Development of Environmentally-Friendly Plasticized Poly (vinyl chloride) – Based Flooring Formulations

Amr El Aghoury

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ABSTRACT

Development of Environmentally-Friendly Plasticized Poly (vinyl chloride) – Based Flooring Formulations

Amr El Aghoury, P.Eng., Ph.D.
Concordia University, 2005

The research aim is to develop alternative cost-effective poly (vinyl chloride) PVC formulation that possesses good mechanical properties, resistant to microbial attack, with low volatile organic compounds (VOC's) emission, as well as to explore a market for lignin, an abundant natural polymer, obtained as a by-product of paper making.

One of the main applications of plasticized PVC for building industry is the production of flooring. Normally in the manufacture industry of the PVC flooring di-ethyl-hexyl-phthalate (DEHP), commercially known as DOP is used as a plasticizer to facilitate the processing of PVC. DOP is environmental pollutant due to its biodegradability that consequently releases VOC's; considering this hazard, the introduction of other biopolymers and other additives in PVC formulation could contribute to a safer and healthier environment. DOP has been used in this research for comparative purpose only.

Series of plasticized PVC formulations were prepared with different types of plasticizers namely: Di-octyl phthalate (DOP), Diethylene glycol dibenzoate (Benzoflex 2-45), Tricresyl phosphate (Lindol) and Alkyl sulfonic acid phenyl ester (Mesamoll). Meanwhile, the role of

lignin within the mixtures was evaluated, as part of the PVC was replaced with different lignins namely Organosolv, Indulin and Tomlinite (20 phr of PVC).

The new proposed alternative flooring material was prepared by melt mixing and compression molding, and tested to evaluate its processibility, thermal properties, mechanical properties (i.e., Young's modulus, tensile strength at break and yield, elongation at break) as well as its morphology.

In addition, the different formulations resistance to fungi attack was studied as a function of the samples weight loss, and their fungal growth was evaluated visually. Also, the impact of this growth on the mechanical and thermal properties of the different presented formulations was studied to evaluate their bio-deterioration.

Moreover, considering the introduction of new formulations, their ageing behavior due to inherent instability of the amorphous glassy state, known as volume recovery or structural relaxation is studied

Finally, the primary emissions (i.e., free non-bound VOC's, which generally have low molecular weight) of VOC's are identified and quantified.

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Dedicated to my father soul;

I am deeply saddened that he is not among us to see his dream coming true; it is done so please rest in peace.

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Acronyms

α	Alpha hydrogen of PVC
δ	Hilderbrand solubility parameter
160	Butyl benzyl phthalate / Santicizer 160
2-45	Di-ethylene glycol dibenzoate / Benzoflex 2-45
AL	Alcell lignin
ASTDR	Agency for toxic substances and diseases registry
ASTM	American society of testing materials
BBP	Butyl benzyl phthalate
$CaCO_3$	Calcium carbonate
$CaSt_2$	Calcium stearate
DBP	Di-n-butyl phthalate
DBTL	Dibutyline dilaurate
DEHP	Di-ethyl hexyl phthalate
DIBP	Diisobutyl phthalate
DIDP	Diisodecyl phthalate
DINP	Diisononyl phthalate
DOP	Dioctyl phthalate
DPP	Dipropyl phthalate
DSC	Differential spectral calorimetry
ECPI	European council for plasticizers and intermediates
EVA	Ethyl vinyl acetate copolymer
FID	Flame ionized detector
FITR	Fourier transform infrared spectroscopy
GC	Gas chromatograph

HCl	Hydrogen chloride
He	Helium
HVAC	Heating, ventilation, and air conditioning
IAQ	Indoor air quality
IL	Indulin lignin
IR	Infrared spectroscopy
IUPAC	International union of pure and applied chemistry
L	Lignin
Lindol	Tri-cresyl phosphate
Mesamoll	Alkyl sulphonic ester of phenol
$MgCO_3$	Magnesium carbonate
min	Minute
mM	Millie mol
mm	Millimeter
Mn	Number average molecular weight
MPa	Mega-pascal
MW	Molecular weight
MWD	Molecular weight distribution
O_2	Oxygen
OH	Hydroxyl group
PF	Phenol-Formaldehyde
pH	Potential of hydrogen
phr	parts per hundred parts resin
PVC	Poly (vinyl chloride)
RH	Relative humidity
rpm	Revolution per minute
TBS	Tight building syndrome
Tg	Glass transition temperature
TGA	Thermogravimetry
TiO2	Titanium dioxide
Tm	Melting temperature

TVOC	Total volatile organic compounds
UF	Urea-formaldehyde
UV	Ultraviolet
VAc	Vinyl acetate
VC	Vinyl chloride
VOC's	Volatile organic compounds

1

Introduction

Poly (vinyl chloride) (PVC) possesses high mechanical properties, low flammability, durability in the natural environment, shows good miscibility with other substances, and its hardness can be altered with the aid of various additives. It has ideal melt viscosity in mold processing and excellent formability with great dimensional accuracy. Its surface is totally process-able by printing, flatting, and has great variety for design. It has excellent processibility and in-site fabrication potentials. Furthermore, it is the only resin that offers practical processing paste due to its fine particles.

1.1 Statement of the problem

In recent years, questions regarding the environmental impact of PVC and mainly of its additives have arisen. Additives introduced during manufacturing of PVC include alkyl phthalate esters. Their ester bonds are broken by the enzymes produced by fungi, resulting in volatile organic compounds (VOC's) that deteriorate indoor air quality. Although, in 1999 the European Council for plasticizers and intermediates reported that medical devices fabricated with DOP cause no harm to people at long exposure, some researchers found that plasticizers incorporated in indoor materials can increase the risk of bronchial obstructions, asthma, and susceptibility to respiratory infections. Considering these risks, there is a tendency to introduce different types of plasticizers that have different chemical structures than the phthalate family.

Moreover the microbial and fungi attack of the PVC have not been thoroughly investigated and needs more research. In order to enhance the PVC resistance to microbial and fungi attack, we introduced lignin to replace part of the PVC. Lignin is a natural polymer, its content in wood is about 25 wt-%, and plays an important role within the mechanical support, water conduction and protection against biodegradation in trees. It is a byproduct with few applications.

1.2 Objective and scope of the study

The aim of this research is to develop a new PVC flooring material, formulated with other plasticizers having different chemical composition than that of alkyl phthalates. Also to study the contributions that lignin can make, when partly replaces the PVC in the new formulations, toward the stability of these formulations to fungi attack. Meanwhile, the emission of VOC's is investigated.

The main objectives of this research program are:

1. Establish compatibility of PVC homopolymer and VC-VAc copolymer - lignin blends with different plasticizers;

2. Examine processibility, thermal and mechanical properties of the new formulations;
3. Increase blends resistance to biodegradation;
4. Decrease the amount of released "VOC's";
5. Explore new applications for lignin in polymer field;
6. Develop a cost-effective material.

To meet these objectives, formulations of PVC/VC-VAc copolymer-lignin filled with calcium carbonate ($CaCO_3$) and different plasticizers were prepared, processed, tested and the results were evaluated and compared to the existing formulation of PVC or VC-VAc copolymer.

1.3 Thesis organization

This research study is presented and outlined in the coming chapters as follows:

Chapter 2: Theoretical consideration

This chapter contains the scientific basis, assumption and approaches of this research, which forms the theoretical foundation and frame work for the analysis of the experimental data presented thereafter.

Chapter 3: Literature review

This chapter contains a review of previous research works, different additives of the PVC-lignin and their effect on the properties of the end product. Moreover the characteristics of PVC, lignin, and different additives are presented.

Chapter 4: Research program

This chapter describes the methodology of this research. Also, the physical and chemical properties of different constituents used, formulations preparation methodology, instruments used and experimental procedure. In addition, a detailed study had been carried out and presented to evaluate the plasticizer concentration and compatibility within the different formulations.

Chapter 5: Results and discussion

In each section the data are presented, analyzed and followed by detailed discussion.

This chapter contains the following seven sections:

- Lignin – plasticizer interaction
- PVC homopolymer – lignin blends
- VC-VAc copolymer – lignin blends
- VC-VAc copolymer versus PVC homopolymer controls and blends
- VC-VAc copolymer microorganisms resistance
- VC-VAc copolymer ageing
- VC-VAc copolymer VOC's emission

Chapter 6: Conclusion and recommendations for future research

This chapter contains the main contributions based on the experimental results and their analysis. Suggestions for further research are presented.

2

Theoretical Consideration

Plasticization process

A plasticizer is a substance or material incorporated in a thermoplastic or elastomer to increase its flexibility and workability. The most common plasticizer classes are dialkyl phthalates and tryaril phosphates typified by di-2-ethylhexyl phthalate (DOP) and trixylil phosphate (TXP) respectively. Although the above two classes account for the plasticizer bulk consumption, it has been possible by the utilization of special plasticizers to use PVC for special applications. The most important theories of polymer plasticization are: the viscosity, the thermodynamic and the lubricity theory.

The viscosity theory is based on the principle that, the plasticizers function by modifying the rheological properties of polymers, and that the interaction with the polymers is physical rather than chemical, the viscosity of miscible plasticizers and, in particular, their viscosity-temperature behavior are factors of prime importance. Furthermore, plasticizers having low temperature coefficients of viscosity derived from the slope of plasticized polymers are less sensitive to temperature change, with respect to mechanical and some physical properties. If polymers are plasticized by liquids having high temperature coefficients of viscosity, they become very hard at low temperature and very soft at high temperature. In other words, their mechanical and physical properties are very sensitive to temperature change.

The thermodynamic theory of plasticization assumes that both polymer and plasticizer are in thermodynamic equilibrium, and that separation phase should occur when the free energy of dilution becomes zero. For a plasticized polymer, therefore, two phases would be formed: one being the swollen polymer and the other almost pure plasticizer. Thus at any given temperature the composition of the swollen polymer represents the maximum plasticizer level that can be tolerated without exudation. If the temperature is raised the free energy will decrease, and therefore that permits more plasticizer to enter the polymer-plasticizer phase. This statement, however, is at variance with the commonly observed phenomenon that plasticizer exudation often takes place when the temperature is raised and not lowered.

The lubricity theory considers that plasticizer function is similar to that of a lubricant in reducing the intermolecular friction between the macromolecules. The lubricant mechanism deems that when a plastic is flexed, the macromolecules must slide backwards and forwards over each other. Intermolecular attractions will oppose such movements, and the plasticizer reduces the internal resistance by the lubrication effect.

Plasticizer can reduce the melt viscosity during processing; lower the second order transition temperature and the elastic modulus of the product. Plasticizer efficiency could be measured by the actual reduction in polymer's Tg per unit weight plasticizer. High efficiency indicates that the plasticizer causes the glassy to rubbery transition over a very broad temperature range.

Generally, plasticizers are high-boiling liquid esters, such as dioctyl phthalate, diethyl phthalate, trixylyl phosphate, dioctyl sebacate, etc. Although materials with boiling points much lower than 250 ^{o}C impart moldability in processing. They are not normally considered as plasticizers since their insufficient finale to impart, any measure of, flexibility to the final product, owing to their high volatile loss at processing temperature. Although plasticizers such as dimethyl phthalate and diethyl phthalate are compatible with PVC, they are too volatile at PVC processing temperatures. Hence, esters of higher molecular weight such as dibutyl phthalate were necessary, as thought of, until it was realized that it is volatile for some applications.

Plasticizers that are susceptible to migration are said to have low permanence. Loss of plasticizer by exudation or biodegradation will lead to a gradual increase in brittleness as the Tg (and therefore the elastic modulus) of the plasticized polymer slowly increases to that of the unplasticized (i.e. glassy) polymer [1]. Although, to some extent plasticizers are a disadvantage because they are not absolutely permanent (i.e. they can be extracted or can volatilize) and can cost more than the PVC itself, they have made PVC a truly versatile material.

Polyblending

Similar mechanical properties modifications to those obtained by plasticizer addition could be achieved by varying the chemical nature of the macromolecules or the degree of polymerization. This effect is usually known as *internal plasticization,* and is most normally achieved by copolymerization. Thus one of the main components used in this research is VC-VAc copolymer that is more flexible than PVC homopolymer. The change in properties is due to the irregularity in the macromolecular chain and the alternation of the intermolecular forces brought by the presence of vinyl acetate as co-monomer.

If homopolymer poly (A)n is hard and horn-like, introduction of co-monomer B can produce a softer, more flexible copolymer poly(A-B)n. We can say, in this case, that the homopolymer poly (A)n has therefore been internally plasticized. The main advantage of internal plasticization is that the effect is permanent unlike the plasticizer effects. Such addition to a polymer does not result in primary valency bonding; it can lead to more variation in physical properties that is likely to result of copolymerization or other internal plasticization techniques.

A polymer blend is a physical mixture (alloy) of two or more polymers. The use of blends of two polymers eliminates problems like migration of one of them from the mixture. The second polymer is being like an additive with high MW that means having high viscosity. Such blends can, in principle, offer a wide variety of morphologies and properties by adjustment of the nature and amount of polymers in the mixture. Both characteristics are strongly depend on the different polymers' *miscibility.* Historically polyblends were developed to improve the impact strength of rigid polymers [2]. Besides the binary systems, ternary blends are gaining importance [3].

In blending different polymers, one may encounter two extreme situations: either a gross phase separation, or a homogeneous mixture at the molecular level. However, the reality is more complex, and many intermediate situations can occur, such as increasing separation at intermolecular level only, formation of co-continuous morphology, dephasing into dispersed heterophase morphologies of increasing phase size.

The formation of two phase systems is not necessarily an unfavorable event since many useful properties and characteristics of a single phase may be preserved in the blend while other properties may be averaged according to the blend composition. Proper control of overall blend morphology and good adhesion between the phases are, in any case, required in order to achieve good mechanical properties. For instance, the toughness properties of immiscible blends, whose components form separate phases, often depend on the dimensions of the dispersed phase and on the degree of *interfacial adhesion* between phases. These issues are largely controlled by melt processing conditions, and by *thermodynamic affinity* of the components of the blend.

There seems to be a general agreement on the fact that there is no compatibility between two polymers when they are not able to develop either weak or strong *specific interactions*. The formation of a polymer blend seems to be due to a balance between self association (P-P, P'-P') and hetero association (P-P'). Much work has been done in order to try to predict whether P and P' polymers are compatible prior blending, mainly using the value of solubility parameter, IR spectroscopy, mechanical techniques or molecular mechanic calculations [4]. The specific interactions between the polymers participating in the blend are: dipole-dipole, hydrogen bond, charge transfer.

In general, polymers scarcely mix with one another, because the combinational entropy (thermodynamic reasons) between polymers is considerably low. Miscibility of polymers strongly depends on polymer-polymer interaction, as a slight difference in conformation of polymer chain sometimes affects this process. Blending does not result in, many cases, a finely stable disperse distribution of one polymer into the other one. Such type of distribution is necessary to get a sufficient interaction between polymers, which results in the formation of *interfaces*, i.e. in the formation of at least one new polymer phase. All the phase behavior displayed by polyblends can be found in mixtures of small molecules, but in different ways, taking into account the differences between micro and macromolecules. For these reasons, the creation of different terms like miscibility and compatibility became necessary for polymer blends studies.

Lignin

The main partner for PVC and VC-VAc copolymer in the introduced blends in this research is lignin. A very small amount of this natural polymer is used around the world in thermosets, as antioxidant or filler in some rubbers, as a component in polyblends with polydimethylsiloxane, acrylic copolymer, polyurethane, epoxy polymer. Lignin is very stable in nature, and one of its functions in trees is to diminish the effects of chemical stress by inhibiting atmospheric degradation, acting as an antioxidant and ultraviolet (UV) light stabilizer. Its phenyl propane units are interconnected by a set of linkages that results in a very complex matrix. This matrix comprises a variety of functional groups –

mainly hydroxyl, methoxyl, carbonyl, and carboxyl – which impart a high polarity to the lignin macromolecules. The functional groups of both lignin and PVC could make the polyblending between them possible, for example that between carbonyl groups of lignin and α hydrogen of PVC or between hydroxyl groups of lignin and chlorine of PVC (i.e., proton/donor acceptor interaction). These interactions are likely to contribute to the miscibility or partial miscibility of these polymers in a blend [5].

* * *

Considering these scientific bases, the proposed formulations in this research will be based on *blends of two polymers (polyblends)*, a synthetic and a natural one, namely PVC – lignin and VC-VAc copolymer – lignin. Moreover, in order to determine the usefulness of the proposed plasticizers for a given polymer, their *compatibility, efficiency and permanence* in the polymeric system will be initially studied and characterized. All these characteristics will be established for the proposed formulations through a methodology that based on the determination of thermal, mechanical properties and the resistance to microorganisms. Details on the methodology are presented in chapter 4.

The initial assumption of the research is that such polyblends for flooring will be able, with an appropriate plasticizer and other necessary additives, to lead to a product having:

-The necessary mechanical and thermal properties;
-Better resistance to fungi attack;
-Lower amount and less health dangerous VOCs released in the process of biodegradation.

3

Literature Review

Plastic products range from sophisticated items such as prosthetic hip and knee joints to disposable food packaging articles. This is due to the tremendous range of properties exhibited by plastics and their ease of processing. Their properties could be tailored by varying the composition of the repeated units, molecular weight, molecular weight distribution and crystallinity.

Polymers are normally categorized according to their physical properties as either thermoplastic, thermosetting, or elastomers. Thermoplastics are capable of being repeatedly softened by increasing temperature and reset on cooling. They are usually produced initially in the form of small granules (pellets) for subsequent fabrication into different items.

PVC is one of the most commonly used members of the broad family of thermoplastics, and is ranked second behind polyethylene in terms of worldwide polymer consumption. 53% of the PVC production in Europe is used in building and construction industry [6]. It has become a very important bulk plastic worldwide in its 70 years history. This is even expected to increase because of its mechanical properties that can be altered over a wide range, yielding everything from rigid to flexible end products [7].

There are two basic forms of PVC: rigid and plasticized. Rigid PVC is an unplasticized polymer that exhibits high rigidity and stiffness, and is used as pipes and ducts, window and door profiles, fencing, shelters, sheeting and roofing membranes, rigid foam. Plasticized PVC that can be formulated to give products with rubbery behavior such as cable and wire covering, wall coverings, handrail, water-stop (bars), and flooring.

3.1 PVC flooring raw materials

Resilient flooring is characterized by its ability to deform and recover from the comprehensive forces caused by the dynamic action of footsteps, cartwheels, and casters, or static load appliances and furniture. Vinyl flooring or PVC flooring is the most commonly used among the family of the resilient flooring materials. Dynamite Nobel AG introduced this material in Europe in 1934 under the name of Nipolan. PVC flooring materials are available in both homogeneous (i.e., system with a constant composition with or without top coat in which the wear layer is the full depth of the composition) and heterogeneous (i.e., system consist of multiple components) form. They are widely used in hospitals, schools, domestic kitchens and bathrooms, where they offer a wide choice of colors and patterns, ease of cleaning, good cushioning, insulation and reasonable price. The last three features represent advantages over linoleum.

The main concern of this study is plasticized PVC. The development of wide scale PVC formulation expertise has enabled the development of a wide range of products, which may not have been possible to produce with a simple polymer. Normally the formulation of PVC flooring contains PVC resin, plasticizer, and thermal stabilizer to prevent thermal decomposition during processing, as well as fillers, pigments, and lubricants.

3.1.1 Poly (vinyl chloride) "PVC"

The abbreviation as well as the full name should specifically denote a homopolymer of vinyl chloride. However both terms, especially the abbreviation has acquired different and wider meaning. PVC is any material or product made of a mixture of a vinyl chloride polymer or copolymer with various additives. For that, the used polymer or copolymer will be identified at the beginning of each section.

PVC is generally obtained by suspension polymerization (about 80% of total commercial production), or by emulsion polymerization (about 10-15%) of vinyl chloride (VC) [8]. Emulsion polymerization is carried out in a heterogeneous medium and involves the dispersion of VC monomer in a continuous water phase with an oil-in-water emulsifier followed by polymerization with a water-soluble initiator. The product is a polymer colloid in which the particles are considerably smaller than the monomer droplets of the initial monomer dispersion. Therefore the reaction mechanism includes particle nucleation and growth.

About 99% of Vinyl Chloride monomer (VC) produced goes into PVC. VC world production in 1996 was 22.9 million tones, out of which 7.4 and 5.72 million tones were produced in North America and Western Europe respectively. The global sales of PVC in 1997 were approximately 23.64 million tones, which reflect the high demand for PVC products. That could be translated into considerably more million of tones of PVC additives as fillers, plasticizers, impact modifiers, etc [9].

PVC has the following microstructure:

$$[-CH_2-CHCl-]_n$$

Where n, is the degree of polymerization, which ranges from 500 to 3500 [10].

10% of PVC is produced as copolymers and terpolymers [11]. This implies the use of two or three different co-monomers in which VC is the basic monomer. Vinyl chloride-vinyl acetate copolymer (VC-VAc) is the most important commercial product which is usually used for producing flooring tiles, whose vinyl acetate content ranges from 3 to 20 wt-%. VAc units present in the copolymer induce an internal plasticization that allows easier processing at a lower temperature in conventional equipment. The VAc also gives pigment wetting characteristics when high levels of filler, are to be used [12].

PVC weight average molecular weight ($\overline{Mw}$) for different applications ranges from 100,000 to 200,000, and number average molecular weight ($\overline{Mn}$) ranges from 45,000 to 64,000, with polydispersity ($\overline{Mw}/\overline{Mn}$) equal approximately 2 [13]. These are among the characteristics that determine the rheological behavior of the melt and the physical-mechanical properties of the end product.

PVC homopolymer consists of 56.8% chlorine, 38.4% carbon, and 4.85% hydrogen. Over 30% of the chlorine produced on a global basis goes to PVC production. Chlorine is not only essential to the chemical composition of PVC; it provides a number of unique properties that give this versatile plastic a distinct advantage in product application and the market place. It makes PVC an inherently low flammable polymer. PVC is the world's leading electrical insulation material. It has over 37% chlorine and as a result it is one of the most energy efficient polymers. In addition, recycling PVC is easier because the chlorine in PVC acts as a marker, enabling automated equipment to sort it [10].

PVC combines good strength and toughness with a wide range of rigidity or flexibility. It possesses excellent resistance to attack from water and many chemicals. It has good weather resistance, electrical insulating qualities, and resistance to flame spread. It is also economical to process, and adversely affected by ultra violet light when exposed to outside environment. Although that our main concern is the development of vinyl flooring, and as mentioned earlier most of the vinyl floorings are fabricated using VC-VAc copolymer, to reduce the complexity of the used formulation for better understanding, the homopolymer was also studied. Homopolymers may be regarded as essentially amorphous [14] with better thermal stability and mechanical properties, while copolymers are easier in melt processing and have greater acceptance to filler in some compositions.

3.1.2 Plasticizers

The development of plasticizers over the past fifty years has closely followed the development of PVC. PVC differs from many polymers in the way that it requires certain additives (plasticizers, stabilizers) to be used with the pure polymer in order to produce a product with useful and significant properties. This may seem to be a disadvantage, but considering the wide variety of products that we end up with, it proves to be a superior advantage. The role of plasticizer is to help processing PVC by reducing the intermolecular forces as well as the glass transition temperature of the polymer, which enables the formation of a product that possesses flexibility and softens.

The Council of the International Union of Pure and Applied Chemistry (IUPAC) adopted the following definition for plasticizer: "A plasticizer is a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility" [4]. In addition, a plasticizer reduces the viscosity, lowers Tg and elastic modulus. Several theories were developed to describe the plasticization mechanisms, which are [15]:

Lubricating theory of plasticization

This theory states that as the system is heated the plasticizer molecules diffuse into the polymer and weaken the polymer-polymer interactions. The plasticizer molecules surround the polymers molecules reducing the polymer-polymer interactive forces and preventing the formation of rigid network. This reduction in the van der Waals forces, along the polymer chains increases the flexibility, softness, and elongation of the polymer.

Gel theory

It considers the plasticized polymer to be neither solid nor liquid but in an intermediate state (i.e., viscoelastic state) loosely held together by a three-dimensional network of weak secondary bonding forces. These bonding forces between plasticizer and polymer are easily overcome by applied external stresses allowing the plasticized polymer to flex, elongate, or compress.

Free volume theory

This is a measure of the internal space available within a polymer. As free volume is increased, more space is provided for molecule or polymer chain movement which induces flexibility. The free volume theory builds on both the lubricity and gel theory of plasticization.

Plasticizer to be effective and useful in PVC, it must contain two types of structural components. The polar part of the molecule must be able to bind reversibly with the polymer while the non-polar portion of the molecule adds free volume and contributes shielding effects at other polar sites on the polymer chain. The balance between the polar and non-polar portions of the molecule is critical; if a plasticizer is either too polar or too non-polar, compatibility problems can arise [16]. The most important plasticizer properties to be considered are:

1.Gelation

Gelation is the measure of the ability of a plasticizer to fuse with the polymer so as to set up a product of maximum elongation and softness. This is measured either as a processing temperature (i.e. the temperature at which the plasticizer and polymer must be heated in order to obtain certain properties), or as a solution temperature (i.e. the temperature at which one grain of polymer dissolves in excess plasticizer), giving a measure of the solving power of the plasticizer. Gelation depends on the plasticizer's polarity (i.e. the greater the polarity of a plasticizer molecule the greater the attraction it has for the PVC polymer and the less heat required to cause the interaction between them). From the molecular size point of view, the smaller the plasticizer molecule the easier it is to enter the PVC matrix. More thermal energy is required to carry the desired interaction with the polymer when larger molecules are used.

2. Migration and Extraction

When plasticized PVC comes into contact with another material, the plasticizer may migrate to that material. The rate of migration depends on the quantity of plasticizer, and its molecular size. The larger it is the less it tends to migrate. It is also depends on the nature of the contact material. Also, the greater is the linearity of the alcohol ester used in fabrication of the plasticizer the greater is the migration of plasticizer. Plasticizer can also be extracted from PVC by a range of solvents including water. The aggressiveness of a particular solvent depends on its molecular size and its compatibility with both the plasticizer and PVC. Water extracts plasticizer very slowly, oils are slightly more aggressive, and low molecular weight solvents are the most aggressive.

3. Compatibility and Miscibility

There are several theoretical techniques, and practical technological tests, by which the plasticizer compatibility with PVC could be assessed. The Hildebrand solubility parameter (δ) is an effective guide, which is related directly to a compound's cohesive energy density, and is constant for any given compound. This is only valid, provided that the degree of hydrogen bonding power, whether the polymer is proton donor or acceptor, the degree of crystallinity of the polymer, the steric effects in the polymer, are taken into consideration. The solubility parameter can be calculated from the structural formula and density of the compound or it can be determined experimentally.

80% of the plasticizers used in the processing of PVC belong to the phthalate esters group, especially that prepared from alcohol in the range C8 to C10, due to the intermediate range of properties. They are extensively produced and widely used (annual production being estimated at about 2 million tons) in many applications (e.g. medical devices, toys, food wraps, shoe soles, and interior building surfaces).

The European Council for Plasticizers and Intermediates (ECPI) [17] revealed that the European plasticizer consumption in 2001 was 958,000 tones, 92% of it was phthalates based, as shown in Figure 3-1. Also, from this Figure we could observe that there is a decreasing trend in using DOP, and an increasing trend in the use of other phthalates plasticizers, in particular Di-isononyl phthalate (DINP) and Di-isodecyl phthalate (DIDP), which is attributed to the phthalates classification carried on by the European Union Risk Assessment in line with ECPI regulation as shown in Table 3-1.

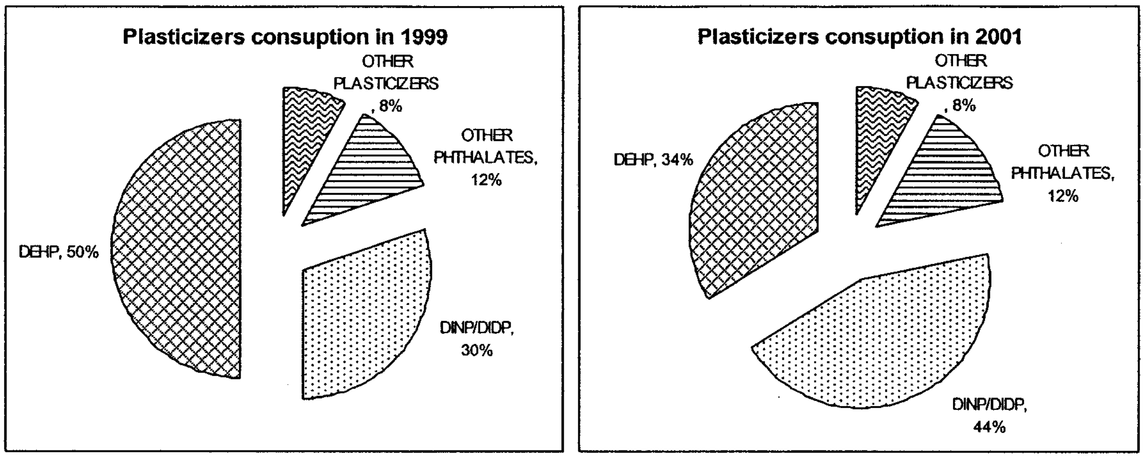


Figure 3-1: The European plasticizers consumption [17]

Table 3-1: Classification and labeling of phthalates plasticizers [17]

	Cancer	Fertility	Developmental
DBP*	None	Category 3	Category 2
DOP	None	Category 2	Category 2
DINP	None	None	None
DIDP	None	None	None
BBP**	None	Category 3	Category 2

Category 1: Substance known to cause effects in humans. Based on epidemiological data. Skull and crossbones.
Category 2: Substance to be regarded as if they cause effects in humans. Based on clear evidence in animal studies. Skull and crossbones.
Category 3: Substance causing concern for humans. Based on sufficient evidence in animal studies to cause suspicions.
* DBP: Di-n-butyl phthalate **BBP: Butyl benzyl phthalate

Plasticizers are not chemically bond to the polymer which facilitates their loss in two simultaneous processes: either by migration, extraction into solid or liquid phase, or by volatilization from polymers in surrounding medium with time and usage. Phthalates have been found everywhere in the environment, both in aquatic and ground mediums, indoor as well as out door environments, in animals and humans, in domestic wastes, in food and in baby milk formula. Therefore they have been considered as ubiquitous environmental contaminates [18]. Latini et al. [19] observed that DOP leakage contributes significantly to material degradation in medical tubes after application. In addition, the sources and air concentrations of phthalates are much higher indoors than outdoors [20-22]. Although, in terms of behavior, DOP has acceptable gelation characteristics, is an odorless oily liquid, and is cheaper comparing to other plasticizers. DOP from coatings and PVC flooring can increase indoor concentrations of phthalates [23-26].

3.1.3 Filler

Fillers serve mainly to reduce the cost and can also offer cheaper alternatives to increase density, modulus of elasticity, hardness, and reduce shrinkage. Loading will be as high as possible, but must not depreciate the end product performance. Mineral fillers have traditionally been used to enhance the mechanical properties of plastics, but increasing attention is being given to how their usage affects the surface properties of finished plastic products. These properties include gloss, smoothness, waviness, profile, porosity, coefficient of friction, conductivity, hardness, scratch resistance, color, homogeneity of pigments, and weathering.

Particle size distribution and the bonding strength between filler particles and polymer matrix are important factors in determining the effectiveness of mineral fillers. Other influencing characteristics include filler particle shape, abrasiveness, and mineral form. Minerals often undergo some form of surface treatment to make their surfaces and the polymer compatible, to optimize processibility and performance. To achieve this goal the most commonly used reagents are coupling and wetting agents.

Coupling agents act by modifying the interfacial region between the inorganic mineral filler and the organic polymer to provide improved bonding between both of them. This allows higher filler loadings and hence cost economics, and improved physical properties of the plastic product, especially when used with high aspect ratio reinforcement fillers. Suitable coupling agents can also increase the utilization range of extender minerals.

Wetting agents serve to wet out the mineral filler to allow a stable homogeneous dispersion to be made in the polymer matrix. This reduces the viscosity of the plastic and often allows higher mineral loadings to be incorporated [27].

Calcium carbonate ($CaCO_3$) is the most widely used filler, available at relatively low cost, and in large quantities from abundant natural sources. Improves flexural modulus, surface finish, and control viscosity, in addition to that the energy required for its processing is low and possesses good thermal resistance during processing. The filler loading in the formulation of flexible PVC range between 17 and 38%, and in PVC floor tiles from 44 to 80%. Almost 60% of calcium carbonate production in Western Europe is used in the PVC industry [27].

The most important selection criteria to be considered when selecting $CaCO_3$ for a given PVC application are [8]: maximum particle size, particle size distribution and mean particle size, color (dry brightness), refractive index, plasticizer absorption, and dispersion characteristics.

3.1.4 Heat stabilizers

PVC and VC-VAc copolymers are subjected to degradation by heat (thermal-degradation) and by light (photo-degradation). In both cases degradation is rapid and is more severe in the presence of oxygen. The main external indications of the thermal degradation of PVC at elevated processing temperatures are deterioration of color, variation of physical and chemical properties, as well as elimination of hydrogen chloride (HCl). Dehydrochlorination involves progressive 'unzipping' of neighboring chlorine and hydrogen atoms along the polymer chain. This HCl is catalyst for further dehydrochlorination. Heat stabilizers are incorporated in all PVC composition to protect the polymer against thermal degradation at high processing temperatures and also subsequently in service, as well as, to react with HCl formed during the reaction and slow autocatalytic effect. The stabilizer used should be non-migratory, non-toxic, odorless, and should not deteriorate the color, clarity or any other properties of the PVC compound. Moreover, it should be readily dispersed in the PVC compound and fully compatible with its components even after extended service, inexpensive and effective in small proportions [8, 28].

3.1.5 Lubricants

The main functions of lubricants in PVC composites are to reduce the friction at, and adhesion to, working metallic surfaces when the composition is being processed (external lubrication), and/or to lower the inter-particle and inter-molecular friction in processing (internal lubrication), which reduces the effective melt viscosity and heat build up. Besides their direct results on melt rheology, substances commonly used as lubricants have other beneficial effects on the properties of compounds and finished articles. For example, the lubrication action of these substances on machine parts and the mold, results with smooth, glossy surfaces in finished articles, and facilitates dispersion of fillers and pigments.

3.1.6 Antimicrobials

Antimicrobials are natural or synthetic [7], mostly of low molecular weight substances that kill or suppress the growth of viruses, bacteria, and/or fungi. Basically two methods of activity can be differentiated. Micro-biostatic activity, wherein only the reproduction of the microorganisms is inhibited (i.e. the cells are not killed but only suppressed in growth), and micro-bicidal activity where the bacteria or fungi are completely killed.

In some cases the same antimicrobial substance can act as both a micro-bicidal and micro-biostatic agent depending on the conditions. The activity of an antimicrobial depends on many parameters: its concentration, pH value, temperature, matrix (i.e., type of polymer) where the antimicrobial was built in, mode of incorporation of the antimicrobial, and the sensitivity of the target microorganisms including the length of time the microorganisms are in contact with the antimicrobial.

In the polymer industry antimicrobials are used for two major purposes: either as a biostabilizer, which protect plastics against microorganisms during service and prevent those products used outdoors from becoming unsightly because of the build up of organic materials, or as antimicrobial active ingredient. They provide a built-in-ability in plastic products to either maintain surfaces in a sanitary and hygienic state, or to provide additional protection and increase shelf life of the plastics.

Flexible PVC is by far the main plastic in which bio-stabilizers are incorporated. PVC itself is resistant to microbial attack, but plasticizers, lubricants, and other organic additives, can be utilized by microorganisms as nutrients [29]. Once biodegradation of the additives starts, microorganisms are capable of utilizing unusual nutrient source and converting it to smaller organic compounds, so the settlement of other microorganisms groups is facilitated, resulting in increased biodegradation.

3.2 Lignin

Lignin is a natural organic material, which together with cellulose and hemicelluloses forms the structural components of trees and various plants as shown in Figure 3-2, and is classified mainly into three major groups: soft wood, hard wood, and grass lignin. Lignins impart rigidity to the cell walls, act as inter cellular binder, and are responsible of wood resistance to compression, impact, and bending. They respond to chemical stresses by inhibiting atmospheric degradation, functioning as an antioxidant and UV absorber. In addition, the presence of lignin renders the wood tissue to resist the action of microorganisms [30].

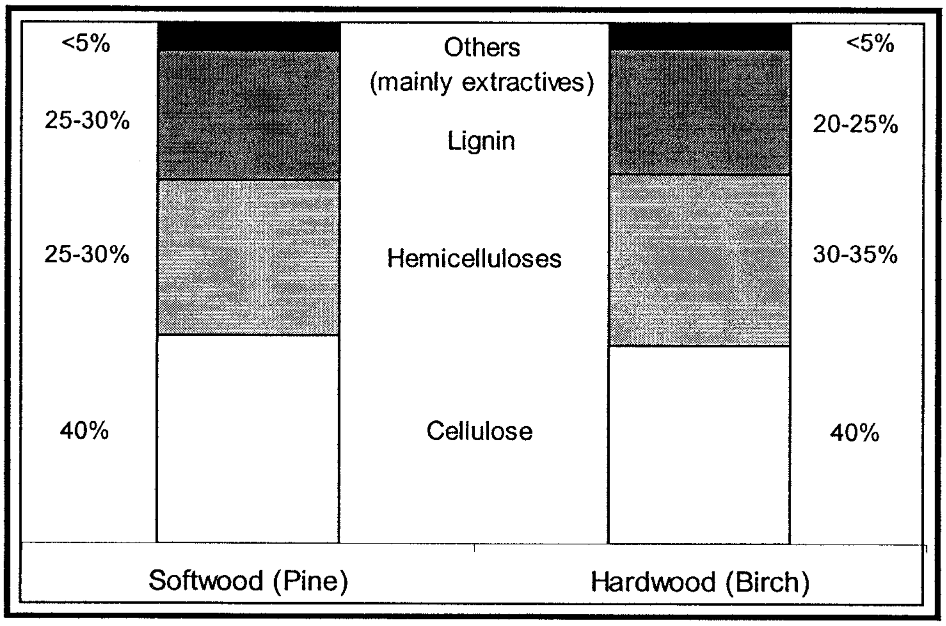
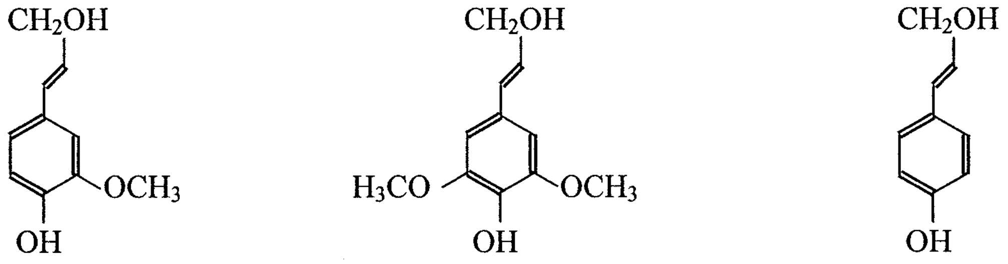


Figure 3-2: Average chemical composition of softwood and hardwood as a percentage of the wood dry solid [31]

Lignin can be defined as polyphenolic material arising preliminary from enzymic dehydrogenative polymerization of three phenylpropanoid units, which are shown in Figure 3-3.



Trans-coniferyl alcohol Trans-sinapyl alcohol Trans-p-coumaryl alcohol

Figure 3-3: The building units (C_6C_3) of lignin [31]

The structural elements of softwood lignin are 90 % trans-coniferyl alcohol and 10 % of trans-p-coumaryl alcohol, while hardwood lignin consists of 50 % trans-coniferyl alcohol and 50 % of trans-sinapyl alcohol. Grass lignins is based on about 40 % trans-coniferyl alcohol, 40 % of trans-sinapyl alcohol, and 20 % other precursors [31].

The approximate elemental mass ratio C:H:O for softwood lignin and hardwood lignin is respectively 64:6:30 and 59:6:35. The main functional groups of native lignin are shown in Table 3-2.

Table 3-2: Functional groups of native lignin (per 100 C_6C_3 units) [24]

Functional group	Softwood lignin	Hardwood lignin
Phenolic hydroxyl	20 – 30	10 – 20
Aliphatic Hydroxyl	115 - 120	110 – 115
Methoxyl	90 – 95	140 – 160
Carbonyl	20	15

Lignin is an amorphous polymer. The chemical structure of lignin is irregular in the sense that different structural elements (phenylpropane units) are not linked to each other in any systematical order. The structural blocks of lignin are joined together by ether linkages (C-O-C) and carbon-carbon bonds (C-C) that form a very complex matrix. Moreover its functional groups impart high polarity to the lignin macromolecule. Lignin, which is present in plant tissues, is referred to as native or natural lignin. The lignin produced through the delignification process, which separates cellulose and removes lignin from wood as a by-product in pulp and paper industry undergoes chemical changes and it is known as technical lignin. It is almost exclusively used as fuel to generate energy.

There are different kinds of technical lignins depending on the chemical processes used for delignification of wood. Kraft lignin (or sulfate lignin), alkali lignin (or soda lignin), and lignosulfonates are derived from kraft, soda, and sulfite pulping of wood respectively. In addition, organosolv lignins, are obtained from the organic solvents (mainly alcohols) pulping of wood.

The technical lignin is in the form of a powder, with densities ranging from 1.3 to 1.4 g/cm^3, and molecular weight ranging from 1000 to 12000. It has a good thermal stability up to 200 °C. It is characterized by high glass transition temperature (Tg) between 100 °C and 180 °C, which could be encountered to the large part of hydrogen bonding caused by the presence of phenolic hydroxyl groups in the main chain [32], or to the chemical structure of lignin, particularly the aromatic rings present in the main chain [33]. However, lignin Tg could be lowered to 70-90 °C with the pretreatment of wood chips by sulfites [34].

Lignin is a renewable, non-toxic material, available commercially at low cost. Lindberg et al. [35] has summarized the positive and promoting factors in the chemical utilization of lignin as follows:

- Readily available in huge amounts;
- High energy content owing to aromatic nuclei;
- The reactive groups on the carbon backbone can be used for a wide range of substitution and addition reaction;
- Good compatibility with several important basic chemicals;
- Excellent colloidal and rheological properties especially in the case of lignosulphonic acid;
- Good absorbent and ion exchange and adhesive properties;
- A direct source of various kinds of phenolic and aromatic compounds;
- The use of the black liquors resulted from sulphate wood delignification process avoids a serious pollution hazard.

Considering these characteristics, lignin appears to be extremely promising material as chemical components in polyblends or as an organic filler. The problems for utilizing lignin in polymer systems include variability, polydispersity, low solubility, high glass transition temperature, its chemical complexity and macromolecular structure, and the presence of different chemicals from the wood processing industry.

Organosolv lignin which is the main type used in this study, is produced through a new delignification process, based on aqueous-organic solvents. This process was developed especially due to environmental concerns related to conventional chemical pulp production [36]. By this means the obtained lignin is in much less unaltered form, than lignin resulting from sulphite and sulphate processes, and is absolutely free of sulfur. It is a fine, brown powder, soluble in some organic solvents and in dilute alkali, but insoluble in water at neutral or acidic pH, and with polydispersity between 2.4 and 6.3 [37]. In addition to organosolv lignin, kraft lignins were used namely Indulin and Tomlinite which are produced from softwood and hardwood respectively.

3.3 Polyblending

Polyblending is the physical mixing of two or more polymers in appropriate proportions, such that the end product has more desirable properties than those of the components. It is one of the most important and inexpensive ways to develop new materials with a high performance at a reduced cost.

Glass transition temperature (Tg) (i.e., the temperature at which amorphous polymer converts from relatively hard, brittle material, to softer plastic material) is an indicator of the polyblends compatibility; a compatible polyblend exhibits a single Tg that is between Tg's of the components and possess optical clarity [38], while the incompatible polyblends have two Tg's which belong to each component and they are usually opaque and show a true two-phase behavior [39].

3.3.1 Lignin polyblends

Seeing the useful features summarized by Lindberg et al. [35], as mentioned earlier, several studies tried to modify polymers using different type of lignins. A short summary for some studies is presented:

One of the most investigated areas is utilizing lignins in the adhesives industry especially with phenol-formaldehyde (PF), urea-formaldehyde (UF), resorcinol-formaldehyde, or melamine-formaldehyde [40]. However, still lignins were not exploiting in high amounts to substitute PF, a fact which is due to the low number of functional groups of lignins that are able to react with formaldehyde in alkaline-catalyzed conditions [41].

Piccolo et al [42] reported that during resol synthesis with lignin from sugar can bagasse, lignin reacted chemically with the phenol growing chain acting as an extender. Molded resins obtained with their formulations using 40% lignin exhibited modulus preservation at elevated temperatures, which showed that the presence of lignin tends to improve the mechanical properties of the blend.

Benar et al [43] achieved a significant reduction in the synthesis time of PF-resol when replaced up to 50% of phenol with modified organosolv lignin, namely acetosolv and formacell lignins from Eucaliptus grandies chips.

Kraft lignin was blended with a acrylic (terpolymer) sealant. Although, this blend shows incompatibility as confirmed by the DSC diagrams, the addition of lignin up to 15 wt-% improved the mechanical properties and the durability of the acrylic sealant. It, also acted as effective reinforcing filler [44].

Feldman et al [45] investigated the modification of epoxy adhesive by polyblending with Tomlinite lignin up to 40% loading. An improvement of the blend adhesion up to 30% lignin content was achieved with maximum results at 20% lignin loading. Only one Tg was detected for blends having up to 20% lignin content indicating complete miscibility. Also, the durability tests in another study carried out by Wang et al [46] showed that epoxy-lignin adhesive blends have better weatherability and photo stability than the epoxy adhesive control.

The goal of adding lignin to polyolefins is to improve its mechanical properties, thermal stability, light stability and biodegradability. Lyubeshkina [47] mentioned that dry sulphate lignin is of considerable interest for the filling and modification of thermoplastics to obtain frost-resistant polypropylene compositions, and also in the reprocessing of polymeric materials waste. Studies have been carried out on the production of composites based on post consumer polyolefins and sulphate lignin as Simionescu et al. [48] obtained blends of polyolefins and lignosulfonates able to impart biodegradation susceptibility to isotactic polypropylene.

Rosch et al. [49] have used organosolv lignin as a filler for polypropylene and poly (ethylene-co-vinyl acetate)-EVA. As a function of the lignin content which was varied between 0-30 wt-%, mechanical properties of the blends were measured. Both lignin filled thermoplastics exhibited obvious matrix reinforcement with the increase of the lignin content. Due to better interfacial adhesion in the EVA-lignin polyblend, an amount of 30 wt-% lignin doubles the Young's modulus of such blends without sacrificing the high elongation at break.

3.3.2 PVC-lignin polyblends

Feldman et al [50] evaluated the blend obtained from unplasticized PVC compound for out door application loaded with 7.5, 5, and 2.5 phr of TiO_2; as this filler has the ability to change the weathering properties of PVC products and the ability to absorb UV radiation falling on the polymer containing kraft lignin (Tomlinite). The presence of lignin did not affect the thermal stability of PVC and its rheological properties during the melt process. The paper shows that the interaction between lignin and PVC to form miscible blends can take place at temperatures higher than Tg of the higher molecular weight fraction of lignin. They also concluded that the increase in tensile strength and the decrease in elongation at break of unweathered PVC-L blends depend on the lignin load. The maximum tensile strength at break is about 9% higher and the elongation at break is about 13% lower than the respective value of PVC-control for PVC-7.5L phr/2.5T phr (where T is TiO_2); meanwhile the PVC-7.5L blend presents the same behavior in tension whereas the elongation is reduced by only 6%.

After a weathering period of 84 days, the tensile strength-strain data reflect an overall cross-linking process occurring in PVC-control as well as in blends. The partial or total replacement of TiO_2 by lignin in different blends did not greatly affect the tensile stress-strain properties of the blend in comparison to PVC-control. However, changes in color as well as the development of crazes on the surfaces exposed to UV light and humidity for PVC-L blends indicate a lower weathering stability in comparison to PVC-control.

Furthermore, blends of unplasticized PVC with organosolv lignin were carried on to develop dark colored and cost effective blend for outdoor applications in building [51]. The scanning electron microscopy study shows that the size of lignin particles in PVC-L blend does not increase with the gradual increase of lignin content. In addition, no signs of coalescence were noticed. This fact indicates that PVC-L blends are not typically miscible thermoplastic blends. Immiscibility of the two polymers was confirmed by Differential Scanning Colorimeter (DSC) analysis, which disclosed the existence of two endothermic relaxation peaks in the Tg region. The fact that the two peaks are not perfectly separated and that the relaxation energy of the principal peak is higher in the blends than in the PVC control, it is an argument for the likely miscibility of the two polymers in blends.

S. El Raghi et al. [52] studied the weathering effect on the properties of rigid PVC and Indulin Lignin (IL). They conclude that IL does not affect the blend processibility and that they form together a miscible blend. Addition of IL led to an increase in the tensile strength and a slight decrease in elongation at yield and at break. Although, that weathering does not affect the mechanical properties with the addition of lignin, both samples blended and unblended showed discoloration.

In another study [36], different lignins and lignin derivatives in blending with rigid PVC for outdoor application were evaluated. Significant differences in mechanical, thermal, and weathering properties as well as thermal stability of lignins were noticed for lignins resulted from different delignification processes. The mechanical properties, particularly strength at yield and break and infrared spectra (IR), demonstrated an interaction between OH groups of lignin and α hydrogen of PVC. A major drawback of all the lignins is that they diminish the impact strength and lower the weathering stability of the blends in comparison to the PVC control which may be partially explained by the slight decomposition of the lignins caused by high temperatures (~ 200°C) required in rigid PVC processing.

A research was carried out by Hui [53] to evaluate the plasticized PVC with Alcell lignin blends (PVC-AL blends) as matrix for highly filled composite flooring application. The lignin replacement of PVC within the matrix varied from 0 to 30 phr, the higher the lignin loading in PVC-Al blends the more difficult it is to be processed. The blends were sticky and difficult to be removed from the mixer parts. Moreover, at levels of 25 and 30 phr the degree of stiffness increases associated with severe losses in strength at break and impact. The study was carried out with different plasticizers (DOP, Benzoflex 2-45 and Santicizer 160) at constant level of 35 phr, as at that level of plasticizer a good efficiency was noticed. It was also concluded that, in the composites formulated with Benzoflex 2-45 and Santicizer 160 as plasticizers, up to 20 parts of PVC was replaced by AL. At these levels the tensile, impact and hardness properties are still appreciable and are in the range of the required values for vinyl flooring materials. From all the plasticizers used Benzoflex 2-45 was better from the mechanical properties point of view, and shows homogenous composite matrix.

Also an investigation was carried out into the use of plasticizers for reducing the degree of association existing within organosolv lignin (Alcell lignin) molecules, to overcome its adverse effects on the mechanical properties when blended with vinyl chloride – vinyl acetate copolymer. The study concluded that plasticization diminishes the high degree of association occurring with Alcell lignin molecules, as confirmed by DSC and FTIR spectroscopy and that the compatibility of Alcell lignin with different plasticizers is strongly influenced by the solubility parameter of the plasticizer. The higher it is the better the compatibility [54].

3.4 Ageing of PVC

Organic materials, both of synthetic and natural origin, readily undergo reaction with oxygen. When polymers oxidize, their mechanical properties are reduced and discoloration may result. The typical signs of oxidation are referred to as “ageing phenomena”, whereas the effect of oxidation on a polymer chemical structure is termed “degradation”. The main factors influencing the degradation of PVC include temperature, humidity, mechanical stress, aggressive media, and ionizing radiation; all leading to changes in the initial properties as a result of simultaneous chemical decomposition of the material. The main process of PVC ageing at room temperature is plasticizer desorption. At higher temperatures thermo-oxidative degradation is possible and is accompanied by dehydrochlorination. The occurrence of thermo-oxidative degradation and dehydrochlorination may be monitored by the changes in molecular weight distribution and the accumulation of double bonds. Meanwhile, it is generally known that the weight loss is linear with the square root of time when the rate of plasticizer reduction is controlled by diffusion and linear with time when the rate is controlled by evaporation [55].

Gumargalieva et al [56] investigated plasticized PVC samples aged in natural and artificial conditions, and samples recovered after use for a long time (15-30 years) at temperature 253-301 K (i.e. -20 to +28 ^{o}C). They used the thermogravimetry (TGA) method to determine the decrease of plasticizer concentration in PVC; it showed that the mass loss for PVC containing various amounts of DOP and heated to 400^{o}C corresponds to loss of plasticizer plus dehydrochlorination and depends linearly up on the plasticizer concentration. They also studied cable insulation articles dismantled after 15 and 30 years to understand the nature and relative contribution of the chemical and physical process occurring in low temperature ageing. The samples used were maintained in darkness at a temperature range of –20°C and +28°C. The main results are shown in Table 3-3. Based on these data the main process of ageing plasticized PVC is desorption of plasticizer, which can be monitored by two indices: the loss of plasticizer, and the increase of the porosity of the polymer as measured by mercury porosimetry.

Table 3-3: Correlation of different aspects of PVC ageing [56]

Exploitation Time, (Years)	DOP amount mass [%]	Shrinkage [%]	Elongation at Break, [%]	Tg [°C]	Pore Volume [cm^3/g]
0	35 ± 1	----	600 ± 40	- 40	0.017
15	27 ± 2	5 ± 2	480 ± 60	- 20	0.05
30	15 ± 6	15 ± 6	300 ± 80	- 20	0.065

Furthermore, Jakubowicz et al [57] investigated the general degradation of plasticized PVC in indoors application to give an estimation of acceleration factors. This information was then used to evaluate technical quality and remaining life time of old products, in order to decide their suitability for mechanical recycling. Results show that the mass loss is dominating process in the ageing of plasticized PVC at low temperatures. Ageing in air at 80 and 90°C for up to 8 weeks caused no significant changes in elongation at break, but at 100 and 110°C it was about one third of the original value, which corresponds to the maximum mass loss of about one third of the original amount of plasticizer. The measurements of residual stability for collected sheathings and cables from (3, 24, 34 years) old buildings show high values, indicating good thermal stability. Some materials were also subjected to accelerated ageing in air at 80°C for 2 and 4 weeks to evaluate the remaining life time, using the assumption that the lowest activation energy calculated is 95 KJ/mol and the Arrhenius relation is also valid for the old materials. From these data it appears that 4 weeks of ageing at 80°C correspond to 44 years of use at room temperature. Accelerated ageing of the old materials did not significantly affect the tensile properties. The maximum change observed was 1%, which shows that the technical quality and the remaining life time are very good, making them suitable for reuse or mechanical recycling.

3.5 Fungi attack

Fungi are natural organisms, carbon heterotrophs because of lacking of chlorophyll, therefore, they required external organic compounds as a carbon source. In order to digest the organic compounds, fungi produce hydrolytic enzymes to break down these nutrients into more simplified ones, and then the simplified nutrients pass into the fungal cell as a watery solution. Since they don't use light to make food, fungi can live in damp and dark places and some of them are anaerobic [58]. A spore is a typical reproductive unit of fungi, which may be resulting from either sexual or nonsexual reproduction. The growth of fungi is mainly influenced by:

1. *Nutrition*

   As carbon, nitrogen, iron, magnesium, and phosphorus.

2. *Moisture*

   Moisture content provides favorable growing conditions for fungi. More than 70% for moisture creates very conducive conditions growth. Fungal growth can be prevented with help of controlling moisture.

3. *Oxygen*

   Most of fungi are aerobic in nature. They require oxygen supply for growth. The absence of oxygen ceases the fungal growth. Fungi may utilize combined oxygen from different components instead of the free molecular oxygen in the absence of atmospheric oxygen [59].

4. *Temperature*

   The optimum temperature for most fungi growth is in the range of 22-27 °C [60].

5. *pH-value*

   Nutrient intake and enzymatic activity in fungi are pH dependent. It alters the cell permeability and affects the enzyme activity; the optimum pH is in the range of 5-6.5 [60].

6. *Light*

The vegetative growth of most fungi is not sensitive to light but the reproduction of fungi is [58].

Plasticizers usually are the main targets attacked by fungi. Webb et al. [61] showed that plasticization with DOP increases adhesion of fungi to plasticized PVC and stimulates its biodegradation. Furthermore, the adhesion to plasticized PVC was strongly dependent on both the pH and electrolyte concentration of the suspension medium, reaching maximum levels at pH 8 and with electrolyte concentration of 10 mM NaCl.

Gumargalieva et al [62] studied the influence of biodegradation by the microscopic fungus on the diffusion desorption of a dialkylphthalate plasticizer from PVC. The conclusion of the study was that the loss of a plasticizer from PVC under the influence of surface biodegradation with the presence of fungal overgrowth is much faster than in it's absence. In the absence of the fungus the rate is limited by volatility of the plasticizer, whereas in the normal case it is limited by diffusion of plasticizer. Fungus acts like a leaching solvent, most probably because it effectively removes plasticizer from the surface of the material by biodegradation.

Inadequate ventilation and insufficient drying of flooded area, as well as faulty cleaning habits lead to rapid fungal growth. Toxic fungi are the class that causes the health hazard to human beings. They produce the mycotoxins like Aspergillus niger, Penicillium…etc, which affect the human health causing allergies, inflammation, infection which can further lead to some sever health problems like asthma and cough.

The biodegradation process often results in reduced durability and life span of the plastic products. The various sign of microbial attack are [29]:

1. Staining

This discoloration can be the result of intracellular pigments or extra cellular dyestuffs (i.e., microorganisms release colored metabolites from the cell). Also, a pink stain can be the result of contamination with microbes (e.g., Sterptoverticillium reticulum). White and black discolorations have also been observed.

2. Effect on electrical properties

Changes in electrical properties, especially insulating power, may be a result of microbial attack. This phenomenon is often caused just by the settlement of microbes on the plastic surface, without any discoloration of the material.

3. Deterioration of mechanical properties

This is the most serious consequence of microbiological degradation. Metabolization of the plasticizers by bacteria and/or fungi may result in brittleness, shrinkage, and loss of tensile strength. The breakdown of plasticizers into smaller molecules also enables microorganisms that are not capable of metabolizing the unbroken ones to grow.

4. Enhanced dirt uptake

The colonization of the plastic surface by microorganisms can cause increased roughness, resulting in a surface on which dirt can accumulate more readily.

5. Odor

As a result of microbial metabolism, unpleasant odors can develop from the production of amines, ammonia or hydrogen sulfide.

3.6 Volatile organic compounds (VOC's)

The "sick building syndrome" is an effect of many synergistic conditions of the indoor environment. The presence of irritants in indoor air is among these conditions, and one of its origins are the VOC's emitted from construction and furnishing materials that with time were changed in composition. That introduced synthetic materials into the home environment with unknown effects on indoor air quality (IAQ), and the health of the occupants. Unlike people in the workplace, a typical family of house occupants displays a wide range of ages, body weights, states of health, and toxicological susceptibilities that range from insensitive to hypersensitive. Furthermore, the level of activity varies considerably from highly active to sleeping over the period of exposure.

Moreover, when the worldwide energy crisis occurred in 1973, the cost per barrel of crude oil jumped suddenly from U.S. $3 to $30, subsequently the cost of heating for homes and offices went high. Similar situation is occurring nowadays, as the crude oil reaches $62 in 2005. In order to save energy, buildings became better insulated and structures more tighten, so that the exchange of heat and air between building and outside environment led to tight building syndrome (TBS). Which results in decreasing the number of air changes per hour (ACH) and increasing in concentration of the building contaminates that had been emitted indoors.

The concentrations of VOC's due to emission are usually quite low, but this does not necessarily mean that the risk to human health is low. It is believed that the sensory reaction of the human body to odorous substance in our surroundings is proportional to the logarithm of the exposure to the specific irritant [63], as well as, long period of exposure to lower concentrations may be more harmful than exposure to isolated peak concentrations [64].

The emissions testing costs are very expensive, which discouraged product manufactures from testing their products. Moreover, increasing ventilation rate is not always the proper way to solve this problem, as higher energy consumption and expensive investments in building HVAC systems could be the consequence.

Mrklie and Kovacic [65], investigate the kinetic parameters of the process of volatilization of DOP from plasticized PVC using isothermal thermogravimetry. The study assured that the process of volatilization of DOP from plasticized PVC proceeds according to the first order of kinetics, and depends on temperature as well as the initial concentration of the plasticizer. It was also found that the influence of temperature is much more important than that of concentration.

For evaporation-controlled emission, the emission rate increases with increasing vapour pressure. Therefore in principle, it can be expected that when the temperature increases the amounts of VOC`s increases. As observed by Sollinger et al. [66] when studied the impact of temperature and humidity on the VOC emission from textile floor coverings by determining the equilibrium concentration (zero air change) at elevated temperatures in the range 23-71°C and at relative humidity (RH) of 0% and 45%. In this case, the equilibrium concentration of VOC`s depends on vapor pressure of the compounds, which is temperature-dependent. This effect may be expected only for initial emission testing under both dynamic and indoor realistic concentration. When materials are ventilated for a long period, the VOC emission will decrease to a low level and become diffusion-controlled, since the increase of diffusion coefficients of the emitted VOC`s within the materials would be less than 10% for a temperature increase from 23 to 35°C, as established by Wolkoff [67] and confirmed by Fang et al. [68]; that under these circumstances the temperature effect becomes less significant. Also the study carried out by Fang et al. [68] concludes that compared with the previously determined strong impact of temperature and humidity on the perception of air quality, the impact of these factors on sensory emissions from building materials has a secondary influence.

DOP were measured in the interior of the new cars by TÜV Nord [69], the results showed that the DOP concentration was 1μg/m^3 below room temperature, while it reach up to 34 μg/m^3 at 65 °C. Wilke et al. [70] tested wallpapers containing DOP in test chamber of 1 m^3 for 28 days at 23°C, and 45% relative humidity; DOP was not detected within the range of detection limit of 0.35 μg/m^3; DOP were only measured up to 2 μg/m^3 when the temperature was increased to 40 °C. In another study, E. Uhde et al. [71] examined the emission behavior of different phthalic esters (i.e., DOP, DINP, Di-n-butyl phthalate (DBP), Diisobutyl phthalate (DIBP) and Dipropyl phthalate (DPP)) from PVC-coated wall coverings under standard room conditions in a test chamber. Phthalic esters emission was inversely proportional to the boiling point of each ester. DBP, which has a lowest boiling point among the tested esters, reached a maximum of 5 μg/m^3, while DPP and DOP, which have higher boiling point, reached about 1-2 μg/m^3.

Bodalal [72] studied the VOC`s emitted from a local vinyl-based tile as well as the floor adhesive. The results showed that the total VOC`s emitted from the vinyl adhesive is much higher than those emitted from the vinyl flooring. Moreover, the vinyl flooring headspace results do not show any of the compounds emitted from the floor adhesive. Furthermore, the research identified that vinyl flooring do not emit nonane, decane, undecane, or dodecane and refers their presence to the system assembly (i.e., vinyl, adhesive, and substrate). The major compounds for vinyl flooring were identified as follows: trichloroethylene, heptanone, octane, 4,7-methano-1H-indene, 1,4-cyclooctadiene, naphthalene, and that the total volatile organic compounds concentration (TVOC) is 0.59 mg/m^3. Table 3-4 list the different emitted VOC's for vinyl flooring, as determined by this researcher.

Table 3-4: Identified compounds in the vinyl-flooring tile [72]

Compound Name	Retention Time	Quality (Q) %	Concentration (mg/m^3)
Acetaldehyde	19.63	72	0.033
Methyl Alcohol	19.83	43	0.021
Acetone	20.05	11	0.041
Butanal	20.94	90	0.017
Propanenitrile, 2-methyl-	21.43	83	0.006
Trichloroethylene	22.75	99	0.059
Toluene	24.70	90	0.010
Hexanal	25.85	86	0.004
Cyclotrisiloxane, hexamethyl	26.11	72	0.003
5 3-Heptanone	29.30	95	0.016
Styrene	29.67	93	0.006
Benzene, (1-methylethyl)-	31.13	91	0.004
Hexanal, 2-ethyl-	32.56	64	0.007
Octane, 2,2,6-trimethyl-	32.71	64	0.008
Bicyclo[2.2.1]hept-2-ene, 5-ethyl-	33.57	90	0.002
4,7-Methano-1H-indene, 3a,4,7,7a-tetr	35.83	83	0.020
Limonene	36.41	56	0.006
Indane	36.77	81	0.012
Heptane, 2,2-dimethyl-	37.46	59	0.008
Hexane, 2,2,5-trimethyl-	37.96	64	0.016
1,4-Cyclooctadiene	40.89	64	0.003
Naphthalene	44.63	94	0.005

4

Research Program

4.1 Outline of the research program

Studies suggest that some plasticizers present in PVC flooring formulation can be a source of VOC's in buildings, leading to poor indoor air quality. This is mainly because these plasticizers are subjected to microbial degradation, which can lead to unsightly fungal growth in flooring products when exposed to humid environment. This research program is a contribution towards developing a new vinyl flooring formulation that possess the basic characteristics of the exciting flooring product, as well as better resistance to microorganism attack, and able to provide a safer indoor environment with higher quality.

The new flooring formulations are different from the existing ones due to:

- Different type of plasticizers;
- Partial replacement of vinyl polymer (20 phr) with lignin.

The function of lignin in rendering wood to resist biodegradation was discussed earlier in the literature review, and the reason for utilizing other plasticizers instead of DOP will be discussed later. Fungi have been shown to produce enzymes that are capable of breaking ester linkages, and they can metabolize the fragment molecules produced. Studies have shown that there are significant differences in the stabilities of different plasticizers. The relative susceptibility to microbial attack is influenced, like the susceptibility to hydrolysis, by steric factors, which dictate the strength of the ester group. In general, linear structures are less resistant to fungal esterase than branched structure.

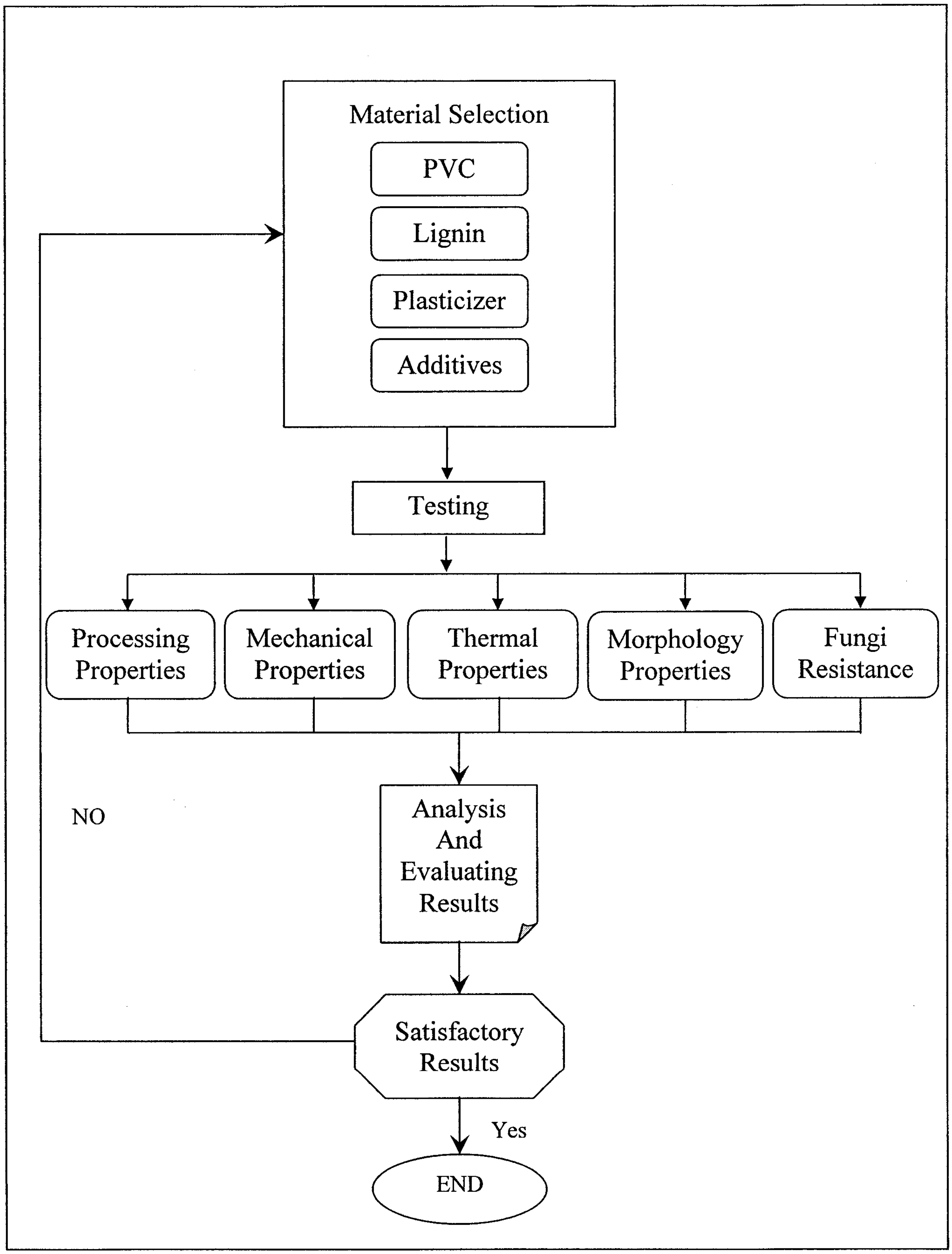
For this reason, one of the objectives of this study is the development of new flooring formulations with other plasticizers that have chemical composition different from that of common dialkyl phtathaltes. Taking into account that in the new formulations the vinyl polymer should be partly replace with lignin, several criteria were into consideration in selecting the new plasticizers:

- Chemical composition;
- Compatibility and efficiency to vinyl polymers (PVC homopolymer, VC-VAc copolymer);
- Compatibility and efficiency to different lignins.

For the first two criteria the literature data provides lot of information, for the third one the literature data are inexistent and some preliminary work were undertaken for finding some of these particular plasticizers. There are several theoretical techniques for assessing the compatibility of a plasticizer with a particular polymer. These include the

Hildebrand solubility parameter δ. The solubility parameter is generally a useful guide in predicting compatibility. Frequently, a polymer will be compatible with a plasticizer if the two have solubility parameters that do not differ more than $\pm$ 1.5 $(\text{cal/cm}^3)^{1/2}$. The solubility parameters of lignins are high and quite close to those of both vinyl polymers as shown in section 4.2.2. The chemical composition and compatibility of the selected plasticizers to vinyl resin was another criterion in this study (i.e., solubility parameters for the different selected plasticizers were approx. 10 $(\text{cal/cm}^3)^{1/2}$ corresponding to that of PVC resins 9.7 $(\text{cal/cm}^3)^{1/2}$). Also, the plasticizer efficiency in lowering the Tg of the polymer was another considered criterion. As the extent of Tg reduction can be related to the magnitude and mode of changes in the polymer chains mobility.

The plasticizer concentration used within this research was initially examined and set on 35 phr as discussed later in section 4.6. Consequently, mixtures of different lignins with 35 phr of three plasticizers corresponding to the first two criteria were prepared by heating. The processing temperature and the extent of Tg reduction was determined by DSC as will be discussed in section 5.1. The methodology that will be followed in achieving the research objectives could be divided into three main stages. These stages are material selection, testing, and analysis of results as shown in the following schema.


Material Selection
PVC
Lignin
Plasticizer
Additives
Testing
Processing Properties
Mechanical Properties
Thermal Properties
Morphology Properties
Fungi Resistance
NO
Analysis And Evaluating Results
Satisfactory Results
Yes
END

A description of the physical and chemical properties of the used polymers, lignins, plasticizers, additives and filler, is given in this section as well as the typical existing formulations of different vinyl flooring materials from which the basic formulation was chosen. The evaluation of various formulations was carried out using processibility and tensile test results, in conjunction with DSC and FTIR analysis. In addition, their morphology was evaluated by optical microscopy.

All the tests were done for each control specimen formulated with different plasticizers and for the respective blends 20 phr of vinyl polymer was replaced with different types of lignin. In addition, the test specimens were inoculated with a mixture of five fungi and incubated for 28 days at 28 °C and 95% relative humidity (necessary conditions for fungal growth). Thereafter, they were examined and rated for fungal growth. The results obtained for PVC homopolymer formulations are given in section 5.2. The VC-VAc copolymer is shown in section 5.3, and a comparison between both resins in section 5.4.

Based on the concluded results from the above mentioned sections, a detailed study for the different formulations resistance to fungi attack was carried out as shown in section 5.5. Following, an evaluation study for the mechanical properties of aged formulations are presented in section 5.6. Finally a comprehensive study of the total volatile organic compounds (TVOC) along with a list of the identified VOC`s and their concentrations are presented for the different formulations.

4.2 Materials

4.2.1 PVC resin

4.2.1.1 PVC homopolymer

The synthetic polymer used is poly (vinyl chloride) homopolymer (OxyVinyls 185), in a powder form for flooring, supplied by OxyVinyls LP, Dallas, Texas. It has the following characteristics: a K value of 56 ($\overline{Mw}$ 38000), solubility parameter (δ) of 9.7 (cal/cm^3)$^{1/2}$ [73], specific gravity of 1.4, the Tg as determined by DSC in our laboratory is 85.5 °C.

4.2.1.2 VC-VAc copolymer

The synthetic polymer used is Oxy 1810, a VC-VAc copolymer supplied by Occidental Chemical Corp. (Dallas, Texas). It is a solid white powder with the following characteristics: K value of 57, $\overline{Mw}$ 54,000, $\overline{Mn}$ 26,000, specific gravity of 1.37, and VAc content of 9.7%.

