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POLYBLENDING OF RIGID PVC WITH KRAFT LIGNIN: APPLICATION TO THE BUILDING EXTERIOR FACADE

Somia Elraghi

A Thesis

in

The Centre For Building Studies

Presented in Partial Fulfillment of the Requirements
for the Degree of Master of Applied Science at
Concordia University
Montréal, Quebéc, Canada

August 1993

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Abstract

Polyblending of Rigid PVC With Kraft Lignin: Application to The Building Exterior Facade

Somia Elraghi

The aim of the project is to obtain a new kind of rigid PVC, cheaper and with better outside weathering properties and to find new application for lignin.

New rigid poly(vinyl chloride) (PVC) formulations were prepared by polyblending with kraft lignin (L), by partial or total replacement of Titanium dioxide (TiO_2). The original unplasticized PVC (UPVC) formulations had different loading of TiO_2 (from 0 to 10 parts per hundred parts of PVC) and the kraft lignin was introduced from 2.5 to 10 parts per hundred parts of PVC.

These new polyblends were tested in a detailed program. The specimens were prepared by melt mixing and compression molding and subjected to accelerated weathering periods from 168 hour to 2016 hour under the effect of UV light and humidity.

The evaluation of polyblends was carried out by comparison of blended PVC with unblended PVC. The tension testing results showed that the kraft lignin improved the tensile strength of PVC. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) displayed a single glass transition temperature very close to that of PVC in all cases, indicating that L - PVC blends are compatible.

Laboratory tests showed that L addition did not change other PVC properties such as:

- rate of burning
- heat distorticn temperature
- percentage water absorption

In short, polyblending of PVC with kraft lignin would reduce the cost of PVC with no effects on its processability and its performance. Improvements can be expected by using a UV stabilized lignin.

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Table of Contents

Abstract III

Acknowledgements V

Table of Contents VI

List of Figures IX

List of Tables XI

List of Symbols XII

1. Introduction 1

2. Rigid PVC 3

  2.1 Definition 3

  2.2 Chemical structure 3

  2.3 Properties 4

  2.4 Thermal degradation 4

  2.5 Photochemical degradation 7

  2.6 Principal components of rigid PVC formulations 10

  2.7 Applications 14

3. Polyblending 17

3.1 Definition 17

3.2 Classification of polyblends 17

4. Lignin as a base for polymeric products 19

4.1 Definition 19

4.2 Different lignin sources 19

4.3 Chemical structure 20

4.4 Polyblends with lignin and applications in building 23

5. Experimental program 27

5.1 Objectives 27

5.2 Raw materials 28

5.2.1 PVC 28

5.2.2 Lignin 29

5.3 Polyblends preparation and processing 29

5.3.1 Fusion and mixing using a torque rheometer 30

5.3.2 Compression molding 32

5.3.3 Specimens preparation 33

5.3.4 Results and discussion 33

5.4 Durability 35

5.4.1 Accelerated weathering test 35

6. Characterization of PVC - Lignin polyblends 38
  6.1 Mechanical properties, tension testing 38
    6.1.1 Results and discussion 41
  6.2 Thermal properties 54
    6.2.1 Differential scanning calorimetry (DSC) 54
      6.2.1.1 Results and discussion 57
    6.2.2 Dynamic Mechanical Analysis (DMA) 64
      6.2.2.1 Results and discussion 66
    6.2.3 Heat Distortion temperature 74
      6.2.3.1 Results and discussion 75
  6.3 Water Absorbtion 78
    6.3.1 Results and discussion 79
  6.4 Laboratory flammability test 82
    6.4.1 Results and discussion 83

7. Cost evaluation 84

8. Conclusions and recommendations 85

9. References 88

List of Figures

No	Title	Page
1.	Chemical structure of lignin	22
2.	Brabender Torque Rheometer	31
4.	Effect of lignin on fusion torque of PVC	32
5.	Accelerated weathering tester	34
6.	Tension testing specimen	37
7.	Mechanical testing, Instron universal testing machine	40
8.	Variation of tensile strength at break with lignin loading before weathering	47
9.	Variation of tensile strength of blended and unblended PVC with weathering period	48
10.	Variation of tensile strength of polyblends (no TiO_2) and PVC with weathering period	49
11.	Variation of elongation at yield for blended and unblended PVC with weathering period	50
12.	Variation of elongation at yield of polyblends (no TiO_2) and PVC with weathering period	51
13.	Variation of elongation at break for blended and unblended PVC with weathering period	52

14. Variation of elongation at break of polyblends (no TiO_2) and PVC with weathering period. 53
15. Thrmal analysis (DSC) apparatus 55
16. DSC diagram for PVC - 0L -10T 59
17. DSC diagram for PVC - 5L - 5T 60
18. DSC diagram for blended and unblended PVC before weathering 61
19. DSC diagram for blended and unblended PVC after weathering 62
20. Effect of weathering on the glass transition temperature of blended and unblended PVC (DSC) 63
21. Thermal analysis (DMA) apparatus 65
22. DMA diagram for PVC - 0L - 10T 69
23. DMA diagram for PVC - 5L - 0T 70
24. DMA diagram for blended and unblended PVC before weathering 71
25. DMA diagram for blended and unblended PVC after weathering 72
26. Effect of weathering on the glass transition temperature of blended and unblended PVC (DMA) 73
27. Heat deflection temperature determination apparatus 75
28. Effect of polyblending on heat deflection temperature 77
29. Effect of polyblending on the percentage water absorption of PVC 81

List of Tables

No	Title	Page
1.	Plastic consumption in western Europe	15
2.	The basic formulation for polyblending	28
3.	Lignin characteristics	29
4.	Effect of lignin on the fusion characteristics of PVC	33
5.	Tensile strength at yield of blended and unblended PVC before and after weathering	41
6.	Percentage elongation at yield for blended and unblended PVC before and after weathering	42
7.	Percentage elongation at break for blended and unblended PVC before and after weathering	43
8.	Results of thermal analysis of blended and unblended PVC before and after weathering using DSC technique	57
9.	Results of thermal analysis of blended and unblended PVC before and after weathering using DMA technique	66
10.	Heat deflection temperature of blended and unblended PVC	75
11.	Percentage water absorption of blended and unblended PVC	79
12.	Cost evaluation of polyblends	84

List of Symbols

Symbol	Description
PVC	Poly(vinyl chloride)
UPVC	Unplasticized poly(vinyl chloride)
L	Lignin
ASTM	American society for testing and materials
DSC	Differential scanning calorimetry
DMA	Dynamic mechanical analysis
Tg	Glass transition temperature
UV	Ultraviolet radiation
Cp	Heat capacity
IR	Infrared radiation
C	Carbon atom
O	Oxygen atom
MW	Molecular weight
HCL	Hydrogen Chloride
Cl	Chlorine atom
HDPE	High density poly ethylene
PP	Polypropylene
PS	Polystyrene

EPS	Extruded polystyrene
ABS	Acrylo - nitrile - butadiene - styrene
LOI	Oxygen index
K	Average molecular weight

1. Introduction

Vinyl chloride has been made commercially in the United States since 1939. Today, the amount of PVC produced worldwide represents about 30% of the total production of thermoplastics, It has good physical properties, water, chemical and abrasion resistance and good strength properties; it also has compounding versatility for a wide variety of applications. The major market of PVC is its use in the building and construction industry [1].

