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Plasticized Lignin-PVC Blends for Flooring

Hui Zhu

A Thesis

in

The Department

of

Building, Civil & Environmental Engineering

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ABSTRACT

Plasticized Lignin-PVC Blends for Flooring

Hui Zhu

The present research, studies the feasibility of replacing part of the PVC in the formulation of flooring materials by lignin, an abundant and renewable natural polymer. The utilization of lignin is aimed to develop more cost-effective flooring materials with appreciable mechanical properties, to decrease their susceptibility to microbial attack, to decrease the amount of VOC's release, and to explore a market for lignin.

To evaluate the role of lignin, a series of flooring materials with different proportions of lignin are obtained, based on the investigation into the use of plasticizers for reducing the degree of association existing within lignin macromolecules. The mechanical and thermal properties, as well as the processibility of the obtained materials are tested.

As a result of the present study, an alternative flooring material is attempted with appreciable properties, such as Young's modulus, tensile strength at break and at yield, elongation at break, as well as impact and hardness tests. In the meantime, the most suitable plasticizer for the specific formulation is determined. The economic advantage is also evaluated.

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160	Butyl benzyl phthalate/Santicizer 160
2-45	Di-ethylene glycol dibenzonate/Benzoflex 2-45
δ	Solubility parameter
ΔF_m	Free energy of mixing
ΔH_m	Enthalpy of mixing
ΔS_m	Entropy of mixing
ABP	Alkyl benzyl phthalate/Santicizer 261
AL	Alcell lignin
ASTM	American society of testing materials
Ba	Barium
Ca	Calcium
$CaCO_3$	Calcium carbonate
CaSt	Calcium stearate
Cd	Cadmium
CED	Cohesive energy density
Cl	Chlorine
C=O	Carbonyl
DAP	Di-alphanyl phthalate
DBS	Di-butyl sebacate
DBTL	Di-butyltin dilaurate

DIOP	Di-isooctyl phthalate
DMA	Dynamic mechanical analyzer
DOP	Di-ethyl hexyl phthalate
DOS	Di-octyl sebacate
DSC	Differential scanning calorimetry
H	Hydrogen
h.	Hour
K-value	Fikentscher constant
Lindol	Tri-cresyl phosphate
min.	Minute
M_n	Number average molecular weight
MPa	Mega-pascal
M_w	Weight average molecular weight
MW	Molecular weight
OCH_3	Methoxyl
OH	Hydroxyl
PE	Polyethylene
pH	Potential of hydrogen
phr	parts per hundred parts resin
PU	Polyurethane
PVC	Poly(vinyl chloride)
RH	Relative humidity
T_g	Glass transition temperature

TiO_2	Titanium dioxide
UV	Ultraviolet
VC	Vinyl chloride
VC-VAc	Vinyl chloride – vinyl acetate
VOC's	Volatile organic compounds
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Poly(vinyl chloride), PVC, has a wide variety of applications. It is second in volume only to polyethylene, with sales in North America of 6.22 billion kg in 1995 [1]. Roughly 64% of PVC resin production was used for construction in U. S. market in 1995 [2]. Indoor applications include wall coverings, resilient flooring, coating, blinds, and profiles for windows and doors. The cost and performance of PVC make it among the most attractive replacement for wood and aluminum.

PVC has been used as the principal component for resilient flooring since 1934, when vinyl flooring was first introduced [3]. Nowadays, many types of vinyl flooring are available in both sheet and tile forms.

Lignin, a second main material used in this study, is a natural polymer which together with cellulose form the structural components of trees and various plants. On average, wood contains about 25 wt-% lignin. The large quantities of lignin produced annually by the pulp and paper industry are used almost exclusively as fuel to generate energy.

Considering the abundance of lignin, its chemical composition, and its functional characteristics in plants, it appears reasonable to examine the contribution lignin can make to the properties of its blends with PVC for vinyl flooring composites.

The objectives of the research program include the development and evaluation of a new flooring material as alternative to existent plasticized flooring by replacing part of the PVC with lignin.

Utilization of lignin in PVC flooring formulations was undertaken for several aims:

- To develop more cost-effective flooring materials with appreciable mechanical properties;
- To decrease the susceptibility to microbial attack of flooring formulations;
- To cultivate a market for lignin.

In order to attain these objectives, calcium carbonate ($CaCO_3$) filled PVC flooring formulations with an organosolv lignin, Alcell lignin (AL) and different plasticizers were obtained and studied in the program. AL is produced through a new delignification process, which is milder and less polluting than traditional sulphite or sulphate processes. The effect of plasticizer type and level on the glass transition temperature (T_g) of AL was determined by differential scanning calorimetry (DSC). The testing of mechanical properties for the flooring materials was also carried out, namely, tensile testing, hardness testing, and impact testing.

1.2 ORGANIZATION OF THE THESIS

The next chapter of the present thesis reviews some theroretical background related to the research. Knowledge of PVC, lignin, and additives which are used for PVC formulation, as well as plasticizers for lignin, is presented. Introduction of flooring materials, processing procedure and standard tests are also addressed. In addition, certain information regarding polymer blends is provided too.

Chapter 3 presents the detailed research program. In this chapter, different phases of the program, including the theoretical logic, formulations, experimental procedures, as well as testing instruments are described and pictured.

In Chapter 4, all the experimental results are presented in the order of different phases of the program. The analysis and explanation of the results of the materials' thermal, mechanical properties and processibility are provided. The performance properties will aid to evaluate these formulations from a practical standpoint. Furthermore, the economic aspect is assessed in comparison to those without lignin.

Finally, conclusions and suggestions for further research on this topic are provided in Chapter 5.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 FLOORING AND DIFFERENT MATERIALS FOR FLOORING

Materials for floor coverings can be classified into different types such as resilient flooring, carpeting, wood, ceramic and stone [3].

The resilient flooring is featured by its ability to deform and recover from the compressive forces caused by the dynamic action of footsteps, cart wheels, and casters, or the static load of appliances and furnishings. The family of resilient flooring includes such materials as vinyl flooring (mainly based on PVC), rubber flooring, linoleum, and asphalt tile.

Linoleum was introduced in 1864 in England and this was essentially the beginning of the resilient flooring industry. Linoleum is based on a binder system of oxidized drying oils, resins, and gums, filled with wood flour, whiting, and sometimes cork dust. Although it has excellent wearing characteristics, linoleum suffers from degradation by alkaline hydrolysis and is, therefore, unsuited to applications where alkaline moisture is present, e.g. on concrete subfloors in contact with the ground. It is also damaged by frequent washing and stripping of wax polish. Due to these factors, linoleum is no longer produced in the United States.

In those applications for which linoleum is not suitable, asphalt tile is used. This product is based on asphalt binders or, for lighter colored tiles, coumarone indene or hydrocarbon resins, and is filled with asbestos and limestone. Asphalt tile is essentially obsolete today and is produced in the United States by only one manufacturer [3].

Linoleum and asphalt tile have been replaced almost completely by resilient flooring based on PVC or, to a lesser extent, rubber.

Generally, the applications for resilient flooring could be divided into two classes, residential and commercial.

With respect to the residential applications, resilient flooring is used primarily in kitchens and bathrooms, with a sizable quantity used also in foyers and family rooms. U.S. Department of Commerce estimated that, of total area of existing residential floor space in 1985 in the United States, 17.8% was covered by resilient ones, either in sheet or tile form.

In terms of the commercial applications, the uses of resilient flooring include those in mercantile, health care, education, light-industry, office, and bank buildings. It was also reported that in 1985, total shipments of hard surface flooring were 5.3×10^8 m^2, and 4.6×10^8 m^2 of resilient flooring [3].

2.1.1 VINYL FLOORING

Although rubber flooring is used on a significant scale, the dominant types of resilient flooring manufactured today are based on PVC.

This material has several attributes that make it apt for flooring applications. For instance, it can tolerate high levels of inert filler, can be effectively plasticized to a wide range of flexibility and it is inherently fire resistant.

Vinyl or PVC flooring was introduced by Dynamit Nobel AG in 1934 under the trade name of *Nipolan*. Today, many types of vinyl flooring are available in both sheet and tile forms.

2.1.2 RAW MATERIALS FOR VINYL FLOORINGS

PVC is one of the most versatile and important polymers produced in the world. On the other hand, it is also one of the least stable polymers. The successful and economical use of PVC in flooring is only possible with the addition of stabilizers and other additives. Following is the brief description of the resin and the additives necessary in producing the vinyl flooring.

2.1.2.1 PVC

PVC is so versatile that it can be compounded for a wide range of properties and used in a wide variety of markets. Most of the products are durable goods and have long life spans. The major uses of PVC are pipe and fittings, window and door frames, flooring materials, film and sheet, wire and cable insulation, automotive parts, adhesive sand coating [2].

Table 2.1 lists PVC's principal usage in the United States in 1995. European uses for PVC are illustrated in Table 2.2.

Table 2.1 Principal uses for U.S. markets in 1995 [1].

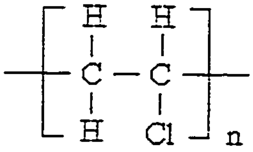
Market	Metric tons
Construction	
Flooring	120,000
Pipe and conduit	2,070,000
Wire and cable	180,000
Siding	640,000
Windows and doors	140,000
Extrusions	240,000
Packaging	
Bottles	80,000
Extrusions	160,000
Calendering	390,000
Custom moldings	50,000
Paste processes	100,000
Texiles and coating	70,000
Exports and resale	850,000
Other	60,000
Total	5,360,000

Table 2.2 European uses for PVC by market share [4].

Market	Market share
Building and construction	53%
Packaging	16%
Wire cable and electrical	9%
Leisure	4%
Transport	3%
Furniture/office equipment	3%
Clothing and footwear	3%
Domestic applications	1%
Other uses	8%

Through Tables 2.1 and 2.2, it can be seen that the applications of PVC in building and construction industry are overwhelming. PVC is now – and probably will remain for some time – the dominant resin used in building and construction industry. Its cost and performance make it among the most attractive replacements for wood and aluminum [5].

PVC is one of the four major, highest-volume thermoplastics; its chemical structure is:



$$\left[-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \overset{\displaystyle H}{\underset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}} - \right]_n$$

where n, the degree of polymerization, or more specifically, the number of repeating units in the molecular chain, ranges between 500 and 3500. However, for a commercial PVC, the average value of n varies from 500 to 1500 [1].

PVC is produced by polymerization of vinyl chloride (VC) by free-radical mechanism, mainly in suspension and emulsion, but bulk and solution processes are also employed to some extent. Suspension polymerization is used for an estimated 82% of total PVC production in U.S., whereas around 10-15% is by emulsion [6].

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.

The most important parameters of the emulsion process are:

- the ratio of monomer to aqueous phase;
- the type and quantity of the emulsifier;
- the type and quantity of the initiator;
- temperature; and
- pH.

Depending on factors such as the type of equipment, type of emulsifier, additives for latex stabilization and expected PVC properties, the ratio between phases (monomer-aqueous phase) varies in the range from 1:1 to 1:2.3. If this ratio is brought to 1:1 or lower, the latex stability decreases and the polymerization slows down. The temperature affects the K-value (Fikentscher constant) which characterizes the degree of polymerization of PVC.

The polymerization temperature is selected on the basis of decomposition kinetics of the particular initiator used and the desired molecular weight of PVC [7].

Suspension polymerization is carried out also in aqueous medium in presence of a suspension agent and a monomer soluble initiator. Methylcellulose or other substances like gelatine, PVA, maleic anhydride-vinyl-acetate copolymers, ethylcellulose, carboxymethyl cellulose and alginates, are used as suspension agents. Polymerization takes place under nitrogen; the stirring rate for the normal compact type is 80 rpm. Polymerization reactors are capable of withstanding pressures of 15 atm (1500 KPa) or above if low molecular weights (MW) are expected. For high MW, pressures are 5-10 atm (500-1000 KPa). The thermal regime and polymerization time depend on the kind of PVC wanted.

Most plants for the production of PVC suspensions run discontinuous for polymerization and continuous for the drying operation, and are able to produce two different, especially from a morphological point of view, PVC's, one called 'compact normal', and the other one 'dry blend'. PVC compact normal is crystalline and composed of spherical particles with superficial adsorption of the plasticizer. The dry blend type is based on amorphous agglomerated particles with a capillary structure which is able to absorb the plasticizer strongly so that the final compound looks dry.

Taking into account the different morphologies of the particles, the normal compact type is recommended to be processed into rigid items, and the dry blend type into plasticized articles.

For PVC, the structural units of the material usually link in a head-to-tail fashion, shown as $-CH_2CHClCH_2CHCl-$, resulting in 1,3 positions for the chlorine atoms (Cl) [6].

PVC molecular weight is one of the characteristics which determines the physical-mechanical properties of the end product, its compatibility with plasticizers and the rheological behavior of the melt. PVC for different applications has a MW in the range of 60,000 to 200,000.

Commercial PVC could be regarded as essentially amorphous even though the crystallite (small crystals) content is about 2-10%. A crystalline structure refers to one where the molecules are shaped so they are packed very tightly, nearly perfectly parallel. The existence of crystals prevents polymer molecules from slipping by each other and act to tightly bind the molecules together. It takes a high level of melting energy to destroy crystals and allow a molecule to flow.

PVC is a material with a wide range of rigidity or flexibility [8]. Although unplasticized PVC is rigid, whereas the plasticized PVC is tough, flexible, and even rubbery at high plasticizer loadings, the plasticized PVC has the same structure as rigid one, except that plasticizer enters in the amorphous phase of PVC, making the molecules more elastomeric [9].

The presence of tertiary carbon as well as irregularities in the PVC chain affects its thermal stability. Its microstructure with a Cl situated on each alternate carbon atom of the polymer chain, leads to a very rigid and relatively tough plastic. However, with the addition of a plasticizer, the dipole bonding, between the polymer chains is much reduced, leading to an increased freedom of chain movement and thus to a flexible material. Thermal stabilizers, UV absorbers, lubricants and processing aids are added for processing and uses and the existence of these additives make PVC's high volume production possible. In other words, additives help overcome the limitation of processing and use for PVC.

2.1.2.2 HOMOPOLYMER & COPOLYMER

Homopolymer is the polymer with the macromolecule consisting of a single type of repeating unit while copolymer is material produced by polymerization of two or more different monomers [10].

In the case of PVC, about 90% of the PVC produced is used in the form of a homopolymer, the other 10% as copolymers and terpolymers [7]. Vinyl chloride can be copolymerized with a variety of monomers. Vinyl chloride-vinyl acetate copolymer (VC-

VAc copolymer) is the most important commercial product, whose vinyl acetate content ranges from 3 to 20 wt-%.

Copolymers are used in place of PVC homopolymer because the internal plasticizing effect of the VAc units make them easier to process at a lower temperature in conventional equipment. The VAc also gives pigment wetting characteristics when high levels of filler, are to be used [11].

As a general rule, VC homopolymers are used primarily in sheet flooring and less in vinyl tiles, whereas vinyl composition tiles usually contain copolymers of VC-VAc.

2.1.2.3 HEAT STABILIZERS

Heat stabilizers are used primarily to inhibit thermal degradation of PVC during processing. At elevated processing temperatures, PVC is subject to dehydrochlorination which will lead to an "unzipping" effect and results in degradation. To make the problem more complicated, the HCl given off during dehydrochlorinaton is a catalyst to further dehydrochlorinaton. Heat stabilizers for PVC must essentially perform two functions. First, they are added to prevent the dehydrochlorinaton from occurring initially. Secondly, the stabilizers are intended to react with the HCl given off, thus to slow the autocatalytic effect.

Some stabilizers perform both functions with a single product while some other stabilization systems require two or more additives to fulfill the entire task.

The development of effective heat stabilizers is one of the major breakthroughs which allows PVC to be commercialized in such a wide variety of applications.

The types of heat stabilizers available for PVC include organotin compounds, mixed metal systems consisting of barium-cadmium (Ba-Cd), barium-zinc (Ba-Zn) or calcium-zinc (Ca-Zn), as well as lead-based systems. The type of heat stabilizer used depends on the applications. Organotin stabilizers are the common compounds used for PVC products. The tin content varies depending on the end-use. It can contain sulfur, such as the mercaptides, or not, such as the maleates.

The stabilizers most commonly used in vinyl flooring are soaps of barium, calcium, and zinc, and certain organotin compounds. Lead and cadmium soaps have been used in the past but, although very effective stabilizers, are not widely used today because of environmental concerns and their tendency to form colored sulfides (a phenomenon referred to as sulfur staining). Epoxidized oils, such as soybean oil, tallate esters, and other partially unsaturated oils, are frequently used as costabilizers with the primary organometallic compounds [2].

2.1.2.4 PLASTICIZERS

Plasticizers are low molecular weight substances which, when added to a polymer, cause an increase in flexibility and workability by reducing intermolecular forces. In the meantime, its T_g is lowered.

As mentioned in Section 2.1.2.1, PVC is particularly well-suited for plasticization. It can thus be obtained in a wide range of stiffness from rigid and somewhat brittle, to very flexible rubber-like products. A few plasticizers impart specific properties for particular applications.

As stated in Section 2.2.1, PVC has around 2-10% crystallinity. The crystals are surrounded by amorphous areas which are tightly bound by strong polar attractions between chlorine (Cl) and hydrogen (H) atom in proximity. Given opportunity (compounding) and motivation (heat and shear), a plasticizer can penetrate the amorphous areas of rigid vinyl and disrupt intermolecular attractions. When enough plasticizer has entered the matrix, a general relaxation ensues and partial mobility is imparted to the polymer chain. At the processing temperature of about 150°C, molecular mixing occurs in a short period of time to give products of greater flexibility [2].

A good plasticizer should have the following general requirements:

- solvency and compatibility;
- efficiency in imparting a desirable property or properties (usually softness and flexibility); and
- permeanence [12].

The addition of plasticizer to PVC changes its mechanical properties. It was demonstrated that the addition of small amounts of plasticizer could cause changes of all mechanical properties[13]. For example, as depicted in Figure 2.1, after adding some certain amount of di-ethyl hexyl phthalate (DOP), it was observed that impact strength went down until 17% were added; then it started to go back up. Tensile strength increased until 8% were added and then decreased [14].

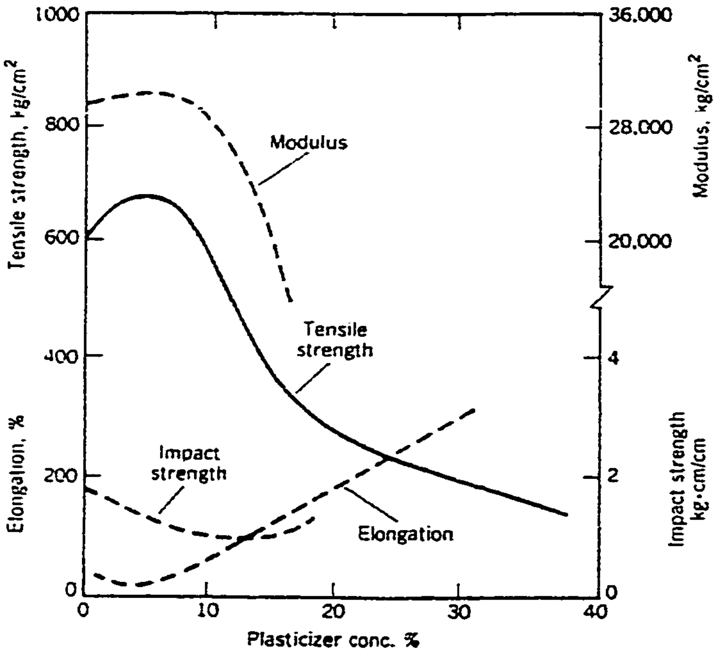


Figure 2.1 Mechanical properties of PVC plasticized with various concentrations of DOP [14].

Plasticizers are essentially nonvolatile solvents for PVC. The choices of commercial plasticizers are extremely abundant, and resource to the experience of polymer manufactures and plasticizer suppliers is advisable to obtain best results at optimum cost [15].

Phthalates prepared from alcohols with about eight carbon atoms are by far the most important class and constitute more than 70% of plasticizers used. For economic reasons, di-isooctyl phthalate (DIOP), DOP, and the phthalate esters of the C7-C9 oxo-alcohols, often known as di-alphanyl phthalate (DAP), are used. DIOP has somewhat less odor, whereas DAP has the greatest heat stability. Di-butyl phthalate and di-isobutyl phthalate are also efficient plasticizers [2].

Phosphate plasticizers are generally used where good flame resistance is required. These materials, however, are toxic and give products with poor low-temperature resistance.

For applications where it is important to have a compound with good low-temperature resistance, aliphatic ester plasticizers are of great value. Di-butyl sebacate (DBS), di-octyl sebacate (DOS), and more commonly, cheaper esters of similar effect derived from mixed acids produced by the petrochemical industry are used.

2.1.2.5 LUBRICANTS

The main function of the lubricants is to prevent sticking of the compound made of PVC and additives to processing equipment. Therefore, lubricants control the frictional and adhesive properties of plastics during processing and in service. Furthermore, lubricants improve the dispersion of fillers and pigments in plastics and better dispersion could improve flow limits that which means better processing as well as material properties.

Lubricants are often classified as external or internal. The external lubricants have limited compatibility such that they will sweat out during processing to form a film between the bulk of the compound and the metal surfaces of the processing equipment. They are considered to retard fusion or to promote metal release. Calcium stearate and lead stearate are often used as external lubricants.

Internal lubricants are mainly intended to improve the flow of the melt, or to reduce the melt viscosity. Unlike external lubricants they are reasonably soluble in PVC and have little effect on fusion. Lubricants are more like plasticizers in their behavior at processing temperatures, whereas at room temperature, this effect is negligible. Wax derivatives, glyceryl monostearate, and long-chain esters such as cetyl palmitate are used as internal lubricants.

2.1.2.6 FILLERS

Fillers are commonly employed in opaque PVC compounds to improve strength, to reduce cost and to improve dimensional stability, to increase the hardness of PVC flooring compound, to improve electrical insulation properties, to control the gloss, and to reduce tackiness of highly plasticized compounds.

Various calcium carbonates are most commonly used fillers for PVC, especially for PVC flooring. Calcium carbonates ($CaCO_3$) are mineral fillers. They are supplied in five particulate forms: water-ground, dry-ground, ultra fine ground, precipitated, and surface treated [16]. The advantages of $CaCO_3$ over other mineral fillers for use in PVC include: lower cost, non-toxicity, transparency, low moisture content, easy coating ability, and the acid-acceptance capability providing a degree of secondary stabilization for PVC during processing. In the meantime, $CaCO_3$ helps PVC flooring improve its hardness [17].

2.1.2.7 PIGMENT

Many pigments are available commercially for use with PVC. Pigment selection should be based on the pigment's ability to withstand process conditions, its effect on stabilizer and lubricant, and its effect on end-use properties.

Most often used pigments are carbon black and titanium dioxide (TiO_2).

2.1.2.8 UV ABSORBERS

UV (ultraviolet) radiation of wavelength 310nm is often considered the most damaging to PVC. This range of wavelength excites the macromolecules of PVC in the sense of imparting excess energy sufficient to break bonds in the molecular chains. As a result, the free radicals formed initiate and participate in the degradation process which is accelerated by the presence of oxygen.

The UV-protective additives which are frequently included in PVC for outdoor use afford additional and complementary protection. They absorb and dissipate the incident UV radiation, essentially before it can initiate degradation.

Carbon black and TiO_2 widely used as pigments for plastics, have a light stabilizing effect on many polymers including PVC. They are often referred to as "light screens". Each compound functions as a physical barrier to both UV and visible radiation. Carbon black absorbs the radiation over both these wavelength ranges and emits the energy in the infrared region. It is also believed to act as an antioxidant by capturing free radicals. TiO_2 has some UV absorption capacity but its screening action is principally due to reflection and scattering of radiation (infrared, visible and UV).

Except for the additives discussed before, impact modifiers and processing aids, foaming agent, antimicrobials, flame retardants, antiblocking and extenders are other additives that can be added to PVC to tailor some desired properties.

2.1.3 FORMULATIONS FOR VINYL FLOORING

As mentioned in Section 2.1.2, PVC resin and additives are used in formulations for flooring materials. Table 2.3 is the illustration of typical formulations for some PVC floorings.

Table 2.3 Typical formulations for some PVC flooring products [3].

Ingredients	Formulation, parts by weight per 100 parts resin				
	A	B	C	D	E
PVC resin	100	100	100	100	100
Plasticizer(s)	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.

Among these, formulation C is the choice for this research, the particular formulations will be discussed in Chapter 3.

The most widely used vinyl flooring material is produced by calendering compounds based on VC-VAc copolymer filled with $CaCO_3$. Tables 2.4 through 2.6 show the mechanical, thermal, physical and processing properties, respectively, of typical PVC flooring filled with $CaCO_3$.

Table 2.4 Mechanical properties of typical $CaCO_3$-filled PVC flooring [18].

Tensile strength at break, MPa	7-24
Elongation at break, %	200-400
Compressive strength (rupture or yield), MPa	7-12

Table 2.5 Processing properties of typical $CaCO_3$-filled PVC flooring [18].

Processing temperature range, °C	140-176
Molding pressure range, MPa	7-14
Compression ratio	2.0

Table 2.6 Thermal and physical properties of typical $CaCO_3$-filled PVC flooring material [18].

Thermal conductivity, 10^{-4}cal.-cm/sec-cm^2-°C	3-4
Specific gravity,	1.3-1.7
Water absorption (0.32 cm thick specimen), % 24hr	0.5-1.0
Dielectric strength (0.32 cm thick specimen), V/mil	250-300

2.1.4 TESTS PERFORMED ON VINYL FLOORING MATERIALS

Tensile and elongation behavior of virgin PVC and composites are evaluated according to ASTM D 638. Tensile strength, elongation and tensile modulus measurements are among the most important indications of strength in a material and are the most widely specified properties of plastic materials. Tensile test, in a broad sense, is a measurement of the ability of a material to withstand forces that tend to pull it apart, and to determine to what extent the material stretches before breaking. Tensile modulus, an indication of the relative stiffness of a material, can be determined from a stress-strain diagram. Different types of plastic materials are often compared on the basis of tensile strength, elongation, and tensile modulus data [19].