4.2.2 Lignin

The main lignin used is an organosolv type produced by Alcell Technologies Inc. (Miramachi, NB), which is characterized by: softening temperature (ring and ball, ASTM E28) of 145 °C, and medium particle size between 20 and 40 μm as determined by the manufacturer, and will be referred to as Alcell.

Indulin AT is a purified form of kraft lignin (softwood) and is completely free of hemicelluloses. It is produced by Westvaco Chemicals. (Charleston Heights, USA), which is free-flowing brown powder, its lignin dry content is 97%, characterized by: 5%moisture content, 3% ash (on dry basis), and bulk density 26, 32 loose and packed respectively, and will be referred to as Indulin.

Tomlinite lignin is also purified from kraft lignin (hardwood); the properties of the different lignins used are summarized in Table 4-1.

Table 4-1: Principle properties of lignins

Characteristics	Alcell	Indulin	Tomlinite
Number molecular weight $\overline{Mn}$	800 – 900 *	1858 [75]	650 [76]
Weight molecular weight $\overline{Mw}$	> 2000*	7050 [75]	2800 [76]
Polydispersity $\overline{Mw}/\overline{Mn}$	2.22	3.79	4.3
Specific gravity	1.27 *	1.3 *	1.3 [77]
Average particle size (μm)	16 *	8 [72]	16 [77]
pH value*	4	6.5	6
Solubility parameter, δ $(cal/cm^3)^{1/2}$	13.7 [74]	≅10 [78]	≅10 [78]
Glass transition temperature, Tg (°C)**	97	142	133

* Producers' data
** As determined by DSC in our laboratory

4.2.3 Filler

The calcium carbonate ($CaCO_3$) used is Pulpro 10, supplied by Omya Ltd. (St. Armand, Quebec), which is characterized by: specific gravity of 2.71, mean particle size of 10 microns, and it contains 95% $CaCO_3$, 2% $MgCO_3$, 3% acid insoluble. This grade is often used in PVC-based floorings; due to its finer particle size it yields better physical properties. The particle size distribution is shown in Figure 4-1.

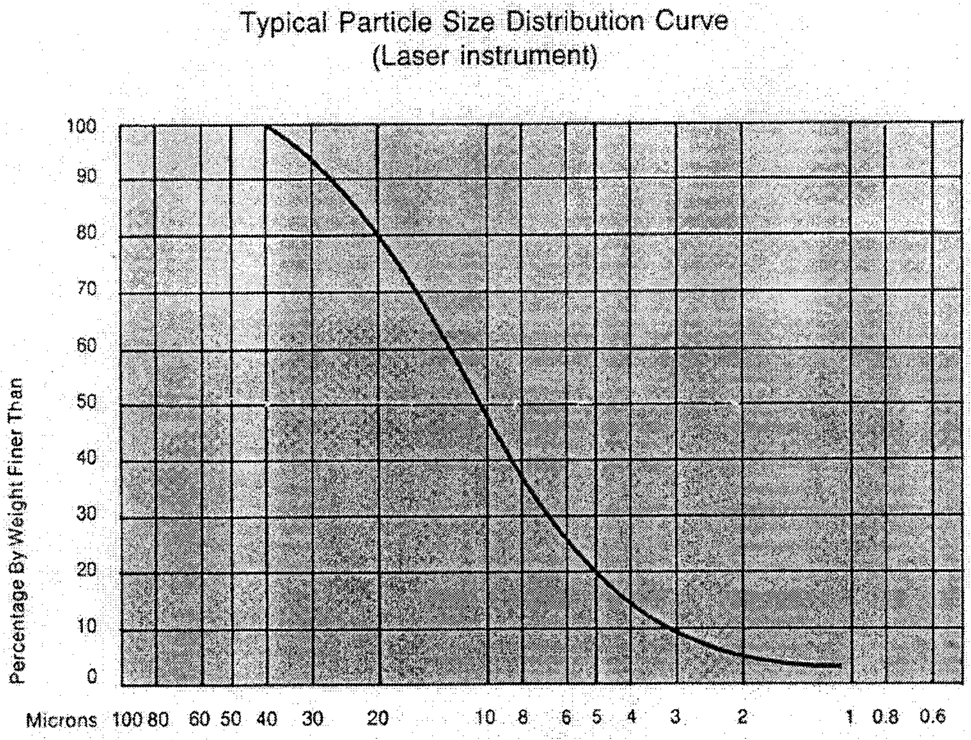


Figure 4-1: Typical particle size distribution of Pulpro 10 [79]

4.2.4 Plasticizers

The plasticizers used in the research study are presented on Table 4-2. Their principal characteristics are listed there after.

Table 4-2: Plasticizers used

Plasticizer / Trade Name	Abbreviation	Supplier
Di-octyl-phthalate	DOP	Fisher scientific, Ottawa, ON
Diethylene glycol dibenzoate / Benzoflex 2-45	2-45	Velsicol, Rosemont, IL
Tricresyl phosphate / Lindol	Lindol	Akzo Nobel, Dobbs Ferry, NY
Alkyl sulfonic acid ester of phenol	Mesamoll	Bayer Corp., Pittsburgh, PA

4.2.4.1 Di-octyl-phthalate (DOP):

DOP is the most PVC industry general purpose plasticizer due to its long use history and excellent balance of properties in non-damaging applications. Its chemical structure is presented in Figure 4-2, while its chemical and physical properties are summarized in Table 4-3.

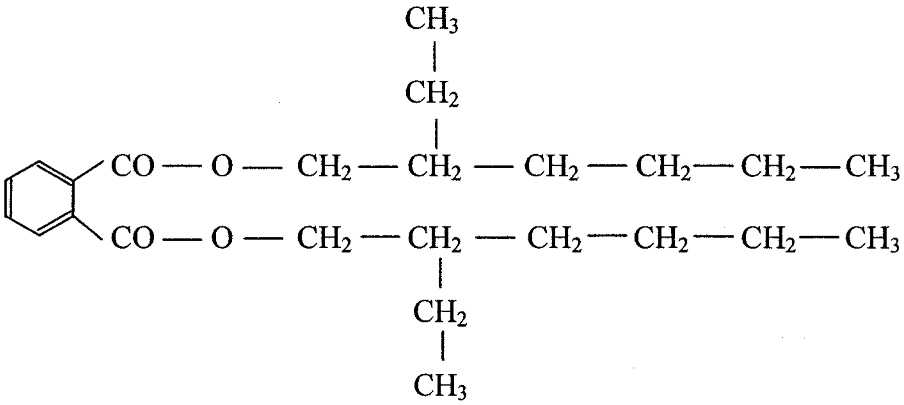


Figure 4-2: DOP chemical structure

Table 4-3: DOP physical and chemical and properties [80]

Characteristics	DOP
Molecular formula	$C_{24}H_{38}O_4$
Molecular weight	390.57
Physical state	Liquid
Color	Colorless to yellow oily liquid
Odor	Very slightly aromatic
Specific gravity [20/20 °C]	0.986
Viscosity [mPa.s at 25°C]	82
Boiling point [°C at 4 mm Hg]	230
Pour point [°C]	-47
Solubility parameter, δ [cal/cm^3] ^{½}	8.23
Solubility in water [mg/liter]	0.23 – 0.34
Glass transition temperature, Tg [°C]*	-80.5

* As determined by DSC in our laboratory

4.2.4.2 Di-ethylene glycol di-Benzoate (Benzoflex 2-45)

Benzoflex 2-45 chemical structure is presented in Figure 4-3, while its chemical and physical properties are summarized in Table 4-4.

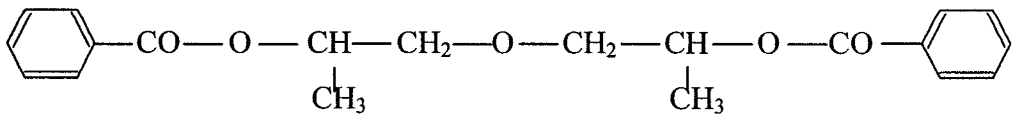


Figure 4-3: Benzoflex 2-45 chemical structure

Table 4-4: Benzoflex 2-45 physical and chemical properties [81]

Characteristics	2-45
Molecular formula	$(C_6H_5CO_2CH_2)_2O$
Molecular weight	314.4
Physical state	Liquid
Color	Clear colorless
Odor	Mild ester
Specific gravity [20/20 °C]	1.178
Viscosity [mPa.s at 25°C]	65-66
Boiling point [°C at 5 mm Hg]	240
Pour point [°C]	28
Solubility parameter, δ $[cal/cm^3]^{1/2}$	10.1
Solubility in water [mg/liter]	38.3 at 30°C
Glass transition temperature, Tg [°C]*	-52

* As determined by DSC in our laboratory

4.2.4.3 Tricresyl phosphate (Lindol)

Lindol chemical structure is presented in Figure 4-4, while its chemical and physical properties are summarized in Table 4-5.

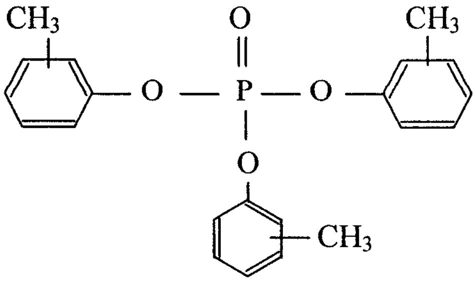


Figure 4-4: Lindol chemical structure

The principle reason for using phosphate ester plasticizers is to enhance the flame retardancy of flexible PVC. Phosphates are used in clear flexible fire retardancy applications in which pigmenting solids can not be used.

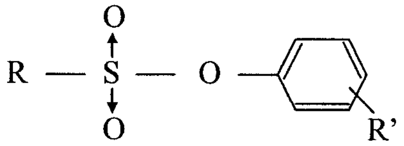
Table 4-5: Lindol physical and chemical properties [82]

Characteristics	Lindol
Molecular formula	$C_{21}H_{21}O_4P$
Molecular weight	368.4
Physical state	Liquid
Color	Colorless
Odor	Very slightly aromatic
Specific gravity [20/20 °C]	1.17
Viscosity [mPa.s at 25°C]	67
Boiling point [°C at 4 mm Hg]	248
Pour point [°C]	-28
Solubility parameter, δ [cal/cm^3]^{½}	9.86
Solubility in water [mg/liter]	0.36
Glass transition temperature, Tg [°C]*	-57.6

* As determined by DSC in our laboratory

4.2.4.4 Alkyl sulfonic acid ester of phenol (Mesamoll)

Mesamoll is characterized by outstanding gelling capacity with a large number of polymers including PVC and polyurethanes, enabling the reduction of processing temperatures and processing times. Possess high saponification resistance, especially when compared to DOP, outstanding resistance to weathering and light. Mesamoll chemical structure is presented in Figure 4-5, while its chemical and physical properties are summarized in Table 4-6.



Where: R = $C_{15}H_{31}$, R' = H and CH_3

Figure 4-5: Mesamoll chemical structure

Table 4-6: Mesamoll physical and chemical properties [83]

Characteristics	Mesamoll
Molecular formula	$C_{15}H_{31}SO_3C_6H_5$
Molecular weight	368.06
Physical state	Liquid
Color	Clear, slightly yellowish
Odor	Very slightly aromatic
Specific gravity [20/20 °C]	1.03-1.07
Viscosity [mPa.s at 25°C]	95-125/20°C
Boiling point [°C at 9.75 mm Hg]	200
Pour point [°C]	≤ -15 (setting point)
Solubility parameter, δ [cal/cm^3]$^{1/2}$	~ 10
Solubility in water [mg/liter]	None
Glass transition temperature, Tg [°C]*	-68.2

* As determined by DSC in our laboratory

All the selected plasticizers used in this research are commercial products that are compatible with PVC homopolymer and VC-VAc copolymer.

4.2.5 Lubricants

4.2.5.1 Calcium stearate ($CaSt_2$)

$CaSt_2$ lubricant grade L-155, obtained from Blachford Ltd. (Mississauga, ON) was used. Its chemical and physical properties are summarized in Table 4-7.

Table 4-7: Physical and chemical characteristics of $CaSt_2$ [84]

Molecular formula	$Ca(CH_3(CH)_{16}COO)_2$
Mean molecular weight	607
Physical state	Fine powder
Color	White to yellowish white
Melting point [^oC]*	155 - 165
Bulk density [mg/liter]	0.16 – 0.38
Solubility in water	0.2
Typical particle size % pass through, 300 mesh	100

* As determined by DSC in our laboratory

Calcium stearate is not only a lubricant but also has a reasonable heat-stabilizing action, and a relatively little light-stabilizing effect. Its non-toxic character promotes certain applications such unplasticized PVC compositions for potable-water pipes in France, as well as bottle formulation and toys.

4.2.5.2 Paraffin wax

A paraffin wax based lubricant commercially known as Marklube 367, obtained from Crampton Vinyl Additives GmbH, Germany was used. It has limited compatibility with PVC and therefore shows a distinct external lubricating action [80]. Its chemical and physical properties are summarized in Table 4-8.

Table 4-8: Physical and chemical characteristics of Paraffin wax [85]

Physical state	Fine powder
Color	Slightly yellow
Melting point [°C]	55 – 67
Bulk density [mg/liter]	0.48 – 0.52
Density [g/cm^3]	0.89 – 0.93
Solubility in water	< 0.1

4.2.6 Heat stabilizers

4.2.6.1 Dibutyltin dilaurate (DBTL)

DBTL was used as a heat stabilizer, obtained from Sigma-Aldrich Canada Ltd. (Mississauga, ON). Its chemical and physical properties are summarized in Table 4-9.

Table 4-9: Physical and chemical characteristics of DBTL [86]

Molecular formula	$(C_4H_9)_2Sn(OOC(CH_2)_{10}CH_3)_2$
CAS number	77-58-7
Relative molecular mass	631.6
Physical state	Oily liquid
Color	Yellow
Melting or freezing point [°C]	22 – 24
Boiling point or range [°C at 9.75 mm Hg]	205
Specific gravity [density]	1.1
Solubility in water	None

DBTL is classified as a di-organotin compound that is known as a non-toxic additive. Two-thirds of the global consumption of organotin compounds is used in heat stabilizing of PVC as reported by the agency for toxic substances and diseases registry (ASTDR) [87]. Its particular importance lies in its outstanding ability to preserve the clarity and the weather-ability of PVC as well as providing excellent heat stability not only when PVC is being processed but also in subsequent service. Also, it is used as a lubricant for its good gelling properties and its suitability for long time processing at high temperatures.

4.2.6.2 Butyltin mercaptide/caboxylate

It was obtained from Crampton Vinyl Additives GmbH, Germany. It is not only used as a heat stabilizer at high processing temperatures but also as a foaming catalyst (Kicker) in rigid and plasticized PVC. Has very good compatibility with PVC, and gives highly transparent finished articles [88]. Its chemical and physical properties are summarized in Table 4-10.

Table 4-10: Physical and chemical characteristics of Butylin mercaptide/caboxylate [88]

Physical state	Liquid
Color	Clear
Boiling point or range [^{o}C]	> 250 at 1.013 kPa
Specific gravity [density]	1.13-1.17
Solubility in water [mg/liter]	< 0.1

4.2.7 Antimicrobial

Sanitized PL 21-60 was used as an antimicrobial, produced by Clariant Huningue S.A. Switzerland. It is a plastisol containing a pyrithyon zinc compound. Its chemical and physical properties are summarized in Table 4-11.

Sanitized PL 21-60 does not contain arsenic, cadmium, mercury or lead and for that it is considered safe for people and environment. Its activity on the cell disrupts the metabolic process of microorganisms and thus interrupts their ability to function, grow, and reproduce [89].

Table 4-11: Physical and chemical characteristics of Sanitized PL 21-60 [89]

CAS number	13463-41-7
Physical state	Plastisol
Color	Beige
Flash point [°C]	> 240
Boiling point or range [°C]	253-257
Specific gravity [density]	1.15-1.21
Solubility in water	Partly soluble

4.3 Formulation

Typical formulations for PVC flooring are summarized in Table 4-12. Among these formulations, formulation C will be our aim in this research, with some modifications to decrease the formulation complexity, as this one is widely used among the others for its cost-performance value, as it possess less plasticizers and high filler loading.

All the composites were formulated with 100 parts per hundred parts (phr) polymer, 200 phr $CaCO_3$; 35 phr plasticizer (DOP for comparative purpose, Lindol, Benzoflex 2-45, Mesamoll), 3 phr dibutyline dilaurate (DBTL) as the heat stabilizer, and 1.5 phr calcium stearate ($CaSt_2$) as a lubricant.

The PVC controls and PVC-L blends were prepared for each plasticizer at 35 phr plasticizer concentration. In the PVC-L blends L replaced 20 parts of PVC proportions.

Table 4-12: Typical formulations for some PVC flooring products [90]

Ingredients	Formulations, parts by weight per 100 parts resin				
	A	B	C	D	E
PVC resin	100	100	100	100	100
Plasticizers	30	60	30	35	40
Epoxidized oil	5	5	4	5	-
Processing aid	-	-	-	-	8
Stabilizers	2.5	2	2	3	2
Fillers or pigments	-	30	210	70	640
Blowing agent	-	5	-	-	-

A: Clear coat for rotogravure flooring;

B: Foam coat for rotogravure flooring;

C: Filled wear layer for inlaid vinyl flooring and vinyl tile;

D: Homogeneous sheet flooring;

E: Vinyl composition tile.

It is interesting to note that from all tested plasticizers DOP has the lower solubility parameter, hence the lowest efficiency in plasticizing lignins. It is known that the solubility parameter is generally a useful guide to predict compatibility. Frequently, a polymer will be compatible with a plasticizer when both of them have solubility parameters that do not differ by more than ± 1.5 $(cal/cm^3)^{1/2}$ [15].

4.4 Experimental methodology

The components of each PVC control and PVC-L blends were weighted, the components in powder state were mixed separately in a vessel, and the liquid components were mixed in another vessel. Then the powder was added to the liquid while mixing for a standard period of time. Subsequently, the formulations were prepared by melt mixing for 8 min at 140 °C for those with copolymer and at 145 °C for those with homopolymer, at a rotor speed of 65 rpm in a Haake Rheomix 600 equipped by roller blades, and with a torque rheometer for the measurement of the mix torque, as well as with thermocouple for continuous measurements of the melt temperature. The mixer was electrically heated and air-cooled. At all mixes, the recorded torque showed that an equilibrium torque plateau was reached about 2 min before the end of the mixing time.

After melt mixing, the batches were grounded to a size of 2-3 mm, while they were still warm, then weighted and placed on the desired mold. The whole assembly of mold was placed between platens of the press, and the mix was molded by compression in a Carver laboratory press equipped with temperature controllers at 155 °C for 6 min; then a pressure of 4 MPa was applied at the same temperature for 2 min.

Afterwards, the molded sheets were cooled from molding temperature to room temperature at a cooling rate of 10 °C/min and under 4 MPa pressure. Those were the procedure carried for preparing sheets with a rectangular shape of 12.7 cm in width, 7 cm in breadth, and 0.15 cm in thickness.

The 1.5 mm thick sheets were cut with a cutting die in shoulder shaped specimens in accordance with ASTM D638-99 type M-III [91]. The tensile strength at yield and break were measured using an Instron universal machine at a cross head speed of 2 mm/min (unless indicated other wise) at a temperature of 23 ± 2 °C. All the specimens for tensile strength were tested one week after their preparation. They were conditioned at 23 ± 2 °C and 50 ± 5 % relative humidity for 48 hr prior testing. The indicated values are an average of at least five determinations. The coefficients of variation inferior to 10 % were taken into consideration for each set of specimens tested.

4.5 Testing

4.5.1 Processibility

The forces involved in mixing a highly viscous melt, which are measured as torque acting on the rotors, can be correlated with the melt viscosity [92]. The Haake Rheocord-M 300 attached to the Rheomix 600 is used for continuous measurements of mixing torque. The torque reading value was then taken as a percentage and multiplied by the machine scale factor. The indicated torque values represent the equilibrium torque.

4.5.2 Tensile strength

The tensile test was performed in accordance with ASTM D638-99 [91], using Instron Universal Testing Machine, model 1125. The machine is of cross-head movement type. It consists of a fixed member carrying one grip at the bottom and a movable one carrying a second grip on the top of it. Self-aligning grips are employed for holding the test specimen between the fixed and movable members to prevent alignment problems. Controlled velocity is the drive mechanisms to control the rate of applied load, as well as a load indicator capable of showing the total tensile load are used. The speed rate was 2 mm/min (unless indicated other wise). Tensile strength at 2% strain, yield point, break point, and total elongation at break were recorded. Modulus of elasticity at 2% strain, tensile strength at yield and break were calculated.

4.5.3 Differential Scanning Calorimetry (DSC)

This is a thermal analysis, in which the quantity of energy absorbed or evolved by the sample, is measured. Consequently, the blend's thermal behavior can be determined. This is achieved by heating a sample and an inert reference material and measuring the difference in energy required to heat both of them over a predetermined time-temperature program. Originally, constant energy input is required to heat both samples at a constant rate, then at a transition point, the sample requires either more or less energy than the reference, depending on whether the change is endothermic or exothermic. The thermal properties of raw materials and the blends were measured using a Dupont 2010 Differential Scanning Calorimeter. The DSC data were analyzed with Dupont DSC Universal Analysis Program Version 4.31E in accordance with ASTM 3417-99 [93].

Samples of about 20 mg weighed with accuracy of ± 0.002 mg were punched from 1.5 mm thick sheets and tested for each blend. All samples were heated from room temperature to 160 °C at a heating rate of 20 °C/min and kept isothermally at 160 °C for 10min to ensure the complete melting of the crystals. Afterwards, at the same rate, they cooled from 160 °C to room temperature then heated again from -50 °C to 160 °C. The indium calibrating sample was scanned at the same heating rate of 20 °C/min, and all the scans were done under nitrogen atmosphere at a flow rate of 20 ml/min. The reported glass transition temperature (Tg) values were estimated from the second run. The peak temperature in the melting range as specified in ASTM D3418-99 [94] represents the temperature of melting, or melting point.

4.5.4 Fourier Transform Infrared Spectroscopy (FTIR)

In this test a beam of electromagnetic radiation attempts to pass through a chemical substance. Accordingly, the beam will be partially transmitted. The remainder is reflected or absorbed in varying degrees, depending on the substance and the frequency of radiation. The absorbed energy is transferred to the atoms or molecules in the sample substance, and as a result, the particles are promoted from lower to higher energy state [95]. Light atom groups absorb at high frequencies, while heavy groups are characterized by low frequencies. Similarly, tightly-bound groups will vibrate at higher frequencies than loosely-bound groups.

The infrared (IR) spectra were recorded with a Fourier transform IR (FTIR) spectrophotometer Magna 550 Nicolet. Samples of 0.0210 g PVC or PVC-Lignin blends resulted from melt compound were precisely weighed (± 0.001 g) and then processed at a temperature of 190°C, under a force of 0.75 ton into a film of 13 mm diameter with a thickness of 50 μm, using a Spectra-Tech universal film maker. The thickness of the films was carefully controlled in order to ensure a uniform thickness for all the specimens. The films were IR analyzed one week after their preparation and conditioned at 23 ± 1 °C and 50 ± 5 % relative humidity. Prior to testing, the films were kept in a vacuum oven for 72 hrs to ensure the complete removal of water.

4.5.5 Gas Chromatography (GC)

4.5.5.1 Sample description

Vinyl sheets were obtained as stated earlier in the experimental procedure with a rectangular shape of 12.7 cm in width, 7 cm in breadth, and 0.15 cm in thickness, and a total surface area of 183.7 cm^2 (include top, bottom surfaces and edges). Immediately, thereafter, each individual sample was placed in a head space bag which is a chemically inert, non-permeable bag, able to contain VOC's with minimum loss. The type used was toddler bag of 0.6 liter capacity, which is suitable for headspace analysis for dry materials, equipped with two plastic valves, to facilitate the gas assemblage directly from the bag. Consequently, each bag was filled with 500 cm^3 of Helium (He), an inert carrier gas, and the samples were maintained at 23 ± 1 °C and 50 ± 5 % RH. The bags were left for a period of 5 days to allow the VOC's in the specimens to reach equilibrium. The headspace testing was carried out in accordance with ASTM D5116-90 [96].

4.5.5.2 Air sampling

Each bag was connected directly using the two valves to the Flame ionizing detector (FID), which generates responses for carbon-containing compounds. FID is considered as a universal, non-selective detector for measuring organic compounds, by producing a flame that will increase the number of ions when contaminates pass through. The FID is connected to Hewlett Packard 5890 Series II Gas Chromatograph.

Subsequently, the bag content is directly swiped and transferred by Helium gas at 40 cm^3/min (i.e., sampling rate) for 3 min (i.e., sampling duration) to a cryogenic condenser (Tekmar 14-6000 modified for on line injection). The condensing medium used is glass beads that are cooled with liquid nitrogen to -100 ^{o}C. This allows all of the sampled helium to condense. During sample condensation, a programmed moisture removal cycle (Moisture Control System – MCS within the Tekmar 6000) removes condensed water from the cryogenic process. The sample is than desorbed at 250 ^{o}C and transferred through a heated and insulated nickel tubing (200 ^{o}C) to a cryogenically cooled (-100 ^{o}C) focuser (Tekmar Cryofocusing Module 14-2530). Once the sample is focused at the tip of a deactivated thin-wall treated stainless steel pre-column (Restek MXT-Guard ID 0.53 cat. 70046), the cryogenic focuser releases the sample by heating the tip to 250 ^{o}C, and hence injecting the sample into a fused silica capillary column (Supelco-VOLCOL 105m x 0.53 mm x 3 μm film), producing a proportional current to each compound of the sample. The current is than translated into a peak using the Chem. station software interface.

The separation of the sample is achieved by setting the GC oven program initially at 30 °C for 2 min than ramping to 180 °C at a rate of 5 °C/min, and left steady at 180 °C for 2 min, with a total duration time of 34 min, setting the Helium (He) flow rate to the column at 10 cm^3/min To ignite the FID, a flow rate of Hydrogen (H_2), Air, and Nitrogen (N_2) gas was set at 30, 300 and 30 cm^3/min respectively.

4.5.5.3 Mass Spectrography (MS)

The Mass Spectrograph is an analytical instrument consisting of three major components: an ion source that ionizes the molecules; a separator that separates ions according to their mass/charge units; and a detector that records the mass of fragments in mass/charge (m/Z) unit form. It is always connected to GC and known as GC/MS system.

4.5.6 Fungi attack test

In order to test the resistance of PVC control and blends to fungi attack, we prepared a nutrient-salts agar by dissolving in 1 liter of water 9 different designated amounts of reagents, as presented on Table 4-13. Then a mix of spore suspension of 5 different fungi (i.e., *Aspergillus niger* (ATCC #9642), *Penicillium pinophilum* (ATCC #11797), *Chaetomium globosum* (ATCC #6205), *Gliocladium virens* (ATCC# 9645) and *Aureobasidium pullulans* (ATCC #15233)) were mixed together as recommended by ASTM G21-2000 [97].

Table 4-13: Compositions of nutrient salts solutions and agar [97]

Compound	Abbreviation	Weight (g)
Potassium dihydrogen orthophosphate	KH_2PO_4	0.7
Magnesium sulfate	$MgSO_4.7H_2O$	0.7
Ammonium nitrate	NH_4NO_3	1.0
Sodium chloride	NaCl	0.005
Ferrous sulfate	$FeSO_4.H_2O$	0.002
Zinc sulfate	$ZnSo_4.7H_2O$	0.002
Manganous sulfate	$MnSO_4.H_2O$	0.001
Agar	-	15.0
Potassium monohydrogen orthophosphate	K_2HPO_4	0.7

Sets of samples similar with those used for the tensile test (i.e. shape and formulation) were prepared. Sufficient nutrient-salts agar was poured into sterile dishes to provide a solidified agar layer from 3 to 6 mm in depth; after the agar was solidified, the specimen was placed on the surface of the agar. Consequently, the dish surface was inoculated, including the surface of the test specimens, with nutrients using an atomizer, and then the dishes were covered. Subsequently, the inoculated test specimens were kept in an incubator at 28 °C and relative humidity 95 ± 2 % for 28 days. Thereafter, a visual examination followed by a microscopic study was carried out to confirm the fungi growth especially for the samples that were rated of traces or no growth, since non-sporulating growth might not be readily observed without the aid of a microscope.

At least two samples or more of the same formulation were examined in order to confirm the fungi growth rating. The fungi growths on the specimens' surface were rated in accordance to ASTM G21-2000 [97] as follows:

0	None	
1	Traces of growth	(less than 10%)
2	Light growth	(10%-30%)
3	Medium growth	(30%-60%)
4	Heavy growth	(60%-Complete coverage)

In order to evaluate the effect of fungi on the physical properties of the samples, they were immersed in an aqueous solution of mercuric chloride for 5 min, cleaned under tap water, air dried overnight at room temperature, and reconditioned at the standard laboratory conditions (i.e. 23 ± 1°C and 50 ± 2 % relative humidity) for 6 days. Considering that the fungi attack results in loosing the additives incorporated in the plastic formulations, the weight loss of the different samples were established. Also, the impact of fungal growth on the mechanical and thermal properties of the different formulations was studied to evaluate their bio-deterioration. The study on fungi growth was done for comparison purposes only and do not reflect the in-use conditions.

4.6 VC-VAc copolymer – lignin - plasticizer mixtures

This section [98] contains experimental results that were thought of as an introduction to evaluate the impact of different plasticizer (i.e., DOP, Benzoflex 2-45, Lindol, and Mesamoll) concentrations on VC-VAc copolymer and VC-VAc copolymer - Alcell polyblend. The different tested plasticizer concentrations were 35, 30 and 28 phr. In addition, and due to the efficiency of Benzoflex 2-45 and Lindol in affecting the different mechanical properties of both controls and blends, other formulations were prepared with 30 phr of several mixtures of these plasticizers. The composition of the plasticizer mixtures are:

- 0.25 parts Benzoflex 2-45 / 0.75 parts Lindol
- 0.5 parts Benzoflex 2-45 / 0.5 parts Lindol
- 0.75 parts Benzoflex 2-45 / 0.25 parts Lindol

4.6.1 Processibility

The amount and type of plasticizers have influences on controls and blends mixing equilibrium torque, as can be seen from Table 4-14. The plasticizer amount reduction is inversely proportional to the equilibrium torque (i.e., decreasing the plasticizers amounts from 35 phr to 30 phr increases the equilibrium torque), which is expected, due to the increasing association degree of VC-VAc copolymer macromolecules. Moreover, all VC-VAc copolymer - AL blends versus their controls exhibit a decreased equilibrium torque value, indicating a lower melt viscosity.

Table 4-14: Equilibrium torque of PVC controls and blends with 35 and 30 phr plasticizers

Plasticizer Type	Equilibrium Torque at 140 ± 1°C [m.g]			
	35 phr Plasticizer		30 phr Plasticizer	
	VC-VAc Control	VC-VAc – Alcell	VC-VAc Control	VC-VAc – Alcell
DOP	925	650	1075	900
2-45	1075	800	1150	1025
Lindol	1125	825	1250	1075
Mesamoll	950	750	1125	925

4.6.2 Thermal properties

The Tg values of VC-VAc copolymer controls and blends with 35, 30 phr plasticizer, as well as the blends with 28 phr plasticizer are shown in Table 4-15 A and B. Also in the same tables the differences in °C between the Tg of control at 35, 30 phr and the different formulations are presented and noted by ΔTg_{c35}, ΔTg_{c30} respectively. As well as, the differences between the Tgs of the blends with 30 and 28 phr plasticizer with respect to blend Tg at 35 phr and noted by ΔTg_{b35}. Data presented in Table 4-15 A and B point out that in comparison to respective controls (ΔTg_{c35}, ΔTg_{c30}) the Tgs of all blends decreased with few °C. Showing that the addition of lignin decreases the intermolecular hydrogen bonding between the VC-VAc copolymer macromolecules, resulting in increasing the plasticization effect.

In most of the cases the blends' Tg reduced values are not comparable with the differences between Tgs of controls plasticized with 35 and 30 phr plasticizer, depicting interactions between plasticizers and Alcell lignin. Moreover, the data show that Tg is inversely proportional to the plasticizer concentrations within all the tested formulations, as revealed by ΔTg_{c35} and ΔTg_{b30}. The Tg increase for both controls and blends, and varies as a function of plasticizer type.

Table 4-15: Tg of VC-VAc copolymer controls and blends; and ΔTg differences between the different VC-VAc copolymer controls and blends with 35 and 30 phr plasticizer concentrations and blends at 35 phr

A

Sample Identification	DOP				2-45			
	Tg [°C]	ΔTg-C35 [°C]	ΔTg-C30 [°C]	ΔTg-B35 [°C]	Tg [°C]	ΔTg-C35 [°C]	ΔTg-C30 [°C]	ΔTg-B35 [°C]
VC-VAc Control 35 phr plasticizer	20.7	-	-	-	22	-	-	-
VC-VAc Control 30 phr plasticizer	25.6	+4.9	-	-	28.2	+6.2	-	-
VC-VAc – Alcell 35 phr plasticizer	8.2	-12.5	-17.4	-	19.3	-2.7	-8.9	-
VC-VAc – Alcell 30 phr plasticizer	20.9	-0.2	-4.7	+12.7	27.1	-5.1	-1.1	+7.8
VC-VAc – Alcell 28 phr plasticizer	22.0	-1.3	-3.6	+13.8	27.7	-5.7	-0.5	+8.4

B

Sample Identification	Lindol				Mesamoll			
	Tg [°C]	ΔTg-C35 [°C]	ΔTg-C30 [°C]	ΔTg-B35 [°C]	Tg [°C]	ΔTg-C35 [°C]	ΔTg-C30 [°C]	ΔTg-B35 [°C]
VC-VAc Control 35 phr plasticizer	30.8	-	-	-	21.9	-	-	-
VC-VAc Control 30 phr plasticizer	35.4	+4.6	-	-	27.7	+5.8	-	-
VC-VAc - Alcell 35 phr plasticizer	25.1	-5.7	-10.3	-	13.7	-8.2	-14	-
VC-VAc - Alcell 30 phr plasticizer	29.4	-1.4	-6.0	+4.3	22.0	-0.1	-5.7	+8.3
VC-VAc - Alcell 28 phr plasticizer	30.0	-0.8	-5.4	+4.9	-	-	-	-

DSC thermograms for the second scan in the temperature interval between –20 and 140 °C for controls and blends formulated with 35 and 30 phr plasticizer reveal a single reproducible Tg which is an indication of the compatibility between the formulations components. Unlike the quite sharp and narrow glass transition range for the blends plasticized with 2-45, Lindol and in a lesser measure with Mesamoll, the Tg region of DOP plasticized blend was broad and less sharp indicating a certain degree of inhomogeneity at the molecular scale. It is interesting to note that from all plasticizers DOP has the lower solubility parameter, hence the lowest efficiency in plasticizing lignin.

When the first scan of DSC thermograms Figure 4-6 & 4-8 were examined, it could be seen that the specific relaxation behavior of VC-VAc copolymer controls at 35 and 30 phr plasticizer exhibited in most of the cases two distinct relaxation peaks located at quite different temperatures, confirming the mixtures heterogeneity. The apparent single broad transition observed in the second scan could be the result of two or more separate overlapping transitions that occurs in a large temperature range.

On the other hand, the blends thermograms Figure 4-7 & 4-9 shows a single Tg at 35 phr, and a shifting for the Tg towards higher values at 30 phr, which reveal the necessity of plasticizer level at 35 phr to reach the relaxation stage of the polymer chains eliminating the execs free void volume to approach the preferred or true equilibrium state of the system. In addition, Alcell lignin acted as a compatibilizer for some polyblends aiding to reach this equilibrium.

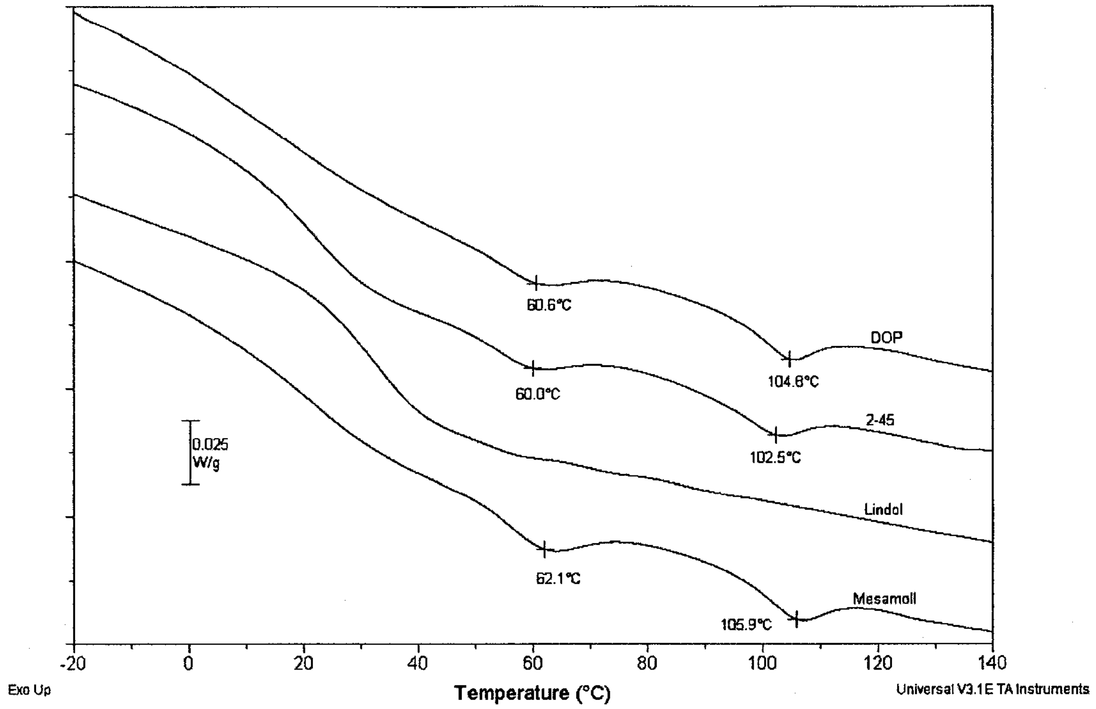


Figure 4-6: DSC thermograms [1st run] of VC-VAc controls with 35 phr plasticizers

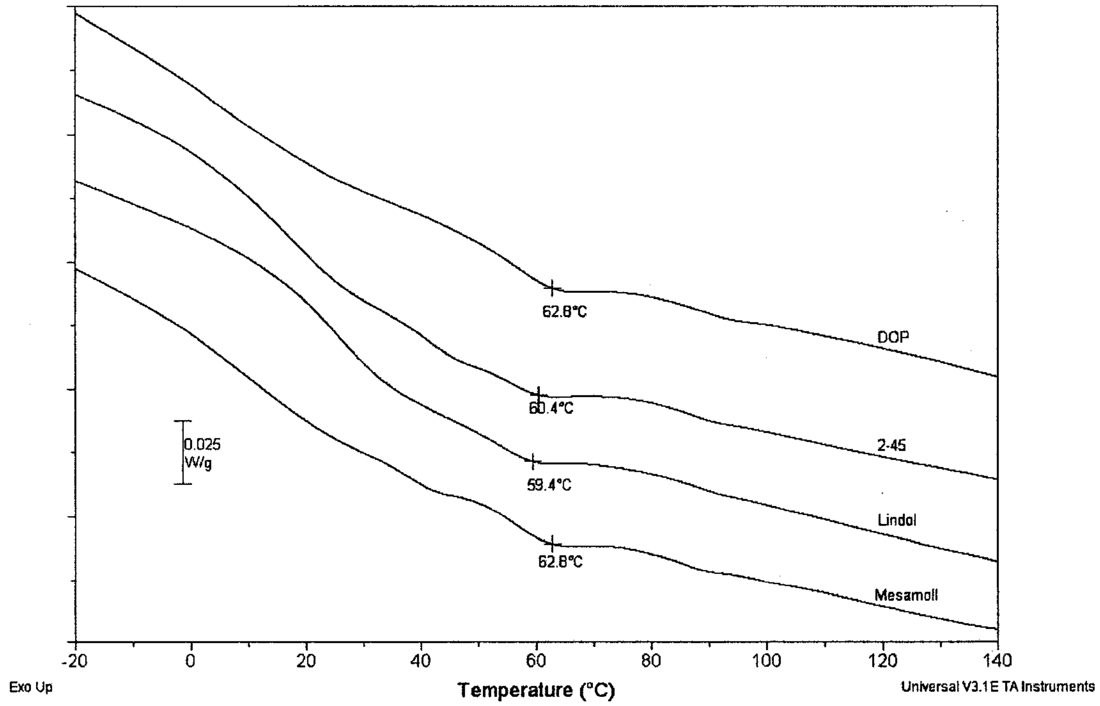


Figure 4-7: DSC thermograms [2nd run] of VC-VAc-AL blends with 35 phr plasticizers

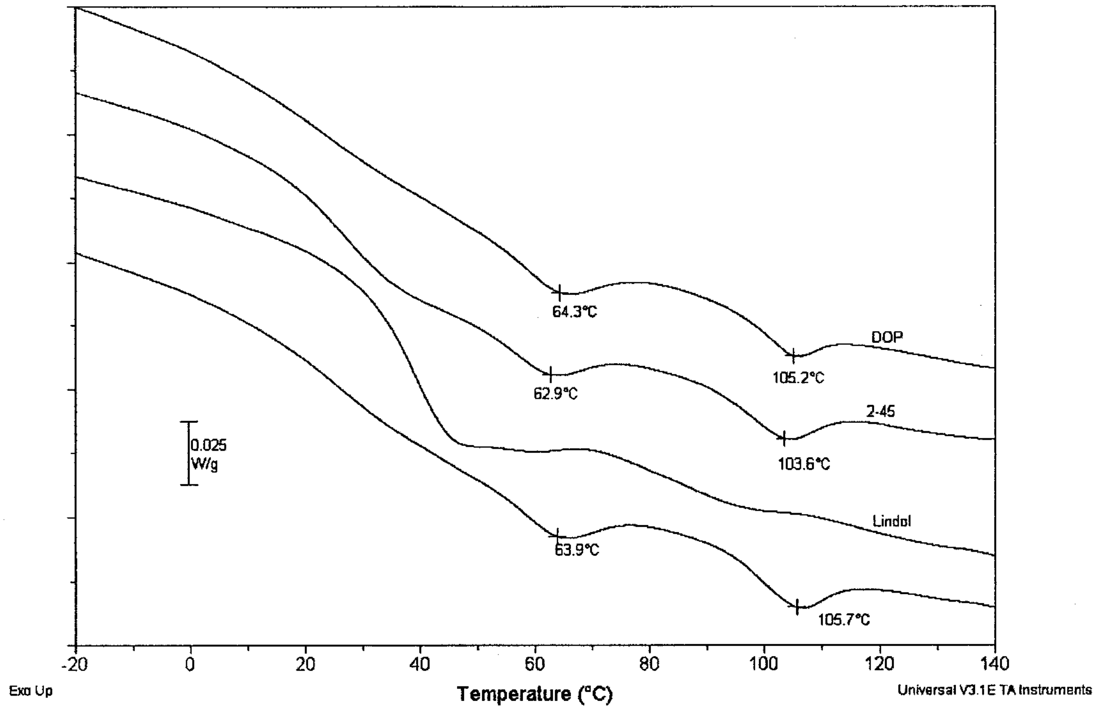


Figure 4-8: DSC thermograms [1st run] of VC-VAc controls with 30 phr plasticizers

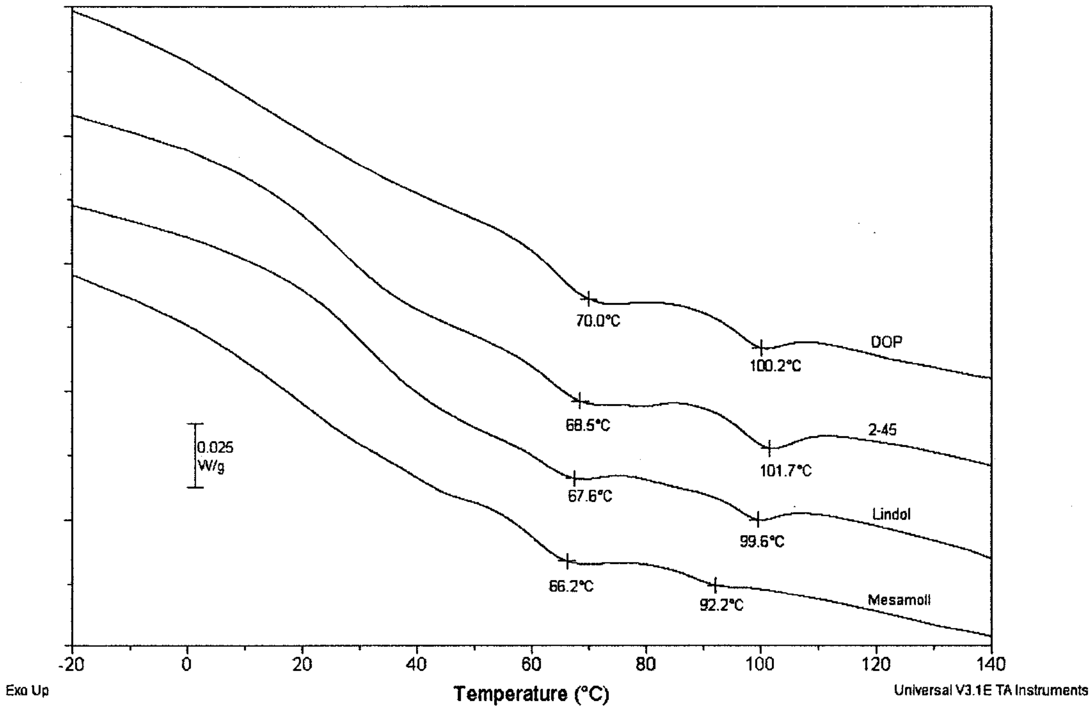


Figure 4-9: DSC thermograms of [2nd run] VC-VAc-AL blends with 30 phr plasticizers

The Tgs' of controls at 35 and 30 phr plasticizer concentrations agree quite well with Fox equation [99] as can be seen in Table 4-16. Control samples formulated with Benzoflex 2-45 show that the experimental data are about 10 and 8 °C lower than the calculated ones for 35 and 30 phr respectively. On the other hand, the blends experimental Tg values are always lower than the calculated ones, that elaborates the effect of plasticizers in lowering the degree of association of Alcell lignin macromolecules, and thus allowing them more molecular mobility at lower temperature than that of Alcell Tg. The calculated Tgs were computed as follows:

$$\frac{1}{Tg} = \frac{W1}{Tg1} + \frac{W2}{Tg2} + \frac{W3}{Tg3}$$

Where: W1, W2 and W3 are the different weight fractions of each component in the calculated formulation.

Tg1, Tg2 and Tg3 are the Tg corresponding to each component in Kelvin's (°K).

Table 4-16: Experimental and calculated Tg's of controls and blends as function of plasticizer type and concentration

Plasticizer Type	Tg [°C]							
	35 phr Plasticizer				30 phr Plasticizer			
	VC-VAc control		VC-VAc - Alcell		VC-VAc control		VC-VAc - Alcell	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
DOP	16.3	20.7	18.5	11.7	21.9	25.6	24.1	20.9
2-45	31.9	22	33.7	19.3	36	28.2	37.9	27.1
Lindol	28.8	30.8	30.6	25.1	33.2	35.4	36	29.4
Mesamoll	23.7	21.9	25.1	13.7	28.3	37.7	30.4	22

Where Calc.: Calculated data; Exp.: Experimental data

4.6.3 Mechanical properties

From the data presented in Table 4-17, it is clear that both the type and amount of plasticizer play a tremendous influence on the mechanical properties. The modulus of elasticity as well as the tensile strength at both yield and break increased by decreasing the amount of plasticizer used. On the other hand, as expected, the elongation increases with the increase of plasticizer amount. This is owed to the plasticizer role, by increasing its amount; it overcomes the intermolecular forces inside the matrix and facilitates the movements of macromolecules with respect to each other.

The trends for the mechanical properties are presented in Tables 4-18 and 4-19. The negative values represent the decreasing trend, in percentage, when VC-VAc - Alcell blends were compared with the corresponding results obtained from VC-VAc controls, and in between the same formulations when different plasticizer concentration is used, while the positive values represent the increasing trend. Due to the fact that the mechanical properties of the formulations are strongly influenced by the Tg, the decrease in Tg values of blends (ΔTg) with respect to the respective controls were restated. It should be also noted that the tensile test was carried using semi-computerized Instron machine.

The specimens were tested at room temperature (i.e., 23 ± 2°C) and as data in Table 4-17 show, the testing temperature was very close or above Tg for the formulations with 35 phr plasticizer and mostly below Tg for that with 30 phr plasticizer. Also it could be notice that the Tgs of the blends are always lower than that of respective controls.

Table 4-17: Mechanical properties of VC-VAc copolymers controls and blends relative to plasticizer type

Sample ID		Tg [°C]	Elastic Modulus [MPa]	Tensile Strength [MPa]		Elongation [%]
				Yield	Break	
DOP						
35 phr	VC-VAc Control	20.7	35.40	3.78	4.86	377
	VC-VAc - Alcell	8.2	16.32	3.55	3.27	335
30 phr	VC-VAc Control	25.6	89.71	4.66	5.47	319
	VC-VAc - Alcell	20.9	48.39	4.26	3.83	271
Benzoflex 2-45						
35 phr	VC-VAc Control	22	31.24	3.48	4.51	477
	VC-VAc - Alcell	19.3	46.46	2.42	3.14	487
30 phr	VC-VAc Control	28.2	92.09	4.47	5.24	394
	VC-VAc - Alcell	27.1	117.88	3.61	3.55	350
Lindol						
35 phr	VC-VAc Control	30.8	211.49	5.86	5.97	281
	VC-VAc - Alcell	25.1	98.33	3.65	3.94	362
30 phr	VC-VAc Control	35.4	279.42	8.60	6.82	208
	VC-VAc - Alcell	29.4	231.48	6.45	4.89	213
Mesamoll						
35 phr	VC-VAc Control	21.9	36.08	3.75	5.16	403
	VC-VAc - Alcell	13.7	25.51	3.40	3.52	342
30 phr	VC-VAc Control	27.7	89.59	5.11	5.99	332
	VC-VAc - Alcell	22	51.51	4.09	4.09	318

The tensile properties are highly dependent on the inter chain and inter molecular attractions. Above Tg, increasing molecular mobility leads to diminished bond strength by inter chain and inter molecular separation [100]. Consequently, modulus and tensile strength at yield and break should decrease and ultimate elongation should increase. These facts are well illustrated by the data reported in Table 4-18 where the changes of mechanical properties of controls and blends formulated with 35 phr plasticizer are presented, whose Tgs are very close or below the room temperature, in relation to the respective data of 30 phr plasticizer formulations, whose Tgs are mostly above room temperature. It is clear that the samples' mechanical properties variations can be easily correlated with their Tg reduction.

Table 4-18: Mechanical properties variations of VC-VAc copolymer controls and Alcell blends formulated with 35 phr plasticizer as percentage of their corresponding values formulated with 30 phr plasticizer

Sample ID		Elastic Modulus	Tensile Strength		Elongation
			Yield	Break	
VC-VAc Control	DOP	-60.5	-18.9	-11.2	18.2
	(2-45)	-66.1	-22.1	-13.9	21.1
	Lindol	-24.3	-31.9	-12.5	35.1
	Mesamoll	-59.7	-26.6	-13.9	21.4
VC-VAc - Alcell Blends	DOP	-66.3	-16.7	-14.6	23.6
	(2-45)	-60.6	-33.0	-11.5	39.1
	Lindol	-57.5	-43.4	-19.4	70.0
	Mesamoll	-50.5	-16.9	-13.9	7.5

On the other hand, comparing the mechanical properties of the blends to those of the respective controls, one can see that the variations are not always in correlation with Tg reduction. Data presented in Table 4-19 show that for blends formulated with DOP and Mesamoll which present appreciable Tg reduction, the modulus and both tensile strength at yield and break decrease and surprisingly the elongation at break decreases too. While the blend formulated with Benzoflex 2-45 shows a slight reduction in its Tg values associated with lower tensile stress at yield and break, elongation increase for 35 phr plasticizer formulation and surprisingly an increase too of its modulus. The only blends where the mechanical properties variation can be well correlated with Tg reductions are those formulated with Lindol.

Table 4-19: ΔTg and mechanical properties variations of Alcell blends formulated with 35 and 30 phr plasticizer as percentage of their corresponding VC-VAc controls

Sample ID		ΔTg [°C]	Elastic Modulus	Tensile Strength		Elongation
				Yield	Break	
35 phr plasticizer	DOP	- 12.5	-53.9	-6.1	-32.7	-11.1
	(2-45)	- 2.7	48.7	-30.5	-30.4	2.1
	Lindol	- 5.7	-53.5	-37.7	-34.0	28.8
	Mesamoll	- 8.2	-29.3	-9.3	-31.8	-15.1
30 phr plasticizer	DOP	- 4.7	-46.1	-8.6	-30.0	-15.0
	(2-45)	- 1.1	28.0	-19.2	-32.3	-11.2
	Lindol	- 6	-17.2	-25.0	-28.3	2.4
	Mesamoll	- 5.7	-42.5	-20.0	-31.7	-4.2

While, blends formulated with only 28 phr plasticizer led to less elastic materials without an appreciable improves of yield and break resistance as can be seen from Figures 4-11 to 4-13. The above data illustrate that the Alcell presence in blend formulations reduces its Tg and that the degree of Tg reduction is influenced by the plasticizer type and concentration. For all the blend formulations the Tg reduction is associated with reductions in the tensile stress at yield and break. It is also interesting to note that the reduction percentage of strength at break for all blends formulations are almost the same, which may be owed to the small-size of Alcell macromolecules ($\overline{Mw} \cong$800-900) as well as to its relatively high polydispersity.

The fact that in some blends the reduction of modulus was associated with reduction in elongation (DOP and Mesamoll plasticizers) and in others the increase in elongation was associated with an increase in modulus (Benzoflex 2-45 plasticizer) indicates that the properties of blends are strongly influenced by degree and mode of Alcell plasticization as well as its dispersion through the VC-VAc copolymer matrix.

It is known that lignin has different molecular weight fraction ranges that vary from low and medium fractions to high molecular weight fractions [33]. Also, that the behavior of formulation plasticized with Benzoflex 2-45 shows that the modulus of elasticity at both concentrations increased, while elongation increased at 35 phr and decreased at 30 phr plasticizer. One may conclude that Benzoflex 2-45 plasticizes mostly the low molecular weight fractions of Alcell that will act as a second plasticizer, pushing apart more the already plasticized VC-VAc copolymer chains, and thus enhance the elongation. The remaining high molecular weight fractions, well be in the glassy state and evenly distributed through plasticized VC-VAc copolymer matrix, in which they will act as reinforcing filler, thus enhancing its modulus. On the other hand Lindol plasticizes both the low and high molecular weight fractions of Alcell lignin, a fact that results in decreasing the modulus and increasing the elongation. This will be further studied and confirmed thoroughly thereafter [101].

PVC controls and blends plasticized with Lindol show better mechanical properties in terms of modulus of elasticity, tensile strength at both yield and break, but with less elongation. While when it comes to elongation, blends with Benzoflex 2-45 are better at both plasticizer levels (i.e., 35 and 30 phr). For that a combination of both plasticizers was carried out at a total of 30 phr plasticizer to evaluate the effectiveness of their mixture. The first scan as presented in Figure 4-10, shows that both Alcell and Lindol presence in the formulations results in one single peak. This observation is in total agreement with the previously noticed one.

The mechanical properties of controls and blends using the plasticizers mixtures (i.e. Benzoflex 2-45 and Lindol) are summarized in Table 4-20. Formulations plasticized with different proportions of Benzoflex 2-45 and Lindol show that by increasing the amount of Lindol, the modulus of elasticity, tensile strength at both yield and break increases, whereas a raise in Benzoflex 2-45 ratio increases the elongation of VC-VAc copolymer controls to a certain limit and then prevented them from further elongation, an occurrence which could be attributable to the influence of Lindol molecules that can block the Benzoflex 2-45 throughout much elongation.

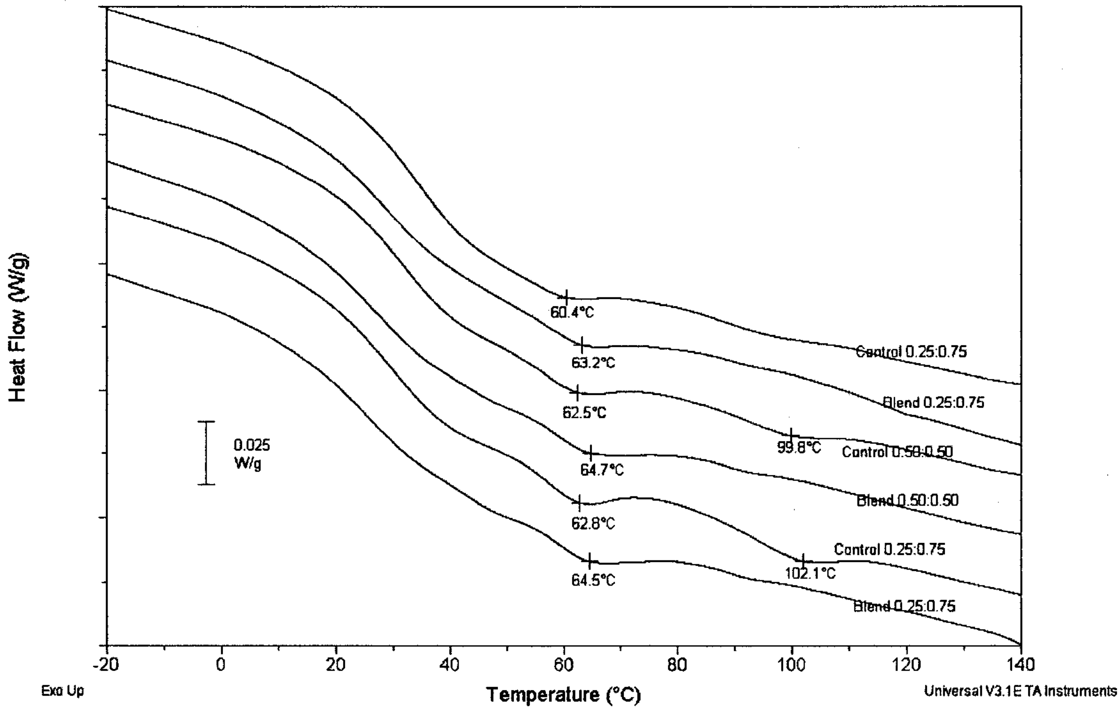


Figure 4-10: DSC thermograms of VC-VAc controls and blends with 30 phr at different ratios of Benzoflex 2-45:Lindol plasticizers

Table 4-20: Mechanical properties of VC-VAc copolymer controls and blends with different ratios of Benzoflex 2-45 to Lindol and the variation of blends properties as a percentage of VC-VAc copolymer controls values

Sample ID	Tg [°C]	Elastic Modulus [MPa]	Tensile Strength [MPa]		Elongation [%]
			Yield	Break	
(0.25) Benzoflex 2-45/(0.75) Lindol					
VC-VAc control	33.2	257.27	7.33	6.41	259
VC-VAc -Alcell	28.6	183.18	5.48	4.52	311
% Variation	- 4.6*	- 28.8	- 25.2	- 29.5	+ 20.0
(0.5) Benzoflex 2-45/(0.5) Lindol					
VC-VAc control	31.8	189.41	5.80	6.23	333
VC-VAc -Alcell	26.6	162.26	4.88	4.14	313
% Variation	- 5.2*	- 14.3	- 15.9	- 33.5	- 6
(0.75) Benzoflex 2-45/(0.25) Lindol					
VC-VAc control	30.4	124.17	4.75	5.66	330
VC-VAc -Alcell	25.6	128.87	3.99	3.83	361
% Variation	- 4.8*	+ 3.8	- 16	- 32.3	+ 9.4

* Variation in °C

Alcell presence in blend formulations enhances and increases the elongation in general and practically the [(0.25) Benzoflex 2-45/ (0.75) Lindol] formulation that reaches almost equal elongation to [(0.5) Benzoflex 2-45/ (0.5) Lindol] formulation, as it is shown in Table 4-20. This confirms the hypothesis that Benzoflex 2-45 plasticized mostly the low molecular weight fractions of Alcell reaching maximum at 0.25 ratio. Considering that the low molecular fraction is constant in Alcell, the left of Benzoflex 2-45 at 0.5 ratio was used to enhance the mechanical properties, and was not enough to get over the Lindol influence. While at 0.75 ratio of Benzoflex 2-45 the access amount successes in breaking the H bonds of VC-VAc copolymer macromolecules and elongate more this formulation overcoming the Lindol influence.

The stress-strain curves for VC-VAc controls and VC-VAc -Alcell blends as function of plasticizer type and concentration are presented from Figure 4-11 to Figure 4-15. One may notice that all curves are representative for ductile materials and exhibit a more or less sharp yield point as well as strain hardening for all controls and for some blends.

It is interesting to note that the key mechanical properties of some blends formulated with 30 phr plasticizer compare very favorably with those of DOP control formulated with 35 phr plasticizer which represents the typical flooring formulation. For example: the blends formulated with Mesamoll, mixtures of Benzoflex 2-45:Lindol in proportions of 0.25:0.75, 0.50:0.50 and in a lesser measure 0.75:0.25 mixture and Benzoflex 2-45 plasticized blend, could represent a successful replacement for the 35 phr DOP control.

Although, at a level of 20 parts VC-VAc copolymer and 5 parts plasticizer reduction these blends compare very favorable with those of DOP control from the mechanical properties point of view, and are superior in terms of economical factors. The research will be continued with 35 phr plasticizer, as a consequence of the second relaxation peaks appearance, as discussed earlier in thermal properties section.

Figure 4-11: Stress-strain curves of controls and blends formulated with different proportions of DOP plasticizer

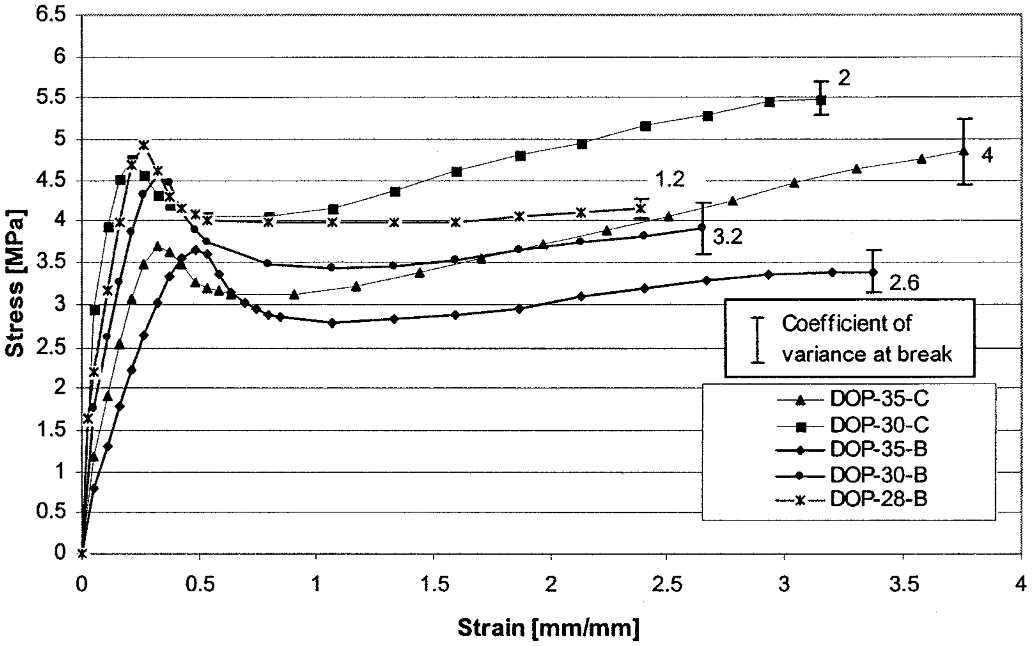
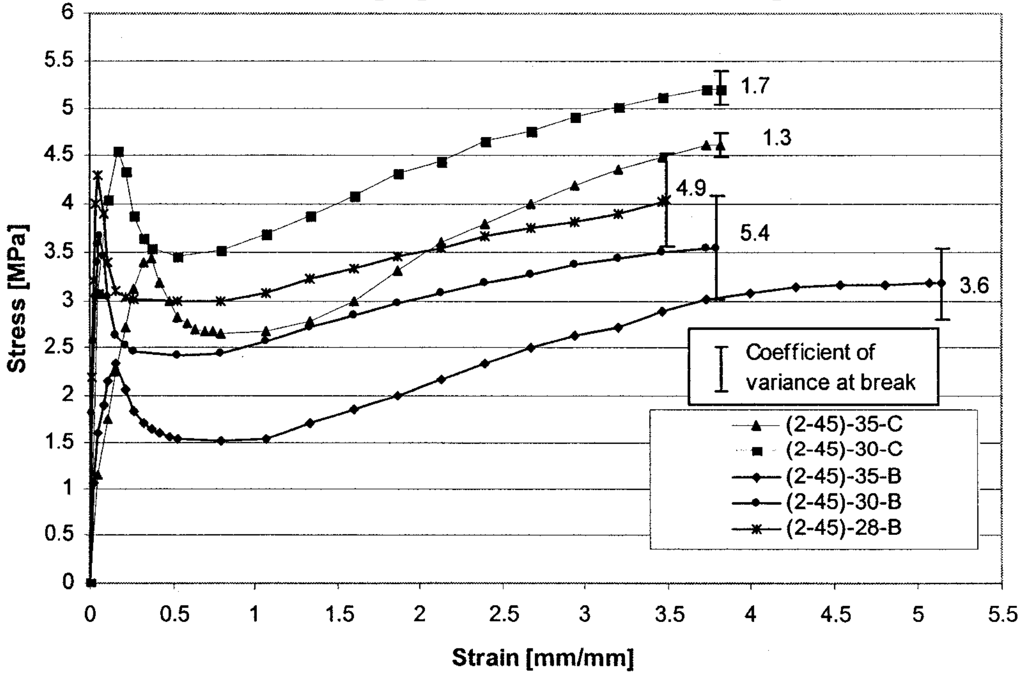


Figure 4-12: Stress-strain curves of controls and blends formulated with different proportions of Benzoflex 2-45 plasticizer



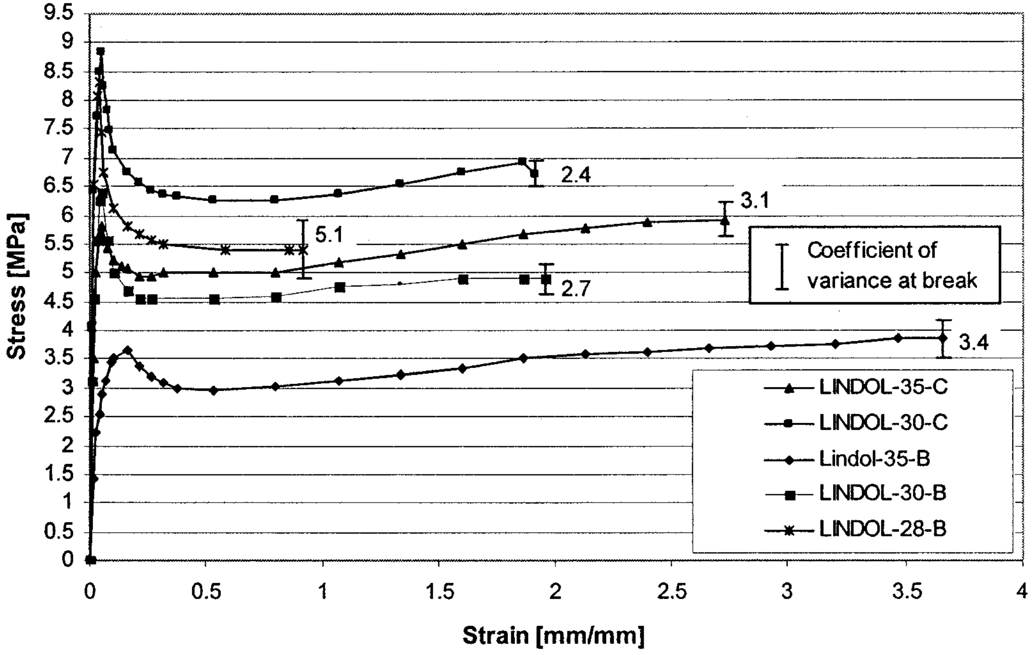


Figure 4-13: Stress-strain curves of controls and blends formulated with different proportions of Lindol plasticizer

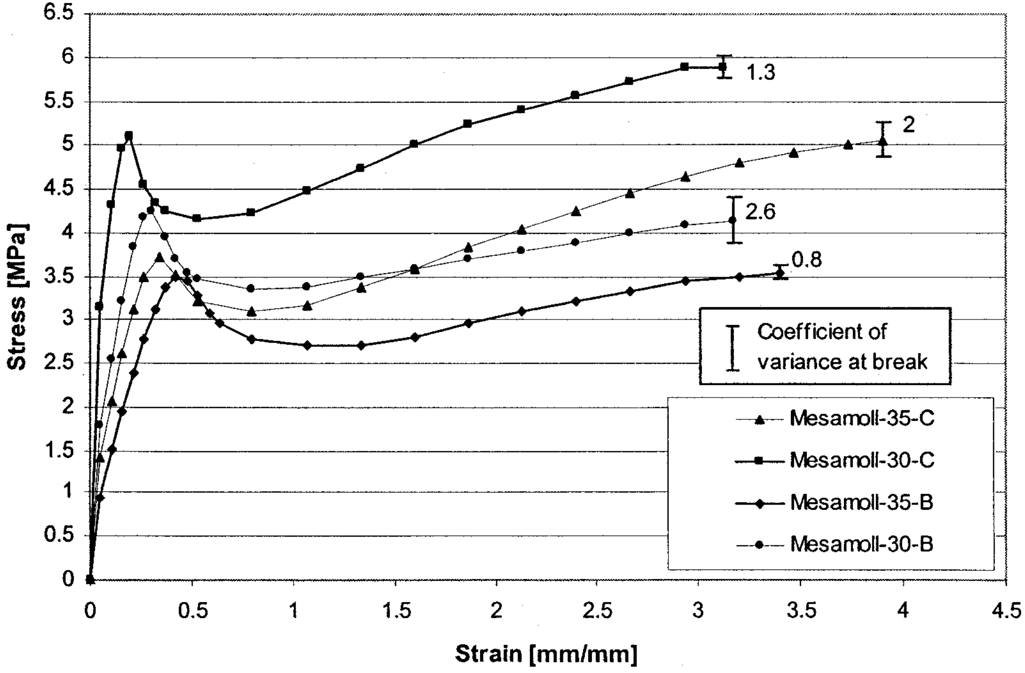
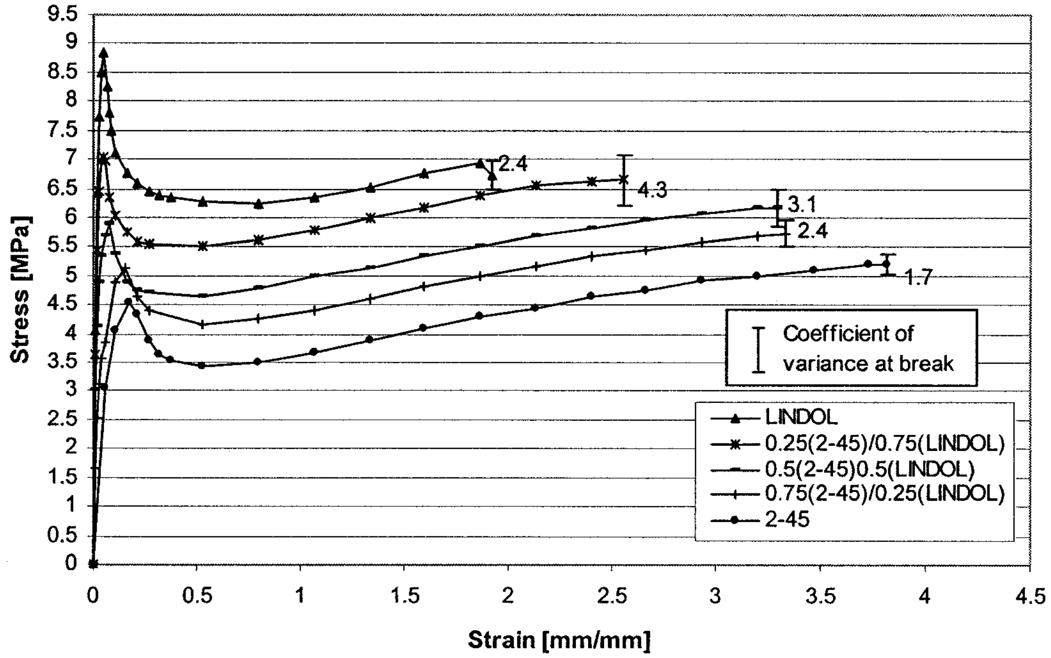


Figure 4-14: Stress-strain curves of controls and blends formulated with different proportions of Mesamoll plasticizer

Figure 4-15: Stress-strain curves of controls formulated with different proportions of 30 phr mixtures of Benzoflex 2-45 and Lindol plasticizers



5

Results And Discussions

5.1 Lignin – plasticizer interaction

The effect of plasticizer efficiency on lignins utilized in the study (i.e. the extent of lowering theirs Tgs) was determined by DSC using mixtures of lignin-plasticizer only to evaluate the plasticization extent of lignin. The mixtures of lignins with 35 phr plasticizer were homogenous powders. However, some of them were really "dry blends", whereas others were slightly "wet-powders", indicating in the last case, traces presence of plasticizer liquid phase on the lignin particle surfaces.