The main problem is that PVC is sensitive to the weathering, UV irradiation and presence of oxygen and humidity induces changes in mechanical properties and colour [2].Titanium dioxide (TiO_2) together with UV stabilisers is usually incorporated in PVC composition to protect the polymer from weathering action; it has a screening action which is due to the reflection and scattering of radiation, however due to the high prices of TiO_2 (1.54 - 2.67 $/Kg) higher than the PVC price, PVC producers are looking for ways to reduce their TiO_2 consumption [3].

The polymer blending is becoming one of the more feasible and economical methods to develop new materials from available base polymers by mixing them with other cheap and abundant polymers [4].

In this research UPVC polymer was blended with kraft lignin (L), a by - product of the pulp and paper industry; it is an inexpensive natural and abundant polymer, and it has good strength and UV absorption properties. The objective of this research is to prepare and evaluate PVC - L polyblends by comparison with unblended PVC characteristics.

The effect of lignin on the processability of PVC as well as the mechanical and thermal properties of polyblends before and after weathering were investigated.

Due to the presence of high concentration of OH groups and high content of carbon and oxygen atoms in the lignin structure, the polyblends were also tested for water absorption and flammability.

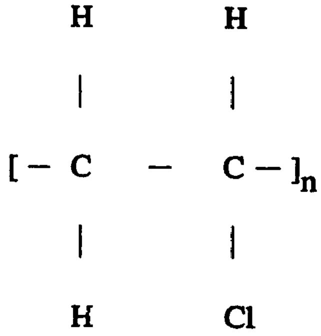
2. Rigid PVC

2.1 Definition:

Rigid PVC is unplasticized. UPVC materials based on homopolymers or copolymers are produced by extrusion or molding.

2.2 Chemical Structure:

The basic repeat unit of the PVC polymer chain is



$$[-\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}} - \overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{Cl}}{|}}{\mathrm{C}}} -]_n$$

where n is the degree of polymerization, i.e. the number of repeating units in the molecular chain. The units are linked head to tail, i.e. $-\mathrm{CH_2}-\mathrm{CHCl}-\mathrm{CH_2}-\mathrm{CHCl}-$, and in a commercial PVC polymer the average value of n ranges between 500 and 1500. Most commercial PVC have K value within the range of 50 - 80 equivalent to about 50,000 - 500,000 MW.

Commercial PVC polymers may be regarded as essentially amorphous although the crystalline material content is of about 2 - 10%. The glass transition temperature (Tg) lies in the range 80 - 84^{o}C.

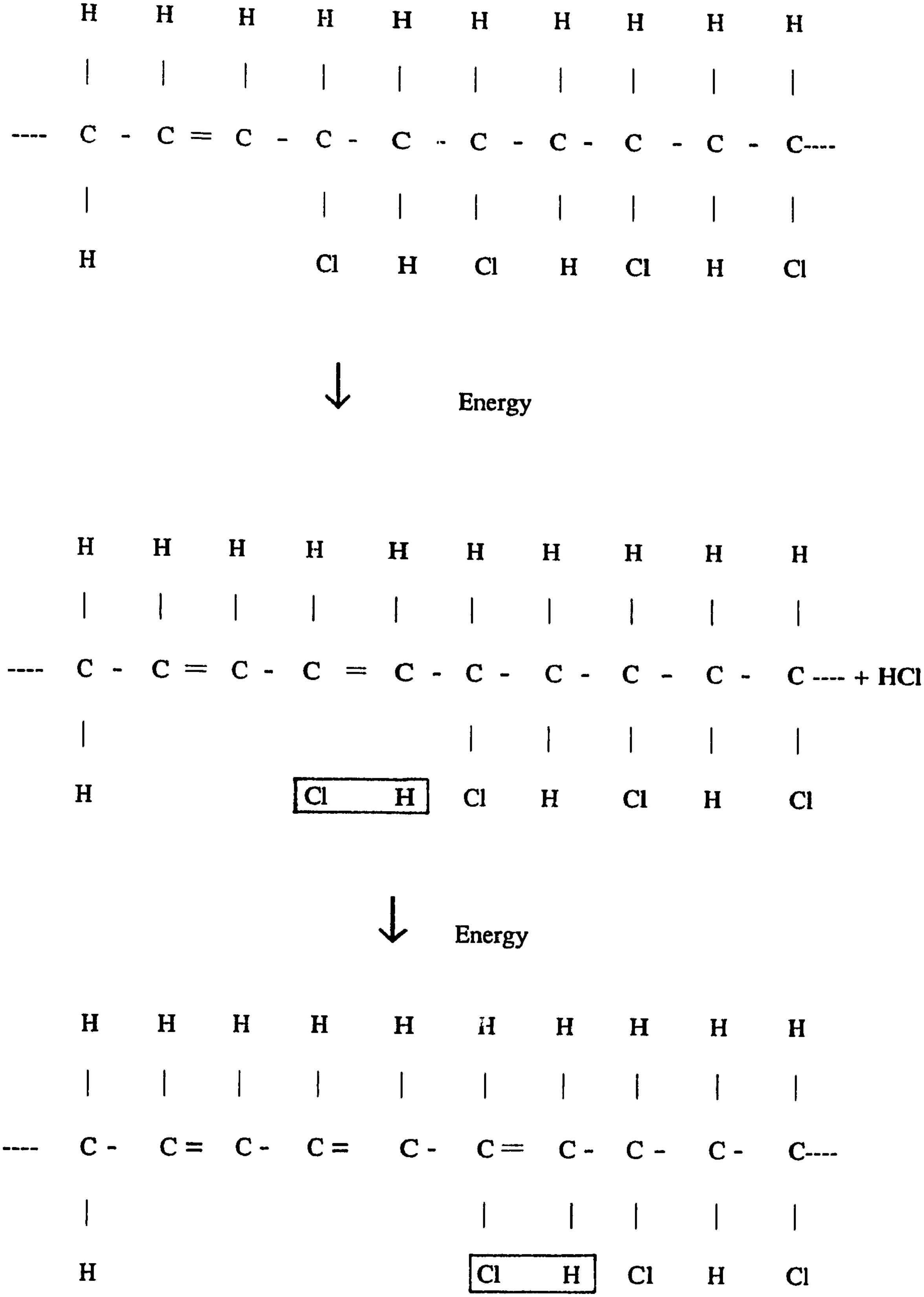
The polymerization techniques used to produce PVC polymers are suspension polymerization (80% of total commercial production), emulsion polymerization (≈10 - 15%), bulk polymerization (10%) and solution polymerization [5].

2.3 Properties:

PVC has achieved a market leadership because of its good physical properties, its easy compounding for a wide variety of applications, its relatively low cost and processing ease. Other desirable properties include self - extinguishing character, water, chemical and abrasion resistance, good strength properties and possibility to be obtained in a complete range of colours. PVC compounds are resistant to most acids, fats, petroleum products and salts.

2.4 Thermal degradation of PVC:

The main manifestations of thermal degradation of PVC are the evolution of hydrogen chloride, change of colour (progressing with the extent of breakdown from light yellow, through reddish brown, to almost black in severe cases) and deterioration of the properties. Due to the elimination of hydrogen chloride double bonds are formed between carbon atoms as follows:


Energy
+ HCl
Energy

The development of the colour is attributed to the conjugated double bond system formed in this process (colour change appears with as few as seven conjugated double bonds in a polyene) whilst it is known that sequences of up to about 30 can arise in the course of dehydrochlorination of PVC [6,7].