Impact resistance is important for handling, installation, and end-use of the composite. It is the ability of a material to resist breaking under a shock loading, or the ability to resist the fracture under stress applied at high speed. The impact strength of polymeric materials is a measure of toughness: the higher the impact strength, the higher the toughness. The notched Izod impact procedure given in ASTM D 256 is commonly used to study this property for both resins and composites. The objective of the Izod impact test is to measure the relative susceptiblility of a standard test specimen to the pendulum-type impact load. The results are expressed in terms of kinetic energy lost by the pendulum in order to break the specimen. This one used in the test is usually notched. The reason for notching the specimen is to provide a stress concentration area that promotes a brittle rather than a ductile failure. A plastic deformation is thus prevented in the specimen [20].

Hardness is defined as the resistance of a material to deformation, particularly permanent deformation, indentation, or scratching.

Resistance to abrasion is an important consideration. Abrasion is roughening or scratching of the surface layer due to removal or displacement of material when hard particles slide or roll across the surface under pressure. The ASTM D1044 standard test is used to study abrasion resistance.

Exposure to ultraviolet (UV) light can lead to fading and yellowing of the flooring tiles over time due to a photodegradation process. The ASTM D5208 test is used to study resistance to discoloration upon exposure to UV light [22].

The thermal behavior of the flooring material is usually described by its T_g which can be determined by using either differential scanning calorimetry (DSC) or a dynamic mechanical analyzer (DMA).

In addition, the emission of volatile organic compounds, VOC's should be evaluated over the use of the vinyl flooring materials.

To study the coatability of the composite for flooring materials covered with a layer of polyurethane (PU) wear, dynamic contact angles between the wear layer and composite should be tested.

2.1.5 PROCESSING OF VINYL FLOORING MATERIALS

A number of steps are required for the processing of PVC-based flooring material.

The first step is compounding, or in other words, the mixing of raw materials in batch mixers, or in screw extruders. Single- and twin-screw extruders, as shown in Figures. 2.2 and 2.3, respectively, are the systems most often specified. These two kinds of extruders offer more consistent product quality and could be operated at lower costs. Raw materials such as PVC, fillers and additives in pellet or powder form enter a twin-screw extruder. The reason for choosing this type of extruder is because PVC is a shear-sensitive material that must be processed under carefully controlled conditions. The function of the extruder is to convert solid feedstock into a homogeneous melt and to pump it through a die at a uniform rate. Following the die, a train of equipment handles the molten extrudate in order to ensure that it cools to precisely the right shape and with the required molecular orientation.

The second operation step is calendering. A fast production of the sheet occurs in this stage. Material from the extruder is fed between two counter-rotating, heated cylinders or rolls and squeezed in the wedge as shown in Figure 2.4. A layer of a thickness corresponding to the shortest distance between the roll surfaces, or the gap, is formed through the nip, and entrained on the surface of one of the rolls. An excess of material forms the bank. The plasticated material undergoes very severe deformations in the nip region, and the viscoelastic character of polymeric materials imposes limitations on the speed of deformation and on the thickness of the sheet formed. The material normally goes through one or more additional roll nips, where the gap becomes progressively smaller, and the roll temperature becomes progressively lower, in order to attain desired sheet thickness and a solid-like consistency in the product.

The final step is stamping if flooring tiles are needed. Flooring sheet produced from the calendering are sectioned by knives into the required dimensions. The usual dimensions for flooring tiles are squares of 30.5cm×30.5cm (1ft×1ft) with thickness around 2.5mm (≈0.100 in.) [11].

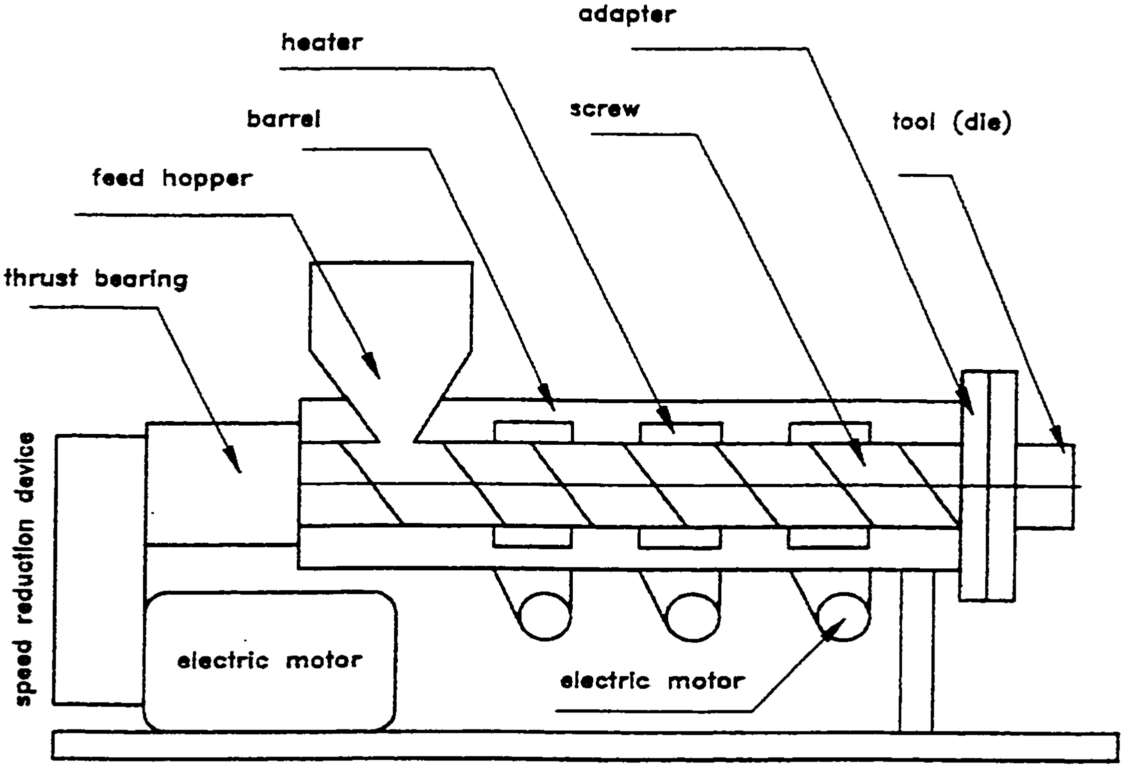


Figure 2.2 Single screw extruder [11].

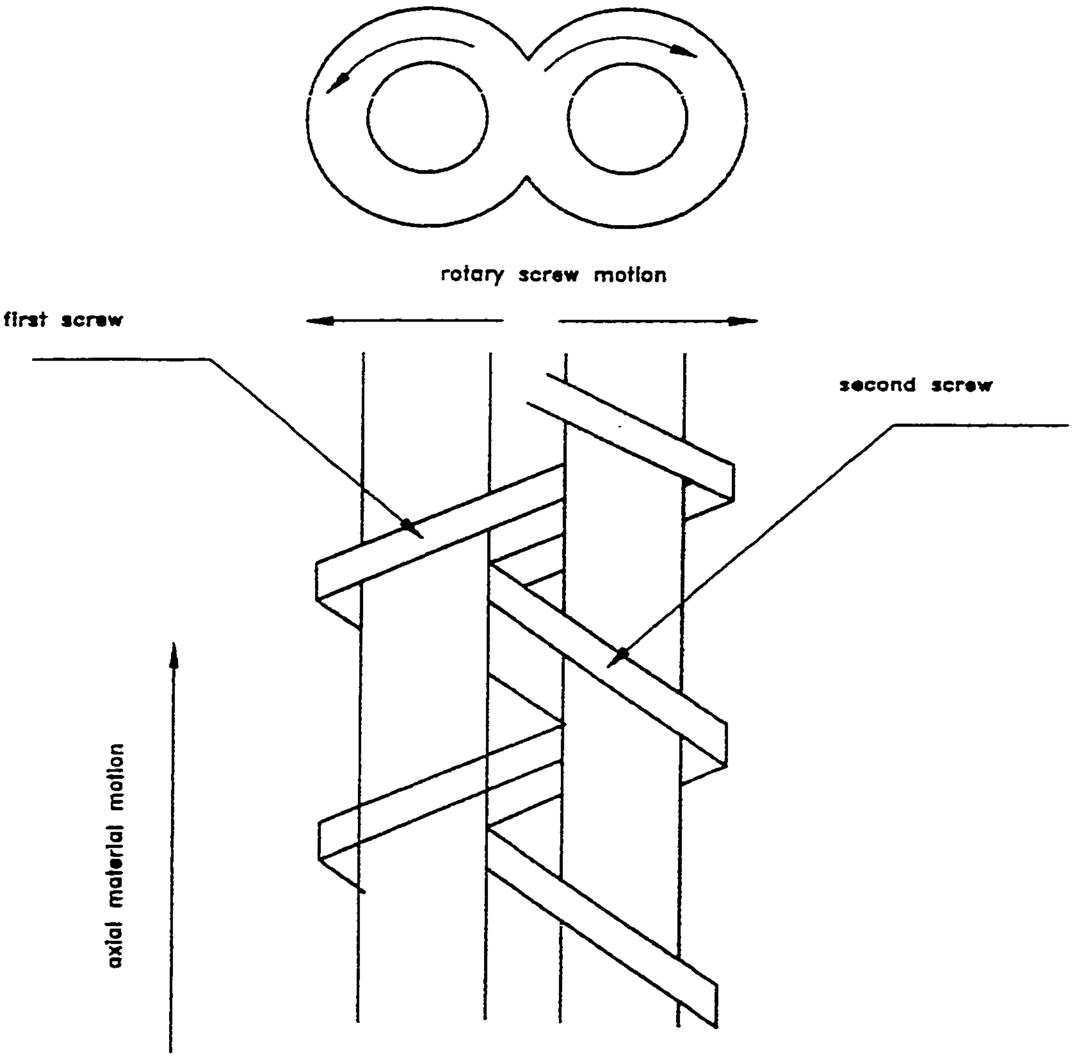


Figure 2.3 Twin screw extruder [11].

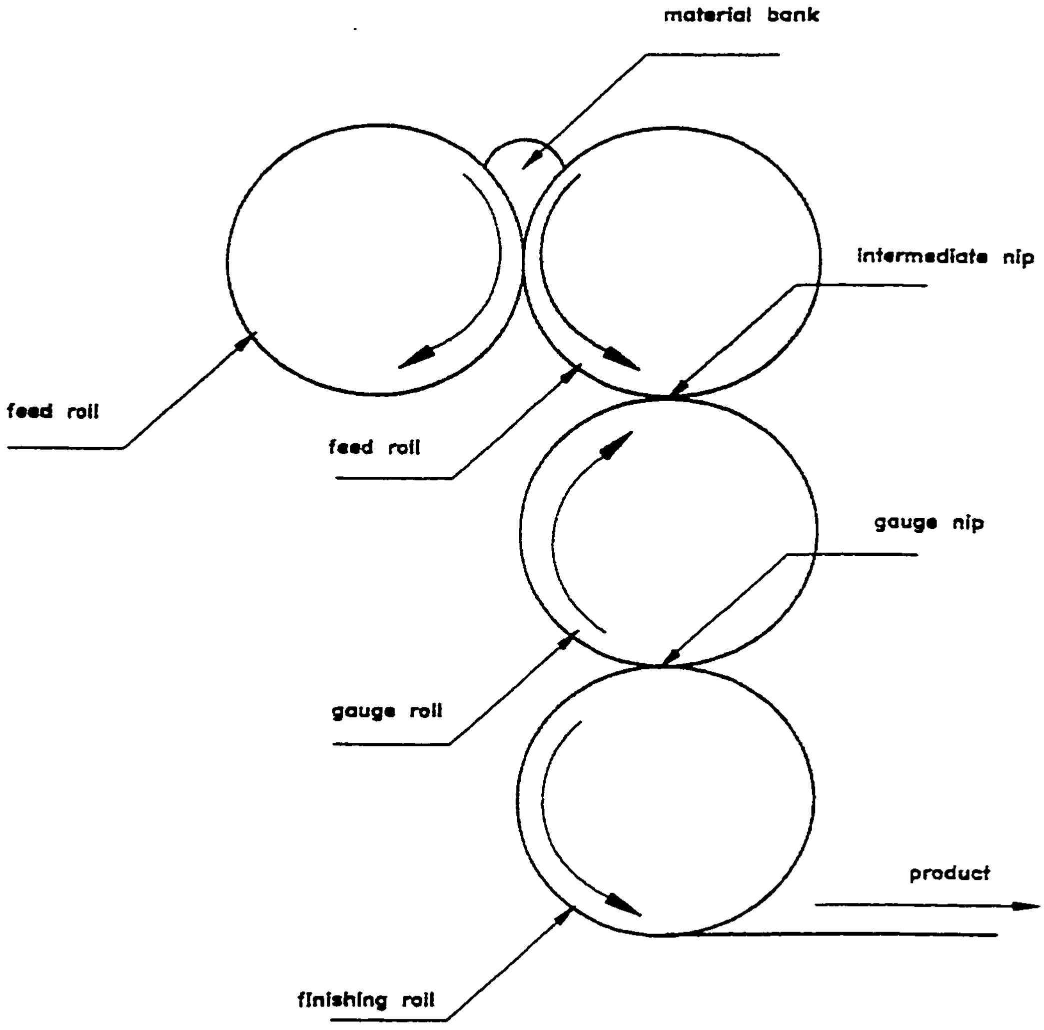


Figure 2.4 Calendering equipment [11].

2.2 POLYMER BLENDS

2.2.1 INTRODUCTION

Various efforts have been made to develop new materials having good balance of efficiency and cost, or more specifically, materials that performing better with lower prices than existing polymers since the 1970's [23]. As a result, polymer blends (or polyblends), which are intimate physical mixtures of two or more polymers, have become an important way for both scientific investigation and commercial product development. Today, polymer blending is one of the powerful and inexpensive ways of tailoring performance using readily available base polymers.

By polymer blending, the aim of the production of good-performance materials at a reduced cost or the modification of some particular properties can be achieved. Thanks to the infinite blending possibilities, the ability to use existing or more flexible processing equipment, and the capacity to combine expensive polymers with ordinary and abundant ones, polymer blending seems to be an ideal way of future supply of materials.

With no covalent bonds between partners, polyblends are the mixtures of two or more polymers of different chemical compositions. In polymer blends, as in interpenetrating polymer networks, the components are different macromolecular compounds, which differentiates them from block and graft copolymers [24, 25, 26].

2.2.2 COMPATIBILITY OF POLYMERS IN BLENDS

Polymers in blends are grouped into incompatible (immiscible, heterogeneous), semi-compatible, or compatible (miscible, homogeneous) blends. When two distinct phases remain upon mixing, the polymers in blend are considered incompatible. In semi-compatible polymer blend, one of the components could be dispersed in a continuous matrix of the other. In compatible polymer blends, and due to mutual solubility, a mono-phase system is formed. However, true compatibility is rare [25].

In the thermodynamic definition, miscibility depends on the free energy of mixing (ΔFm). This may be written as:

$$\Delta F_m = \Delta H_m - T \cdot \Delta S_m$$

where ΔH_m is the enthalpy and ΔS_m the entropy of mixing [25, 27]. When small molecules of different liquids are mixed, the increase in randomness and enthalpy is very high and outweights the endothermic heat of mixing. The result is negative free energy and thus miscibility. When macromolecules are mixed, thousands of atoms in each molecule remain together, decreasing the mixing randomness and resulting in lower enthalpy gain. This in turn lowers the possibility to outweigh the endothermic heat of mixing, making true mixing and miscibility more difficult.

A simple and usually reliable approach for determining whether a blend system is miscible or not is to examine its glass-transition behavior using thermal-mechanical, or dielectric techniques. Miscible blends show a single, composition-dependant T_g reflecting the mixed environment of the blend, whereas two-phase blends show two T_g's characteristic of each phase. This method is of limited usefulness when the glass transitions of the two polymers are very close together and cannot be adequately resolved [28].

2.2.3 PROPERTY RELATIONSHIPS

The relationship between the physical properties of a polymer blend and those of its components would depend on the thermodynamic interaction between the components as well as many other factors [28].

Fully miscible polymers generally represent the simplest case. In the absence of crystallinity, most properties follow some additive relationship, as suggested in Figure 2.5; miscible polymer blends are similar to random copolymers in this regard. The T_g, and hence the softening point, is generally a monotonic function of composition. As a rule, most mechanical properties, permeation (logarithmic scale) to small molecules, etc, follow nearly linear relations with composition in such systems.

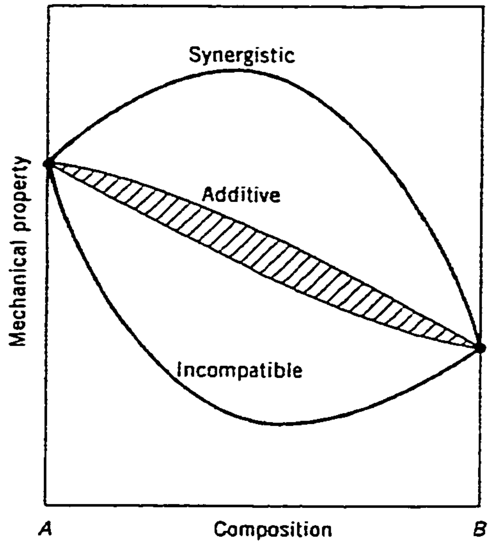


Figure 2.5 Illustration of the subsequent modification of property responses [28].

For polymer blends where the components form separated phases, properties depend on the arrangement of these phases in space and the nature of the interface between the phases.

Such immiscible blends behave like composite materials in many respects. Properties like softening temperature, modulus, permeation, etc, are dominated by the characteristics of the component that forms the continuous phase. Failure properties, especially those related to ductility, e.g., elongation at break and impact strength, often depend on the dimensions of the phases and the degree of interfacial adhesion between the components. The nature of the interface is related to the thermodynamic interaction between the components, which then governs morphology generation in the melt via interfacial tension, and adhesion in the solid state via the thickness of the interfacial zone and the degree to which chains from the two phases entangle [28].

2.2.4 PROPERTIES OF POLYMER BLENDS

The properties of polymer blends depend, apart from the properties of the constituent polymers, upon the morphology of the blend. The size, shape, distribution and degree of separation of the dispersed and continuous phase will in turn depend on the following [26, 29, 30]:

(1) Rheological and interfacial adhesion properties of the polymers;

(2) Volume ratio of the components;

(3) Composition of constituent polymers;

(4) Molecular weight and structure of each polymer;

(5) Blending conditions including temperature and pressure; and

(6) Method of blend preparation, i.e., mixing, open-rolls blending, or extrusion.

A property of the polymer blends, of value P, is described by the following equation [31]:

$$P = P_1C_1 + P_2C_2 + I\,P_1\,P_2$$

where P_1 and P_2 are property values for constituent polymers, and C_1 and C_2 their respective concentrations. I defines the level of synergism created by polyblending. When I is positive, the blend properties exceed the expected arithmetic averages of those of the components (synergistic blend). For a negative I, the blend properties are below the predicted values (nonsynergistic blend). While synergistic blends are usually termed alloys, polymer blends with properties corresponding closely to the predicted values ($I = 0$) are sometimes called additive blends, as also can be found in Figure 2.5.

2.3 LIGNIN

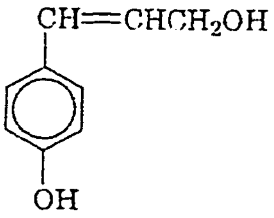
2.3.1 SOURCE AND STRUCTURE OF LIGNIN

The word lignin is derived from the Latin word *lignum* meaning wood. It is a natural polymer which together with cellulose form the structural components of trees and various plants. It is, after polysaccharides, the principal constituent of the woody structure. Concentrating in the outer layers of wood cells, lignin performs multiple functions that are essential to the life of plants [32].

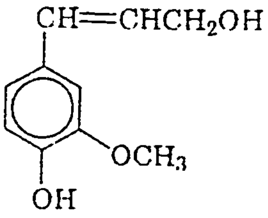
Lignin imparts rigidity to the plants and acts as a binder between wood cells; it decreases the penetration of water across the cell walls and thus plays an important role in the internal transport of water, nutrients, and metabolites; it acts as an antioxidant and UV stabilizer, and impends penetration of destructive enzymes into the cell walls [33].

On average, wood contains about 25 wt-% of lignin. It contributes 24-33% and 19-28%, respectively, to dry wood weight of softwoods and temperate-zone hardwoods [32]. Lignin content in a given wood species varies from tree to tree and with the location in the tree.

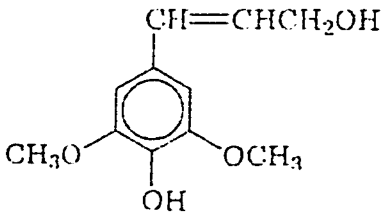
Lignin is always closely associated with cellulose. Its exact chemical structure, as it occurs in wood, is not known and the extreme difficulty in separating it from other wood components in an unchanged form suggests that the exact structure in wood of native lignin may never be determined. Analysis performed on lignin indicates that it has an aromatic nature. Functional groups such as hydroxyl (OH), methoxyl (OCH_3), and carbonyl (C=O) are contained within all kinds of lignins (separated from different species). Lignin may be defined as an amorphous, polyphenolic material arising from enzymatic dehydrogenative polymerization of three phenyl propane monomers, namely, coniferyl alcohol (2), sinapyl alcohol (3), and *p*-coumaryl alcohol (1).



(1)
p-coumaryl alcohol



(2)
coniferyl alcohol



(3)
sinapyl alcohol

These monomers are naturally bonded together by random coupling reactions resulting in a three-dimensional amorphous polymer. More than two-thirds of phenyl propane units in lignin are linked by ether bonds and the rest by carbon-carbon bonds.

The phenyl propane units are interconnected by about ten different linkages in a complex matrix. This matrix comprises a variety of functional groups, including the already mentioned OH, OCH_3, and C=O units, which impart polarity to the lignin macromolecules [32, 33, 34, 35].

2.3.2 GENERAL PROPERTIES

The lignins isolated experimentally or available commercially are friable solids, usually powders, without any observable crystalline form under the electron microscope. They have densities of 1.3 –1.4g/cm^3. The molecular weight of lignin ranges from 1,000 to 12,000, depending on the conditions under which it is isolated.

The T_g, of lignin is between 100°C and 180°C. It seems higher when compared to those of common synthetic polymers. The reason for the high T_g is probably due in large part to hydrogen bonding caused by the presence of phenolic hydroxyl groups in the main chain of lignin. It is also understood that the chemical structure of lignin, particularly the aromatic rings present in the main chain, contributes to the high T_g. This characteristic of lignin is profoundly affected by moisture and, as already mentioned, by hydrogen bonding [33, 36, 37].

The T_g of lignin could be lowered to 70-90°C in commercial thermo-mechanical pulping, with the pretreatment of wood chips by sulfites [38].

Lignin possesses a strong absorption capacity (surface area 180m^2/g) [39]. It has a characteristic ultraviolet (UV) absorption spectrum, with maximum absorptance at 210nm, and weaker at 280nm.

Lignin has good thermal stability up to 200°C. Carbonization begins at a temperature a little above 200°C and slight changes in structure take place up to 300°C. At elevated temperature (up to 460°C), the lignin macromolecules undergo depolymerization, decarboxylation, dehydration and low molecular weight compounds are therefore formed.

2.3.3 DELIGNINFICATION PROCESSES AND DIFFERENT KINDS OF LIGNIN

Technical lignins are obtained as by-products in pulp and paper industry through certain delignification processes that separate cellulose and remove lignin from wood or other plants.In nature, lignin is always bonded with cellulose. Delignification in pulping processes consists, in its early stages, of breaking the connecting bonds between these two polymers thus allowing the separation of lignin from cellulose. Later, the lignin macromolecule is partly degraded into soluble fragments and the cellulose is recovered for papermaking and other products. Delignification processes can be classified as [35]:

(1) sulphate and soda pulping process;
(2) sulphite or acid process; and
(3) organosolv and wood steaming.

In both sulphate and sulphite processes, lignin undergoes significant chemical changes and the technical lignins thus obtained are not identical in their structure to native ones.

In the sulphate and soda pulping process, wood is cooked with a solution (white liquor) containing sodium hydroxide and sodium sulphide. This process results in spent liquors, called black liquors, from which alkali or kraft lignin may be obtained.

In the sulphite or acid process, wood is cooked with salts of sulphurous acid. This results in lignosulphonate spent liquors as a by-product. The residue of this process has often been disposed of by discharge into the sewer system thus becoming a source of pollution [34].

The physical and chemical properties of kraft lignin differ greatly from those of lignosulphonate. Table 2.7 is the summary of these differences.

Table 2.7 Properties of kraft lignins and lignosulfonates [32].

	Kraft lignins	Lignosulfonates
Molecular weight	2,000-3,000	20,000-50,000
polydispersity	2-3	6-8
Sulfonate groups, meq/g	0	1.25-2.5
Organic sulfur, %	1-1.5	4-8
	soluble in alkali (pH>10.5), acetone, dimethylformamide, methyl cellosolve	soluble in water at all pHs; insoluble in organic solvents
Color	dark brown	light brown
Functional groups	many phenolic hydroxyl, carboxyl, and catechol groups; some side-chain saturation	fewer phenolic hydroxyl, carboxyl, and catechol groups; little side-chain saturation

The organosolv process is a new delignification process, based on aqueous-organic solvents [40]. In high-temperature wood steaming processes, the delignification occurs as a result of such a treatment of wood with steam. They were developed in the last decade around the world, especially due to environmental concerns related to conventional chemical pulping processes. The lignin thereafter separated by this means is in a much less unaltered form than lignins resulting from sulphite and sulphate processes and is essentially free of sulfur.

Organosolv lignin is a fine, brown, free-flowing powder. Its properties are different from those of conventional lignins. This kind of lignin is soluble in some organic solvents and in dilute alkali. It is insoluble in water at neutral or acidic pH. It has number average molecular weight lower than 1000 and polydispersity between 2.4 and 6.3 [32].

2.3.4 UTILIZATION OF LIGNIN

Lignin is primarily used as an energy source. The calorific value of this organic material in the spent liquors is a significant economic factor when considering the comparative cost of oil required to sustain a similar process.