The only pair, which presented two distinct phases, was Alcell-DOP mixture. The Tgs of lignin-35 phr plasticizer mixtures, as determined in the second run, and the differences between Tgs of lignins (Table 4-1), and those of the respective lignin-plasticizer mixtures

(ΔTg), as well as their external aspect are presented in Table 5-1. Figures 5-1 to 5-4 represent their thermograms for the first and second DSC scan.

Table 5-1: Tg of lignins-35 phr plasticizer mixtures and differences between the Tg of lignin and Tg of lignin-35 phr plasticizer mixtures (ΔTg)

Plasticizer type	Alcell			Indulin			Tomlinite		
	Aspect	Tg [°C]	ΔTg [°C]	Aspect	Tg [°C]	ΔTg [°C]	Aspect	Tg [°C]	ΔTg [°C]
2-45	Dry powder	32	65	Dry powder	62	80	Dry powder	47	86
Mesamoll	Wet powder	83	14	Wet powder	121	21	Wet powder	130	3
DOP	Two phases	-	-	Wet powder	126	16	Wet powder	123	10
Lindol	Dry powder	42	55	Dry powder	114	28	Dry powder	55	78

An inspection of the data presented in Table 5-1 shows that there are appreciable differences in efficiency of each plasticizer on the three tested lignins. Benzoflex 2-45 and Lindol induce sensible reduction of lignins Tg, and in the meantime all the mixtures are truly solid phases. The results are not surprising taking into account their high and closed solubility parameter. Mesamoll and DOP seem to be poorer plasticizers for lignins than Benzoflex 2-45 and Lindol. They induce modest reduction in Tg, and traces of liquid phase are observed in their mixtures with lignins.

The sensible differences in Tg reduction extent of the different pairs lignin-plasticizer suggest that the magnitude and mode of changes in lignins chains mobility are different and are strongly influenced by the plasticizer type. Although each plasticizer-lignin mixture presents apparently a single Tg, as can be seen from Figures 5-1 to 5-4, the transitions are very broad indicating a somewhat less than homogenous blend.

According to the literature data a sharp transition (Tg interval < 15 °C) is typical for a material that is homogenous on thermal measurement scale, with a resolution scale of 100-500 nm. A broad transition, on the other hand, is characteristic for a less homogenous blend [102]. In order to deeply elucidate the phase behavior and the morphology of these lignin-plasticizer blends the enthalpy relaxations, as they appear in the first DSC scans, were also studied.

The appearance of multiple enthalpy relaxations in the first DSC scans is an indication of heterogeneous blends. If the mix is homogeneous on a molecular level, the co-operative nature of the relaxation process implies that a single enthalpy relaxation would be observed whose position and magnitude reflects the mixture and not the pure components [103]. The enthalpy relaxation, which is a time related phenomenon, is due to polymer chains relaxation eliminating the excess free volume in an effort to approach the preferred or true equilibrium state of the system. This behavior is manifested through a slow decrease in volume (densification), decrease in enthalpy (enthalpy relaxation) or other state function variables. The excess free volume is quenched in the system when the respective system is cooled from the melt. The rapid rise in viscosity that occurs as Tg is approached, freezes the polymer chains in a non-equilibrium conformation and configuration [104].

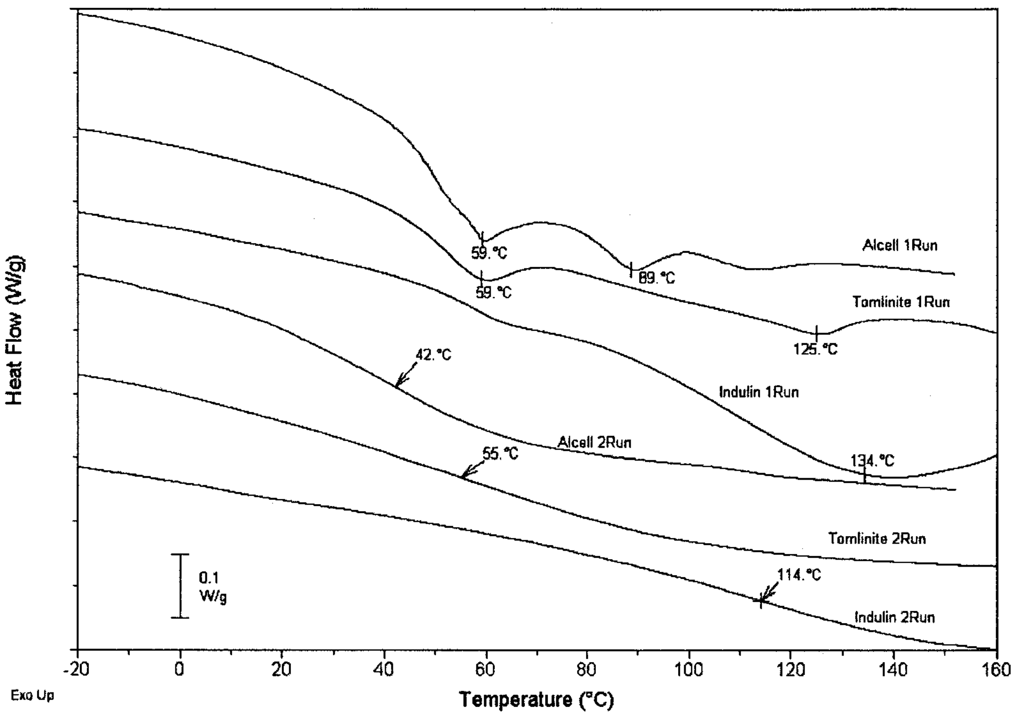


Figure 5-1: DSC thermograms of mixtures of different lignins with 35 phr Lindol

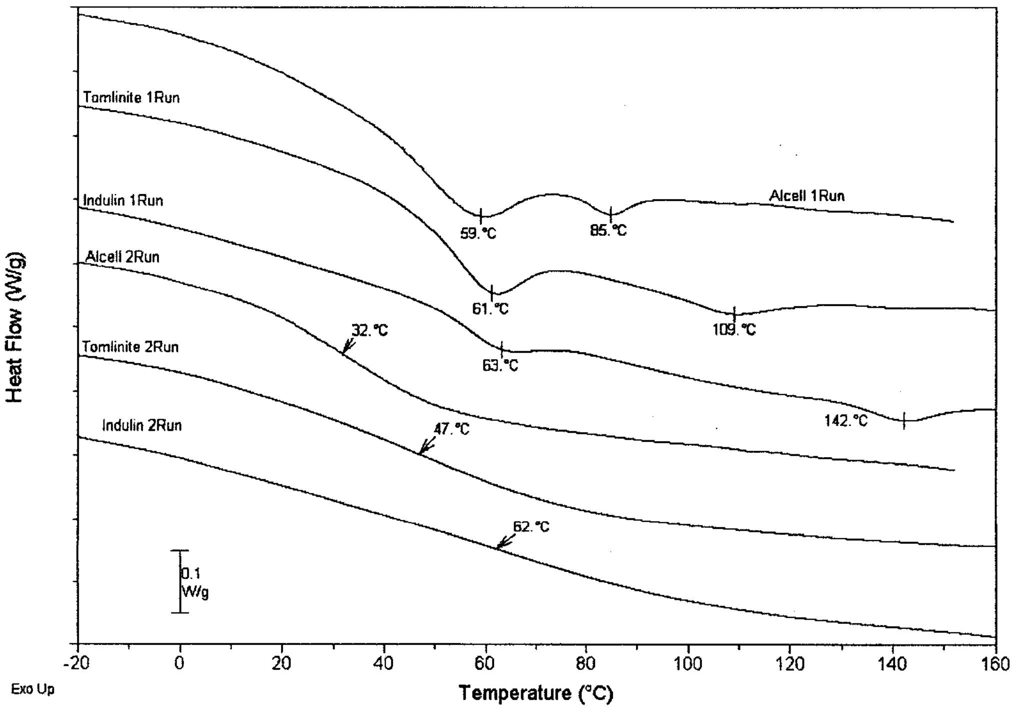


Figure 5-2: DSC thermograms of mixtures of different lignins with 35 phr Benzoflex 2-45

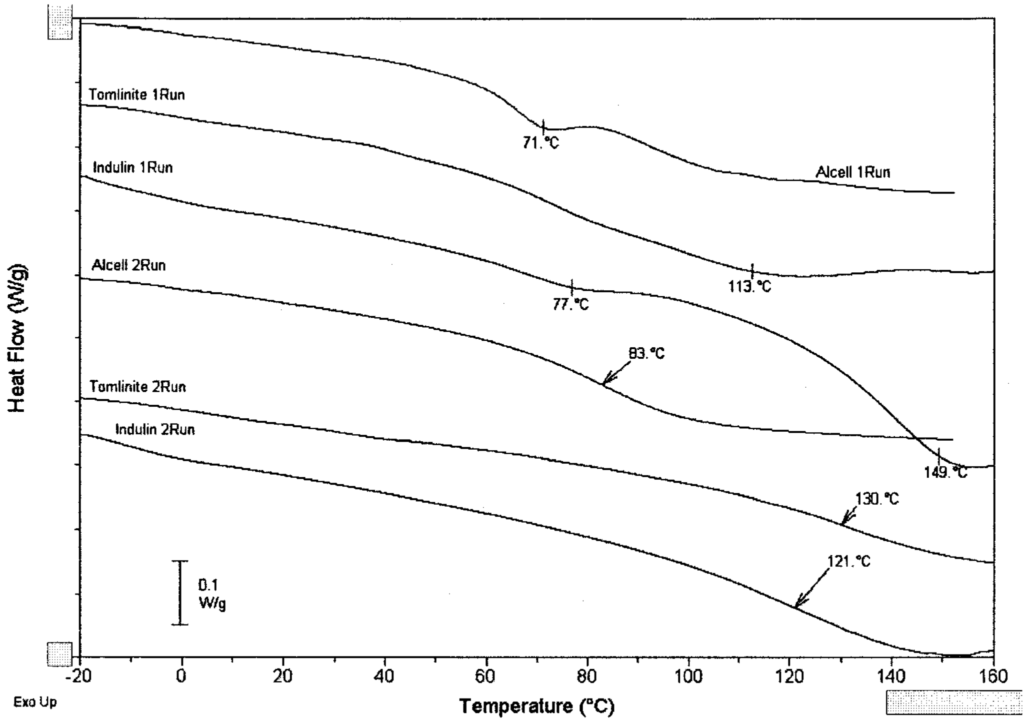


Figure 5-3: DSC thermograms of mixtures of different lignins with 35 phr Mesamoll.

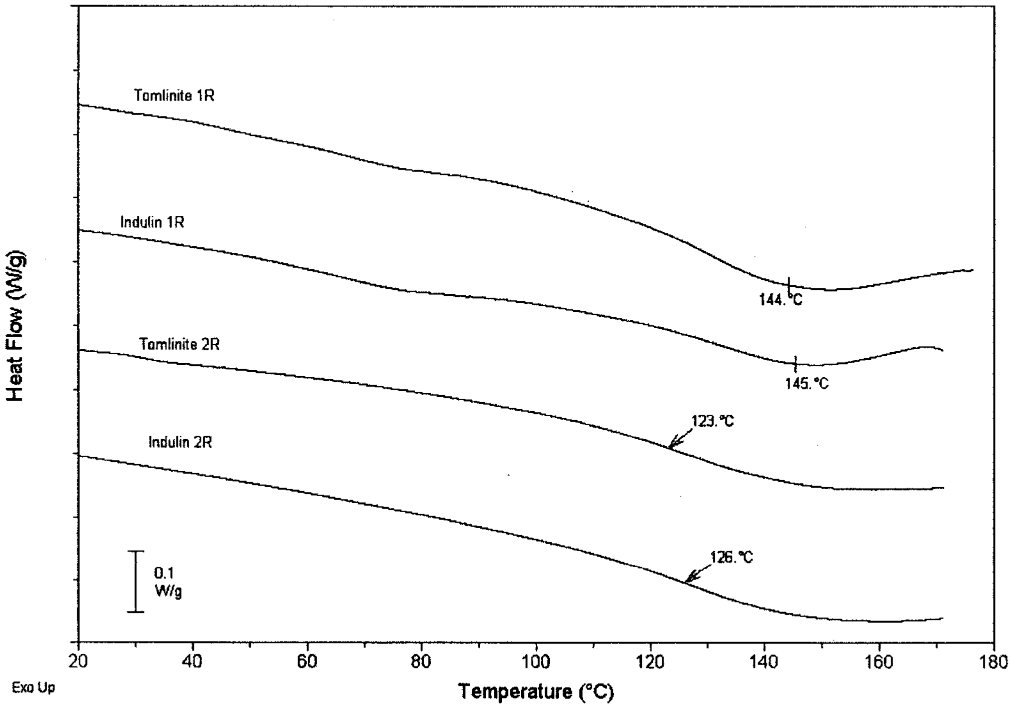


Figure 5-4: DSC thermograms of mixtures of different lignins with 35 phr DOP

From the first scan of DSC thermograms, Figures 5-1 to 5-4, each pair of plasticizer-lignin mixture exhibits a specific relaxation behavior comprising in most of the cases two distinct relaxation peaks located at quite different temperatures, confirming the mixtures heterogeneity. The apparently single broad transition observed in the second scan could be the result of two or more separate overlapping transitions that occur in a large temperature range.

As it can be seen from Table 4-1 the molecular weight distribution of lignins is very broad. In addition, due to the presence of many OH phenolic groups, strong intermolecular bonds are formed between lignin fractions of different molecular weights. Literature data indicate that, the temperature range of the glass transition of the different molecular weight fractions of lignins increases significantly with increasing their molecular weight [33]. By analyzing the position and the intensity of the relaxation peaks in the first scans, Figures 5-1 to 5-4, one may conclude that each plasticizer, depending on its characteristics and chemical configuration, solvates the low and medium molecular weight fractions, within a particular lignin and partially swells some high molecular weight fractions. Depending on the lignin's degree of solvation and swelling, the size and the position of the transitions occurring at different temperature intervals will be different and reflecting the overlapping transitions values. In the meantime the degree of solvation and swelling of lignin by a particular plasticizer will influence the mechanical properties of the respective blends as will be further discussed.

5.2 PVC homopolymer – lignin blends

The present section evaluates the impact of blending organosolv and kraft lignins with plasticized PVC. The initial experimentation with homopolymer was carried out in view to reduce the complexity of the system, aiming for better understanding of the polyblending of the main constituents' behavior (i.e., PVC and Lignins). In the meantime the impact of replacing Di-octyl phthalate (DOP), with Diethylene glycol dibenzoate (Benzoflex 2-45), Tricresyl phosphate (Lindol), Alkyl sulfonic acid phenyl ester (Mesamoll) in these formulations was examined [101].

In the PVC blends the two polymers represent 100 parts and the ratio PVC: lignin was 80: 20. The plasticizer loading (35phr) was calculated for the 100 parts polymer. If the lignin loading is not taken into account, the quantity of plasticizer relative to PVC only is 42 phr. In order to establish if indeed there is an interaction between the lignins and the plasticizers in the blends, in parallel PVC controls with 42 phr plasticizer were prepared.

5.2.1 Morphology

The dispersion extent of lignins in the various blends was examined by taking photomicrograph at 100x magnification of razor-cut samples. These micrographs allowed a comparative determination of dispersion by visual inspection of lignin agglomerates size and distribution through polymer matrix in each blend. The results will be discussed together with the mechanical properties data.

5.2.2 Processibility

All PVC-lignin blends versus their controls exhibit a decreased equilibrium torque value, indicating a lower melt viscosity, as can be seen from the Table 5-2. The equilibrium torque values of controls with 42 phr plasticizer are lower than that of the respective blends. That means that viscosity decreased, as expected, at a higher plasticizer concentration. For the respective blends the viscosity is slightly lower indicating that not all the plasticizer is disposable for PVC chains. However, for the same plasticizer, the equilibrium torque value of blends is largely influenced by the type of lignin, pointing to the possibility of morphological differences existing within the blends.

Table 5-2: Equilibrium torque of PVC controls with 35 and 42 phr plasticizers and blends with 35 phr plasticizer

Plasticizer type	Equilibrium Torque at 145 ± 1°C [m.g]				
	PVC Control		PVC-Alcell	PVC-Indulin	PVC-Tomlinite
	35 phr	42 phr			
DOP	1200	1025	1025	1075	1075
Benzoflex 2-45	1350	1100	1175	1200	1200
Lindol	1375	1150	1175	1325	1275
Mesamoll	1300	1050	1050	1200	1175

5.2.3 Thermal properties

The Tg values of PVC controls and blends formulated with 35 phr plasticizer, as well as controls with 42 phr plasticizer are shown in Table 5-3. Also in Table 5-3 the differences in °C between the Tg of controls and respective blends (ΔTg) are shown, in addition the differences between the Tgs of controls with 42 and 35phr plasticizer are stated. DSC thermograms in the temperature interval between –20 and 140 °C, as shown in Figure 5-5 to 4-8 reveal single Tgs for all blends, which indicates a relatively homogenous structure. Unlike the quite sharp and narrow glass transition range for the blends plasticized with 2-45, Lindol and in a lesser measure that with Mesamoll, the Tg region of DOP plasticized blend was broad and less sharp indicating a certain degree of in-homogeneity at the molecular scale. Data presented in Table 5-3 point out that in comparison to the respective controls the Tgs of all blends (ΔTg) decreased with a few °C. In most cases the decreased values of blends Tgs' are not comparable with the differences between the Tgs of the controls plasticized with 35 and 42 phr plasticizer, depicting interactions between plasticizers and lignins. However, the degree of interactions varies as a function of plasticizer and lignin type as ΔTg data suggest. A correlation between the blends Tg reduction and their mechanical properties variations will be further discussed.

Table 5-3: Tg of PVC controls and blends and differences (ΔTg) between the Tg of controls and respective blends, and differences between controls with 35 and 42 phr

Sample Identification	Lindol		Benzoflex 2-45		Mesamoll		DOP	
	Tg [°C]	ΔTg [°C]	Tg [°C]	ΔTg [°C]	Tg [°C]	ΔTg [°C]	Tg [°C]	ΔTg [°C]
Control 35 phr plasticizer	25.7	-	20.8	-	11.8	-	9.3	-
Control 42 phr plasticizer	21.1	4.6	10.9	9.9	3.6	8.2	1.1	8.2
Alcell Blend	22.1	3.6	16.9	3.9	9.7	2.1	2.2	7.1
Indulin Blend	21.8	3.9	15.1	5.7	2.5	9.3	1.8	7.5
Tomlinite Blend	22.5	3.2	13.1	7.7	4.6	7.2	2.3	7.0

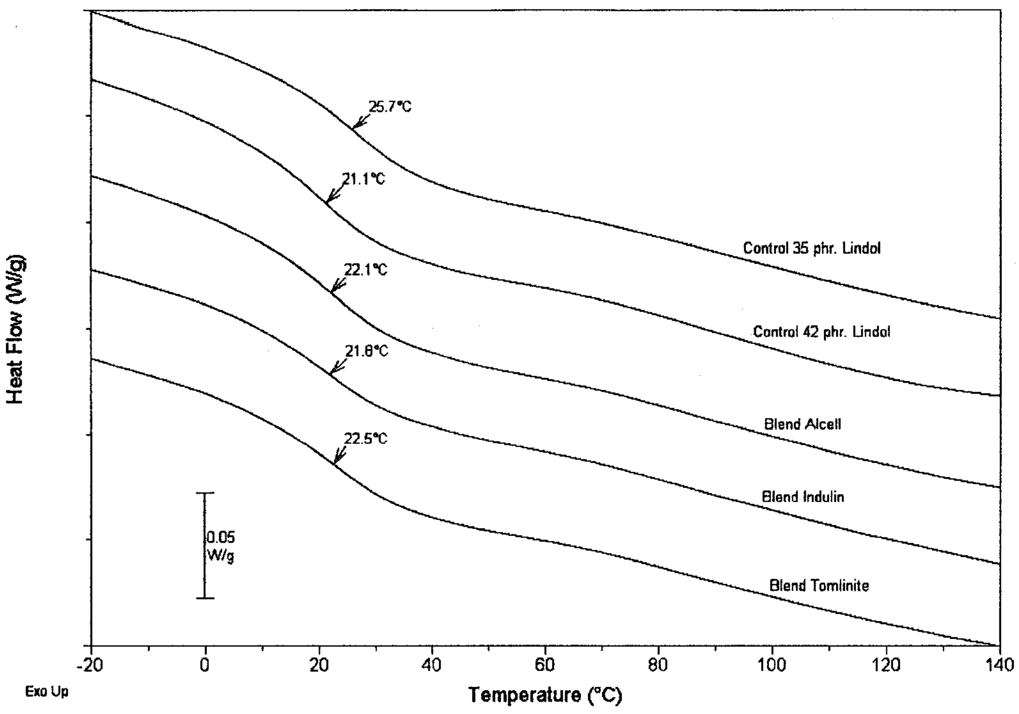


Figure 5-5: DSC thermograms of PVC control and blend with Lindol

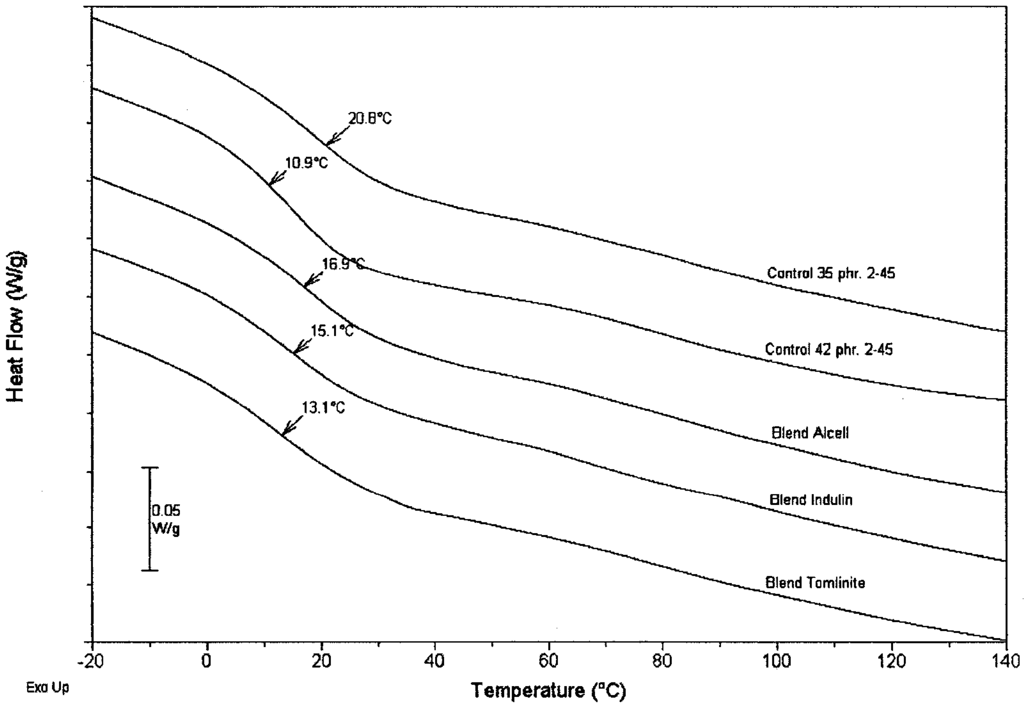


Figure 5-6: DSC thermograms of PVC control and blend with Benzoflex 2-45

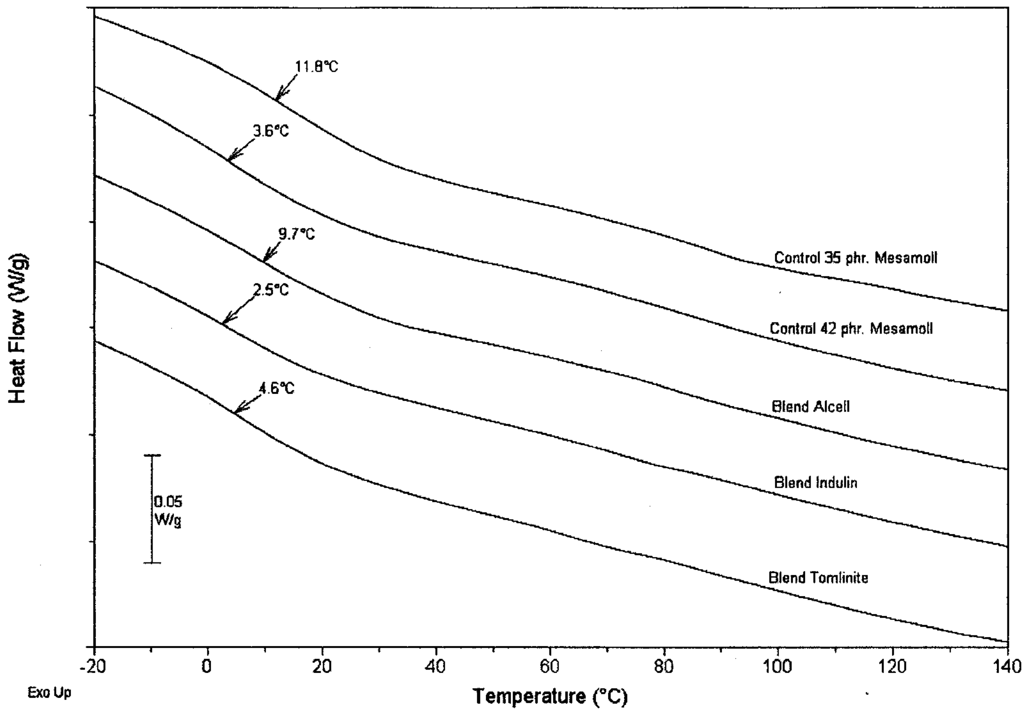


Figure 5-7: DSC thermograms of PVC controls and blends with Mesamoll

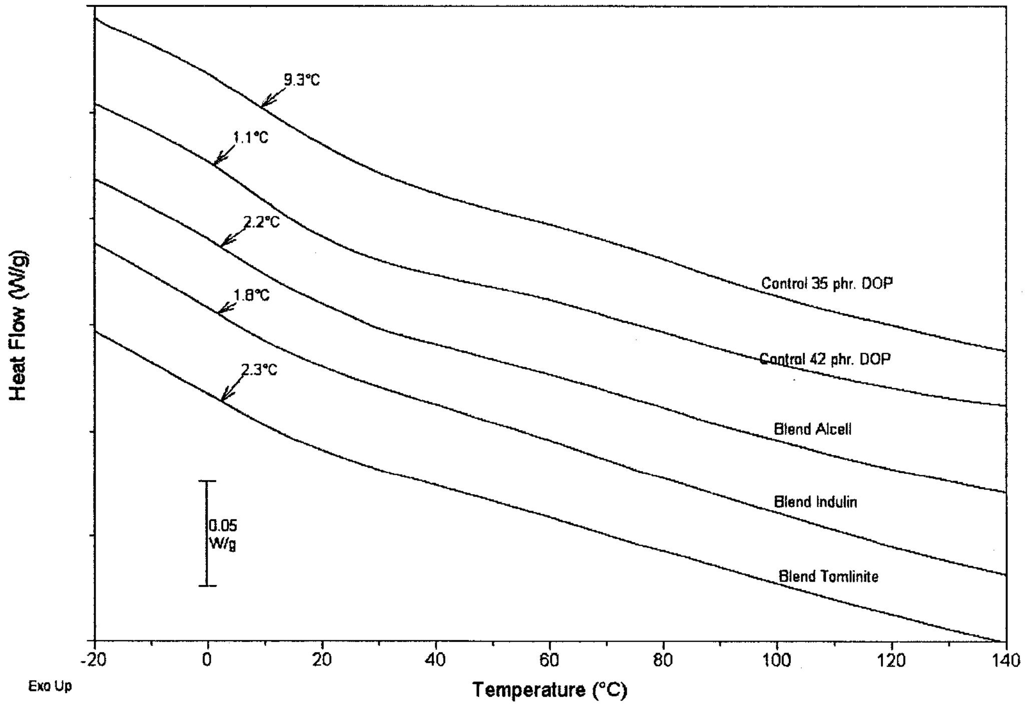


Figure5-8: DSC thermograms of PVC controls and blends with DOP

5.2.4 Mechanical properties

General considerations

The mechanical properties data of PVC controls and blends as function of plasticizer type are presented in Table 5-4 and their respective stress-strain curves in Figures 5-9 to 5-12. Those Figures indicate that the stress-strain curves are representative of ductile materials. They exhibit a distinct yield and the failure is ductile with neck propagation and strain hardening for all the controls and for a few blends. In Table 5-5 the variation in percentages of the blends mechanical properties relative to their respective PVC controls are presented. Due to the fact that the mechanical properties of the formulations are strongly influenced by their thermal characteristics, the reduction in Tg values of blends (ΔTg) with respect to their respective controls are restated in Table 5-5. All the specimens were tested at room temperature (i.e., 23 ± 1 °C) which was in all the cases above or very close to specimens' Tg as seen in Table 5-3.

Analyzing the data presented in Table 5-5 two extremes can discern in PVC-lignin blends. On one extreme there are the blends plasticized with Lindol characterized by similar Tg values of about 22°C which are about 3°C lower than that of the respective controls. At the other extreme there are blends plasticized with DOP characterized by Tg values of about 2°C and which are with about 7 °C lower than that of the respective controls. For all these blends the modulus values are reduced by about 45% in comparison with the respective controls.

Table 5-4: Mechanical properties of PVC controls and blends relative to plasticizer type

Sample Identification	Modulus [MPa]	Tensile strength [MPa]		Elongation [%]
		Yield	Break	
DOP plasticizer				
PVC control	56.53	4.26	4.44	148
Blend Alcell	31.12	4.11	3.44	126
Blend Indulin	32.16	3.37	2.72	151
Blend Tomlinite	31.01	3.73	3.19	187
2-45 plasticizer				
PVC control	48.31	4.31	5.41	267
Blend Alcell	55.84	3.19	3.84	302
Blend Indulin	42.89	3.64	4.23	203
Blend Tomlinite	33.09	4.70	4.24	206
Lindol plasticizer				
PVC control	146.3	5.86	5.87	118
Blend Alcell	82.1	4.41	4.50	197
Blend Indulin	73.8	3.74	3.82	166
Blend Tomlinite	75.2	5.28	4.77	125
Mesamoll plasticizer				
PVC control	40.04	4.01	4.84	179
Blend Alcell	38.08	3.99	3.88	170
Blend Indulin	33.38	3.47	3.02	171
Blend Tomlinite	34.70	3.84	3.46	190

Table 5-5: Mechanical properties variations of PVC-lignin blends as percentage of the respective values of controls and differences between the Tgs of control and the Tgs of the blends

Sample Identification	Δ Tg [°C]	Modulus @2% Elongation [%]	Tensile Strength [%]		Elongation [%]
			Yield	Break	
DOP					
Blend Alcell	7.1	-44.95	-3.52	-22.52	-14.86
Blend Indulin	7.5	-43.11	-20.89	-38.74	2.03
Blend Tomlinite	7.0	-45.14	-12.44	-28.15	26.35
Benzoflex 2-45					
Blend Alcell	3.9	15.59	-25.99	-29.02	13.11
Blend Indulin	5.7	-11.22	-15.55	-21.81	-23.97
Blend Tomlinite	7.7	-31.50	9.05	-21.63	-22.85
Lindol					
Blend Alcell	3.6	-43.88	-24.74	-23.34	66.95
Blend Indulin	3.9	-49.56	-36.18	-34.92	40.68
Blend Tomlinite	3.2	-48.60	-9.90	-18.74	5.93
Mesamoll					
Blend Alcell	2.1	-4.90	-0.50	-19.83	-5.03
Blend Indulin	9.3	-16.63	-13.47	-37.60	-4.47
Blend Tomlinite	7.2	-13.34	-4.24	-28.51	6.15

Figure 5-9: Stress-strain curves of PVC control and blends plasticized with DOP

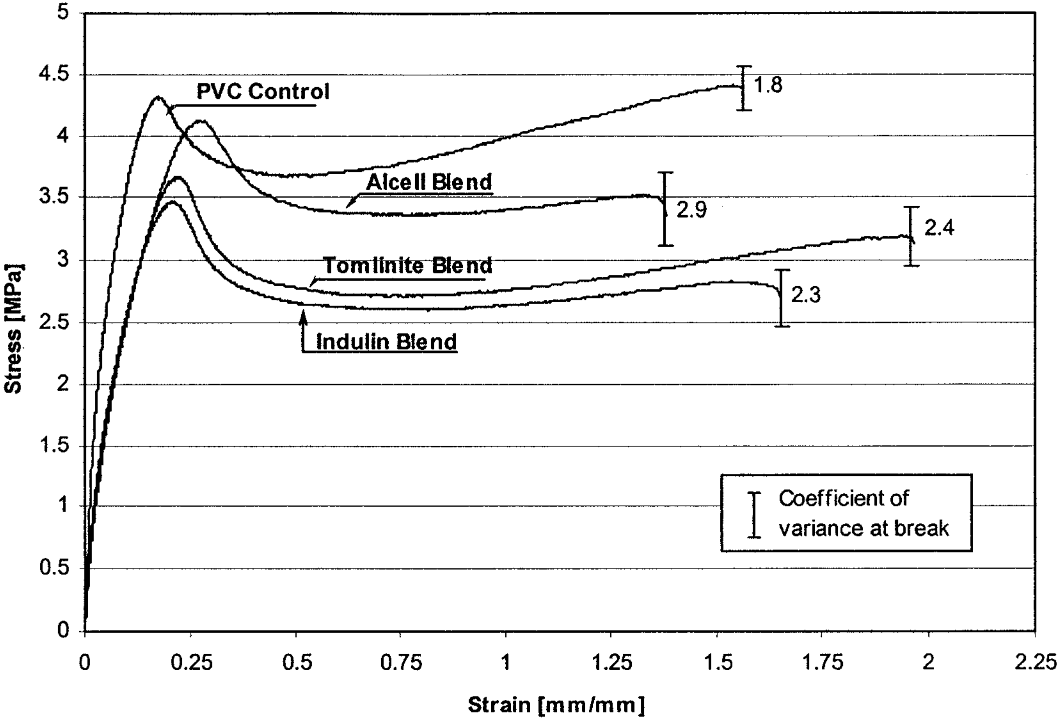


Figure 5-10: Stress-strain curves of PVC control and blends plasticized with Benzoflex 2-45

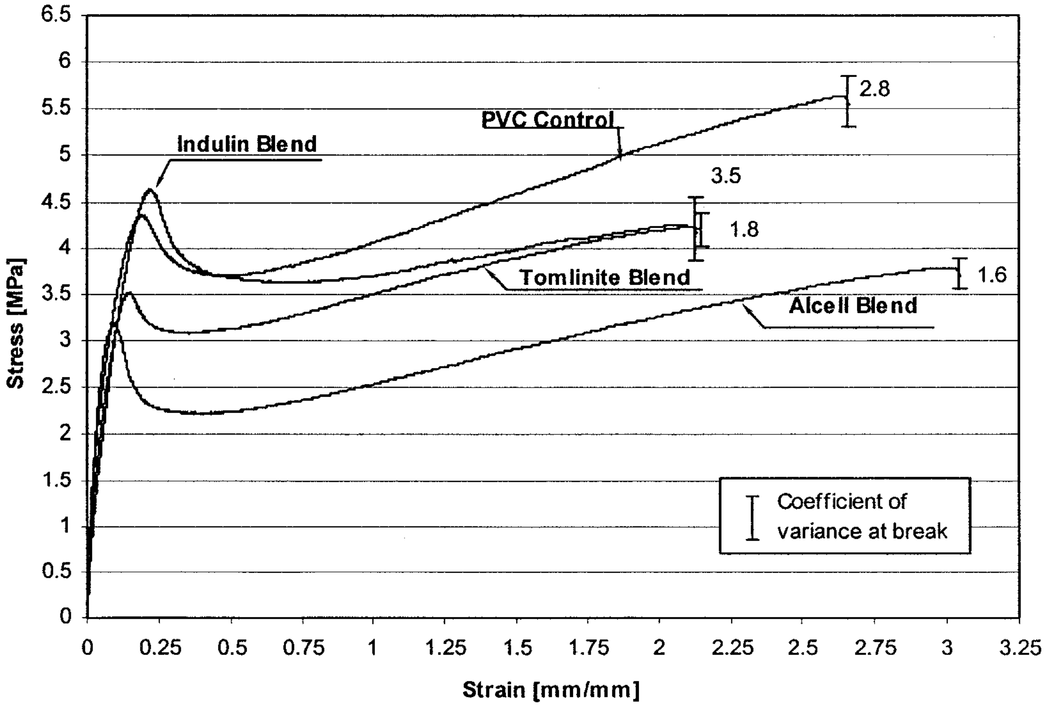


Figure 5-11 : Stress-strain curves of PVC control and blends plasticized with Lindol

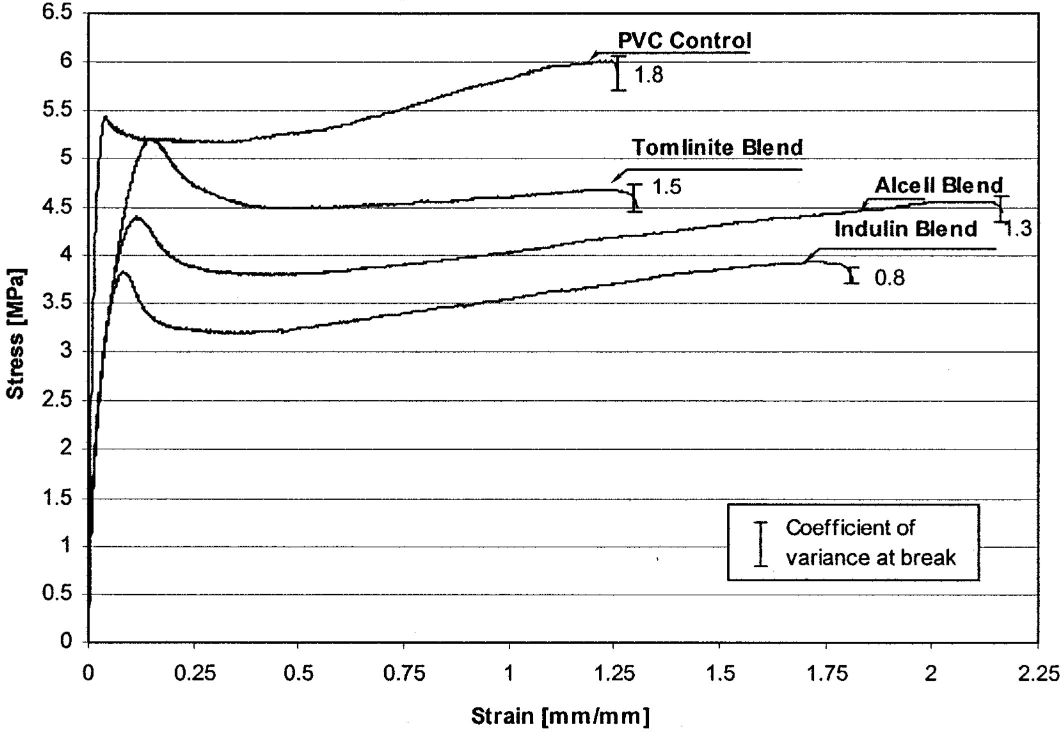
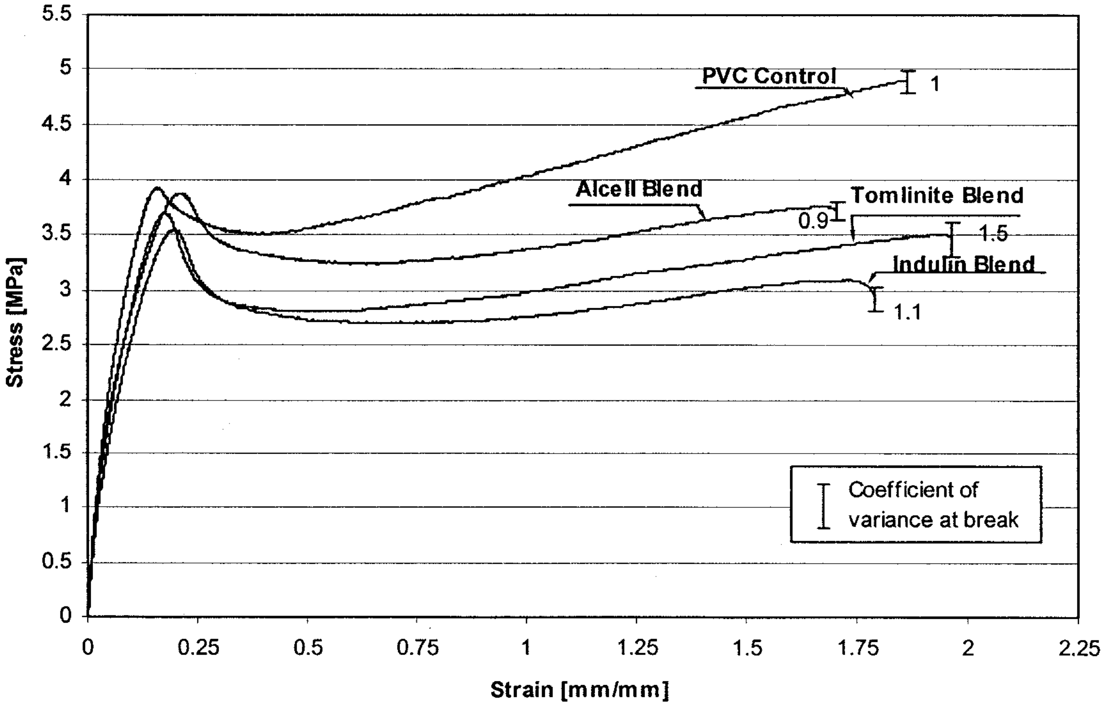


Figure 5-12: Stress-strain curves of PVC control and blends plasticizied with Mesamoll



The tensile properties are highly dependent on intermolecular PVC-PVC, lignin-lignin PVC-lignin, PVC-plasticizer, lignin-plasticizer and matrix-filler attractions. Above Tg, increasing molecular mobility leads to diminished bond strength by interchain or intermolecular separation [100].

Considering that room temperature, which is the testing temperature, is higher than Tg values of blends plasticized with DOP and closed to that plasticized with Lindol, the molecular mobility should increase, inducing an increase in elongation. A decrease in modulus as well as tensile strength values at yield and break for DOP plasticized blends higher than that of Lindol plasticized blends were recorded. Indeed Lindol plasticized blends generally present these features, whereas DOP plasticized blends are characterized by much modest increase in elongation or even decrease (as for Indulin blend), and comparable decreases in tensile strength at break. The tensile strength at yield values decrease less than those of Lindol plasticized blends. All these results suggest that different factors affect the mechanical properties of Lindol and DOP plasticized blends.

DOP plasticized blends

By examining Table 5-3 and Figure 5-8 it is clear that DOP is a poor plasticizer for lignins. Consequently quite large size lignin particle are present in the blends and probably more plasticizer are available for the PVC matrix, which will become softer as Tg data indicate. (See also Figure 5-16). Presence of poorly plasticized lignin with a quite high Tg, in the glassy state, will act as reinforcing filler and will enhance the modulus of PVC matrix in blends. In the meantime the quite large size particles of lignin will impede the PVC matrix from undergoing cold drawing and therefore the material will elongate less. These facts may explain why the modulus values reduction corresponding to ΔTg of 7 °C in DOP plasticized blends are of the same order of magnitude as in Lindol plasticized blends where ΔTg was only 3 °C, and why elongation increases less in DOP plasticized blends.

Lindol plasticized blends

Data presented in Table 5-3 and Figure 5-5 show that generally Lindol is a good plasticizer for lignins. It reduces the Tgs of Alcell and Tomlinite and in a lesser measure that of Indulin. The relaxation peaks from Figure 5-5 suggest that Lindol plasticizes both the low and high molecular weight fractions of Alcell and Tomlinite, whereas Indulin seems to be only partially plasticized. The morphology of blends plasticized with Lindol illustrates well its effectiveness in plasticizing different lignins. Thus, the morphology of Alcell and Tomlinite blends are seen to be quite different from that of Indulin blends, where large lignin domains are evident (Figure 5-13). Presence of these large Indulin domains may indicate that more plasticizer is available for PVC matrix, which will become softer as can be seen from data presented in Table 5-4 and Figure 5-11. On the other hand the well plasticized Alcell and Tomlinite may have a plasticizing effect on the PVC matrix as can be seen from the Figure 5-11 and Table 5-5.

Benzoflex 2-45 plasticized blends

Benzoflex 2-45 seems also to be good plasticizer for all lignins as can be seen from Table 5-3. In addition all blends have a comparable morphology, all lignins being evenly distributed through the PVC matrix (Figure 5-14). The mechanical properties of these blends display some interesting characteristics when compared with the respective data of the control. Alcell blend's Tg is 3.9 °C lower, the elongation value is higher and the strength at yield and break values are lower. In addition a certain degree of strain hardening is noticeable depicting a higher degree of plasticization with respect to control. However, the blend modulus, which expected to be lower, is higher. This is a surprising behavior, due to the fact that modulus values are very sensitive to temperature. DSC data of Alcell-Benzoflex 2-45 mixture (Table 5-1 and Figure 5-2) indicate that Benzoflex 2-45 is good plasticizer for Alcell, reducing its Tg from 97 to 32 °C. However the relaxation peaks located at relatively low temperature suggest that Benzoflex 2-45 plasticizes mostly the low molecular weight fractions of lignins. The remaining high molecular weight fractions that are in glassy state and evenly distributed through plasticized PVC matrix will act as reinforcing filler thus enhancing its modulus. On the other hand the low molecular plasticized Alcell fractions will act as a plasticizer, pushing apart more the already plasticized PVC chains, and thus enhancing the elongation.

Comparing the control specimens Tgs to that of Indulin and Tomlinite blends, one can noticed that ΔTgs decreased by 5.7 and 7.7 °C respectively and the modulus decreases in the same order. The tensile strength at yield is higher than that of Alcell blend and both elongate less than Alcell blend and even than PVC control (Tables 5-4 and 5-5). The DSC thermograms indicate that Benzoflex 2-45 plasticizes to a certain degree the high molecular fractions of these two lignins. These partially plasticized fractions probably develop some interactions with PVC chains and due to their high molecular weight a higher force is needed for their chain segments to be able to slip past each other at yield. In addition they are less evenly distributed through PVC matrix than Alcell (Figure 5-14), fact which explains why their blends elongate less.

Mesamoll plasticized blends

The properties of PVC-lignin blends plasticized with Mesamoll can also be quite well correlated with the degree of its plasticization for each lignin. Data presented in Table 5-1 show that Mesamoll is rather a poor plasticizer for the three tested lignins. It modestly reduces their Tg and all the plasticizer-lignin mixtures are rather wet powders. However, their DSC thermograms (Figure 5-3) are characteristic for a quite homogenous mixture judging from the aspect of the first runs which suggest that all fractions of Tomlinite and Indulin, and in a lesser measure those of Alcell, are participating into the transition (Figure 5-15). This fact may explain the higher Tgs of these mixtures in comparison with other plasticizer-lignin mixtures.

The Tg values for Alcell, Tomlinite and Indulin blends are lower than that of PVC control plasticized with Mesamoll by 2.1, 7.2 and 9.3 °C respectively, with a modest decrease in modules for such decreases in Tg. Surprisingly their tensile strength at yield as well as their elongation at break do not vary much in relation to their respective control properties, except Indulin blend whose yield strength reduction is below the average reduction and Tomlinite blend whose elongation at break is above the average decline.

As in DOP plasticized blends case, a lack of correlation between the blends Tg reduction and their modulus and elongation values can be observed. Probably in this case, too, (Mesamoll plasticizer) more plasticizer is available for PVC matrix, which becomes softer as the Tg data and Figure 5-12 indicate. Presence of only partially plasticized lignins with high Tg will act as a reinforcing filler and will enhance the modulus but in the meantime will impede the PVC matrix to elongate.

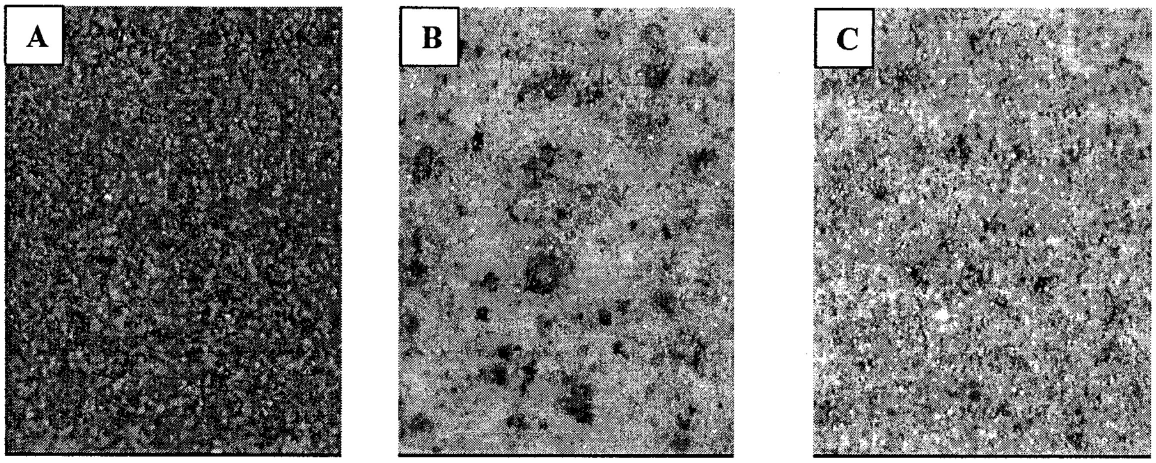


Figure 5-13: Photomicrographs (100x) of PVC control and blends with Lindol as plasticizer; A=Alcell; B=Indulin; C=Tomlinite

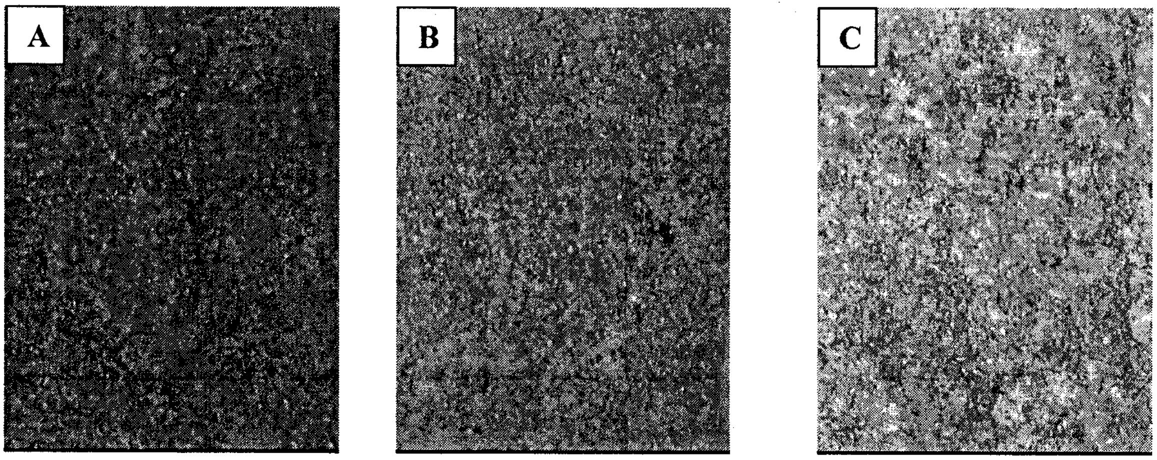


Figure 5-14: Photomicrographs (100x) of PVC control and blends with Benzoflex 2-45 as plasticizer; A=Alcell; B=Indulin; C=Tomlinite

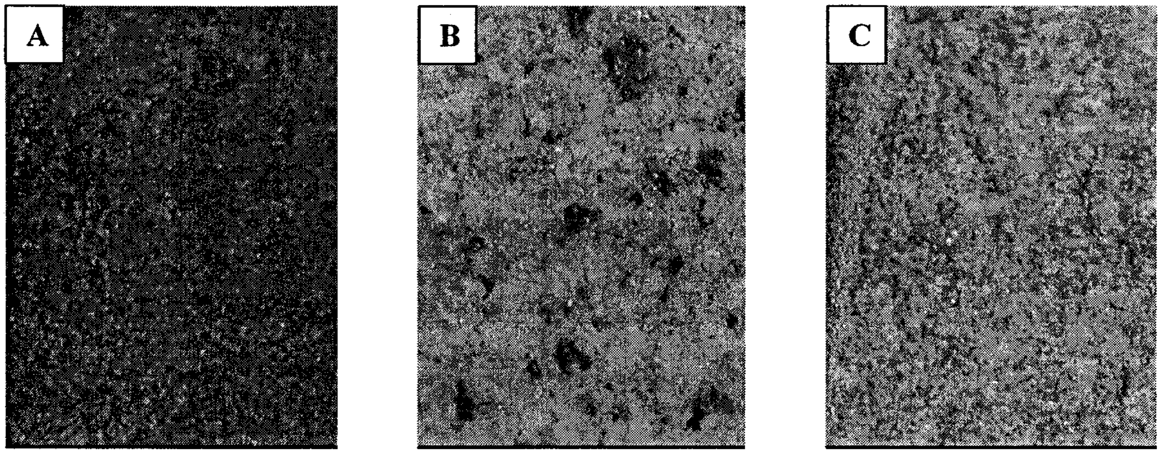


Figure 5-15: Photomicrographs (100x) of PVC control and blends with Mesamoll as plasticizer, A=AL; B=Indulin; C=Tomlinite

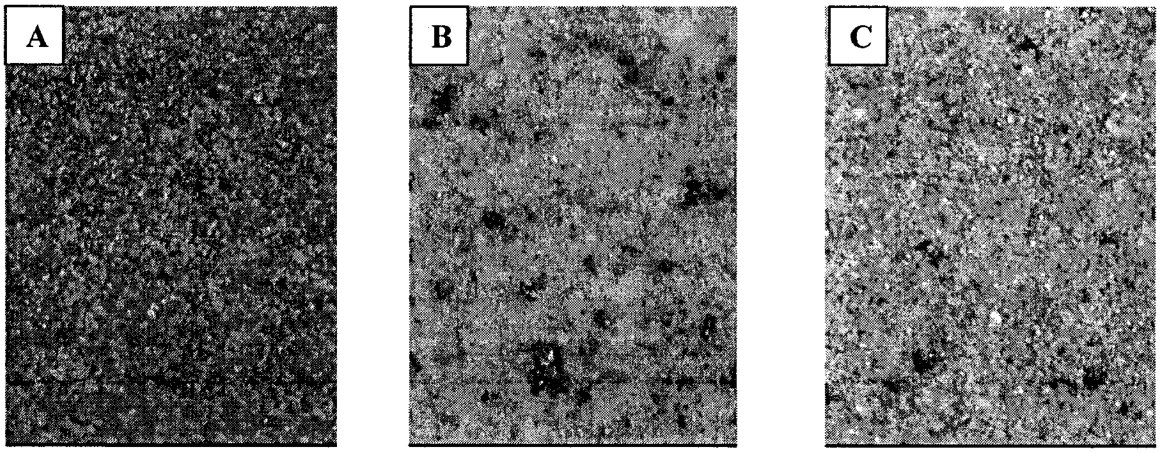


Figure 5-16: Photomicrographs (100x) of PVC control and blends with DOP as plasticizer; A=AL; B=Indulin; C=Tomlinite

5.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

The Infrared spectra of PVC controls and blends is very complex due to the strong spectral contributions of the calcium carbonate filler, which represents 58.9%-wt. of the formulations, as well as the spectral contributions of other additives. The complexity of spectra restricts the amount of information that can be gained concerning the changes that have occurred due to blending PVC with lignins. Most of the prominent lignin absorption peaks are barely detectable in blends spectra, except the absorption band of hydroxyl group. Shifts in frequencies and changes in the shape of the absorption band of OH group may be interpreted as evidence of interactions between hydroxyl groups of lignins with other components of the formulation, particularly with the carbonyl group of plasticizer, α hydrogen of PVC homopolymer.

When hydrogen bonding occurs between OH groups and other groups of the components of the formulations, the force constant for stretching the O-H bond will be reduced, and so the frequency of hydroxyl stretch absorption. However, hydroxyl-hydroxyl interaction can take place in lignin, and association with other functional groups may produce either an increase or a decrease of hydroxyl stretching frequency, depending on the relative strength of the hydroxyl-hydroxyl and hydroxyl-other functional groups interactions [105].

The OH absorption bands of all lignins are presented in Figure 5-17. The shape of these bands is similar, as well as their absorption maxima. In Figures 5-18 to 5-20, the bands of

Alcell mixtures with Benzoflex 2-45, Lindol and Mesamoll (100 parts Alcell and 35 parts plasticizer) are presented as well as of Alcell mixtures with the respective plasticizers and calcium carbonate (100 parts Alcell, 35 parts plasticizer and 200 parts calcium carbonate).

It can be seen from these Figures that for the mixtures of Alcell with Benzoflex 2-45 and Lindol, which are effective plasticizers for Alcell, the absorption maxima decreases from 3427 cm^{-1} to 3416 cm^{-1} (Figure 5-18) and 3417 cm^{-1} respectively (Figure 5-19), depicting a lower degree of association by hydrogen bonding between the Alcell components. The mixture prepared with Mesamoll (Figure 5-20), which is a less effective plasticizer for Alcell, presents a higher absorption maxima located at 3432 cm^{-1}. The slight increase in frequency suggests that during the mixture preparation (8 min. at 145 °C) a higher degree of association occurred between the Alcell components.

All mixtures prepared with calcium carbonate show an increase in absorption maxima which is located at 3433 cm^{-1} for mixtures prepared with Lindol, at 3434 cm^{-1} for Benzoflex 2-45 and at 3436 cm^{-1} for Mesamoll (Figures 5-18 to 5-20). These increases in OH absorption maxima may be due to the fact that some fractions of Alcell OH groups are involved in hydrogen bonding with calcium carbonate, through the absorbed water film present on the surface of the filler. It is known that the apparent surface of a filler particle is that of the absorbed water film and not of the filler [106].

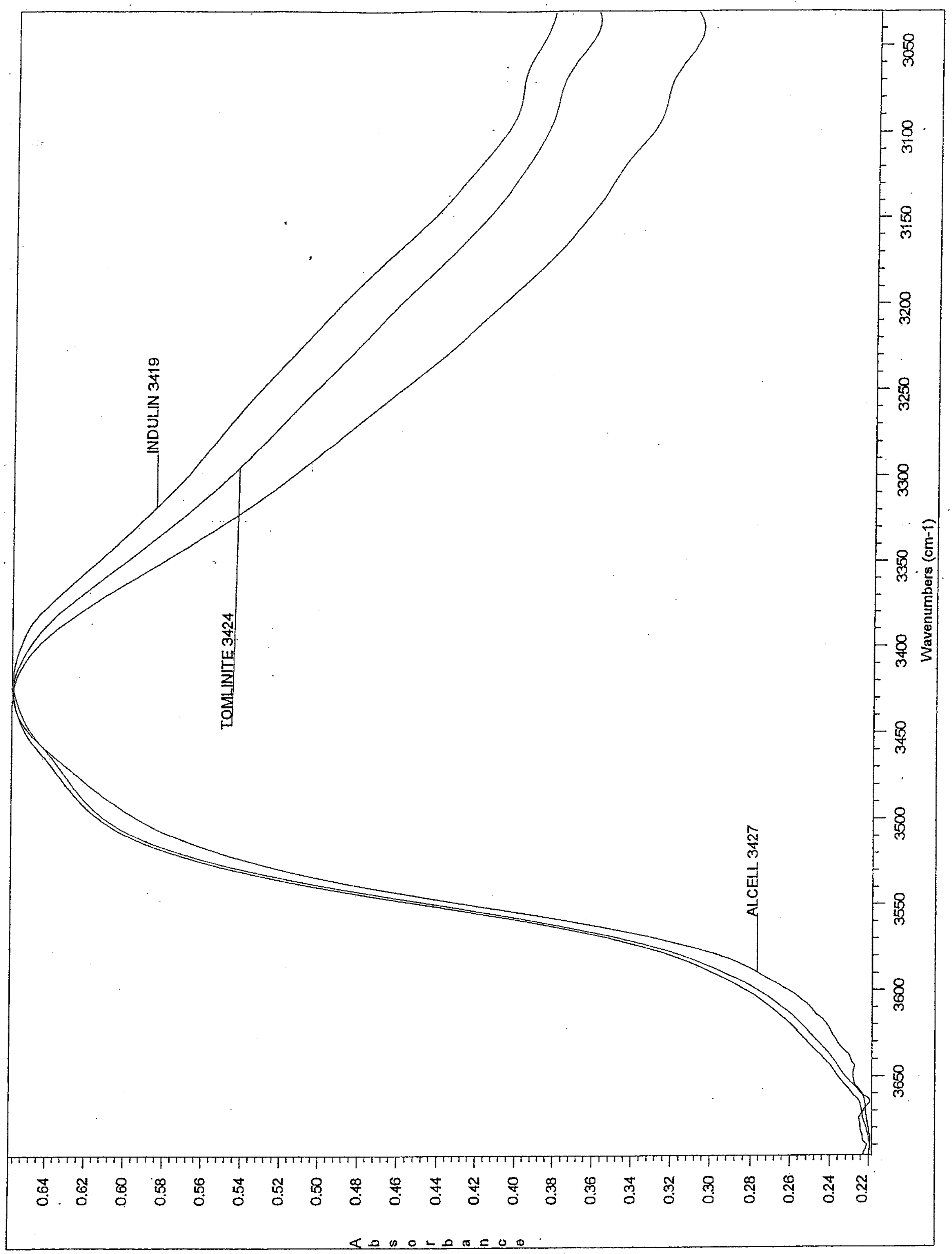


Figure 5-17: FTIR spectra of different lignins

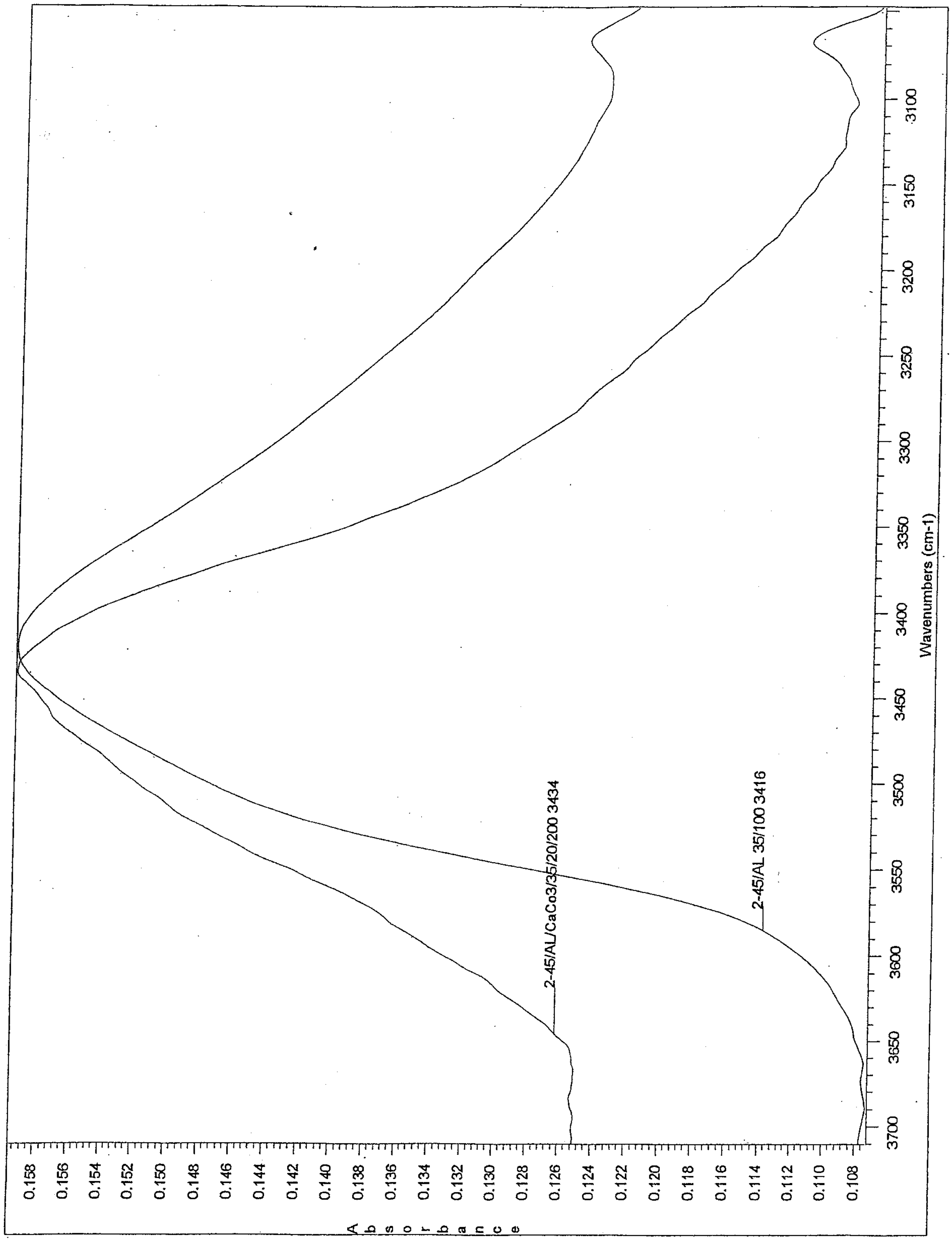


Figure 5-18: FTIR spectra of Alcell lignin mixture with calcium carbonate plasticized with 35 phr Benzoflex 2-45

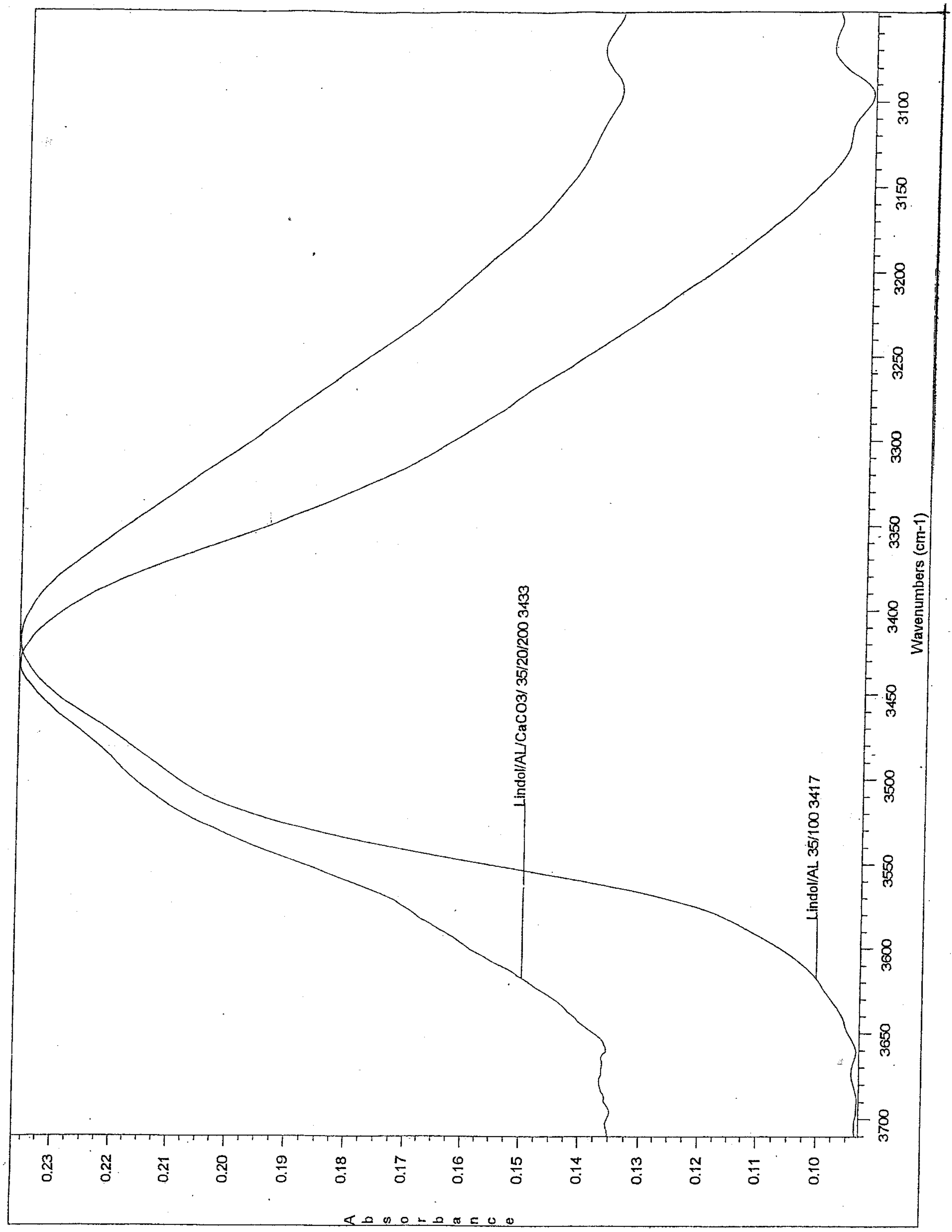


Figure 5-19: FTIR spectra of Alcell lignin mixture with calcium carbonate plasticized with 35 phr Lindol

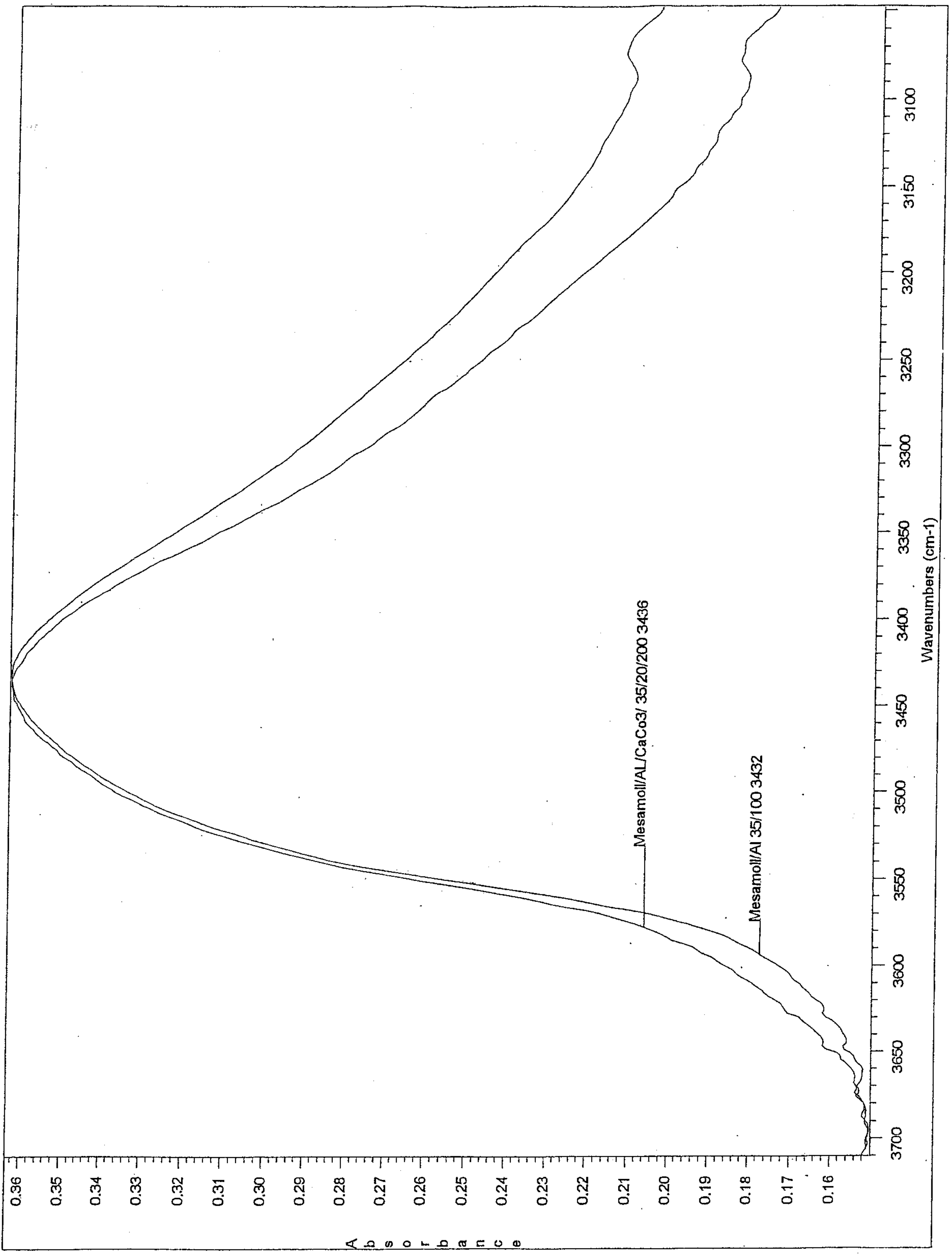


Figure 5-20: FTIR spectra of Alcell lignin mixture with calcium carbonate plasticized with 35 phr Mesamoll

The FTIR spectra of homopolymer blends with different lignins are presented in Figure 5-21 for formulations plasticized with Benzoflex 2-45, Figure 5-22 for formulations plasticized with Lindol and Figure 5-23 for those plasticized with Mesamoll. In Table 5-6 are shown the value of OH absorption maxima as well as the increase or decrease of the tensile strength at yield of the blend in percentages of the respective value of the control.