Dehydrochlorination can occur even at moderately elevated temperature (about 100°C); it is catalyzed by HCl evolved and can also be promoted by other strong acids. In addition to dehydrochlorination, thermal degradation of PVC polymer in the presence of oxygen also involves oxidation with the formation of hydroperoxide, cyclic peroxide, ketone groups. Chain scission and crosslinking can also take place as degradation proceeds both in air and in an inert atmosphere. Thermal degradation varies with the process of manufacture of PVC polymer. The thermal stability decreases in the following sequences:

Mass polymer ----> suspension polymer ----> emulsion polymer

This is normally attributable to the amount of impurities present, which increases in the same sequences. In compounds, the stability of the PVC resin can be adversely influenced by other constituents (e.g plasticiser, antistatic agents and some colorants), and every PVC composition should be treated as having an individual stabilisation problem.

2.5 Photochemical degradation:

All the main external manifestations associated with thermal degradation of PVC appear also as a result of photolysis i.e dehydrochlorination, development of colour and deterioration of properties. Embrittlement and cracking can also occur in varying degrees [8].

The dissociation energy of carbon - chlorine bond is about 77 k cal mol^{-1}; this corresponds to the energy of light wavelength of 375 nm [9]; therefore light of this wavelength (in the near - UV part of the spectrum) should be able to cause photodegradation of PVC. In practice the process requires higher photo energy (UV light of shorter wavelengths). It is known that the UV band between about 290 and 315 nm is mainly responsible for the photochemical degradation of polymers including PVC.

However the mechanisms of this process in PVC are less well understood than those of thermal degradation. The main features indicated by available evidence may be briefly summarised as follows:

1) Photo - oxidation begins as chromophoric groups as hydroperoxide and ketone absorb light of wavelengths > 250 nm. After that free radicals (highly reactive atoms or groups of atoms with unpaired electrons) are formed; further these radicals react with other PVC macromolecules, removing HCl from the polymer. As a result more longer polyene sequences are formed (polyene sequences are defined as $(C = C)n$ where n= 2, 3, 4, 5 etc

double bonds). As the polyene sequences increase (i.e ≥ 8), the light absorption is shifted to longer wavelengths thus producing discoloration (from yellow to dark red). The severity of discoloration may decrease with extended UV radiation (bleaching effect), oxygen presence reduces the extent of the discoloration in UV - irradiated PVC. This bleaching process results from reaction of polyenyl radical with oxygen and it will lead to a step by step shortening of polyene sequences (crosslinking). These short polyenes do not absorb light in the visible region and subsequently reduce the rate of discoloration [11,13].

2) Oxidation products (alcohols, ketone, aldehydes) may also be formed from the free radicals according to the following stages: free radicals ----> peroxides from free radicals and oxygen ----> peroxi radicals from unstable peroxide structures ----> alcohols, aldehydes, ketones from peroxi radicals. They are light absorbing units and are sensitive to water. Rain loosens these products and gradually erodes the PVC surface. The surface becomes brittle due to the erosion as well as to the chain scission which occur during photo - oxidation. For a properly compounded PVC this embrittlement would occur slowly over many years [12,13].

The effect of UV is combined with other environmental factors such as:-

a) **Heat:-**

It has been noticed that combined effects of UV light and heat produce greater damage than that produced by each one separately [14].

b) **Moisture:-**

Moisture, whether liquid water or water vapour may accelerate the deterioration of PVC sheets during outside exposure. Alcohols, ketones and aldehydes are produced as dehydrochlorination occurs during oxidation process; these products are very sensitive to water. Rain loosens these products and gradually erodes the PVC surface [13,29].

2.5.1 **Properties affected through degradation:**

Change of mechanical properties:

For plastics which are initially tough, degradation may cause embrittlement (reduction of strain prior to failure). Crosslinking and molecular chain scission are principal causes of this embrittlement. Photooxidative molecular chain scission results in decrease of MW (and therefore a decrease in strength), and the increase in crosslinking increases stiffness and reduces elongation. Warshaw [15] reported about the elongation at break and tensile strength of PVC compounds exposed to outdoor weathering for 10 years. It was found that there was a slight increase in tensile strength from 330 N/cm^2 as manufactured,to 365 N/cm^2 after 10 years which was explained as an effect of crosslinking occurring during UV degradation.

Change in optical properties:-

Discoloration and a reduction in reflectance are caused by environmentally - induced degradation. Discoloration is the first change observed in plastics. Factors detemining the extent of colour change include chemical nature of the resin and technique of manufacture [16].

2.6 Main components of rigid PVC formulations:

2.6.1 Heat Stabilisers:

Heat stabilisers may be divided into:-

1. Lead compounds
2. Organotin stabilisers
3. Compounds of other metals such as of lithium, cadmium, aluminum, sodium, calcium, zinc ...etc
4. Organic stabilisers

These are additives incorporated in the PVC by physical mixing. Examples of this approach to stabilisation include treatment of PVC polymer with triphenyl aluminum to substitute phenyl groups for liable Cl atoms in the chain. Also replacement of the liable Cl can be done by mercaptide groups through reaction of PVC polymer with dibutyltin mercaptide salts. [17].

2.6.2 Antioxidants and UV absorbers:

Many heat stabilisers have antioxidant action. Primary antioxidants (without heat - stabilising action) are also used as additives in PVC either incorporated individually or as constituents of composite commercial stabiliser system. These additives are in general phenol derivatives. Primarily antioxidants are essentially scavengers of free radicals. Additives with secondary antioxidant action are able to remove peroxide radicals and to decompose hydroperoxide groups (which can act as free radical initiators in the oxidative degradation process) converting them to inactive derivative through chemical reaction. Incorporation of antioxidants can improve the heat stability of PVC compositions and stability to light.

2.6.3 UV Absorbers:

UV radiation of wavelength 310 nm is often considered the most damaging to PVC. This wavelength range excites the PVC macromolecules in the sense of imparting excess energy sufficient to break bonds in the molecular chains. The free radicals formed as a result 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 Titanium dioxide widely used as pigments for plastics, have a light stabilising effect on many polymers including PVC. They are often referred to as "light screens"; each functions as a physical barrier to radiation both UV and visible. Carbon black absorbs the radiation over both these wavelength ranges and emits the energy in IR region. It is also believed to act as antioxidant by capturing free radicals. TiO_2 has some UV absorption but its screening action is principally due to reflection and scattering of radiation (IR, visible and UV) [18].

2.6.4 Fillers in PVC:

Fillers defined as solid particulate or fibrous materials, chemically inert, are incorporated in plastic compositions to modify the properties (hardness) or to reduce material cost, in the ideal case when no processing difficulties and no rise in the process/production cost occur.

Glass fibre and mineral fillers as calcium carbonate are usually used in the PVC compositions. In the rigid compositions, fillers are not normally included to reduce material cost, but to improve the processing or physical properties of the end product. For example the presence of calcium carbonate increases the internal friction and the mixing shear of the melt during compounding, Thus improving the dispersion of the other additives [19].

2.6.5 Lubricants:

The principal function of an external lubricant is to reduce the friction against and (sticking to) the surfaces of the processing machinery and mold. The internal lubricant lowers the internal friction of the compound in processing, reducing the effective melt viscosity and frictional heat build - up. Both internal and external lubrication can improve the heat stability of rigid PVC through the reduction of internal and external friction.