On the other hand, it is evident that lignin is an ideal polymer that can be utilized in more areas other than fuel because of the fact that lignin is an abundant, renewable and less expensive nature polymer and due to its functional groups and its properties. However, the application of lignin as macromolecules in material systems is relatively small, its uses include: as thermosetting resin, as antioxidant and reinforcement in rubber, and as components in polyblends [41]. The rest is used almost exclusively as fuel to generate energy. Recent data showed that of the 50 million tons of technical lignins produced annually in the world, only 3 million tons of lignosulfonates and 100,000 tons of alkali lignins are used for other purposes than fuel [42].

Although lignin is currently underutilized, it has the potential of becoming major source of polymer-based products for different industries including building and construction industry, from adhesives, insulation, elastomers, to polymer blends.

2.3.5 LIGNIN IN POLYMER BLENDS

Considering the abundance of lignin, its chemical composition, and its functional characteristics in plants, studies at the Center for Building Studies (CBS) of Concordia University have been undertaken to examine the contribution that lignin can make to the properties of polymer blends with PVC. Previous work done has reported on the evaluation of blends of rigid PVC with different types of lignin [40, 43, 44,]. The data demonstrated an interaction between the two polymers occurring between the OH groups of lignin and the α hydrogen of PVC. The addition of lignin was possible up to 10 parts per 100 PVC (phr), and produced matrix reinforcement as indicated by an increase in Young's modulus. This increase, however, was accompanied by substantial losses in both strength and elongation at break, as well as in impact strength. Some decomposition of the lignin resulted from the high temperatures required to process the rigid PVC.

Technical grades of lignin have already been incorporated into a variety of thermoplastics and thermosets. However, these blends are typically characterized by a high degree of brittleness, and by poor viscoelastic properties. Chemical modification of lignin by oxyalkylation or hydroxyalkylation has been proposed as a promising technique for overcoming its frequently adverse effects on the mechanical properties of polymers [45]. The aim of these modifications has been to block or eliminate various oxygen-containing functional groups, especially hydroxyl groups, responsible for the high degree of association of lignin macromolecules. Recently published data for a kraft lignin-poly(vinyl acetate) blend, containing about 85% lignin, show that mechanical properties are strongly influenced by the degree of association of the lignin macromolecules [46].

2.3.6 LIGNIN PLASTICIZATION

Besides the chemical modifications, another possible method of decreasing the degree of association and, consequently, the T_g of lignin would be through the use of plasticizers. Plasticized PVC is probably the best example of a plasticizer's effectiveness, and most of the theoretical and practical aspects of plasticization follow the development of this polymer.

Earlier it was shown that a good plasticizer should have the following general requirements: solvency and compatibility, efficiency in imparting a desirable property or properties (usually softness and flexibility), and permanence. There are several techniques for assessing the compatibility of a plasticizer with a particular polymer. These include the Hildebrand solubility parameter, δ, and the Flory-Huggins interaction parameter. The solubility parameter is generally a useful guide to predicting compatibility. Frequently, a polymer will be compatible with a plasticizer when the two have solubility parameters that do not differ by more than ± 1.5 $(\text{cal/cm}^3)^{1/2}$. This relationship has been developed based on the thermodynamic free energy of mixing. The square root of δ or cohesive energy density (CED), is a measure of the intensity of the intermolecular interactions in a pure liquid or solid. The strength of the solvent-solvent bonds and polymer-polymer bonds are thus related to CED [47]. Another criterion for plasticizer efficiency is the extent to which the T_g of the polymer is lowered by the introduction of a given amount of plasticizer. The extent of T_g reduction can be related to the magnitude and mode of changes in polymer chain mobility [48, 49].

2.3.7 ECONOMIC CONSIDERATION

The price for organosolv lignin is $ 0.20 Cdn. per kg, which is much less expensive when compared to other polymers, such as the price for Oxy 1810 (the specific PVC used in the present study) of $ 2.93 Cdn. per kg. It is apparent that a big economic advantage could be achieved if part of the PVC used for the flooring formulations was substituted by organosolv lignin.

Hence the use of lignin, an abundant and relatively low priced material, in a system with compatible polymers would serve not only to improve properties, but also to reduce final product cost.

CHAPTER 3

RESEARCH PROGRAM

3.1 OUTLINE OF RESEARCH PROGRAM

This research program is a contribution towards testing the feasibility of lignin to replace part of the vinyl polymer in the flooring formulation. Based on this main purpose, the research program is subdivided into four phases, as illustrated in Figure 3.1.

In the first phase of the experimental program, polymer blends of VC-VAc copolymer with Alcell lignin (AL) were prepared by compounding the most commonly used plasticizer – di-ethyl hexyl phthalate (DOP), dibutyltin dilaurate (DBTL) as heat stabilizer, calcium stearate (CaSt) as lubricant, $CaCO_3$ as filler, and several proportions of AL, i.e. 15, 20, 25, 30 and 40 phr. Further, for convenience, the VC-VAc copolymer with 9.7% VAc will be referred to as PVC. The evaluation of the various formulations was made using tensile tests in conjunction with impact and hardness tests. The mechanical testing results indicated that AL produced a certain extent of matrix embrittlement (higher moduli and losses on tensile strength at break and elongation). Results of this stage are provided in Section 4.1.

Consequently, in order to obtain more elastic formulations with lignin, the study of lignin plasticization was conducted. So in some formulations plasticized lignin was used instead of lignin. A number of plasticizers were formulated with AL. The effect of plasticizer type and level (15, 30, and 45 phr) on the T_g of AL was determined by differential scanning calorimetry (DSC) and by visual, examination of the homogeneity of AL-plasticizer blends. The following criteria were taken into consideration in selecting the AL plasticizers: their solubility parameter, which should be close to that of AL which is 13.7 $(\text{cal/cm}^3)^{1/2}$, their compatibility with PVC and their availability on the market. An analysis of the results obtained from this phase permitted a more rational choice to be made concerning the plasticizers suitable for the specific formulations to use. The results are shown in Section 4.2.

For proving the effect of plasticizers on lignin, further blends of PVC-AL and selected types and proportions of plasticizers were prepared and tested, and the results are compared with similar data obtained for PVC controls. Except the selected "good" platicizers, AL blends were also prepared with DOP which is not compatible with AL. It was chosen as a plasticizer for comparative purposes.

The last phase of the research involved preparation of polymer blends of PVC-AL and plasticizers chosen from the third phase, with the common additives for the flooring formulations, which were outlined at the beginning of the chapter. In these blends, AL replaced PVC in proportions of 15, 20, 25 and 30%. Mechanical properties as modulus, tensile strength at yield and at break, elongation, hardness, and impact tests were carried out.

A description of the raw materials, general formulations, detailed experimental procedures, as well as the description of test methods and characterization techniques will be given in the following sections.

Phase 1

- The study of the influence of different AL loading: 15, 20, 25, 30, 40 phr on a typical flooring formulation by mechanical testing: modulus, tensile strength at yield and break and elongation.

Phase 2

- The study of the AL plasticization by using plasticizers selected in function of solubility parameter, compatibility with PVC and availability on the market;
- The study of the effect of compatible plasticizers level on the AL.

Phase 3

- The preparation, testing and comparison of PVC controls and PVC-AL blends with the different type and level ofplasticizers selected in phase 2. For comparative purposes control and blends with DOP were prepared and tested;
- The determination of their processibility;
- The determination of their mechanical properties: modulus, tensile strength at yield and at break, and elongation;
- Thermal properties (T_g's of the blends).

Phase 4

- The preparation, testing and comparison of PVC controls and PVC-AL blends (AL replaced PVC in proportion of 15, 20, 25 and 30%) from the point of view of flooring formulations with plasticizers selected from phase 3;
- The determination of their processibility;
- The determination of their mechanical porperties: modulus, tensile strength at yield and at break, and elongation;
- Thermal properties (T_g's of the composites).

Figure 3.1 Outline of the research program.

3.2 RAW MATERIALS

3.2.1 PVC

The synthetic polymer used in the program, Oxy 1810, a vinyl chloride-vinyl acetate copolymer, was supplied by Occidental Chemical Corporation, TX, U.S.. For convenience, this copolymer will be referred to as PVC. The properties of this resin is presented in Table 3.1.

Table 3.1 Properties of Oxy 1810 PVC copolymer [53].

K-value	57
M_w	54,000
M_n	26,000
Specific gravity	1.37
Bulk density, g/cm^3	0.63
Particle size	
% retained, mesh 40 (in μm)	10
% through, mesh 200 (in μm)	-
Comonomer VAc content, %	9.7

3.2.2 LIGNIN

Lignin used in the research is an organosolv-type, Alcell lignin produced at the pilot scale by Alcell Technologies Inc., Miramachi, New Brunswick. This grade is obtained through a new, more efficient and less polluting delignification process.

The characteristics of AL as determined by the manufacturer are provided in Table 3.2. T_g as determined by DSC in our laboratory is 97°C.

Table 3.2 Characteristics of Alcell lignin [54].

M_w	< 2,000
M_n	800 –900
Specific gravity	1.27
Softening temperature (ring and ball, ASTM E28), °C	145
Median particle size, µm	20 - 40
Solubility parameter δ, $(cal/cm^3)^{1/2}$	13.7*

* [48]

3.2.3 ADDITIVES

3.2.3.1 HEAT STABILIZER

Dibutyltin dilaurate (DBTL) is used as heat stabilizer, and was obtained from Sigma-Aldrich Canada Ltd..

3.2.3.2 PLASTICIZER

The plasticizers studied in the research are presented in Table 3.3, and their principal characteristics are summarized in Table 3.4.

Table 3.3 Plasticizers used in the research.

Plasticizer / Trade name	Abbreviation	Supplier
Di-ethyl hexyl phthalate	DOP	Fisher Scientific
Butyl benzyl phthalate / Santicizer 160	160	Monsanto
Alkyl benzyl phthalate / Santicizer 261	ABP	Monsanto
Di-butyl sebacate	DBS	Fisher Scientific
Di-ethylene glycol dibenzoate / Benzoflex 2-45	2-45	Velsicol
Tri-cresyl phosphate / Lindol	Lindol	Akzo Nobel

Table 3.4 Principal characteristics of the plasticizers [55].

Characteristic	DOP	160	ABP	DBS	2-45	Lindol
Molecular weight	390	312	368	314	314	368
Specific gravity, 20/20°C	0.986	1.119	1.070	0.933	1.178	1.170
Viscosity, mPa.s @25°C	82	46	57	20 @ 0°C	65-66	67
Boiling point, °C@4mm Hg	230	240@10mm	252@10mm	160@1mm	240@5mm	248
Pour point, °C	-47	< -45	-45	-11	16&28*	-28
Solubility parameter, $(cal/cm^3)^{1/2}$	8.23	9.88	9.55	8.68	10.1	9.86

*freezing point °C, two crystal forms

3.2.3.3 FILLER

Calcium carbonate ($CaCO_3$) is used as the filler for the formulations. It is obtained from Steep Rock Resources in Perth, Ontario. The grade used was Snowhite 12. Typical particle size distribution is presented in Figure 3.2. This grade is often used in PVC-based floorings because finer particle size yields better physical properties. Table 3.5 is the summary of its properties.

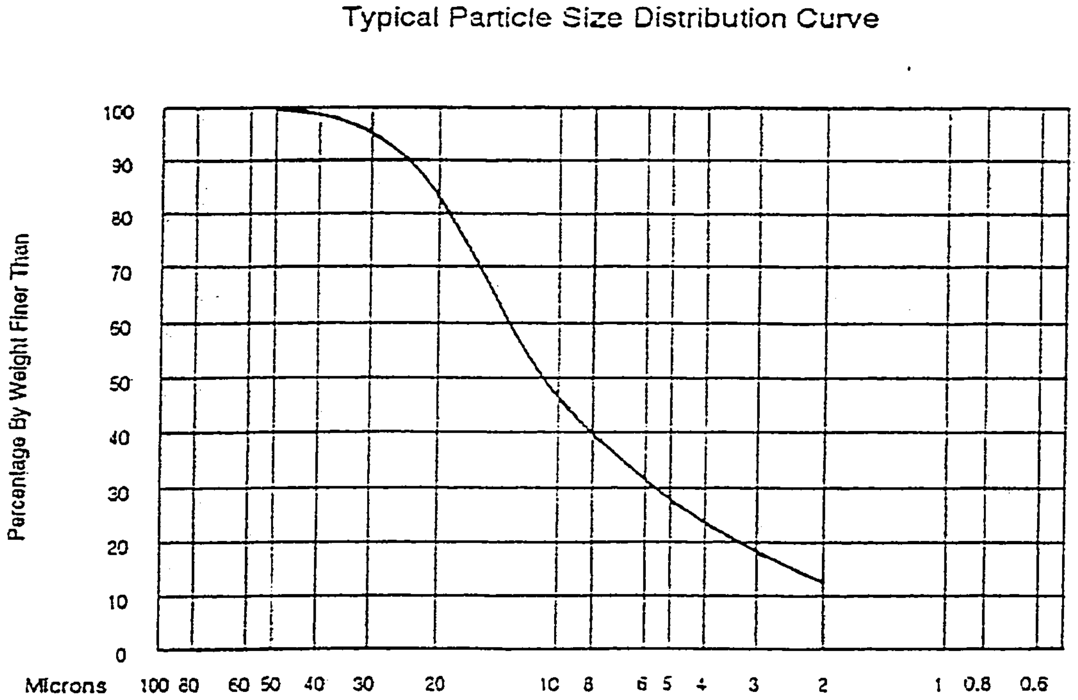


Figure 3.2 Typical particle size distribution curve of Snowhite 12 [56].

Table 3.5 Properties of the $CaCO_3$, Snowhite 12 [56].

Typical physical properties	Bulk density (loose), g/cm^3	0.8
	Bulk density (packed), g/cm^3	1.4
	Specific gravity	2.71
Typical particle size	% retained, 325 mesh	0.1
	Mean particle size	12 microns
Typical chemical analysis	$CaCO_3$ (%)	96.0
	$MgCO_3$ (%)	2.0
	Acid insolubles (%)	2.0

3.2.3.4 LUBRICANT

Calcium stearate (CaSt) lubricant grade L-155, obtained from Blachford Ltd. Canada, is used in the study.

3.3 GENERAL FORMULATIONS

3.3.1 PHASE 1

As addressed in the previous section, only DOP is used as the plasticizer in the first phase. The formulation is shown in Table 3.6.

Table 3.6 Formulation for Phase 1 (35 phr plasticizer).

Ingredient	Composition (phr)					
Resin: VC-VAc copolymer	100	85	80	75	70	50
Lignin: Alcell lignin	0	15	20	25	30	50
Pasticizer: DOP	35	35	35	35	35	35
Heat stabilizer: DBTL	3	3	3	3	3	3
Lubricant: CaSt	1.5	1.5	1.5	1.5	1.5	1.5
Filler: $CaCO_3$	200	200	200	200	200	200

3.3.2 PHASE 2

In this phase, blends of AL with 15, 30 and 45 phr plasticizers which are shown in Table 3. 3, are prepared to study the homogeneity of the blends and to determine their Tg's. Formulation for this specific step is presented in Table 3.7.

Table 3.7 Formulation for Phase 2.

Ingredient	Composition (phr)		
Plasticizer*	15	30	45
Alcell lignin	100	100	100

* corresponding to Table 3.3

3.3.3 PHASE 3

Based on the selection of phase 2, blends and controls are formulated with Lindol, 160, and 2-45 as plasticizers whereas DOP is also chosen for the comparative purpose. Formulations for this phase are provided in Tables 3.8 and 3.9. The AL loading is always 30 phr.

Table 3.8 Formulation for Phase 3 (35 phr plasticizer).

Ingredient	Composition (phr)	
Resin: VC-VAc copolymer	100	100
Lignin: AL	0	30
Pasticizer: DOP 160 2-45 Lindol	35	35
Heat stabilizer: DBTL	3	3
Lubricant: CaSt	1.5	1.5

Table 3.9 Formulation for Phase 3 (44 phr plasticizer).

Ingredient	Composition (phr)	
Resin: VC-VAc copolymer	100	100
Lignin: AL	0	30
Pasticizer: DOP 160 2-45 Lindol	44	44
Heat stabilizer: DBTL	3	3
Lubricant: CaSt	1.5	1.5

3.3.4 PHASE 4

The flooring formulation for phase 4 can be seen in Table 3.10.

Table 3.10 Formulation for Phase 4 (35 phr plasticizer).

Ingredient	Composition (phr)				
Resin: VC-VAc copolymer	100	85	80	75	70
Lignin: Alcell lignin	0	15	20	25	30
Pasticizer: DOP 160 2-45	35	35	35	35	35
Heat stabilizer: DBTL	3	3	3	3	3
Lubricant: CaSt	1.5	1.5	1.5	1.5	1.5
Filler: $CaCO_3$	200	200	200	200	200

3.4 EXPERIMENTAL PROCEDURES

3.4.1 LIGNIN-PLASTICIZER BLENDS

Blends of Alcell lignin with 15, 30, and 45 phr plasticizer were prepared by mixing these components for eight minutes in an open bowl in order to obtain a reasonably uniform blend, followed by a period of eight-minute heating at 145±1°C in a forced air oven. This temperature corresponds to the softening temperature of AL. At the end of the heating period, the resulted melts were examined for homogeneity and subsequently cooled at room temperature in a desiccator. After cooling for 2 hours, the blends are ground to a fine powder in an agate mortar. A control AL sample containing no plasticizer is also prepared in the same manner.

3.4.2 PVC CONTROLS AND PVC-LIGNIN BLENDS

For blends of PVC-AL in phase 3 and those composites for flooring formulations in phase 4, the experimental procedures were the same. They will be addressed in the following sections.

3.4.2.1 SPECIMEN PREPARATION

The preparation of PVC-lignin blends for testing involved a few steps. They were: melt mixing and grinding, compression molding, specimen preparation, specimen conditioning, and testing. Detailed description will be introduced in the following sections.

The ingredients of all the blends were carefully weighted, manually dry mixed for a standard period of time and then introduced into the mixer for melt mixing. The filling coefficient was 67% for a net chamber volume of 60 cm^3.

Subsequently, the melt mixing was homogenized for 8 minutes at 141°C, with a rotor speed of 65rpm in the Haake Rheomix 600. This apparatus consists of a batch mixer equipped with roller blades and accurate temperature controllers which maintain constant temperature in each mixer zone. The mixer is electrically heated and air-cooled. The Haake Rheomix 600 is equipped with a torque rheometer, the Haake Rheocord-M 300, for continuous measurement of mixing torque, and with a thermocouple for continuous measurement of melt temperature. The thermocouple is connected to a temperature recorder as shown in Figure 3.3. In all mixtures, the recorded torque showed that a plateau is reached about two minutes before the end of the mixing time.

Several batches were prepared for each formulation. After melt mixing, the material was ground to small chips with thickness of 2-3mm and maximum length of 10mm.

Following the grinding, sheets of 1.5mm thickness were molded by compression at 155°C and under the pressure of 4.37 MPa. The compression molding was carried out on a Carver Laboratory Press equipped with temperature controllers as shown in Figure 3.4. Certain amount of material was placed in the mold and the mold was placed between the platens of the press which were set at the desired temperature, 155°C. A heating period of 6 minutes with no pressure was allowed. Then the pressure was applied for a determined period of time, 2 minutes, followed by cooling with air at a rate of 10°C/min., under the pressure of 2.18 MPa.

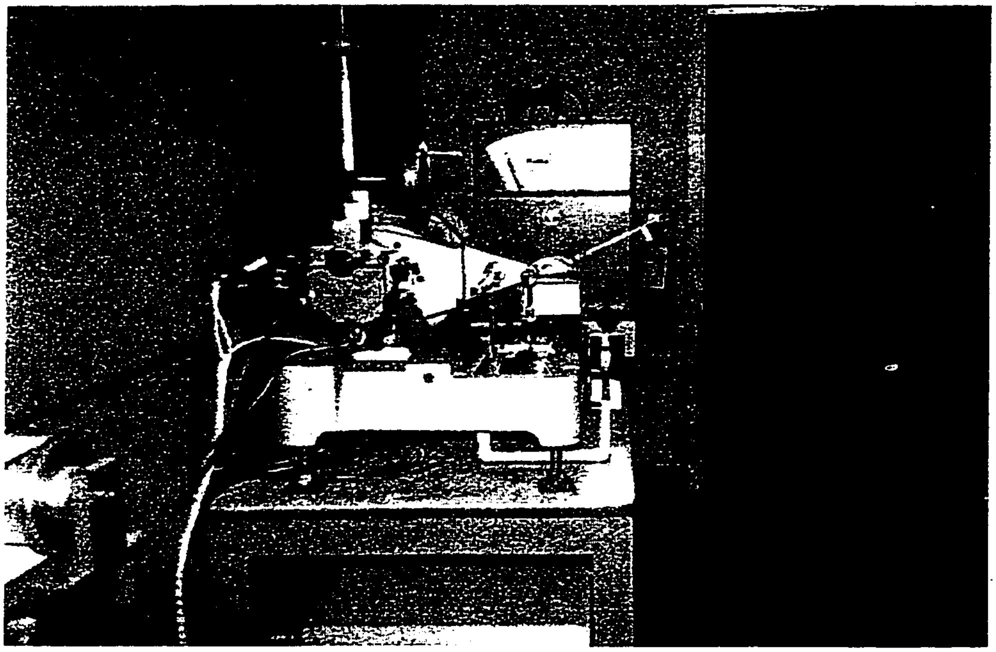


Figure 3.3 Haake Rheomix 600 for mixing.

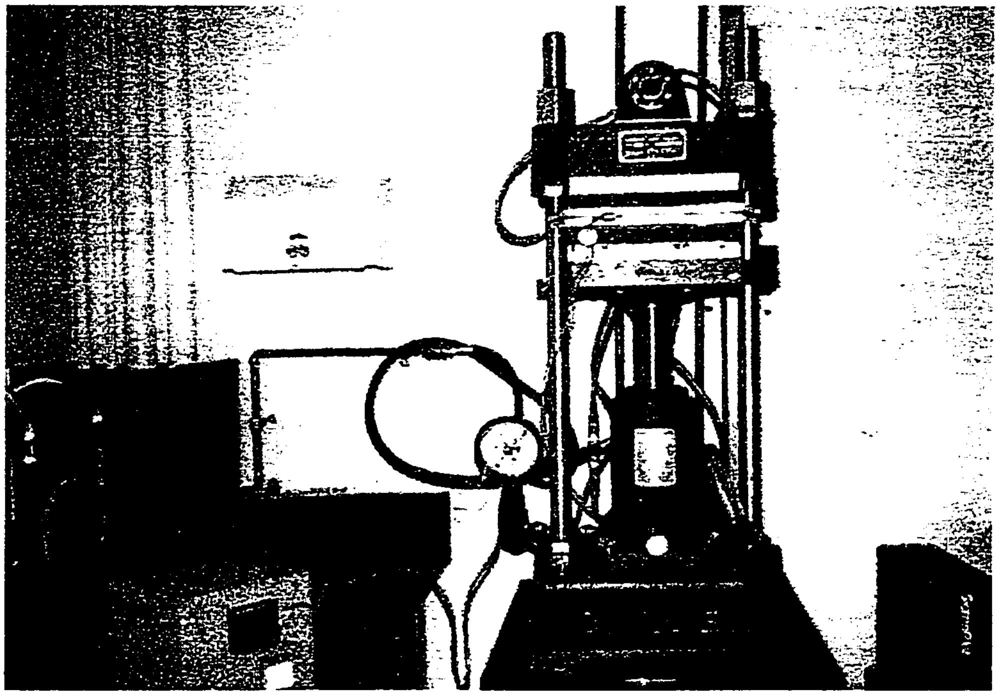


Figure 3.4 Carver Laboratory Press for compression molding.

After cooling, specimens were sectioned with a cutting die into dog-bone shaped for tensile testing, in accordance with ASTM D638. Specimens for impact tests were cut in compliance with ASTM D250. Figure 3.5 is the illustration of specimen shape for tensile tests, and Figure 3.6 for impact tests.

Specimens were conditioned at 23±2°C, with relative humidity (RH) of 50±5%, for at least 7 days prior to testing.

3.4.2.2 TESTING

(1) PROCESSIBILITY

It has long been known that the forces involved in mixing a highly viscous melt, which are measured as the torque acting on the rotors, can be correlated with the melt viscosity. A torque rheometer, the Haake Rheocord-M 300 which is attached on the Haake Rheomix 600 is used for continuous measurement of mixing torque. The presented data (shown in Tables 4.5 and 4.10) represent the values of constant torque which occurs at the last two minutes before the end of the mixing.

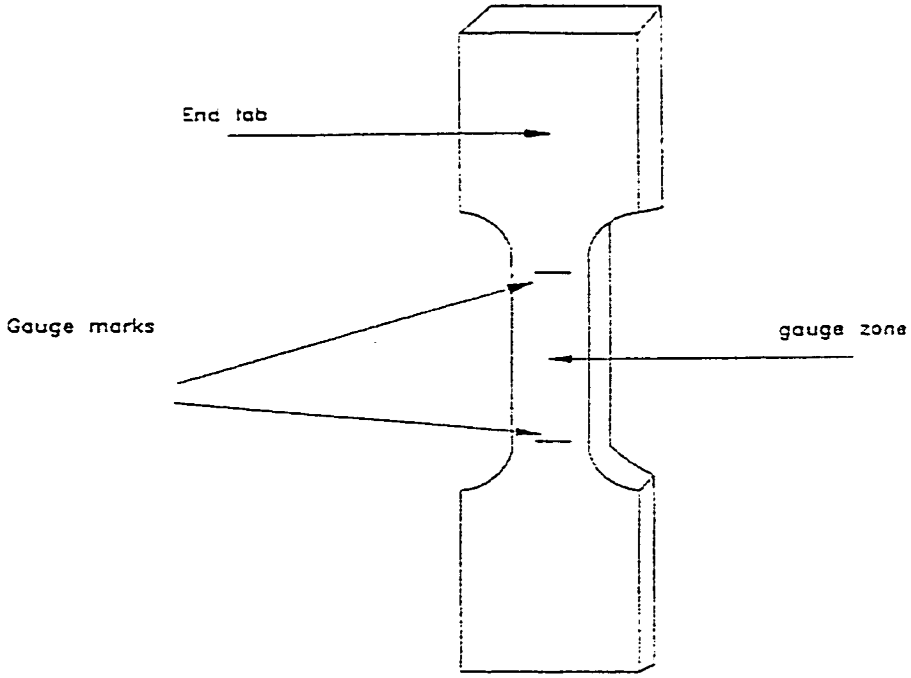


Figure 3.5 Illustration of specimen for tensile tests.