Table 5-6: Position of OH absorption maxima and tensile strength at yield change in comparison with respective control for PVC – Lignin blends as function of plasticizer and lignin type

Benzoflex 2-45			Lindol			Mesamoll		
Lignin Type	OH absolute maxima [cm^{-1}]	[%] Change of Yield Strength	Lignin Type	OH absolute maxima [cm^{-1}]	[%] Change of Yield Strength	Lignin Type	OH absolute maxima [cm^{-1}]	[%] Change of Yield Strength
Alcell	3337	74.0	Indulin	3386	65.1	Indulin	3409	86.5
Indulin	3404	84.5	Alcell	3402	76.7	Alcell	3469	99.5
Tomlinite	3426	109.0	Tomlinite	3495	79.7	Tomlinite	3493	95.6

Figure 5-21 to 5-23 show that the shape and the maxima of these absorption bands are different for each lignin and vary as a function of plasticizer type, due to the different conformations adopted by increasing or decreasing lignin plasticized portion in the polymer blend matrix of the final product. It is interesting to note that the increase or decrease of absorption maxima for each formulation correlates quite well with the tensile strength at yield of the respective formulation in correlation to the yield strength of the respective control.

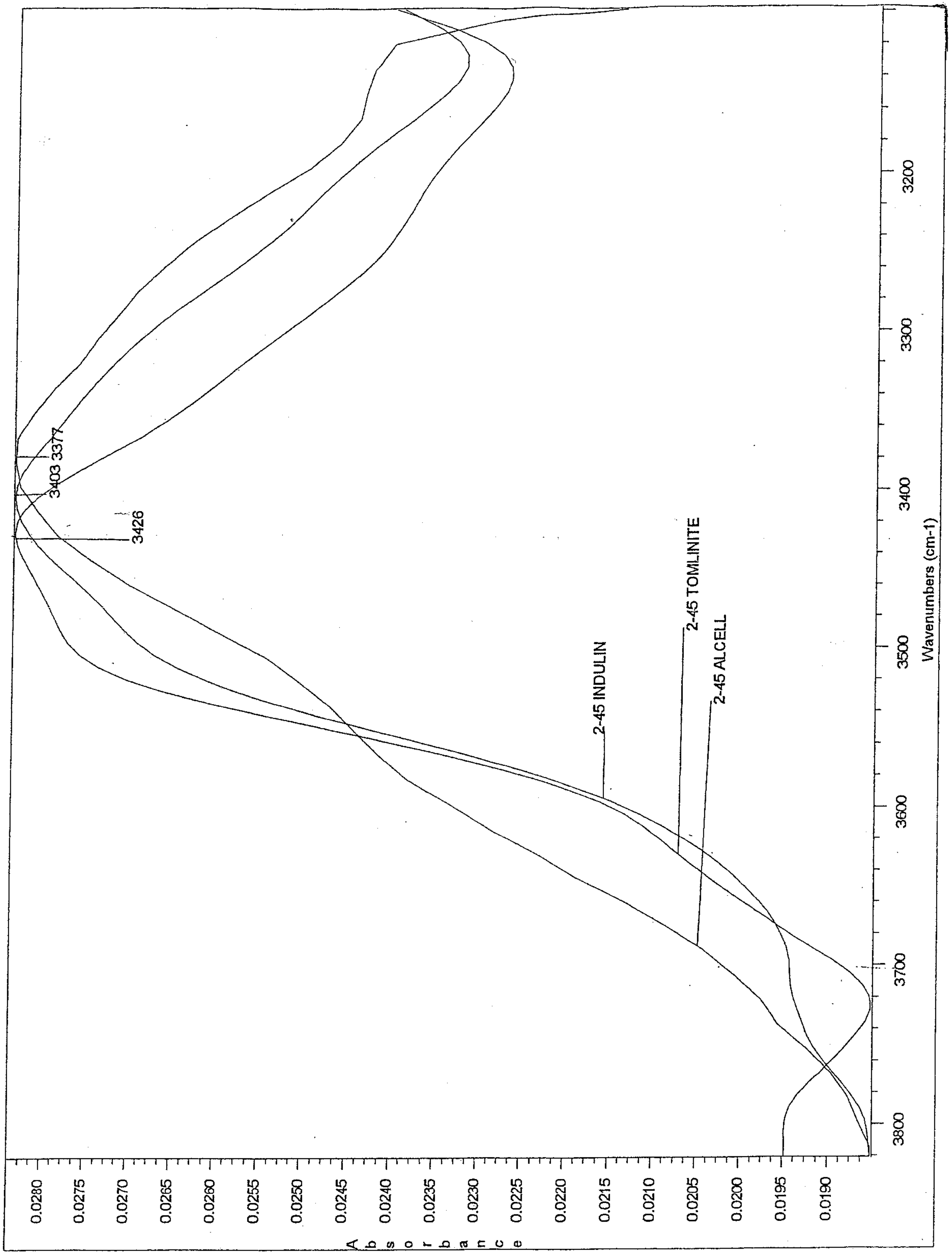


Figure 5-21: FTIR spectra of PVC-lignin's blend plasticized with 35 phr Benzoflex 2-45

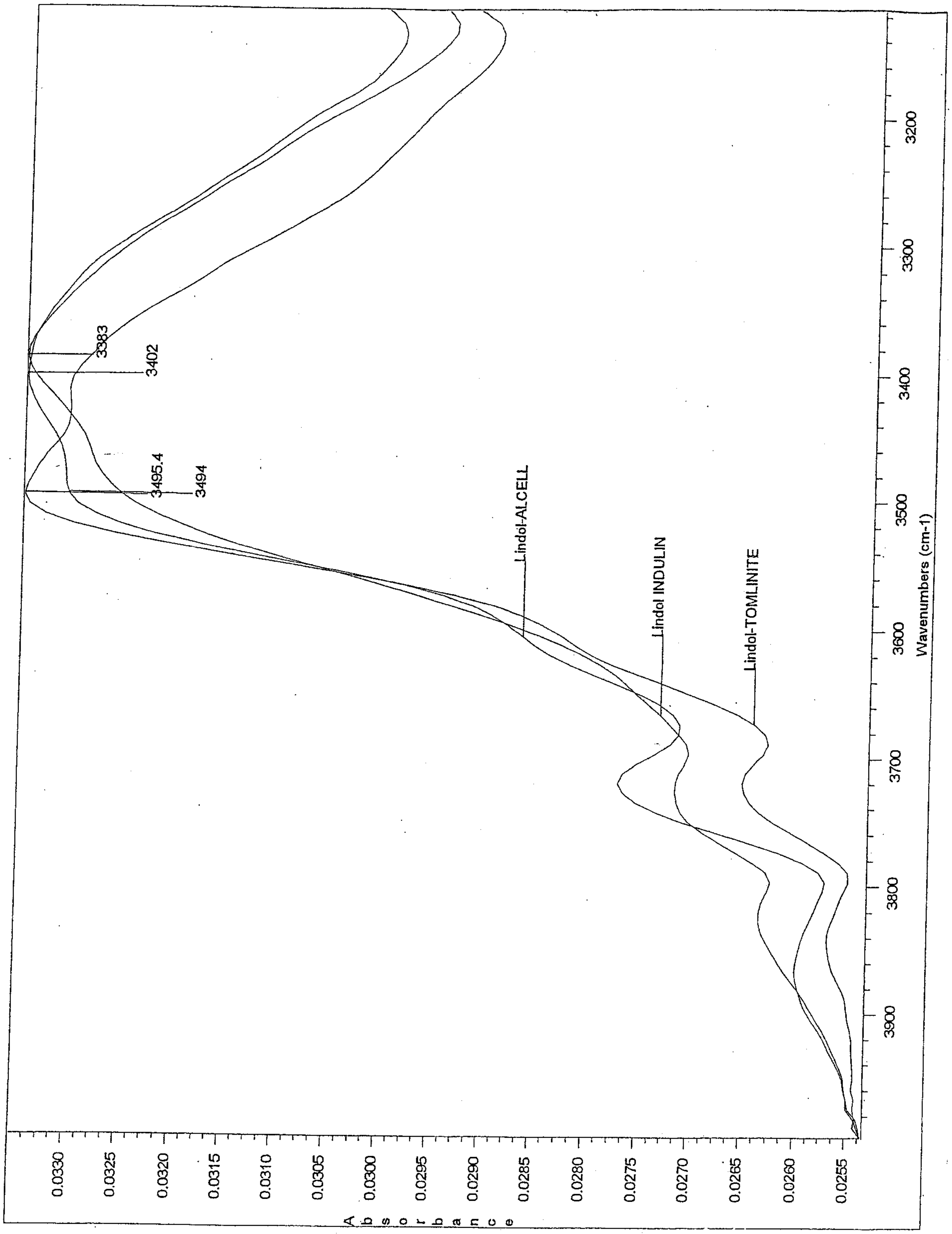


Figure 5-22: FTIR spectra of PVC-lignin's blend plasticized with 35 phr Lindol

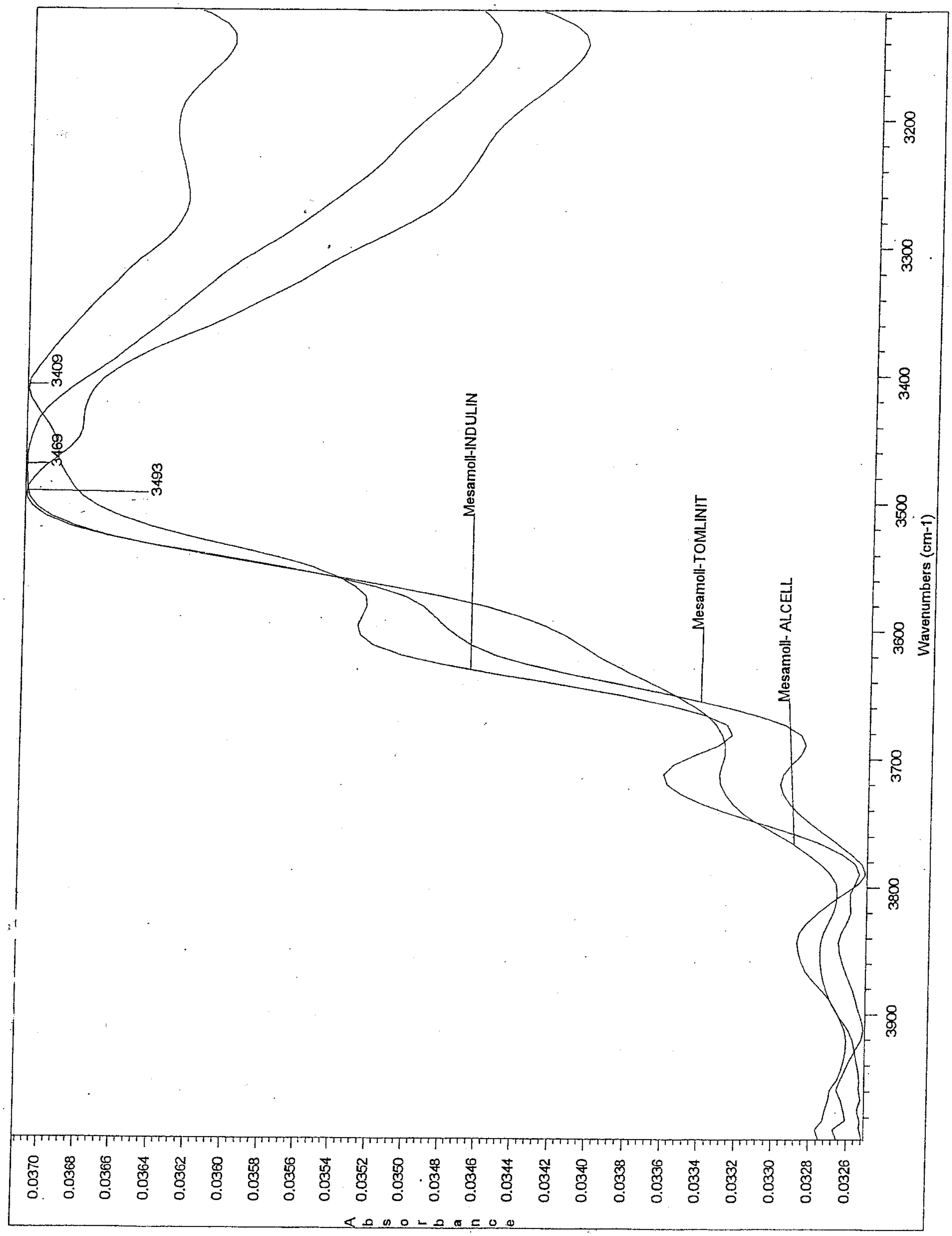


Figure 5-23: FTIR spectra of PVC-lignin's blend plasticized with 35 phr Mesamoll

The increase or decrease of OH group absorption maxima suggests that more or less fractions of lignin are involved in hydrogen bonding with calcium carbonate through the absorbed water film present on the surface of the filler. If more fractions of lignin are involved in this particular bonding the force at yield would increase. These bodings are conditioned by the degree of lignin plasticization as well as the degree of lignin dispersion through the matrix. It is also interesting to note that for a certain plasticizer the variations of tensile strength at yield does not correlate with the Tg of the blend, in contrast with the modulus values, which are much more sensitive to the Tg.

The above-presented data of PVC-lignin blends illustrate that plasticizers seem to play complex roles in determining the polyblend morphology and mechanical properties. However these properties of the blends are the result of several combined factors such as:

- Plasticizer effectiveness in lowering the degree of interaction between both PVC chains and lignin macromolecules;
- Plasticizer effectiveness in filler and lignin dispersion;
- Specific type of intermolecular bonding between plasticized PVC and plasticized lignins;
- The degree of adhesion between the PVC and/or lignins and calcium carbonate filler.

In addition the data demonstrate that the presence of certain plasticizers, which interfere with the intermolecular interactions existing in lignins, may allow the lignin molecules more molecular mobility. The morphology and the properties of PVC plasticized lignin blends are strongly influenced by the degree and mode of lignin plasticization and its dispersion within the PVC matrix.

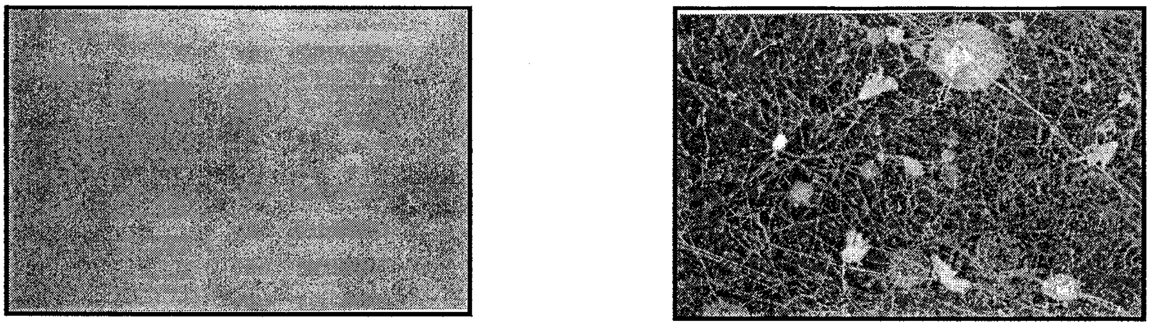
5.2.6 Fungi growth rating

Evaluation of the fungi growth on samples surface was carried on, after 28-days of incubation using an optical microscope with a 500x magnification as shown in Figure 5-24 to 5-27. Fungi radically grow on all samples, the PVC blends showed an extensive growth when compared to PVC controls. Although, all PVC controls showed fungi growth, it had not caused any visible change on the surface, only PVC control with Benzoflex 2-45 showed white spots on the surface indicating that such composites with Benzoflex 2-45 were degraded by fungi.

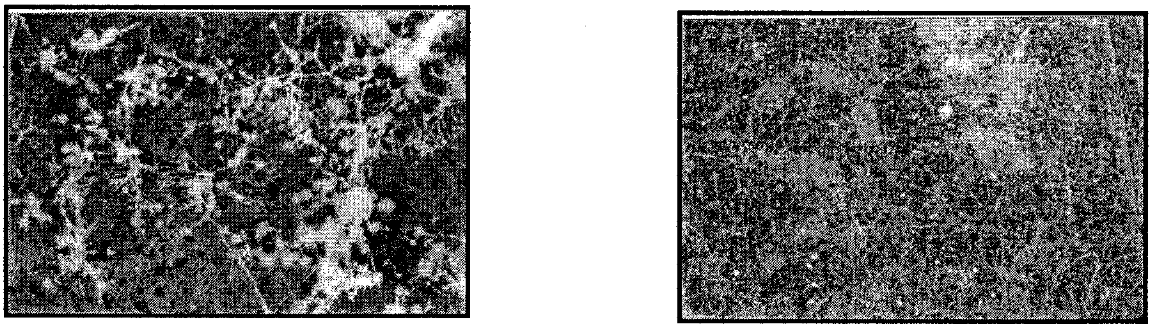
Given that lignins were the only brown (i.e., dark) color among the mixing components, the discoloration of PVC blends could be justified as a chemical change of lignin structure. The fungal growth rating for the different controls and blends are shown in Table 5-7. From the data we could notice that PVC-Tomlinite with Lindol and Mesamoll showed a similar growth to PVC controls. The plasticizer used in this study as a function of the fungi growth could be ordered as Benzoflex 2-45 > DOP > Mesamoll and Lindol.

Table 5-7: Fungi growth rating on specimens' surface

Sample ID	Fungi Rating			
	DOP	Benzoflex 2-45	Lindol	Mesamoll
PVC – Control	2	3	2	2
PVC – Alcell	3	4	3	3
PVC – Indulin	4	4	3	3
PVC – Tomlinite	3	4	2	2

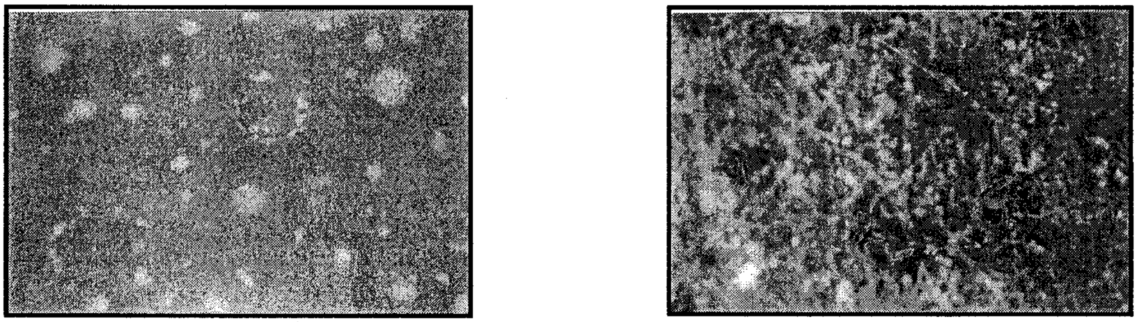


DOP - Control DOP - Alcell

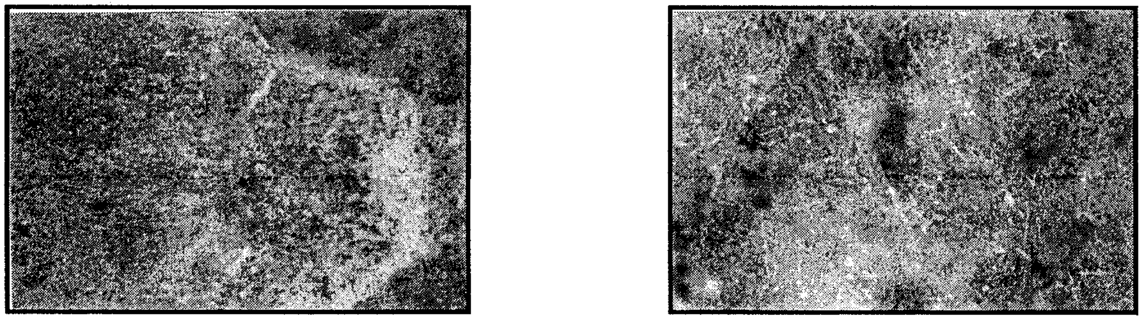


DOP - Indulin DOP - Tomlinite

Figure 5-24: The fungal growth (500x) on the surface of PVC controls and blends with respect to DOP

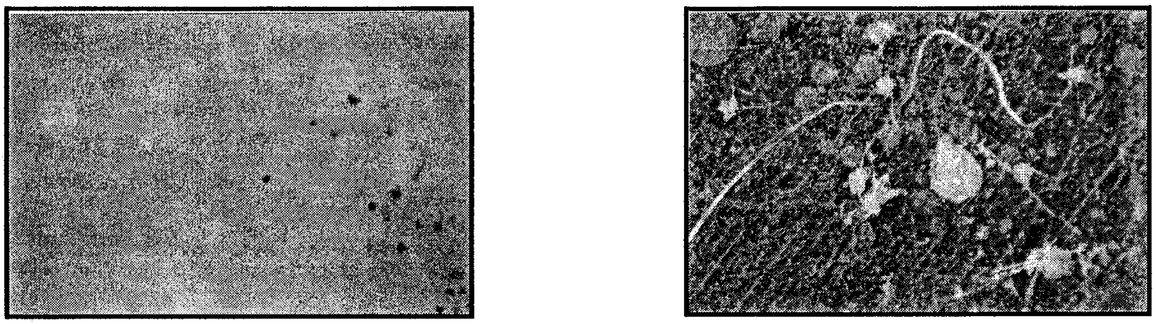


2-45 Control 2-45 Alcell



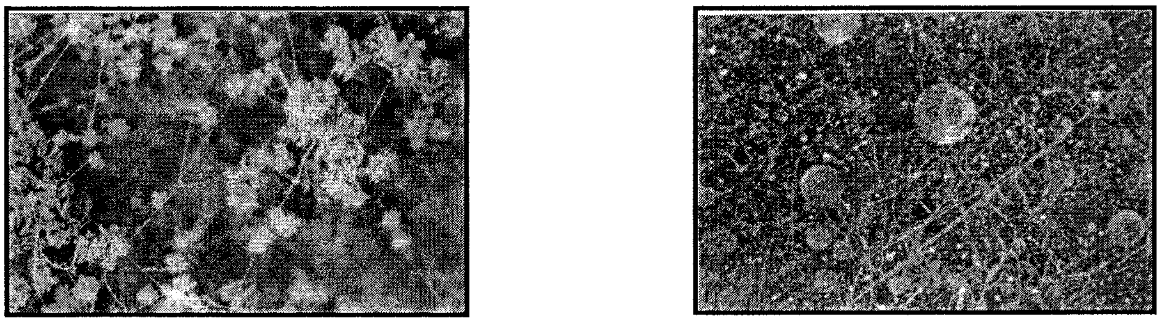
2-45 Indulin 2-45 Tomlinite

Figure 5-25: The fungal growth (500x) on the surface of PVC controls and blends with respect to Benzoflex 2-45



Lindol - Control

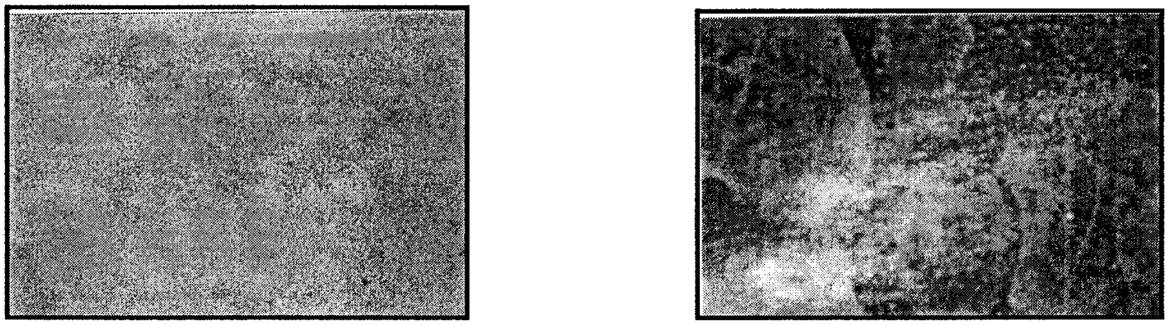
Lindol - Alcell



Lindol - Indulin

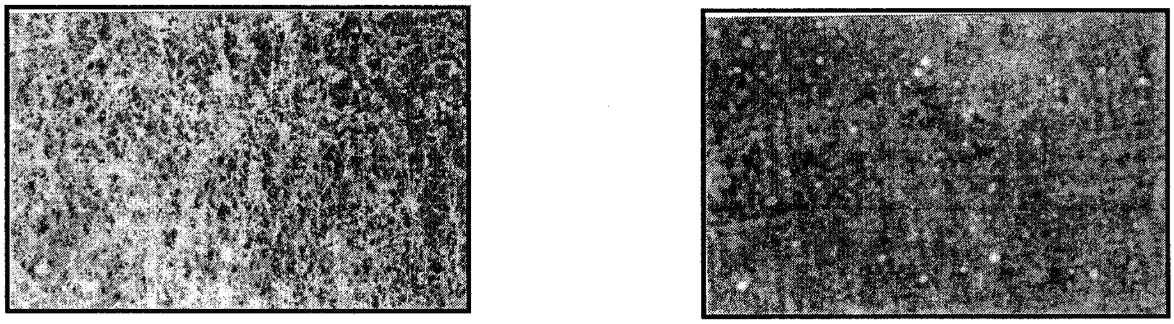
Lindol - Tomlinite

Figure 5-26: The fungal growth (500x) on the surface of PVC controls and blends with respect to Lindol



Mesamoll - Control

Mesamoll - Alcell



Mesamoll - Indulin

Mesamoll - Tomlinite

Figure 5-27: The fungal growth (500x) on the surface of PVC controls and blends with respect to Mesamoll

5.3 VC-VAc Copolymer – Lignin blends

This section [107-109] evaluates the impact of blending organosolv and kraft lignins with plasticized vinyl chloride–vinyl acetate copolymer in flooring formulations. Also it examines the impact of replacing DOP, with Benzoflex 2-45, Lindol and Mesamoll in these formulations.

5.3.1 Processibility

All VC-VAc copolymer-lignin blends versus their controls exhibit a decreased equilibrium torque value, indicating a lower melt viscosity, as can be seen from the Table 5-8. For the same plasticizer, the equilibrium torque value of the blends is largely influenced by the type of lignin and it increases in the order of Alcell > Indulin > Tomlinite, pointing out to the possibility of morphological differences existing within the blends. In addition for the same blend formulations the equilibrium torque with respect to the plasticizer type where in the order of DOP > Mesamoll > Benzoflex 2-45 > Lindol.

Table 5-8: Equilibrium torque of VC-VAc controls and blends with 35 phr plasticizers

Plasticizer Type	Equilibrium Torque at 140 ± 1°C [m.g]			
	PVC Control	PVC – Alcell	PVC – Indulin	PVC – Tomlinite
DOP	925	650	825	875
Benzoflex 2-45	1075	800	875	925
Lindol	1125	825	1025	1050
Mesamoll	950	750	850	900

5.3.2 Thermal properties

The Tg values of PVC controls and their respective blends, are shown in Table 5-9. Their Tgs differences are also shown in the same Table in °C and noted by (ΔTg). DSC thermograms for the second run in the temperature interval between –20 and 140 °C (Figures 5-28 to 5-31) reveal single Tgs for all blends which indicates a relatively homogenous structure. Similarly to homopolymer formulations a quite sharp and narrow glass transition range for blends plasticized with 2-45, Lindol and in a lesser measure with Mesamoll was observed. The Tg region of DOP plasticized blends was broad and less sharp indicating a certain degree of in-homogeneity at the molecular scale (similar to homopolymer).

Table 5-9: Tg of VC-VAc controls and blends and differences between the Tg of controls and respective blends (ΔTg)

Sample Identification	DOP		Benzoflex 2-45		Lindol		Mesamoll	
	Tg [°C]	ΔTg [°C]	Tg [°C]	ΔTg [°C]	Tg [°C]	ΔTg [°C]	Tg [°C]	ΔTg [°C]
VC-VAc Control	20.7	-	22.0	-	30.8	-	21.9	-
Alcell Blend	8.2	-12.5	19.3	-2.7	25.1	-5.7	13.7	-8.2
Indulin Blend	8.4	-12.3	17.9	-4.1	24.5	-6.3	10.1	-11.8
Tomlinite Blend	6.9	-13.8	19.2	-2.8	25.2	-5.6	8.9	-13.0

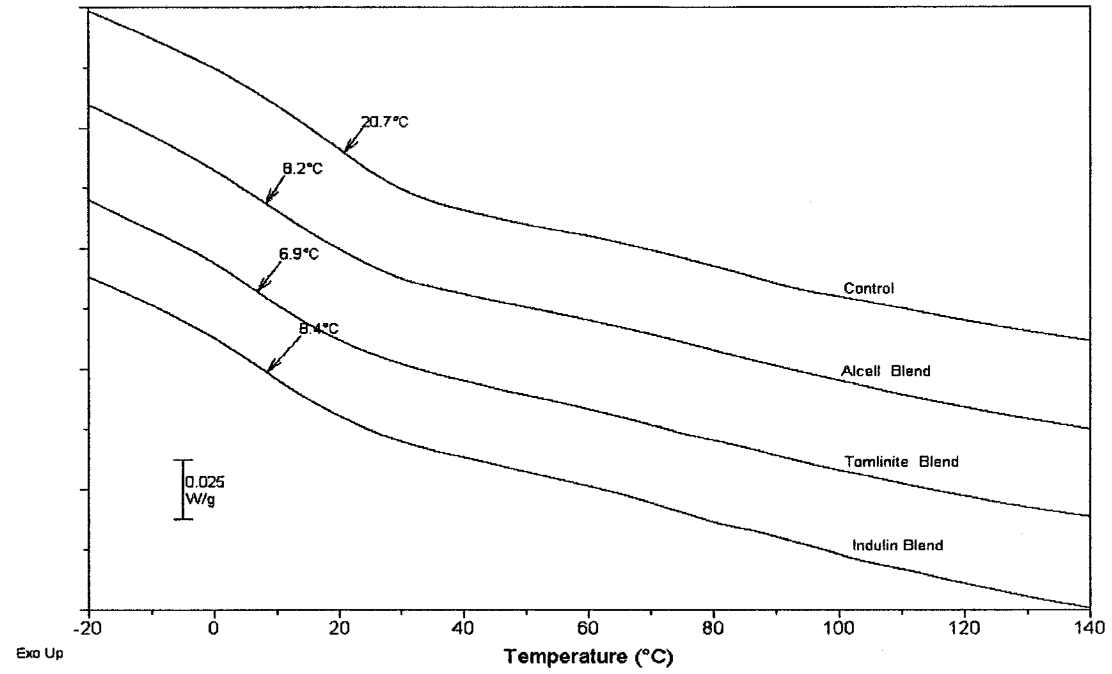


Figure 5-28: DSC thermograms of VC-VAc control and different lignin's blend with DOP

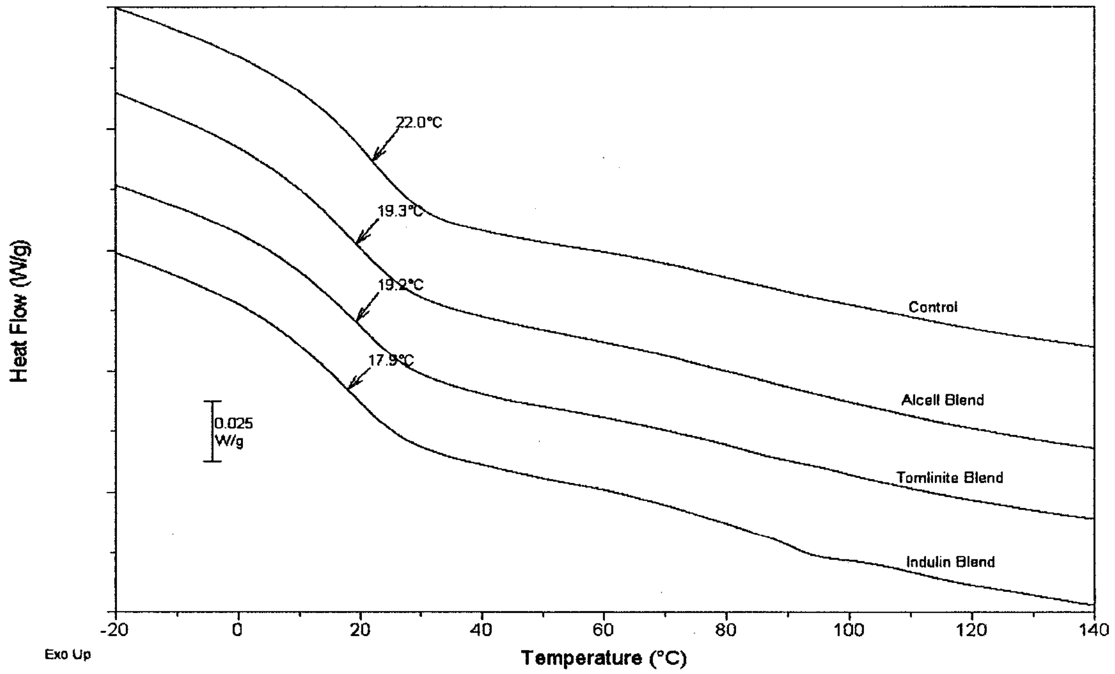


Figure 5-29: DSC thermograms of VC-VAc control and different lignin's blend with Benzoflex 2-45

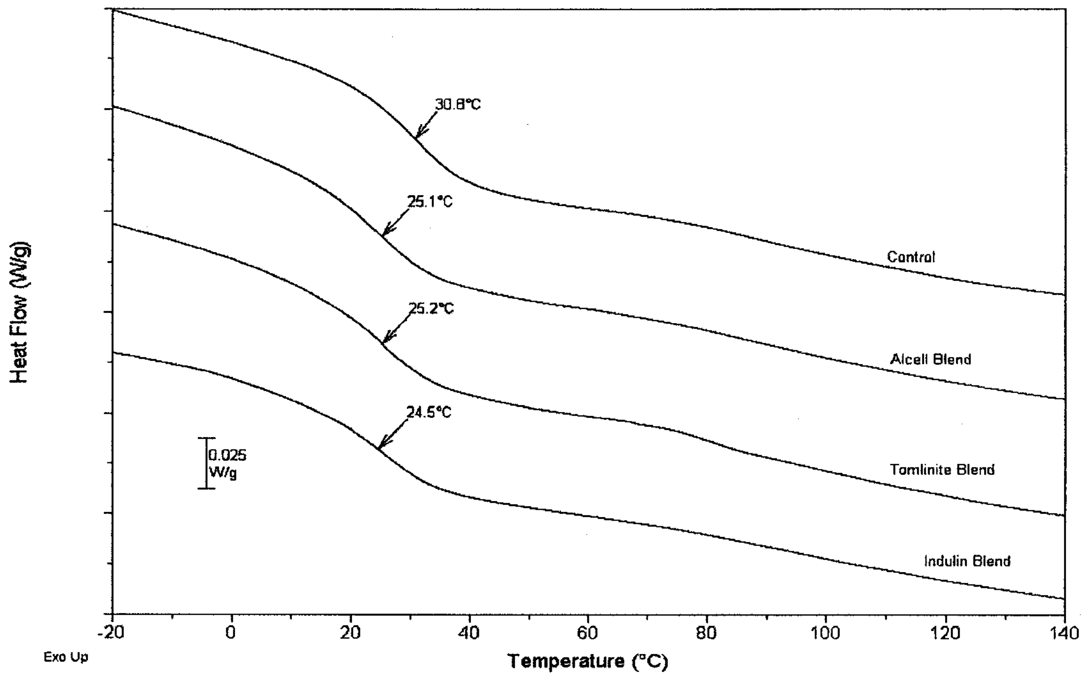


Figure 5-30: DSC thermograms of VC-VAc control and different lignin's blend with Lindol

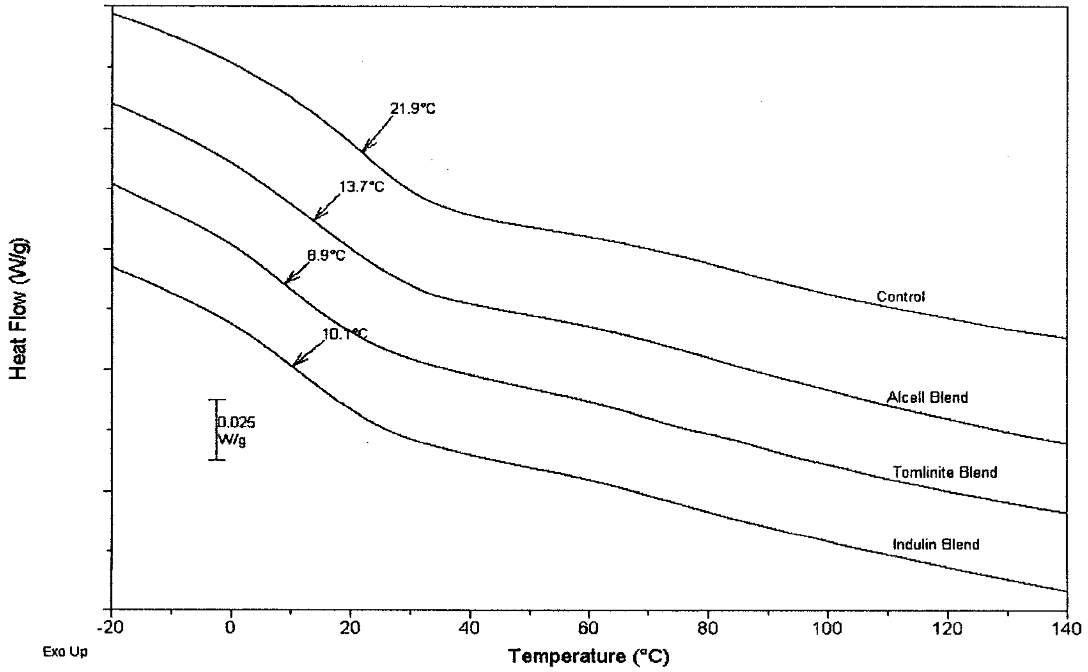


Figure 5-31: DSC thermograms of VC-VAc control and different lignin's blend with Mesamoll

Data presented in Table 5-9 point out that in comparison to the respective controls the Tgs of all blends decreased with few °C, and that the reduction (ΔTg) varies as a function of plasticizer and lignin type. There are appreciable differences in efficiency of each plasticizer on different lignins. Benzoflex 2-45 and Lindol reduce the Tg of all lignin blends by 3-5 °C. The results are not surprising taking into account their own Tg that are close to each other (-52 and -57.6 °C respectively). On the other hand Mesamoll and DOP reduce the Tg of the blends by 8-14 °C. These data are in total agreement with the data obtained from the homopolymer study but they are higher. The VC-VAc copolymer blends Tgs are higher in comparison to that of homopolymer, due to the vinyl acetate presence that tends to favorite the adhesion of the chains more to each other. The presence of polar carbonyl group is responsible for enhancing the polymer-polymer interaction [110].

Although each plasticizer-copolymer and plasticizer-lignin mixture presents apparently a single Tg as the second run suggests, an inspection of DSC thermograms of the first run (Figures 5-32 to 5-35) imply differently and shows that each mixture exhibit a specific relaxation behavior comprising in most of the cases two distinct relaxation peaks located at quite different temperatures. This may be interpreted as mixtures heterogeneity and that the apparently single broad transition observed in the second scan could be the result of two or more separate overlapping transitions that occur in a large temperature range.

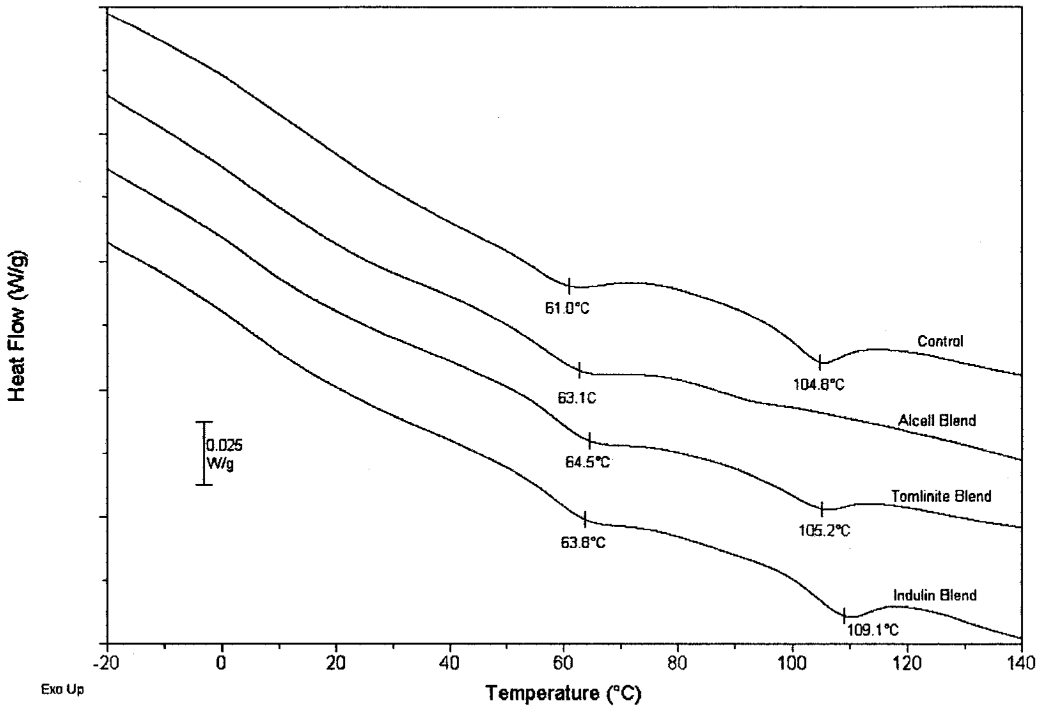


Figure 5-32: DSC thermograms of VC-VAc control and different lignin's blend with DOP

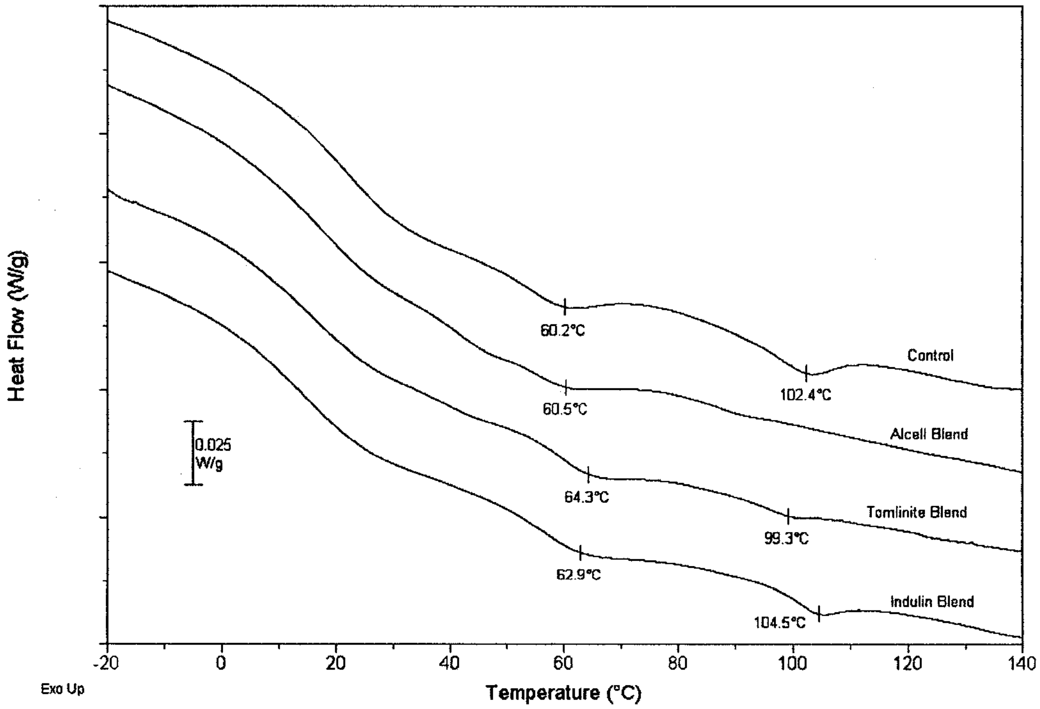


Figure 5-33: DSC thermograms of VC-VAc control and different lignin's blend with Benzoflex 2-45

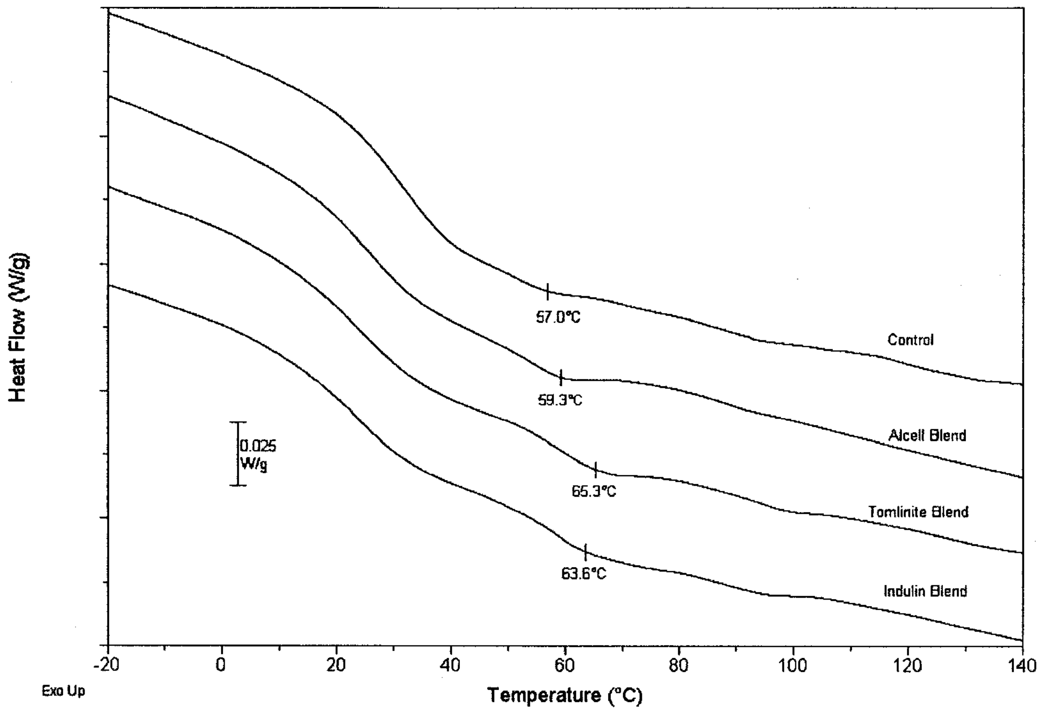


Figure 5-34: DSC thermograms of VC-VAc control and different lignin's blend with Lindol

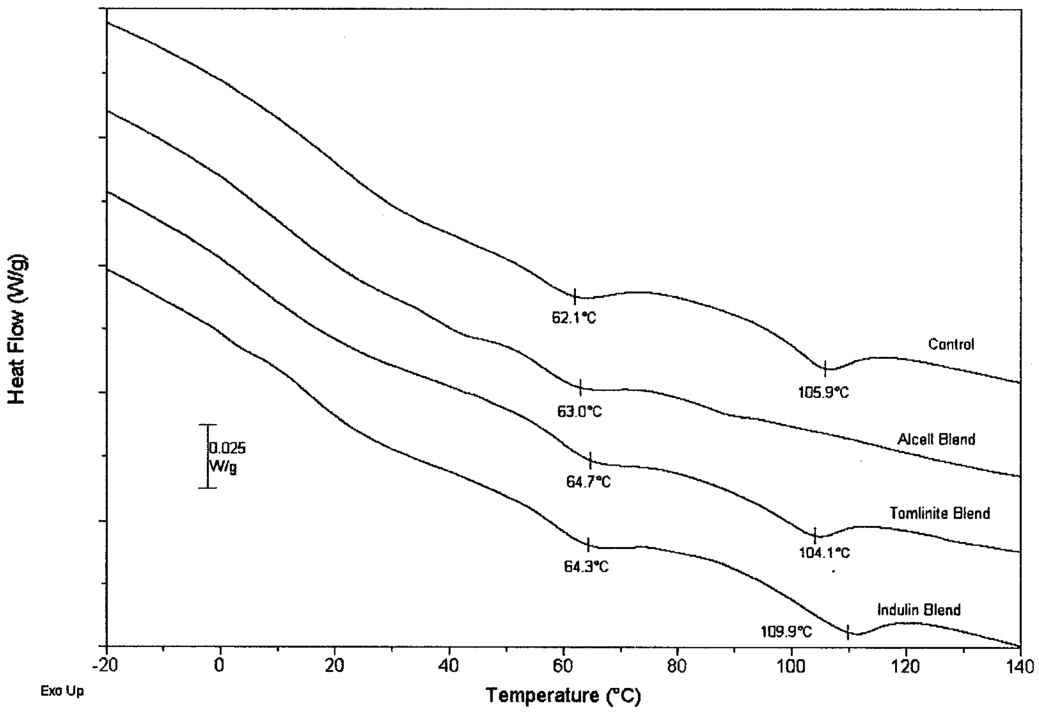


Figure 5-35: DSC thermograms of VC-VAc control and different lignin's blend with Mesamoll

As mentioned earlier, the enthalpy relaxation is due to the relaxation of polymer chains eliminating the excess free volume in an effort to approach the system preferred equilibrium state. The excess free volume is quenched in the system when the respective system is cooled from the melt. The rapid rise in viscosity that occurs as Tg is approached, freezes the polymer chains in a non-equilibrium conformation and configuration [104]. The free volume and viscosity of the blend is dependent on the molecular weight distribution (MWD=$\overline{Mw}/\overline{Mn}$) of its constituent, [8].

Larger molecules in a sample weigh more than smaller molecules, the $\overline{Mw}$ as well as molecular MWD should be smaller for small-size molecules and bigger for large-size molecules. Table 4-1 shows that Alcell, Indulin and Tomlinite lignins MWD is 2.22, 3.79, 4.3 respectively. Alcell lignin MWD is the least among the lignin used, approaching that of PVC (MWD=2.1). Seeing that, the association of Alcell lignin molecules within the blends will be more effective, decreasing the free volume that results in more miscible blend and for that a single transition endotherm is observed with Alcell lignin.

Furthermore, it is interesting to note that the formulation plasticized with Lindol shows one distinct relaxation peak. This could be owed to the solubility parameter of Lindol (δ=9.86 $(cal/cm^3)^{1/2}$) that is the least among the tested plasticizers and the nearest approaching that of copolymer (δ=9.7$(cal/cm^3)^{1/2}$). In addition different lignins show better compatibility when plasticized with Lindol due to its ability to plasticize both the lower and higher molecules fractions.

5.3.3 Mechanical properties

General considerations

The mechanical properties data of VC-VAc copolymer controls and blends as a function of plasticizer type are presented in Table 5-10, and their respective stress-strain curves in Figures 5-36 to 5-39. In Table 5-11 the variation in percentages of blends mechanical properties relative to their respective VC-VAc copolymer controls are indicated. Due to the fact that the mechanical properties of the formulations are strongly influenced by the Tg, the decrease in Tg values of blends (ΔTg) with respect to their respective controls are restated in Table 5-11. All the specimens were tested at room temperature (i.e., 23 ± 1 °C) which was in all the cases above or very close to specimens' Tg as seen in Table 5-9.

Analyzing the data presented in Table 5-11 two extremes may discern in VC-VAc-lignin blends. On one extreme there are the blends plasticized with Benzoflex 2-45 and Lindol characterized by similar Tg values of about 19 and 25 °C respectively, which are about 3-6°C lower than that of the respective controls. At the other extreme there are the blends plasticized with DOP and Mesamoll characterized by Tg values range of about 7-14 °C and which are about 8-14 °C lower than that of the respective controls. For most of these blends the modulus values are reduced by about 50-70 % in comparison with their respective controls.

Table 5-10: Mechanical properties of VC-VAc copolymer controls and blends relative to plasticizer type

Sample ID	Elastic Modulus [MPa]	Tensile Strength[MPa]		Elongation [%]	Toughness [MPa]
		Yield	Break		
DOP					
VC-VAc control	45.63	3.44	4.6	357	13.18
VC-VAc - Alcell	21.19	3.17	3.2	359	9.86
VC-VAc - Indulin	17.43	2.35	2.3	307	5.66
VC-VAc - Tomlinite	12.26	2.37	2.22	295	5.5
Benzoflex 2-45					
VC-VAc control	52.06	3.28	4.61	470	16.8
VC-VAc - Alcell	38.86	2.54	3.12	485	10.98
VC-VAc - Indulin	26.04	2.67	2.64	337	7.57
VC-VAc - Tomlinite	17.43	3.27	2.9	306	8.03
Lindol					
VC-VAc control	196.68	5.47	6.04	313	16.8
VC-VAc - Alcell	112.64	4.41	4.04	359	13.43
VC-VAc - Indulin	62.73	3.33	2.91	253	6.84
VC-VAc - Tomlinite	56.45	3.8	3.21	183	6.14
Mesamoll					
VC-VAc control	56.07	3.71	5.13	383	15.49
VC-VAc - Alcell	29.24	3.45	3.46	357	10.96
VC-VAc - Indulin	15.53	2.43	2.67	336	6.87
VC-VAc - Tomlinite	14.76	2.57	2.59	325	6.72

Table 5-11: Mechanical properties of VC-VAc-Alcell, VC-VAc -Indulin, and VC-VAc -Tomlinite blends versus VC-VAc controls at 35 phr of different plasticizers

Sample ID	ΔTg [°C]	Elastic Modulus [%]	% Tensile Strength		Elongation [%]	Toughness [%]
			Yield	Break		
DOP						
VC-VAc – Alcell	9.0	-53.56	-7.85	-30.43	0.56	-25.19
VC-VAc - Indulin	12.3	-61.80	-31.69	-50.00	-14.01	-57.06
VC-VAc - Tomlinite	13.8	-73.13	-31.10	-51.74	-17.37	-58.27
Benzoflex 2-45						
VC-VAc – Alcell	2.7	-25.36	-22.56	-32.32	3.19	-34.64
VC-VAc - Indulin	4.1	-49.98	-18.60	-42.73	-28.30	-54.94
VC-VAc - Tomlinite	2.8	-66.52	-0.30	-37.09	-34.89	-52.20
Lindol						
VC-VAc – Alcell	5.7	-42.73	-19.38	-33.11	14.70	-20.06
VC-VAc - Indulin	6.3	-68.11	-39.12	-51.82	-19.17	-59.29
VC-VAc - Tomlinite	5.6	-71.30	-30.53	-46.85	-41.53	-63.45
Mesamoll						
VC-VAc – Alcell	8.2	-47.85	-7.01	-32.55	-6.79	-29.24
VC-VAc - Indulin	11.8	-72.30	-34.50	-47.95	-12.27	-55.65
VC-VAc - Tomlinite	13.0	-73.68	-30.73	-49.51	-15.14	-56.62

Figures 4-36 to 4-39 indicates that the stress-strain curves are representative for ductile materials. They exhibit a distinct yield and ductile failure with neck propagation and strain hardening for all the controls and for a few blends.

Figure 5-36: Stress-strain curves of VC-VAc control and blends plasticized with DOP

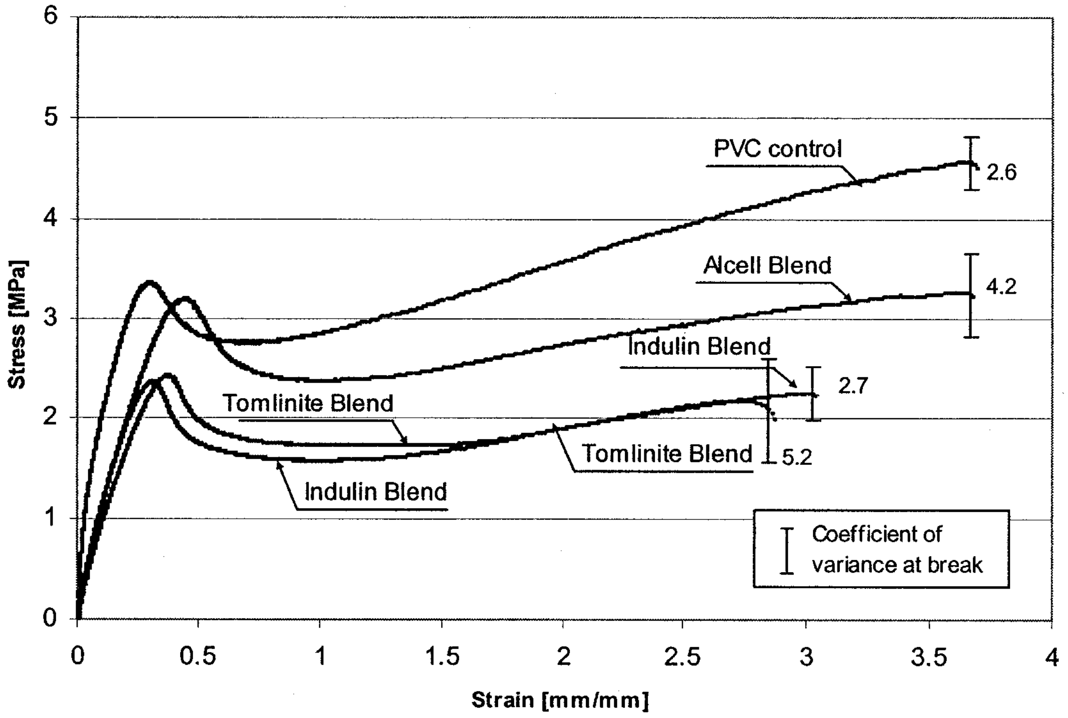


Figure 5-37: Stress-strain curves of VC-VAc control and blends plasticized with Benzoflex 2-45

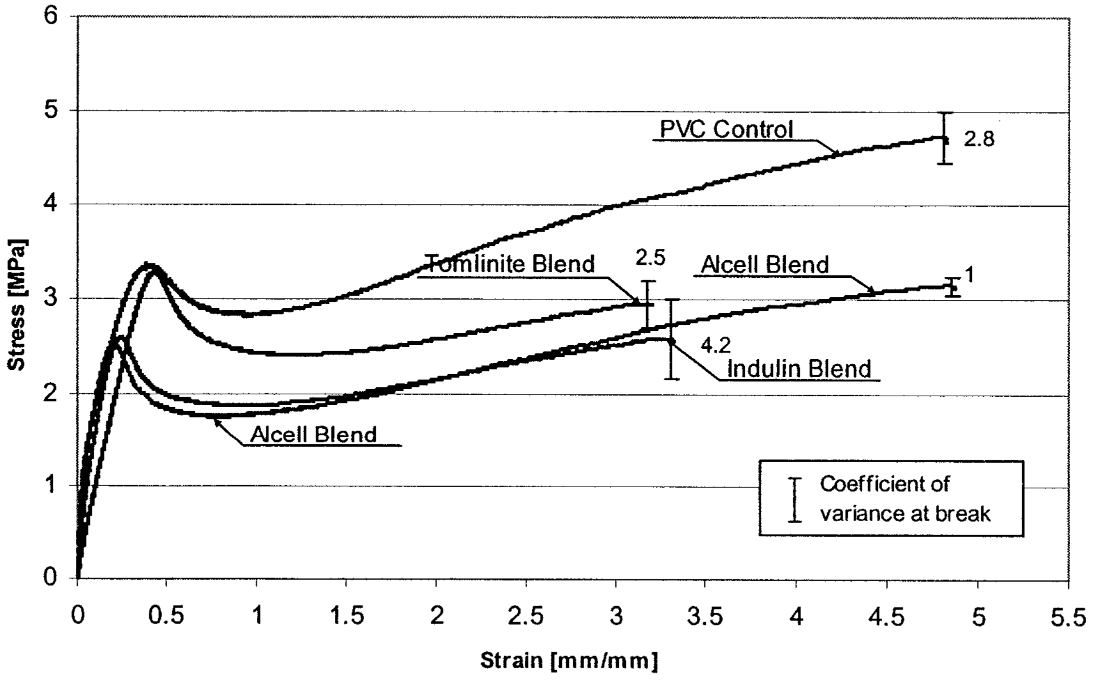


Figure 5-38 : Stress-strain curves of VC-VAc control and blends plasticized with Lindol

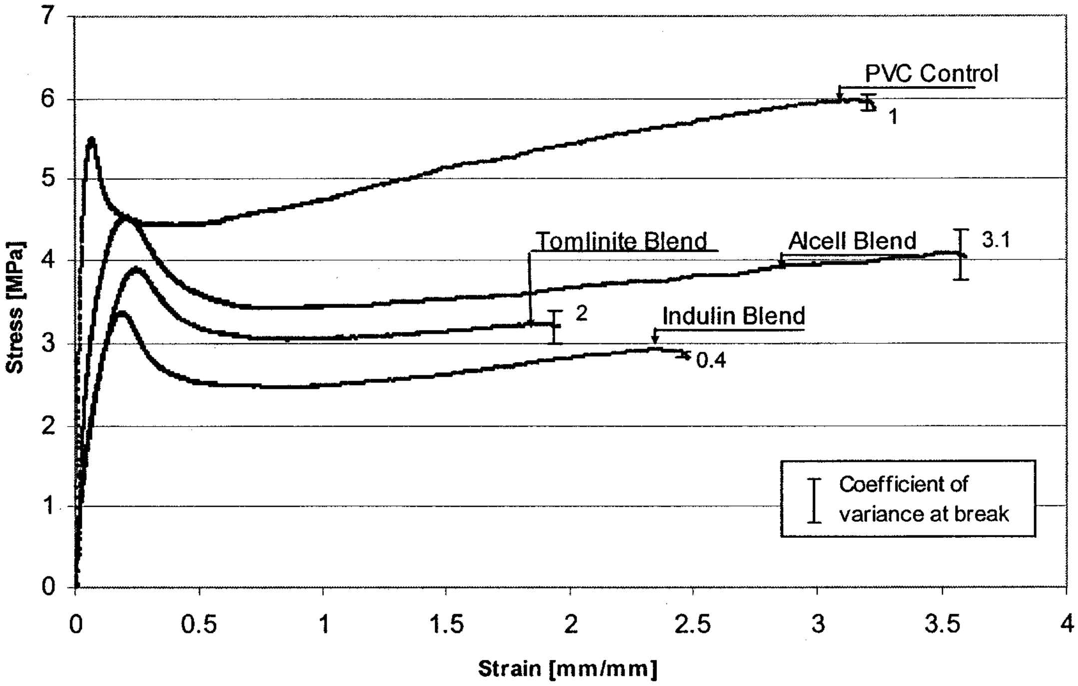
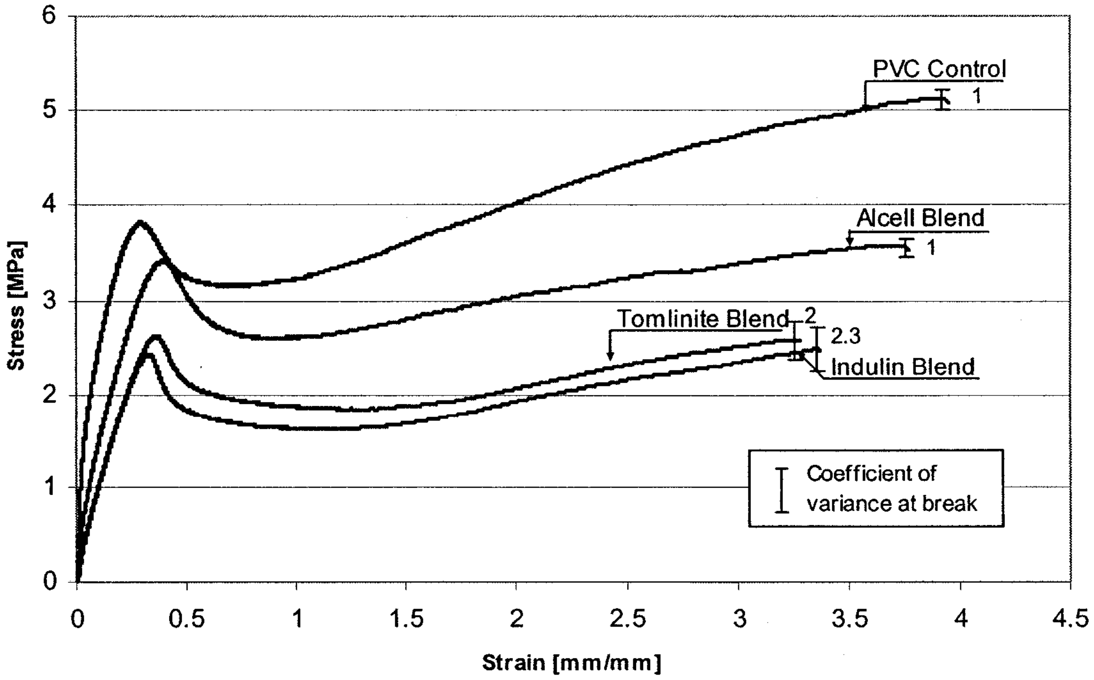


Figure 5-39: Stress-strain curves of VC-VAc control and blends plasticizied with Mesamoll



The tensile properties are highly dependent on intermolecular copolymer - copolymer, lignin-lignin, VC-VAc copolymer - lignin, VC-VAc copolymer - plasticizer, lignin-plasticizer and matrix-filler attractions. Above Tg, increasing molecular mobility leads to diminished bond strength by interchain or intermolecular separation [100].

Considering that room temperature, which is the testing temperature, is higher than Tg values of DOP and Mesamoll blends and close to that of Lindol and Benzoflex 2-45 blends, the molecular mobility should increase inducing an increase in elongation and a decrease in modulus, as well as tensile strength values at yield and break for DOP and Mesamoll plasticized blends higher than that of Lindol and Benzoflex 2-45 plasticized blends. Indeed Lindol plasticized blends generally present these features, whereas DOP plasticized blends are characterized by much modest increase in elongation and comparable increases in tensile strength at break. The tensile strength at yield values decreases less than those of Lindol plasticized blends. All these results suggest that different factors affect the mechanical properties of the different tested plasticizers.

DOP and Mesamoll plasticized blends

By examining Table 5-11, it is clear that elastic modulus is reduced for blends as a function of Tg decline (i.e., elastic modulus reduction is directly proportional to the Tgs decrease). The reduction in modulus is accompanied by tensile strength at break, elongation, and toughness reduction. The mechanical properties reduction for the different lignins are in order of Alcell > Indulin > Tomlinite. Although, the ΔTg of DOP and Mesamoll plasticized blends are higher than that of Lindol and Benzoflex 2-45, the mechanical properties depreciation are in the same order of magnitude. This is due to the presence of poorly plasticized lignin with a quite high Tg, in the glassy state, that will act as reinforcing filler and enhance the modulus of the blends plasticized with DOP and Mesamoll reaching that of Lindol and Benzoflex 2-45.

Lindol plasticized blends

Lindol plasticizes both the low and high molecular weight fractions of Alcell and Tomlinite, and partially that of Indulin (i.e., low molecular weight fractions). As observed previously it reduces the Tgs of Alcell and Tomlinite and in a lesser measure that of Indulin. Alcell, the most plasticize lignin shows an increase in elongation by 14.7 % when compared to VC-VAc control, while the reduction in modulus is obvious due to lignin toughness nature. On the other hand Indulin blend, the least plasticized one, shows an increase in modulus than expected, tacking into consideration that its' ΔTg is higher than both Alcell and Tomlinite blends. This is owed to its poor plasticization with Lindol that reinforced the matrix and consequently allows more plasticizer for the VC-VAc matrix inducing elongation reduction by only 19.2 %. Considering that Tomlinite blend ΔTg is almost equal to that of Alcell blend, same behavior was expected, but surprisingly it shows high reduction in modulus and elongation. This is owed to Lindol ability to plasticize Tomlinite blend reducing the available plasticizer for VC-VAc matrix that consequently reduces the modulus. In addition, Tomlinite high polydispersity (MWD=4.3 the highest among the tested lignins), reflects the presence of large-size molecules which are able to restrict the elongation of the blend.

Benzoflex 2-45 plasticized blends

Although, the ΔTg of different lignins is in the range of 3 °C, while that plasticized with Lindol is 6 °C, and that of all lignins plasticized with Benzoflex 2-45 is below room temperature, while those plasticized with Lindol is above room temperature. Lignins plasticized with Benzoflex 2-45 followed the same trend as formulations plasticized with Lindol. In addition, their moduli of elasticity reduction are less than that of Lindol. These increases in modulus as well as the increase in the tensile strength at break, support the argument that Benzoflex 2-45 plasticizes mostly the low molecular weight fractions. The remaining high molecular weight fractions are in the glassy state, and evenly distributed through plasticized VC-VAc copolymer matrix will act as reinforcing filler thus enhancing its modulus.

Moreover, Benzoflex 2-45 seems to be good plasticizer for all lignins. The mechanical properties of these blends display some interesting characteristics when compared with the respective data of the control. The Alcell blend's Tg is with 2.7 °C lower, the elongation value is higher and the strength at yield and break values lower. In addition a certain degree of strain hardening is noticeable depicting a higher degree of plasticization in relation with the control. While for Indulin and Tomlinite blends, the ΔTgs decreased by 4.1 and 2.8 °C respectively. The tensile strength at yield is higher than that of Alcell blend, and both elongate less than Alcell blend. As mentioned previously (i.e., see PVC homopolymer) Benzoflex 2-45 plasticizes to a certain degree the high molecular fractions of these two lignins. These partially plasticized fractions probably develop some interactions with the VC-VAc copolymer chains and due to their high polydispersity (i.e., MWD=3.79, 4.3 respectively) a high force is needed for chain segments to be able to slip past each other at the yield. In addition they are less evenly distributed through VC-VAc matrix than Alcell, which explains why their blends elongate less.

5.3.4 Fungi growth rating

Evaluation of the fungi growth on the sample surfaces was carried out, after 28-days of incubation using visual examination and optical microscopy at a 500x magnification. Fungi grew up on all samples; the VC-VAc blends showed discoloration and extensive growth when compared to VC-VAc controls. Although, all VC-VAc controls showed an extent of fungi growth, this had not cause any visible change on the surface except for VC-VAc control plasticized with Benzoflex 2-45, that showed white spots on the surface, indicating that composites containing Benzoflex 2-45 were degraded by fungi. The fungal growth rating for different controls and blends are shown in Table 5-12. From which we could notice that VC-VAc -Alcell polyblend plasticized with Lindol shows a similar growth to VC-VAc controls. The plasticizers used in this study as a function of fungi growth could be ordered as 2-45 > DOP $\geq$ Mesamoll > Lindol.

Table 5-12: Fungi growth rating on specimens' surface

Sample ID	Fungi Rating			
	DOP	Benzoflex 2-45	Lindol	Mesamoll
VC-VAc – Control	1	2	1	1
VC-VAc – Alcell	3	4	1	3
VC-VAc – Indulin	2	4	2	2
VC-VAc – Tomlinite	2	4	2	2

5.4 VC-VAc copolymer versus PVC homopolymer

In this section an evaluation of the processibility, thermal and mechanical properties, as well as the fungi resistance of different VC-VAc copolymer formulations are discussed versus their PVC homopolymer formulations. This is carried in order to understand better the behavior of these complex formulations highly filled with calcium carbonate, and to evaluate the effect of vinyl acetate present in the copolymer.

5.4.1 Processibility

All VC-VAc copolymer controls and VC-VAc copolymer-lignin blends exhibit a decreased mixing equilibrium torque value versus that of PVC homopolymer, indicating a lower melt viscosity, as can be seen in Table 5-13.

Table 5-13: Equilibrium torque differences between VC-VAc copolymer versus PVC homopolymer controls and blends with 35 phr plasticizers

Plasticizer Type	Equilibrium Torque at 140-145 ± 1°C [%]			
	VC-VAc Control	VC-VAc – Alcell	VC-VAc – Indulin	VC-VAc – Tomlinite
DOP	- 22.9	- 36.6	- 23.3	- 18.6
Benzoflex 2-45	- 20.4	- 31.9	- 27.1	- 22.9
Lindol	- 18.2	- 29.8	- 22.6	- 17.6
Mesamoll	- 26.9	- 28.6	- 29.2	- 23.4

The reduction in equilibrium torque magnitude is around 30 % with maximum reduction for formulation obtained with Alcell lignin. This supports the argument that the presence of vinyl acetate acts as internal plasticizer facilitating the macromolecules movements, and hence reduces the mixing equilibrium torque. VC-VAc copolymer has lower softening point than that of PVC homopolymer, can be processed at lower temperature (i.e., economical value), and has generally an inferior long term heat stability [111].

5.4.2 Thermal properties

The differences in glass transition temperature (ΔTg) between copolymer and homopolymer formulations are shown in Table 5-14. As data suggest, the VC-VAc copolymer Tgs are higher than that of PVC homopolymer for controls and blends, the presence of vinyl acetate comonomer enhance the bonding in between the copolymer chains. A careful review of the different ΔTgs reveals that Lindol and Benzoflex 2-45 plasticizers have less effect on the Tgs increase, which may be due to their own Tgs that are the lowest among the tested plasticizers (i.e., -57.6 and – 52 °C respectively).