2.6.6 Polymeric modifiers:

Are used to improve the impact strength of the product and/or serve as processing aids. Important contribution of acrylic processing aids include greater output speeder fluxing and therefore improved mixing, eliminating or reducing of melt fracture, improved tensile and impact strength.

2.6.7 Colorants:

Colorants should be resistant to HCl. TiO_2 is used as a white pigment to enhance the brightness of colour produced by an associated colorant and to provide opacity. TiO_2 lowers moisture pick - up and improves durability by ease of dispersion.

2.6.8 Antistatic Agents:

If it is necessary to have methods of preventing static electricity charge built - up, incorporation of an "antistatic agent" in the PVC material may enable any charge build - up to be neutral. Antistatic agents are chemicals which are either incorporated in a plastic or applied externally to reduce charge build - up and promote charge dissipation. Examples of these agents are amines, amides and ammonium compounds.

2.7 Applications:

PVC products range from soft, flexible films to rigid high strength materials. Plasticiser, lubricants, fillers and stabilizers are used to produce this versatility and it is possible to make a compound with the right balance of properties for almost any application.

It is seen from table 1 that in Western Europe PVC showed a growth rate over the 1980 - 1990 decade of 3% per annum [20].

Table 1 - Plastic consumption in Western Europe

Material	Consumption (tonnes x 10^6)		
	1980	1990	Growth Rate (%/year)
HDPE	1320	2070	4
PP	1230	2550	
PS/EPS	1535	1900	2
PVC	3710	5140	3
ABS	280	390	3.5
Nylons	180	335	6
Acrylic	130	190	3.5
Polyesters	104	420	15
Polycarbonate	60	130	8
Polyacetal	48	80	5

Principal market of rigid PVC includes pipe, pipe fittings, pressure pipe for potable water and drainage. Rigid PVC sheeting is produced by extrusion or calendering (thick sheets are made by compression) and the main applications of this kind include roofing, external and internal cladding, lining of tanks for chemicals or food storage. Rigid extruded profile used for external cladding of building (siding) represents a substantial outlet in North America. UPVC window and door frames and complete window systems are produced from special compositions formulated for resistance to weathering and impact.

Flexible PVC is used for baby pants, dolls, bottles, films,tubes sheeting, gaskets. Both rigid and flexible PVC compositions are used in packaging applications as bottles; rigid thermofoil are widely used for nestings in cake, biscuit, thin films are used in packaging of food staffs especially meat, fruits, vegetables, and cheese. The insulation and sheathing of cables constituted the first important use for plasticized PVC.

Foamed PVC flooring is manufactured from several layers of spread paste with a chemically foamed layer sandwiched below the top near layer.

3. Polyblending

3.1 Definition:

Polyblends constitute a group of materials that are simple to obtain by physical mixing of different polymers. The properties of polymers can be varied by blending carefully selected polymers, such that the end product has more desirable properties than those of its components. Polyblending has become one of the most important commercial way to develop materials to meet the specific functional needs in industry or to change the properties to suit industrial requirements. One of the main aims of polyblending is the production of good performance materials with low cost. This is achieved through an infinite possibilities of blending, the ability to use the available processing equipment and the capacity to combine expensive polymers with cheap and abundant ones [21,22].

3.2 Classification of Polyblends:

Polyblends are classified into incompatible (immiscible), semi compatible and compatible (miscible). Usually blending two polymers leads to a class of materials whose properties are due to the presence of two components. When two distinct phases remain upon mixing, the polyblends are considered immiscible, and in miscible blends a single - phase system is formed [23]. In this last case the level of molecular mixing is adequate to yield the macroscopic properties expected of a single phase material [21]. In practice the degree of compatibility is defined with respect to the resulting properties of the polyblends. The properties of polyblends depend apart from the properties of the constituent polymers upon the morphology of the blend [21,22,23]. The size, shape, the distribution and degree of separation of the dispersed and continuous phases will in turn depend by the following:

1- Interfacial adhesion properties of the polymers
2- Volume ratio of the components
3- Composition of constituent polymer
4- MW and structure of each polymer
5- Blending conditions including temperature and pressure
6- Method of blend preparation, i.e mixing, compression, and so on.

In general, compatible polyblends exhibit optical clarity, a single glass transition temperature which is between the Tg's of the components and which has a sharpness of the transition similar to that of the components, and homogeneity at a submicroscopic level (50 - 100 Angstroms) [24,25].

The mechanical properties of these blends are usually superior to those of incompatible ones. Incompatible polyblends have two Tg's which belong to each component, are usually opaque and show true two phasic behaviour [20,25].

With miscible polyblends, a range of price/performance characteristics between the component polymers can lead to a large number of different and useful products. The versatility places miscible polymer blends in a unique situation with potential commercial importance [21].

4. Lignin as a base for polymeric products

4.1 Definition:

Lignin is considered as the second constituent of wood after cellulose. Cellulose represents about 70% and lignin about 30% of the weight of dry wood [26]. Lignin is concentrated in the outer layers of wood cells contributing to the strength of the mature plant by holding these cells together.

4.2 Different lignin sources:

Plant lignin can be divided into three broad classes, which are commonly called softwood (gymnosperm), hardwood (dicotyledonous angiosperm), and the grass or annual plant (monocotyledonous angiosperm) lignin.

In plants, cellulose fibres are bonded to lignin. There are two main methods for making chemical pulp, i.e isolating cellulosic fibres by chemical means which consists mainly of removing the lignin from wood or other plants:

1. The acidic sulphite method
2. The alkaline kraft pulping method

In the acidic sulphite method, wood is cooked with salts of sulphurous acid, whereas in the alkaline process, it is cooked with a solution (white liquor) containing sodium hydroxide and sodium sulphide. The dark solution of the degraded lignin dissolved out of the wood is called spent sulphite liquor in the sulphite process and black liquor in the kraft process. In the alkaline kraft process the black liquor is concentrated and used as a source of heat for the manufacture of steam which is necessary for the production of paper.

4.3 Chemical structure:

The chemical structure of lignin is not completely known. Lignin is a highly branched, randomly structured, three dimensional polymer consisting of phenylpropane units held together by ether and carbon - carbon bonds as shown in figure 1. The analysis shows that lignin has an aromatic nature and numerous functional groups (as shown in table 3) [27].

Lignin is an amorphous polydisperse polymer (no definite melting point), and the molecular weight of lignin ranges from 1000 to 12,000 depending on the conditions of isolation. It has a strong absorption capacity (surface area 180 m^2/gm) [29]. It has a characteristic ultraviolet absorption spectrum, with maximum absorption at 210 nm, and weaker absorption at 280 nm. The infrared absorption ranges between 800 cm^{-1} and 3600 cm^{-1}.

Lignin possesses a good thermal stability (Carbonization begins at a temperature slightly 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 formed.

Lignin is a natural, non toxic, brown powderlike polymer, commercially available in huge quantities and a low cost resource which can be used as a basic component for new polymeric materials [29].