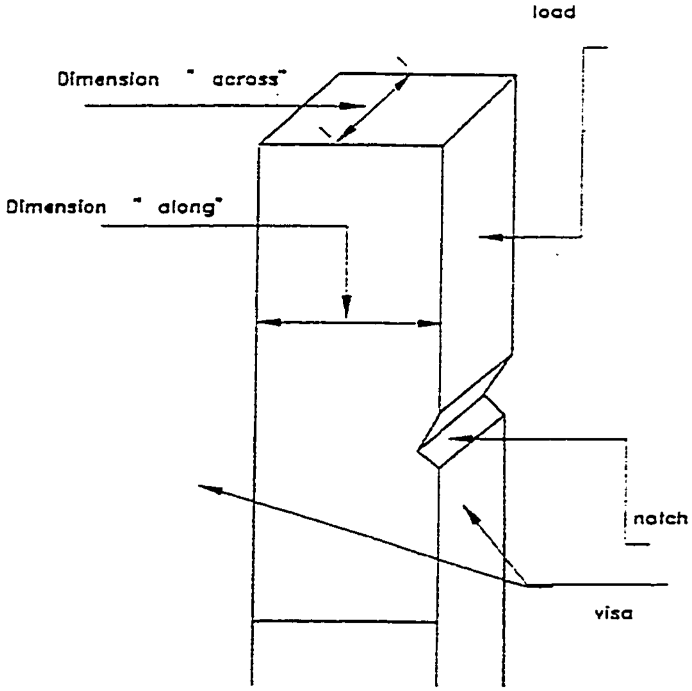


Figure 3.6 Illustration of specimen for impact tests.

(2) MECHANICAL PROPERTIES

Tensile tests were performed for all PVC-AL polymer blends and tensile, hardness and impact tests on PVC-AL blends for flooring formulations.

The tensile strength tests were carried out in accordance with the procedures outlined in ASTM D638, using an Instron Universal Testing Machine model 1125, which is shown in Figure 3.7. The machine is of the cross-head movement type, comprising of a fixed member carrying one grip and a movable member carrying a second grip. Self-aligning grips employed for holding the test specimen between the fixed member and the movable member prevent alignment problem. A controlled velocity drive mechanism is used. A load-indicating mechanism capable of indicating total tensile load is employed. An extension indicator, commonly known as the extensometer, is used to determine the distance between two designated points located within the gauge length of the test specimen as the specimen is stretched. The speed of testing that produces rupture of specimens in 5 min. is selected for each type of formulation. The tensile strength at yield was calculated by dividing the load at yield recorded on the chart by the cross sectional area of the specimen. Tensile strength at break was calculated by dividing the load recorded at break on the chart by the cross sectional area of the specimen. Percent elongation at break was calculated by dividing the extension at break from the chart (change in the gage length) by the original gage length and multiplying by 100.

Impact tests were carried out using the notched Izod procedure given in ASTM D256 with a model 92T Tinius Olsen impact tester illustrated in Figure 3.8. In the Izod impact test the specimen is held as a vertical cantilever beam, and is broken by a single swing of the Pendulum with the line of initial contact at a fixed distance from the specimen clamp, and from the centerline of the notch and on the same face as the notch. The impact strength is read directly in J/m from the calibrated scale on the instrument.

Hardness tests are based upon the increase in the depth of penetration of a rigid indentor (spherical, conical or otherwise) into a flat pad of rubber (or similar elastomeric materials) when an applied load is increased by a standard amount. The hardness tests were carried out on the Durometer hardness tester which consists of a pressure foot, an indentor, and an indication device, shown in Figure 3.9. The indentor is spring loaded. This test is performed in compliance with ASTM D2240. The sample for hardness is around 2.54cm (1in.) wide and at least 0.64cm (0.25in.) thick, it can be either molded or cut from a sheet. Several thin specimens may be piled to form a 0.64cm (0.25in.) thick sample.

For each formulation, at least five samples were tested. All of the indicated values are an average of all the determinations. The coefficients of variation inferior to 10% were taken into account for each set of specimens tested.

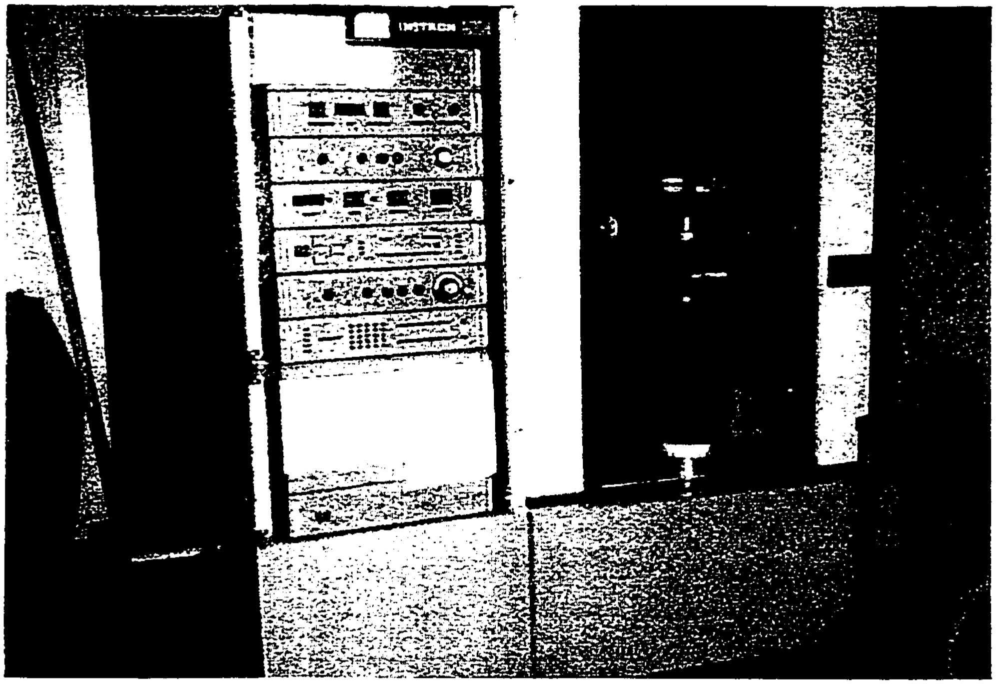


Figure 3.7 Instron universal testing machine.

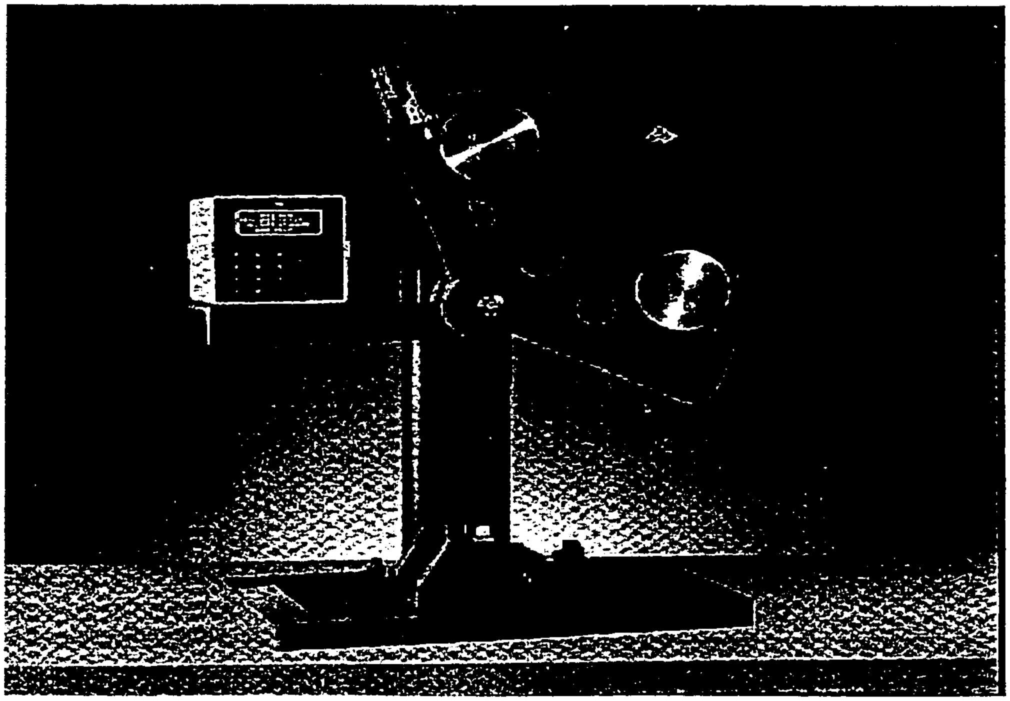


Figure 3.8 Notched Izod impact testing machine.

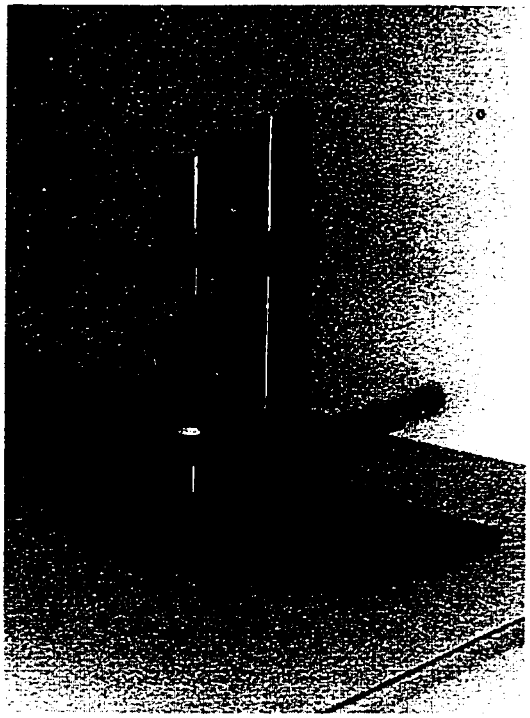


Figure 3.9 Durometer hardness tester.

(3) THERMAL PROPERTIES

In order to understand the thermal behavior of the blends, their T_g's are determined by using DSC tests.

The DSC method uses the differences in heat capacity of a reference and sample material analyzed over a predetermined time-temperature program. Reference and sample specimens are placed in individual cells or pans which sit on a thermoelectric disk. Heat is transferred at a constant rate to the disk and into both reference and sample via the specimen pans. The differential temperature of the specimens is monitored by area thermocouples located on the underside of the disc beneath each specimen pan. Since the thermal resistance of the specimens is held constant, differential temperatures are directly proportional to differential heat flows. At a transition point, T_g, the sample requires either more or less energy than the reference, depending on whether the change is endothermic or exothermic. The DSC cell is illustrated in Figure 3.10.

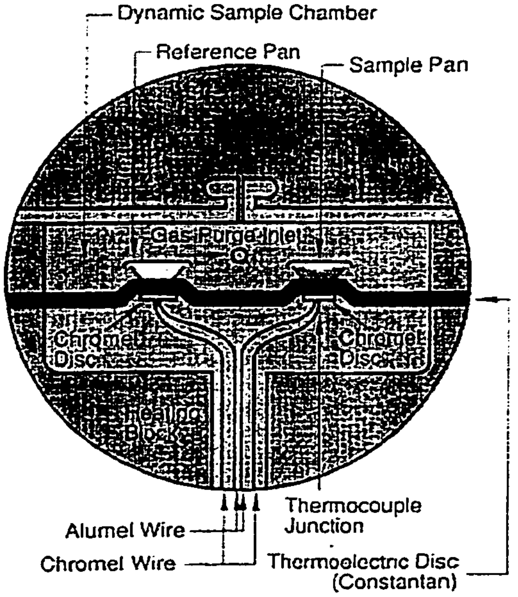


Figure 3.10 DSC cell.

The thermal properties of the blends were measured using a 912 Du Pont differential scanning calorimeter connected with a 2100 Du Pont Thermal Analyzer. The DSC data are analyzed with the Du Pont DSC Standard Data Analysis Program version 4.0. At least two specimens of about 5-6 mg for AL-plasticizer blends, and of about 14-15 mg for PVC-AL blends, were scanned at a heating rate of 20°C/min., under nitrogen atmosphere, between –40°C and 160°C for 15 and 30 phr formulations, and from -80°C to 160°C for 45 phr formulations. The reported T_g represents the inflection point of the heat flow versus temperature curve. Moreover, the width of the T_g peak, or ΔT_g, which represents the difference between the final and onset, is also measured in the case of AL-plasticizer blends. The T_g's are measured after the blends had been aged 24 and 336 hours at room temperature. Five different specimens of an AL-160 (30 phr) were scanned to determine precision of the method.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 PHASE 1 – FLOORING COMPOSITES BASED ON PVC-AL BLENDS AND DOP AS PLASTICIZER

By following the formulations shown in Table 3.6, PVC-AL flooring materials with the most popular plasticizer DOP were obtained. Composites where AL replaced 15, 20, 25, 30 and 40 parts PVC with 200 phr $CaCO_3$ (filler), 35 phr DOP (plasticizer), 3 phr DBTL (heat stabilizer), 1.5 phr CaSt (lubricant) were prepared and tested.

The composites with 40 parts AL were very sticky and difficult to be removed from the mixer parts. For reducing the adherence of the composite melt to the machine parts, besides calcium stearate, other lubricants are also recommended in processing of plasticized PVC were used, such as:

(a) Hostalub FA which is an amide wax of the bis-stearoyl-ethylene diamine type;
(b) Wax E which is a montan wax; and
(c) Wax PE 250 which is a polyolefine wax.

All these lubricants were obtained from Clariant Canada Inc.. None of these waxes were suitable and consequently only formulations with 15, 20, 25 and 30 parts AL were tested.

Table 4.1 shows the tensile properties for composites with 15, 20, 25, and 30 parts AL along with the controls with DOP as plasticizer. Their hardness and impact strength are presented in Tables 4.2 and 4.3.

The Young's modulus of these composites, which is a measure of the material stiffness, decreases when part of the PVC is replaced by lignin. However, it increases again at 30 parts AL but is still lower in respect to that of PVC control. This trend is illustrated in Figure 4.1.

In Figures 4.2 and 4.3, the tensile strength at break and yield versus AL content are presented. Both decrease simultaneously with increasing AL content. However, with increasing lignin content, tensile strength at break decreases more dramatically than tensile strength at yield does. As can be seen from Figure 4.3, the tensile strength at yield for all the composites is almost constant and reflects a quite good interfacial adhesion between the two polymers.

In contrast with tensile strength at break, the decrease of elongation at break shown in Figure 4.4 is very moderate up to 25 parts AL but much stronger at 30 parts AL content.

Overall, the tensile data show that the presence of AL in the blends leads to a decrease of all the tensile properties in relation to the respective data of PVC control, as can be seen in Table 4.1. At the highest AL loading, i.e. 30 parts, the Young's modulus is still lower than that of PVC control but higher in comparison with the other AL loadings and both tensile strength at break and elongation decrease dramatically.

With respect to the hardness of tested DOP/PVC-AL-filler composites, a trend of very slight reduction with increasing lignin content is demonstrated in Table 4.2. On the other hand, the data appear to be very close within the different AL loadings and quite close to the data of PVC control.

The DSC curves for the control and composites are shown in Figure 4.6. For all the compositions they present apparently a single transition which is distributed over a wider temperature interval as the AL content in the blends is higher.

The fluctuation of the T_g data as determined by DSC is somehow erratic for the different composites with differences of about ±10°C for a similar composition. For example, for the five different samples taken from the composite 85PVC-25AL, the values of T_g's (°C) are 1.5; 10.6; 2.1; 7.3; 3.4°C, respectively.

For PVC control the data are constant and the value of T_g is 18°C. An explanation of this behavior which suggests a degree of heterogeneity at a microscale could be the presence of coarse, irregularly shaped lignin particles in the PVC-AL blends.

In order to obtain more homogenous formulations with well-dispersed and smaller lignin particles as well as possibly better mechanical properties, the study of AL plasticization was undertaken and the results of this study will be further presented as in Phase 2.

Table 4.1 Tensile properties for DOP/PVC-AL-filler composites.

Sample identification	Young's modulus (at 5% elongation)		Tensile strength at yield		Tensile strength at break		Elongation at break	
	(MPa)	% of control	(MPa)	% of control	(MPa)	% of control	(%)	% of control
PVC control	2.98	100	3.51	100	6.01	100	336	100
85 PVC-15 AL	-	-	3.10	88.3	4.07	67.7	334	99.4
80 PVC-20 AL	1.63	54.7	3.06	87.2	4.00	66.6	312	92.9
75 PVC-25 AL	1.68	56.4	2.92	83.2	3.56	59.2	304	90.5
70 PVC-30 AL	2.21	74.2	2.99	85.2	2.95	49.1	229	68.2

Table 4.2 Hardness for DOP/PVC-AL-filler composites.

Sample identification	Hardness shore	
		% of control
PVC control	96.3	100.0
85 PVC-15 AL	92.9	96.5
80 PVC-20 AL	94.0	97.6
75 PVC-25 AL	93.7	97.3
70 PVC-30 AL	93.4	97.0

Table 4.3 Impact strength for DOP/PVC-AL-filler composites.

Sample identification	Impact strength	
	(J/m)	% of control
PVC control	152.9	100.0
85 PVC-15 AL	142.3	93.1
80 PVC-20 AL	91.8	60.0
75 PVC-25 AL	80.0	52.3
70 PVC-30 AL	66.3	43.4

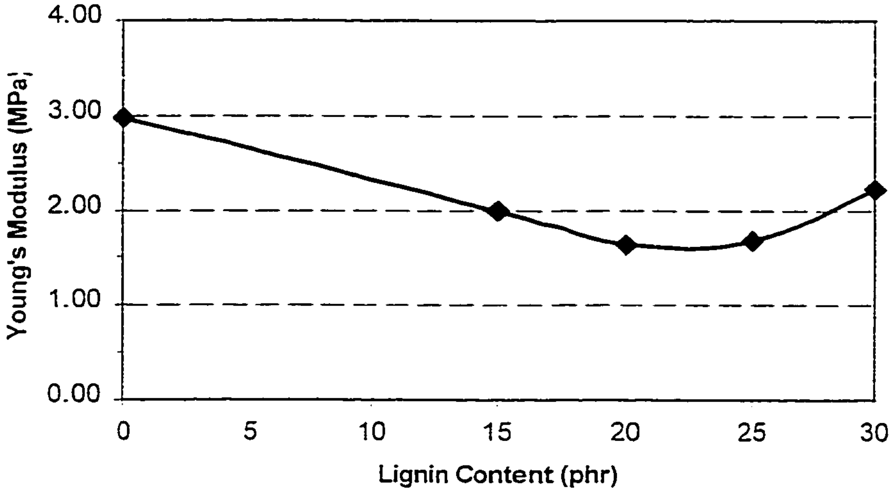


Figure 4.1 Effect of lignin content on Young's modulus for DOP/PVC-AL-filler composites.

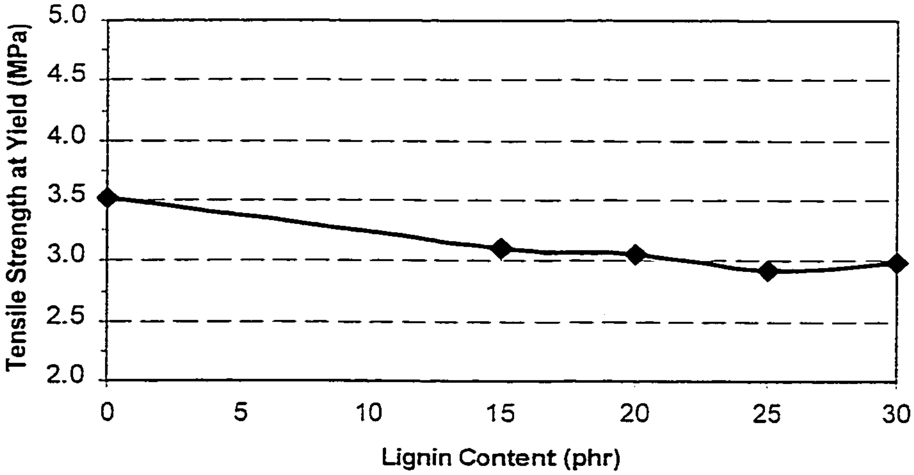


Figure 4.2 Effect of lignin content on tensile strength at yield for DOP/PVC-AL-filler composites.

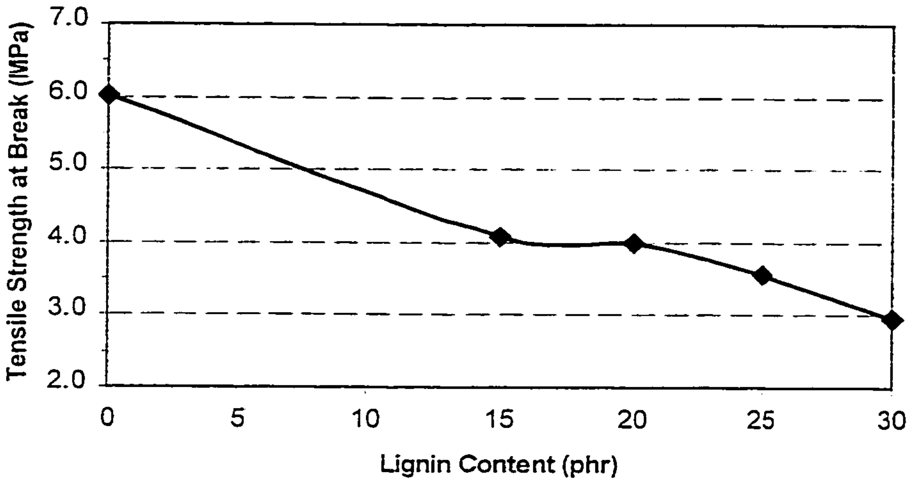


Figure 4.3 Effect of lignin content on tensile strength at break for DOP/PVC-AL-filler composites.

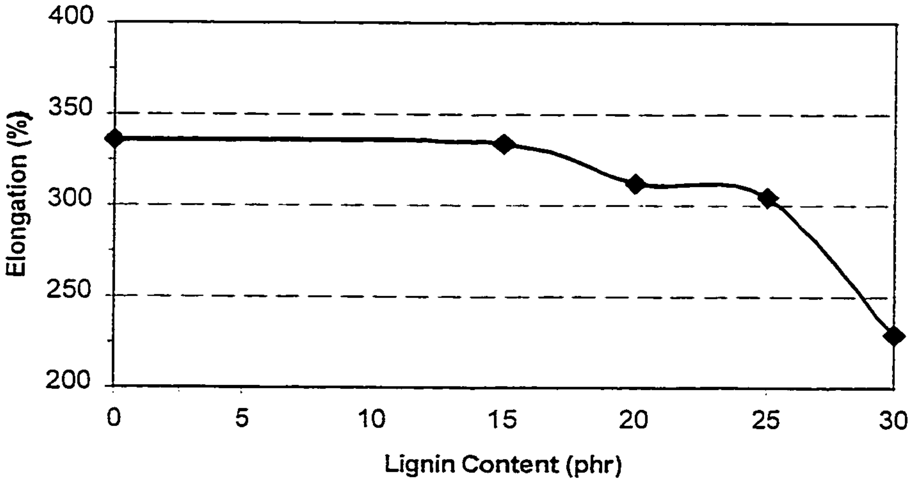


Figure 4.4 Effect of lignin content on elongation at break for DOP/PVC-AL-filler composites.

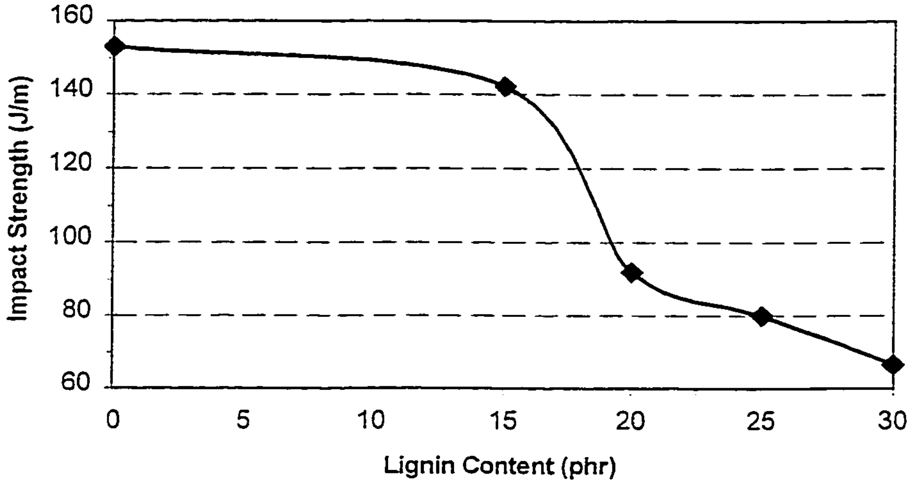


Figure 4.5 Effect of lignin content on impact strength for DOP/PVC-AL-filler composites.