Table 5-14: Tg differences (ΔTg) between VC-VAc copolymer versus PVC homopolymer controls and blends with 35 phr plasticizers

Sample Identification	ΔTg [°C]			
	DOP	Benzoflex 2-45	Lindol	Mesamoll
VC-VAc – Control	11.4	1.2	5.1	10.1
VC-VAc – Alcell	6.0	2.4	3.0	4.0
VC-VAc – Indulin	6.6	2.8	2.7	7.6
VC-VAc – Tomlinite	4.6	6.1	2.7	4.3

5.4.3 Mechanical properties

The elastic modulus at 2% elongation, tensile strength at yield and break, as well as elongation differences of the copolymer versus homopolymer are showed in Table 5-15 in percentage. The calculations are carried in accordance to the formula:

$$\% \, Change = \frac{Copolymer - Homopolymer}{Homopolymer} X \, 100$$

Although, the glass transition temperature is very effective factor in controlling the mechanical properties, as higher the Tg is, the higher the mechanical properties. The mechanical properties (i.e., modulus, tensile strength at yield and break) show a declining trend accompanied with an increase in elongation when VC-VAc copolymer control, and blend formulations are compared to their corresponding PVC homopolymer formulations.

Even though, the VC-VAc copolymer controls and blends Tgs' are higher than that of PVC homopolymer. Their Tgs, in most of the cases are lower or very close to room temperature (i.e., 23 ± 1 °C). For that, vinyl acetate is suspected to play a dual role. It attracts the polymeric chains together resulting in considerably higher Tgs, and at the same time acts as a lubricant in between the chain macromolecules it self, resulting in decreasing the modulus and increasing the elongation.

Table 5-15: Mechanical properties [%] of VC-VAc copolymer versus PVC homopolymer controls and blends with 35 phr plasticizers

Sample ID	% Elastic Modulus	% Tensile Strength		Elongation [%]
		Yield	Break	
DOP				
VC-VAc control	-19.28	-19.25	3.60	141.22
VC-VAc - Alcell	-31.91	-22.87	-6.98	184.92
VC-VAc - Indulin	-45.80	-30.27	-15.44	103.31
VC-VAc - Tomlinite	-60.46	-36.46	-30.41	57.75
Benzoflex 2-45				
VC-VAc control	7.76	-23.90	-14.79	76.03
VC-VAc - Alcell	-30.41	-20.38	-18.75	60.60
VC-VAc - Indulin	-39.29	-26.65	-37.59	66.01
VC-VAc - Tomlinite	-47.33	-30.43	-31.60	48.54
Lindol				
VC-VAc control	34.44	-6.66	2.90	165.25
VC-VAc - Alcell	37.20	0.00	-10.22	82.23
VC-VAc - Indulin	-15.00	-10.96	-23.82	52.41
VC-VAc - Tomlinite	-24.93	-28.03	-32.70	46.40
Mesamoll				
VC-VAc control	40.03	-7.48	5.99	113.97
VC-VAc - Alcell	-23.21	-13.53	-10.82	110.00
VC-VAc - Indulin	-53.48	-29.97	-11.59	96.49
VC-VAc - Tomlinite	-57.46	-33.07	-25.14	71.05

The modulus of elasticity reduction in blends were in the order of Alcell > Indulin > Tomlinite when lignin type was considered. Meanwhile when the increase in elongation is considered the same order is valid. Seeing that, Alcell lignin seems to be the most proper lignin in altering the formulations mechanical behavior

Among the tested plasticizers Lindol enhance both the modulus and elongation of PVC control and Alcell blend while its modulus reduction for Indulin and Tomlinite formulations were the lowest.

5.4.4 Fungi resistance

An inspection of the fungi rating for both copolymer and homopolymer shows that the copolymer formulations are more resistible to fungi. The fungi rating were downgraded for all VC-VAc copolymer controls, and most of its blend formulations plasticized with Lindol and DOP. That could be owed to the VAc presence that enhance the interaction between the copolymer chains resulting in tied structure with smaller-size pores. The denser the structure is, the better its resistance to microorganisms attack.

5.5 VC-VAc copolymer microorganism resistance

Previously the fungi resistance of the different formulations was based on the visual assessment and microscopy followed by fungi rating in accordance to ASTM G21-2000 [97]. Although this method was helpful to identify which formulations is initially better to continue with, further methods of assessments are required to confirm the results. Considering that the visual assessment is in two dimension only (i.e., the samples surface) and is not able to identify or measure the harmful effect of the fungi in the third dimension (i.e., the surface depth). The results of this preliminary test indicated that fungal growth was similar on all the surfaces of control specimens, except those formulated with Benzoflex 2-45 plasticizer, which was quite surprising. Alkyl sulphonic phenyl ester group present in Mesamoll should have a higher resistance to hydrolysis and consequently to fungi attack than aryl phosphate ester present in Lindol and much higher than alkyl carbonyl ester present in DOP. This observation was an indicative that other additives present in these formulations could be the fungi targets. The heat stabilizer (i.e., dibutyltin dilaurate) and the lubricant (i.e., calcium stearate), both derivatives of fatty acids, were considered to enhance the adhesion of fungi to the exposed surfaces due to the high affinity of fungi to fatty acids derivatives [112, 113].

Consequently other formulations were prepared in the same conditions and proportions. The only difference was the chemical nature of the heat stabilizer and lubricant. Butyltin mercaptide/carboxylate, commercially known as Mark TK 262 GV, as a heat stabilizer with a paraffin wax base lubricant commercially known as Marklube 367 were used.

Controls and blends were formulated with the previous heat stabilizer and lubricant as well as with the new ones. In addition, other compositions were formulated with the both sets of heat stabilizer and lubricant, and an antimicrobial agent in proportion of 0.6 %-wt based on the total weight of the final formulation. The components of each formulation, as well as the designation of each formulation are presented in Table 5-16.

A total of 16 formulations representing control specimens and 16 formulations representing blend specimens were prepared. Three sheets (7 x 12.7 x 0.15 cm) were pressed for each formulation. Two out of three sheets were inoculated with the fungi suspension (inoculated specimens) and incubated for 28 days at 28 ± 1°C and 95 ± 2 % RH. After the incubation period each sheet was examined for fungal growth then disinfected with a solution of mercuric chloride, washed and dried at room temperature for 24 hrs.

Consequently, one out of these two sheets was dried for another 6 days and thereafter 5 dog and bone specimens were cut and tested for tensile properties, while the other sheet was used for determining the weight loss. The non-inoculated sheets (sterile specimens) were incubated in similar conditions. After the incubation period they were examined for fungal growth and after 6 days drying, 5 dog and bone specimens were cut and tested for tensile properties.

Table 5-16: Composition in phr of the different VC-VAc copolymer and Alcell blend tested formulations

Formulation Components/Designation	Controls				Blends.			
	I	I-A	II	II-A	I	I-A	II	II-A
VC-VAc copolymer	100	100	100	100	80	80	80	80
Alcell lignin	0	0	0	0	20	20	20	20
Plasticizer	35	35	35	35	35	35	35	35
Ca CO_3 filler	200	200	200	200	200	200	200	200
DBTDL[1] heat stabilizer	3	3	0	0	3	3	0	0
Ca Stearate lubricant	1.5	1.5	0	0	1.5	1.5	0	0
Mark TK 262 GV heat stabilizer[2]	0	0	3	3	0	0	3	3
Marklube 367 lubricant[3]	0	0	1.5	1.5	0	0	1.5	1.5
Sanitized PL-21-60 antimicrobial[4]	0	2	0	2	0	2	0	2

Where (1) Dibutyltin dilaurate (2) Butyltin mercaptide/carboxylate
(3) Paraffin wax (4) Phyrithion compound

The susceptibility of control and blend formulations to fungi attack were evaluated [114] by the determination of:

- Intensity of fungal growth;
- Loss in weight;
- Changes in mechanical properties (modulus, tensile strength at yield and break, elongation at break);
- Glass transition temperature.

5.5.1 Visual assessment

The visual assessment of the inoculated samples was carried out and the fungi growth was rated as presented in Table 5-17. In formulations I the fungi growth covered less than 10% of all the control specimens' surfaces, except the control plasticized with Benzoflex 2-45 that shows a light growth (i.e., 10%-30%). The fungi growth was more visible on the blend specimens' surfaces that range from medium growth to heavy growth, except formulation plasticized with Lindol that shows a growth similar to the control samples (i.e., less than 10%). Presence of the antimicrobial agent in formulations I-A seems to prevent the fungal growth on all controls surfaces. However, traces of fungal growth were observed on blends' surfaces plasticized with DOP and Mesamoll.

Table 5-17: Fungi growth rating on specimens' surfaces after 28 days incubation period

Sample ID		DOP	Benzoflex 2-45	Lindol	Mesamoll
Formulation I	Control	1	2	1	1
	Blend	3	4	1	3
	Control - A	0	0	0	0
	Blend - A	1	0	0	1
Formulation II	Control	0	1	0	0
	Blend	3	4	2	3
	Control - A	0	0	0	0
	Blend - A	0	2	0	0

All control specimens obtained with formulation II (except formulation plasticized with Benzoflex 2-45) show an absence of fungi growth. This observation could confirm the fact that the heat stabilizer and/or lubricant - both derivatives of fatty acids - are fungi principal target in formulation I. Nevertheless, the new additives seems not to be effective in the presence of Alcell lignin as the blends in formulation II indicated, the fungi growth rating being similar to that observed in formulation I. Therefore it may be presumed that in all blends the lignin is the favored fungi' carbon source. The efficiency of the added antimicrobial agent in formulation II, i.e. formulation II-A, seems better than in formulation I. From all the examined blend specimens only blend plasticized with Benzoflex 2-45 presented a light fungi growth. In addition, it should be noted that all blend samples in all the tested formulations (i.e., formulation I, I-A, Π, Π-A) plasticized with Benzoflex 2-45 shows discoloration signs that vary from severe discoloration to light one even for the sample rated with no fungi growth. This indicates that Benzoflex 2-45 is the most susceptible plasticizer among the tested ones.

5.5.2 Weight loss assessment

The weight loss data (i.e., desorption) after 28 days incubation period and subsequent drying are shown in Table 5-18. In addition in the same table the percentages of weight increase after the incubation period are shown, which represent, in reality, the percentages of water absorption.

As can be seen in this table the weight loss values for all controls and blends in the different formulations are very small, and vary between 0.1-0.2 %, except again the controls formulated with Benzoflex 2-45 plasticizer. In addition, the weight loss is slightly higher for all blends. As a general rule, but with some exceptions, there is a slight decrease of weight loss for all the specimens formulated with the antimicrobial agent.

Table 5-18: Increase in weight after 28 days incubation period and loss in weight after incubation period and subsequent drying of controls and blends specimens expressed as percentages of their initial weight

Sample Identification	Formulation							
	I		I-A		II		II-A	
	Weight Incr.%	Weight Loss %	Weight Incr.%	Weight Loss %	Weight Incr.%	Weight Loss %	Weight Incr.%	Weight Loss %
DOP control	0.503	0.119	0.488	0.103	1.637	0.093	1.324	0.093
DOP blend	0.863	0.197	1.076	0.186	0.859	0.197	0.894	0.155
Mesamoll C.	0.518	0.128	0.479	0.094	1.358	0.096	1.667	0.085
Mesamoll B.	0.204	0.204	1.119	0.211	0.868	0.170	0.945	0.168
Lindol C.	0.245	0.075	0.233	0.035	1.145	0.130	1.487	0.128
Lindol B.	0.423	0.200	0.450	0.163	1.652	0.198	0.914	0.148
2-45 control	-	0.298	-	0.208	2.099	0.302	2.719	0.286
2-45 blend	1.105	0.584	1.336	0.440	1.142	0.790	1.509	0.609

The drying time was quite long, between 5 to 15 days, depending on the type of formulation. As a general trend it was higher for the specimens formulated with the antimicrobial agent, and generally higher for blends than for controls specimens.

Presence of high amounts of calcium carbonate filler could be responsible for the different drying times, due to the different levels of water absorption/desorption within the filler. It could also be possible that the polymer matrix structures during the incubation period become more compact as a result of the temperature influence. This compacted structure would slow down the water desorption out of the sheet. The changes occurring in material structure due to the effect of temperature and time will be discussed later.

All the tested specimens contain 58.9% mineral filler and 29.5% vinyl polymer in %-weight. Both these constituents are not biodeteriorated materials. This narrows the biodeterioration to the plasticizers and additives used for controls, in addition to Alcell lignin in blends formulations. The total amount of plasticizers and additives present in both formulation I and I-A in %-wt are 11.63 and 11.56 respectively, while the plasticizer presence in formulation Π and Π-A are 10.31 and 10.25 respectively (considering that neither the heat stabilizer nor the lubricant used in this formulations are a fungi target). Also the Alcell presence in blends formulations is 5.89 %-wt. for formulation I and Π, and 5.85 %-wt for formulation I-A and Π-A.

For a rough estimation of the plasticizer and additives loss in %-weight, the obtained loss in weights were reported to the biodegraded additives within formulation I and I-A. The same estimation was made for the controls obtained with the formulation II and II-A. For these formulations the total weight loss was reported to the plasticizer content only, as the other additives presumably being not affected by the fungi mixture as it was commented above. While for blends, Alcell %-wt was added to the plasticizer or plasticizer, and additives depending on the formulation type as a possible fungi target. All this estimations are presented in Table 5-19.

Estimated % weight loss of the susceptible additives in the different formulations is calculated as follows:

$$\%\,\mathit{Weight\ loss} = \frac{\%\,\mathit{Total\ weight\ loss\ of\ the\ specimen}\ (\mathit{values\ reported\ in\ Table}\ 4-18)}{Z}\ X\ \ 100$$

Where for controls		for blends
Z = 11.63	Formulation I	Z = 17.52
Z = 11.56	Formulation I-A	Z = 17.41
Z = 10.31	Formulation Π	Z = 16.2
Z = 10.25	Formulation Π-A	Z = 16.1

Although, the fungi rating for Lindol among the VC-VAc copolymer control samples within formulation I and I-A are similar to those of DOP and Mesamoll, the weight loss data presented in Table 5-19 reveal that Lindol is the least susceptible plasticizer to fungi attack.

Also the data show that even if formulations plasticized with Benzoflex 2-45 show no fungi growth with formulation I-A and Π-A its weight loss is high, which may be an indicator of the plasticizer hydrolysis. The weight loss calculated for the blends formulation shows that formulation I-A and Π-A plasticized with Lindol is the least susceptibility to fungi attack.

Table 5-19: Estimated percentage of plasticizers and additives loss in weight for controls in Formulations I and IA, of plasticizers loss in weight for controls in Formulation II and IIA and of AL loss in weight for blends in all Formulations

Sample Identification	Formulation			
	I	I-A	II	II-A
	Plasticizer& Additives Loss [%]	Plasticizer&. Additives Loss [%]	Plasticizer Loss [%]	Plasticizer Loss [%]
Controls				
DOP	1.02	0.89	0.90	0.91
Mesamoll	1.10	0.81	-	0.83
Lindol	0.64	0.30	1.25	1.25
2-45	2.56	1.80	2.92	2.79
Blends (+ Alcell % loss)				
DOP	1.12	1.07	1.2	0.96
Mesamoll	1.16	1.2	1.05	1.04
Lindol	1.14	0.94	1.2	0.92
2-45	3.36	2.53	4.88	3.78

5.5.3 Mechanical properties assessment

All the mechanical properties reported in this section resulted from a tensile strength test that was carried out at cross-head speed of 15 mm/min. The mechanical properties of the inoculated specimens and of the sterile controls, after 28 days incubation period, as well as % changes of these properties as a consequence of the biodegradation process are presented in Table 5-20 to 5-23. Modulus at 2% elongation, tensile strength at yield and break and % elongation at break data are presented. The % changes for each property were calculated according to the following formula:

$$\%\,Change \;=\; \frac{[Inoculated\ specimen - Sterile\ specimen\,]\ tensile\ test\ value}{Sterile\ specimen\ tensile\ test\ value} \quad X \quad 100$$

The Tg values of inoculated and sterile specimens are shown in Table 5-24. To facilitate the analysis of the results of the different test methods, the fungal growth rating, the changes in mechanical properties and the differences in the Tg values (ΔTg) of inoculated specimens versus sterile specimens are all presented in Table 5-25. A discussion concerning all these results for each particular formulation is presented thereafter. The mechanical properties variations are means of measuring the physical changes that takes place as a consequence of chemical change. The microbial degradation resulted in loss of different plasticizer and existing additives reduces the elastic behavior of the plastic material. The general mechanical behavior expected for the plasticized PVC that was exposed to fungi attack is an increase in elastic modulus and the tensile strength at yield accompanied with elongation reduction.

Table 5-20: Elastic modulus at 2% elongation [MPa] of controls and blends specimens after 28 days incubation period

Sample ID	Controls			Blends		
	Sterile	Inoculate	% change	Sterile	Inoculate	% change
DOP						
Formulation I	80.7	87.5	8.4	83.8	74.6	-11.0
Formulation I - A	96.7	103.7	7.2	93	88.5	-4.8
Formulation Π	91.6	110.2	20.3	109.5	111.7	2.0
Formulation Π - A	76.6	81.6	6.5	98.4	87.5	-11.1
Benzoflex 2-45						
Formulation I	92.8	97.2	4.74	157.3	178	13.2
Formulation I - A	116.9	120	2.7	155.3	159.8	2.9
Formulation Π	100.5	130.6	30.0	237.6	272.9	14.9
Formulation Π - A	71.8	82.1	14.3	224.1	193.3	-13.7
Lindol						
Formulation I	287.2	304.5	6.0	309.8	327.7	5.8
Formulation I - A	258.6	279.3	8.0	303	313.3	3.4
Formulation Π	279.2	310.7	11.3	318.6	337.7	6.0
Formulation Π - A	236.3	257.7	9.1	281.4	261.9	-6.9
Mesamoll						
Formulation I	-	-	-	-	-	-
Formulation I - A	106.8	109.8	2.8	122.3	127.8	4.5
Formulation Π	109.6	129.1	17.8	135.4	129.2	-4.6
Formulation Π - A	106.4	102.1	-4.0	114.1	109.4	-4.1

Table 5-21: Tensile strength at yield [MPa] of controls and blends specimens after 28 days incubation period

Sample ID	Controls			Blends		
	Sterile	Inoculate	% change	Sterile	Inoculate	% change
DOP						
Formulation I	4.42	4.59	3.8	3.48	3.13	-10.1
Formulation I - A	4.72	4.77	1.1	3.85	3.82	-0.8
Formulation Π	5.57	5.97	7.2	-	-	-
Formulation Π - A	5.57	5.84	4.8	-	-	-
Benzoflex 2-45						
Formulation I	3.84	4.09	6.5	3.99	4.58	14.8
Formulation I - A	4.31	4.43	2.8	3.79	4.05	6.9
Formulation Π	5.95	6.26	5.2	6.35	6.74	6.1
Formulation Π - A	5.47	5.52	0.9	5.91	5.43	-8.1
Lindol						
Formulation I	7.39	7.45	0.8	7.32	7.38	0.8
Formulation I - A	6.89	7.15	3.8	7.34	7.06	-3.8
Formulation Π	9.11	10.17	11.6	-	-	-
Formulation Π - A	8.4	6.38	-24.0	-	-	-
Mesamoll						
Formulation I	-	-	-	-	-	-
Formulation I - A	5.25	5.26	0.2	4.48	4.58	2.2
Formulation Π	6.3	6.47	2.7	-	-	-
Formulation Π - A	6.55	6.38	-2.6	-	-	-

Table 5-22: Tensile strength at break [MPa] of controls and blends specimens after 28 days incubation period

Sample ID	Controls			Blends		
	Sterile	Inoculate	% change	Sterile	Inoculate	% change
DOP						
Formulation I	6.1	6.32	3.6	4.17	4.1	-1.7
Formulation I - A	6.05	6.42	6.1	4.36	4.44	1.8
Formulation Π	5.67	5.81	2.5	8.79	9.24	5.1
Formulation Π - A	5.44	5.59	2.8	9.2	8.96	-2.6
Benzoflex 2-45						
Formulation I	6.35	6.36	0.2	4.21	4.5	6.9
Formulation I - A	6.31	6.69	6.0	4.51	4.51	0.0
Formulation Π	6.03	6.04	0.2	4.33	4.06	-6.2
Formulation Π - A	5.51	5.51	0.0	3.89	3.98	2.3
Lindol						
Formulation I	7.65	8.09	5.8	5.67	5.72	0.9
Formulation I - A	7.78	8.15	4.8	5.6	5.48	-2.1
Formulation Π	6.95	9.09	30.8	10	10.13	1.3
Formulation Π - A	6.92	8.1	17.1	9.41	9.06	-3.7
Mesamoll						
Formulation I	-	-	-	-	-	-
Formulation I - A	6.83	6.87	0.6	4.68	4.69	0.2
Formulation Π	6.3	6.31	0.2	8.67	8.85	2.1
Formulation Π - A	5.9	5.83	-1.2	9	8.83	-1.9

Table 5-23: Elongation at break [%] of controls and blends specimens after 28 days incubation period

Sample ID	Controls			Blends		
	Sterile	Inoculate	% change	Sterile	Inoculate	% change
DOP						
Formulation I	273	285	4.4	212	209	-1.4
Formulation I - A	264	252	-4.5	216.1	204	-5.6
Formulation Π	231	212	-8.2	35	38	8.6
Formulation Π - A	247	329	33.2	40	42	5.0
Benzoflex 2-45						
Formulation I	287	283	-1.5	214	207	-3.3
Formulation I - A	284	278	-2.1	269	258	-4.1
Formulation Π	239	194	-18.8	209	158	-24.4
Formulation Π - A	272	252	-7.4	216	245	13.4
Lindol						
Formulation I	132	171	29.5	121	104.7	-13.5
Formulation I - A	182	176	-3.3	128	148	15.6
Formulation Π	87	95	9.2	6	6	0.0
Formulation Π - A	114	93	-18.4	10	10	0.0
Mesamoll						
Formulation I	-	-	-	-	-	-
Formulation I - A	276	264	-4.3	187	171	-8.6
Formulation Π	231	200	-13.4	29	30	3.4
Formulation Π - A	180	202	12.2	34.8	35.5	2.0

Table 5-24: Tg [°C] of controls and blends specimens after 28 days incubation period

Sample Identification	Formulation							
	I		I-A		II		II-A	
	Sterile	Inoculate	Sterile	Inoculate	Sterile	Inoculate	Sterile	Inoculate
DOP Control	22.5	21.3	21.0	21.9	16.9	19.1	14.4	-
DOP Blend	12.4	14.5	11.8	12.1	12.6	12.8	10.4	-
Mesamoll C.	-	-	21.8	21.9	21.5	20.9	-	-
Mesamoll B.	-	-	15.1	14.0	15.2	15.8	-	-
Lindol C.	33.4	32.4	31.2	30.2	29.3	30.2	-	-
Lindol B.	27.8	28.6	27.5	27.7	29.0	29.1	-	-
2-45 Control	24.3	23.9	23.4	23.3	22.6	23.0	21.3	-
2-45 Blend	21.2	22.6	22.2	22.2	23.2	23.0	21.3	-

Table 5-25: Fungi rating, Δ Tg values, % loss in weight and % changes of mechanical properties of inoculate specimens versus sterile ones for controls and blends specimens after 28 days incubation period

	DOP		Mesamoll		Lindol		Benzoflex 2-45	
	Control	Blend	Control	Blend	Control	Blend	Control	Blend
	Formulation I							
Fungi rating	1	3	1	3	1	1	2	4
Δ Tg [°C]	-1.2	2.1	n.a.	1.9	-1.0	0.8	-0.4	1.4
Loss in weight	0.119	0.197	0.128	0.204	0.035	0.163	0.298	0.584
Modulus	8.4	-11	n.a.	n.a.	6.0	5.8	4.5	13.2
Yield Strength	3.8	-10.1	n.a.	n.a.	0.8	0.8	6.5	14.8
Break Strength	3.6	-1.7	n.a.	n.a.	5.8	0.9	0.2	4.5
Elongation	4.4	-1.4	n.a.	n.a.	29.5	-13.5	-1.5	-3.3
	Formulation I-A							
Fungi rating	0	1	0	1	0	0	1	0
Δ Tg [°C]	0.9	0.3	0.1	0.3	-1.0	0.2	-0.1	0
Loss in weight	0.103	0.186	0.094	0.211	0.075	0.200	0.208	0.440
Modulus	7.2	-4.8	2.8	4.5	8.0	3.4	2.7	2.9
Yield Strength	1.1	-0.8	0.2	2.2	3.8	-3.8	2.8	6.9
Break Strength	6.1	1.8	0.6	0.2	4.8	-2.1	6.0	-
Elongation	-4.5	-5.6	-4.3	-8.6	-3.3	15.6	-2.1	-4.1
	Formulation II							
Fungi rating	0	3	0	3	0	2	1	4
Δ Tg [°C]	2.2	0.2	2.2	0.6	0.9	0.1	0.4	-1.7
Loss in weight	0.093	0.197	0.096	0.170	0.130	0.198	0.302	0.790
Modulus	20.3	2.0	17.8	-4.6	11.3	6.0	30.0	14.9
Yield Strength	7.2	-	2.7	-	11.6	-	5.2	6.1
Break Strength	2.5	5.8	0.2	2.1	9.0	1.3	0.2	-6.2
Elongation	-8.2	8.6	-13.4	3.4	9.2	0.0	-18.8	-24.4
	Formulation II-A							
Fungi rating	0	0	0	0	0	0	0	2
ΔTg [°C]	n.a	n.a.	n.a.	n.a.	n.a.	n.a.	n.a	n.a
Loss in weight	0.093	0.155	0.085	0.168	0.128	0.148	0.286	0.609
Modulus	6.5	-11.1	-4.0	-4.1	9.1	-6.9	14.3	-13.7
Yield Strength	4.8	-	-2.6	-	-24.1	-	0.9	-8.1
Break Strength	2.8	-2.6	-1.2	-1.9	17.1	-3.7	0	2.3
Elongation	33.2	5.0	12.2	2.0	-18.4	0.0	-7.4	13.4

DOP Plasticized Controls

Formulation I: Fungi rating less than 10%, weight loss, increases in modulus, as well as increases in yield and break strength indicate that this formulation is degraded in a certain measure. Surprisingly, the ΔTg is negative. A decrease of inoculated specimen Tg is an indication that the heat stabilizer and lubricant, both fatty acids derivatives, were the fungi nutrients rather than DOP plasticizer. This could be observed from the data presented in Table 5-24; in the absence of these additives, respectively in formulation II the DOP plasticized control's Tg value is sensibly lower. Not expected is a slight increase of elongation at break. The only explanation, is that although the fungi succeeded in attacking part of the existing additives by the testing time these additives were just partially broken, but free to move, resulting in this elongation.

Formulation I-A: Fungi rating 0, slightly lower weight loss, lower increases of modulus, and strength at yield than that in formulation I accompanied by a slight increase in Tg and decrease of elongation. All these data show that the antimicrobial agent had provided a certain protection without completely preventing the biodegradation. Meanwhile, the slight increase of Tg would indicate that now the plasticizer rather than the additives is deteriorated. Literature data strengthen the fact that the visual assessment of fungi growth on a surface in not always in agreement with other methods of evaluation. The fungal growth on a surface of a plastic material can be invisible or uneven. Furthermore, the extent of fungal growth is not always necessarily related to the degree of biodeterioration [115-118]. On the other hand, the slight deterioration of the material, even in the presence of the antimicrobial agent may result from its insufficient inhibitory concentration and on its ability to diffuse out of the material. The hampered diffusion of the antimicrobial agent out of the material will be discussed later.

Formulation II: Fungi rating is 0, weight loss is slightly lower than in formulation I, Tg increases and the material presents a higher degree of embrittlement than in formulation I. This embrittlement increase of formulation II evidences clearly a loss of plasticizer. It can be ascribed to physical heterogeneity of the material. In contrast to formulation I the level of water absorption was sensibly higher. Literature data show that in general, polymers' resistance to biodegradation and particularly that of plasticized PVC is reduced in heterogeneous systems that facilitate penetration of moisture and growth of fungi in the interfacial regions [115, 119].

Formulation II-A: Fungi rating is 0, weight loss similar as in formulation II, but the modulus, yield and break strength are lower than in formulation II. All these data indicate a certain efficiency of the antimicrobial agent. Not expected is the increase in elongation at break (same observation as in formulation I).

DOP Plasticized Blends

Formulation I: Fungi rating 3, weight loss higher than that of the respective control, Tg slightly increased, elongation slightly decreased but surprisingly the modulus and strength at yield and break decreased, too. The reason for the modulus and strength reduction may arise from the attack of Alcell by fungi. The Alcell macromolecules are very complex and present the tendency to association, which made them very resistant to biodegradation. As it was shown earlier DOP partly plasticize Alcell and consequently some fewer lignins' low molecular weight fractions are free to interact with polar VC-VAc copolymer resulting in H-bonds between OH groups of Alcell and α-hydrogen of PVC or carbonyl group of VAc [120]. If these low molecular Alcell fractions are partially destroyed by specific enzymes or acids produced by fungi, some of the secondary bonds between Alcell and copolymer will vanish, and the strength of the matrix will be reduced.

Formulation I-A: fungi growth decreased, and the changes follow the same trend as in formulation I, but in a lesser measure. Similar to DOP control formulation I-A, the slight deterioration of the material, points to the insufficient concentration of the antimicrobial agent or to the reduction of its ability to diffuse out of the material.

Formulation II and II-A: both sterile and inoculated samples are very stiff in comparison with the respective blends obtained with formulation I and IA, and characterized by a high strength at break and low elongation. The difference between the Tg of control and blend sterile samples is around 4°C, whereas the same difference is around 10°C in formulation I. The reason of the high degree of stiffness of these specimens is not immediately clear, although there is a possibility that the presence of paraffin wax lubricant (totally non-polar) prevents the Alcell dispersion through the polymer matrix. The stiffness of the blends and their Tg suggest a higher degree of association within the Alcell components.

Li et al [121] reported that the tensile behavior of lignin-based blends is directly dependent on the degree of association between the lignin macromolecules. Higher is the degree of lignin components association, higher is the blend stiffness. Assuming that the morphology of these blends is different than that obtained with Formulation I, the fungal influence behaviour will be different too. Comparing the intensity of microorganism's growth in Formulation I and II-A, sensible differences is noticed, from medium growth (30 to 60% of the surface) to none respectively. In the meantime the changes of mechanical properties as effect of fungal deterioration are very close. Based on these observations it could be concluded that a correlation between the intensity of fungal growth and changes in mechanical properties is hardly to be done. Other authors concluded the same observation [116].

Mesamoll Plasticized Controls

The changes in mechanical properties and Tg, as well as weight loss of all the controls specimens, as effect of biodeterioration, match the changes observed in similar formulations plasticized by DOP. The only exception represents the formulation II-A where the modulus and tensile strength decrease and elongation increases. The material seems to be more plasticized. This effect of plasticization may be attributed to water traces that are still present into the formulation at the testing time. It was shown that bound water molecules could disrupt the interaction between vinyl polymer chains, introducing further plasticization [122].

Mesamoll Plasticized Blends

In general the susceptibility of these blends to microorganisms attack is comparable to that of DOP plasticized blends. It is interesting to note that the loss in weight of formulation I-A specimen, where the fungal rating was 1, is higher than that of formulation I specimen with a 3 fungal rating. The results of an international cooperative experiment [123], on biodegradation of plasticized PVC films by a mixture of six fungi (four similar as in ASTM G21-2000 and the *Chaetomium globosum* replaced by *Aspergillus versicolor* ATCC #22730 and *Pullularia pullulants* ATCC #9348), have indicated that the weight losses are related to the degradation of the plasticizer in the film. Plasticizer loss, however, was greater than the weight loss as it was confirmed by a precise and reproducible extraction method. This discrepancy was explained by the fact that apparently, the biodegradable component of the plastic formulation is only partly broken down. Non-extractable metabolic residues must remain within the plastic film. Although the author did not negate the value of the weight loss data, he indicated that caution is necessary in interpreting these data. As the biodegradable components of these blends are probably plasticizer, additives and Alcell it is possible that sometimes, metabolic residues of partially broken down Alcell have more chances to remain within the material.

Lindol Plasticized Controls

Formulation I: The trend of mechanical properties changes after the incubation period is similar to control samples plasticized by DOP. However, its weight loss value is the smallest one among all the tested controls obtained within this formulation. Bearing in mind the earlier observation regarding the interpretation of loss in weight data is hard to discern if the weight loss reflects a better resistance of this plasticizer to fungi attack in comparison to the other plasticizers. Similarly to the DOP plasticized blends the elongation at break had unexpectedly increased.

Formulation I-A: The fungi rating and the weight loss confirm the efficiency of the antimicrobial agent, but a comparison of the changes in mechanical properties with those observed in formulation I leads to opposite conclusion. The same observation is applicable if one compares changes of mechanical properties between formulation II and II-A.

Lindol Plasticized Blends

Formulation I: Tg increases, weight loss, as well as fungi rating are the lowest among all the blends obtained with this formulation. In contrast to the blend plasticized with DOP, Lindol plasticized blend shows that the Tg increased less and the modulus, strength at yield and break increased and elongation decreased. All this changes are picturing a loss of plasticizer rather than Alcell deterioration, which may indicate a particular morphology of this blend.

Formulation I-A: there was no visible fungal growth on the specimen surface and the weight loss was also the lowest among the other blends obtained in this formulation. Probably its own structure impedes in a higher measure the fungal attack without preventing it completely. Its mechanical properties change (except that slight increase in modulus) appear as a result of an extra plasticization that could be owed to the water traces effect, as discussed earlier and observed for the control specimen plasticized by Mesamoll with in formulation II-A.

Formulation II and II-A: these blends are very stiff and similar to those plasticized by DOP and Mesamoll among the same formulations. Generally the changes of the mechanical properties and weight losses, as effect of biodeterioration, are similar too but curios the fungi rating is 2 in formulation II

Benzoflex 2-45 Plasticized Controls

Formulation I and I-A: from all the controls obtained with formulation I and I-A those plasticized with Benzoflex 2-45 exhibit the highest fungi rating 2 and 1 respectively, the highest loss in weight and the lowest decrease in Tg. In addition modulus increase and elongation decrease, as well as the increase of yield and break strength correlates quite well with fungi rating and weight loss indicating without doubt a loss of plasticizer and additives in both formulations. Similar to other formulations the antimicrobial agent presence helped in a certain measure the microorganisms' growth reduction without inhibiting it completely.

Formulation II and II-A: data presented in Table 5-25 show that the different controls within formulation II have no fungal growth on their respective surfaces, although their mechanical properties changes as well as their weight losses suggest a loss in plasticizer as effect of biodegradation. Only controls plasticized with Benzoflex 2-45 show traces of fungal growth, and in the meantime the weight losses and the changes of mechanical properties indicate a higher loss in plasticizer than in other controls.

Benzoflex 2-45 Plasticized Blends

Formulation I: after 28 days incubation there was a massive growth of sporing fungi on blend samples surfaces (>60%) associated with strong discoloration, substantial changes in mechanical properties as well as the highest weight loss among all the different blends. All these data demonstrate that both the plasticizer and Alcell suffer serious changes as effect of fungi attack. Probably the higher damages in this formulation are owed to the attack of the lower molecular Alcell fractions that are most plasticized with Benzoflex 2-45.

Formulation I-A: fungal growth 0, accompanied by a substantial weight loss; this formulation represents a typical example of the fact, discussed earlier, that although the fungal growth on a specimen surface can be invisible the biodeterioration took place as can be seen from the data presented in Table 5-25.

Formulation II and II-A: in contrast with the other blends prepared with these formulations, the Benzoflex 2-45 blends are tougher and characterized by high modulus and yield strength values as well as high break elongations, as can be seen in Tables 5-20 to 5-23. Surprisingly paraffin wax lubricant did not impede, as it did in the presence of other plasticizers, Alcell dispersion within the polymer matrix.

The specific conclusions that can be drawn from the analysis of the above-presented results are:

1. Based on the visual examination of the control specimens the susceptibility to fungi attack of DOP, Mesamoll and Lindol are similar in formulation I (less than 10% of the surface) and that of 2-45 plasticizer slightly higher (10 to 30% of the surface). Based on the weight loss the susceptibility of the plasticizers to fungi can be rated as: 2-45 > Mesamoll ≥ DOP > Lindol. However the degree of fungal growth and the loss in weight did not correlate with changes in mechanical properties.

2. No fungal growth was detected on the control specimens' surfaces plasticized with DOP, Mesamoll and Lindol and only traces (less than 10%) were observed on the specimen's surface plasticized with Benzoflex 2-45 in formulation II. It is obvious that the heat stabilizer and lubricant used in formulation I represented an easy nutrient source for the fungi. The order of weight loss of formulation II with respect to plasticizer type was similar to that of Formulation I, and also the mechanical properties changes (examined after 28 days inoculation and one week reconditioning) did not correlate with the fungal growth and weight losses.

3. The antimicrobial did provided a certain protection against fungi, as can be seen from the fungal rating reduction on all the specimens formulated with it. However, the weight losses as well as mechanical properties and Tg changes indicated that the protection was incomplete as long as certain deterioration still occurred within these particular protected formulations. Initially it was believed that the deterioration was due to its insufficient concentration and /or its reduced ability to diffuse out of the material. The antimicrobial concentration was indicated by the producer. On further reflection, it was possible to suggest a possible reason for its incomplete ability to protect the materials. Under the effect of time and temperature during the incubation period a physical ageing will occur in all the constituents, depending on their molecular mobility. An increase in chemical structure order or the formation of a three dimensional network in which entanglements and small crystallites act as junction points or physical cross-links of the structure are the results of physical ageing and the main consequence of these phenomenon is that the polymer matrix becomes more compact [124]. As discussed above, the raise of the polymer matrix compaction will prevent the absorbed water desorption, thus increasing the drying period. Also, a more compact structure may encapsulate the biocide, preventing its migration to the surface where biodeterioration is mainly taking place. Literature confirms this possible mechanism [125].

4. The fungi have shown stronger degradation ability for blends than controls. In comparison with the respective controls the blend specimens exhibited higher

fungi growth rates or at similar fungal growth, higher weight loss. Our previous data had shown that this particular fungi mixture does not affect Alcell alone. Visual examination did not detected fungal growth on the inoculated Alcell samples after the same incubation period, fact that was confirmed by FTIR spectra, which did not reveal evident changes in its spectral bands [126]. So it is evident that the Alcell attack occurred, in a higher or lower measure, in the presence of specific plasticizers when the degree of association between lignin's macromolecules is decreased. The molecular weights of the dissociated Alcell's structures are smaller, that can be easily broken down and assimilated by microorganisms. The blends formulated with Benzoflex 2-45 plasticizer, which is the most effective plasticizer for the lower molecular weight portion of Alcell among the four tested plasticizers, displayed the highest degree of deterioration. It is interesting to note that Lindol, as well, is a good plasticizer for Alcell. However in comparison with the blends plasticized by DOP and Mesamoll most of the Lindol plasticized blends are the less susceptible to fungi attack. After the fungal attack most of the blends, which are initially brown, present a certain degree of discoloration with highest degree of discoloration for blends formulated with Benzoflex 2-45 and the lowest for Lindol plasticized blends. Conjugated aryl-α carbonyl and conjugated carbon-carbon double bonds structures are the principal cromophoric groups in Lignin. It was demonstrated that degradation and discoloration process of lignin is due to the formation of peroxy radicals, from these groups as effect of mild UV light [127]. It could be possible that the various types of acids produced by the fungi were able to break these structures or part of them, and consequently induce the discoloration of Alcell.

5.5.4 Incubation effect

The purpose of this section [128] is to better understand the mechanical properties behavior after inoculation, as they were not correlating properly with the other methods of assessments (i.e., Visual, weight loss and thermal assessments). The expected reason, as thought of, is the time length of the experiment, considering that the mechanical testing was always carried one week after the inoculation period. In addition to that evaluate the incubation conditions role (i.e., high humidity and temperature) on the tested formulations.

For that, three sets of samples were prepared from each formulation as follows:

- One set was inoculated and incubated for 28 days at 28 ± 1°C and 95 ± 2 % relative humidity and will be referred to as inoculated specimens.
- Another set was only incubated at the same conditions (i.e., 28 days at 28 ± 1°C and 95 ± 2 % R.H.) without inoculation, which represent sterile specimens.
- The third set was kept 7 days at standard laboratory conditions 23 ± 1°C and 50 ± 2 % R.H., which represent zero control specimens.

Following the incubation period, the inoculated samples were disinfected with a solution of mercuric chloride, washed and dried at room temperature for 24 hrs. After 20 days (previously 6 days) the three sets of specimens were cut and tested for thermal and mechanical properties. During this period the samples were kept in standard laboratory conditions. The tensile strength test was carried out using a semi-computerized Instron machine at a cross-head speed of 2 mm/min.

5.5.4.1 Thermal properties

The Tg data of PVC controls and blends as a function of plasticizer type, for both inoculate and sterile specimens are presented in Table 5-26. Due to the fact that PVC formulations are strongly influenced by the presence of humidity and temperature, the primarily Tg (after one week) of the different formulation at standard laboratory conditions are restated to emphasis their role (zero control). In addition, the difference in Tg between zero control formulations and their corresponding sterile formulations, as well as between inoculate and sterile specimens are presented and noted by $\Delta Tg_{(2-1)}$, $\Delta Tg_{(3-1)}$, $\Delta Tg_{(3-2)}$ respectively.

A careful review of the $\Delta Tg_{(2-1)}$ data shows that as effect of temperature and humidity the Tg values of all controls and blends increased with several degrees as a function of the plasticizer type. Moreover by examining $\Delta Tg_{(3-2)}$, it surprisingly shows that the influence of fungi on the different formulations is negligible comparing to that of humidity and temperature. This could be due to the time length of the experiment, as temperature and relative humidity creates the necessary environment for fungi growth. After that the effect of fungi attack will take place.

Table 5-26: Tg [°C] of VC-VAc controls and blends specimens after 28 days incubation period as well as at normal condition; and ΔTg differences between them

Sample Identification	Tg [°C] Zero Control (1)	Tg [°C] after 28 days @ 28°C & 100% R.H.		$\Delta Tg_{(2-1)}$ [°C]	$\Delta Tg_{(3-1)}$ [°C]	$\Delta Tg_{(3-2)}$ [°C]
		Sterile, (2)	Inoculate, (3)			
Control-DOP	20.7	21.8	22.5	1.1	1.8	0.7
Blend-DOP	11.7	13.4	12.8	1.7	1.1	-0.6
Control-(2-45)	22	25.2	24.3	3.2	2.3	-0.9
Blend-(2-45)	19.3	23.9	22.4	4.6	3.1	-1.5
Control-Lindol	30.8	33.9	34	3.1	3.2	0.1
Blend-Lindol	25.1	28.6	28.9	3.5	3.8	0.3
Control-Mesamoll	21.9	23.5	23.7	1.6	1.8	0.2
Blend-Mesamoll	13.7	15.5	15.8	1.8	2.1	0.3

5.5.4.2 Mechanical properties

Although the DSC results do not show any significant change due to the effect of microbial degradation, the mechanical properties acted differently as data suggested in Table 5-27. The percent changes in mechanical properties between inoculate and sterile samples are also reported in the same table.

Control specimens

Shows that due to incubation the modulus of elasticity increased for all the VC-VAc copolymer controls with different plasticizers by approximately 25%, and consequently the elongation decreased by approximately 14, 37, and 9 % for DOP, 2-45, Mesamoll respectively while Lindol elongation increased by only 4%. This could be due to the great affinity of fungi towards the plasticizers, and as a result their amount decreased and the modulus increased. In the case of Lindol due to its bulk structure the fungi enzymes were capable only of partly breaking it, as discussed earlier. Meanwhile the tensile strength at yield and break were approximately unchanged.

Blend specimens

The elastic modulus variation increases for all blend formulations except that formulated with DOP. When elongation is the issue, it acted as a function of the plasticizer structure, tacking into consideration that our plasticizers structure range from bulk structure (i.e., Lindol) passing by Mesamoll and DOP to reach the most linear one among the studied plasticizers (i.e., Benzoflex 2-45), we end up with two behaviors:

First: elongation decreased with Lindol and Mesamoll formulations and its reduction was inversely proportional to the modulus of elasticity, as expected, which could be due to the structure complexity of this plasticizers. Given that Lindol has higher compatibility with Alcell lignin, the elongation reduction with it was higher then that of Mesamoll, as fungi enzymes were capable of destroying the hydrogen bond of the plasticized Alcell portion, especially that of low molecular weight fractions.

Second: elongation decreased with DOP and Benzoflex 2-45 and its reduction was directly proportional to the modulus of elasticity. This surprising behavior could be accounted for the humidity and the plasticizer linearity. The elongation reduction with Benzoflex 2-45 was higher than that of DOP due its higher linearity.

Inoculated blends vs. VC-VAc control specimens

All blends versus their controls exhibit reduction in their mechanical properties; fungi presence changes the behavior of elastic modulus with the most bulk plasticizer (i.e., Lindol) and the most linear one (i.e., Benzoflex 2-45). In the case of Benzoflex 2-45 fungi were able to break its linearity, surviving and reproducing on this organic nutrients, subsequently increasing the elastic modulus and reducing its elongation. On the other hand, with Lindol due to its bulk structure it was hard for the fungi to extract it (partly broken), that influences the modulus reduction, also resulting in minimizing the elongation reduction.

The mechanical properties decline results from a physical deterioration as a consequence of fungi attack. This process is time dependent as data demonstrated, it requires either a longer inoculation period (i.e., more than the 28 days mentioned earlier in ASTM G21-2000) or a longer period after the inoculation period to establish the mechanical deterioration.

Table 5-27: Mechanical properties of PVC control and Alcell blend formulations after 28 days inoculation period and at normal conditions

Sample ID	PVC Control				Alcell Blend			
	Zero control	Sterile	Inoculate	% change*	Zero control	Sterile	Inoculate	% change*
Modulus of Elasticity [MPa]								
DOP	35.4	37.5	46.26	23.4	16.32	41.1	36	-12.4
Benzoflex 2-45	31.24	56.7	72.26	27.4	46.46	160	162.7	1.7
Lindol	211.49	232.1	283.5	22.1	98.33	168.5	263.8	56.6
Mesamoll	36.08	37.3	49	31.4	25.51	56.4	72	27.7
Tensile Strength at Yield [MPa]								
DOP	3.78	4.16	4.16	0.0	3.55	4.15	4.17	0.5
Benzoflex 2-45	3.48	4.43	4.61	4.1	2.42	4.58	4.62	0.9
Lindol	5.86	8.09	8.38	3.6	3.65	6.44	6.4	-0.6
Mesamoll	3.75	4.5	4.64	3.1	3.4	4.9	4.96	1.2
Tensile Strength at Break [MPa]								
DOP	4.86	4.61	4.44	-3.7	3.27	3.24	3.21	-0.9
Benzoflex 2-45	4.51	4.49	4.06	-9.6	3.14	3.11	3.17	1.9
Lindol	5.97	6.55	6.59	0.6	3.94	4.7	4.77	1.5
Mesamoll	5.16	5.44	5.4	-0.7	3.52	3.72	3.79	1.9
% Elongation								
DOP	377	347	299	-13.8	335	179	162	-9.5
Benzoflex 2-45	377	242	152	-37.2	487	101	76	-24.8
Lindol	281	145	151	4.1	362	165	108	-34.5
Mesamoll	403	337	305	-9.5	342	152	131	-13.8

* % change is for inoculate sample versus sterile sample

Humidity and temperature

To establish the effect of humidity and temperature, the variation between sterile samples and zero control samples are presented in Table 5-28.

Table 5-28: Mechanical properties variations [%] of VC-VAc controls and blends with 35 phr plasticizer at normal conditions versus test environment

Sample ID		Elastic Modulus [%]	Tensile Strength [%]		Elongation [%]
			Yield	Break	
VC-VAc zero controls vs. sterile	DOP	+ 5.90	+ 10.05	- 5.14	- 7.96
	Benzoflex2-45	+ 81.47	+ 27.30	- 0.44	- 35.81
	Lindol	+ 9.72	+ 38.05	+ 9.72	- 48.40
	Mesamoll	+ 3.33	+ 20.00	+ 5.43	- 16.38
Blends zero controls vs. sterile	DOP	+ 151.78	+ 16.90	- 0.92	- 46.57
	Benzoflex2-45	+ 250.13	+ 89.26	- 0.96	- 79.26
	Lindol	+ 71.40	+ 76.44	+ 19.29	- 54.42
	Mesamoll	+ 121.25	+ 44.12	+ 5.68	- 55.56

VC-VAc zero controls vs. sterile samples

In Tables 5-28 we could notice that the modulus of elasticity for the sterile samples versus the zero control ones had greatly increased (i.e., 81.5%) for specimens plasticized with Benzoflex 2-45. Meanwhile its elongation has decreased to a great extent (i.e., 35.8%). Specimens plasticized with Lindol also have a great loss in elongation (i.e., 48.4%) but their modulus was increased by 9.7%. For the samples plasticized with DOP and Mesamoll the modulus increased by approximately 5%, while the reduction in elongation for samples plasticized with Mesamoll was double that of DOP. Exposing high filled polymer samples with calcium carbonate to harsh environment results in increasing the filler absorption of water vapor that enhances the bonding between filler particles and the polymer matrix as indicated by the tensile strength results at yield which is in the order of DOP > Mesamoll > Benzoflex 2-45 > Lindol, the same order of elongation reduction was established. The modulus of elasticity increases and subsequently elongation is reduced as a function of plasticizer type.

Blends zero controls vs. sterile samples

On the other hand, blends shows different status. The presence of lignin affected all the samples. The modulus of elasticity increased tremendously accompanied with a reduction in elongation especially for formulation plasticized with Benzoflex 2-45 where the loss was approximately 80%. The tensile strength at yield for all samples increased dramatically accompanied with elongation reduction. Alcell presence modifies the formulation humidity absorption behavior that results in increasing its particles bonding to the VC-VAc copolymer matrix.

5.6 VC-VAc copolymer ageing

Materials are said to age when their properties change with time, usually the change is adverse. For polymers, ageing may be due to a diversity of reasons: oxidation, with or without UV light, hydrolysis, gradual loss of plasticizer or other additives. This section is confined to ageing that is due to the inherent instability of the amorphous glassy state, known as volume recovery or structural relaxation. Products of glassy polymers are usually made by shaping them in the molten (rubbery) state, followed by a fixation of the shape by rapid cooling to below the glass transition temperature. During the cooling process the material solidifies and gains its stiffness. Due to the short time of cooling, material continues its solidification and stiffening during its service life that affects the material properties. Seeing that, the impact of ageing on the thermal and mechanical properties of VC-VAc copolymer blended with Alcell lignin was studied.

5.6.1 Thermal properties after ageing

The Tg values of the aged VC-VAc copolymer controls and respective blends are shown in Table 5-29. Also in Table 5-29 are shown the differences in °C between the Tg of controls and their respective blends (ΔTg). DSC thermograms for the second run in the temperature interval between –20 and 140 °C (Figures 5-40 to 5-43) reveal single Tgs for all the controls and blends, which indicates a relatively homogenous structure. Unlike the quite sharp and narrow glass transition range for the blends plasticized with 2-45, Lindol and in a lesser measure with Mesamoll, the Tg region of DOP plasticized blends was broad and less sharp indicating a certain degree of in-homogeneity at the molecular scale.

Table 5-29: Tg of VC-VAc controls and blends and differences between the Tg of controls and respective blends (ΔTg) after ageing for 1, 10, 39 weeks

Sample ID		Tg [°C]			ΔTg[°C]		
		1 Week (1)	10 week (2)	39 week (3)	$\Delta Tg_{(2-1)}$	$\Delta Tg_{(3-2)}$	$\Delta Tg_{(3-1)}$
Control	DOP	20.7	20.1	21.9	-0.6	1.8	1.2
	Benzoflex 2-45	22.0	21.8	24.2	-0.2	2.4	2.2
	Lindol	30.8	29.7	32.3	-1.1	2.6	1.5
	Mesamoll	21.9	21.7	23.2	-0.2	1.5	1.3
Alcell Blend	DOP	8.2	9.1	9.2	0.9	0.1	1
	Benzoflex 2-45	19.3	19.7	21.8	0.4	2.1	2.5
	Lindol	25.1	25.2	26.3	0.1	1.1	1.2
	Mesamoll	13.7	13.0	14.9	-0.7	1.9	1.2

The data show two different trends as indicated by ΔTg_{2-1}. All controls showed a decreasing in Tg, while blends showed an increase after an ageing period of 9 weeks (except Mesamoll blend). That could be due to lignin presence, which decreases the free volume due to its small-size molecules that stiffening the VC-VAc matrix resulting in accelerating the achievement of equilibrium state for the blend. On the other hand, when the ageing period of 39 weeks is compared to the 10-week results, one observes an increasing trend for all the aged samples as indicated by ΔTg_{3-2}. After 39 weeks of ageing all the formulations showed an average increase of 1.3 °C, except formulation plasticized with Benzoflex 2-45 which showed an increase of 2.5 °C as indicated by Tg_{3-1}. This can be explained by the high linearity of this plasticizer that facilitates its macromolecules movements to reach equilibrium rapidly.

A careful inspection of the DSC thermograms for the first run presented in Figures 5-44 to 5-47 shows that VC-VAc copolymer controls exhibit a specific relaxation behavior comprising in most of the cases two distinct relaxation peaks located at quite different temperatures. The first endothermic peak near 60 °C shifted with respect to time to 70 °C while the other one near 102 °C when aged shifted around 4 °C. The change in position of the Tg peak accompanied with an increase of Tg, is due to the quenching of the free volume with respect to time (i.e., Physical Ageing or Annealing), due to the relaxation of the intermolecular chains [129-131] in an effort to approach the preferred or true equilibrium state. Cooling a polymeric melt induces a rapid rise of viscosity that occurs as the Tg of the polymer is approached. The macromolecules are frozen in a non equilibrium confirmation and configuration leaving a free volume in the system.

Considering that the second endothermic peak is due to the presence of calcium stearate (melting temperature (Tm) = 127 °C, as determined in our laboratories), and that it appears with VC-VAc copolymer controls and does not appear with VC-VAc-Alcell blends until its aged 39 weeks start to appear. That supports the argument that fractions of Alcell lignin reacted with calcium stearate, neutralizing its presence, however when the samples were aged 39 weeks this portion degraded resulting in calcium stearate reappearance.

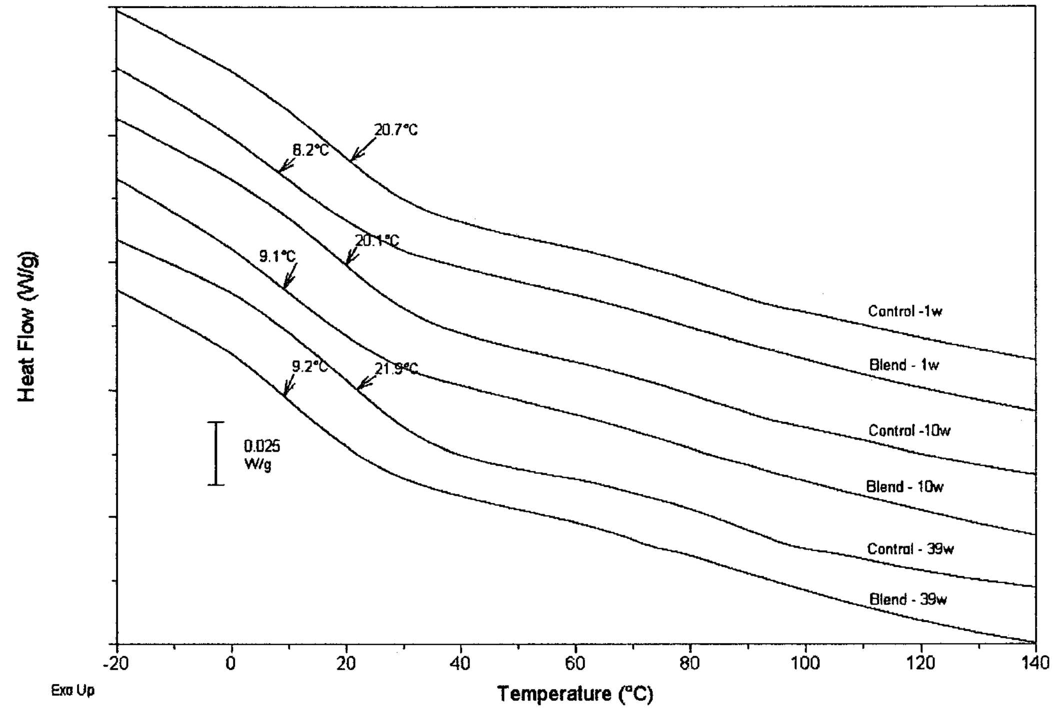


Figure 5-40: DSC thermograms [2nd run] of VC-VAc control and blend aged at 1, 10 and 39 weeks plasticized with DOP

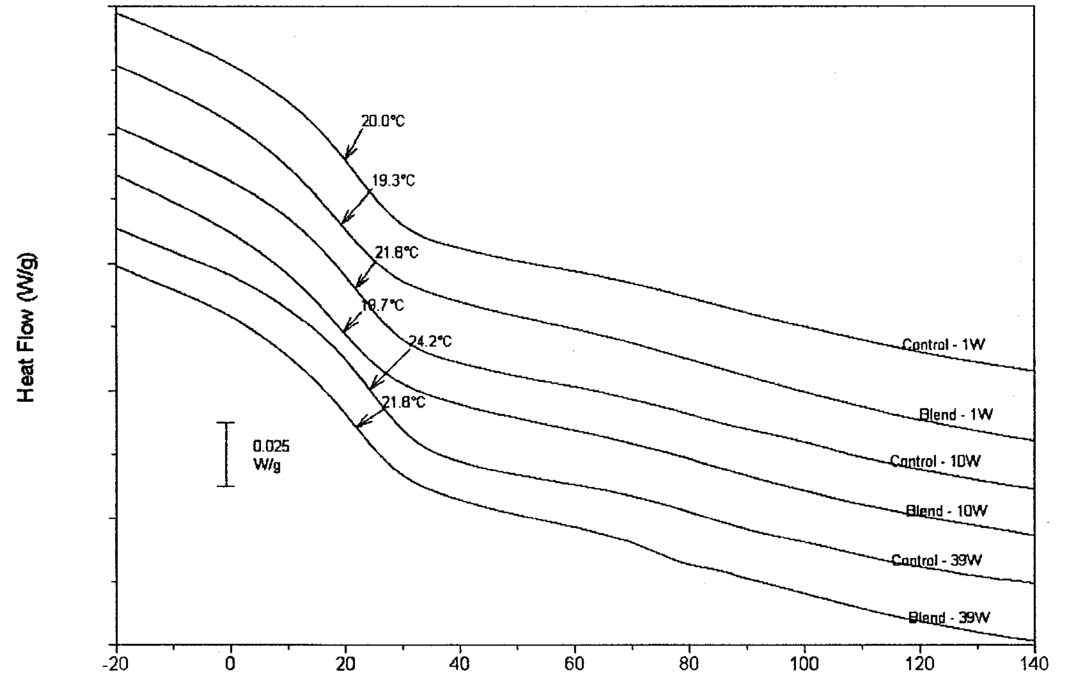


Figure 5-41: DSC thermograms [2nd run] of VC-VAc control and blend aged at 1, 10 and 39 weeks plasticized with Benzoflex 2-45

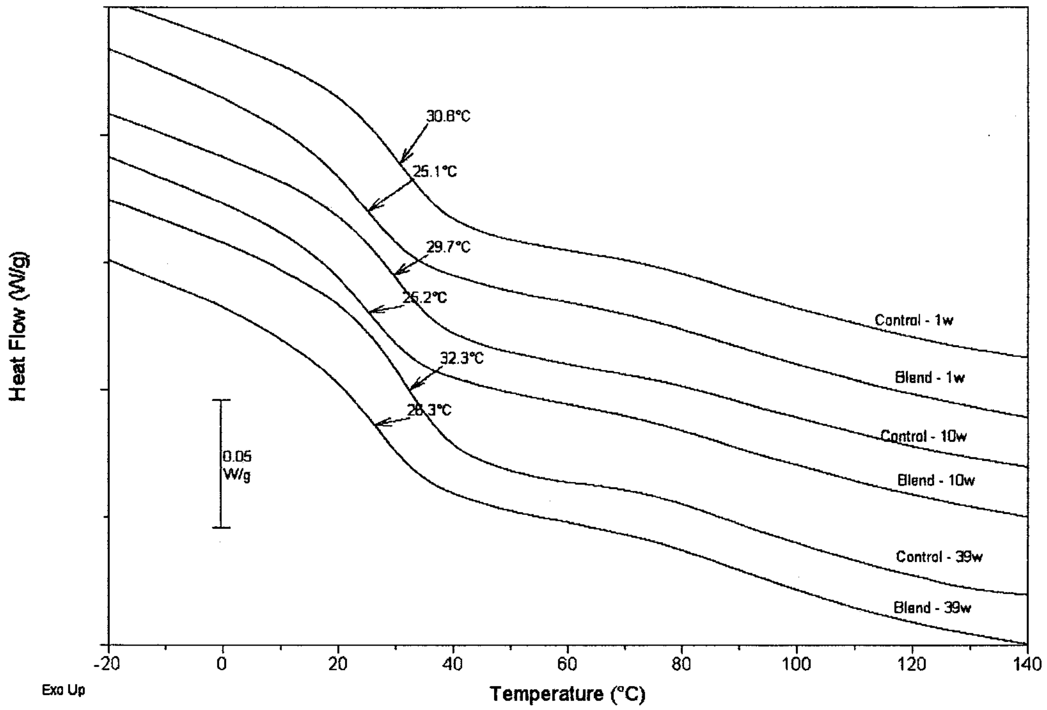


Figure 5-42: DSC thermograms [2nd run] of VC-VAc control and blend aged at 1, 10 and 39 weeks plasticized with Lindol

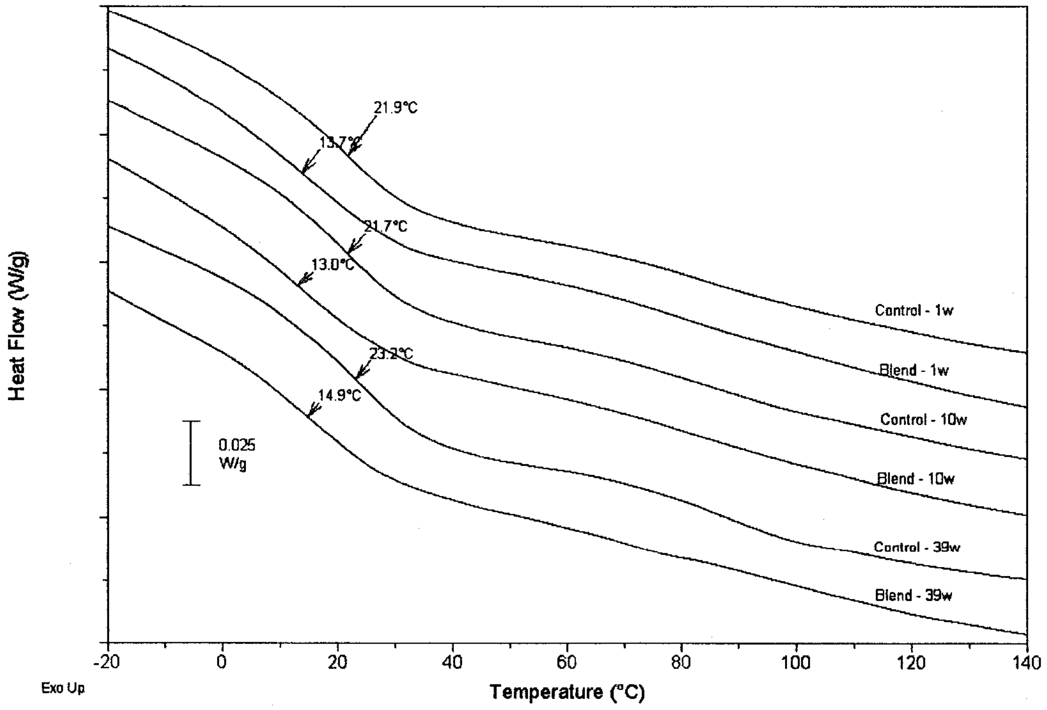


Figure 5-43: DSC thermograms [2nd run] of VC-VAc control and blend aged at 1, 10 and 39 weeks plasticized with Mesamoll

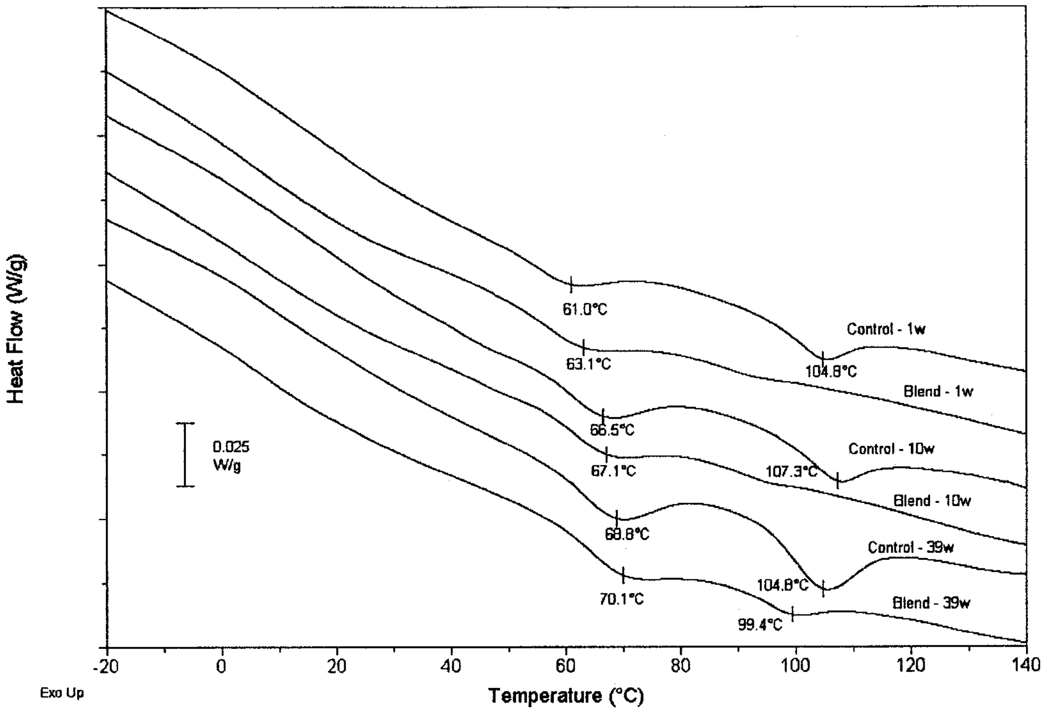


Figure 5-44: DSC thermograms [1st run] of VC-VAc control and blend aged at 1, 10 and 39 weeks plasticized with DOP

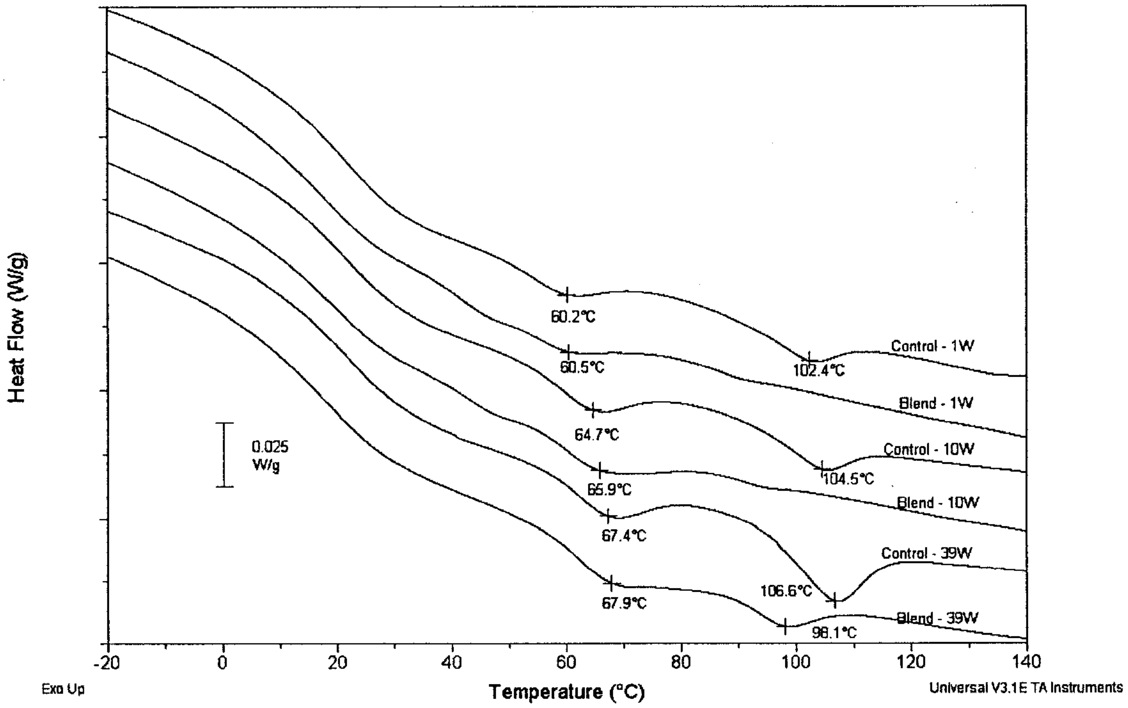


Figure 5-45: DSC thermograms [1st run] of VC-VAc control and blend aged at 1, 10 and 39 weeks plasticized with Benzoflex 2-45

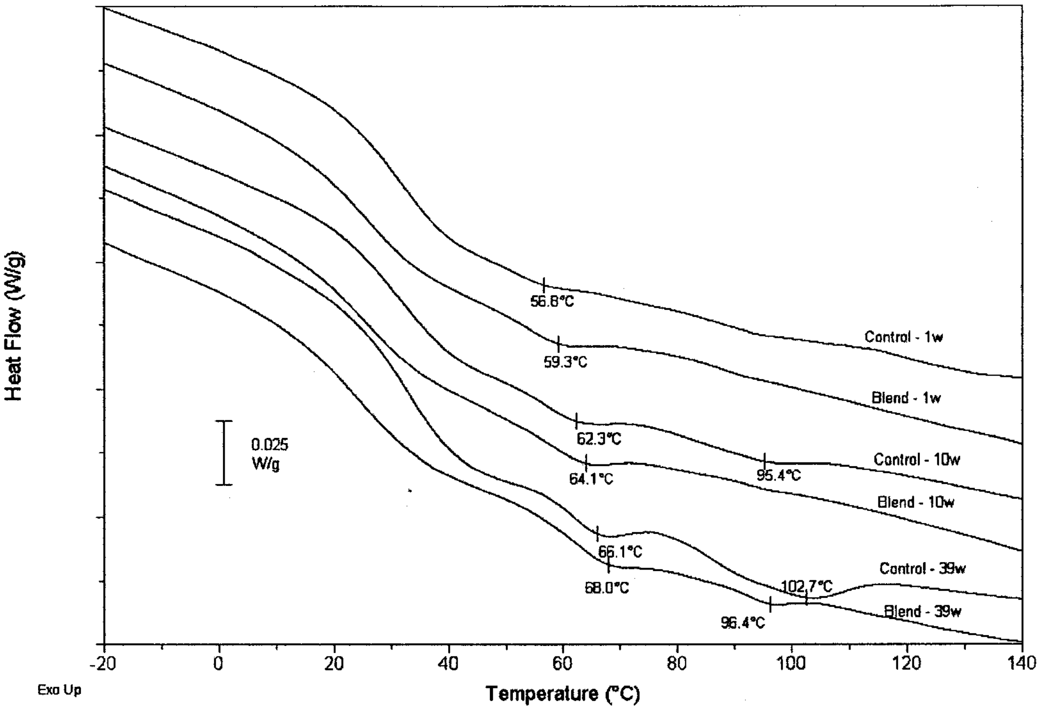


Figure 5-46: DSC thermograms [1st run] of VC-VAc control and blend aged at 1, 10 and 39 weeks plasticized with Lindol

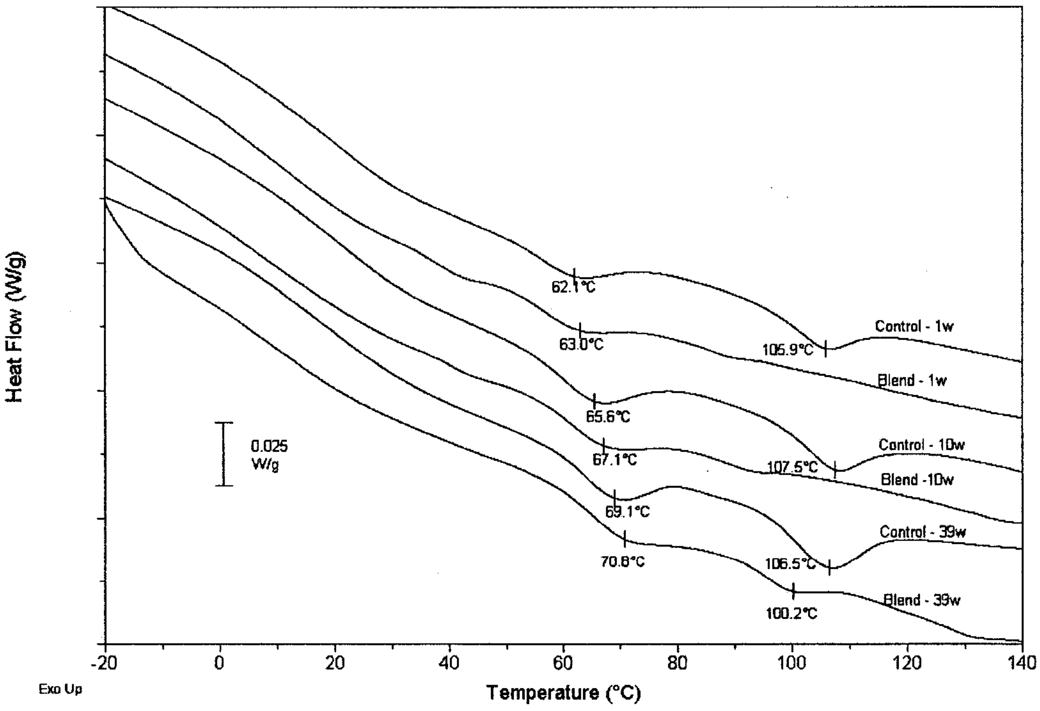


Figure 5-47: DSC thermograms [1st run] of VC-VAc control and blend aged at 1, 10 and 39 weeks plasticized with Mesamoll

5.6.2 Mechanical properties after ageing

Ageing affects large number of properties such as density, modulus of elasticity, and the rate of stress, strain, enthalpy, and volume relaxation [132, 133]. In addition little is known about the natural indoor ageing of plasticized PVC, and how effective is the simulation of accelerated ageing in simulating the natural indoor conditions.