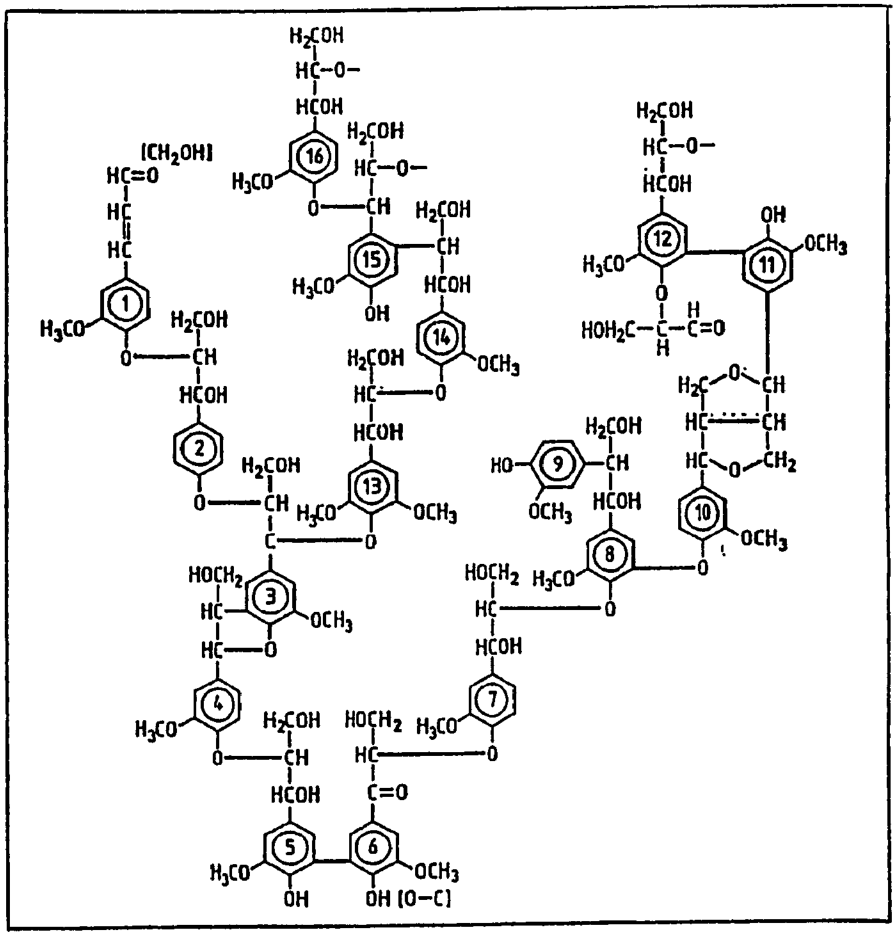


Figure 1 Chemical structure of lignin

4.4 Polyblends with lignin and applications in buildings:

The yearly growth of the world forests is about 7 - 9 billion cubic meters of biomass. During the production of 140 million tons of cellulose and pulp from a part of this biomass, about 50 million tons of lignin are formed. Over 95% of the lignin residue is used as an energy source for the recovery of pulping chemicals or disposed of as a waste [30].

In the last years a lot of research has been done world wide in order to utilize lignin in plastics production as an active filler reinforcer or component of polyblends.

Lignin is cosidered as a high - impact - strength, thermally resistant thermoset polymer. It thus inherently has properties similar to those sought in some uses of engineering plastics. Glasser et al [30] have focused particularly on the possible use of chemically modified lignin as a component in engineering plastics.

The use of lignin in polyblends, example with poly(vinyl alcohol) with no sign of phase separation is a new promising technique [31].

Montogemery improved the strength of poly(vinyl chloride) through blending with a mixture of lignin and butadiene - styrene copolymer [32].

Various attempts have been made to prepare lignin based adhesives. Fuhrman has used lignin as a component in an adhesive for plywood, particle board and fibreboard [31,33].

From studies on the coextrusion of lignosulphonates with vinyl polymers, only part of the sulphur is evolved as sulphur dioxide. A considerable amount of the residual sulphur is converted during the pyrolysis to sulphonyl and sulphur bridges between the basic polymers; model studies indicate that these bridges make the base polymer thermally stable . These reactions permit the use of lignin containing sulphuric acid groups as stabilisers for polymers as polyethylene, polypropylene and poly(vinyl chloride) [34].

Szalay and Jehnson have shown that lignosulphonate increases the thermal stability of poly(vinyl chloride) [30].

According to Leven et al [34] a blending of lignosulphonate with polyethylene in a plasticorder increases the stability as indicated by rheogical behaviour (the flow behaviour of the blends is almost the same as the flow behaviour with increase of temperature of pure polyethylene).

It is evident from general chemical and photochemical properties of nitroxide radicals that nitroxide derivatives of lignin could be used as processing stabilisers for polymers [35].

Gul et al found that lignin derivatives increase the low temperature and UV light resistance of polypropylene [30].

Moorer et al employed lignin in the formation of polyurethane foams [30].

Nicholas employed kraft lignin as a reinforcing agent and antioxidant in elastomeric compositions and he concluded that modified lignin could be incorporated into the matrix of polymers due to functionalization [30].

Chodak et al increased the thermal oxidative stability of polypropylene through blending with kraft lignin [36].

Yoshidiha et al used kraft lignin as a chemical component in the production of polyurethanes. The obtained product has good mechanical properties and high thermal stability [37].

Also Shiroishic et al patented a chemically synthesized kraft lignin/epoxy adhesive having good strength and water resistance [30].

At the Centre for Building Studies (Concordia University), Beznaczuk [38] showed that kraft lignin improves the mechanical performance of a silicone sealant. Khoury studied polyblending of epoxy adhesives with kraft lignin. The resulting polyblends presented an improvement of adhesive tensile strength [39]. Lacasse [40] showed that kraft lignin improves the tensile properties of polyurethane, acrylic and butyl based sealants and recently J. Wang used lignin in an epoxy - lignin system without modifications, resulting in a significant improvement of adhesive joint shear strength up to 178% of that of the epoxy and a considerable cost advantage [27].

It is evident from the discussion that lignin is still a material of the future in the area of structural plastics [30]. However, the ever - increasing demand for a clean environment hastens the day when lignin will be used on a large industrial scale; from this point of view, it is obvious that research should continue and more funds should be allocated to research work on lignin new applications.

5. Experimental Program

5.1 **Objectives:**

The experimental research program was undertaken for the development of a rigid more economic poly(vinyl chloride) formulation for the building industry. It is hoped that further research in the area of lignin - polymer systems will cultivate new markets for lignin, a low cost renewable material which is readily available from the pulp and paper industry.

The main objectives of the research program are:

1. To obtain PVC - lignin polyblends by replacing partially or totally the TiO_2 filler in PVC composition with lignin.
2. To evaluate the properties of the obtained polyblends in comparison with those of unblended PVC.

The effect of lignin on the mechanical, thermal and viscoelastic properties of polyblends was investigated and the durability of the blends, as measured by the change in the above properties as effect of artificial weathering was also examined.

Due to particular characteristics of lignin (high content of OH groups which imparts hygroscopicity and high content of carbon and oxygen atoms which impart flammability), the polyblends were also tested for water absorption and flammability.

5.2 Raw Materials:

5.2.1 PVC

B.F Goodrich unplasticized already compounded PVC commercial resin (GEON 8586) was used for preparing the polyblends with lignin. The PVC is a suspension polymer having a high molecular weight (K value = 67) and the formulation is compounded for outdoor applications. Five batches of the compound containing 0, 2.5, 5, 7.5 and 10 parts TiO_2 (non chalking silica coated) were used in the present study. The basic formulation used is given below:

Table 2 - The basic formulation for polyblending

Ingredient	Level (phr)
PVC resin	100
Dimethyl tin dithioglycolate (stabiliser)	2
Acrylic (processing aid)	1.5
N.butyl acrylate (based impact modifier)	6
Lubricants	3.75
Titanium dioxide	Variable

5.2.2 Lignin:

Kraft lignin (L) was obtained from Domtar Research Center, Seneville, Que. Lignin was separated by sulphuric acid precipitation of black liquor which resulted from the pulping of various hard woods (beech, maple, elm).