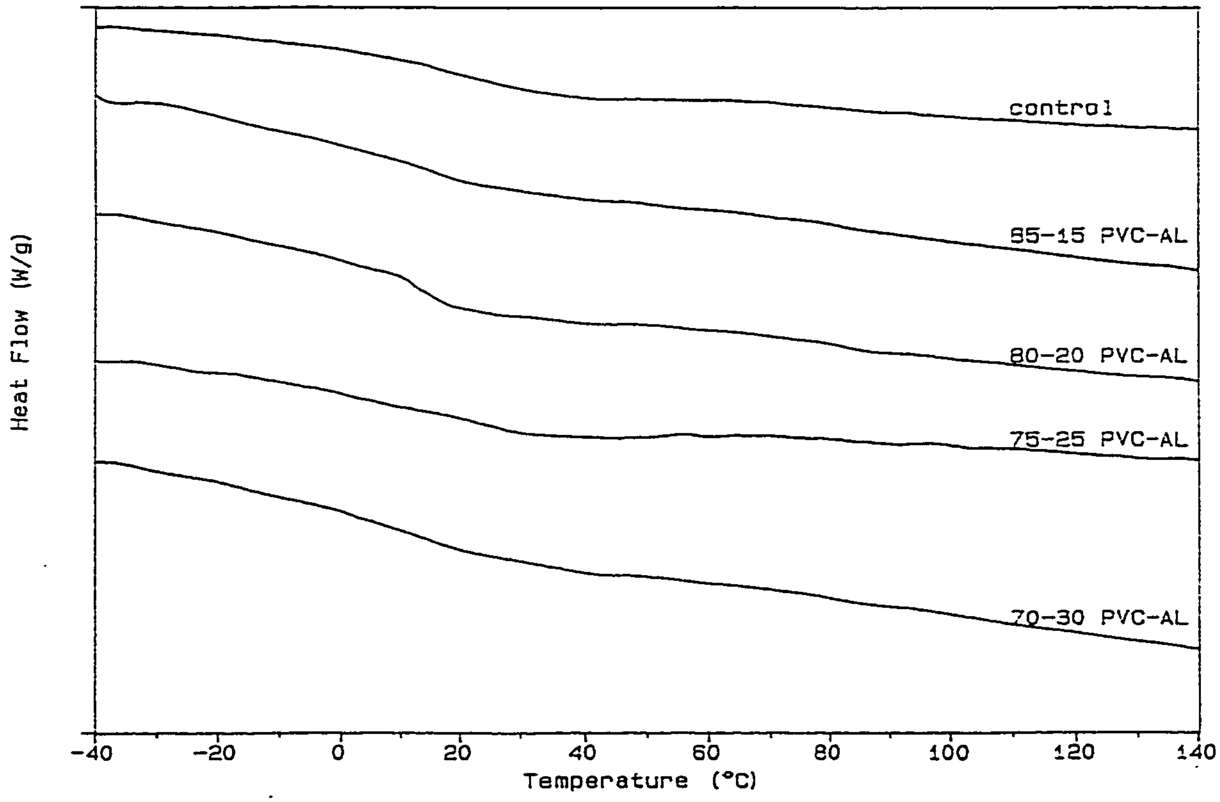


Figure 4.6 DSC curve for DOP/PVC-AL-filler composites and control.

4.2 PHASE 2 – STUDY OF LIGNIN PLASTICIZATION

A series of plasticizers utilized in the study are presented in Table 3.3 and their principal characteristics in Table 3.4.

Of the six plasticizers tested, only DOP and DBS were not retained in the blends at any concentration. Two separated phases are clearly discerned after mixing, which indicates incompatibility of these plasticizers with AL. As can be seen in Table 3.4, these two plasticizers also possess the lowest solubility parameter δ's. A third plasticizer, ABP forms homogenous blends with AL only at a 15 phr loading.

Table 4.4 Changes in T_g and ΔT_g as function of plasticizer content in AL-plasticizer blends.

Sample identification	T_g, °C	ΔT_g, °C
AL control	97	22
AL treated @ 140°C	97	22
AL-160, 15 phr.	66	35
AL-160, 30 phr.	38	31
AL-2-45, 15 phr	65	34
AL-2-45, 30 phr	35	28
AL-Lindol, 15 phr	69	34
AL-Lindol, 30 phr	51	28
AL-ABP, 15 phr	66	40

The data in Table 4.4, which give the changes in T_g and ΔT_g in AL (control and thermally treated) and AL-plasticizer blends (plasticized lignin), show a number of interesting results. The appearance of a single transition in the DSC thermograms of the blends is a first indicative of a homogenous structure. The tabulated T_g's of the AL-plasticizer blends decrease markedly with the plasticizer content. Moreover, it seems that the magnitude of the decrease in T_g is insensitive to plasticizer's chemical structure, with the exception of the relatively bulky Lindol molecule. At the 45 phr plasticizer level, all the blends exhibit a very broad transition range and the precise location of T_g is very difficult to assign. ΔT_g is quite high in all the blends, indicating a certain degree of heterogeneity, especially at the 15 phr plasticizer content. According to the literature, a sharp transition ($\Delta T_g < 15°C$) is typical for a material that is homogeneous on the scale of thermal measurement. A broad transition, on the other contrary, suggests a somewhat less homogenous blend [50]. The ΔT_g values correlate quite well with the plasticizer solubility parameters, demonstrating the influence of δ on the homogeneity of the blends.

The first scan of the blends aged for 335 hr with different plasticizer contents are shown as dashed lines in Figures 4.7 through 4.9. These figures show that the least homogenous blends are those containing 45 phr plasticizer, which exhibit at least two broad peaks in the dashed DSC curve. According to the literature, the presence of multiple enthalpy recovery peaks in aged blends can be used as an indication of the heterogeneity of the blends [51].

It can be concluded that the DSC results discussed above show the effectiveness of plasticizers in decreasing the high degree of association occurring between AL macromolecules. The compatibility of a given plasticizer with AL is strongly influenced by both concentration in the blend, and by the solubility parameter. For the compatible plasticizers studied in this work, concentrations near 30 phr appear to give the best results.

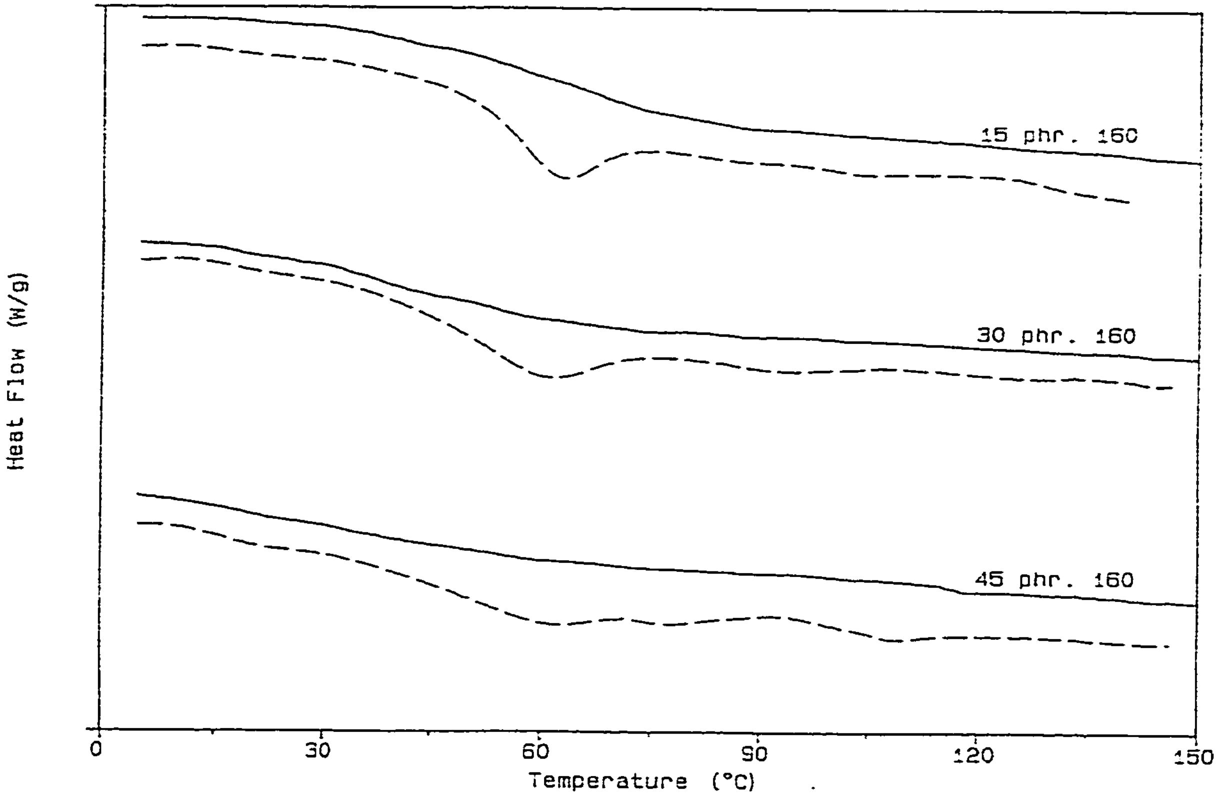


Figure 4.7 DSC thermogram of AL-160 blends.

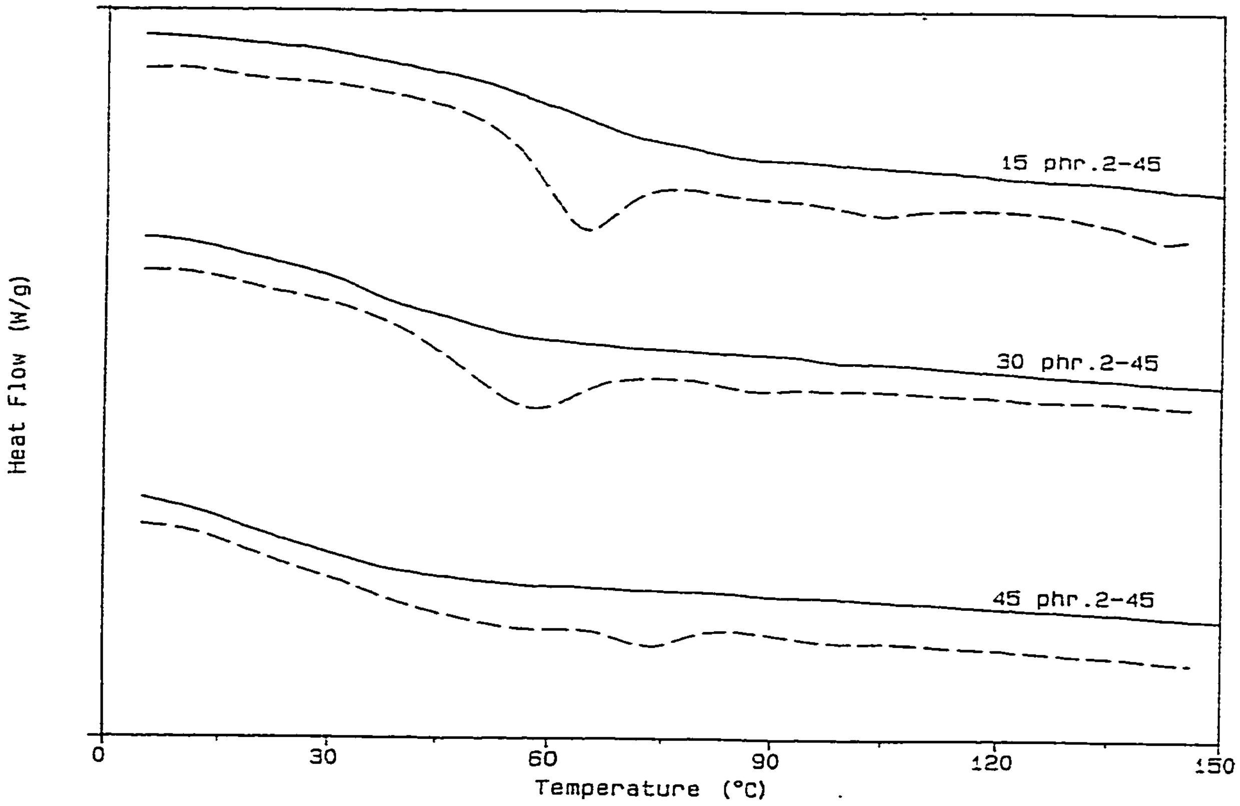


Figure 4.8 DSC thermogram of AL-2-45 blends.

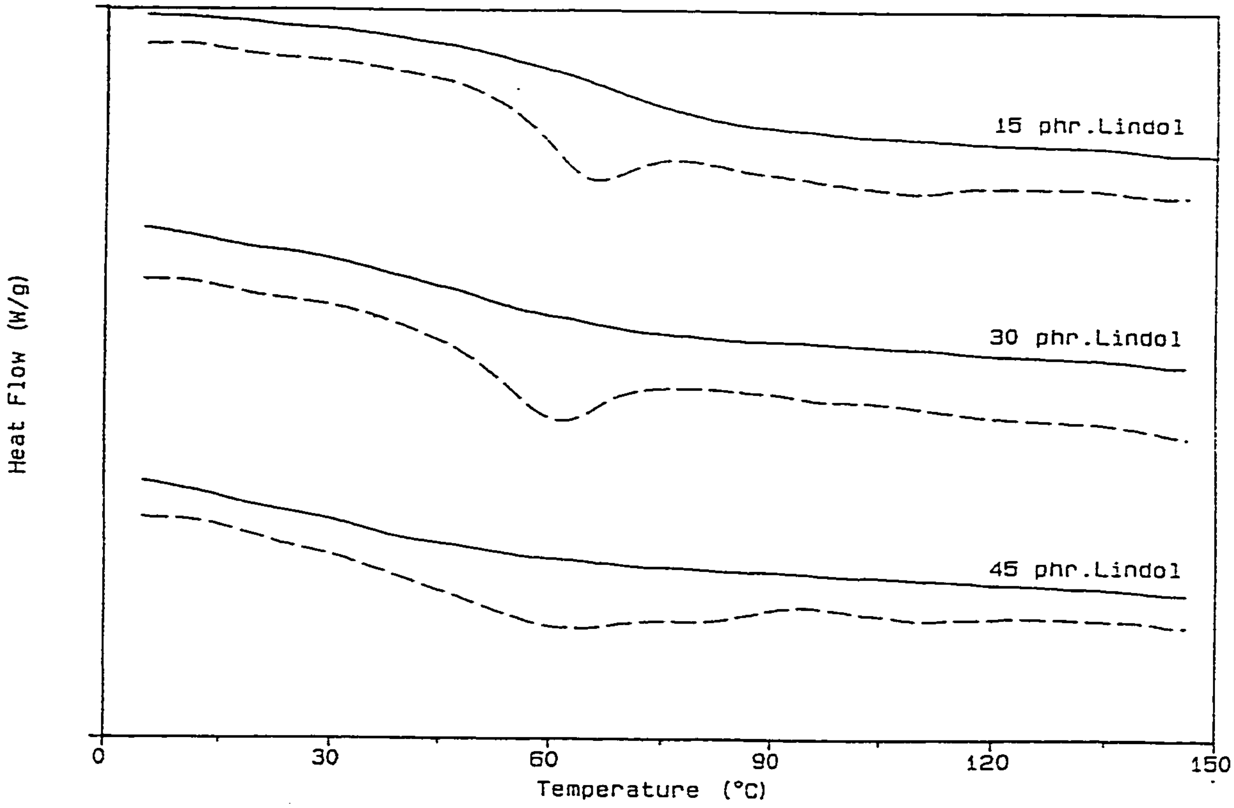


Figure 4.9 DSC thermogram of AL-Lindol blends.

4.3 PHASE 3 – PVC-AL BLENDS WITH PLASTICIZERS SELECTED FROM PHASE 2

The extensive literature concerned with PVC plasticization reveals that when plasticizers are compared at equal efficiency, that is using amounts which produce similar reductions in T_g, the final blend properties can be similar. However, properties of compounds containing the same amounts of plasticizer can show significant variations. Based on this, it was tried to determine whether AL plasticization would overcome the adverse effects on the mechanical properties of its blends with PVC. Blends of AL with PVC and several plasticizers were prepared and tested, and the results were compared with similar data obtained for PVC controls.

Blends and controls were formulated with the following plasticizers: 2-45, 160, and Lindol, and their formulations are presented in Tables 3.8 and 3.9. DOP is not compatible with AL; however, it is also chosen as a plasticizer for comparative purposes.

The blends were formulated with 35 and 44 phr plasticizer, which are equivalent to 27 and 34 parts per hundred parts polymers, i.e. PVC and AL together. This range of concentration appears to represent the optimal level from the AL plasticization results discussed earlier. The AL content in all the blends was always the same, i.e. 30 phr.

The processibility, manifested as steady state torque, for each studied formulation, can be seen in Table 4.5; T_g's of the blends can be found in Table 4.6; and tensile properties of the plasticized PVC-AL blends are presented in Table 4.8. All the results are compared with the data obtained for the PVC controls. The stress-strain curves for PVC controls with 35 phr plasticizer, and blends with 35 and 44 phr plasticizer are presented in Figures 4.12 through 4.14.

4.3.1 PROCESSIBILITY

From the data shown in Table 4.5, it can be seen that both type and level of plasticizer have distinct influences on the control and blend mixing torque. It has long been known that the forces involved in mixing a highly viscous melt, which are measured as the torque acting on the rotors, can be correlated with the melt viscosity [52]. PVC-AL blends all exhibit a decreased torque value in relation to their respective controls, indicating a lower melt viscosity. The decrease in mixing torque is also seen to be a function of the plasticizer type. According to the experimental results shown in Table 4.5, the melt viscosity of the blends decreases in the following order: DOP > Lindol >160 > 2-45. It is interesting to note that this order corresponds to the effective lowering of AL's T_g by the same plasticizers as shown in Table 4.4.

Table 4.5 Steady state torque of blends as function of type and amount of plasticizer.

Sample identification	Steady state torque, m g	
	35 phr plasticizer (27 parts/100 parts PVC+AL)	44 phr plasticizer (34 parts/100 parts PVC+AL)
DOP control	780	-
DOP/PVC-AL blend	650	531
Lindol control	819	508
Lindol/PVC-AL blend	620	459
160 control	685	454
160/PVC-AL blend	550	401
2-45 control	700	380
2-45/PVC-AL blend	500	331

4.3.2 THERMAL PROPERTIES

The T_g values of PVC controls and PVC-AL blends are shown in Table 4.6. The DSC thermograms of the blends, in the temperature interval between –40 and 120°C, at both 35 and 44 phr plasticizer concentration levels are shown in Figures 4.10 and 4.11, respectively. At both levels a single T_g is observed which indicates a relatively homogenous structure. However, for the DOP blends the drop in heat flow is much less pronounced, which may signify a certain degree of heterogeneity for this particular blend in comparison with the others.

Table 4.6 T_g of blends and controls as function of type and amount of plasticizer.

Sample identification	T_g, °C	
	35 phr plasticizer (27 parts/100 parts PVC+AL)	44 phr plasticizer (34 parts/100 parts PVC+AL)
DOP-PVC control	16.0	15.5
DOP/PVC-AL blend	19.4	17.6
Lindol-PVC control	33.1	23.3
Lindol/PVC-AL blend	35.3	28.3
160-PVC control	25.0	16.3
160/PVC-AL blend	27.2	18.1
2-45-PVC control	18.1	14.4
2-45/PVC-AL blend	25.5	21.8

When compared to the PVC controls all blends exhibit a slightly higher T_g except for those containing plasticizer 2-45, where the differences are more remarkable. The differences between PVC-AL blends and their corresponding controls are shown in Table 4.7.

Table 4.7 Increase in T_g's (°C) for the PVC-AL blends relative to the controls.

Type of plasticizer	Plasticizer content, phr	
	35	44
DOP	3.4	2.1
Lindol	2.2	5.0
160	2.2	1.8
2-45	7.4	7.4

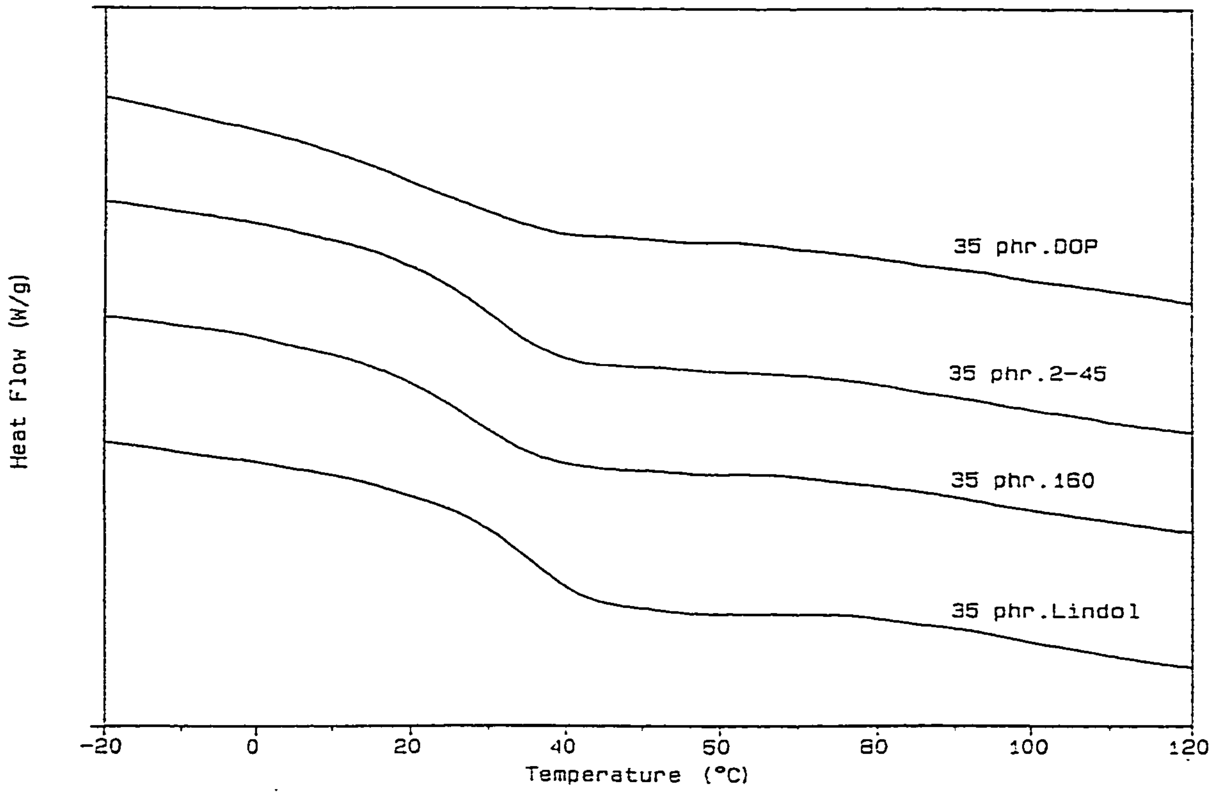


Figure 4.10 DSC thermograms of PVC-AL blends with 35 phr plasticizer.

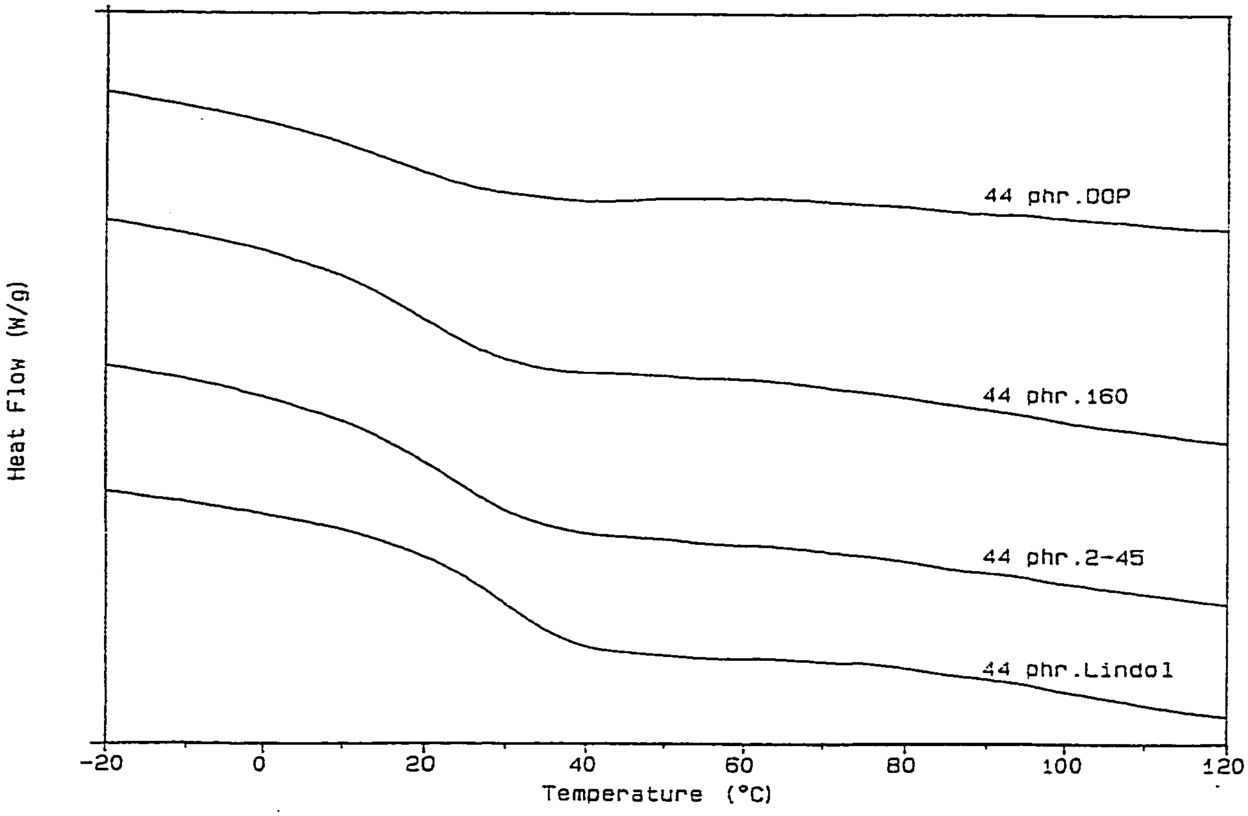


Figure 4.11 DSC thermograms of PVC-AL blends with 44 phr plasticizer.

4.3.3 MECHANICAL PROPERTIES

The mechanical properties of the PVC controls and PVC-AL blends are shown in Table 4.8, and the stress-strain curves in Figures 4.12 through 4.14. From the data presented in Table 4.8 and Figure 4.12, it can be seen that most of the PVC control samples behave as soft elastic materials undergoing ductile failure with uniform yielding. The PVC control with Lindol has a relatively elevated T_g in comparison with the other controls due to the bulky structure of Lindol molecule. Consequently, its modulus at testing temperature is high with a discrete yield point on the stress-strain diagram.

Table 4.8 Mechanical properties of blends as function of type and amount of plasticizer.