The mechanical properties data of PVC controls and blends as function of plasticizer type are presented in Tables 5-30 and 5-31 and their respective stress-strain curves in Figures 5-48 to 5-55. Figures 5-48 to 5-55 indicate that the stress-strain curves are representative for ductile materials and that their general profile appearance does not change with respect to time. But we could notice that with increasing the ageing time the slope of the elastic range increases.

Their profiles exhibit a distinct yield and their failure are ductile with neck propagation and strain hardening for all controls and blends. The profiles also show that the different formulations are toughening with ageing reaching their maximum at 39 weeks, as indicated by the strain retreat.

Table 5-30: Mechanical properties of VC-VAc controls relative to plasticizer type

Sample ID	Elastic Modulus [MPa]	Tensile Strength[MPa]		Elongation [%]	Toughness [MPa]
		Yield	Break		
DOP					
1 week	45.63	3.44	4.60	357	13.18
10 week	57.93	4.14	4.57	284	11.14
26 week	30.11	3.84	4.33	315	10.98
39 week	32.17	4.23	4.47	276	10.76
52 week	20.68	3.48	4.49	347	12.31
Benzoflex 2-45					
1 week	52.06	3.28	4.61	470	16.80
10 week	54.43	3.86	4.71	407	15.51
26 week	29.16	3.34	4.41	427	15.17
39 week	44.35	3.44	4.39	339	12.03
52 week	20.42	2.92	4.45	421	14.42
Lindol					
1 week	196.68	5.47	6.04	313	16.80
10 week	202.60	6.03	5.88	226	13.25
26 week	134.79	6.07	6.10	232	13.14
39 week	150.03	5.88	5.79	164	8.90
52 week	85.64	4.99	5.77	214	11.42
Mesamoll					
1 week	51.20	3.71	5.13	383	15.49
10 week	51.90	4.09	5.21	353	14.91
26 week	27.05	3.73	5.00	367	13.43
39 week	29.11	3.85	5.08	301	12.06
52 week	23.55	3.82	4.96	347	13.83

Table 5-31: Mechanical properties of VC-VAc-Alcell blends relative to plasticizer type

Sample ID	Elastic Modulus [MPa]	Tensile Strength[MPa]		Elongation [%]	Toughness [MPa]
		Yield	Break		
DOP					
1 week	21.19	3.17	3.20	359	9.86
10 week	29.32	3.55	3.13	270	7.6
26 week	17.84	3.32	3.10	270	7.60
39 week	20.14	3.65	2.99	203	6.12
52 week	13.55	3.35	3.13	271	7.70
Benzoflex 2-45					
1 week	57.67	2.54	3.12	485	10.89
10 week	62.94	2.86	2.95	393	9.29
26 week	60.44	2.82	2.99	384	9.61
39 week	54.58	2.82	2.67	323	7.26
52 week	44.94	2.65	2.97	383	9.44
Lindol					
1 week	112.64	4.41	4.04	359	13.43
10 week	116.06	4.62	4.05	299	11.48
26 week	90.50	4.19	3.96	285	10.47
39 week	59.24	3.95	3.64	224	7.93
52 week	61.07	3.84	3.61	236	8.11
Mesamoll					
1 week	29.24	3.45	3.46	357	10.96
10 week	31.46	3.94	3.55	285	9.14
26 week	19.15	3.19	3.31	281	7.67
39 week	26.90	3.47	3.19	219	6.44
52 week	17.85	3.45	3.43	252	7.78

Figure 5-48: Stress-strain curves of VC-VAc control aged at 1, 10, 26, 39 and 52 weeks plasticized with DOP

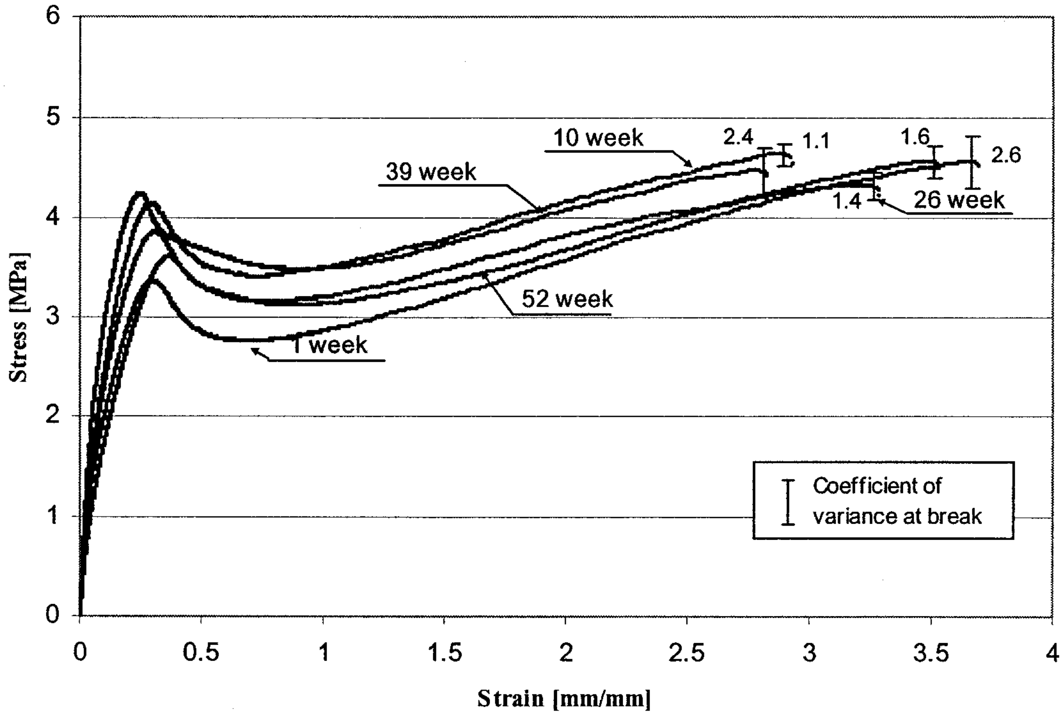


Figure 5-49: Stress-strain curves of VC-VAc control aged at 1, 10, 26, 39 and 52 weeks plasticized with Benzoflex 2-45

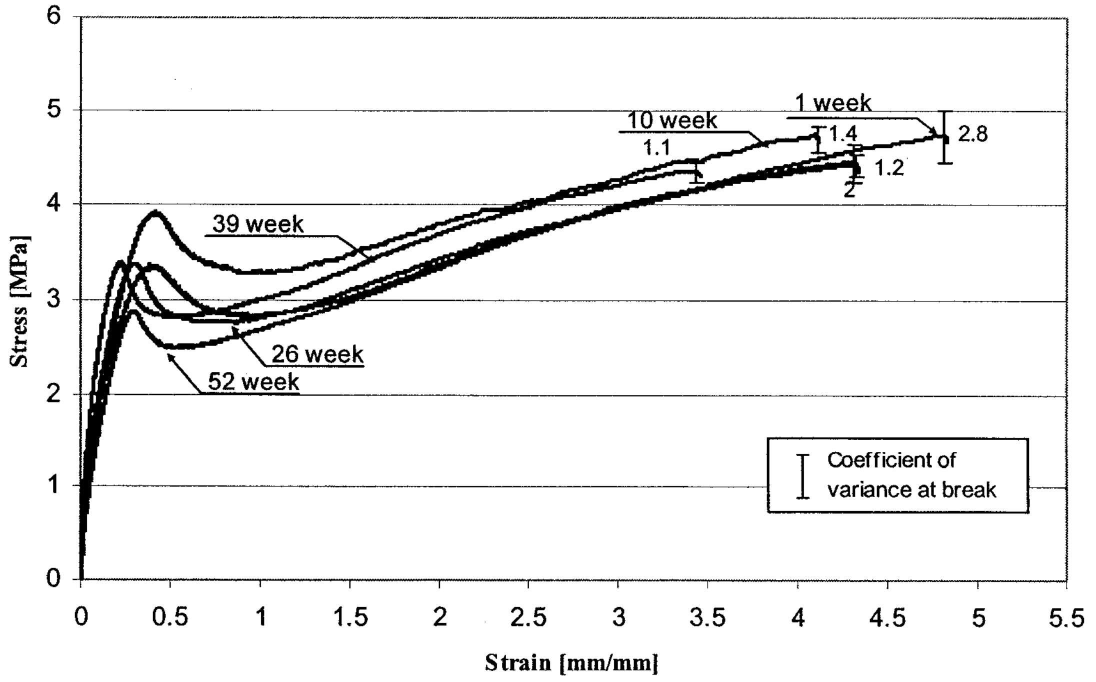


Figure 5-50: Stress-strain curves of VC-VAc control aged at 1, 10, 26, 39 and 52 weeks plasticized with Lindol

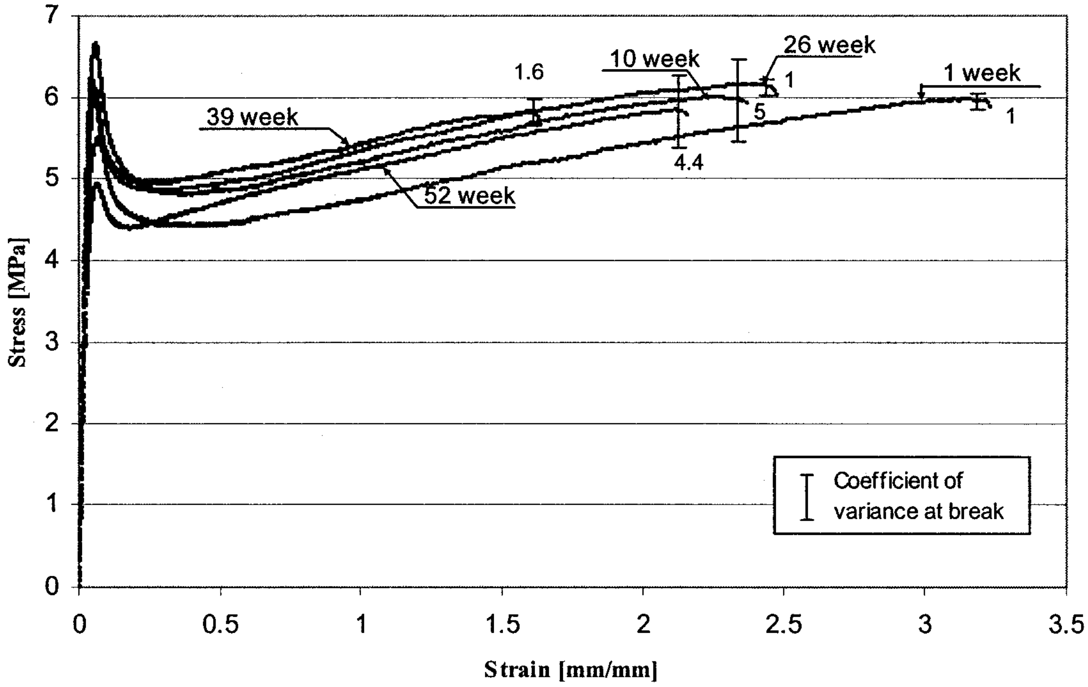


Figure 5-51: Stress-strain curves of VC-VAc control aged at 1, 10, 26, 39 and 52 weeks plasticized with Mesamoll

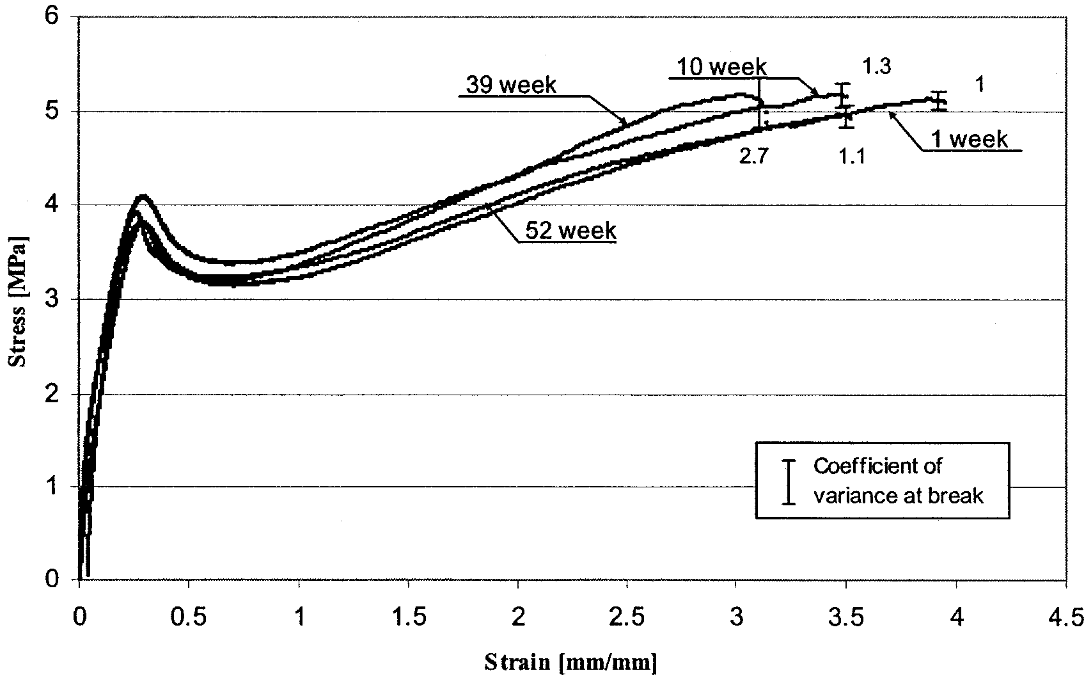


Figure 5-52: Stress-strain curves of VC-VAc-Alcell blend aged at 1, 10, 26, 39 and 52 weeks plasticized with DOP

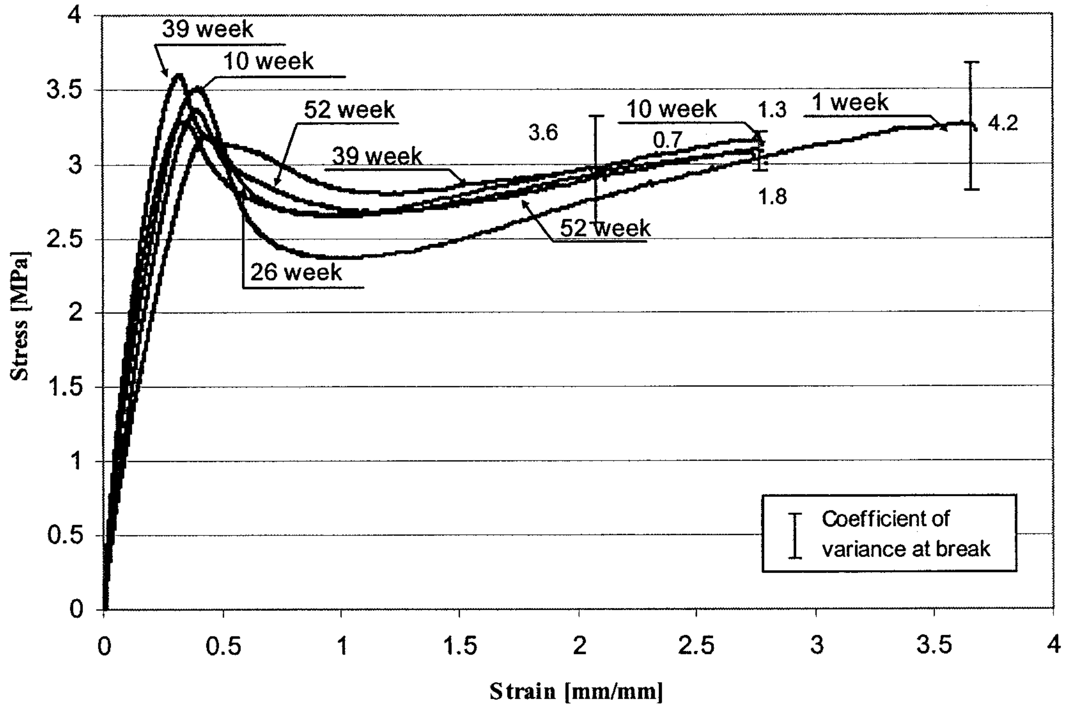


Figure 5-53: Stress-strain curves of VC-VAc-Alcell blend aged at 1, 10, 26, 39 and 52 weeks plasticized with Benzoflex 2-45

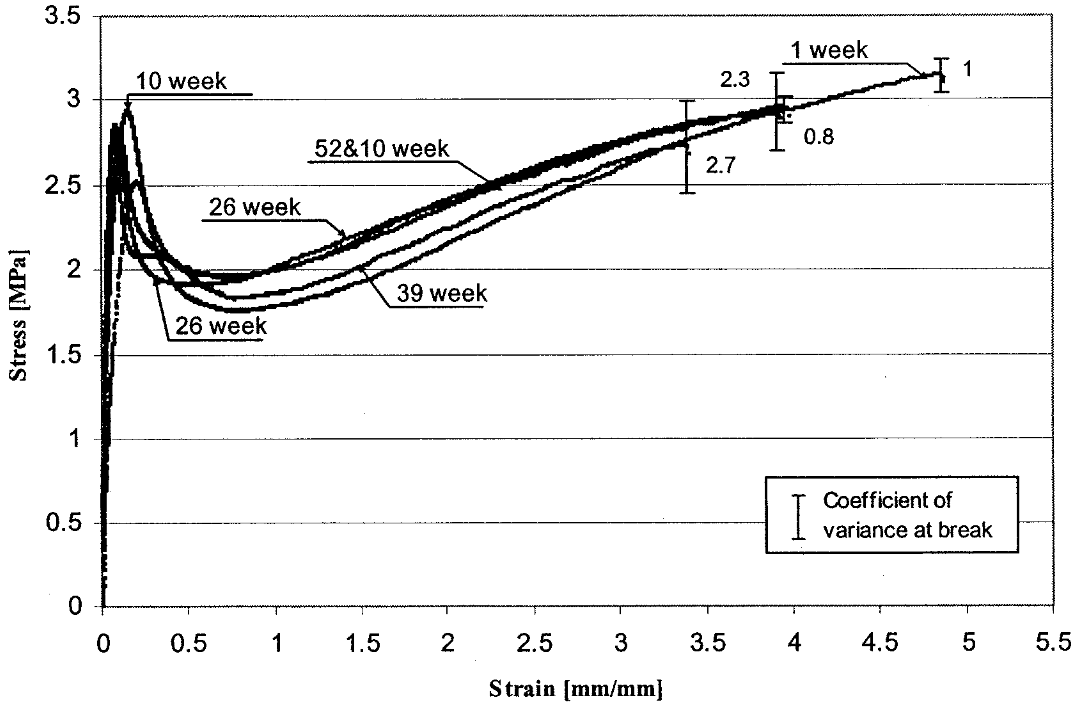


Figure 5-54: Stress-strain curves of VC-VAc-Alcell blend aged at 1, 10, 26, 39 and 52 weeks plasticized with Lindol

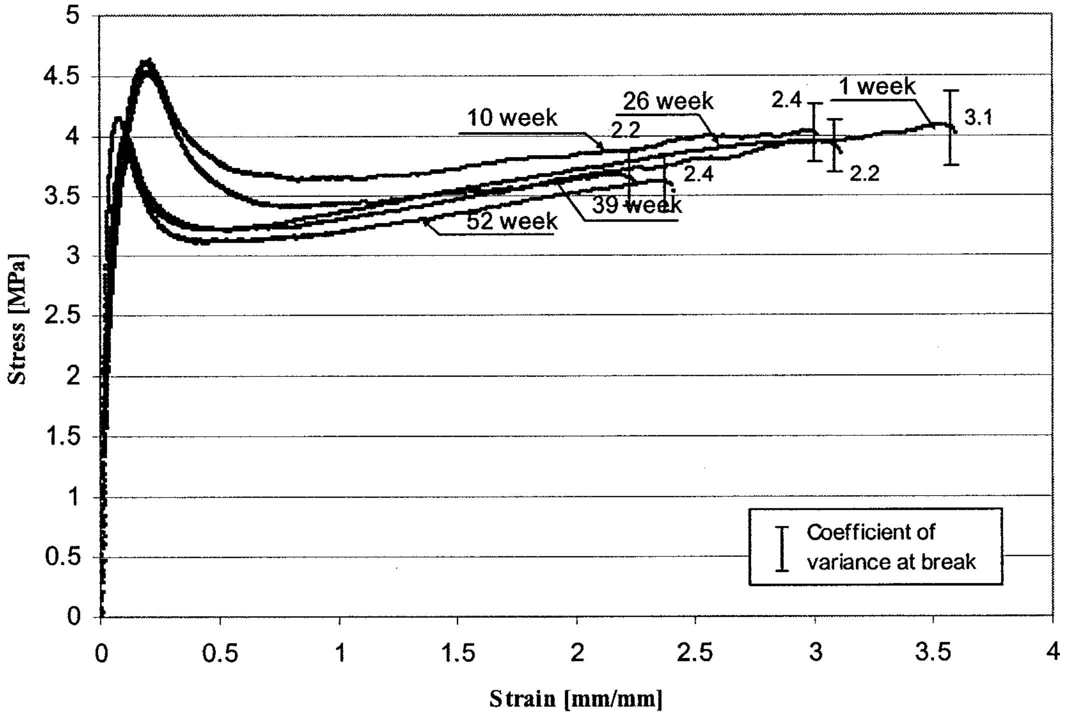
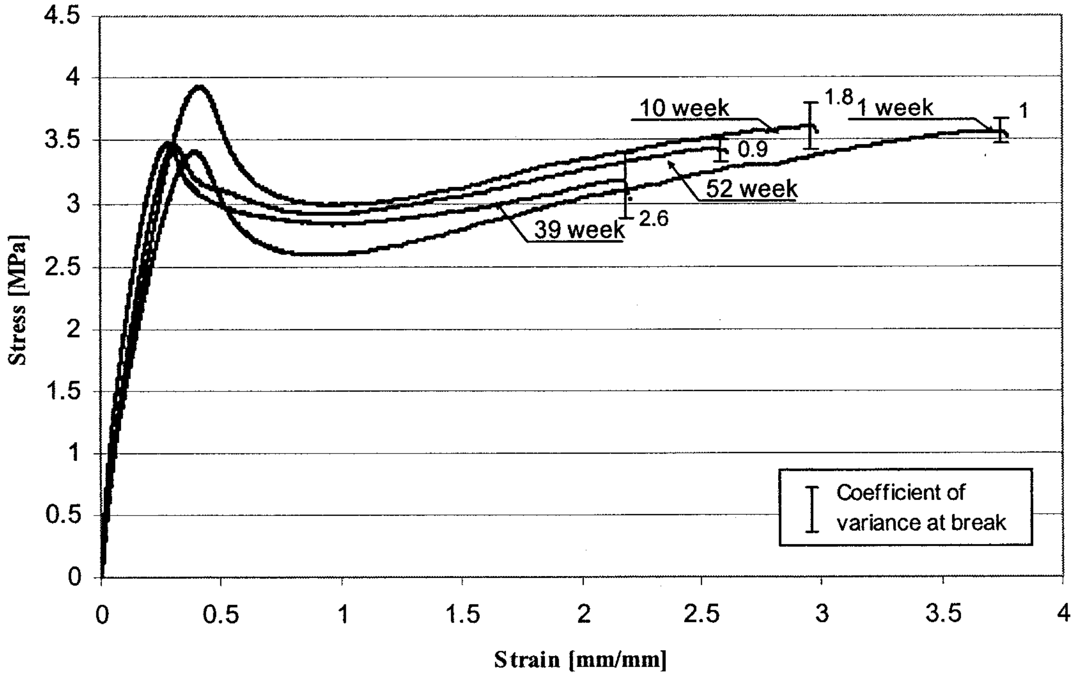


Figure 5-55: Stress-strain curves of VC-VAc-Alcell blend aged at 1, 10, 26, 39 and 52 weeks plasticized with Mesamoll



The modulus of elasticity and elongation are plotted versus ageing time as shown in Figure 5-56 to 5-63. The Figures show that elastic modulus of VC-VAc controls and blends is inversely proportional to elongation, and as a general trend both modulus of elasticity and elongation decreased with increasing the ageing time. The process of ageing indicates the existence of several stages:

First stage: after 10 weeks of ageing the specimens show an increase in modulus with a reduction in elongation, considering that room temperature, which is the testing temperature, is higher than Tg values of formulations plasticized with DOP, Benzoflex 2-45, Mesamoll, and approaching that of Lindol. In the different formulations surface plasticizers tend to exudate. As the main process in ageing of plasticized VC-VAc copolymer at low temperature is the diffusion desorption of the plasticizer [56]. Desorption or evaporation is believed to be the rate-controlling factor being dependent on the temperature and the vapor pressure over the surface of the material [57].

Second stage: after 26 weeks, and due to the first stage, the macromolecules tendencies are to re-array and to re-structure the voids or free volume created by the plasticizer desorption. That induces a relatively high decrease in modulus due to the struggle of the macromolecules to overcome the internal attraction bonding forces, accompanied with a slight increase in elongation, as the molecules are just proceeding with the overcoming of the internal forces.

Figure 5-56: Modulus of elasticity versus elongation of aged VC-VAc control plasticized with DOP

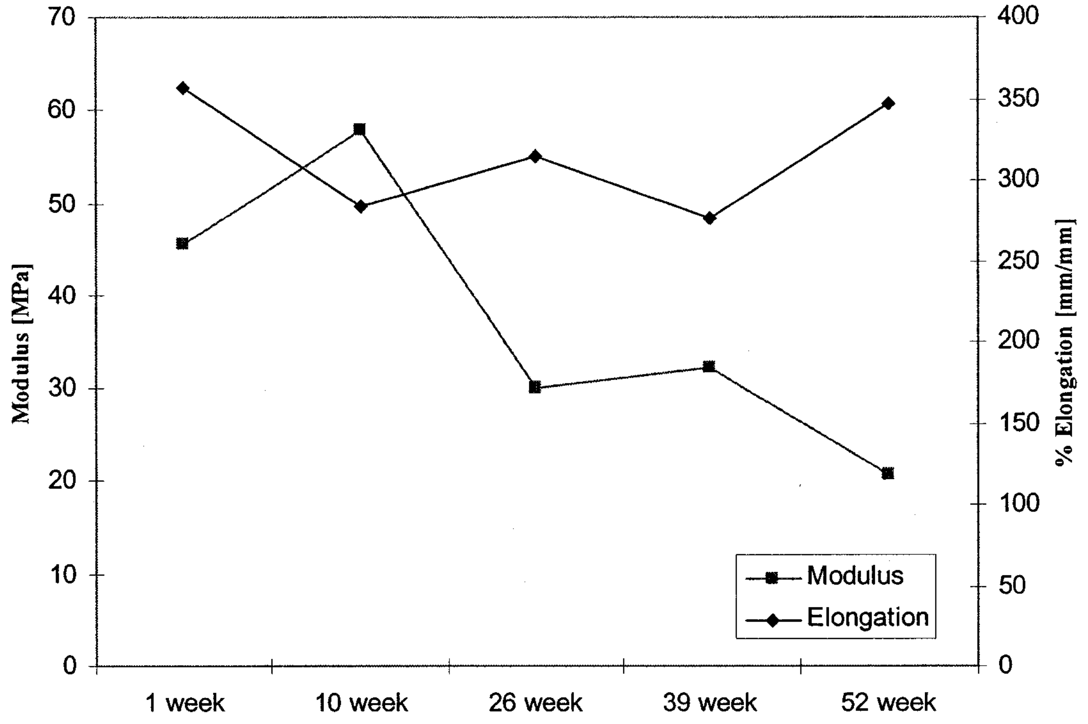


Figure 5-57: Modulus of elasticity versus elongation of aged VC-VAc control plasticized with Mesamoll

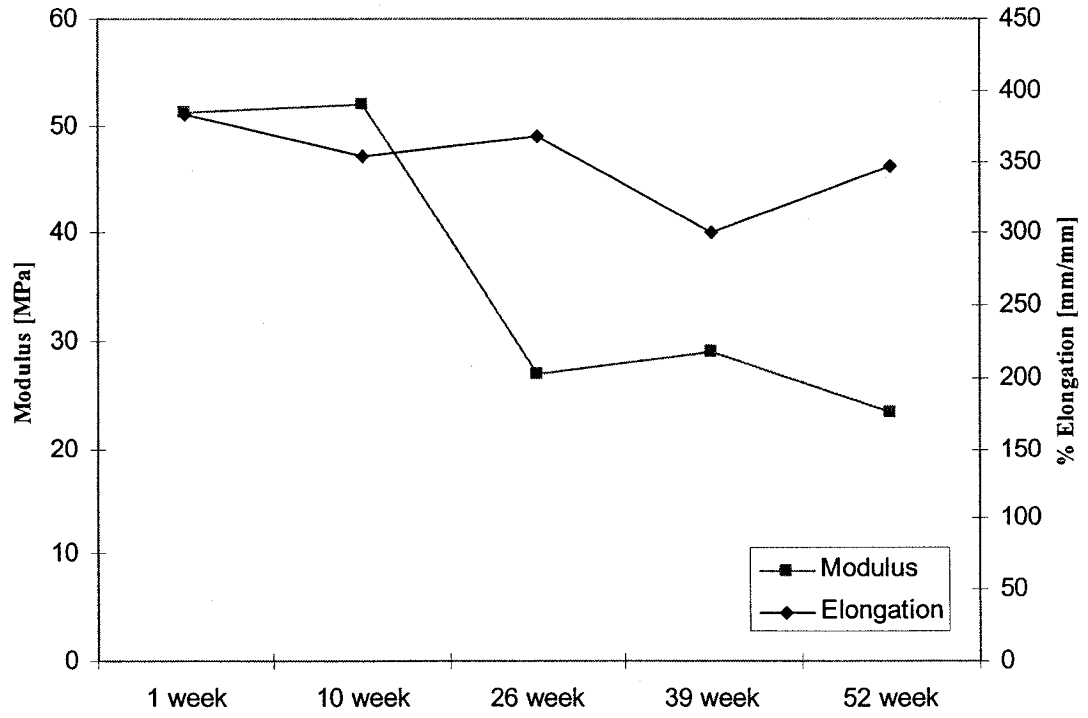


Figure 5-58: Modulus of elasticity versus elongation of aged VC-VAc control plasticized with Benzoflex 2-45

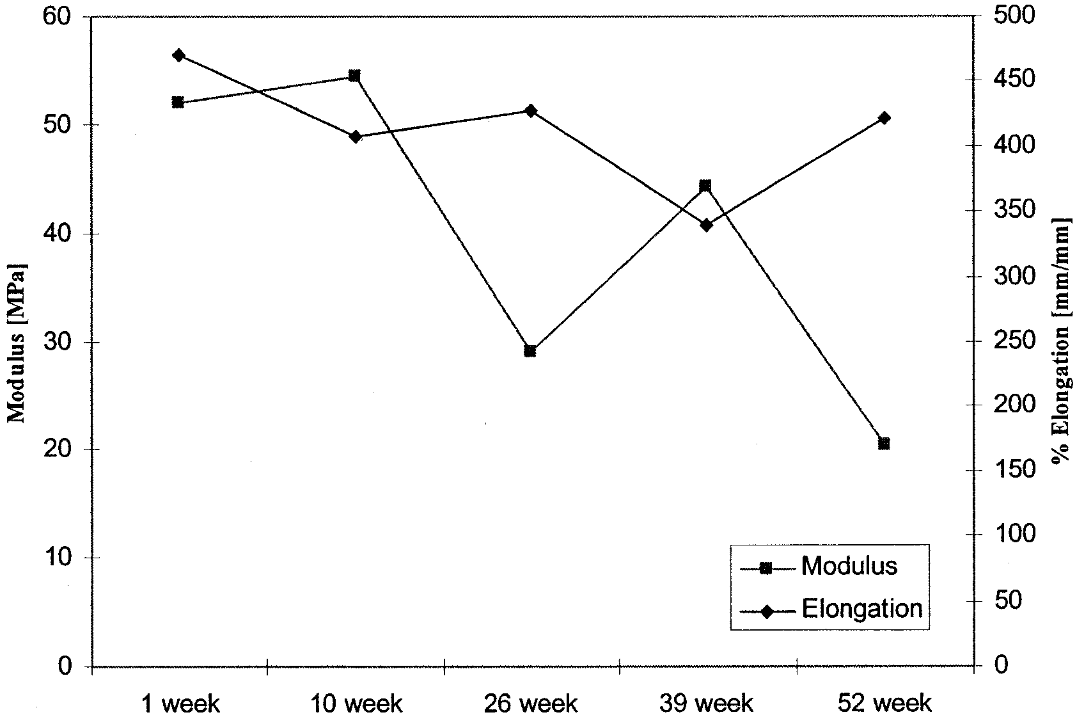


Figure 5-59: Modulus of elasticity versus elongation of aged VC-VAc control plasticized with Lindol

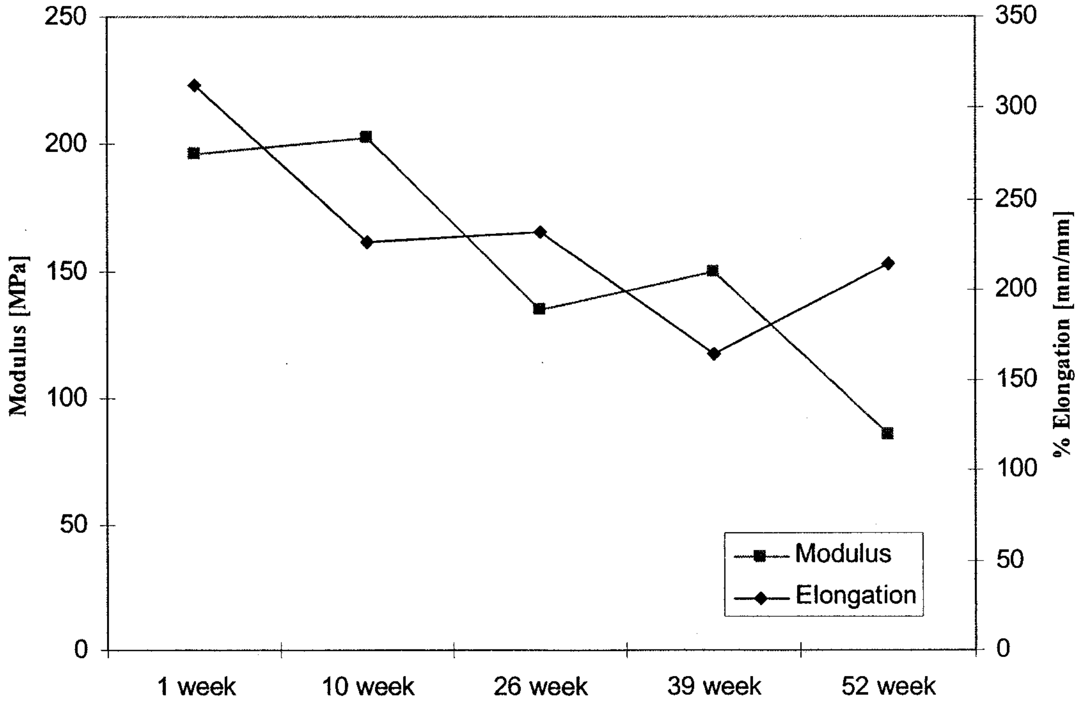


Figure 5-60: Modulus of elasticity versus elongation of aged VC-VAc-Alcell blend plasticized with DOP

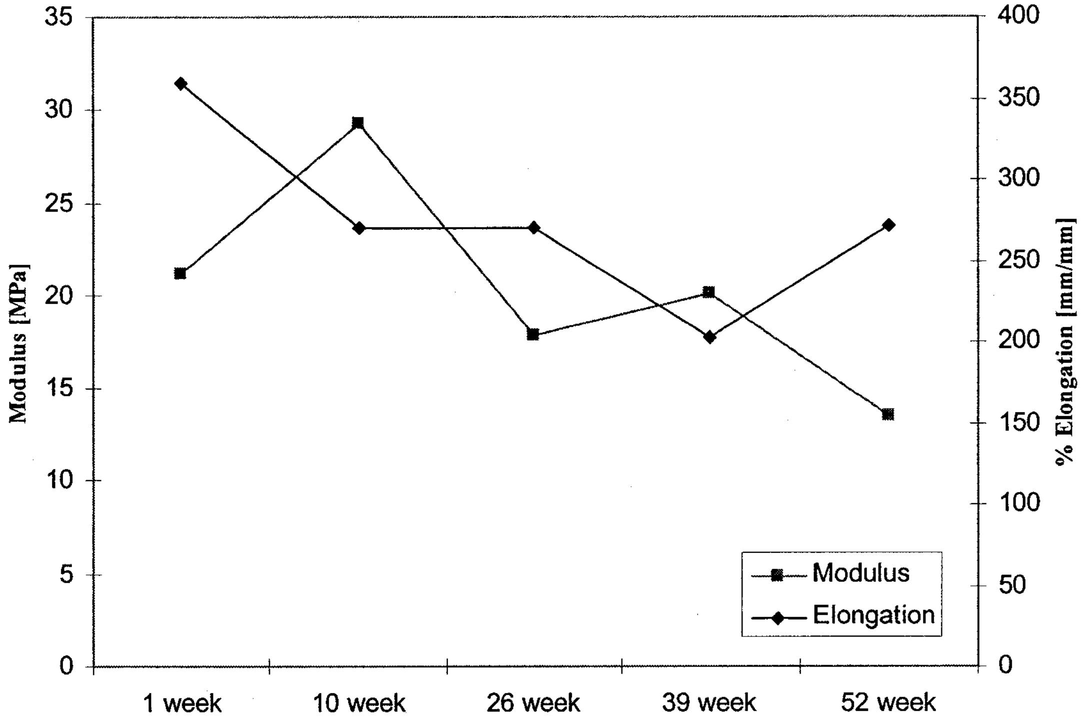


Figure 5-61: Modulus of elasticity versus elongation of aged VC-VAc-Alcell blend plasticized with Mesamoll

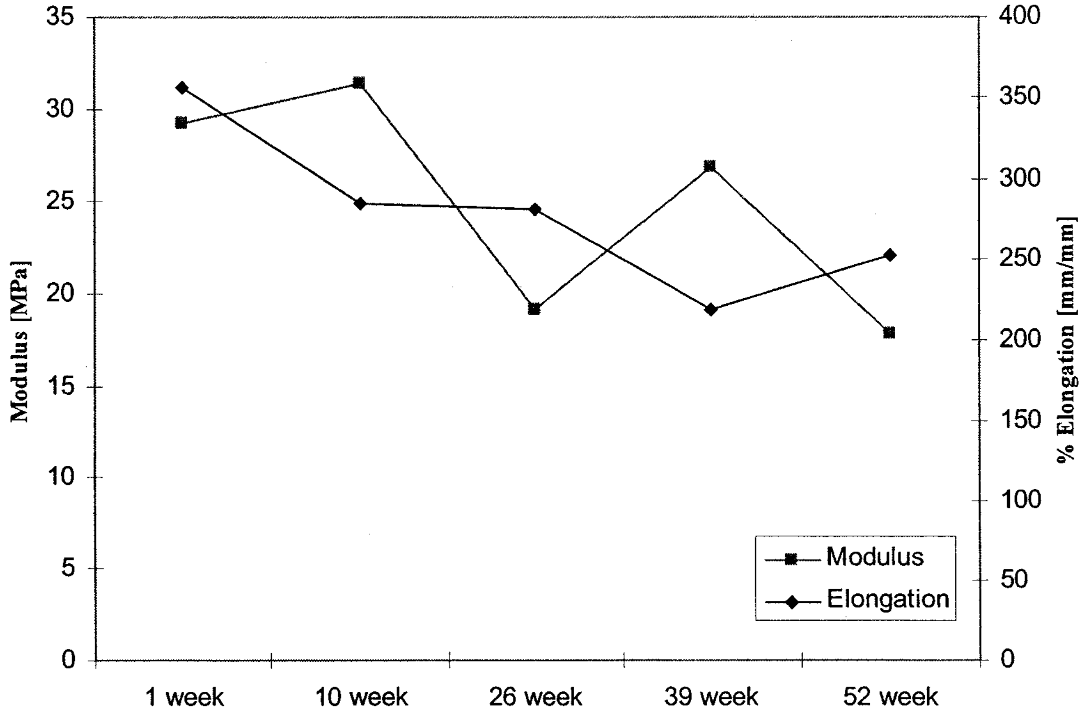


Figure 5-62: Modulus of elasticity versus elongation of aged VC-VAc-Alcell blend plasticized with Benzoflex (2-45)

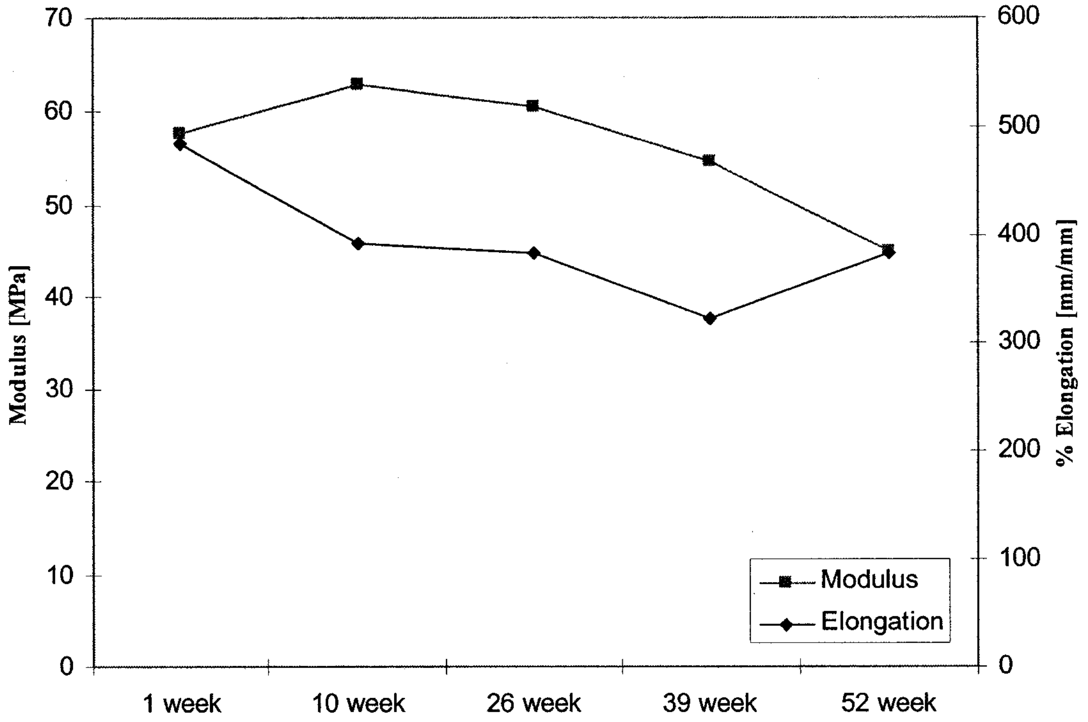
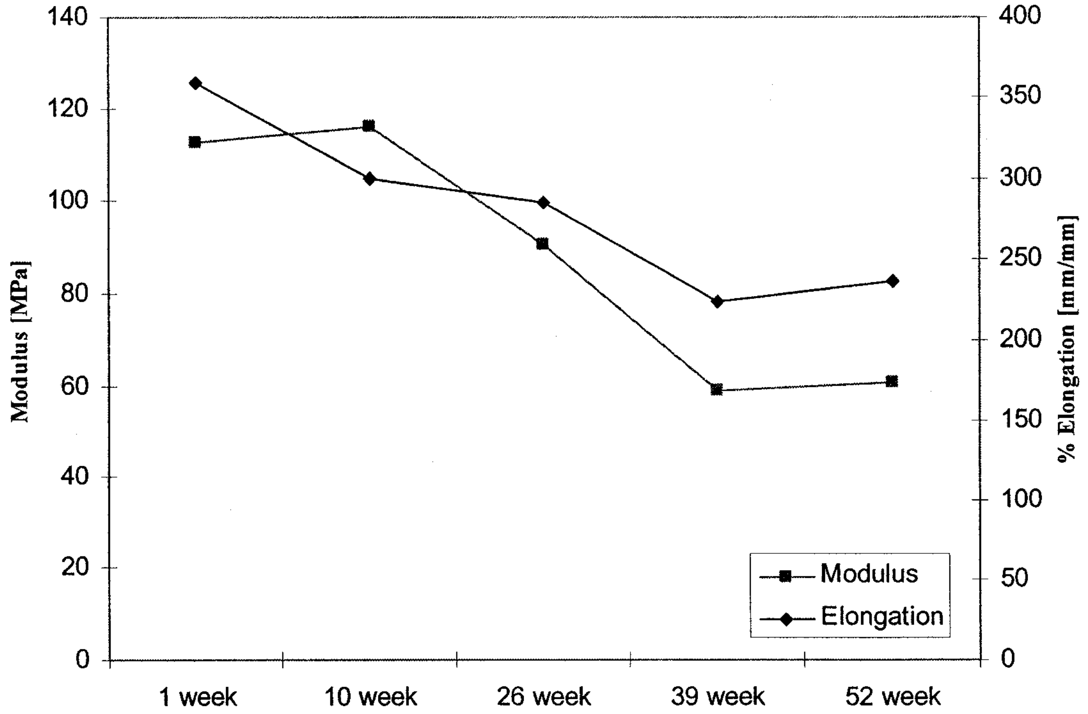


Figure 5-63: Modulus of elasticity versus elongation of aged VC-VAc-Alcell blend plasticized with Lindol



These two stages will be repeated until the polymer chains eliminate the excess free volume in an effort to approach the preferred or true equilibrium state of the system. This behavior is manifested through a slow decrease in volume (densification), along with other state function variables that are controlled by the existing temperature, humidity, and latter on will involve the used stabilizer. The properties of an amorphous polymer are dependent not only on the free volume but also on how that free volume is distributed, that is, on the degree, type, and distribution order in the sample.

In addition, it should be mentioned that the over all profile of ageing and changing of both modulus and elongation (Figure 5-56 to 5-63) are influenced by the plasticizer properties. As seen in VC-VAc controls, formulation plasticized with Lindol showed a more cohesive and compact profile and in less measure that of Benzoflex 2-45, while formulation plasticized with DOP and Mesamoll acted differently and showed a loose profile. On the other hand when Alcell lignin is added, it affects the profile according to its own plasticization, showing a compact profile for formulation plasticized with DOP and Mesamoll, and showed an almost linear profile with the most linear plasticizer (i.e., Benzoflex 2-45), while with Lindol it almost achieves the equilibrium state.

Tensile strength at yield and elastic modulus are plotted versus ageing time for both VC-VAc controls and blends as shown in Figure 5-64 to 5-71. Tensile strength at yield is directly proportional to the elastic modulus as their profile similarity suggested with respect to time. The rise in yield stress would result from a better packing of macromolecules, greater force being required to initiate their movement with respect to each other (i.e., higher modulus). On the other hand, tensile strength will decrease when the chain links is already directed and settled.

Figure 5-64: Modulus of elasticity versus tensile strength at yield of aged VC-VAc control plasticized with DOP

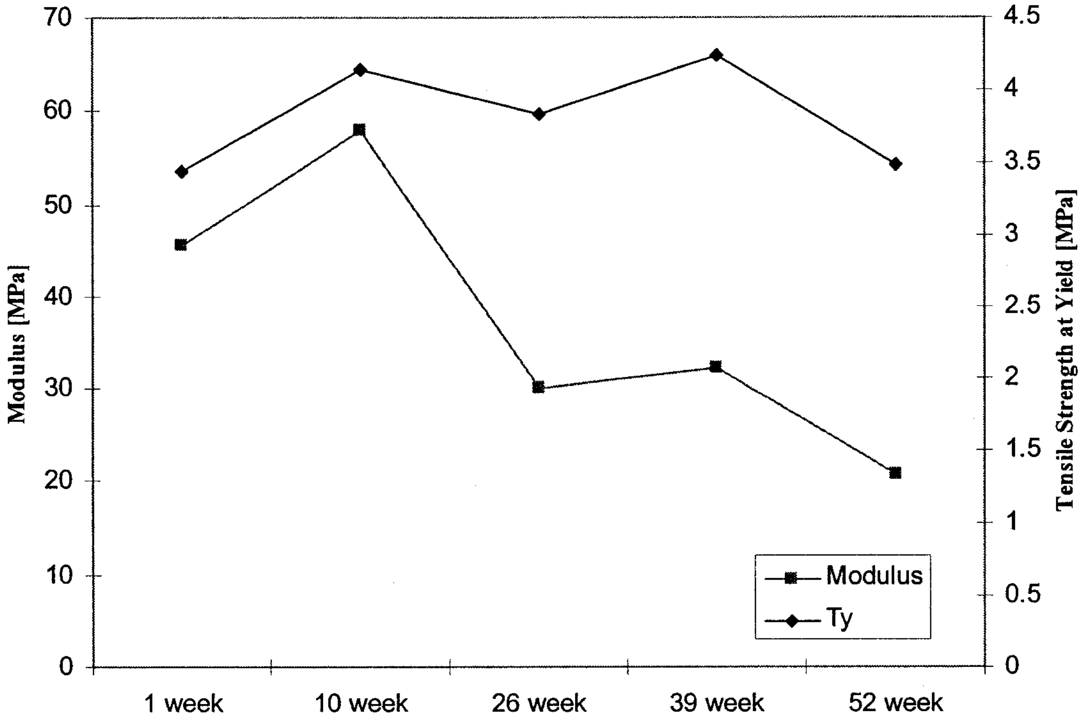


Figure 5-65: Modulus of elasticity versus tensile strength at yield of aged VC-VAc control plasticized with Mesamoll

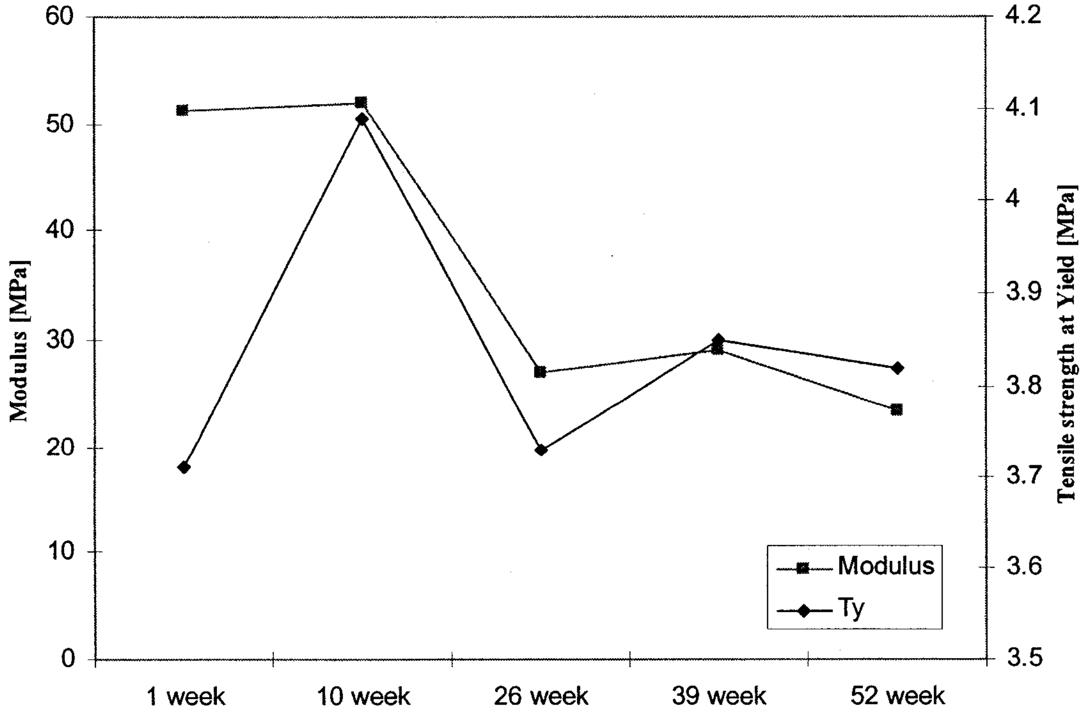


Figure 5-66: Modulus of elasticity versus tensile strength at yield of aged VC-VAc control plasticized with Benzoflex 2-45

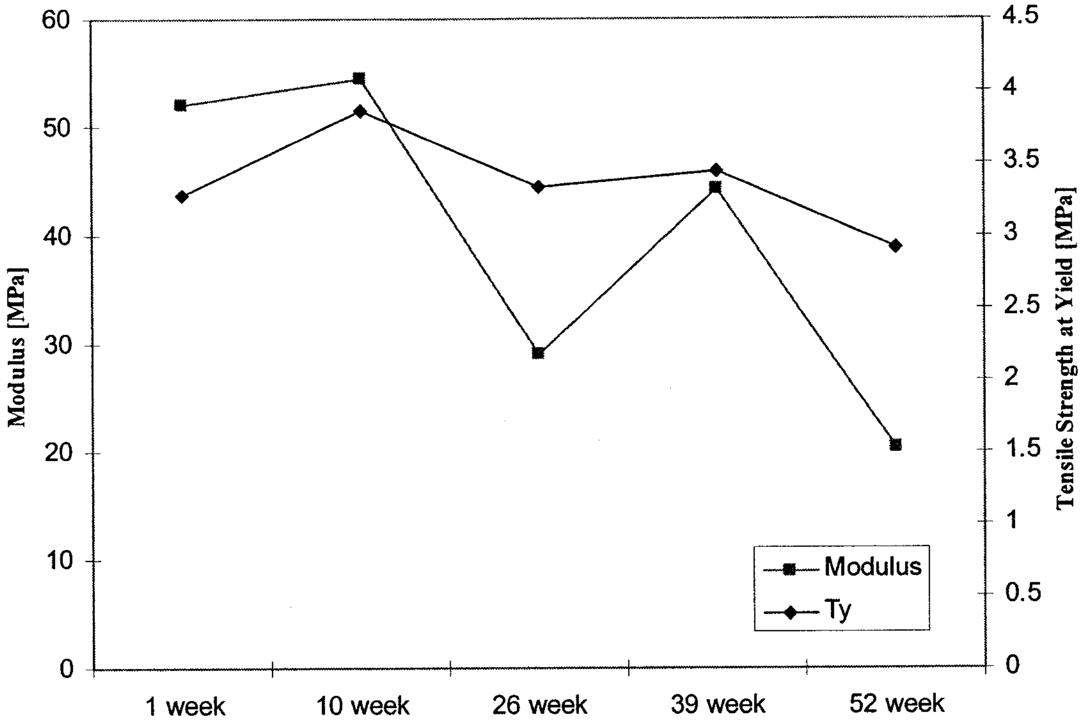


Figure 5-67: Modulus of elasticity versus tensile strength at yield of aged VC-VAc control plasticized with Lindol

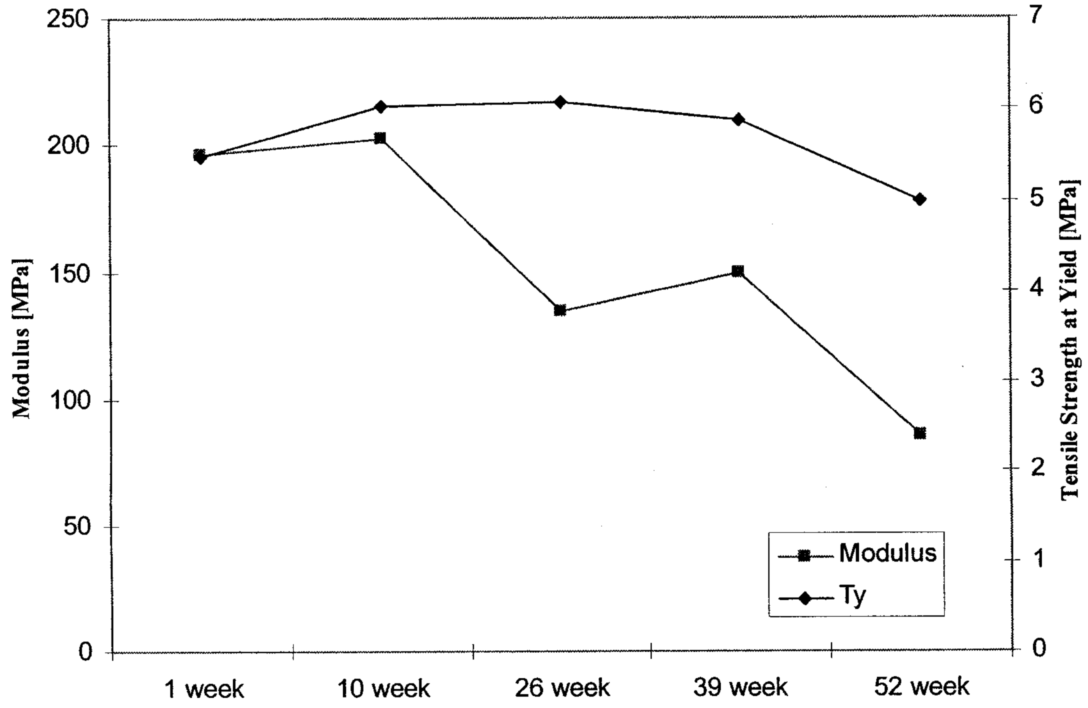


Figure 5-68: Modulus of elasticity versus tensile strength at yield of aged VC-VAc-Alcell blend plasticized with DOP

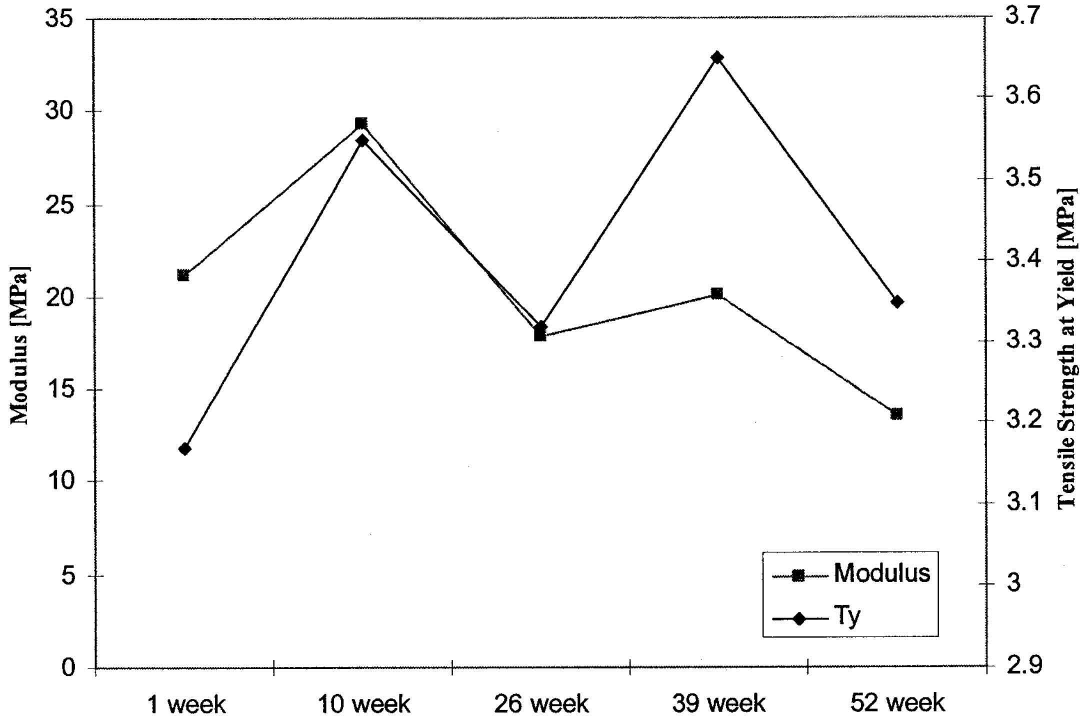


Figure 5-69: Modulus of elasticity versus tensile strength at yield of aged VC-VAc-Alcell blend plasticized with Mesamoll

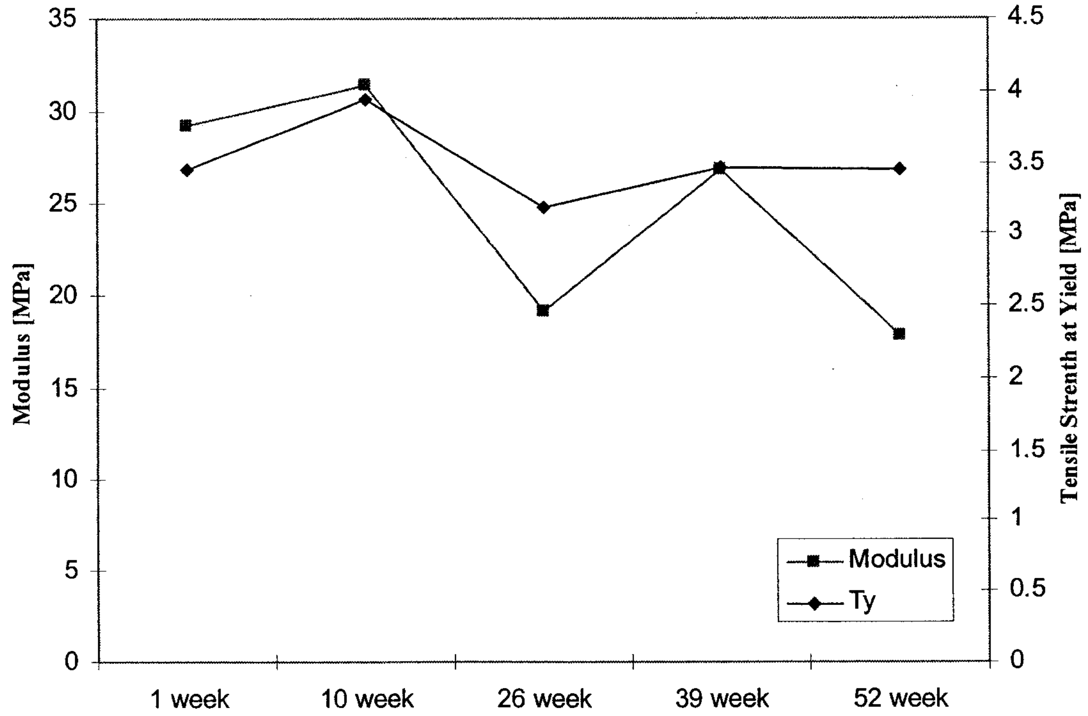


Figure 5-70: Modulus of elasticity versus tensile strength at yield of aged VC-VAc-Alcell blend plasticized with Benzoflex 2-45

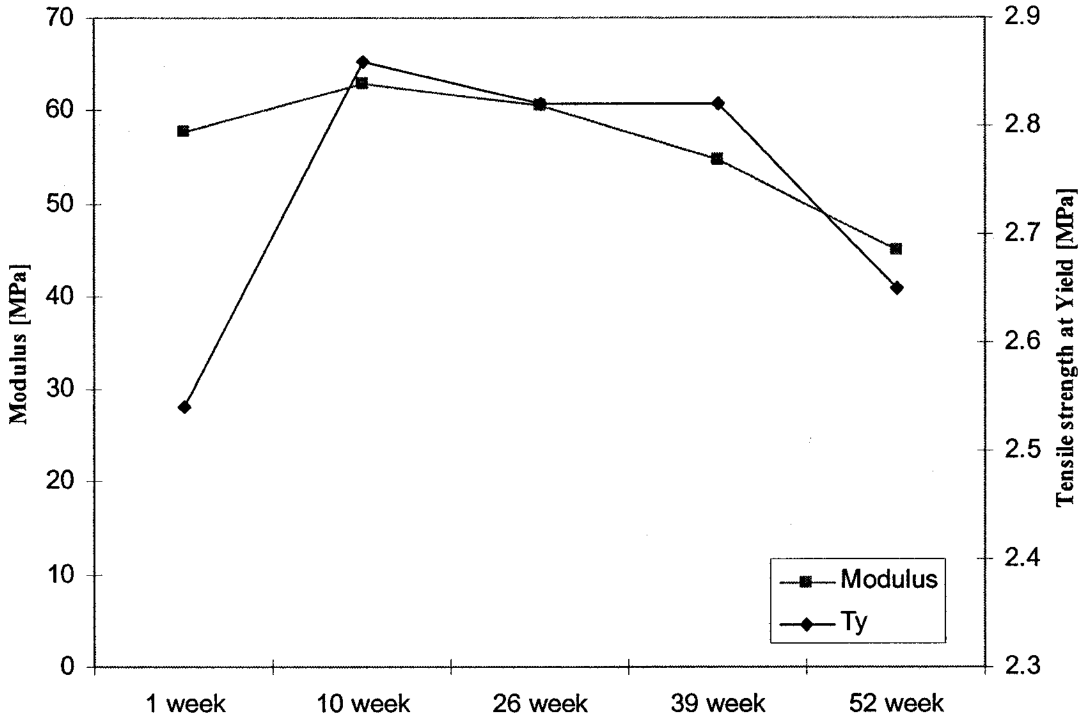
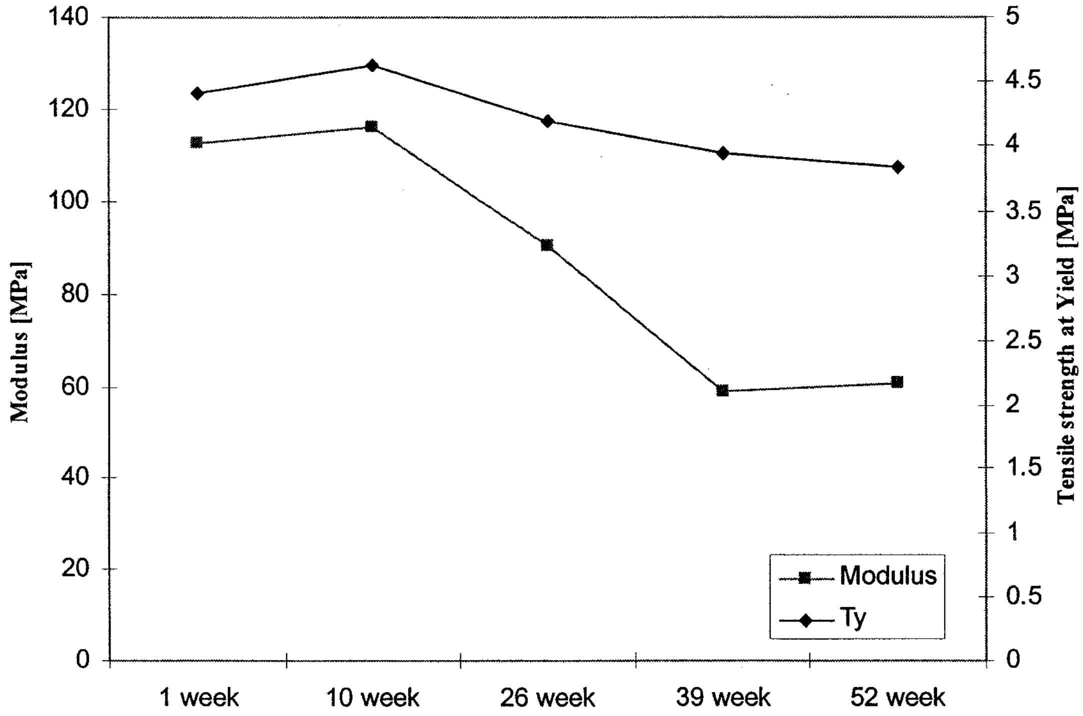


Figure 5-71: Modulus of elasticity versus tensile strength at yield of aged VC-VAc-Alcell blend plasticized with Lindol



5.7 VC-VAc copolymer VOC's emission

For new or renovated buildings, the primary emissions (free non-bound VOC's, which generally have low molecular weight, like solvents, additives) of VOC's from building products dominates for a period of up to some months. Ageing of building materials, by chemicals (e.g., maintenance products, moisture) or physical (e.g., heat, weariness, UV-light, etc) decomposition may result in secondary emissions, which is significantly lower than those of the primary emissions [134].

The VOC's emitted from building materials have been acknowledged as being pollutants that may deteriorate indoor air quality (IAQ) in terms of sensory reactions such as odor annoyance, eye and airway irritation which may be associated with sick building syndrome, like headache [135,136]; these emissions may be influenced by temperature and humidity.

IAQ investigators used variety of methods to determine the chemical emissions from indoor materials. This study carried only the fundamental composition investigation using static headspace direct analysis (i.e., the gas space above a test specimen in a closed container). This is very sufficient for carrying on the comparison between the different formulations with regard to the VOC`s emitted. Moreover, an identification and quantification of the VOC`s emitted from the different compositions of the vinyl flooring materials were classified and evaluated using GC/MS system.

Headspace analysis is the only reliable source of information. In the absence of other sources such product labels and technical data sheets that do not elaborate enough regarding the chemical composition. Vinyl flooring is considered as a "Dry product" which is characterized by relatively low emission rates of VOC's that decay slowly. Although some manufactures can argue that the vinyl flooring is a complex chemical system which consists of different components that undergoes chemical and physical changes after fabrication, resulting in different compounds that differ from those stated in the vinyl technical data sheet. The recognition that the quality of indoor air could be deteriorated due to the VOC`s emitted from the building and finishing materials was the motive to carry on this study.

5.7.1 GC calibration

Figure 5-72, represent the results of a five point system calibration attained using five certified permeation tubes. Each data point is the average of 5 direct on-line injection (i.e., n=5). Coefficient of variation of FID response to each standard generated atmosphere ranges from 2 % (for higher concentrations) to 8 % (for lower concentrations). This indicates that concentrations generated by permeation tubes in the above system including variations in tubes, emission rates, oven temperature and flow rates are steady [137].

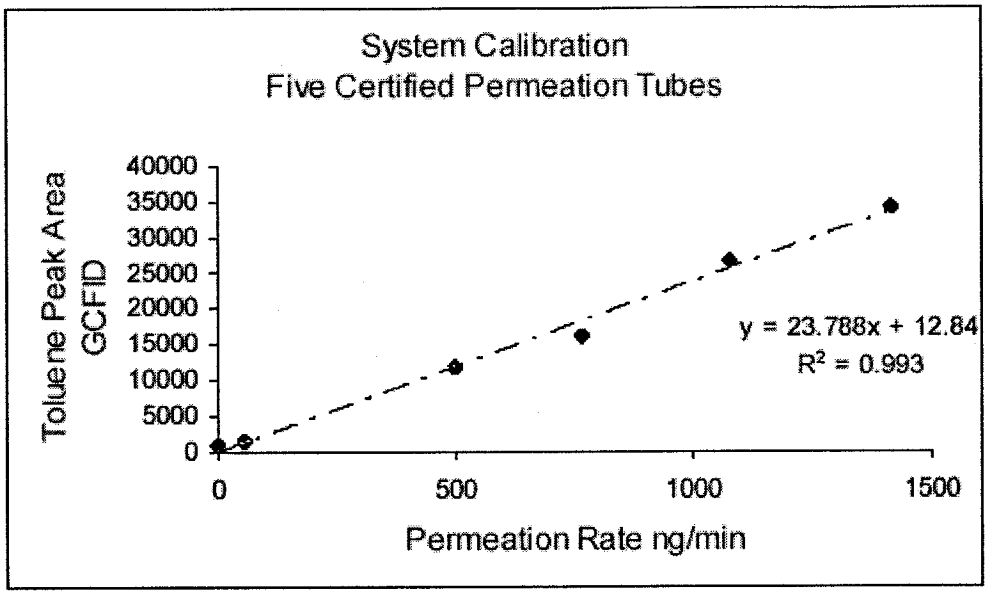


Figure 5-72: Responses of the FID cryogenic system to low-level Toluene emissions by five certified permeation tubes – The sixth point in the figure (close to the Y-intercept) is the baseline response of the system [137].

This step is necessary to relate the peak area/height of contaminates to their concentrations. All conditions of the system (i.e., flow rate, temperature, relative humidity, sampling and analysis procedures) are kept to that of the conditions used during sampling of the standard generated atmosphere. In addition, before running each sample a base line is established.

Using the curve equation Y = 23.788 X + 12.84

Where flow rate=388 cm^3/min. and Sampling loop=2 cm^3.

Calibration Factor = 0.0002

5.7.2 Head space analysis

The gas chromatographs of the different tested formulations are presented in Appendix [A]. The peaks response shows that the emitted compounds have a boiling point ranging from 60 °C to 104-134 °C, which indicates that those compounds are in the VOC's range. Considering that a VOC is an organic compound that has a vapor pressure greater than 10^{-2} kPa at 25 °C and a boiling point below 250 °C at standard atmospheric pressure. Organic compounds with boiling points below 50 °C are considered very volatile (VVOC).