Table 3 - Lignin Characteristics [27]

Analysis percentage	C= 65, H = 6, S= 1.5, OH= 10 methoxyl = 17.2, carboxyl= 5, ash= 1.39
Molecular weight	M_w= 2800, M_n= 650, Polydispersity= 4.3
Specific gravity	1.295
Average particle size (micron)	16
Tg °C.	132.7 ± 2%

5.3 Polyblends Preparation And Processing:

The amounts of kraft lignin introduced in the polyblends were 2.5, 5, 7.5 parts per hundred parts (phr) of PVC compound containing TiO_2 and are designated in the text as PVC - 7.5T -2.5L, PVC - 5T - 5L, PVC - 2.5T - 7.5L.

The other three polyblends prepared from lignin and PVC compound without TiO_2 are designated as PVC - 0T - 5L, PVC - 0T - 7.5L, PVC - 0T - 10L. The polyblends were compared with unblended PVC which is designated as PVC - 10T - 0L. All the formulations were prepared by dry blending in a mixer for 5 minutes at room temperature and the processing was carried out in three steps:

5.3.1 Fusion and Mixing Using A Torque Rheometer:

When PVC resins are mixed under appropriate conditions of heat and shear, a fluxed mass is produced. This mass has certain melt characteristics that can be defined with a torque rheometer operated under fluxed conditions of shear and temperature.

C.W 1636 Brabender plasticorder torque rheometer was used according to ASTM D 2538 [41] for mixing the blends and also to study the fusion characteristics of the polyblends, i.e reformulated compounds, in comparison with those of unblended PVC. The apparatus consists of a batch mixer measuring head equipped with roller blades. The mixing head is electrically heated and the temperature was measured by a thermocouple detector as illustrated in figure 2. Several batches of 20.5 gram each were prepared for each formulation. The roller mixer was operated at 195°C and 80 rpm at a time of 8 minutes for each sample. The mixing temperature was suggested by the manufacturer and the mixing time was obtained experimentally.

The resulting torque rheometer curves were used to determine the fusion characteristics of different polyblends (relation between the torque and the time). The maximum point of the curve is the fusion torque; all the values were an average of seven determination for each formulation.

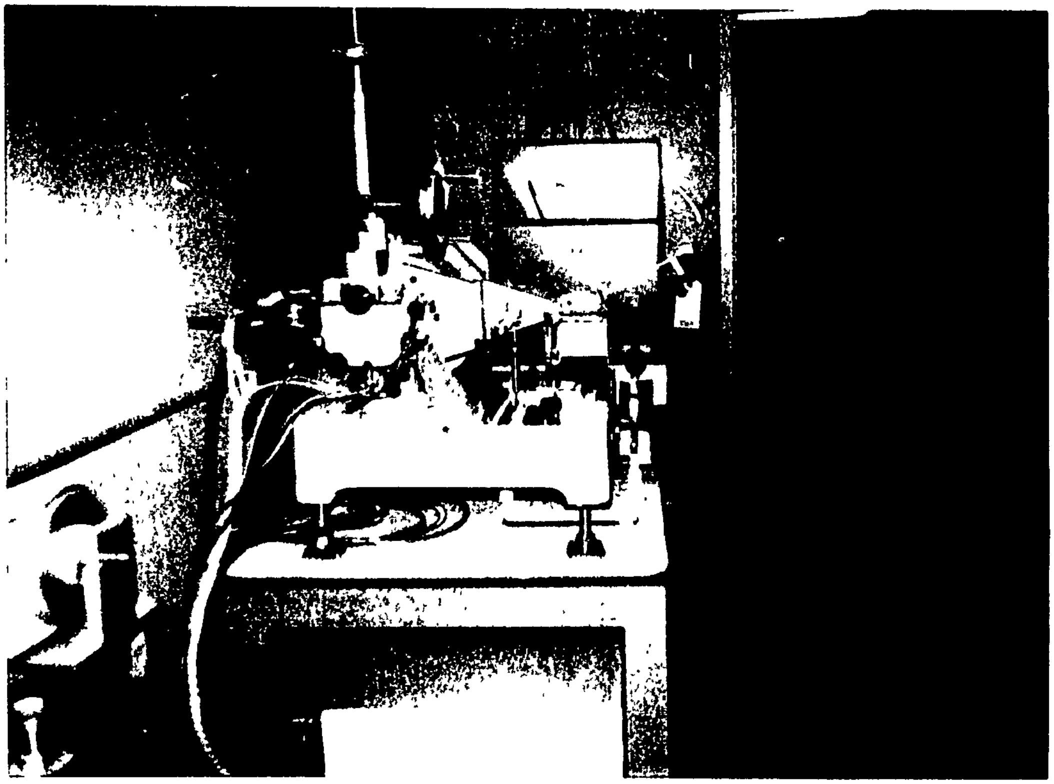


Figure 2 Brabender torque rheometer

5.3.2 Compression Molding:

The fluxed materials produced in the mixer were cut immediately into small chips when still hot, and sheets of about 3mm thick were obtained by compression molding. The mold was heated at $195^{o}C$ in a CARVER laboratory press 2833 - 39X illustrated in figure 3. The molding time was 10 minutes at 6.9 MPa pressure.