Sample identification	35 phr plasticizer (27 parts/100 parts PVC+AL)			
	Modulus at 100% elongation, MPa	Tensile strength at yield, MPa	Tensile strength at break, MPa	Elongation at break, %
DOP-PVC control	4.13	-	15.89	775
DOP/PVC-AL blend	5.32	11.06	11.56	557
Lindol-PVC control	7.73	-	22.90	730
Lindol/PVC-AL blend	-	11.76	17.76	572
160-PVC control	3.10	-	15.71	764
160/PVC-AL blend	6.61	10.77	13.34	685
2-45-PVC control	2.78	14.71	14.77	852
2-45/PVC-AL blend	8.73	11.57	16.04	715
	44 phr plasticizer (34 parts/100 parts PVC+AL)			
DOP-PVC control	1.92	-	9.65	800
DOP/PVC-AL blend	3.16	7.42	7.64	580
Lindol-PVC control	2.88	13.84	14.69	852
Lindol/PVC-AL blend	5.94	10.91	12.51	656
160-PVC control	1.44	-	9.57	788
160/PVC-AL blend	2.58	8.32	8.88	733
2-45-PVC control	1.50	-	9.60	937
2-45/PVC-AL blend	3.03	9.33	11.68	823

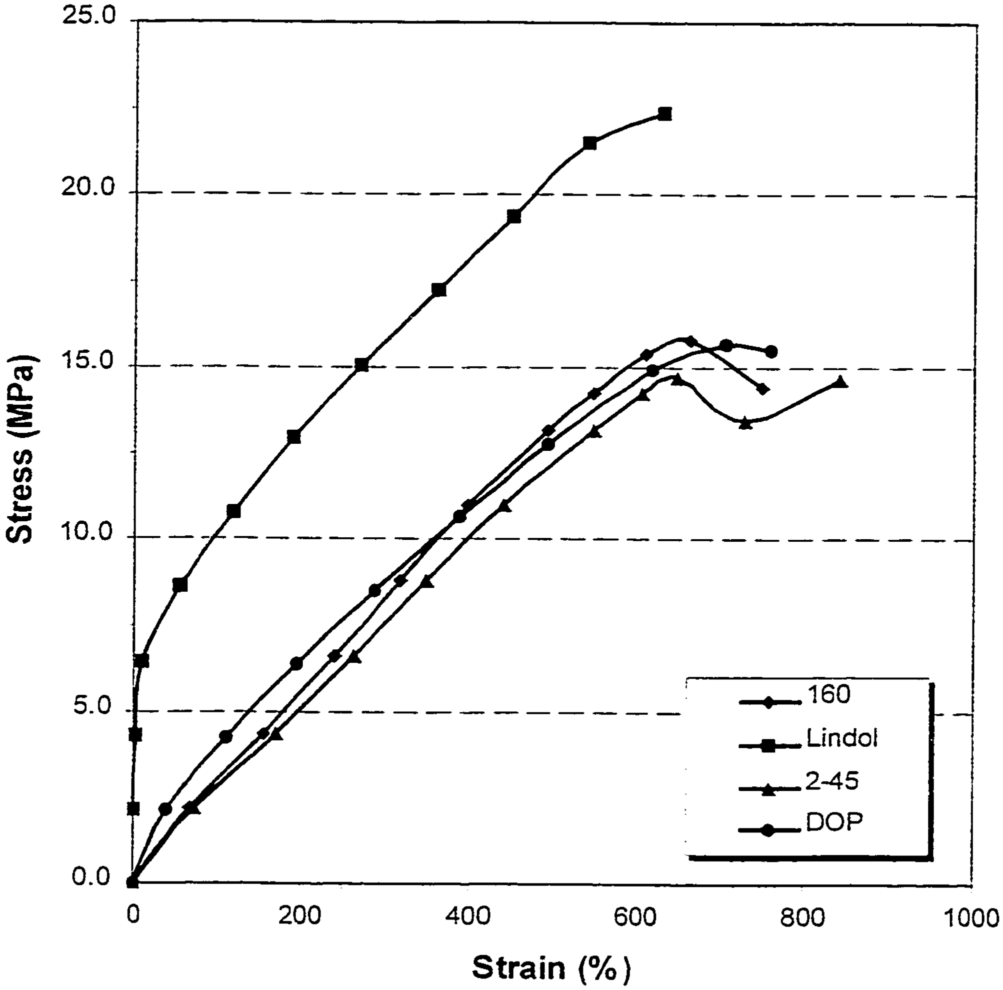


Figure 4.12 Stress-strain curve for PVC controls with 35 phr plasticizer.

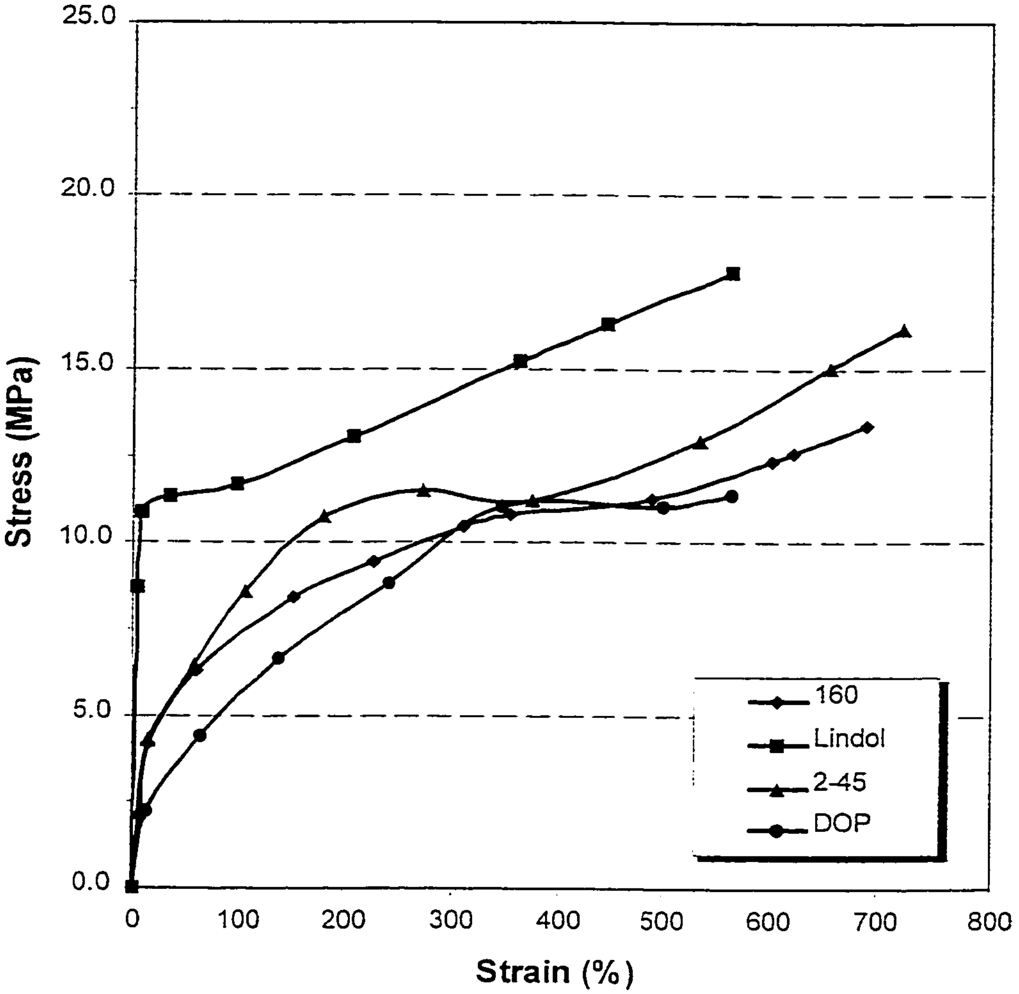


Figure 4.13 Stress-strain curve for PVC-AL blends with 35 phr plasticizer.

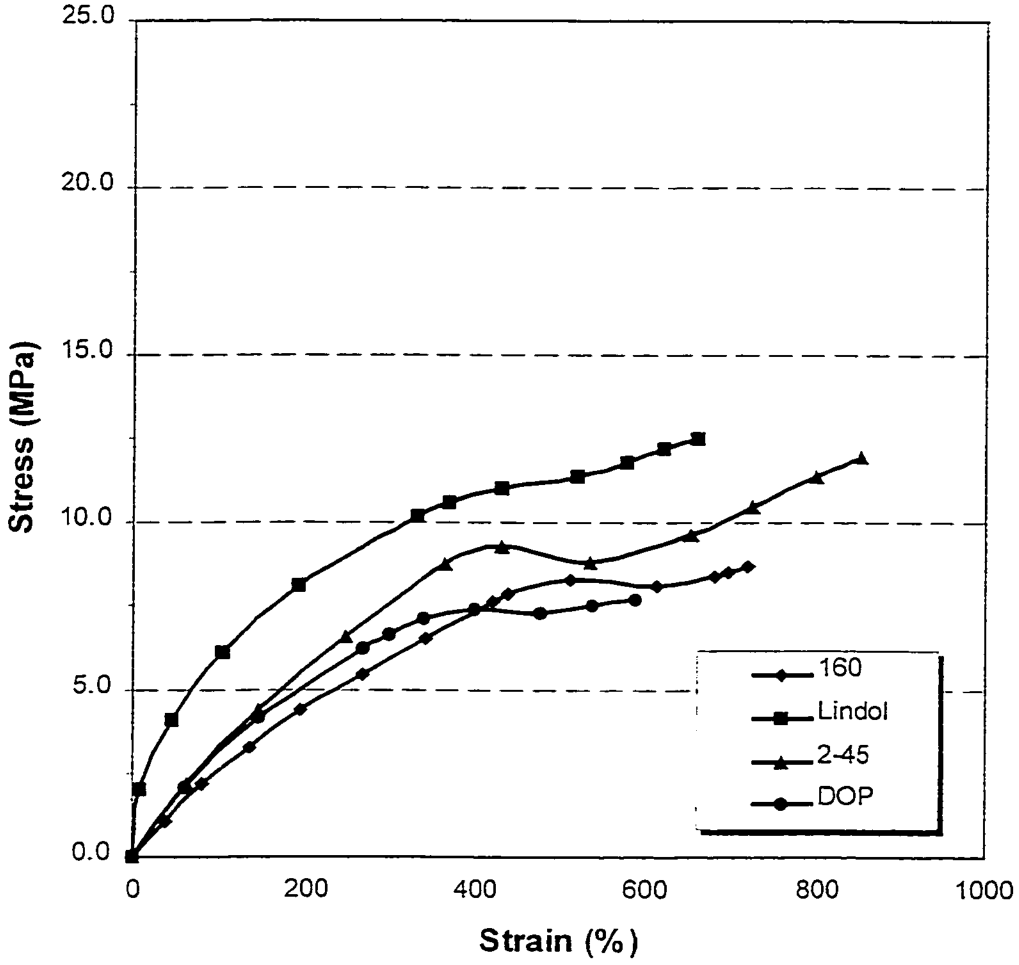


Figure 4.14 Stress-strain curve for PVC-AL blends with 44 phr plasticizer.

A full stress-strain curve is an ideal way of interpreting the tensile behavior. By studying Figures 4.12 through 4.14, it can be concluded that the PVC-AL blends are rather tough elastic materials. All present a distinct yielding point, and the failure mode is ductile with neck propagation and strain hardening, as can be seen in Figures 4.13 and 4.14. For both plasticization levels studied, the mechanical properties of the PVC-AL blends determined at room temperature are not dependent, as expected, on corresponding T_g's. When the blends are ordered with respect to increasing T_g, certain trends are evident in the tensile properties relative to the PVC controls. These trends are summarized in Table 4.9.

Table 4.9 Mechanical properties of PVC-AL blends relative to the PVC controls.

PVC-AL blends with 35 phr plasticizer			
Plasticizer	Increase in modulus, %	Decrease in breaking strength, %	Decrease in elongation, %
DOP	28.8	27.2	28.1
2-45	214.0	(8.6)	16.1
160	113.0	15.9	10.0
Lindol	-	22.4	21.6
PVC-AL blends with 44 phr plasticizer			
Plasticizer	Increase in modulus, %	Decrease in breaking strength, %	Decrease in elongation, %
DOP	64.0	20.8	27.5
2-45	79.0	(21.7)	12.2
160	102.0	7.2	7.0
Lindol	106.0	14.8	23.0

* the values with parentheses represent the increases in breaking strength relative to the corresponded control, instead of decreases

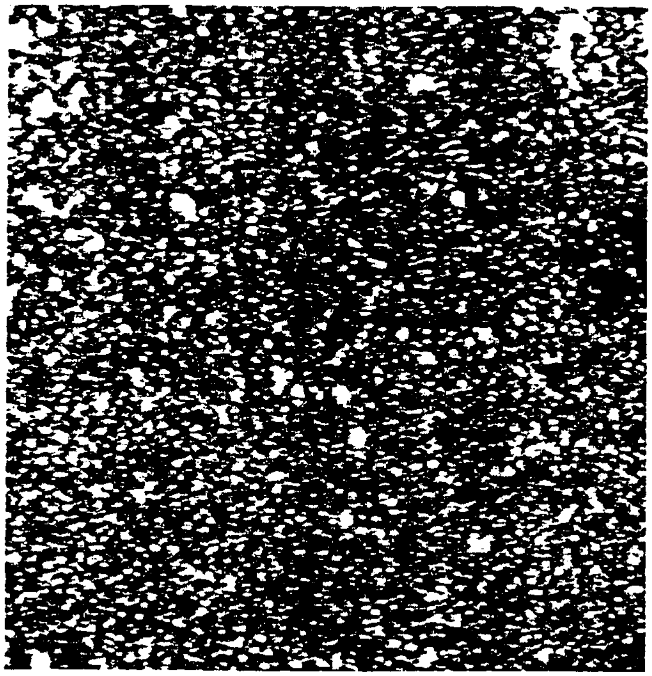


Figure 4.15 35 phr DOP with 30 phr lignin in 100 phr PVC, 100x magnification.

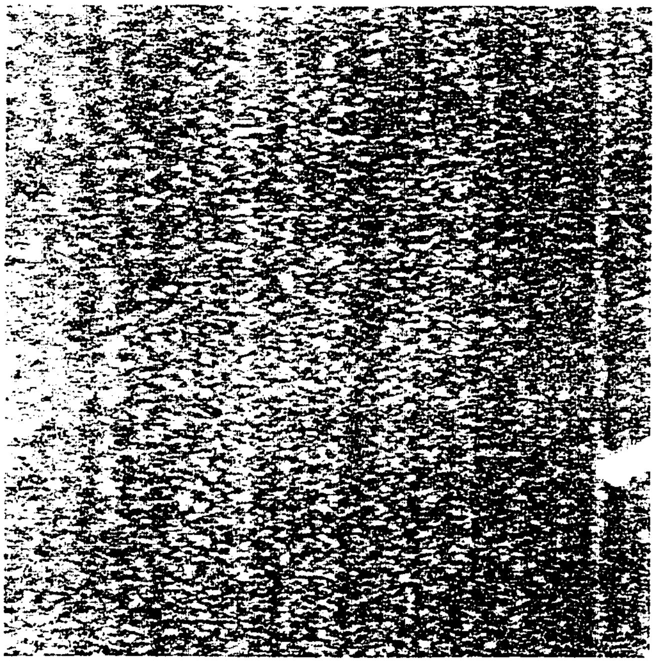


Figure 4.16 35 phr 2-45 with 30 phr lignin in 100 phr PVC, 100x magnification.

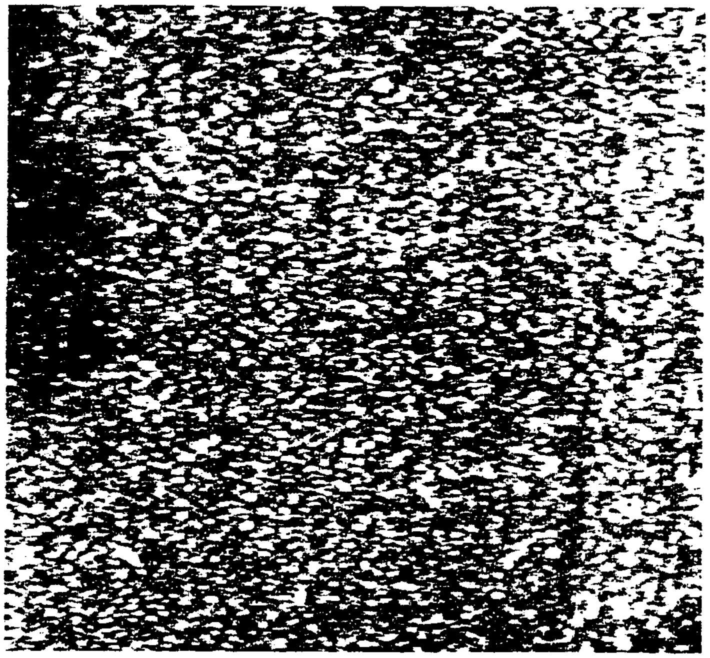


Figure 4.17 35 phr 160 with 30 phr lignin in 100 phr PVC, 100x magnification.

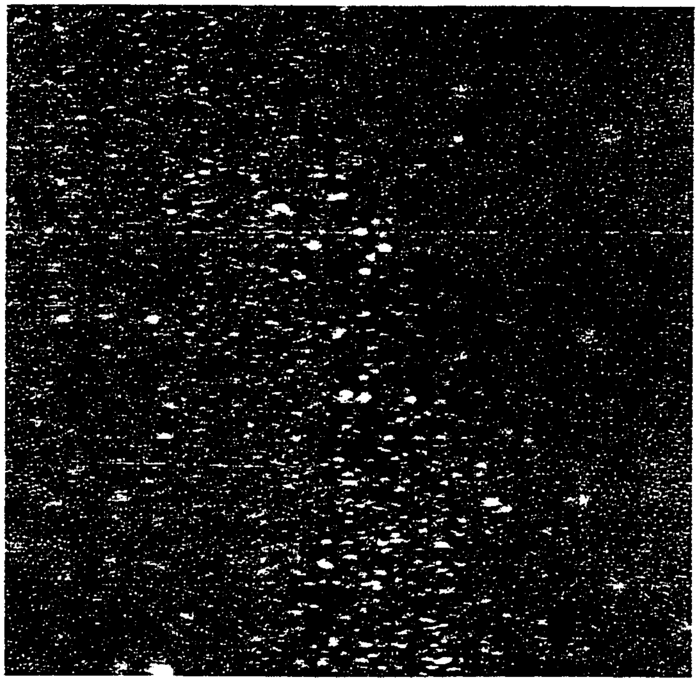


Figure 4.18 35 phr Lindol with 30 phr lignin in 100 phr PVC, 100x magnification.

A tensile force acting on a specimen below T_g introduces the energy necessary for the chains to overcome secondary forces which are due to inter-molecular bonding and slip past each other. The secondary forces became greater as temperature decreases below T_g. This temperature dependence of inter-molecular forces leads to the expectation that the modulus of the blends would be an ordered function of the T_g, that is, modulus should be the highest for Lindol and the lowest for DOP. The same trend should be noted for tensile strength at break and for decrease in elongation.

The data presented in Tables 4.8 and 4.9 do not bear out these expectations. An inspection of the tabulated data suggests that another mechanism is responsible for the mechanical properties, characterized by the blends with plasticizer 2-45 at one extreme and the blends with plasticizer DOP at the other. It is interesting to note that the same extremes are observed during mixing, with the highest melt viscosity for the blends with plasticizer DOP, and the lowest for the blends with plasticizer 2-45. This result points out the possibility of morphological differences of the blendsaffecting the mechanical properties.

4.3.4 MORPHOLOGY OF THE PVC-AL BLENDS

Photomicrographs at 100x magnification were obtained to examine the morphology of the samples. These photomicrographs are shown in Figures 4.15 through 4.18 for the samples with 35 phr plasticizer. The morphology of the 2-45 and Lindol blends seem to be quite different from the samples with plasticizers DOP and 160, where large lignin domains are evident. There are thus significant differences in dispersion among the four 35 phr samples. Plasticizers DOP and 160 clearly give the poorest lignin dispersion, while plasticizers Lindol and 2-45 both result in excellent dispersions. It has long been known that the toughness of a polymer composite is strongly influenced by filler size and dispersion quality. The toughness of the samples tested here could be estimated by calculating the areas under the stress-strain curves in Figures 4.13 and 4.14. The exercise reveals that Lindol and 2-45 give tougher composites than DOP and 160 do. This result is not surprising of giving the different lignin dispersion in the four polyblend samples. It is supposed that for an amount of 45 phr lignin samples, the same results can be obtained.

The plasiticizers therefore appear to play complex roles in determining the morphology and mechanical properties of blends and composites. Plasiticization efficiency, as determined by changes in T_g, cannot be used alone to determine the impact on mechanical properties. The effect of each plasiticizer on polymer morphology must also be taken into account. If samples having similar morphologies are compared, then T_g seems to correlate well with mechanical properties. For instance, plasticizers 2-45 and Lindol both produce samples exhibiting excellent dispersion. The T_g of the samples with plasticizer 2-45 is considerably lower than that of the samples with plasticizer Lindol. As expected in this case, the plasiticizer 2-45 is considerably less detrimental to the mechanical properties of the blends relative to the control (see Tables 4.6 and 4.9) than plasticizer Lindol is at both concentrations tested.

From Figures 4.13 and 4.14, it can be seen that the highest degree of strain hardening, or cold drawing, takes place within the blends with plasticizer 2-45. The degree of strain hardening depends on particular molecular structures and is the result of the increased intermolecular forces between the aligned neighboring polymers or polymer chains thus making the material stronger.

The highest degree of strain hardening which occurs in blends with plasticizer 2-45 indicates again a better opportunity of dissociated and more mobile AL macromolecules to interact with PVC polymer chains.

The experiments performed disclose the incompatibility of DOP with AL. This incompatibility might explain the worst mechanical properties of the blends obtained with this plasticizer in relation with the other blends. Only one transition is observed for these blends; this is an indication of homogenous structure. However, the degree of homogeneity appears to be different in relation with the other blends resulting from the comparison of DSC thermograms sharpness in the T_g region (Figures 4.10 and 4.11). Interestingly, the T_g values of DOP blends are the lowest of the series. The presented data show that the dispersion of the AL in PVC-AL blends is highly influenced by the type of used plasticizer. Their efficiency in AL dispersion, as indicated by the photomicrographs (Figures 4.15 through 4.18), can be rated in the following order: DOP<160<Lindol<2-45.

Although Lindol is a good plasticizer, it was not used in the following phase because of the relatively high values of T_g's for both control and PVC-AL blends.

4.4 PHASE 4 – FLOORING COMPOSITES BASED ON PVC-AL BLENDS AND PLASTICIZERS RESULTED FROM PHASE 3

Based on the result obtained in Phase 3 regarding the study of PVC-AL blends, two plasticizers 160 and 2-45 were considered worthy candidates for flooring material formulations. Composites identical in composition as that presented in Phase 1 (see Tables 3.6 and 3.10) were prepared with 35 phr 2-45 or 160 as plasticizer. As indicated in Table 3.10, composites with 200 phr filler ($CaCO_3$), 35 phr plasticizer (2-45 or 160), 3 phr heat stabilizer (DBTL), and lubricant (CaSt), where AL replaced 15, 20, 25. and 30 parts PVC were prepared and tested. These formulations were tested in the same way and the obtained results correlated with the similar data from Phase 1, in which DOP was used as a plasticizer.

Once again, for comparative purposes all the testing results obtained in Phase 1 are indicated again.

4.4.1 PROCESSIBILITY

As addressed in Section 4.3.1, the steady state torque of mixing is the manifestation of the processibility of the material and of the viscosity of the melt. Table 4.10 presents steady state torque of PVC-AL-filler composites with various plasticizers.

Table 4.10 Steady state torque of PVC-AL-filler composites as function of AL content and type of plasticizer.

Sample identification	Steady state torque, m.g		
	2-45 as plasticizer	160 as plasticizer	DOP as plasticizer
PVC control	920	924	962
85 phr PVC-15 phr AL	768	912	782
80 phr PVC-20 phr AL	799	887	779
75 phr PVC-25 phr AL	784	871	763
70 phr PVC-30 phr AL	726	758	686

Similar to those PVC-AL blends without filler discussed in Section 4.3.1 of Phase 3, decreased torque values of all PVC-AL-filler composites compared to their respective controls were observed. This leads to the conclusion that less viscous melt is obtained when part of PVC is replaced by lignin. Based on the experimental results presented in

Table 4.10, the melt viscosity values for the control samples are found to be quite close to each other and practically with the same trend as observed in the case of control samples obtained in Phase 3 (Table 4.5).

At 15, 20 and 25 parts AL, the viscosities of the composites are decreasing slightly and at 30 parts AL , the decrease is remarkable being the lowest in the blends with DOP as plasticizer. It should be pointed out that the torque values are almost two times higher for the filled compositions than for unfilled ones (Table 4.5) due to the presence of calcium carbonate.

The viscosity trends and values of the PVC-AL composites studied in this phase are different from those of blends studied in Phase 3, with the lowest values occurring with DOP as plasticizer and higher values with 160 as plasticizer. In Phase 3, the lowest value is obtained for plasticizer 2-45 and the highest for plasticizer DOP.

4.4.2 THERMAL PROPERTIES

The values of T_g's for the composties prepared with 2-45 and 160 as determined by DSC analysis are presented in Table 4.11. The results of DSC analysis for the composites with DOP were discussed in Section 4.1 of Phase 1.

Table 4.11 T_g of PVC-AL-filler composites as function of AL content and type of plasticizer.

Sample identification	T_g, °C	
	2-45 as plasticizer	160 as plasticizer
PVC control	21.5	24.2
80 phr PVC-20 phr AL	21.3	20.2
75 phr PVC-25 phr AL	19.1	17.3
70 phr PVC-30 phr AL	18.9	15.9

In contrast to the PVC-AL blends, which show that the presence of AL led to increased T_g values (Table 4.6) in $CaCO_3$ filled composites, it acts in an opposite mode leading to decreased T_g values in comparison to those of respective controls. In the blends with 160 as plasticizer, the T_g decreases are substantially higher than those with 2-45 as plasticizer. These results point to the possibility of morphological differences between the PVC-AL blends and the filled composites.

The DSC thermograms of the blends, in the temperature interval of –40 to 140°C, are shown in Figures 4.19 and 4.20.