The total volatile organic compounds (TVOC) based on the detectors response to toluene (i.e., toluene response factor) are determined and presented in Table 5-32; the concentration of the TVOC emitted from each sample is calculated in accordance to the following equation:

Total mass (ng) = Total area of all peaks x Calibration factor Eq.1

TVOC Concentration (ng/cm^3) =

Total Mass (ng) / (Sampling rate (cm^3/min.) x Sampling Duration (min.))........Eq.2

Where Sampling rate is 40 cm^3/min.

Sampling duration is 3 min.

Table 5-32: Total volatile organic compounds concentrations in the different tested formulation

Sample ID	Total Area (mm^2)	Total Mass (ng)	TVOC (ng/cm^3)	TVOC (mg/m^3)
VC-VAc – DOP	950880	190.176	1.585	1.6
VC-VAc – Benzoflex 2-45	4521037	904.207	7.535	7.5
VC-VAc – Lindol	137796	27.559	0.23	0.2
VC-VAc – Mesamoll	3954664	790.933	6.591	6.6
Alcell blend – DOP.	6315404	1263.08	10.526	10.5
Alcell blend – Benzoflex 2-45	1330267	266.053	2.217	2.2
Alcell blend – Lindol	1244084	248.817	2.073	2.1
Alcell blend – Mesamoll	7345245	1469.05	12.242	12.2

The data presented in Table 5-32 show that generally the VOC's emitted from the different vinyl flooring formulation are very small. These are in total agreement with the literature findings; although they are little higher than the literature findings, but this is due to that the presented tested data are initial concentrations. Knowing that the higher concentration is the initial one obtained within the first 150 hrs of the emission test [138]. VC-VAc–Lindol formulation is the least VOC's emitting among the tested formulations. Although, when Alcell lignin is added the VOC's show an increasing trend, VC-VAc–Alcell blends plasticized with both Lindol and Benzoflex 2-45 show a very comparative emission to that of VC-VAc–DOP.

5.7.3 Gas Chromatography/Mass Spectrography (GC/MS) analysis

The objective of this analysis is to identify the different VOC's emitted from the prepared vinyl formulations. Considering that the test is carried out for air samples and not liquid samples, and due to the unavailability of MS in our laboratories, and that the collaboration with Environment Canada (Ottawa) was not achievable, the samples were sent to Precision Analytical Laboratories a private one in Phoenix, Arizona, U.S.A. The data provided are shown in appendix [B], and summarized in Table 5-33, while their irritation and carcinogenic effects are summarized in Table 5-34.

The separation of the sample is achieved by setting the GC oven program initially at 35 °C for 5 min. than ramping to 150 °C at a rate of 5 °C/min., ramping again to 220 °C at a rate of 15 °C/min., and left steady at 220 °C for 2min., with a total duration time of 34.67 min.

The major identified VOC's among the tested formulation are 1-Butanol (Butyl Alcohol), Butanal, Butane, Vinyl Acetate, Acetaldehyde, and Trimethyldecane. These identified VOC's are in a way different than that identified earlier in the literature findings. This is not surprising, due to the know-how secrecy that allows the different manufactures to adjust the material characteristics as well as the cost without any proper notification or clarification.

Table 5-33: Identification and quantification of the different VOC's [ppbv] emitted from the different formulations

VOC's Compounds	Chemical characteristics			PVC Control - Emission [ppbv]				Alcell Blend - Emission [ppbv]			
	Molecular form	Molecular weight	Boiling Point[°C]	DOP	(2-45)	Lindol	Mesamoll	DOP	(2-45)	Lindol	Mesamoll
1-Butanol(Butyl Alcohol)	$C_4H_{10}O$	74.12	117.7	300	400	500		1000	500	90	2000
1-Chloropropane	C_3H_7Cl	78.54	46.5							30	200
1-Undecanol	$C_{11}H_{24}O$	172.31	243			400				10	
2-Butanol	$C_4H_{10}O$	74.12	99.5	300	300	300				20	200
Acetone(2-Propanone)	C_3H_6O	58.08	56							20	200
Butanal	C_4H_8O	72.11	74.8	3000	3000	5000	3000	2000	700	200	3000
Butane	C_4H_{10}	58.12	-0.5	3000	3000	2000	800	4000	1000	300	6000
Chloromethane	CH_3Cl	50.49	-24							60	600
Ethyl Acetate	$C_4H_8O_2$	88.11	77.1					300		40	600
Methyl ester acetic acid	$C_3H_6O_2$	74.08	56.8							20	300
Propene(Propylene)	C_3H_6	42.08	-47.6			200				80	500
Vinyl Acetate	$C_4H_6O_2$	86	70	5000	5000	9000	6000	7000	3000	500	9000
Acetaldehyde	C_2H_4O	44.05	20.1	3000	3000	2000	2000	500		50	1000
Ethanol	C_2H_6O	46.07	78.2					1000	400	100	2000
1-Chlorobutane	C_4H_9Cl	92.57	78.6		300	200					
2-Methyl-2-Propanol	$C_4H_{10}O$	74.12	82.4			200					
Undecane	$C_{11}H_{24}$	156.31	195.9			300					
Trimethyldecane	$C_{13}H_{28}$	184	-	500	600		200	200			200
2-Butanone	C_4H_8O	72.11	75.6	200							
1-Undeccene	$C_{11}H_{22}$	154.29	193		300						

Table 5-34: The effect of different VOC's emitted on human health [141]

VOC's compounds	CAS #	Physical constants			Remarks
		Molecular form	Molecular weight	Boiling point [°C]	
1-Butanol(Butyl Alcohol)	71-36-3	$C_4H_{10}O$	74.12	117.7	Severe skin and eye irritant
1-Chloropropane	540-54-5	C_3H_7Cl	78.54	46.5	skin and eye and mucous irritant
1-Undecanol	112-42-5	$C_{11}H_{24}O$	172.31	243	Moderately toxic by ingestion, skin irritant
2-Butanol	78-92-2	$C_4H_{10}O$	74.12	99.5	Skin and eye irritant, fire hazard
Acetone(2-Propanone)	67-64-1	C_3H_6O	58.08	56	Moderately toxic by several routes, severe skin and eye irritant
Butanal	123-72-8	C_4H_8O	72.11	74.8	Moderately toxic by several routes, severe skin and eye irritant
Butane	106-97-8	C_4H_{10}	58.12	-0.5	Asphyxiate, fire hazard
Chloromethane	74-87-3	CH_3Cl	50.49	-24	Suspected carcinogen, fire hazard
Ethyl Acetate	141-78-6	$C_4H_8O_2$	88.11	77.1	Eye irritant
Methyl ester acetic acid	79-20-9	$C_3H_6O_2$	74.08	56.8	Moderately toxic by several routes, moderate skin and eye irritant, fire hazard
Propene(Propylene)	115-07-1	C_3H_6	42.08	-47.6	Suspected carcinogen, Asphyxiate, fire hazard
Acetaldehyde	75-07-0	C_2H_4O	44.05	20.1	Carcinogen, severe skin and eye irritant
Ethanol	64-17-5	C_2H_6O	46.07	78.2	Human carcinogen
1-Chlorobutane	109-69-3	C_4H_9Cl	92.57	78.6	Skin and eye irritant, dangerous fire hazard
2-Methyl-2-Propanol	75-65-0	$C_4H_{10}O$	74.12	82.4	Dangerous fire hazard
Undecane	1120-21-4	$C_{11}H_{24}$	156.31	195.9	Moderately toxic by intravenous route

In addition the data presented in Table 5-33 show that Alcell presence in the blend formulations suppress the amounts of Butanal, Butane, Acetaldehyde with the different used plasticizers as well as Vinyl Acetate with formulations plasticized with Benzoflex 2-45 and Lindol. However, its presence introduces other VOC's as Ethyl Acetate but in small amounts. As well as Chloromethane, Methyl ester acetic acid, 1-Chloropropane, Acetone (2-Propanone) for formulation plasticized with Lindol and Mesamoll.

The airway irritation estimate is considered the upper odor threshold. A comparison of odor threshold with airway irritation estimates for about 100 common VOC's shows that for most VOC's their airway irritation are at least one order of magnitude higher than the corresponding odor threshold, except sensory reactive VOC's, like methanol, formaldehyde, methyl vinyl ketone, methyl acetate, and compounds of very low odor intensity [134]. Sensory effect (i.e., eye and airway irritation) may vary in between people as some may be more sensitive to the VOC's normally measured indoors. Considering this reason, it is generally recommended to use low emitting building products wherever possible [136]. In another study [139] removing pollution sources and/or the systematic use of low polluting materials, improve the perceived air quality by reducing the chemical and sensory pollution.

However those limits and sensory effect can not protect against carcinogens or allergens. This can be accommodated for by exclusion of individual VOC that classified carcinogenic in national occupational guidelines, or by the World Health Organization above 1 $\mu g/m^3$ based on emission test [140]. The different VOC's emitted in $\mu g/m^3$ are shown in Table 5-35. Acetaldehyde and Ethanol are carcinogenic, in addition Chloromethane, Propene (Propylene) are suspected carcinogenic [141]. Acetaldehyde is reduced in all plasticized blends below 1 $\mu g/m^3$, although Alcell introduced Ethanol in the blended formulations, it is still below the allowable levels, as well as Chloromethane, and Propene.

One of the most important conclusions of this research is the fact that although Alcell lignin, a natural polymer, introduced more volatile compounds within the formulations, it proves to be very valuable in reducing the levels of the emitted volatile organic compounds below the harmful levels as identified by the World Health Organization (1 $\mu g/m^3$ based on emission test).

Formulations based on VC-VAc copolymer – Alcell lignin blends plasticized with Lindol show to be the best from the point of view of the amount and composition of the emitted VOC's.

Table 5-35: Identification and quantification of the different VOC's [μg/m^3] emitted from the different formulations

VOC's Compounds	Chemical characteristics			PVC Control - Emission [μg/m^3]				Alcell Blend - Emission [μg/m^3]			
	Molecular form	Molecular weight	Boiling point [°C]	DOP	(2-45)	Lindol	Mesamoll	DOP	(2-45)	Lindol	Mesamoll
1-Butanol(Butyl Alcohol)	$C_4H_{10}O$	74.12	117.7	0.36	0.49	0.61		1.21	0.61	0.11	2.43
1-Chloropropane	C_3H_7Cl	78.54	46.5							0.04	0.26
1-Undecanol	$C_{11}H_{24}O$	172.31	243			1.13				0.03	
2-Butanol	$C_4H_{10}O$	74.12	99.5	0.36	0.36	0.36				0.02	0.24
Acetone(2-Propanone)	C_3H_6O	58.08	56							0.02	0.19
Butanal	C_4H_8O	72.11	74.8	3.54	3.54	5.90	3.54	2.36	0.83	0.24	3.54
Butane	C_4H_{10}	58.12	-0.5	2.85	2.85	1.90	0.76	3.80	0.95	0.29	5.71
Chloromethane	CH_3Cl	50.49	-24							0.05	0.50
Ethyl Acetate	$C_4H_8O_2$	88.11	77.1					0.43		0.06	0.86
Methyl ester acetic acid	$C_3H_6O_2$	74.08	56.8							0.02	0.36
Propene(Propylene)	C_3H_6	42.08	-47.6			0.14				0.06	0.34
Vinyl Acetate	$C_4H_6O_2$	86	70	7.03	7.03	12.66	8.44	9.85	4.22	0.70	12.66
Acetaldehyde	C_2H_4O	44.05	20.1	2.16	2.16	1.44	1.44	0.36		0.04	0.72
Ethanol	C_2H_6O	46.07	78.2					0.75	0.30	0.08	1.51
1-Chlorobutane	C_4H_9Cl	92.57	78.6		0.45	0.30					
2-Methyl-2-Propanol	$C_4H_{10}O$	74.12	82.4			0.24					
Undecane	$C_{11}H_{24}$	156.31	195.9			0.77					
Trimethyldecane	$C_{13}H_{28}$	184	-	1.51	1.81		0.60	0.60			0.60
2-Butanone	C_4H_8O	72.11	75.6	0.24							
1-Undeccene	$C_{11}H_{22}$	154.29	193		0.76						

6

Contributions and Recommendations For Further Research

The current research was necessitated by the concerns evolved with regard to health hazards induced by synthetic building materials within tight building enclosure as in cold regions like Canada. On the other hand, use of biologically derived polymers is emerging as an important component for economic development and as effective solution to reduce health hazards.

6.1 Contributions

- This study shows the possibility of using a natural polymer, lignin, in formulations for flooring materials based on synthetic polymers.

- An indoor pollutant source di-octyl-phthalate used currently in some building materials was effectively replaced by tri-cresyl phosphate (Lindol) plasticizer. Lindol plasticized VC-VAc copolymer – lignin blend can be used as a matrix for a high level filled vinyl tile composition.

- The new proposed formulation "*VC-VAc copolymer – Alcell lignin plasticized with Lindol*" is an environmental friendly formulation, which compared with the PVC one plasticized with DOP, possesses the following characteristics:
    - Lower melt viscosity and lower mixing equilibrium torque;
    - Higher glass transition temperature, modulus and tensile strength at yield;
    - Equivalent elongation, toughness and fungi growth rating;
    - No fungi growth, in the presence of an antimicrobial, similar to the formulation based on DOP and antimicrobial;
    - Stable mechanical and thermal properties, even after fungi attack;
    - The amount of emitted VOCs by the new formulation is far below those emitted by the formulation with DOP;
    - The amount of acetaldehyde (suspected as carcinogenic) emitted by the new formulation is 0.04 $\mu g/m^3$ compared to 2.16 $\mu g/m^3$ emitted by the formulation with DOP.

Summarizing the main contribution of the present research we arrive to the following:

- Lignin plasticization is the first study in this field. This process is a new contribution to the polymer science and technology. It opens up possibilities for using lignin in formulations with other synthetic polymers, and effectively replaces partially PVC or VC-VAc copolymer in vinyl formulations.

- The new formulation's superior properties are due to the proved interactions and compatibility between the main components of the system such as vinyl polymer – lignin, vinyl polymer-plasticizer and lignin-plasticizer.

- The presence of tricresyl phosphate enhances the indoor air quality in terms of reducing sensory and sick building syndrome. The amount of its VOCs emission is much below the harmful levels identified by the World Health Organization. This is due to the chemical composition of Lindol.

6.2 Recommendations for further research

1. The research is to be continued in evaluating and experimenting different kinds of technical lignins, eventually with higher purification and in higher loading amounts. Studying other families of plasticizers, by considering initially their interaction with lignin and afterwards their role within the different synthetic polymer polyblends.

2. Modeling the proposed formulation and its mechanical properties by employing non-classical continuum mechanics and discrete approaches. Considering that the undertaken work in this study provided information regarding the properties of the formulations at the macro-scale level. The further research will involve the material constituent characterizations at the micro-scale level, using more sensitive analysis methods such as: transition electron microscopy and nanoindentation technique.

3. Study the possibility of changing the inoculation period from 28 days, as specified in the ASTM G 21-2000, to a longer time. In order to establish the influence of microorganisms namely "fungi" on the plastic materials mechanical properties. As in accordance to our findings, mechanical properties variation could be an excellent indication for the polymeric materials biodeterioration, if the time length of the experiment is sufficient to draw a valid conclusion.

4. Develop a methodology that utilizes the environmental impact of building materials (in cost element form $) to be added to the standard life cycle cost of a giving material to establish a total life costing measure. This method will be more effective in determining the real value of a given material, considering its health hazards. This could be carried out by:
    1. Quantify the environmental impact of that material;
    2. Convert that identified quantity impact to a real value ($);
    3. Calculate the normal life cycle cost based on its environmental value.

References

[1] J. R. Fried, Polymer Science and Technology, Prentice Hall PTR, N.J., 1996

[2] Burke, D.M., Ambient mechanical properties of impact modified PVC and MMA copolymer blends, Journal Vinyl Additives Technology, 1996, Vol. 2(3), pp. 202-206.

[3] Hsu W. P., Phase behavior of ternary polymer blends with hydrogen bonding, Journal of Applied Polymer Science, 2004, Vol. 92(5), p.p. 2797-2802.

[4] Tiller A. R., Estimation of polymer compatibility from molecular mechanics calculations, Polymer, 1994, Vol. 35(15), p.p. 3251-3259.

[5] Robinson L. M., Journal Vinyl Technology, 1992, Vol. 12, p.p.89.

[6] http://www.compulink.co.uk/~plasticsdata/pvc/pvcuse.htm, Browsed in May 2000.

[7] H. Zweifel, Plastics Additives Handbook, 2001, 5th Edition, Hanser Gardner Publishers Inc., Cincinnati. pp. 427.

[8] W.V. Titow, PVC Technology Handbook, 1984, 4th Edition, Elsevier Applied Science Publishers, London and New York.

[9] C.D. Craver, C.E. Carraher, "Applied Polymer of Science – 21st Century", 2000, Elsevier Applied Science Publishers, London, pp. 107-156.

[10] J.W. Summers, a Review of Vinyl Technology, Journal of Vinyl and Additive Technology, June 1997, Vol. 3, No.2.

[11] Feldman D. and Barbalata A., Synthetic Polymers: Technology, Properties, and Applications, 1996, Chapman and Hall, London.

[12] Charrier J.M., Polymeric Materials and Processing: Plastics, Elastomers, and Composites, 1991, Hanser Publishers, NY.

[13] Brydson J.A., Plastics Materials, Butterworth-Heinemann, 6th Ed, Oxford, 1995, pp. 307.

[14] Haward R.N., "The Physics of Glassy Polymers", Applied Science Publishers, London, 1973, pp. 201-206.

[15] J.K. Sears and J.R. Darby, "The Technology of Plasticizers", John Wiley & Sons, New York, 1982, pp. 35-74.

[16] A.D. Godwin, "Plasticizers in: Applied Polymer of Science – 21st Century", 2000, Elsevier Applied Science Publishers, London, pp. 161.

[17] D. Cadogon, "Health and Environmental Impact of Phthalates", Plastics Additives and Compounding, June 2002, pp. 28-29.

[18] Latini G., "Potential Hazards of Exposure to Di-(2-Ethylhexyl)-Phthalate in Babies", Biol Neonate, 2000, Vol. 78, pp. 269-276.

[19] Latini G., Avery GB., Materials Degradation in Endotracheal Tubes: A Potential Contribuation to Brochopulmonary Dysplasia, Acta Paediatr, 1999, Vol. 88, pp. 1174-1175.

[20] Sheldon L., Whitaker D., Keever J., Clayton A., and Perrit R., "Phthalate and PAHs in Indoor and Outdoor Air in Southern California Community", in: Proceedings of Indoor Air, International Conference on Indoor air Quality and Climate, Helsinki, Finland, 1993, Vol. 3, pp. 109-114.

[21] Weschler C.J., "Indoor-Outdoor Relationship for Non Polar Organic Constituents of Aerosol Particles", Environmental Science and Technology, 1984, Vol. 18, pp. 648-652.

[22] Wolfgang L., Sigrist G., Otto H.H., "Moisture Indicating Emissions of Phthalates and their Effects", In: Proceedings of Healthy Building , Espoo, Finland, 2000, Vol. 4, pp. 405-410.

[23] Bortoli M.D., Pecchio E., Schauenburg H., Schlitt, Helmut and Vissers H., "Emission of Formaldehyde, Vinyl Chloride, VOC's and Plasticizers from Different Wall Coating Materials", in: Proceedings of Indoor Air, International Conference on Indoor air Quality and Climate, Helsinki, Finland, 1993, Vol. 2, pp. 413-418.

[24] Jann O., Wilke O., Brödner D., "Procedure for the Determination and Limitation of VOC Emissions from Furniture and Coated Wood Based Products", In: Proceedings of Healthy Building, Washington DC, USA, 1997, pp. 593-598.

[25] Pleil J.D. and Whiton R.S., "Determination of Organic Emissions from New Carpeting", Applied Occupational and Environmental Hygiene, 1990, Vol. 5, pp. 693-699.

[26] Reitzig M., Mohr S., Heinzow B., Knöppel H., "VOC Emissions after Building Renovations: Traditional and Less Common Indoor Air Contaminants, Potential Sources and Reported Health Complaints", Indoor Air, Vol. 8, pp. 91-102.

[27] J. Griffiths, European Markets for Minerals in Plastics, Industrial Minerals Information Ltd., 1997, United Kingdom.

[28] Chanda M., Roy S. K., Plastics Technology Handbook, 1993, 2nd Edition, Marcel Dekker Inc.

[29] Sloss R.I., "Development of Biocides for the Plastic Industry", Industry Paper, Zeneca Biocides, 1993, pp. 36-51

[30] Feldman, D., "Some Consideration on Thermosetting Polymers as Matrices for Composites", Journal of Prog. Polymer Science, 1990, vol.15, pp.603-628.

[31] Per Stenius, Forest Products Chemistry, Papermaking Science and Technology Series, Book 3, 2000, Fapet Oy, Helsinki, Finland.

[32] H.Yoshida, R. Morck, and K. P., Holzforshung, 1987, Vol. 41, pp. 171-176.

[33] T. Hatakeyama, K. Nakamura, and H. Hatakeyama, Polymer, 1978, Vol. 19, pp. 593.

[34] Lyubeshkina, E. G., Lignin as Components of Polymeric Composite Materials, in: Chemical Reviews, 1983, Vol. 52 (7), pp.675-692.

[35] J. J. Lindberg, T. A. Kuusela and K. Levon, Specialty Polymers from Lignin, Lignin Properties and Materials edit by W. G. Glasser and S. Sarkanen (ACS Symposium Series 397, Washington, 1989), pp. 190-204.

[36] Feldman, D. and Banu, D., Contribution to the Study of Rigid PVC Polyblends with Different Lignins, Journal of Applied Polymer Science, 1997, vol.66, pp.1731-1744. John Wiley & Sons, Inc.

[37] Lin, S. Y., Stuart, E., and Lebo, J. R., Lignin, in: Encyclopedia of Chemical Technology, 1995, 4th Edition, Vol. 15, pp. 269-289. John Wiley & Sons, NY.

[38] D. J. Williams, Polymer Science and Engineering, Prentice Hall, 1971, New Jersey.

[39] O. Olabisis, L. M. Robenson, M. T. Show, Polymer-Polymer Miscibility, Academic Press, 1979, New York.

[40] E. Roffael, B. Dix, "Lignin and Lignosulfonates in Non-Conventional Bonding – An Overview", Holz als Roh Undwerkstoff, 1991, Vol. 49, pp. 199-205.

[41] A. Pizzi, F. A. Cameron, G. H. Van der Klashorst, "Soda Bagasse lignin Adhesives For Particle Board", Adhesives from Renewable Source, Edited by: R. W. Hemingway, A. H. Conner, S. H. Branham, ACS Symposium, Series 385, 1987, pp. 82-95.

[42] R. S. G. Piccolo, F. Santos, E. Frollini, "Sugar Cane Bagasse Lignin in Resol-type Resin: Alternative Applications for Lignin-Formaldehyde Resins", J. M. S. Pure Applied Chemistry, 1997, Vol. A34 (1), pp. 153-164.

[43] P. Benar, A. G. Goncavles, D. Mandelli, U. Shuchardt, "Eucalyptus Organosolv Lignins: Study of the hydroxymethylation and Use of Resols", Bioresource Technology, 1999, Vol. 68, pp. 11-16.

[44] D. Feldman, M. Lacasse and D. Banu, "Contribution to the Modification of an Acrylic Sealant with Lignin", Journal Polymer Materials, 1988, Vol. 5, pp.131-139.

[45] D. Feldman, D. Banu, A. Natansohn and J. Wang, "Structure-Properties Relations of Thermally Cured Epoxy-Lignin Polyblends", in Journal of Applied Polymer Science, 1991, Vol. 42, pp.1537-1550.

[46] J. Wang, D. Banu and D. Feldman, "Epoxy-Lignin Polyblends: Effects of Various components on adhesive properties", Journal Adhesive Science Technology, 1992, Vol. 6(5), pp.587-598.

[47] E. G. Lyubeshkina, "Lignin as Components of Polymeric Composite Materials", Russian Chemical Reviews, 1983, Vol. 52(7), pp.1196-1224.

[48] Cr. I. Simionescu, M. M. Macoveanu, M. C. Pascu, J. H. Choi, C.Sung and W.Baker, "Isotactic Polyproplyne/Epoxy – Modified Lignin Blends", Cellulose Chemical Technology, 1998, Vol. 32, pp.61-88.

[49] J. Rosch and R. Mulhaupt, "Mechanical Properties of Organosolv Lignin Filled Thermoplastics, Polymer Bulletin", 1994, Vol. 32, pp.361-365.

[50] Feldman, D., Banu, D., and S. El-Raghi, Poly (vinyl chloride)-Lignin Blends for Out Door Application in Building, in Journal of Macromolecular Science-Pure Applied Chemistry, 1994, A31 (5), pp.555-571.

[51] Feldman, D., Banu, D., J. Lora, and S. El-Raghi, Rigid Poly (vinyl chloride)-Organosolv Lignin Blends for Application in Building, in: Journal of Applied Polymer Science, 1996, Vol.61, pp. 2119-2128. John Wiley & Sons, Inc.

[52] S. El Raghi, R. R. Zahran, B. E. Gebril, Effect of Weathering on some Properties of Polyvinyl Chloride / Lignin Blends, Materials Letters, 2000, Vol. 46, pp. 332-342, Elsevier Science.

[53] Hui Zhu, Plasticized Lignin-PVC blends for flooring, M.Sc., Concordia University, August 2000.

[54] D. Feldman, D. Banu, J. Campanelli and H. Zhu, "Blends of Vinylic Copolymer with Plasticized Lignin: Thermal and Mechanical Properties", Journal of Applied Polymer Science, 2001, Vol. 81, pp.861-874.

[55] Murase A., Sugiura M., Polymer Degradation and Stability, 1994, Vol. 43, pp. 415.

[56] K. Z. Gumargalieva, V. B. Ivanov, G. E. Zaikov, Ju. V. Moiseev, T. V. Pokholok, Problems of Ageing and Stabilization of Polyvinyl Chloride, Polymer Degradation and Stability, 1996, Vol. 52, pp. 73-79.

[57] Ignacy Jakubowicz, Nazdaneh Yarahmadi, Thomas Gevert, Effects of Accelerated and Natural Ageing on Plasticized Polyvinyl Chloride, Polymer Degradation and Stability, 1999, Vol. 66, pp. 415-421.

[58] Moore-Landecker E., "Fundamentals of Fungi", 2nd Edition, 1982, Prince Hall Inc., Englewoods Cliffs, New Jersey.

[59] Smith D. and Onions A.H.S., "the Preservation and Maintenance of Living Fungi", 1994, CAB International, New York.

[60] Ingold C. T., The Biology of Fungi, 5th Edition, 1984, Hutchinson & Co. Ltd., London.

[61] Webb JS, Van der Mei HC, Nixon M. East-wood LM, Greenhalgh M, Read SJ, Robson GD, Handley PS, Plasticizers Increase Adhesion of the Deteriogenic Fungus, in: Aureobasidium Pullulates to Polyvinyl Chloride. Applied Environmental Microbial, 1999, Vol. 65, pp. 3575-3581.

[62] K. Z. Gumargalieva, G. E. Zaikov, S. A. Semenov, O. A. Zhdanova, The Influence of Biodegradation on the Loss of a Plasticizer from Polyvinyl Chloride, Polymer Degradation and Stability, 1999, Vol. 63, pp. 111-112.

[63] Berglund B., Measurements of Formaldehyde Odor Indoor, Proceedings of the Climate 2000 world Congress on Heating, Ventilating and Air-conditioning, Copenhagen, 1985, VVS Kongress Vol. 4 indoor climate, pp.251-256.

[64] Holmberg B., Some Ideas on Chemically Induced Cancer, from a Toxicological View, Swedish Board of Occupational Health, Report 1977:37.

[65] Zeljko Mrklie and Tonka Kovacic, Thermochimica Acta, 1998, Vol. 322, pp. 129-135 Elsevier Science B.V.

[66] Sollinger S., Levsen K., Wunsch G., Indoor Pollution by Organic Emissions from Textile floor coverings: Climate Test Chamber Studies under Static Conditions, Atmospheric Environment, 1994, Vol. 28, pp. 2369-2378.

[67] Wolkoff P., Impact of Air Velocity, Temperature, Humidity, and Air Long Term VOC Emissions from Building Products, Atmospheric Environment, 1998, Vol. 32, pp. 2659-2668.

[68] Fang L., Clausen G., Fanger P.O., Impact of Temperature and Humidity on Chemical and Sensory Emission from Building Materials, Indoor Air, 1999, Vol. 9, pp. 193-201.

[69] TÜV Nord, Entwicklung und Erprobung von Standerd-Messverfahren für die Bewertung des fahrzeugeigenen Beitrages zu organischen Luftverunreinigungen in fahrgasträumen von personenkrftwagen, Band I: Zusammenfassung, Hamburg, Eigenverlag, 1996.

[70] Wike O., Jann O., Bestimmung von Weichmacheremissionen aus unterschiedlichen Materialien in Meßkammern, Freiberger Polymertag, Forschungsinstitut für Lederund Kunstledertechnologie, Freiberg, G/1-G/11, 1999, Proceedings 4.

[71] E. Uhde, M. Bednarek, F. Fuhrmann, T. Salthammer, Phthalic Esters in the door Environment Test Chamber Studies on PVC-Coated Wall coverings, Indoor Air, 2001, vol.11, pp.150-155, Munksgaard.

[72] Bodalal A., Fundamental Mass Transfer Modeling of Emission of Volatile Organic Compounds from Building Materials, Ph.D. Thesis, department of Mechanical and Aerospace Engineering, Carleton University, Ottawa, Canada, May 1999.

[73] A. Andrady, Photodegradation of Rigid PVC, Journal of Applied Science, 1989, Vol. 37, pp. 935-946.

[74] Y. and Hu Q., Journal of Applied Polymer Science, 1995, Vol.57, pp.1441 John Wiley & Sons, Inc.

[75] Gonzalez, J.L. Salager, M.R. Brunetto, M. Gallignani, J.L. Burguera, M. Burguera and Y. Petit de Pena, J. High Resol.Chromatogr. 2000, 23 pp. 693-696

[76] D. Feldman, D. Banu, C. Luchian, and J. Wang, Journal of Applied Polymer Science , 1991, 42, pp.1307-1318.

[77] Lacasse, "Functional Properties of Polyurethane Based Sealants Blended with Polymeric Modifiers", PhD thesis, 1991, Concordia University.

[78] Y. Lin in Ullman's Encyclopedia of Industrial Chemistry, Vol. A15, Wiley, New York, 1990, pp. 305-315.

[79] Omya LTD., Technical Data Sheet, Pulpro 10, St. Armand.

[80] Guidelines for Drinking-water Quality, Health Criteria and other Supporting Information, 2nd Edition, World Health Organization, 1996, Geneva, Vol. 2, pp. 530-540.

[81] Product Information Bulletin, Velsicol Chemical Corporation, 2001.

[82] Environmental Health Criteria (EHC) 110, 1990, World Health Organization.

[83] Technical Data Sheet, 2001, Bayer AG Inc., U.S.A.

[84] Loyd V. Allen Jr., Calcium Stearate in Kibbe AH Edition, Handbook of Pharmaceutical Excipients, 3rd Edition, Washington DC, American Pharmaceutical Association.

[85] Safety Data Sheet, Crampton Vinyl Additives GmbH, Germany, 2003.

[86] International Chemical Safety Cards (ICSCs): 1171, 1995.

[87] ttp://www.atsdr.cdc.gov/toxprofiles/tp55-c5.pdf, Browsed in May 2004.

[88] Safety Data Sheet, Crampton Vinyl Additives GmbH, Germany, 2003.

[89] Sanitized PL 21-60, Product Data Sheet, Clariant Huningue S.A. Switzerland.

[90] Elvers B., Rounsavill J. F. and Schulz G., Floor Coverings, in: Ulmann's Encyclopedia of Industrial Chemistry, 5th Ed., 1988, Vol. A11, pp. 269-277, Wiley-VCH.

[91] ASTM D 638-99, 1999, Test Method for Tensile Properties of Plastics, American Society for Testing and Materials.

[92] Mckinney P. V., Journal of Applied Polymer Science, 1965, Vol. 9, pp.3359 John Wiley & Sons, Inc.

[93] ASTM D 3417-99, 1999, Test Method for Determining Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry, American Society for Testing and Materials.

[94] ASTM D 3418-99, 1999, Test Method for Determining Transition Temperatures of Polymers by Thermal Analysis, American Society for Testing and Materials.

[95] K.E. Stine, Modern Practices in Infra Red Spectroscopy, Beckman InstrumentInc., Fullerton, California, 1975, Vol. 1, pp.3-12.

[96] ASTM D 5116, 1990, Standard Guide for Small-Scale Environmental Determinations of Organic Emissions from Indoor Materials/Products, American Society for Testing and Materials.

[97] ASTM G 21, 2000, Slandered Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi, American Society for Testing and Materials.

[98] A. EL-Aghoury, D. Banu and D. Feldman, "Plasticizers Concentration effect on VC-VAc Copolymer – Alcell Lignin Polyblend: Thermal and Mechanical Properties", 3rd International Conference in Building Physics/Science (IBPC3), submitted January 2005

[99] Shalabi, W.S., Bair E.B., in Thermal Characterization of Polymeric Materials, Turi, E.A. Ed., Academic Press: New York 1981, pp. 412.

[100] Birley, A., Haworth, B. and Batchler, J., in Physics of Plastics, 1995, Hanser, Oxford University, New York, pp. 253-258.

[101] D. Banu, A. EL-Aghoury and D. Feldman, Contributions to the characterization of PVC – Lignin Blends, Journal of applied Polymer Science, accepted may 2005.

[102] H. Bair, in Thermal Characterization of the Polymeric Materials, E. Turi, Ed. 1981, Academic Press, New York, pp. 878-892.

[103] G. ten Brinke, L. Oudhuis, T. Ellis, Thermochimica Acta, 1994, 238, pp. 75-98.

[104] L.C. E. Struick, Physical Aging in Amorphous Polymers and other Materials, 1978, Eelsevier, New York, pp.1-5.

[105] A. Graton "Infrared Spectroscopy of Polymer Blends, Composites and Surfaces" Hanser New York, 1992 pp. 176-190.

[106] H.Katz and J.V. Milewski "Handbook of Filler for Plastics", Van Nostren Reinhold, New York, 1987 pp. 24-25.

[107] D. Feldman, D. Banu, and A. El-Aghoury, Plasticized PVC – Lignin Blends, 11th annual International Conference on Composites/Nano Engineering, ICCE-11, August 8-14 2004, South Carolina, USA.

[108] A. El-Aghoury, D. Banu, and D. Feldman, "Plasticizers Effects on the Properties of Vinyl Chloride-Vinyl Acetate Copolymer-Lignin Blends", 5th International Conference on Advanced Polymer via Macromolecular Engineering (APME-5), June 21-26, 2003, Montreal, Canada

[109] D. Banu, D. Feldman and A. El-Aghoury, Plasticized Vinyl Copolymer - Lignin Blends; Correlation between Mechanical and Thermal Properties, 13th Annual Technical Meeting and Exhibition, June 3-4 2003, Carlton University, Ottawa, Ontario, Canada.

[110] Glasser W. G., Knudsen J. S., Chang C. S., Journal of Wood Chemistry Technology, 1988, Vol. 8 (2), pp. 221.

[111] J.A. Brydson, "Plastics Materials", Fourth Edition, 1983, Butterworth Scientific, pp. 316.

[112] J.R. Darby and J.K. Sears, in L.I. Nass (Ed.) Encyclopedia of PVC,1976, Marcel Decker, New York, Vol. II, pp. 249-253.

[113] I. Melan, The Behavior of Plasticizers, Pergamon Press, 1961, New York, pp. 249-253.

[114] A. EL-Aghoury, R.K. Vasudeva, D. Banu, M. Elektorowicz and D. Feldman, "Contribution to the Study of Fungal Attack on some Plasticized Vinyl Formulations", Journal of Polymers and Environment, submitted April 2005

[115] S.A. Semenov, K.Z. Gumargalieva and G.E. Zaikov, Biodegradation and Durability of Materials under Effect of Microorganisms, 2003, VSP Boston, pp. 7-77.

[116] H.R. Hitz, A. Mertz and R. Zinkernagel, Material and Organismen 2, 1967, pp. 271-296.

[117] W. Hazeu, International Biodeteriration Bulletin 3, 1967, pp.15-19 cf. Chemical Abstract.

[118] D. Bretislav, G. V. Akimov, *British Plastics* 40, 1967, pp. 109-112.

[119] G.G. Bochareva, Yu. V. Ovchinnikov, L.N. Kurganova and L.N. Beirekhova Plastcheskie Massy 9, 1975, pp.60-61, cf. Chemical Abstract.

[120] D.Feldman and D. Banu, Journal of Adhesion Science Technology 17, 2003, pp. 2065-2083.

[121] Y.Li, J. Mlynar and S. Sarkanen, Journal Polymer Science, Part B: Polymer Physics 35, 1997, pp. 1899-1910.

[122] V. V. Tsukruk, *Polym. Intl.* 49, 2000, pp. 441-444.

[123] R. E. Klausmeier, *Intl. Biodetn.* Bull. 8, 1972, pp. 3-7.

[124] M. Gilbert (1994) *J.M. S. – Rev. Macromol. Chem. Phys.* C37, pp. 77-135.

[125] P.F. Hamlyn (1990) *Textile* 19, pp. 46-50.

[126] H.Wang, M. Electorowicz, R. Chifrina, D. Banu and D. Feldman (2003) Annual Conference of the Canadian Society of Civil Engineering, Moncton, New Brunswick, June 4-7 pp. ENM 548-1-548-10.

[127] G.Gellerstedt (1993) in A. S. Scalbert (Ed.) Polyphenolic Phenomena, INRA, Paris pp.199-204.

[128] A. EL-Aghoury, R.K. Vasudeva, D. Banu, M. Elektorowicz and D. Feldman, "Biodegradation of VC-VAc copolymer under the effect of Microorganisms", 3rd International Conference in Building Physics/Science (IBPC3), submitted January 2005

[129] Foltz, C. R., Mckinney, P.V., "Journal of Applied Polymer Science", 1969, Vol. 13, pp. 2235.

[130] Wysgoski, M.G., "Journal of Applied Polymer Science", 1980, Vol. 25, pp. 1455.

[131] Chan, A.H., Paul, D.R., "Journal of Applied Polymer Science", 1979, Vol. 24, pp. 1539.

[132] Struik, L. C. E., "Physical Ageing in Amorphous Polymers and other Materials", Elsevier, Amsterdam, 1978.

[133] Kovacs, A. J., Aklonis, J. J., Hutchinson, J. M., Ramos, A. R., "Journal of Polymer Science", Polymer physics Edition, 1979, pp. 1097.

[134] Wolkoff P., "How to Measure and Evaluate Volatile Organic Compound Emissions from Building Products. A Perspective", Science of the Total Environment, 1999, Vol. 227, pp. 197-227.

[135] Seife C., "Headache in Orbit", New Scientist, July 1999, Vol. 5.

[136] Wolkoff P., Nielsen G. D., "Organic Compounds in Indoor air-their Relevance for Perceived Indoor Air Quality?", Atmospheric Environment, 2001, Vol. 35, pp. 4407-4417.

[137] S. Rastan, T. Brodie, D. Bouchard, J. Kozinski, F. Haghigat and J. P. Farant, "A Comparative Study of the Flec and Small Environmental Chamber Using a Novel Reference Emitting Material (REM)", Indoor Air Proceedings, 2002, pp. 908-913.

[138] J. F. Van der wal, A. W. Hoogeveen and P. Wouda, "The Influnce of Temperature on the Emission of Volatile Organic Compounds from PVC Flooring, Carpet and Paint", International Journal of Indoor Air Quality and Climate, 1997, Vol. 7, No. 3, pp. 215-221.

[139] P. Wargocki, Z. Bakó-Biró, G. Clausen and P. Ole Fanger, "Air Quality in a Simulated Office Environment as a Result of Reducing Pollution Sources and Increasing Ventilation", Energy and Buildings, 2002, Vol. 34, pp. 775-783.

[140] Anderson NexØ B., "A View on Risk Assessment Methodologies for Carcinogenic Compounds in Indoor Air", Scand Journal Work Environmental Health, 1995, Vol. 21, pp. 376-381.

[141] Richard J. Lewis, SR., "SAX'S Dangerous Properties of industrial Materials, 9th edition, 1996, New York.

Appendix [A]
Gas Chromatography Spectra

```
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===================================================================================
                                 Area Percent Report
===================================================================================

Data File Name    : C:\HPCHEM\1\DATA\AMR\NV-F0197.D
Operator          : Amr                                   Page Number       : 1
Instrument        : ANALYZER1                             Vial Number       :
Sample Name       :                                       Injection Number  :
Run Time Bar Code:                                        Sequence Line     :
Acquired on       : 17 Apr 03   08:05 AM                  Instrument Method: AMRPVC.MTH
Report Created on: 17 Apr 03   08:39 AM                   Analysis Method   : AMRPVC.MTH
Sample Info       :


Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0197.D
    Pk#  Ret Time        Area           Height        Type   Width      Area %
   |---|----------|--------------|--------------|----|---------|----------|

Total area = 0

===================================================================================
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Gas chromatogram base line for GC only

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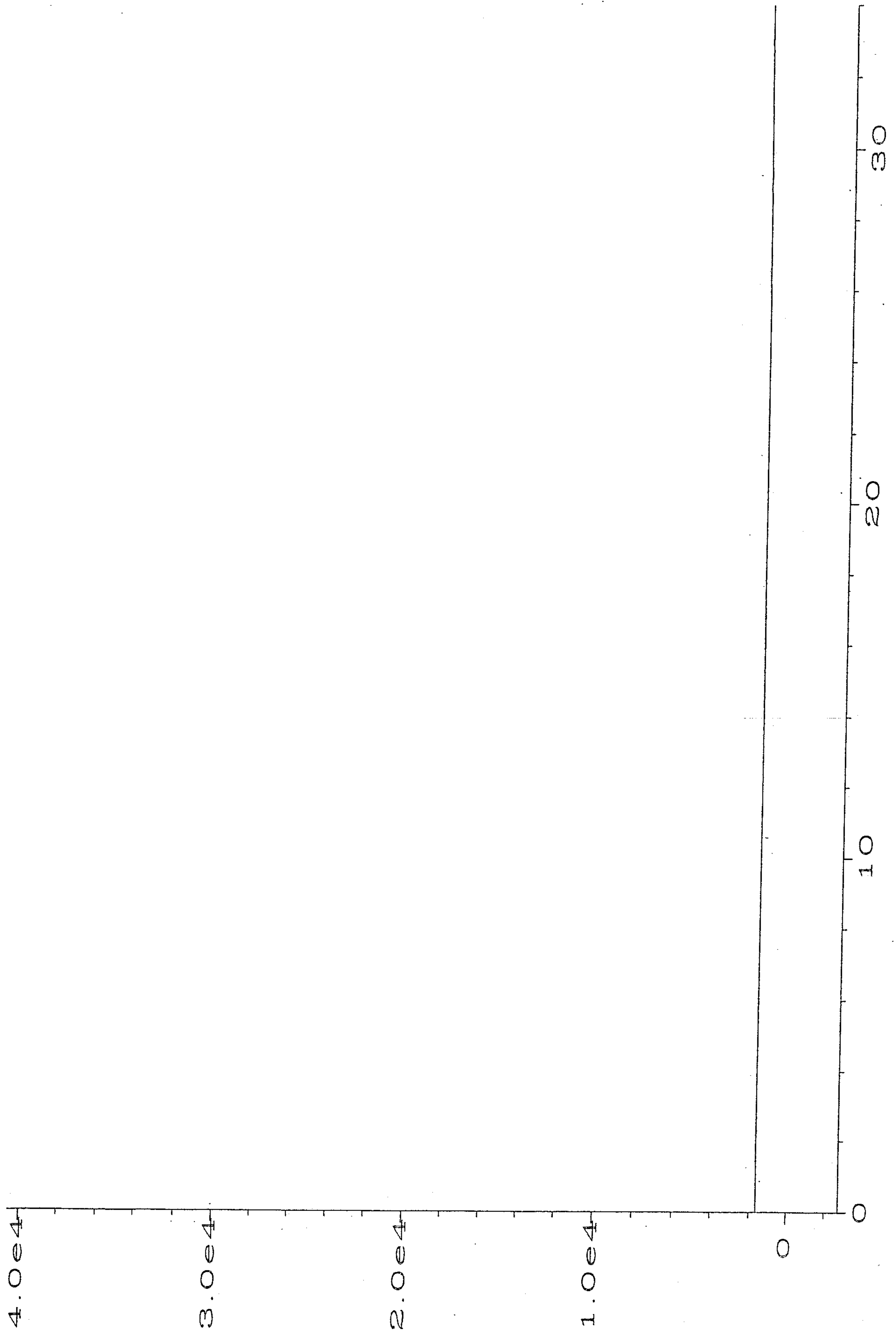

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Calibrated report not possible because no calibration table exists
=====================================================================
                          Area Percent Report
=====================================================================

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Operator          : Amr                      Page Number       : 1
Instrument        : ANALYZER1                Vial Number       :
Sample Name       :                          Injection Number  :
Run Time Bar Code:                           Sequence Line     :
Acquired on       : 17 Apr 03   08:59 AM     Instrument Method: AMRPVC.MTH
Report Created on: 17 Apr 03   09:34 AM      Analysis Method   : AMRPVC.MTH
Sample Info       :

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   Pk#  Ret Time        Area            Height       Type   Width       Area %
  |---|----------|--------------|--------------|----|---------|----------|

Total area = 0

=====================================================================
```

Gas chromatogram base line for GC and FID

```
Calibrated report not possible because no calibration table exists
===============================================================================
                             Area Percent Report
===============================================================================

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Instrument        : ANALYZER1                          Vial Number       :
Sample Name       :                                    Injection Number  :
Run Time Bar Code:                                     Sequence Line     :
Acquired on       : 17 Apr 03   10:09 AM               Instrument Method: AMRPVC.MTH
Report Created on: 17 Apr 03   10:43 AM                Analysis Method   : AMRPVC.MTH
Sample Info       :


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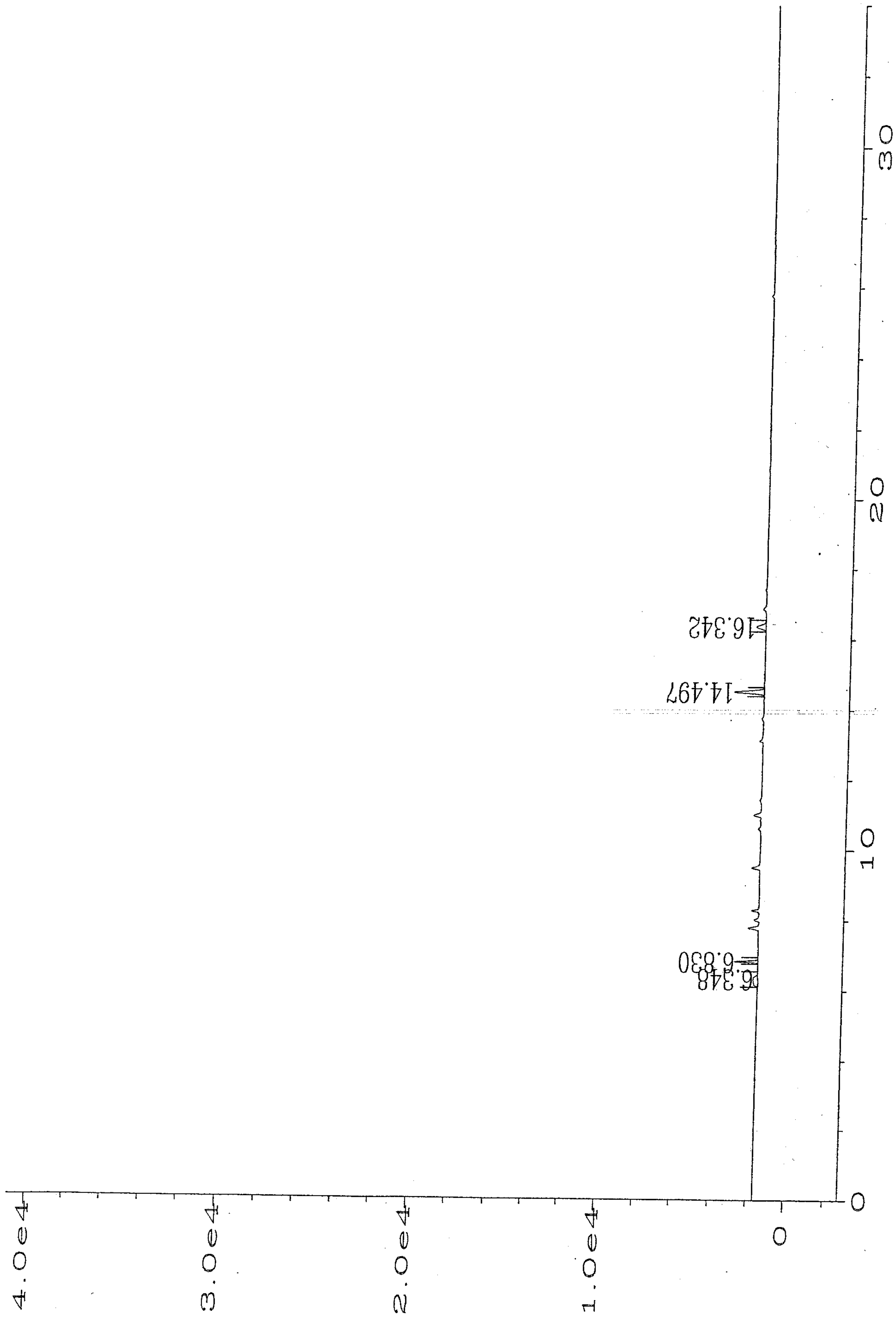
   Pk#  Ret Time         Area            Height     Type   Width      Area %
  |---|----------|--------------|--------------|----|----------|-----------|
     1    6.348             3826             228  BB     0.231     20.6951
     2    6.830             3209            1267  BB     0.039     17.3608
     3   14.497             8108            1576  BB     0.080     43.8569
     4   16.342             3344             480  BB     0.107     18.0873

Total area = 18486

===============================================================================
```

Gas chromatogram base line for Nitrogen (carrying gas)

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0199.D



```
Calibrated report not possible because no calibration table exists
===========================================================================
                         Area Percent Report
===========================================================================

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Sample Name       :                              Injection Number :
Run Time Bar Code:                               Sequence Line    :
Acquired on       : 17 Apr 03   09:53 PM         Instrument Method: AMRPVC
Report Created on: 17 Apr 03   10:27 PM          Analysis Method  : AMRPVC
Sample Info       :

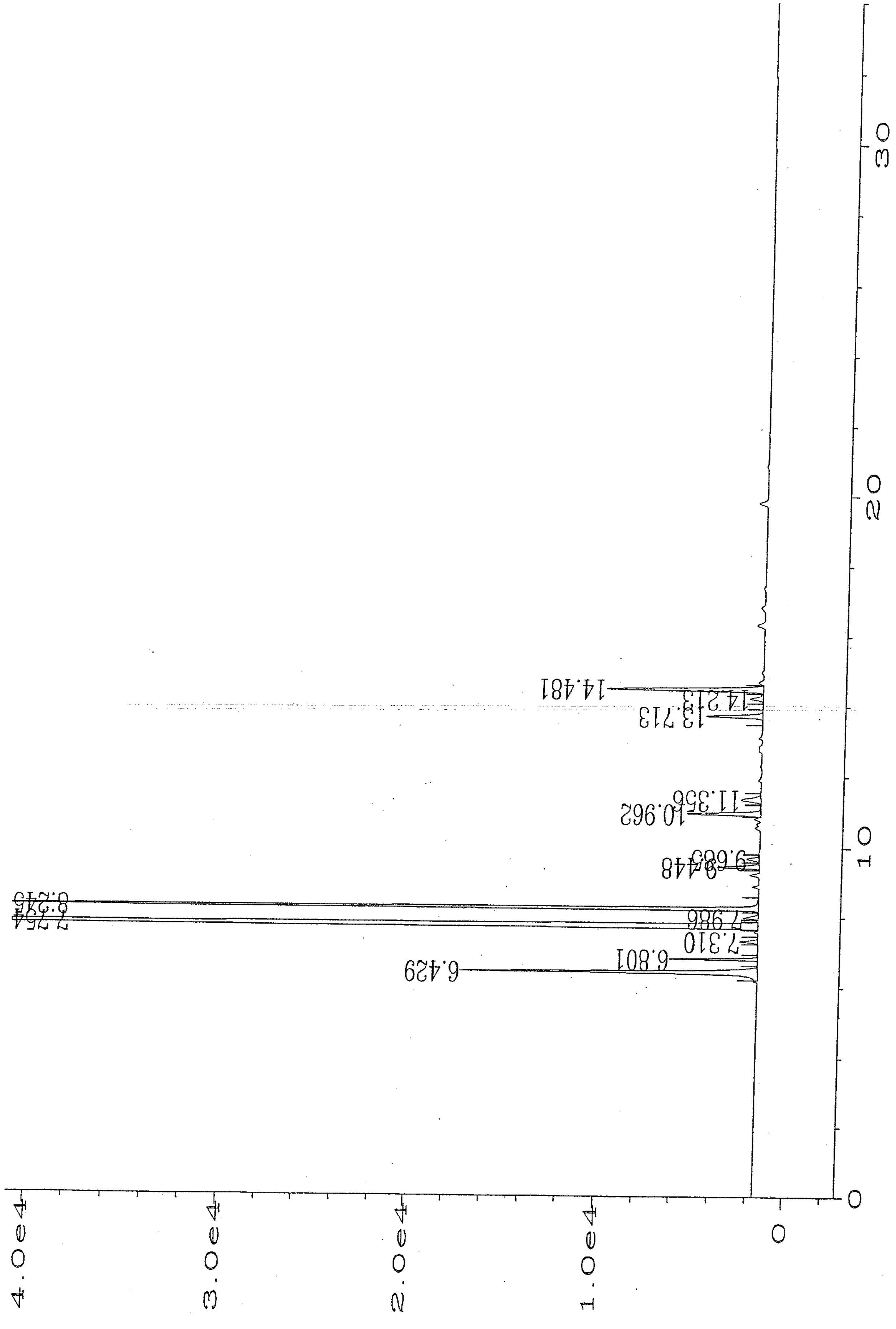

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0208.D
   Pk#  Ret Time       Area            Height       Type   Width      Area %
  |---|----------|--------------|--------------|----|---------|---------
    1    6.295              0            425    Fsho  0.000     0.0000
    2    6.338              0            878    Fsho  0.000     0.0000
    3    6.429          72225          15827    VV    0.065     7.5956
    4    6.801          13073           4685    VB    0.044     1.3748
    5    7.310           3906            958    BB    0.064     0.4108
    6    7.754         576741         138100    VV    0.065    60.6534
    7    7.986           3728            829    VV    0.064     0.3920
    8    8.053              0            248    Rsho  0.000     0.0000
    9    8.245         179789          54430    VB    0.052    18.9076
   10    9.448           9544           2226    BV    0.066     1.0037
   11    9.685           3833            667    VV    0.089     0.4031
   12   10.962          18843           3844    VB    0.077     1.9816
   13   11.356           7463           1072    BB    0.111     0.7848
   14   13.713          14964           2993    BB    0.078     1.5738
   15   14.213           4219            692    BV    0.093     0.4437
   16   14.481          42553           8316    VV    0.080     4.4751

Total area = 950880

===========================================================================
```

Gas chromatogram of the VOC's emitted from VC-VAc copolymer – 35 phr DOP

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0208.D



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Calibrated report not possible because no calibration table exists
=====================================================================
                          Area Percent Report
=====================================================================

Data File Name    : C:\HPCHEM\1\DATA\AMR\NV-F0201.D
Operator          : Amr                          Page Number      : 1
Instrument        : ANALYZER1                    Vial Number      :
Sample Name       :                              Injection Number :
Run Time Bar Code:                               Sequence Line    :
Acquired on       : 17 Apr 03  11:06 AM          Instrument Method: AMRPVC.
Report Created on: 17 Apr 03  11:41 AM           Analysis Method  : AMRPVC.
Sample Info       :

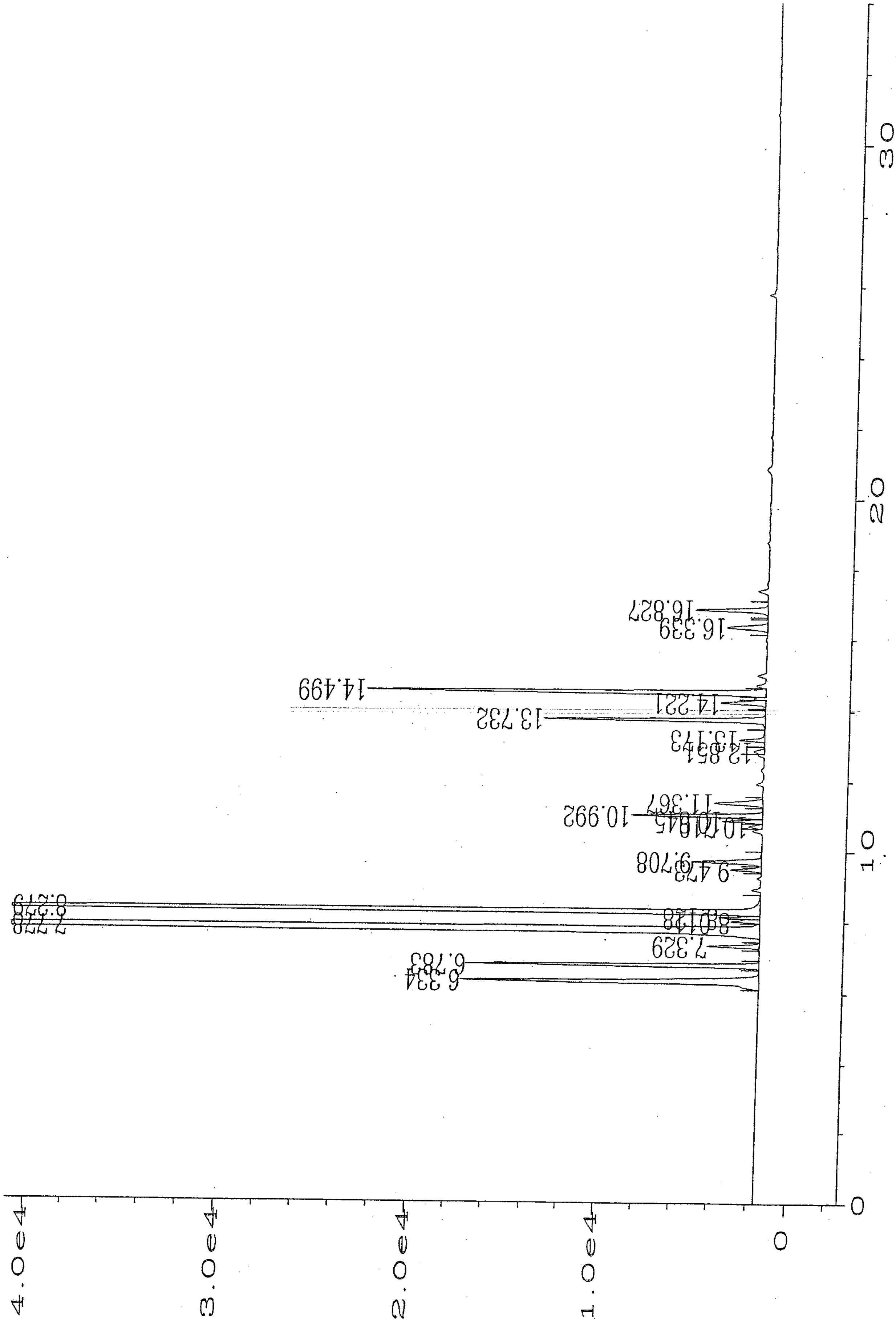

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0201.D
  Pk#  Ret Time       Area            Height      Type   Width      Area %
 |---|----------|--------------|--------------|----|---------|----------
    1     6.208              0            934  Fsho   0.000      0.0000
    2     6.305              0          12431  Fsho   0.000      0.0000
    3     6.334         105403          15800  BV     0.089      2.3314
    4     6.783          69432          15544  PV     0.073      1.5357
    5     7.329          11808           2666  BV     0.070      0.2612
    6     7.597              0           1060  Fsho   0.000      0.0000
    7     7.659              0           3484  Fsho   0.000      0.0000
    8     7.778        2575627         587460  PV     0.069     56.9698
    9     7.911              0            301  Rsho   0.000      0.0000
   10     8.011           6744           1489  VV     0.063      0.1492
   11     8.073              0            861  Rsho   0.000      0.0000
   12     8.128           7173           2101  VV     0.052      0.1587
   13     8.279        1430227         408682  VB     0.055     31.6349
   14     9.473           6977           1577  BV     0.068      0.1543
   15     9.708          21299           3607  VB     0.092      0.4711
   16    10.710           3152            666  VV     0.073      0.0697
   17    10.845           8185           2016  VV     0.063      0.1810
   18    10.992          34279           6873  VV     0.078      0.7582
   19    11.367          16916           2451  PV     0.108      0.3742
   20    12.851           3527            543  VV     0.099      0.0780
   21    13.173           6179           1285  PV     0.074      0.1367
   22    13.732          58311          11667  VB     0.078      1.2898
   23    14.221          12860           2273  BV     0.088      0.2844
   24    14.499         108086          21061  VV     0.081      2.3907
   25    16.339          14465           2053  BB     0.111      0.3200
   26    16.827          20388           3714  BB     0.085      0.4510

Total area = 4521037

=====================================================================
```

Gas chromatogram of the VOC's emitted from VC-VAc copolymer – 35 phr Benzoflex 2-45

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0201.D



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Calibrated report not possible because no calibration table exists
=====================================================================
                          Area Percent Report
=====================================================================

Data File Name    : C:\HPCHEM\1\DATA\AMR\NV-F0207.D
Operator          : Amr                           Page Number       : 1
Instrument        : ANALYZER1                     Vial Number       :
Sample Name       :                               Injection Number  :
Run Time Bar Code:                                Sequence Line     :
Acquired on       : 17 Apr 03  05:40 PM           Instrument Method: AMRPVC.MTH
Report Created on: 17 Apr 03   06:15 PM           Analysis Method   : AMRPVC.MTH
Sample Info       :

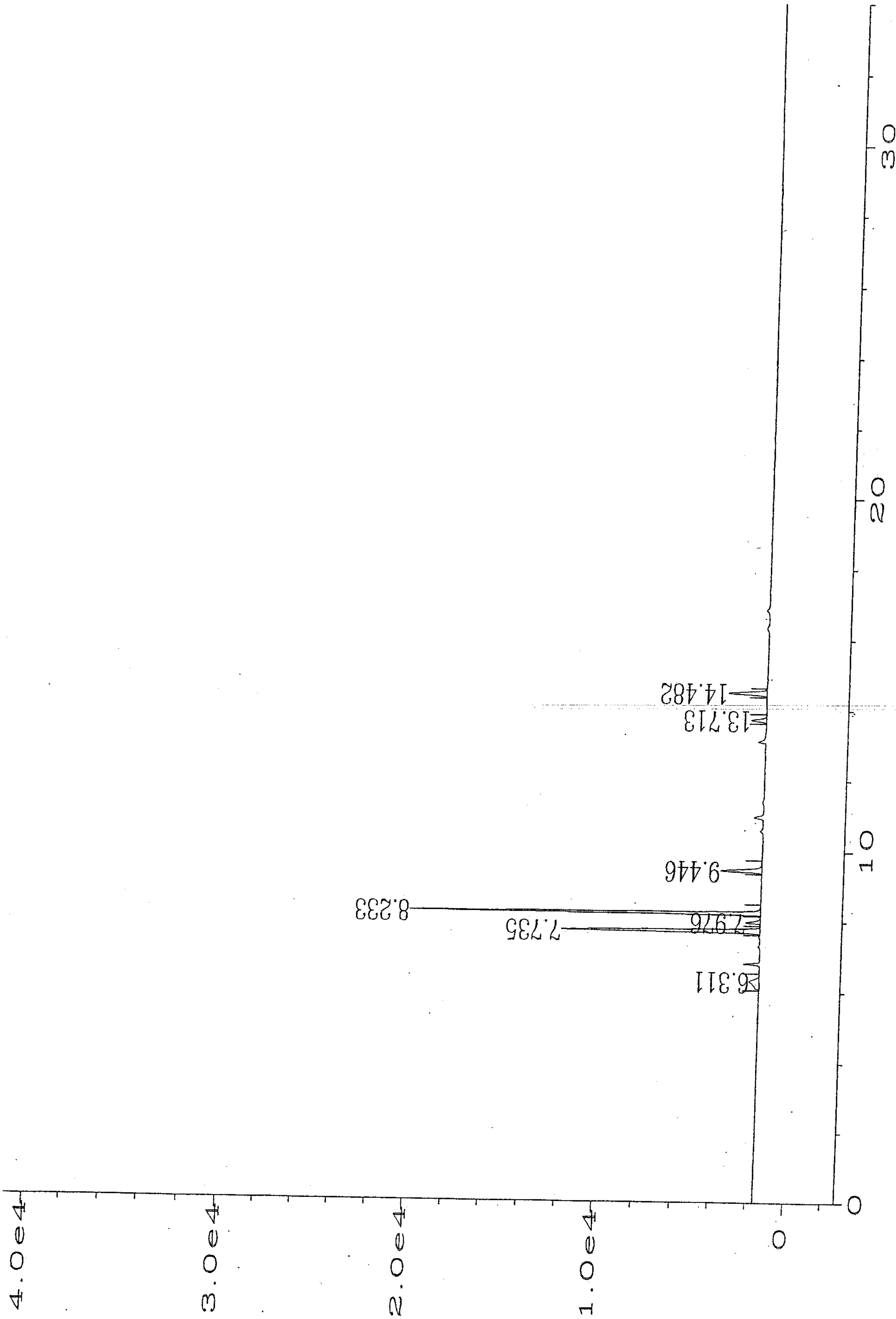
Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0207.D
   Pk#  Ret Time       Area            Height      Type   Width      Area %
  |---|----------|--------------|--------------|----|---------|----------|
    1     6.216              0            342   Fsho   0.000      0.0000
    2     6.277              0            454   Fsho   0.000      0.0000
    3     6.311           6654            521   BB     0.175      4.8287
    4     7.735          44198          10450   PV     0.067     32.0748
    5     7.976           3002            783   PV     0.056      2.1785
    6     8.233          59544          18479   VB     0.050     43.2119
    7     9.446          10123           2205   BB     0.070      7.3460
    8    13.713           3899            783   BB     0.078      2.8295
    9    14.482          10377           2037   BV     0.079      7.5305

Total area = 137796

=====================================================================
```

Gas chromatogram of the VOC's emitted from VC-VAc copolymer – 35 phr Lindol

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0207.D



```
Calibrated report not possible because no calibration table exists
=====================================================================
                        Area Percent Report
=====================================================================

Data File Name    : C:\HPCHEM\1\DATA\AMR\NV-F0202.D
Operator          : Amr                       Page Number       : 1
Instrument        : ANALYZER1                 Vial Number       :
Sample Name       :                           Injection Number  :
Run Time Bar Code:                            Sequence Line     :
Acquired on       : 17 Apr 03  11:54 AM       Instrument Method: AMRPVC.MTH
Report Created on: 17 Apr 03  12:29 PM        Analysis Method   : AMRPVC.MTH
Sample Info       :

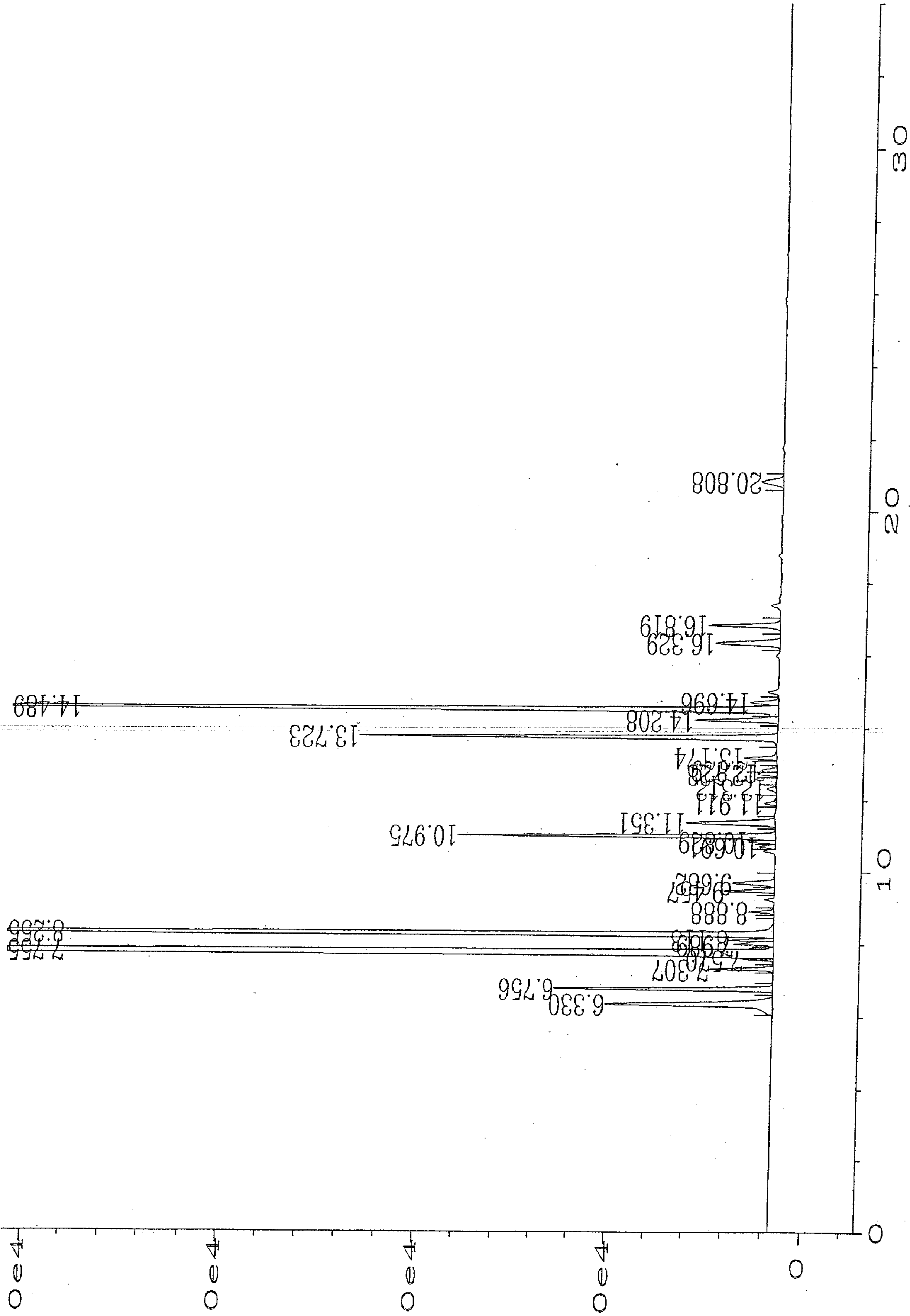
Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0202.D
  Pk#  Ret Time        Area          Height     Type   Width      Area %
 |---|----------|--------------|--------------|----|---------|----------|
    1     6.114              0            367 Fsho   0.000      0.0000
    2     6.179              0            576 Fsho   0.000      0.0000
    3     6.295              0           5697 Fsho   0.000      0.0000
    4     6.330          66360           8626 BV     0.114      1.6780
    5     6.432              0           1786 Rsho   0.000      0.0000
    6     6.490              0            400 Rsho   0.000      0.0000
    7     6.756          52287          11303 VV     0.076      1.3222
    8     7.307          14318           3216 BV     0.070      0.3621
    9     7.570           3839           1502 PV     0.043      0.0971
   10     7.726              0         322015 Fsho   0.000      0.0000
   11     7.755        2302175         512888 VV     0.070     58.2142
   12     7.989           9721           1988 VV     0.068      0.2458
   13     8.055              0            983 Rsho   0.000      0.0000
   14     8.113           7605           2262 VV     0.051      0.1923
   15     8.255         827338         239882 VB     0.054     20.9206
   16     8.888           4607           1266 BV     0.056      0.1165
   17     9.457          10914           2530 PV     0.066      0.2760
   18     9.682          13727           2102 VB     0.101      0.3471
   19    10.691           3792            797 VV     0.073      0.0959
   20    10.829           5340           1322 VV     0.062      0.1350
   21    10.975          82402          16430 VV     0.079      2.0837
   22    11.351          30701           4493 PV     0.108      0.7763
   23    11.911           3143            585 BV     0.081      0.0795
   24    12.312           3220            488 PV     0.107      0.0814
   25    12.728           4836            953 BV     0.077      0.1223
   26    12.829           4322            739 VV     0.088      0.1093
   27    13.174           7691           1623 VB     0.074      0.1945
   28    13.691              0          13177 Fsho   0.000      0.0000
   29    13.723         107501          21712 BB     0.078      2.7183
   30    14.208          23862           4221 BV     0.088      0.6034
   31    14.489         304457          59378 VV     0.080      7.6987
   32    14.696           7282           1360 VV     0.083      0.1841
   33    16.329          22532           3206 PV     0.111      0.5697
   34    16.819          19912           3603 PB     0.085      0.5035
   35    20.808          10783           1072 BB     0.160      0.2727

Total area = 3954664

=====================================================================
```

Gas chromatogram of the VOC's emitted from VC-VAc copolymer – 35 phr Mesamoll

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0202.D



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 Calibrated report not possible because no calibration table exists
=====================================================================
                         Area Percent Report
=====================================================================