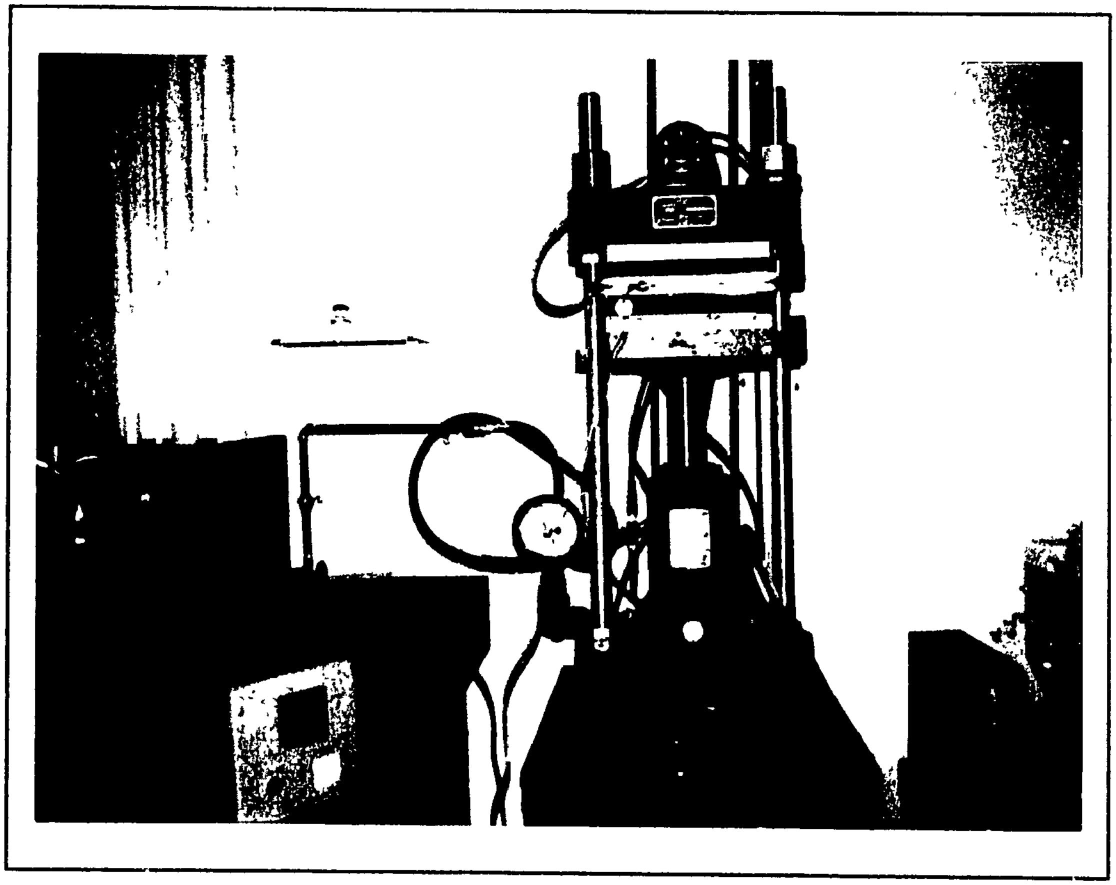


Figure 3 Compression molding

After that the press cooled down to room temperature with air. Several sheets of about 3mm thick were produced from unblended and blended mixtures.

5.3.3 **Specimens Preparation:**

The sheets were cut out to shoulder shape specimens (ASTM D 638 type V) and bar shape specimens having different dimensions by using a cutting die.

5.3.4 **Results And Discussion:**

In table 4 and figure 4 there are indicated the average fusion characteristics of blended and unblended mixtures. It can be seen that the fusion torque as well as the maximum temperature are very close in all the cases, indicating that the processability of PVC was not affected by addition of lignin; in addition the processing was carried out without any problems and without any manifestation of degradation.

Table 4 - Effect of lignin on the fusion characteristics of PVC

Property	**Formulation**						
	With TiO_2				**Without TiO_2**		
	0L	**2.5L**	**5L**	**7.5L**	**5L**	**7.5L**	**10L**
Fusion Torque (m - g)	383	351	377	395	383	410	405
Maximum Temp.°C	196	198	197	195	195	195	195

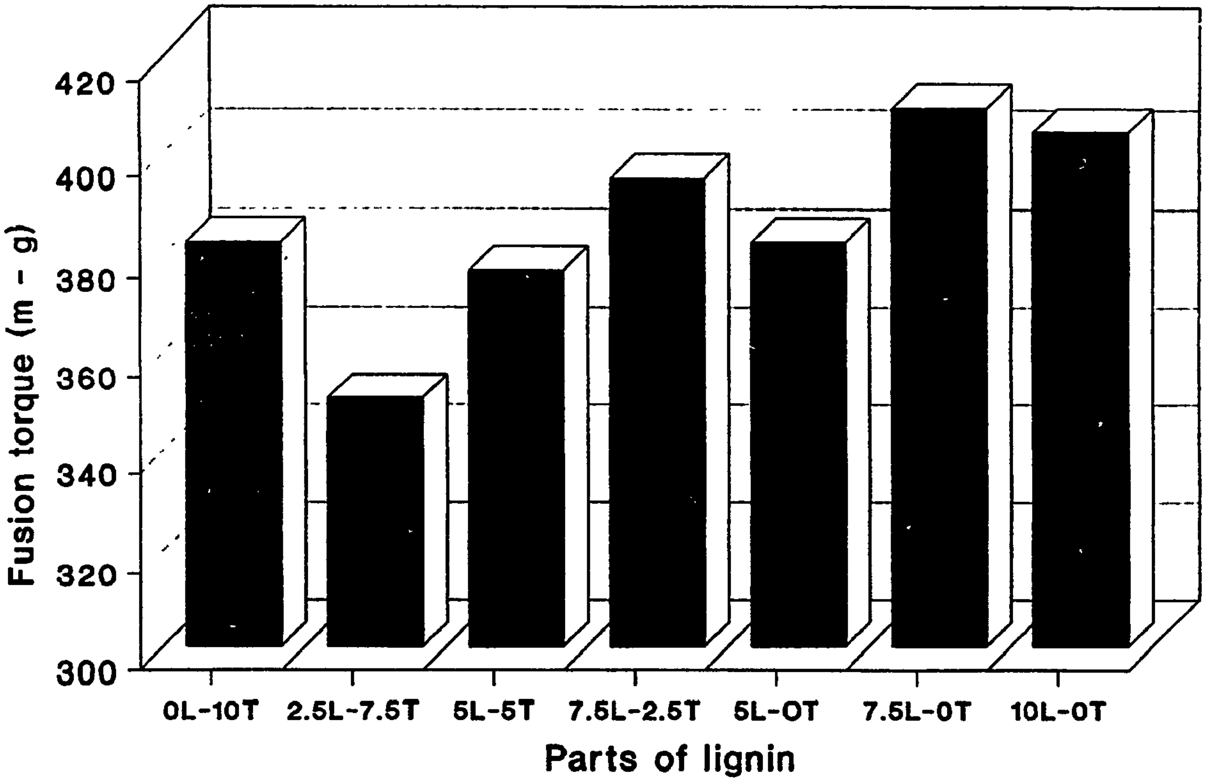


Figure 4 Effect of lignin on fusion torque of PVC

5.4 **Durability:**

The durability of a building material is regarded as its ability to continue to perform satisfactory through the period of use. A durable product is one that retains its essential properties for a period consistent with its application in building [42].

The aging of polymer materials depends on their formulation, conditions of fabrication and of use. The problem is the production of a long life material (in France, the minimum life demanded of building material is 10 - 20 years) [46].

From the point of view of PVC durability it should be pointed out that PVC is a polymer which is very sensitive to the weathering action, due to the change in mechanical properties and colour as effect of UV radiation. In the presence of oxygen and moisture, it undergoes a very fast dehydrochlorination and peroxidation process with the formation of polyene and subsequent scission of the chains, formation of water "washable" products as well as crosslinking [43].

5.4.1 **Accelerated Weathering Test:**

When new materials are developed it is often important to determine how durable they will be when exposed to the weather, i.e how they will retain reasonable percentage of original appearance and properties.

Today, the chemist can no longer afford to wait a year or two for outdoor exposure tests to show whether his latest "improved" formulation is really an improvement. In this time we need weathering data in a matter of weeks, not years. With today accelerated weathering tester, it is possible to generate reliable weathering data in a matter of days or weeks [44].

The durability of PVC - L blends was tested using a Q.U.V accelerated weathering tester according to ASTM G53 [45]. This tester simulate the deterioration caused by water as rain or dew and the ultraviolet energy in sunlight. It contains a series of UV - B lamps with a peak emission at 313 nm and a spectral energy distribution between 280 - 390 nm wavelengths which are responsible for most polymer damage.

The Q.U.V accelerated weathering tester Q - Panel Company Cleveland, OHIO USA consists of a corrosion resistant material test chamber enclosing eight fluorescent UV lamps, a heated water pan, test specimens racks and provisions for controlling and indicating operating times and temperatures as shown in figure 5.

Specimens are alternately exposed to ultraviolet light alone (4h UV at 60^oC) and to condensation alone (4h condensation at 50^oC) in a repetitive cycle without interruption twenty - four hour a day.