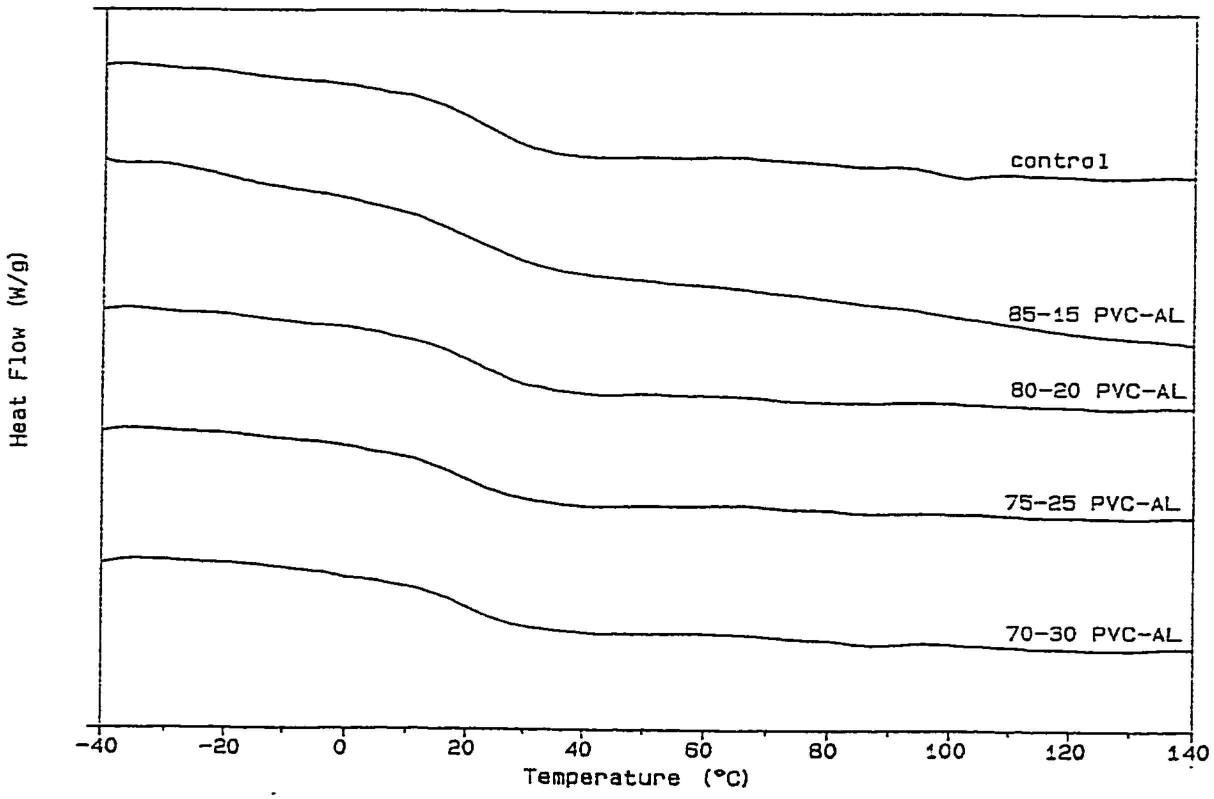


Figure 4.19 DSC curve for 2-45/PVC-AL-filler composites and control.

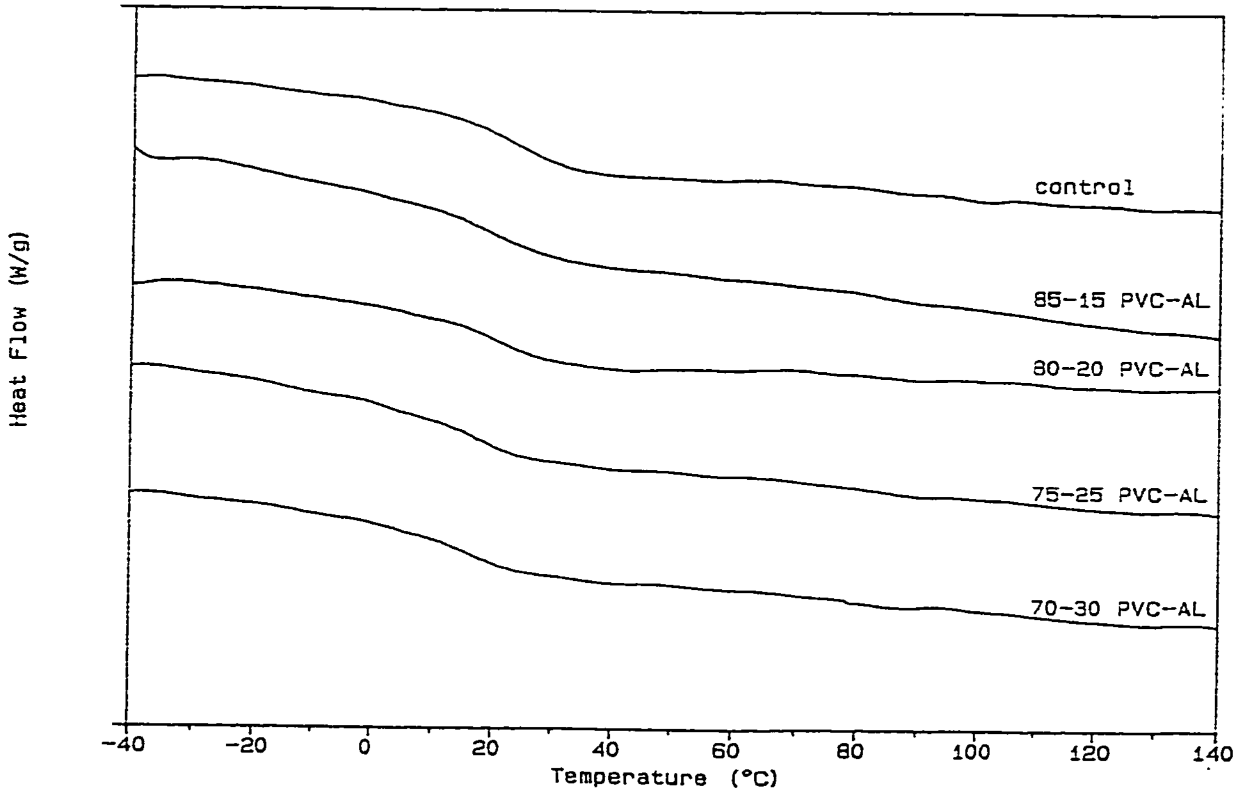


Figure 4.20 DSC curve for 160/PVC-AL-filler composites and control.

4.4.3 MECHANICAL PROPERTIES

4.4.3.1 TENSILE PROPERTIES

The results of PVC-AL-filler composites with 2-45, 160, and DOP as plasticizers are given in Table 4.12 and the variations of the properties relative to the controls are presented in Table 4.13. Figures 4.21 through 4.24 show the tensile properties of the composites, namely, Young's modulus, tensile strength at yield and at break, elongation at break, as function of lignin content for each type of plasticizer, and Figures 4.25 through 4.29 are the stress-strain curves for PVC controls and blends.

As can be seen from Figure 4.21 for blends with DOP, the modulus decreases when 20 parts PVC were replaced by AL and at 25 and especially 30 parts AL, it increases but it is still lower than that of PVC control. The same observation for the composites with plasticizer 160 with the note that at 30 parts AL, the modulus is of about 39% higher than that of the corresponding control. For samples with plasticizer 2-45 the increases in modulus are noticeable for all the lignin loadings, and the increase becomes appreciably greater for 25 and 30 parts lignin.

A comparison of 160 control and composites' modulus data with plasticizer 2-45 similar data show a correlation between the stiffness of all the compositions and T_g's. PVC control with plasticizer 160 has a higher T_g than PVC control with plasticizer 2-45 and a higher modulus. The same investigation is available for the composites. All the composites with 2-45 have a higher T_g than the ones with plasticizer 160 (Table 4.11) and a higher modulus. However, within the composites obtained, with the same plasiticizer, the effect of lignin is not the same. For instance, for composites with plasticizer 2-45 in comparison to PVC control, the T_g decreases moderately with AL loading while the modulus increases substantially, especially for 25 and 30 parts lignin. At 30 parts lignin loading, the same observation applies for composites with plasticizer 160 where the T_g reduction is of about 10°C, and modulus increasing of about 38%. Taking into account the relatively low values of T_g's (all below room temperature), it could be expected that, the lower T_g's, the lower modulus values. This is due to the fact that at the temperatures above T_g the mobility of macromolecules would be higher, therefore, inter-molecular bonding would be lower and consequently the modulus would be lower too. These results again point out the possible morphological differences as a result of plasticizer type.

The effect of AL on the tensile strength at yield is shown in Figure 4.22 and it can be seen that the lignin loading and type of plasticizer affected the yield strength and modulus in a qualitatively similar manner.

The experimental results indicate a continuous decrease of the tensile strength at break (Figure 4.23) which correlates well with AL concentration and with data obtained for controls. The effect of lignin content and type of plasticizer on the elongation at break are presented in Figure 4.24. In relation to respective data of PVC controls, elongation at break decreases very moderately for composites with plasticizer 2-45 and has an unexpected high value at 30 parts lignin loading, when taking into account the respectively high values of modulus at this particular concentration. For composites with plasticizer DOP, the elongation also decreases moderately with lignin loading up to 25 parts lignin and with 30 parts lignin, it decreases in a higher degree. For composites with plasticizer 160 elongation data are almost identical or quite higher than those of the controls up to 25 parts lignin and at 30 parts lignin, it decreases in a much lower measure than in the case of DOP plasticized composites. As in the case of 2-45 plasticizer, the values of the elongation at break are unpredictably high.

The behavior of PVC-AL-filler composites with the three studied plasticizers will be further illustrated by stress-strain curves shown as Figures 4.25 through 4.29. From these curves, it can be seen all the composites behave like a tough elastic material. The failure mode is ductile with neck propagation and strain hardening. In comparison with the PVC-AL blends without filler, the materials obtained in Phase 4 are less strong but quite tough and elastic. These qualities are in agreement with the function of the filler, which is to impart strength and to lower mechanical property to acceptable extent. From Figures 4.26 through 4.29, it seems obvious that the performance of plasticizer 2-45 and 160 are quite similar. Overall, 2-45 appears to be superior to other plasticizers, 160 and DOP, especially when the lignin content increases. These figures show that the highest degree of strain hardening (cold drawing) always takes place within composites with 2-45 as plasticizer, suggesting that this plasticizer induces the best dissociation of AL macromolecules as it is observed from the data of Phase 2 too. As predicted, the composites with DOP do not perform as well as those with other two plasticizers, especially at the high loading of lignin. Nevertheless, the properties are still in the range of the required values for vinyl flooring materials, as shown in Chapter 2.

Table 4.12 Mechanical properties of PVC-AL-filler composites as function of AL content and type of plasticizer.

Sample identification	2-45 as plasticizer			
	Modulus at 5% elongation, MPa	Tensile strength at yield, MPa	Tensile strength at break, MPa	Elongation at break, %
PVC control	2.99	3.82	6.33	366
85 phr PVC-15 phr AL	-	3.49	4.95	365
80 phr PVC-20 phr AL	3.43	3.44	4.30	350
75 phr PVC-25 phr AL	5.34	3.39	3.60	366
70 phr PVC-30 phr AL	6.29	3.52	3.31	343
	160 as plasticizer			
	Modulus at 5% elongation, MPa	Tensile strength at yield, MPa	Tensile strength at break, MPa	Elongation at break, %
PVC control	3.80	4.07	6.06	312
85 phr PVC-15 phr AL	-	3.49	4.95	326
80 phr PVC-20 phr AL	2.38	3.05	4.04	352
75 phr PVC-25 phr AL	3.70	3.00	3.20	315
70 phr PVC-30 phr AL	5.28	3.58	2.67	281
	DOP as plasticizer			
	Modulus at 5% elongation, MPa	Tensile strength at yield, MPa	Tensile strength at break, MPa	Elongation at break, %
PVC control	2.98	3.51	6.01	336
85 phr PVC-15 phr AL	-	3.10	4.07	334
80 phr PVC-20 phr AL	1.63	3.06	4.00	312
75 phr PVC-25 phr AL	1.68	2.92	3.56	304
70 phr PVC-30 phr AL	2.21	2.99	2.95	229

Table 4.13 Mechanical properties of PVC-AL-filler composites relative to the PVC controls.

Sample Identification	2-45 as plasticizer		
	Decrease in modulus, %	Decrease in breaking strength, %	Decrease in elongation, %
85 phr PVC-15 phr AL	-	21.9	0.3
80 phr PVC-20 phr AL	(14.7)	32.1	4.4
75 phr PVC-25 phr AL	(78.6)	43.1	0
70 phr PVC-30 phr AL	(110.4)	47.7	6.3
	160 as plasticizer		
	Decrease in modulus, %	Decrease in breaking strength, %	Decrease in elongation, %
85 phr PVC-15 phr AL	-	18.3	(4.5)
80 phr PVC-20 phr AL	37.4	33.3	(12.8)
75 phr PVC-25 phr AL	2.6	47.2	(10.0)
70 phr PVC-30 phr AL	(38.9)	55.9	9.9
	DOP as plasticizer		
	Decrease in modulus, %	Decrease in breaking strength, %	Decrease in elongation, %
85 phr PVC-15 phr AL	-	32.3	0.6
80 phr PVC-20 phr AL	45.3	33.4	7.1
75 phr PVC-25 phr AL	43.6	40.8	9.5
70 phr PVC-30 phr AL	25.8	50.9	31.8

* the values with parentheses represent the increases of the properties relative to the corresponded control, instead of decreases

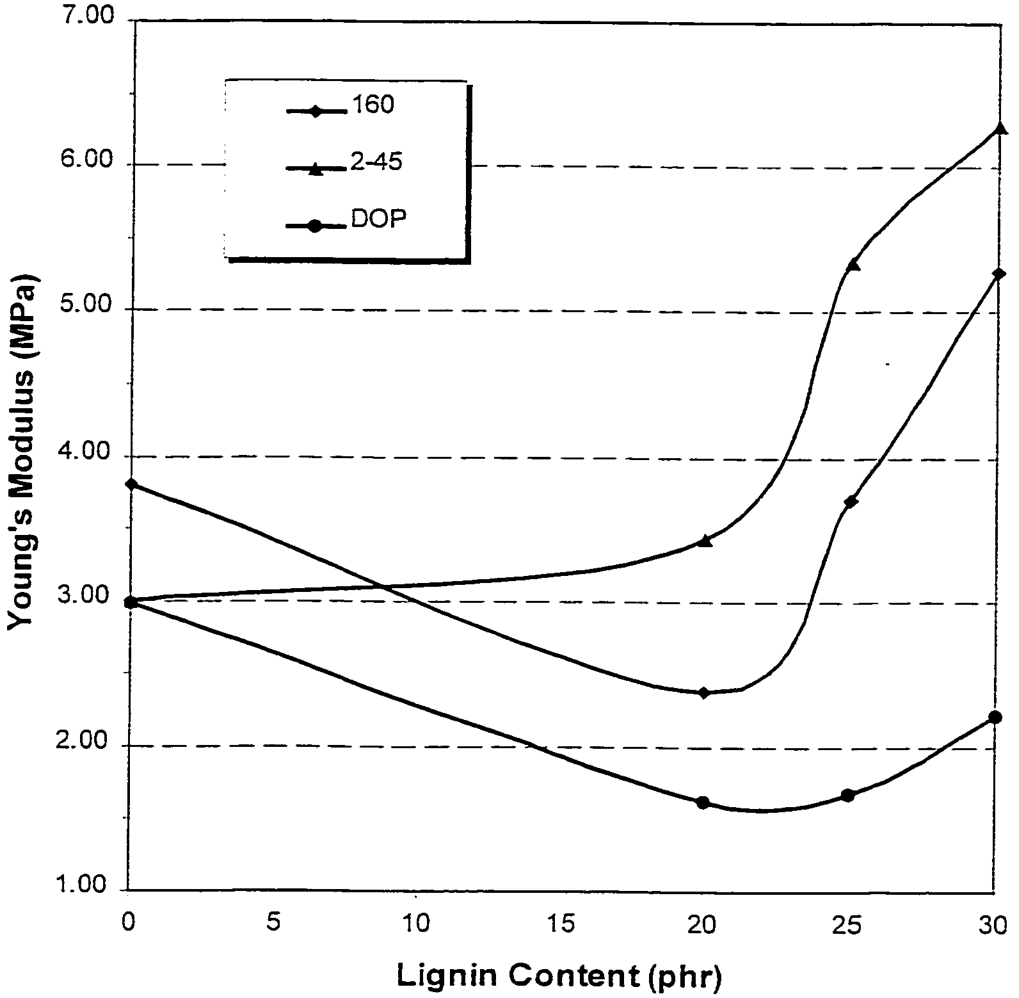


Figure 4.21 Young's modulus of PVC-AL-filler composites as function of lignin content with different plasticizers.

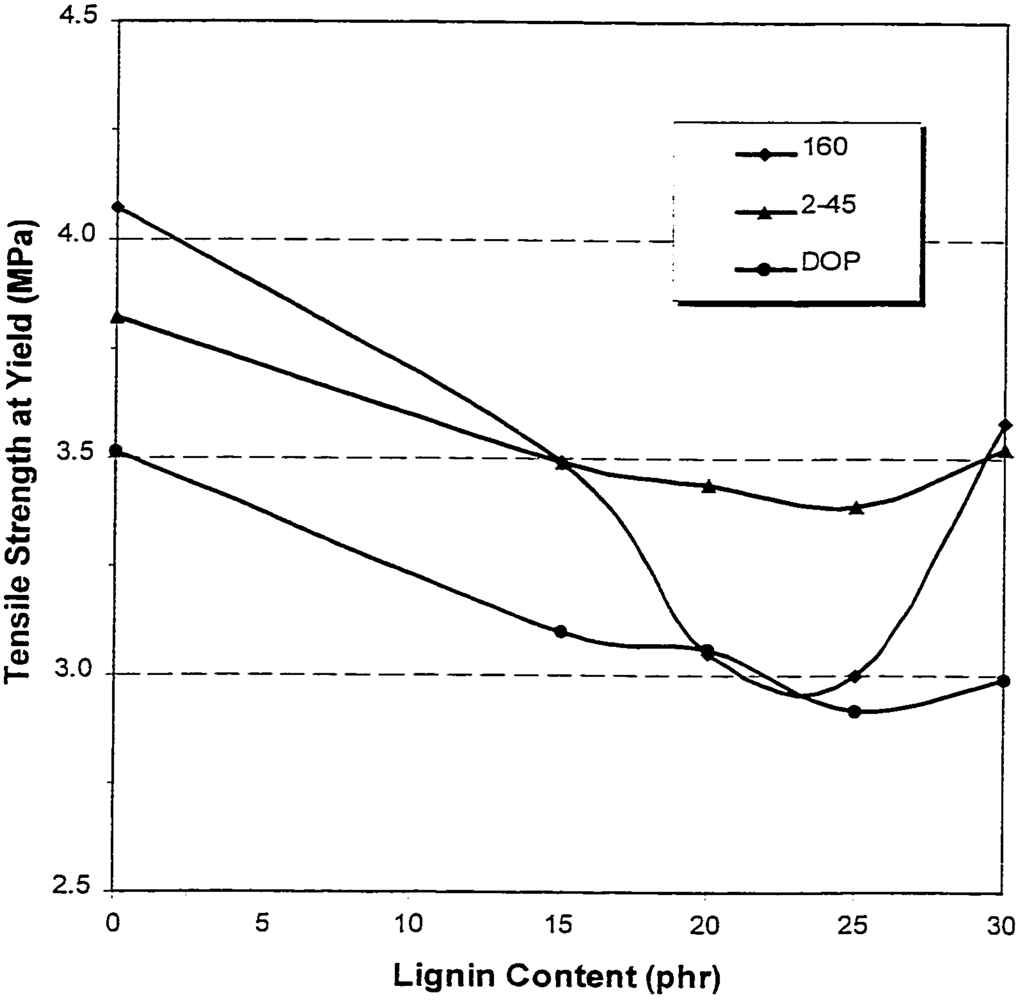


Figure 4.22 Tensile strength at yield of PVC-AL-filler composites as function of lignin content with different plasticizers.

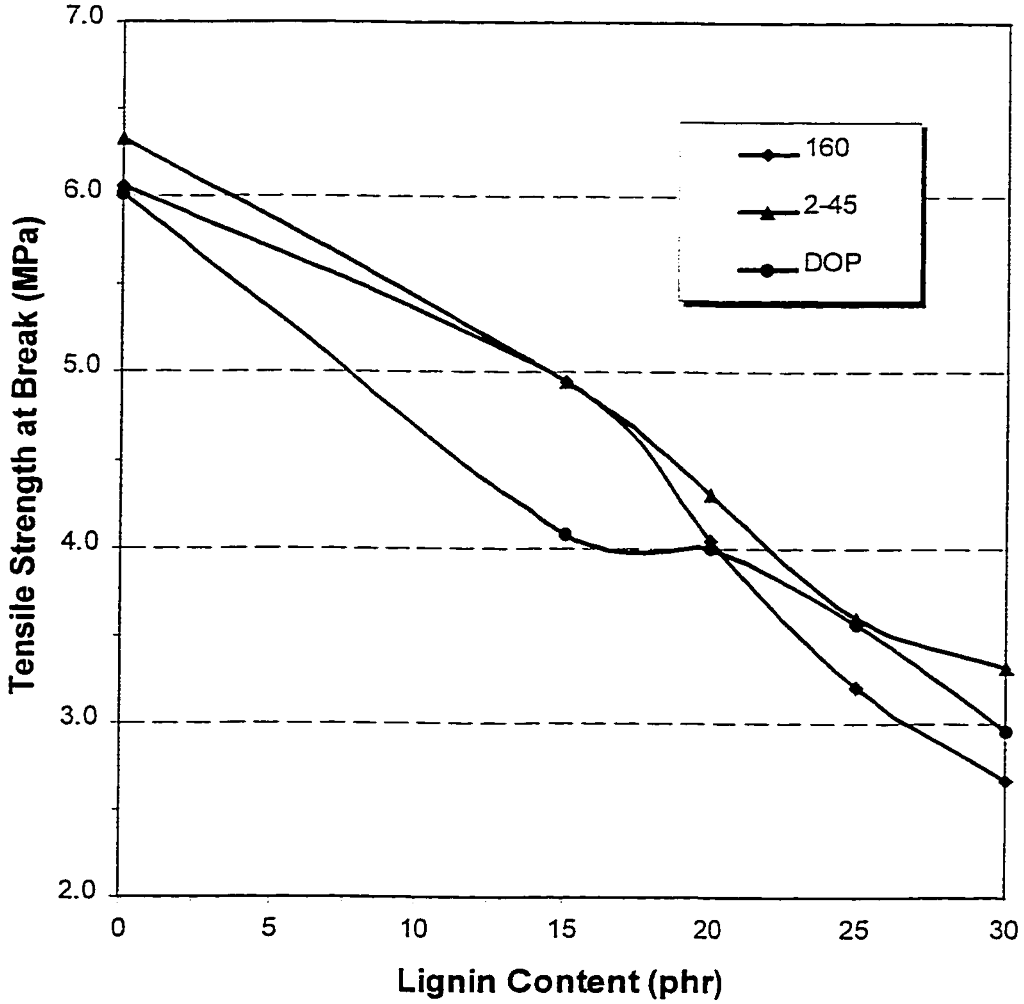


Figure 4.23 Tensile strength at break of PVC-AL-filler composites as function of lignin content with different plasticizers.

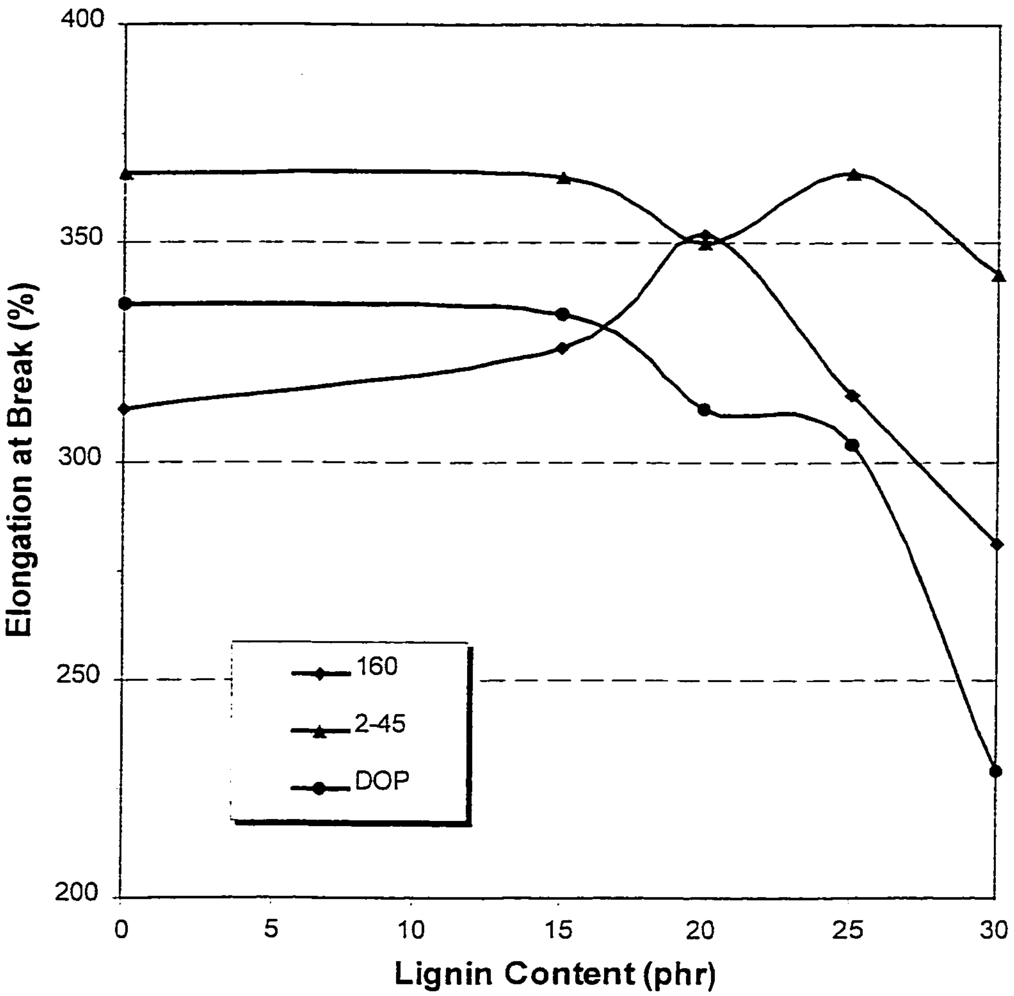


Figure 4.24 Elongation at break of PVC-AL-filler composites as function of lignin content with different plasticizers.