Data File Name    : C:\HPCHEM\1\DATA\AMR\NV-F0204.D
Operator          : Amr                          Page Number        : 1
Instrument        : ANALYZER1                    Vial Number        :
Sample Name       :                              Injection Number   :
Run Time Bar Code:                               Sequence Line      :
Acquired on       : 17 Apr 03   01:34 PM         Instrument Method: AMRPVC.MTH
Report Created on: 17 Apr 03   02:09 PM          Analysis Method   : AMRPVC.MTH
Sample Info       :

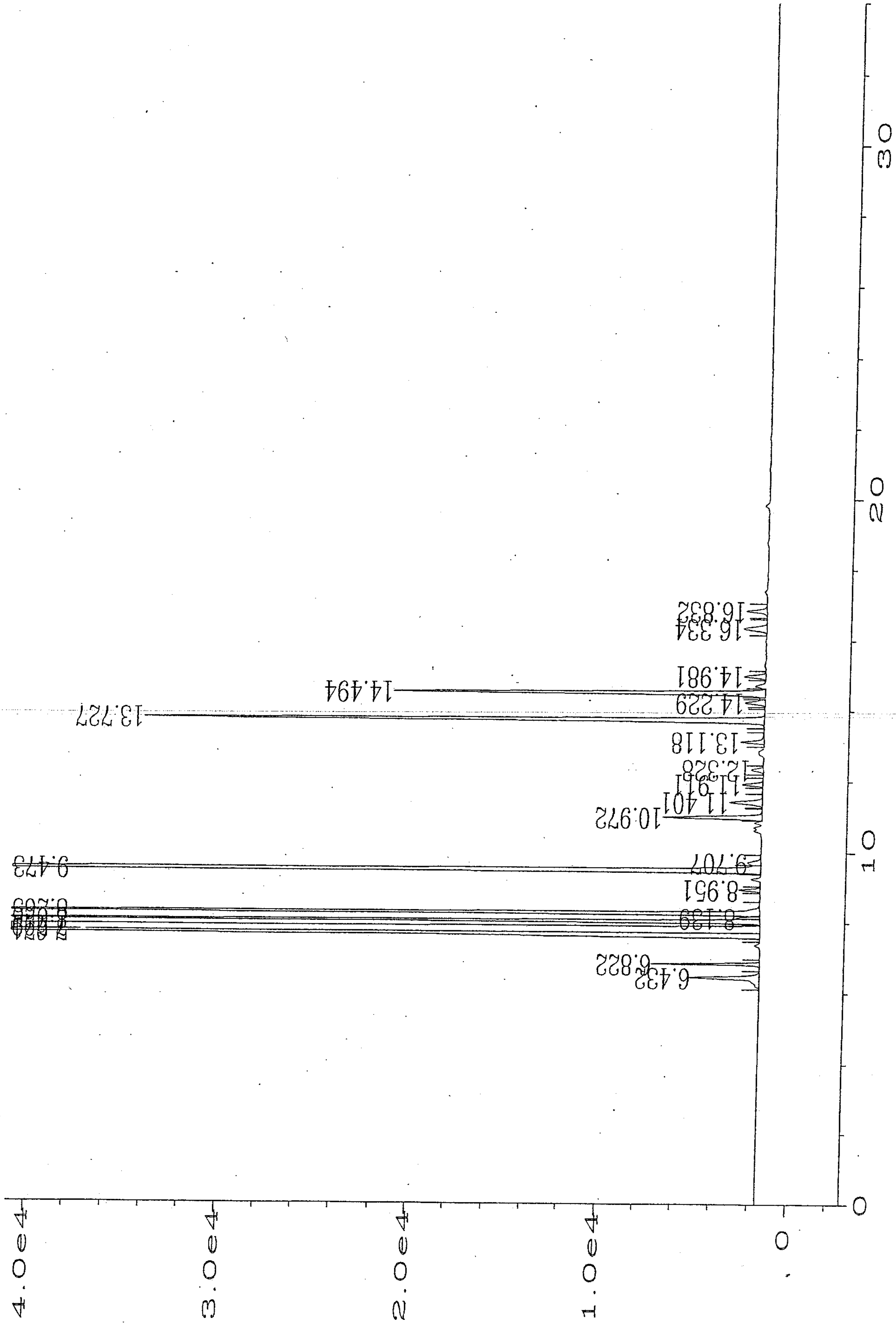

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0204.D
   Pk#  Ret Time         Area            Height      Type   Width      Area %
  |---|----------|--------------|--------------|----|---------|----------|
    1     6.283             0            324    Fsho   0.000     0.0000
    2     6.383             0           1740    Fsho   0.000     0.0000
    3     6.420             0           3316    Fsho   0.000     0.0000
    4     6.432         22369           3649    BV     0.082     0.3542
    5     6.822         15997           5680    PV     0.044     0.2533
    6     7.604             0          12146    Fsho   0.000     0.0000
    7     7.671        254237          57876    PV     0.065     4.0257
    8     7.799       4732500        1068132    VV     0.069    74.9358
    9     8.026        171646          56153    VV     0.047     2.7179
   10     8.139          3869           1219    VV     0.053     0.0613
   11     8.265        216455          63770    VV     0.053     3.4274
   12     8.364             0            621    Rsho   0.000     0.0000
   13     8.951          4123           1091    BV     0.059     0.0653
   14     9.473        552631         144416    PV     0.060     8.7505
   15     9.707          4684            676    VB     0.104     0.0742
   16    10.972         25956           5161    VB     0.079     0.4110
   17    11.401         10654           1687    BB     0.098     0.1687
   18    11.911          5175           1072    BB     0.075     0.0819
   19    12.328          3265            597    BB     0.085     0.0517
   20    13.118          5564           1198    PB     0.072     0.0881
   21    13.727        160257          32646    BB     0.077     2.5376
   22    14.229          5751           1012    BV     0.088     0.0911
   23    14.494        100497          19602    VV     0.080     1.5913
   24    14.981          5605           1089    PB     0.081     0.0888
   25    16.334          8242           1159    BB     0.112     0.1305
   26    16.832          5926           1038    BB     0.087     0.0938

Total area = 6315404

=====================================================================
```

Gas chromatogram of the VOC's emitted from VC-VAc copolymer – Alcell plasticized with 35 phr DOP

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0204.D



```
Calibrated report not possible because no calibration table exists
=====================================================================
                        Area Percent Report
=====================================================================

Data File Name     : C:\HPCHEM\1\DATA\AMR\NV-F0205.D
Operator           : Amr                         Page Number       : 1
Instrument         : ANALYZER1                   Vial Number       :
Sample Name        :                             Injection Number  :
Run Time Bar Code:                               Sequence Line     :
Acquired on        : 17 Apr 03   03:12 PM        Instrument Method: AMRPVC.MTH
Report Created on: 17 Apr 03   03:46 PM          Analysis Method  : AMRPVC.MTH
Sample Info        :

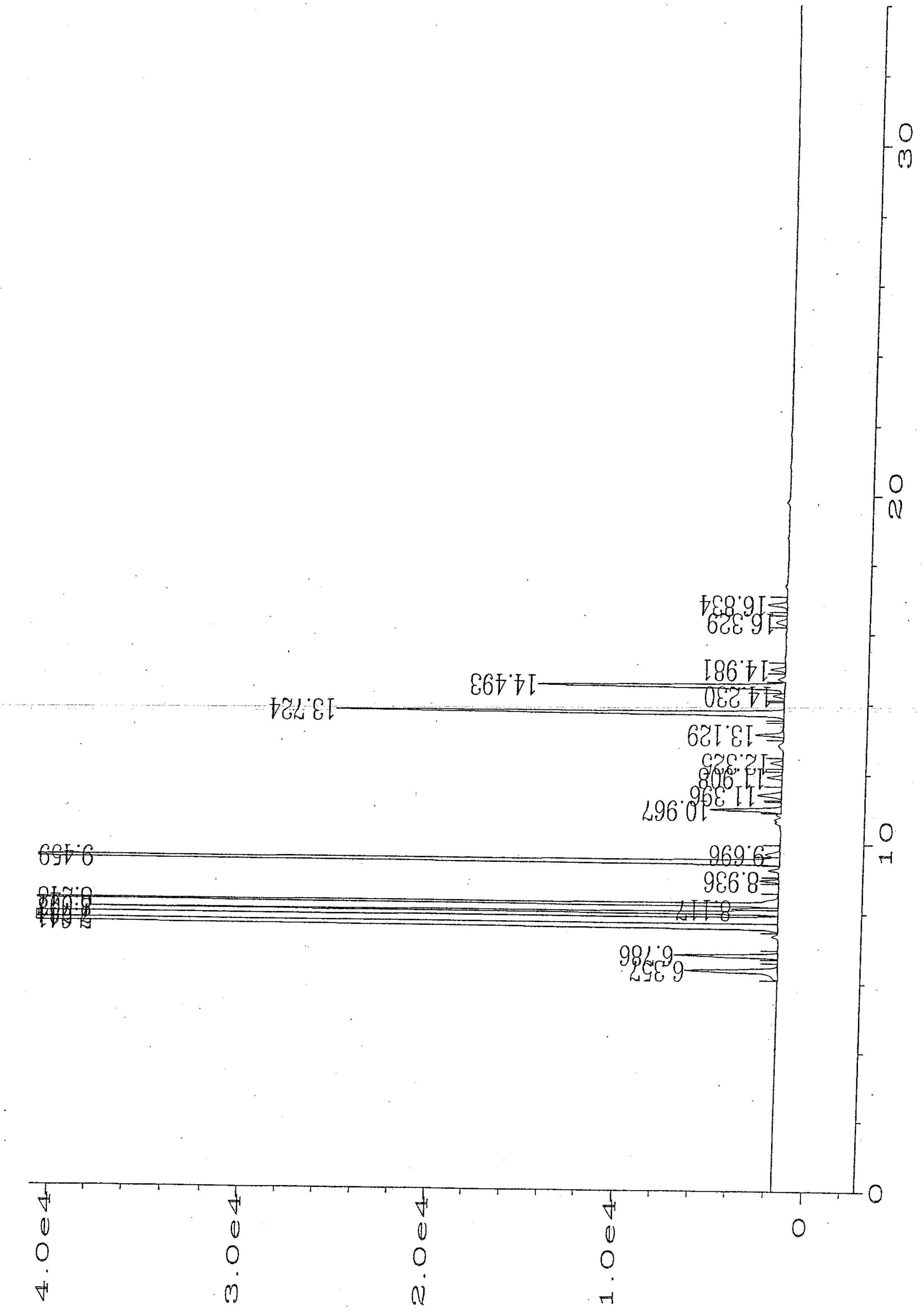

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0205.D
  Pk#  Ret Time      Area          Height      Type   Width      Area %
 |---|----------|--------------|--------------|----|---------|----------|
   1     6.138            0            263   Fsho   0.000      0.0000
   2     6.300            0           2324   Fsho   0.000      0.0000
   3     6.342            0           4449   Fsho   0.000      0.0000
   4     6.357        30689           4887   BB     0.087      0.4178
   5     6.760            0           4253   Fsho   0.000      0.0000
   6     6.786        24929           5422   BV     0.065      0.3394
   7     7.501            0            393   Fsho   0.000      0.0000
   8     7.580            0          30549   Fsho   0.000      0.0000
   9     7.641       464007          90735   PV     0.076      6.3171
  10     7.784      5882833        1308237   VV     0.070     80.0904
  11     8.007       113937          36668   VV     0.048      1.5512
  12     8.117         8487           2394   VV     0.053      0.1155
  13     8.248       195874          57479   VV     0.053      2.6667
  14     8.345            0            733   Rsho   0.000      0.0000
  15     8.936         3607            967   VV     0.058      0.0491
  16     9.459       371733          96417   PV     0.060      5.0609
  17     9.696         5190            735   VB     0.109      0.0707
  18    10.967        18658           3702   VB     0.079      0.2540
  19    11.396         7610           1198   BV     0.096      0.1036
  20    11.908         3856            773   VB     0.077      0.0525
  21    12.325         3437            616   BB     0.087      0.0468
  22    13.129         6965           1420   PB     0.075      0.0948
  23    13.724       118626          23831   BB     0.078      1.6150
  24    14.230         3296            581   BV     0.087      0.0449
  25    14.459            0           7968   Fsho   0.000      0.0000
  26    14.493        68293          13066   VV     0.081      0.9298
  27    14.981         3899            749   PB     0.081      0.0531
  28    16.329         3833            539   BB     0.111      0.0522
  29    16.834         5488            970   BB     0.086      0.0747

Total area = 7345245

=====================================================================
```

Gas chromatogram of the VOC's emitted from VC-VAc copolymer – Alcell plasticized with 35 phr Mesamoll

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0205.D



```
Calibrated report not possible because no calibration table exists
=====================================================================
                        Area Percent Report
=====================================================================

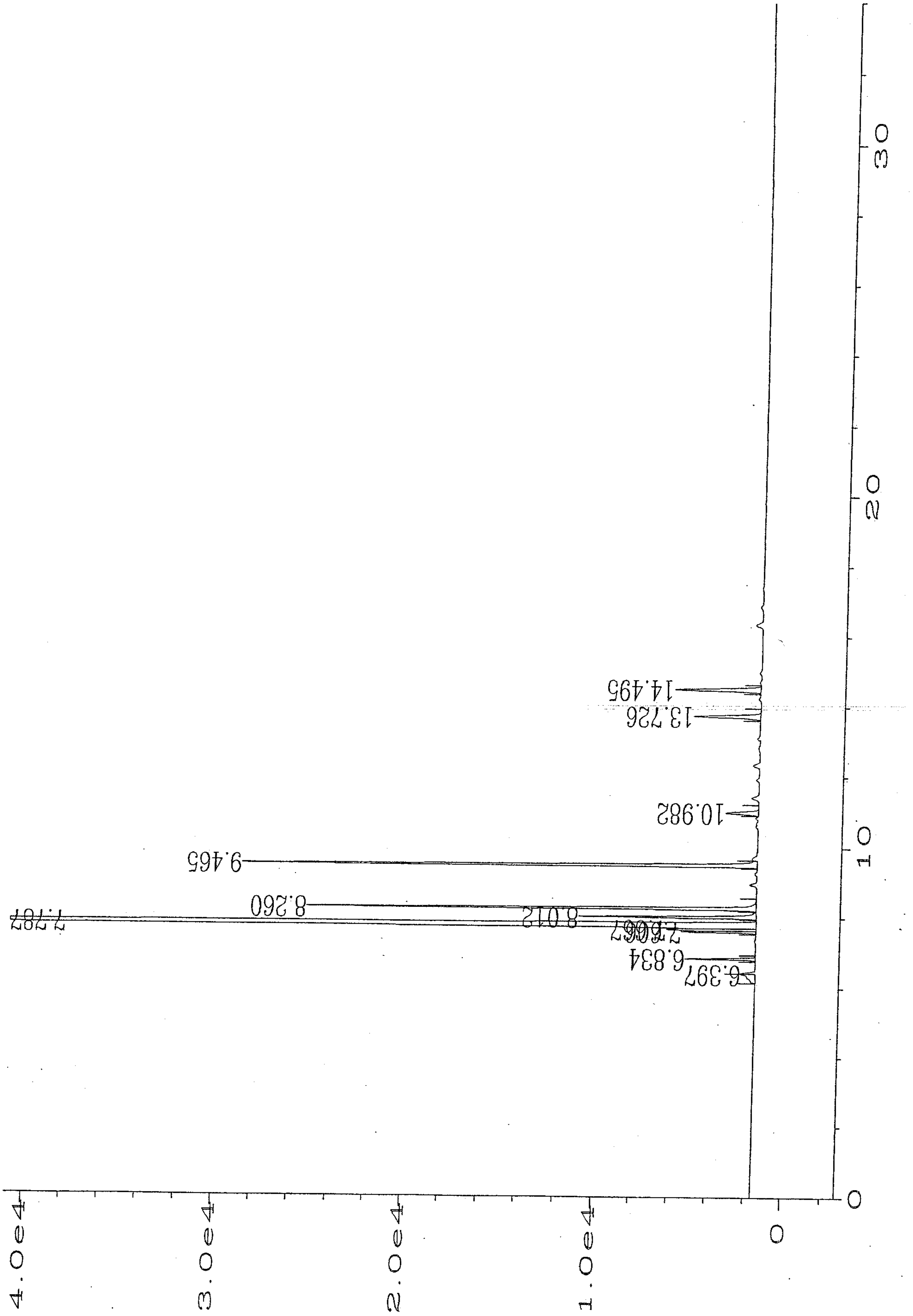
Data File Name    : C:\HPCHEM\1\DATA\AMR\NV-F0203.D
Operator          : Amr                       Page Number       : 1
Instrument        : ANALYZER1                 Vial Number       :
Sample Name       :                           Injection Number  :
Run Time Bar Code:                            Sequence Line     :
Acquired on       : 17 Apr 03   12:44 PM      Instrument Method: AMRPVC.MTH
Report Created on: 17 Apr 03   01:18 PM      Analysis Method   : AMRPVC.MTH
Sample Info       :


Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0203.D
   Pk#  Ret Time         Area           Height      Type   Width       Area %
  |---|----------|--------------|--------------|----|---------|----------|
    1     6.223             0            245   Fsho   0.000      0.0000
    2     6.338             0            459   Fsho   0.000      0.0000
    3     6.397          6146            756   BV     0.107      0.4620
    4     6.834          9452           3718   BV     0.040      0.7105
    5     7.606         10916           3931   BV     0.042      0.8206
    6     7.667         15269           4730   VV     0.048      1.1478
    7     7.787       1026128         243950   VV     0.066     77.1370
    8     8.012         29035           9419   VV     0.047      2.1826
    9     8.260         78722          23774   VB     0.052      5.9177
   10     8.369             0            210   Rsho   0.000      0.0000
   11     9.465        106350          27234   BV     0.061      7.9946
   12    10.982          8309           1722   VB     0.076      0.6246
   13    13.726         17146           3495   BB     0.077      1.2889
   14    14.495         22795           4524   BV     0.079      1.7136

Total area = 1330267
=====================================================================
```

Gas chromatogram of the VOC's emitted from VC-VAc copolymer – Alcell plasticized with 35 phr Benzoflex 2-45

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0203.D



```
Calibrated report not possible because no calibration table exists
=====================================================================
                         Area Percent Report
=====================================================================

Data File Name    : C:\HPCHEM\1\DATA\AMR\NV-F0206.D
Operator          : Amr                       Page Number       : 1
Instrument        : ANALYZER1                 Vial Number       :
Sample Name       :                           Injection Number  :
Run Time Bar Code:                            Sequence Line     :
Acquired on       : 17 Apr 03   03:58 PM      Instrument Method: AMRPVC.MTH
Report Created on: 17 Apr 03   04:33 PM       Analysis Method   : AMRPVC.MTH
Sample Info       :

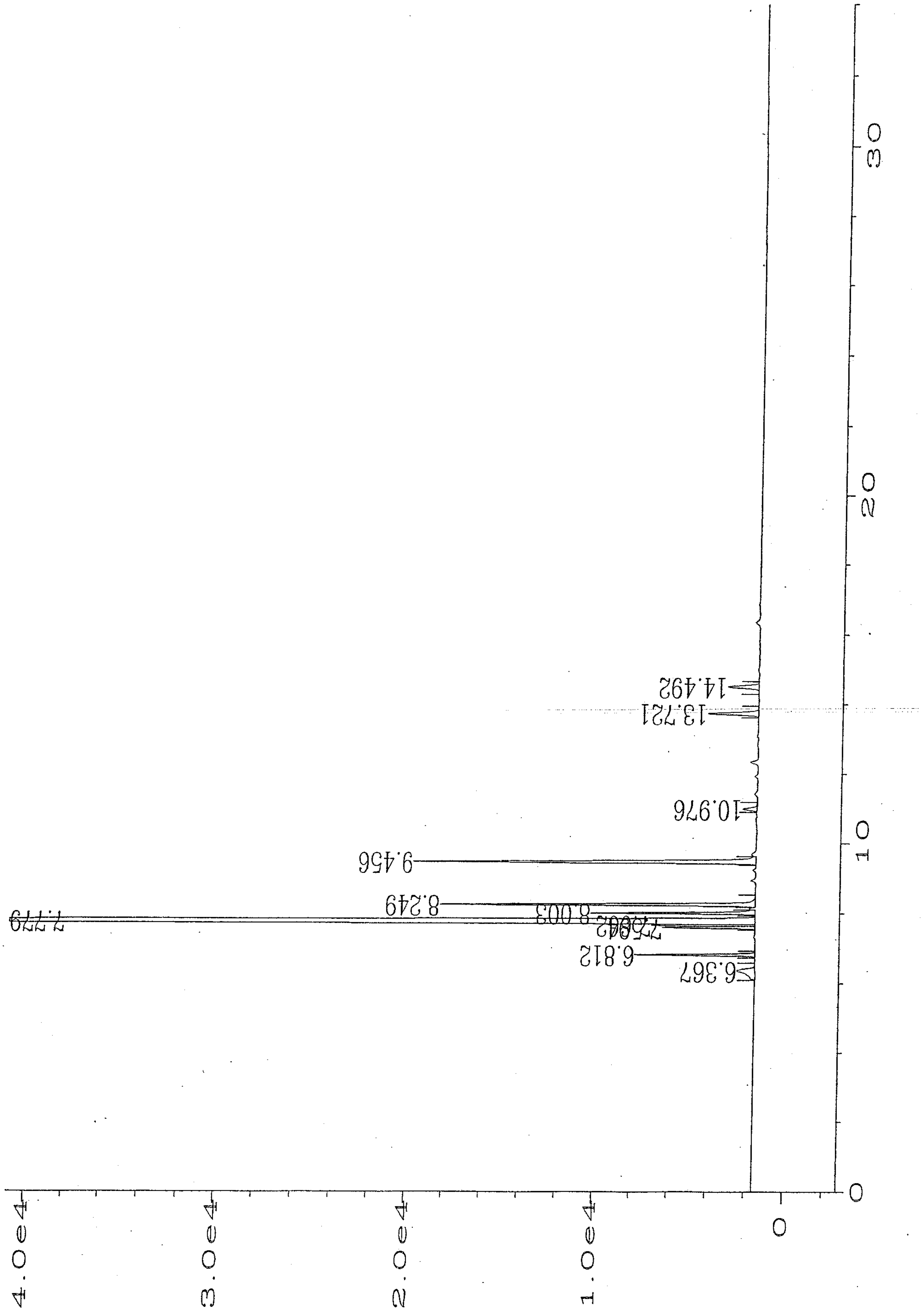

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0206.D
    Pk#  Ret Time          Area          Height    Type   Width     Area %
   |---|----------|--------------|--------------|----|---------|----------|
     1     6.168              0            249  Fsho   0.000     0.0000
     2     6.237              0            386  Fsho   0.000     0.0000
     3     6.301              0            560  Fsho   0.000     0.0000
     4     6.367           9883            923  BB     0.152     0.7944
     5     6.812          17310           6292  BB     0.043     1.3914
     6     7.594          13793           4838  BV     0.043     1.1087
     7     7.662          17184           5402  VV     0.047     1.3813
     8     7.779        1008005         238381  VV     0.066    81.0239
     9     8.003          25673           8767  VV     0.045     2.0636
    10     8.249          55839          16855  VB     0.052     4.4883
    11     9.456          71877          18307  BV     0.061     5.7775
    12    10.976           3564            734  VB     0.075     0.2865
    13    13.721          12888           2611  BB     0.077     1.0360
    14    14.492           8067           1583  BV     0.079     0.6484

Total area = 1244084

=====================================================================
```

Gas chromatogram of the VOC's emitted from VC-VAc copolymer – Alcell plasticized with 35 phr Lindol

Sig. 1 in C:\HPCHEM\1\DATA\AMR\NV-F0206.D



Appendix [B]

Gas Chromatography/Mass Spectrography-Identification And Quantification Tables

Aerotech Environmental

Date: *17-Nov-03*

CLIENT:	Concordia University	**Client Sample ID:**	(DOP-1) 1
Lab Order:	03101300	**Tag Number:**	
Project:		**Collection Date:**	10/23/2003
Lab ID:	03101300-01A	**Matrix:**	AIR

Analyses	Result	Limit	Qual	Units	DF	Date Analyzed
TENTATIVELY IDENTIFIED COMPOUNDS IN AIR	**TICS**					Analyst: **JG**
1-Butanol	300	200	T4D2	ppbv	20	11/3/2003
2-Butanol	300	200	T4D2	ppbv	20	11/3/2003
2-Butanone	200	200	T4D2	ppbv	20	11/3/2003
Butanal	3000	200	T4D2	ppbv	20	11/3/2003
Butane	3000	200	T4D2	ppbv	20	11/3/2003
C4H8 Hydrocarbon	3000	200	T4D2	ppbv	20	11/3/2003
Trimethyldecane	500	200	T4D2	ppbv	20	11/3/2003
Unknown Hydrocarbon	300	200	T4D2	ppbv	20	11/3/2003
Vinyl Acetate	5000	200	T4D2	ppbv	20	11/3/2003
Acetaldehyde	3000	200	T4D2	ppbv	20	11/3/2003

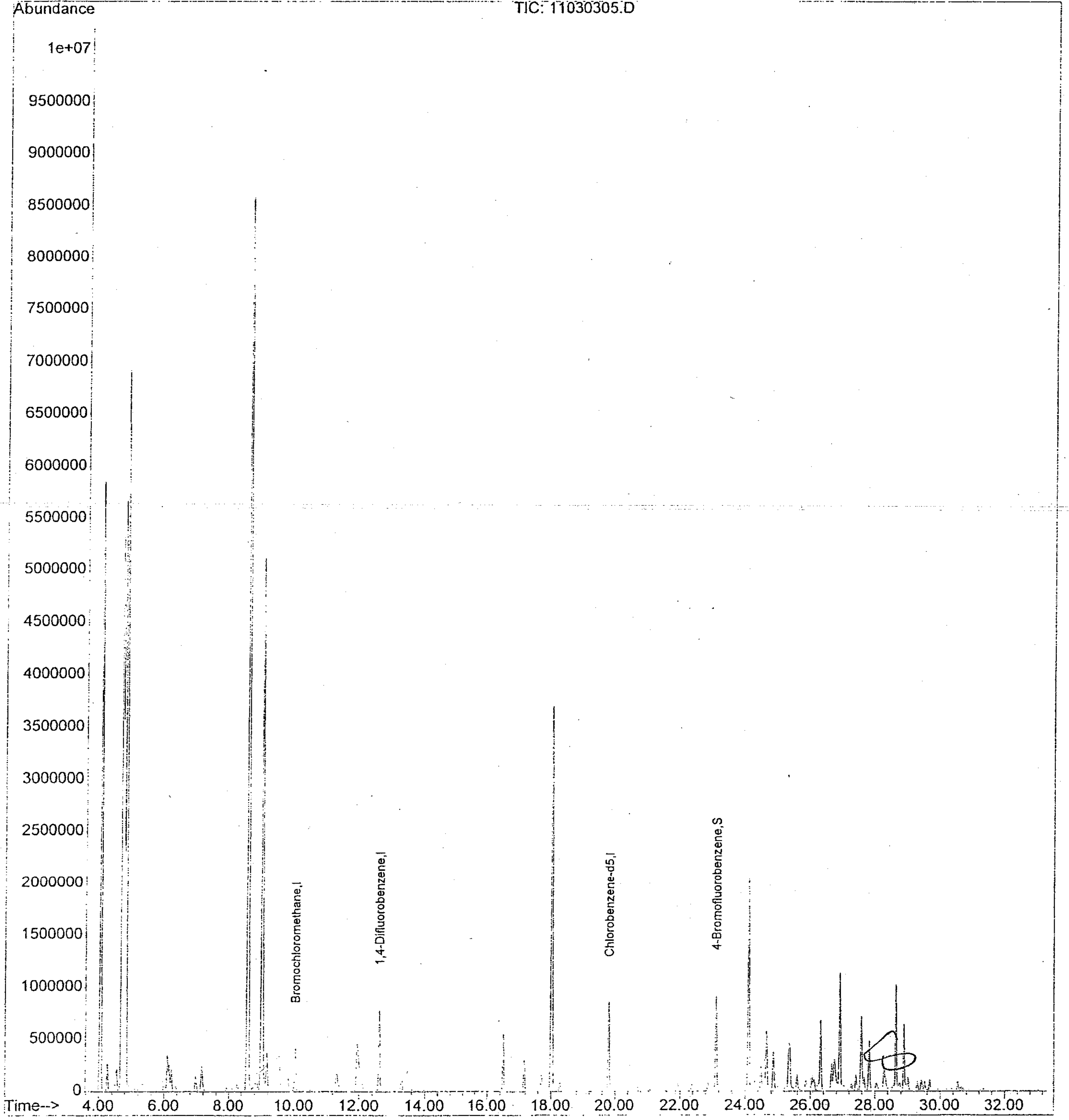
Qualifiers:

ND - Not Detected at the Reporting Limit	S - Spike Recovery outside accepted recovery limits
J - Analyte detected below quantitation limits	R - RPD outside accepted recovery limits
B - Analyte detected in the associated Method Blan	E - Value above quantitation range
* - Value exceeds Maximum Contaminant Level	

Quantitation Report (QT Reviewed)

```
Data File : C:\MSDCHEM\1\MS005\110303\11030305.D          Vial: 1
Acq On    :  3 Nov 2003  12:23 pm                      Operator: JJG
Sample    : TO15 03101300-01A X20                      Inst    : MS005
Misc      : IS/SS C-100803-01  10mL                    Multiplr: 1.00
MS Integration Params: RTEINT.P
Quant Time: Nov  3 13:47 2003                Quant Results File: TO-15 102803

Method         : C:\MSDCHEM\1\METHODS\TO-15 102803.M (RTE Integrator)
Title          : TO-15   Standards for 7 points calibration
Last Update    : Wed Oct 29 17:20:14 2003
Response via   : Initial Calibration
```



11/03/03

Aerotech Environmental

Date: *17-Nov-03*

CLIENT:	Concordia University	**Client Sample ID:**	((2-45)-1) 2
Lab Order:	03101300	**Tag Number:**	
Project:		**Collection Date:**	10/23/2003
Lab ID:	03101300-02A	**Matrix:**	AIR

Analyses	Result	Limit	Qual	Units	DF	Date Analyzed
TENTATIVELY IDENTIFIED COMPOUNDS IN AIR		**TICS**				Analyst: **JG**
1-Butanol	400	200	T4,D2	ppbv	20	11/3/2003
1-Chlorobutane	300	200	T4,D2	ppbv	20	11/3/2003
1-Undecene	300	200	T4,D2	ppbv	20	11/3/2003
2-Butanol	300	200	T4,D2	ppbv	20	11/3/2003
Butanal	3000	200	T4,D2	ppbv	20	11/3/2003
Butane	3000	200	T4,D2	ppbv	20	11/3/2003
C4H8 Hydrocarbon	2000	200	T4,D2	ppbv	20	11/3/2003
Trimethyldecane	600	200	T4,D2	ppbv	20	11/3/2003
Unknown Hydrocarbon #1	200	200	T4,D2	ppbv	20	11/3/2003
Unknown Hydrocarbon #2	200	200	T4,D2	ppbv	20	11/3/2003
Unknown Hydrocarbon #3	400	200	T4,D2	ppbv	20	11/3/2003
Unknown Hydrocarbon #4	200	200	T4,D2	ppbv	20	11/3/2003
Vinyl Acetate	5000	200	T4,D2	ppbv	20	11/3/2003
Acetaldehyde	3000	200	T4,D2	ppbv	20	11/3/2003

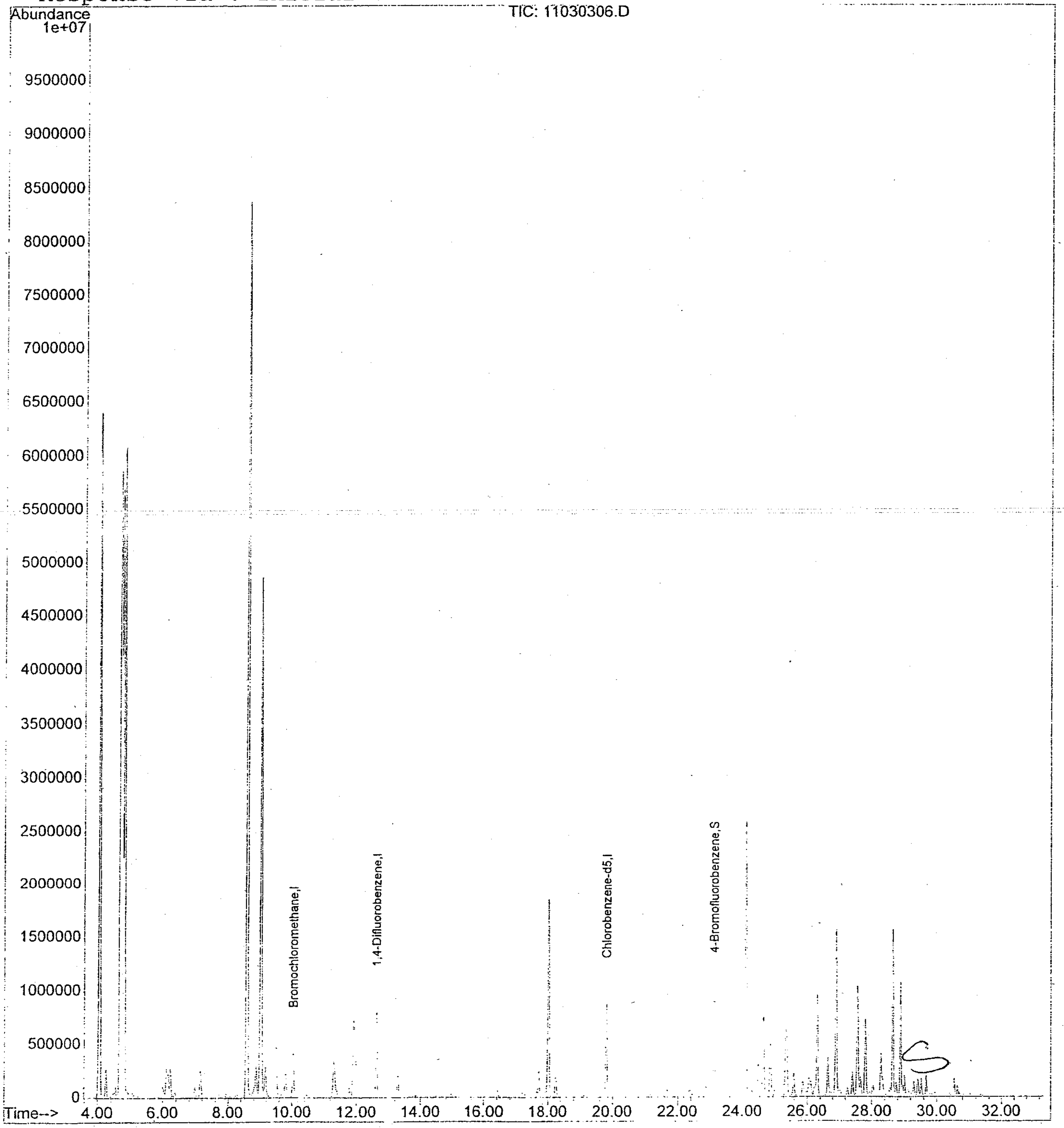
Qualifiers:

ND - Not Detected at the Reporting Limit
J - Analyte detected below quantitation limits
B - Analyte detected in the associated Method Blank
* - Value exceeds Maximum Contaminant Level
S - Spike Recovery outside accepted recovery limits
R - RPD outside accepted recovery limits
E - Value above quantitation range

Quantitation Report   (QT Reviewed)

```
Data File : C:\MSDCHEM\1\MS005\110303\11030306.D          Vial: 2
Acq On    :  3 Nov 2003   1:06 pm                     Operator: JJG
Sample    : TO15 03101300-02A,X20                     Inst    : MS005
Misc      : IS/SS C-100803-01  10mL                   Multiplr: 1.00
MS Integration Params: RTEINT.P
Quant Time: Nov  3 13:49 2003                Quant Results File: TO-15 102803

Method         : C:\MSDCHEM\1\METHODS\TO-15 102803.M (RTE Integrator)
Title          : TO-15  Standards for 7 points calibration
Last Update    : Wed Oct 29 17:20:14 2003
Response via   : Initial Calibration
```



PAL

Precision Analytical Laboratorie
a division of Aerotech Laboratories, In

Precision Analytical Laboratories

Date: *05-Sep-03*

CLIENT:	Concordia University	**Client Sample ID:**	(Lindol-1) PVC Control
Lab Order:	03080652	**Tag Number:**	
Project:		**Collection Date:**	
Lab ID:	03080652-01A	**Matrix:**	AIR

Analyses	Result	Limit	Qual	Units	DF	Date Analyzed
TENTATIVELY IDENTIFIED COMPOUNDS IN AIR	**TICS**					Analyst: **JG**
1-Butanol	500	200	T4D2	ppbv	20	8/18/2003
1-Chlorobutane	200	200	T4D2	ppbv	20	8/18/2003
1-Undecanol	400	200	T4D2	ppbv	20	8/18/2003
2-Butanol	300	200	T4D2	ppbv	20	8/18/2003
2-Methyl-2-propanol	200	200	T4D2	ppbv	20	8/18/2003
Butanal	5000	200	T4D2	ppbv	20	8/18/2003
Butane	2000	200	T4D2	ppbv	20	8/18/2003
Propene	200	200	T4D2	ppbv	20	8/18/2003
Undecane	300	200	T4D2	ppbv	20	8/18/2003
Unknown Hydrocarbon #1	800	200	T4D2	ppbv	20	8/18/2003
Unknown Hydrocarbon #2	200	200	T4D2	ppbv	20	8/18/2003
Unknown Hydrocarbon #3	300	200	T4D2	ppbv	20	8/18/2003
Unknown Hydrocarbon #4	300	200	T4D2	ppbv	20	8/18/2003
Unknown Hydrocarbon #5	400	200	T4D2	ppbv	20	8/18/2003
Unknown Hydrocarbon #6	300	200	T4D2	ppbv	20	8/18/2003
Vinyl Acetate	9000	200	T4D2	ppbv	20	8/18/2003
Acetaldehyde	2000	200	T4D2	ppbv	20	8/18/2003

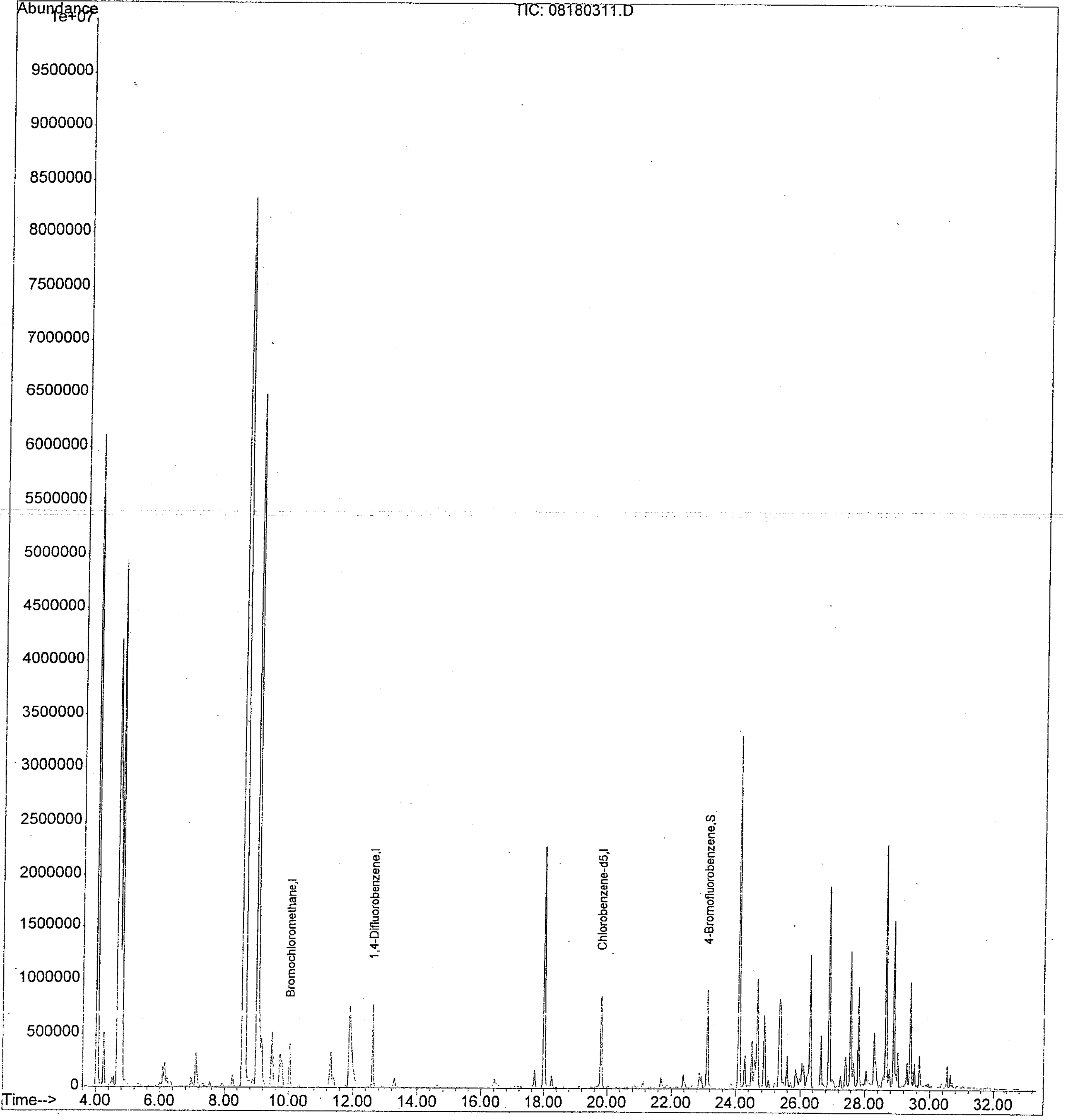
Qualifiers:

ND - Not Detected at the Reporting Limit
J - Analyte detected below quantitation limits
B - Analyte detected in the associated Method Blank
* - Value exceeds Maximum Contaminant Level
S - Spike Recovery outside accepted recovery limits
R - RPD outside accepted recovery limits
E - Value above quantitation range

```
                         Quantitation Report    (QT Reviewed)

  Data File : C:\MSDCHEM\1\MS005\081803\08180311.D          Vial: 6
  Acq On    : 18 Aug 2003   4:42 pm                     Operator: JJG
  Sample    : TO15 03080652-01A X20                     Inst    : MS005
  Misc      : IS/SS C-081503-01  10mL                   Multiplr: 1.00
  MS Integration Params: RTEINT.P
  Quant Time: Aug 19 13:29 2003                  Quant Results File: TO-15 081503

  Method         : C:\MSDCHEM\1\METHODS\TO-15 092303.M (RTE Integrator)
  Title          : TO-15  Standards for 7 points calibration
  Last Update    : Wed Oct 01 12:16:29 2003
  Response via   : Initial Calibration
```



Aerotech Environmental

Date: *17-Nov-03*

CLIENT:	Concordia University	**Client Sample ID:**	(Meswell-1) 19
Lab Order:	03101300	**Tag Number:**	
Project:		**Collection Date:**	10/23/2003
Lab ID:	03101300-05A	**Matrix:**	AIR

Analyses	Result	Limit	Qual	Units	DF	Date Analyzed
TENTATIVELY IDENTIFIED COMPOUNDS IN AIR		**TICS**				Analyst: **JG**
Butanal	3000	200	T4,D2	ppbv	20	11/3/2003
Butane	800	200	T4,D2	ppbv	20	11/3/2003
Trimethyldecane	200	200	T4,D2	ppbv	20	11/3/2003
Vinyl Acetate	6000	200	T4,D2	ppbv	20	11/3/2003
Acetaldehyde	2000	200	T4,D2	ppbv	20	11/3/2003

Qualifiers:

ND - Not Detected at the Reporting Limit

J - Analyte detected below quantitation limits

B - Analyte detected in the associated Method Blan

* - Value exceeds Maximum Contaminant Level

S - Spike Recovery outside accepted recovery limits

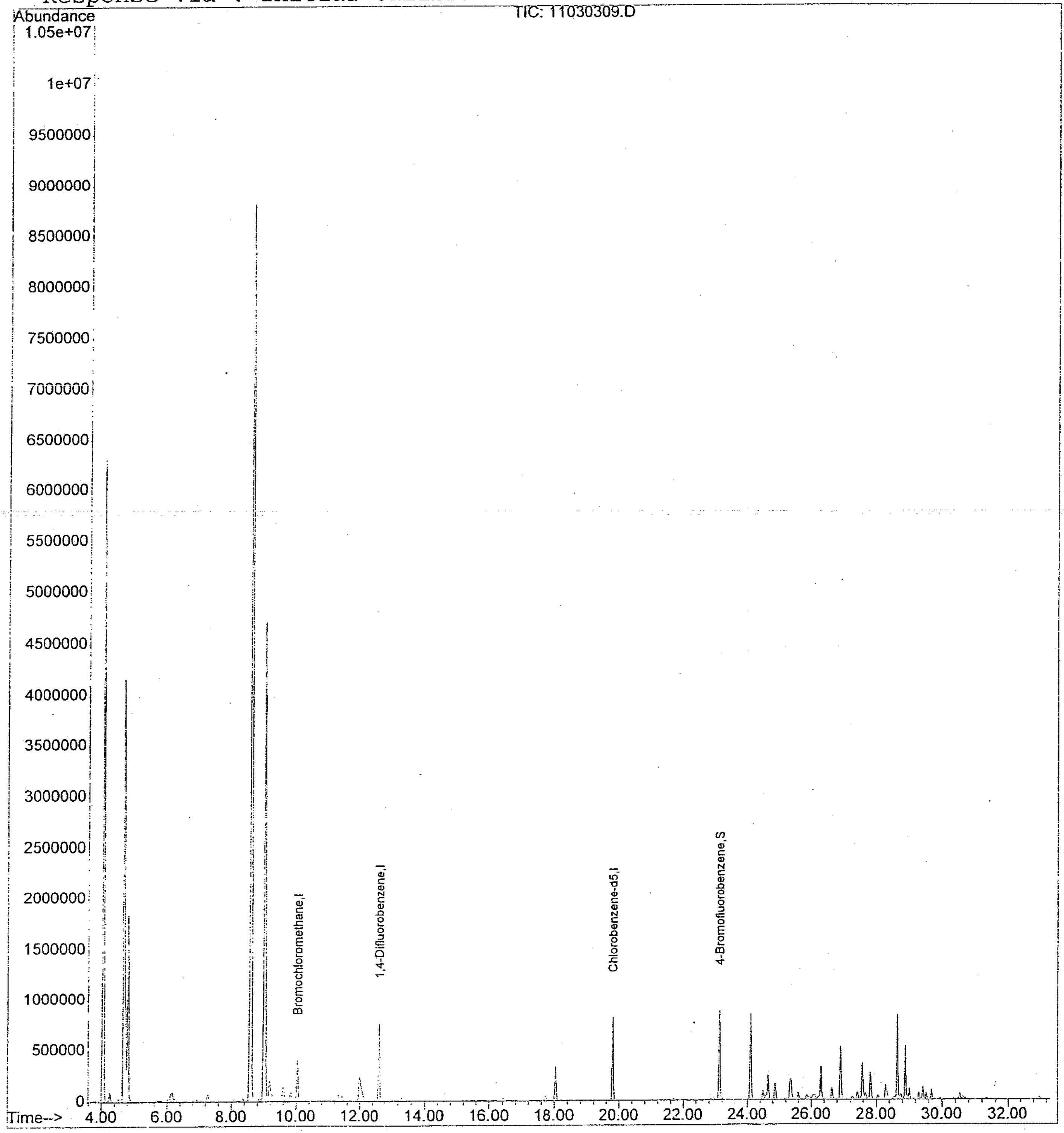
R - RPD outside accepted recovery limits

E - Value above quantitation range

```
                    Quantitation Report     (QT Reviewed)

Data File : C:\MSDCHEM\1\MS005\110303\11030309.D          Vial: 5
Acq On    :  3 Nov 2003   3:16 pm                     Operator: JJG
Sample    : TO15 03101300-05A X20                     Inst     : MS005
Misc      : IS/SS C-100803-01  10mL                   Multiplr: 1.00
MS Integration Params: RTEINT.P
Quant Time: Nov  3 16:13 2003              Quant Results File: TO-15 102803

Method         : C:\MSDCHEM\1\METHODS\TO-15 102803.M (RTE Integrator)
Title          : TO-15  Standards for 7 points calibration
Last Update    : Wed Oct 29 17:20:14 2003
Response via   : Initial Calibration
```



11/03/03

Aerotech Environmental

Date: *17-Nov-03*

CLIENT:	Concordia University	**Client Sample ID:**	(DOP-2) 4
Lab Order:	03101300	**Tag Number:**	
Project:		**Collection Date:**	10/23/2003
Lab ID:	03101300-03A	**Matrix:**	AIR

TENTATIVELY IDENTIFIED COMPOUNDS IN AIR TICS

Analyst: JG

Analyses	Result	Limit	Qual	Units	DF	Date Analyzed
1-Butanol	1000	200	T4D2Q1	ppbv	20	11/3/2003
Butanal	2000	200	T4D2Q1	ppbv	20	11/3/2003
Butane	4000	200	T4D2Q1	ppbv	20	11/3/2003
C4H8 Hydrocarbon	300	200	T4D2Q1	ppbv	20	11/3/2003
Ethyl Acetate	300	200	T4D2Q1	ppbv	20	11/3/2003
Trimethyldecane	200	200	T4D2Q1	ppbv	20	11/3/2003
Vinyl Acetate	7000	200	T4D2Q1	ppbv	20	11/3/2003
Acetaldehyde	500	200	T4D2Q1	ppbv	20	11/3/2003
Ethanol	1000	200	T4D2Q1	ppbv	20	11/3/2003

Qualifiers:

ND - Not Detected at the Reporting Limit

J - Analyte detected below quantitation limits

B - Analyte detected in the associated Method Blank

* - Value exceeds Maximum Contaminant Level

S - Spike Recovery outside accepted recovery limits

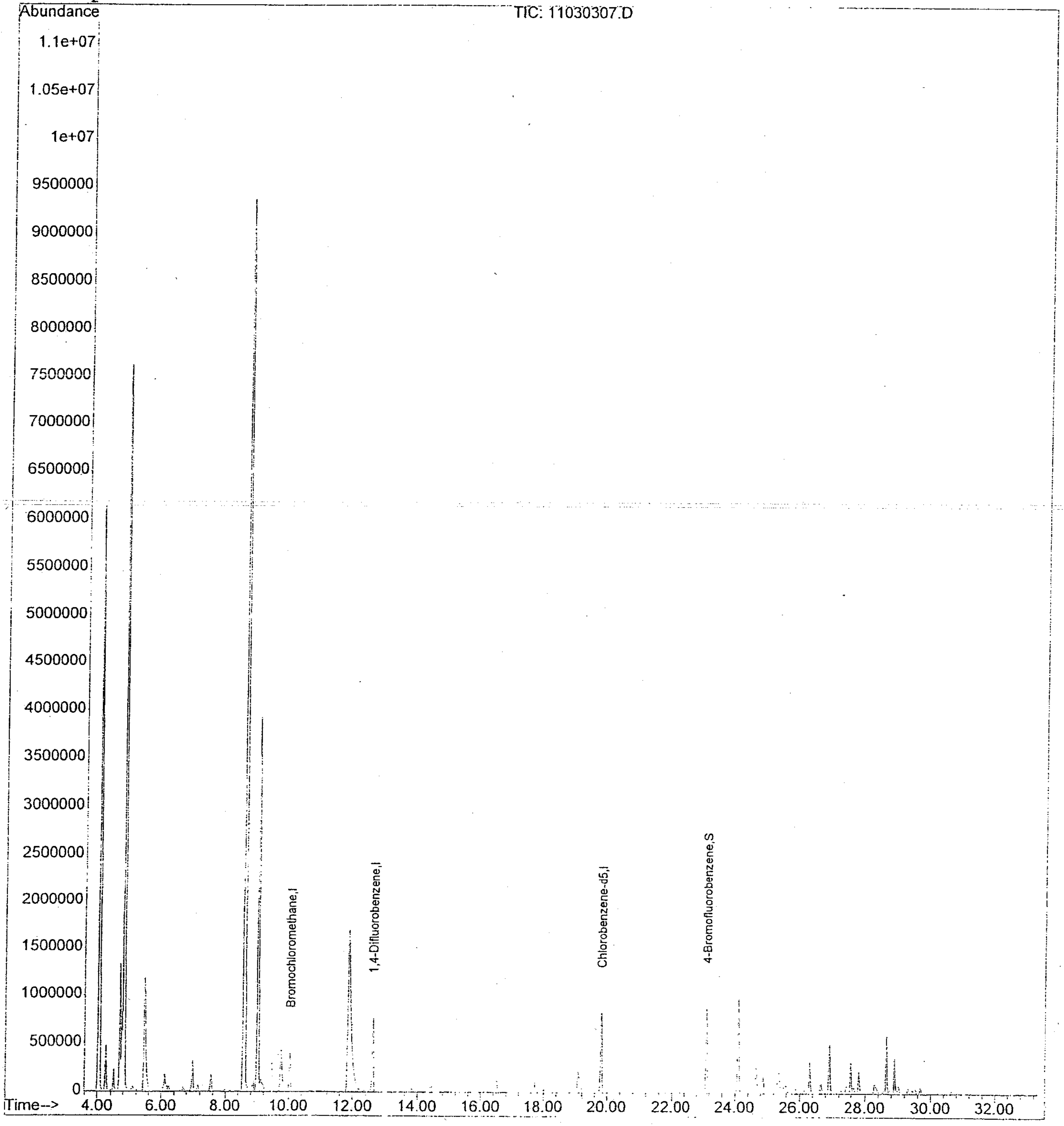
R - RPD outside accepted recovery limits

E - Value above quantitation range

```
                    Quantitation Report     (QT Reviewed)

  Data File : C:\MSDCHEM\1\MS005\110303\11030307.D          Vial: 3
  Acq On    :  3 Nov 2003   1:50 pm                     Operator: JJG
  Sample    : TO15 03101300-03A X20                     Inst    : MS005
  Misc      : IS/SS C-100803-01  10mL                   Multiplr: 1.00
  MS Integration Params: RTEINT.P
  Quant Time: Nov  3 14:46 2003                 Quant Results File: TO-15 102803

  Method         : C:\MSDCHEM\1\METHODS\TO-15 102803.M (RTE Integrator)
  Title          : TO-15  Standards for 7 points calibration
  Last Update    : Wed Oct 29 17:20:14 2003
  Response via   : Initial Calibration
```



JJG 11/03/03

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Aerotech Environmental

Date: *17-Nov-03*

CLIENT:	Concordia University	**Client Sample ID:**	((2-45)-2) 5
Lab Order:	03101300	**Tag Number:**	
Project:		**Collection Date:**	10/23/2003
Lab ID:	03101300-04A	**Matrix:**	AIR

Analyses	Result	Limit	Qual	Units	DF	Date Analyzed
TENTATIVELY IDENTIFIED COMPOUNDS IN AIR TICS						Analyst: **JG**
1-Butanol	500	200	T4D2Q1	ppbv	20	11/3/2003
Butanal	700	200	T4D2Q1	ppbv	20	11/3/2003
Butane	1000	200	T4D2Q1	ppbv	20	11/3/2003
Vinyl Acetate	3000	200	T4D2Q1	ppbv	20	11/3/2003
Ethanol	400	200	T4D2Q1	ppbv	20	11/3/2003

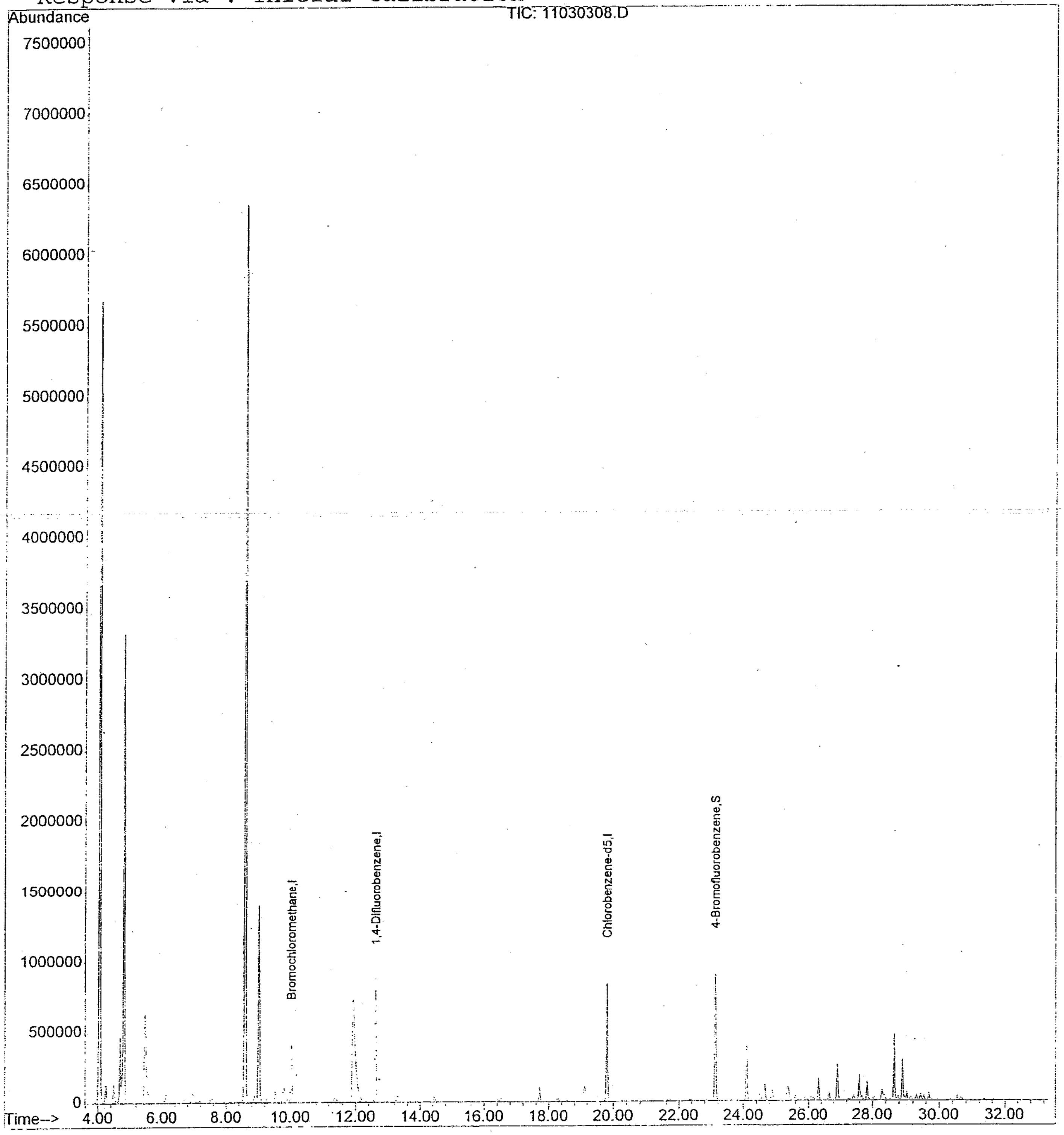
Qualifiers:

ND - Not Detected at the Reporting Limit
J - Analyte detected below quantitation limits
B - Analyte detected in the associated Method Blank
* - Value exceeds Maximum Contaminant Level
S - Spike Recovery outside accepted recovery limits
R - RPD outside accepted recovery limits
E - Value above quantitation range

Quantitation Report (QT Reviewed)

```
Data File : C:\MSDCHEM\1\MS005\110303\11030308.D          Vial: 4
Acq On    :  3 Nov 2003    2:33 pm                     Operator: JJG
Sample    : TO15 03101300-04A X20                      Inst    : MS005
Misc      : IS/SS C-100803-01  10mL                    Multiplr: 1.00
MS Integration Params: RTEINT.P
Quant Time: Nov  3 16:11 2003                Quant Results File: TO-15 102803

Method         : C:\MSDCHEM\1\METHODS\TO-15 102803.M (RTE Integrator)
Title          : TO-15  Standards for 7 points calibration
Last Update    : Wed Oct 29 17:20:14 2003
Response via   : Initial Calibration
```



Precision Analytical Laboratories

Date: *21-Oct-03*

CLIENT: Concordia University
Lab Order: 03080652
Project:
Lab ID: 03080652-02A

Client Sample (Lindol-2) PVC(1810)
Tag Number:
Collection
Matrix: AIR

Analyses	Result	Limit	Qual	Units	DF	Date Analyzed
TENTATIVELY IDENTIFIED COMPOUNDS IN AIR		**TICS**				Analyst: **JG**
1-Butanol	90	200	T4D2	ppbv	20	8/18/2003
1-Chloropropane	30	200	T4D2	ppbv	20	8/18/2003
1-Undecanol	10	200	T4D2	ppbv	20	8/18/2003
2-Butanol	20	200	T4D2	ppbv	20	8/18/2003
Acetone	20	200	T4D2	ppbv	20	8/18/2003
Butanal	200	200	T4D2	ppbv	20	8/18/2003
Butane	300	200	T4D2	ppbv	20	8/18/2003
C4H8 Hydrocarbon	50	200	T4D2	ppbv	20	8/18/2003
Chloromethane	60	200	T4D2	ppbv	20	8/18/2003
Ethyl Acetate	40	200	T4D2	ppbv	20	8/18/2003
Methyl ester acetic acid	20	200	T4D2	ppbv	20	8/18/2003
Propene	80	200	T4D2	ppbv	20	8/18/2003
Unknown Hydrocarbon #1	30	200	T4D2	ppbv	20	8/18/2003
Unknown Hydrocarbon #2	10	200	T4D2	ppbv	20	8/18/2003
Unknown Hydrocarbon #3	10	200	T4D2	ppbv	20	8/18/2003
Unknown Hydrocarbon #4	15	200	T4D2	ppbv	20	8/18/2003
Vinyl Acetate	500	200	T4D2	ppbv	20	8/18/2003
Acetaldehyde	50	200	T4D2	ppbv	20	8/18/2003
Ethanol	100	200	T4D2	ppbv	20	8/18/2003

Qualifiers:

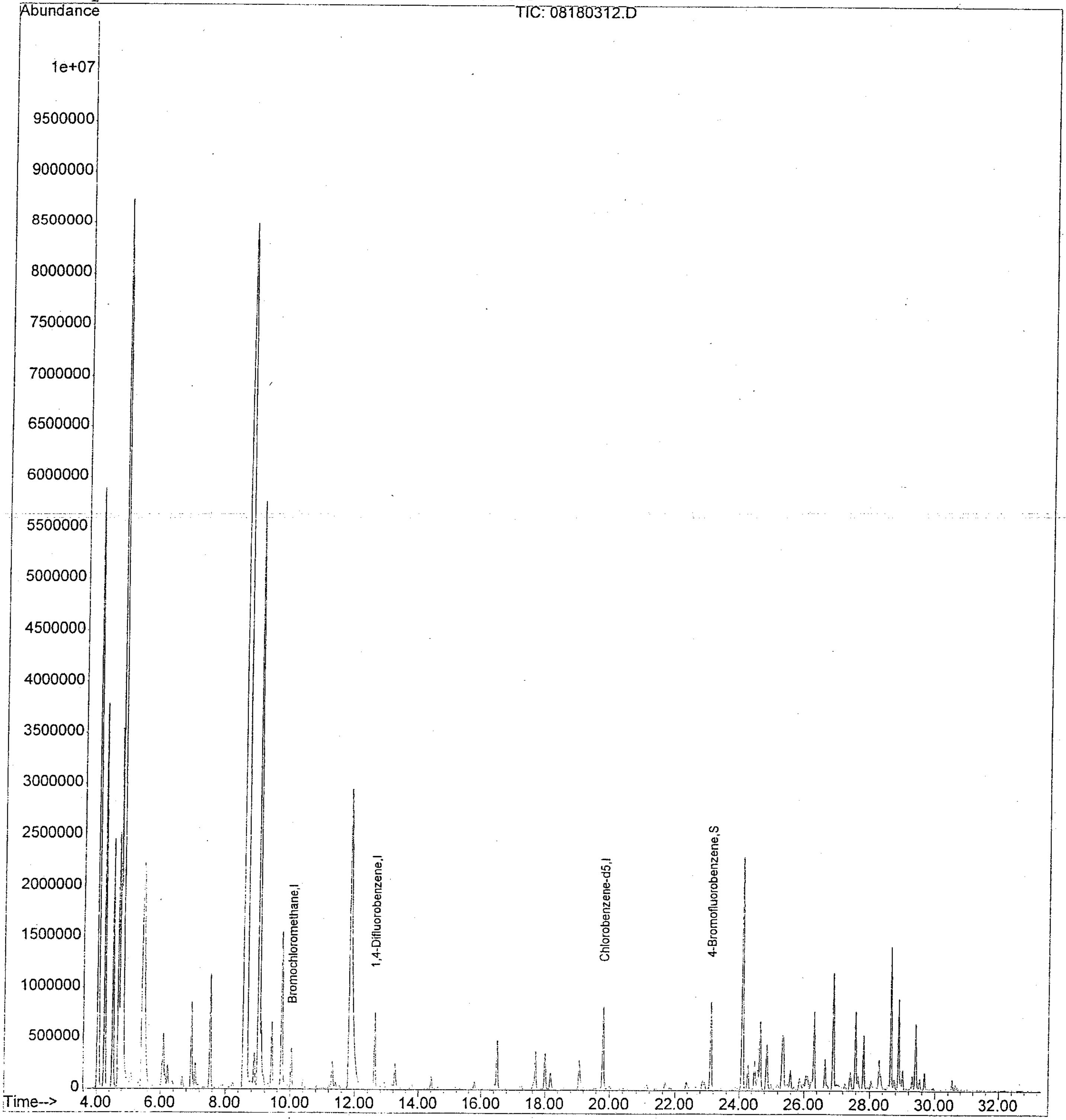
ND - Not Detected at the Reporting Limit
J - Analyte detected below quantitation limits
B - Analyte detected in the associated Method Blank
* - Value exceeds Maximum Contaminant Level

S - Spike Recovery outside accepted recovery limits
R - RPD outside accepted recovery limits
E - Value above quantitation range

Quantitation Report (QT Reviewed)

```
Data File : C:\MSDCHEM\1\MS005\081803\08180312.D          Vial: 7
Acq On    : 18 Aug 2003   5:27 pm                      Operator: JJG
Sample    : TO15 03080652-02A X20                      Inst     : MS005
Misc      : IS/SS C-081503-01  10mL                    Multiplr: 1.00
MS Integration Params: RTEINT.P
Quant Time: Aug 19 13:31 2003                  Quant Results File: TO-15 081503

Method       : C:\MSDCHEM\1\METHODS\TO-15 092303.M (RTE Integrator)
Title        : TO-15  Standards for 7 points calibration
Last Update  : Wed Oct 01 12:16:29 2003
Response via : Initial Calibration
```



Aerotech Environmental

Date: *17-Nov-03*

CLIENT:	Concordia University	**Client Sample ID:**	(Meswell-2) 21
Lab Order:	03101300	**Tag Number:**	
Project:		**Collection Date:**	10/23/2003
Lab ID:	03101300-06A	**Matrix:**	AIR

Analyses	Result	Limit	Qual	Units	DF	Date Analyzed
TENTATIVELY IDENTIFIED COMPOUNDS IN AIR	**TICS**					Analyst: **JG**
1-Butanol	2000	200	T4,D2	ppbv	20	11/3/2003
1-Chloropropane	200	200	T4,D2	ppbv	20	11/3/2003
2-Butanol	200	200	T4,D2	ppbv	20	11/3/2003
Acetone	200	200	T4,D2	ppbv	20	11/3/2003
Butanal	3000	200	T4,D2	ppbv	20	11/3/2003
Butane	6000	200	T4,D2	ppbv	20	11/3/2003
C4H8 Hydrocarbon	500	200	T4,D2	ppbv	20	11/3/2003
Chloromethane	600	200	T4,D2	ppbv	20	11/3/2003
Ethyl Acetate	600	200	T4,D2	ppbv	20	11/3/2003
Methyl ester acetic acid	300	200	T4,D2	ppbv	20	11/3/2003
Propene	500	200	T4,D2	ppbv	20	11/3/2003
Trimethyldecane	200	200	T4,D2	ppbv	20	11/3/2003
Vinyl Acetate	9000	200	T4,D2	ppbv	20	11/3/2003
Acetaldehyde	1000	200	T4,D2	ppbv	20	11/3/2003
Ethanol	2000	200	T4,D2	ppbv	20	11/3/2003

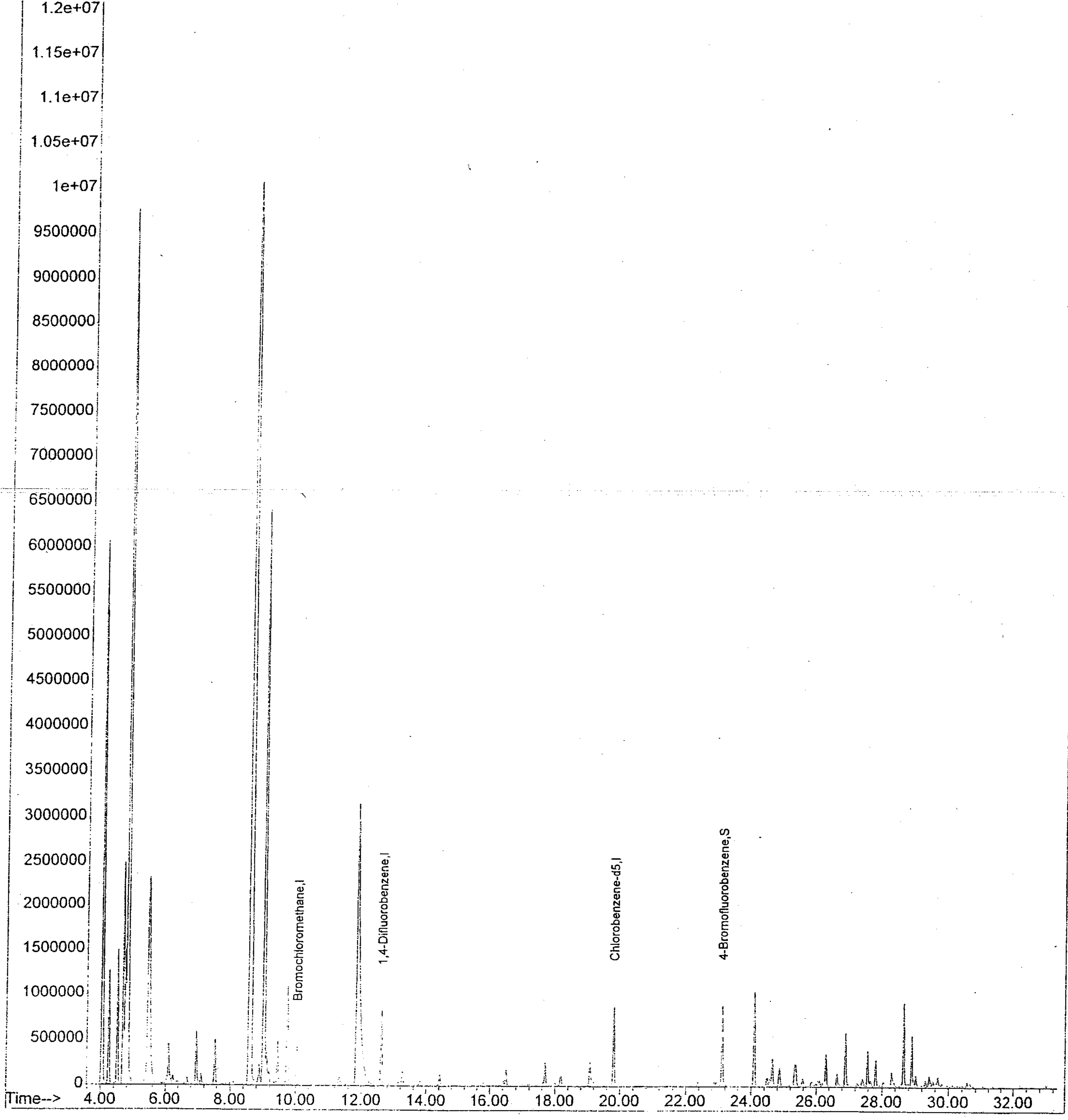
Qualifiers:

ND - Not Detected at the Reporting Limit
J - Analyte detected below quantitation limits
B - Analyte detected in the associated Method Blank
* - Value exceeds Maximum Contaminant Level
S - Spike Recovery outside accepted recovery limits
R - RPD outside accepted recovery limits
E - Value above quantitation range

```
                    Quantitation Report    (QT Reviewed)

  Data File : C:\MSDCHEM\1\MS005\110303\11030310.D         Vial: 6
  Acq On    :  3 Nov 2003   4:00 pm                    Operator: JJG
  Sample    : TO15 03101300-06A X20                    Inst    : MS005
  Misc      : IS/SS C-100803-01  10mL                  Multiplr: 1.00
  MS Integration Params: RTEINT.P
  Quant Time: Nov  3 16:37 2003                 Quant Results File: TO-15 102803

  Method          : C:\MSDCHEM\1\METHODS\TO-15 102803.M (RTE Integrator)
  Title           : TO-15  Standards for 7 points calibration
  Last Update     : Wed Oct 29 17:20:14 2003
  Response via    : Initial Calibration
```



11/03/03