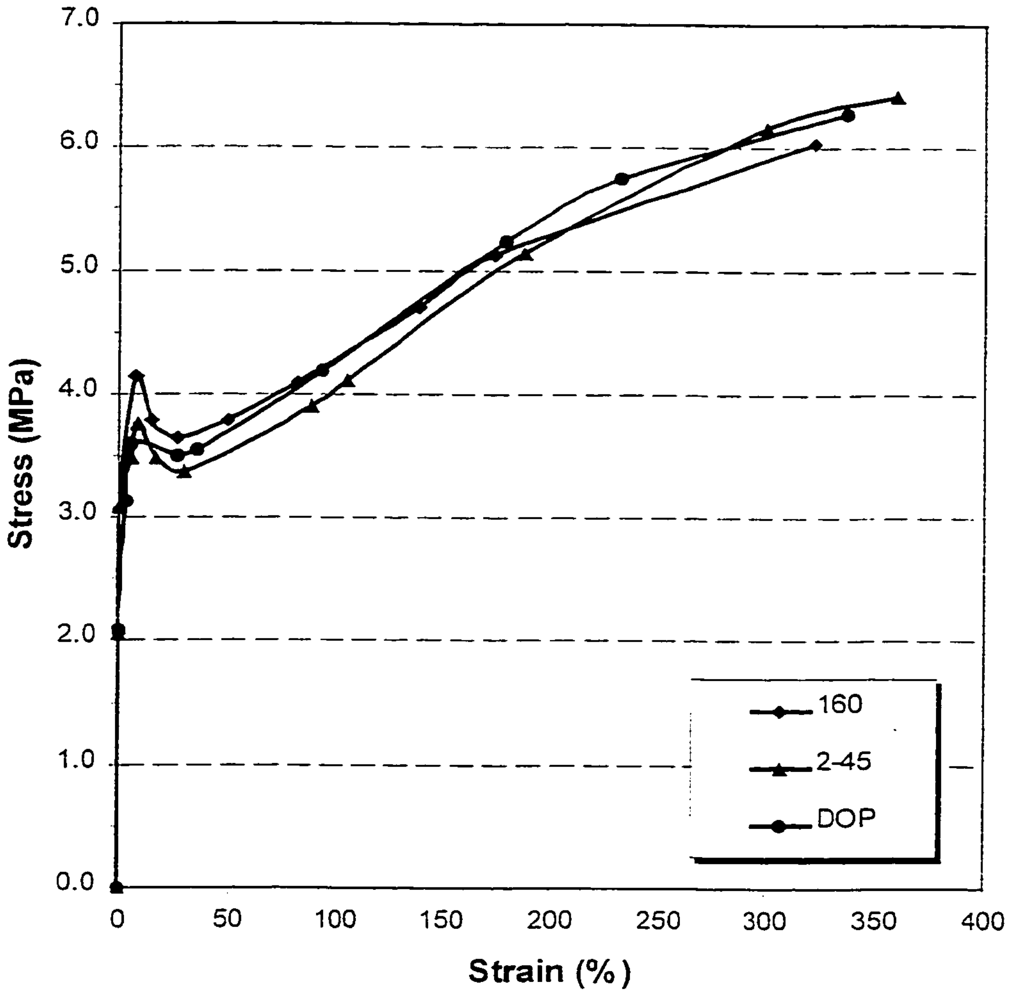


Figure 4.25 Stress-strain curve for controls of PVC-filler composites with different plasticizers.

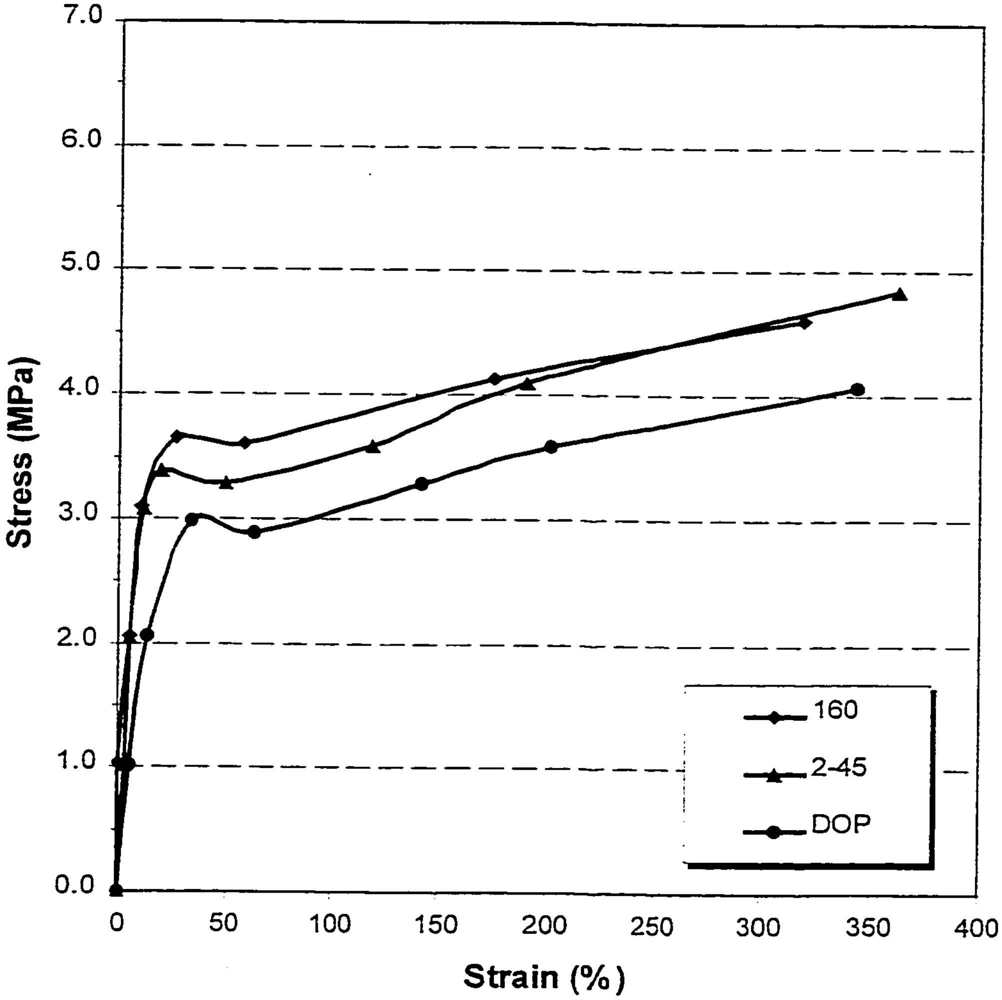


Figure 4.26 Stress-strain curve for PVC-AL-filler composites with 15 phr AL and different plasticizers.

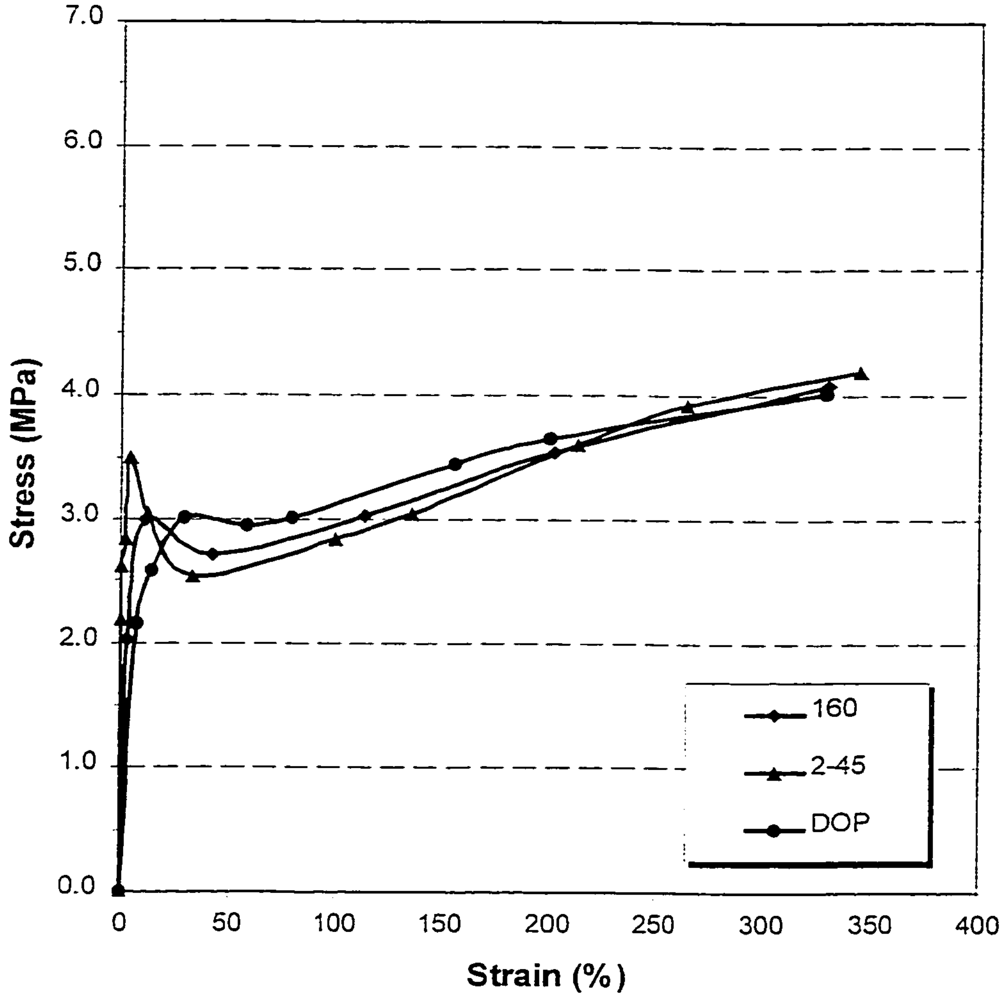


Figure 4.27 Stress-strain curve for PVC-AL-filler composites with 20 phr AL and different plasticizers.

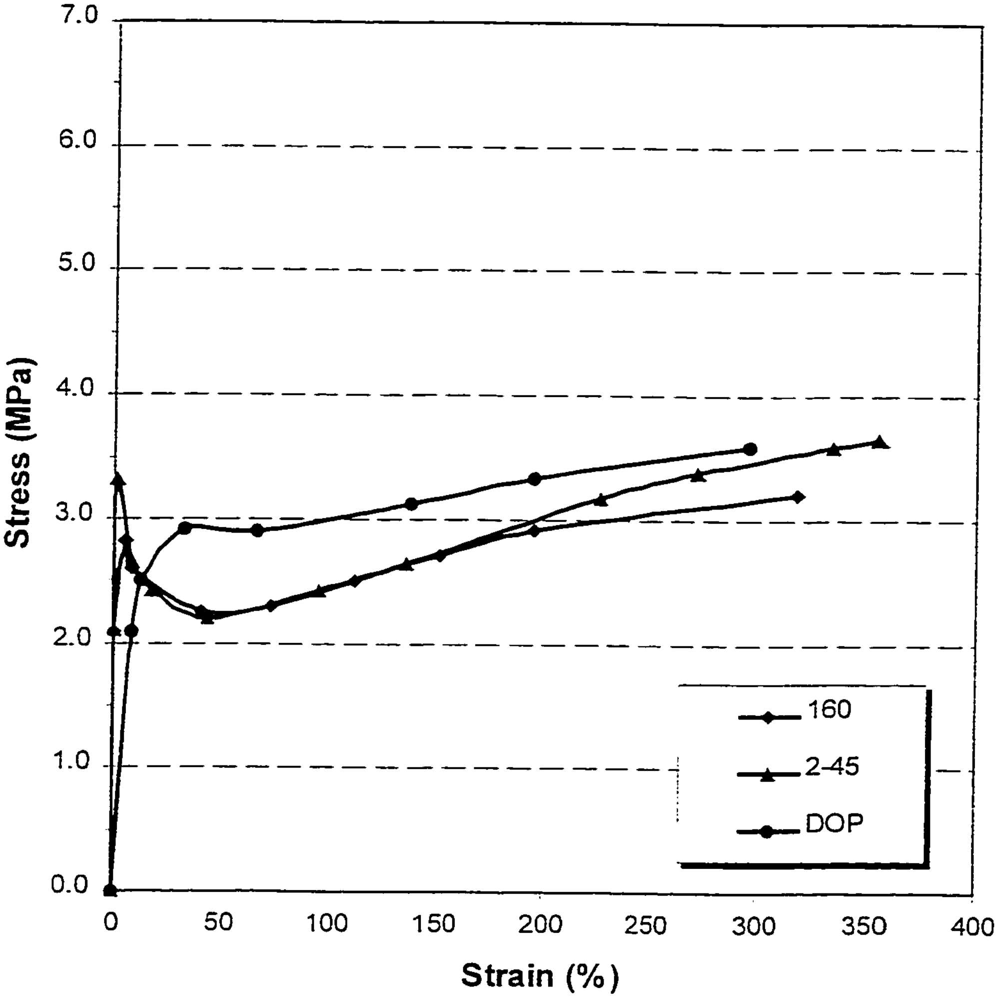


Figure 4.28 Stress-strain curve for PVC-AL-filler composites with 25 phr AL and different plasticizers.

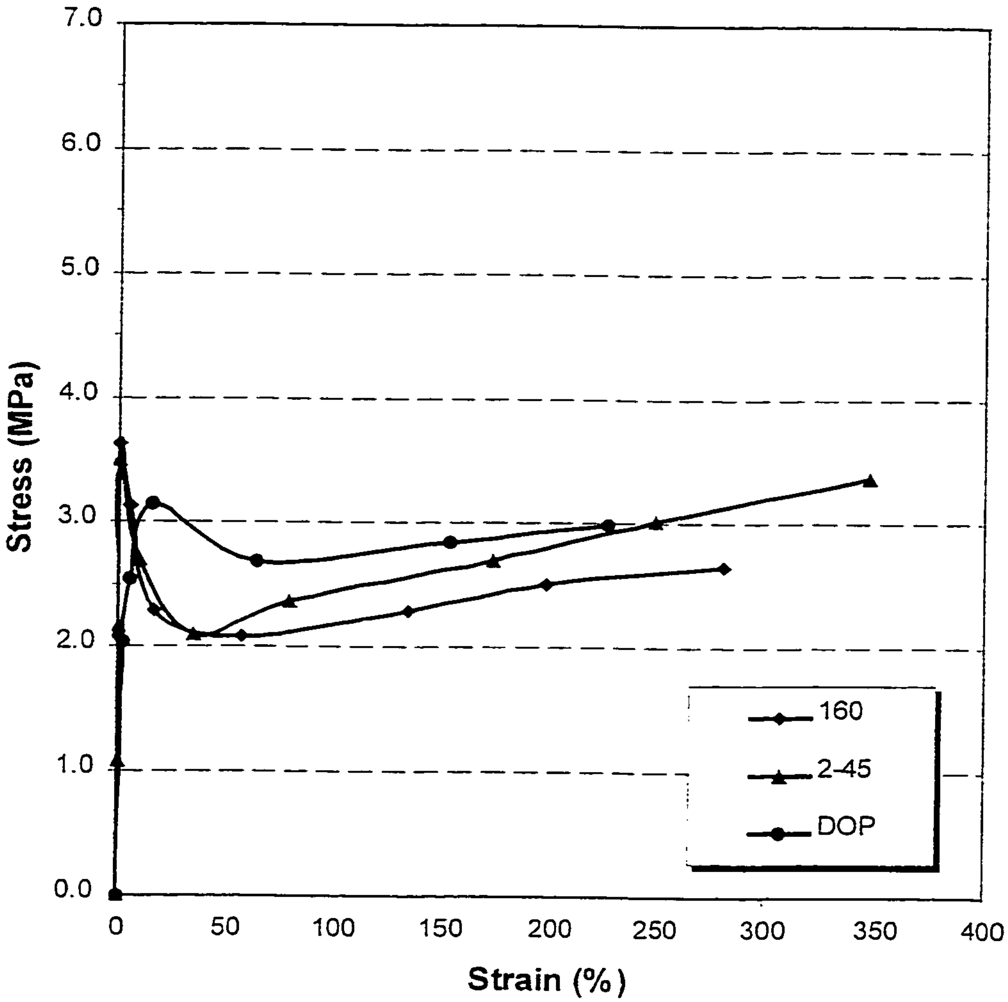


Figure 4.29 Stress-strain curve for PVC-AL-filler composites with 30 phr AL and different plasticizers.

4.4.3.2 HARDNESS

The values of hardness for PVC controls and PVC-AL-filler composites are indicated in Table 4.14. These data show that the gradual replacement of PVC with lignin has little effect on hardness.

Table 4.14 Hardness of PVC-AL-filler composites as function of lignin content and plasticizer.

Sample identification	Hardness		
	2-45 as plasticizer	160 as plasticizer	DOP as plasticizer
PVC control	96.9	97.1	96.3
85 phr PVC-15 phr AL	95.6	94.7	92.9
80 phr PVC-20 phr AL	97.5	95.9	94.0
75 phr PVC-25 phr AL	95.5	96.4	93.7
70 phr PVC-30 phr AL	97.1	94.0	93.4

4.4.3.3 IMPACT STRENGTH

Table 4.15 presents the impact strength of PVC-AL-filler composites and Figure 4.30 is the illustration of impact strength of composites as function of lignin content and type of plasticizer.

The type of plasticizer and the AL content in composites have an important effect on impact properties of composites. For PVC controls the highest impact values are obtained with DOP, suggesting that this plasticizer is the most efficient in dispersing filler particles. Data from Figure 4.30 indicate a continuous decrease of the impact values which correlate with AL concentration in composites. At 25 and 30 parts AL in composites the impact values are only of about 50% and 40% of the values of respective controls regardless to the type of plasticizer. Up to 25 parts AL in composites the decrease in impact strength has a particular trend for each type of plasticizer, the lowest decreasing being for 2-45 plasticizer and the highest for DOP. These results also point out the possibility of morphological differences as function of AL content and as function of plasticizer type affecting the impact properties.

Table 4.15 Impact strength of PVC-AL-filler composites as function of lignin content and plasticizer.

Sample identification	Impact strength, J/m		
	2-45 as plasticizer	160 as plasticizer	DOP as plasticizer
PVC control	106.4	97.7	152.9
85 phr PVC-15 phr AL	103.7	78.2	142.3
80 phr PVC-20 phr AL	94.6	83.4	91.8
75 phr PVC-25 phr AL	56.7	67.1	80.0
70 phr PVC-30 phr AL	42.7	38.7	66.3

If we analyze the tensile, impact and hardness data resulted for the composites obtained with several AL loadings and different plasticizers, it is immediately apparent that it is possible to replace up to 20 parts PVC by AL in composites having 2-45 as plasticizer. At these values of PVC replacement with AL, the mechanical properties of the resulted composites are still appreciable and in the range of the required values for vinyl flooring materials, as shown in Chapter 2.

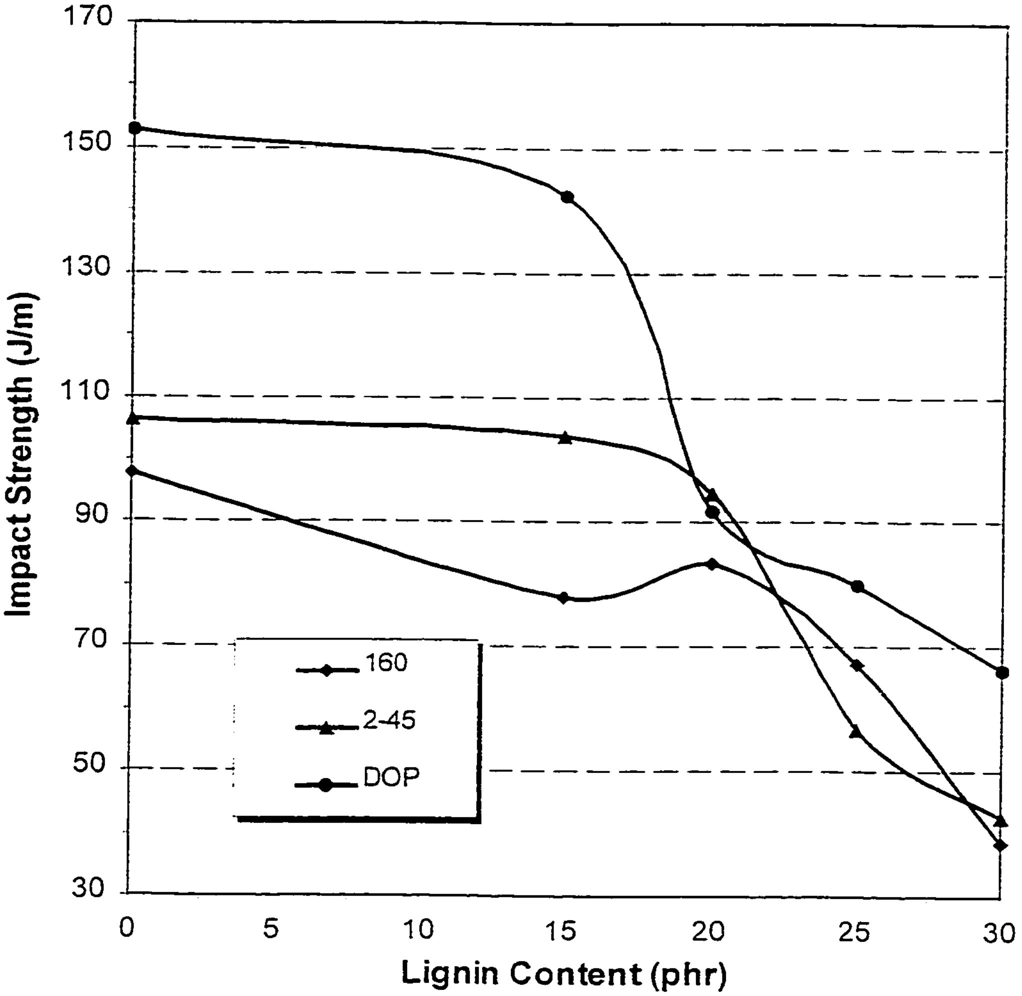


Figure 4.30 Impact strength of PVC-AL-filler blends as function of lignin content.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

5.1 CONCLUSIONS

The present research was carried out to obtain and evaluate PVC-AL blends as matrix resin for composites for flooring application, as flexible tiles and sheets.

In these blends the matrix resin level was always the same, i.e. 100 phr to 200 phr calcium carbonate filler but its composition varied from 85-15, 80-20, 75-25, and 70-30 parts PVC-AL. DOP, 160 and 2-45 were used as plasticizers at level of 35 parts per 100 parts resin. All the plasticizers used in this study were compatible with PVC but only plasticizers 160 and 2-45 were compatible with AL. In order to obtain an effective plasticizer for AL the research was done in several steps.

Based on the results of each step the following conclusions may be made:

(1) lignin can be plasticized and its plasticization diminishes the high degree of association occurring within AL macromolecules, as confirmed by DSC determination of T_g;

(2) The compatibility and efficiency of an AL plasticizer is strongly influenced by the solubility parameter (δ) of the plasticizer. High values of the δ imply good compatibility;

(3) Blends of AL and PVC (0 to 30 phr AL) in the presence of different plasticizers representing a range of variation in regard to their efficiency in AL show that most of the blends are homogeneous exhibiting one sharp T_g which is close to room temperature;

(4) A good efficiency of the plasticizers in PVC-AL blends was found at a level of 35 parts per 100 parts resin;

(5) In these blends the presence of AL produces a slight degree of stiffness increase accompanied by moderate losses of strength and elongation at break;

(6) Mechanical properties of these blends correlate well with the degree of lignin dispersion in the blends and with plasticizer efficiency for AL. In these respect, the best plasticizer seems to be 2-45 and the worst is DOP;

(7) In the composites with 200 phr calcium carbonate as filler, the replacement of PVC by AL can be done by up to 30 phr without processing problems. At higher AL concentration the material becomes very sticky and difficult to be removed from the mixer parts;

(8) At levels of 25 and 30 parts in composites, AL produces a quite high degree of stiffness increase associated with severe losses in strength at break and impact strength. The decrease in elongation is very moderate for DOP and slight for 2-45 and 160 plasticizers;

(9) In the composites formulated with 2-45 and 160 as plasticizers, it is possible to replace up to 20 parts PVC by AL. At these levels of PVC replacement the tensile, impact and hardness properties are still appreciable and in the range of the required values for vinyl flooring materials;

(10)In terms of the economic factors, the degree of price reduction with the addition of AL is outstanding and the prices can be seen in Table 5.1.

Table 5.1 Comparison of the prices of flooring materials with 20 parts lignin/without lignin.

	Prices with the use of AL (20 parts), \$ Cdn. per kg	Prices without the use of lignin, \$ Cdn. per kg	Decrease of price with the use of lignin, %
2-45 as plasticizer	1.15	1.31	11.5
160 as plasticizer	1.15	1.31	11.5

5.2 RECOMMENDATIONS FOR THE FUTURE STUDIES

The present study reveals that the replacement of PVC with up to 20 parts organosolv lignin in flooring formulations is feasible. Besides tensile and impact tests other tests specific for flooring materials and in accordance with existing standard methods should be included in the future studies.

Emission of volatile organic compounds (VOC's) should be tested as well in order to establish the efficiency of AL in this respect.

In addition, taking into account that lignin plasticization was undertaken for the first time in this study, recommendations may be made with respect to continuous studies on this issue and with respect to studies which incorporated plasticized lignin in other polymeric based building materials.

So far a satisfactory standard test for VOC's of flooring materials does not exist, and the future study has to insist in the finding of such a method.

More fundamental research has to be done to explain better the effects of lignin and plasticizer on composite properties.

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