The UV source is an array of fluorescent lamps (UV - B) with peak emission of 313 nm and a spread energy distribution between 280 to 390 nm. Condensation is produced by exposing the test surface to a heated, saturated mixture of air and water, while the reverse

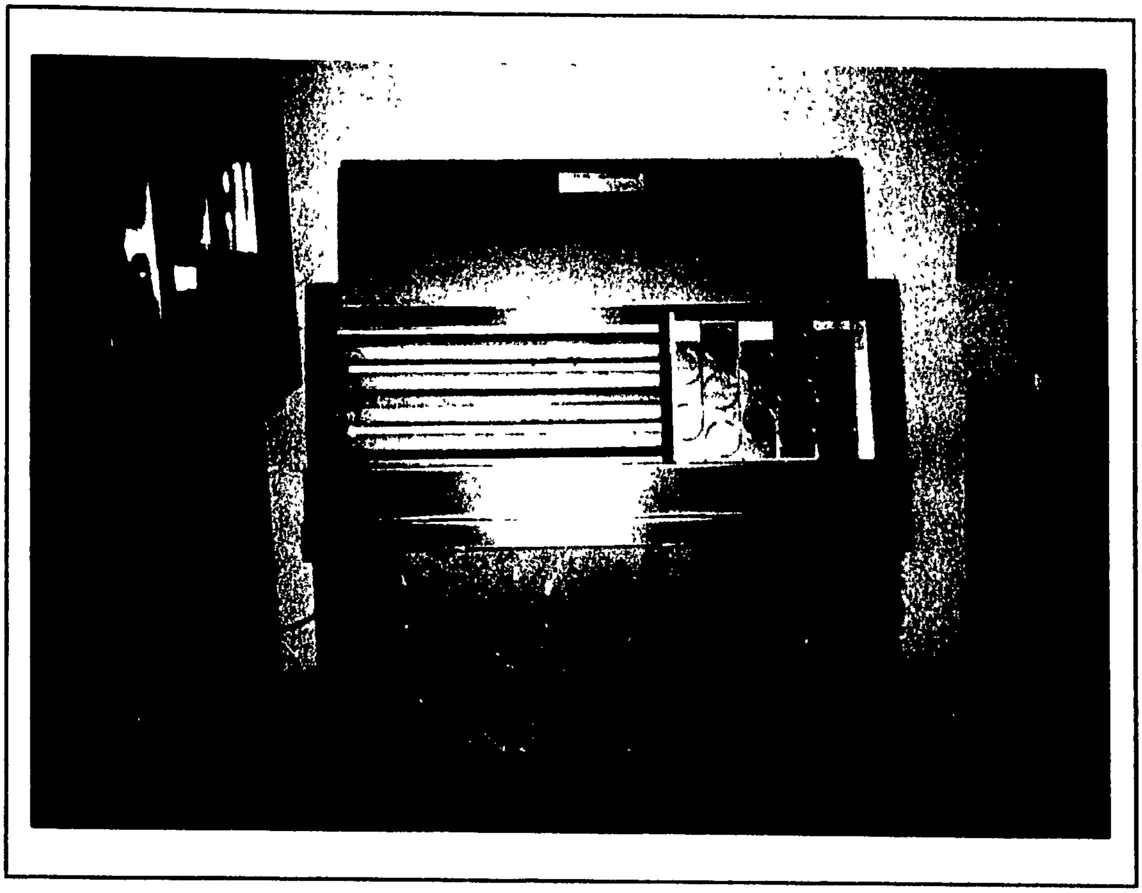


Figure 5 Accelerated weathering tester

side of the test specimen is exposed to the cooling effect of ambient room air. The durability of each blend was evaluated by comparing the mechanical properties and thermal behaviour between unweathered and weathered specimens at different periods of aging from 168 h to 2016 h.

6. Characterization of PVC - Lignin Polyblends

The characterization of PVC - L polyblends was based on the application of the following techniques:

1. Tension testing (tensile strength, elongation at yield and at break).
2. Differential Scanning Calorimetry (DSC).
3. Dynamic Mechanical Analysis (DMA).
4. Flammability .
5. Heat distortion temperature.
6. Water absorption.

6.1 Mechanical Properties, Tension Testing:

The tensile properties of blended and unblended PVC were determined according to ASTM D 638 [46]; test specimens were prepared by die cutting from material in sheet (thickness ≈ 3mm); the selected dimension of specimens are shown in figure 6.

The test was carried out in several series for unblended and blended PVC . The first series was carried out to determine the tensile properties (tensile strength and elongation at yield and at break) for unweathered specimens. The test was repeated for weathered specimens after periods of 168, 480, 672, 1512, 2016 hour. All the specimens were conditioned before testing at 23 ± 2^{o}C and 50% relative humidity for 40 hour according to ASTM D 618 [47].

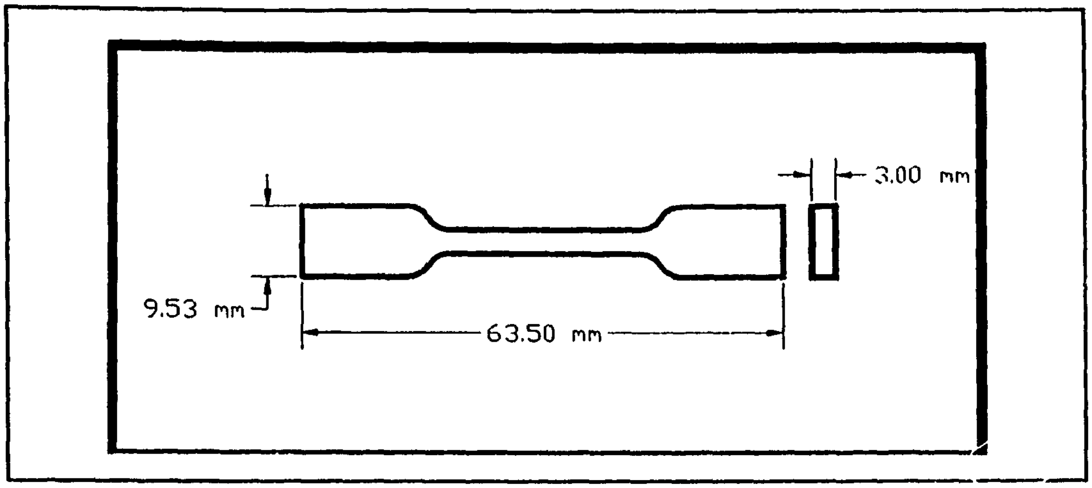


Figure 6 Tension testing specimen

The Instron universal testing machine model 1125 (figure 7) was used for tension testing. The machine consists of cross head movement type comprising of fixed member carrying one grip and movable member carrying a second grip. The grips are used for holding the test specimens between the fixed and the movable members. The specimens should be aligned as perfectly as possible with the direction of pull so that no rotary motion that may cause slippage will occur in the grips during testing.

The control unit contains load indicator capable of showing the total tensile load carried by the test specimen and extension indicator to determine the gage length of the test specimen or any change in it as a function of the load on the specimens or of the elapsed time from the start of the test.

The cross head frame moves in the upward direction, causing tensile forces to develop along the specimen interface. A cross head speed of 1 mm/min was used in conjunction with 20 mm/min chart speed according to ASTM recommendation and 50 Kg load was used to test the specimens. Testing was conducted until failure occurs; the tensile strength was calculated by dividing the maximum load recorded on the chart by the original minimum cross section area of the specimen which is equal ≈ 8.12 mm^2 (2.8 x 2.9 mm).

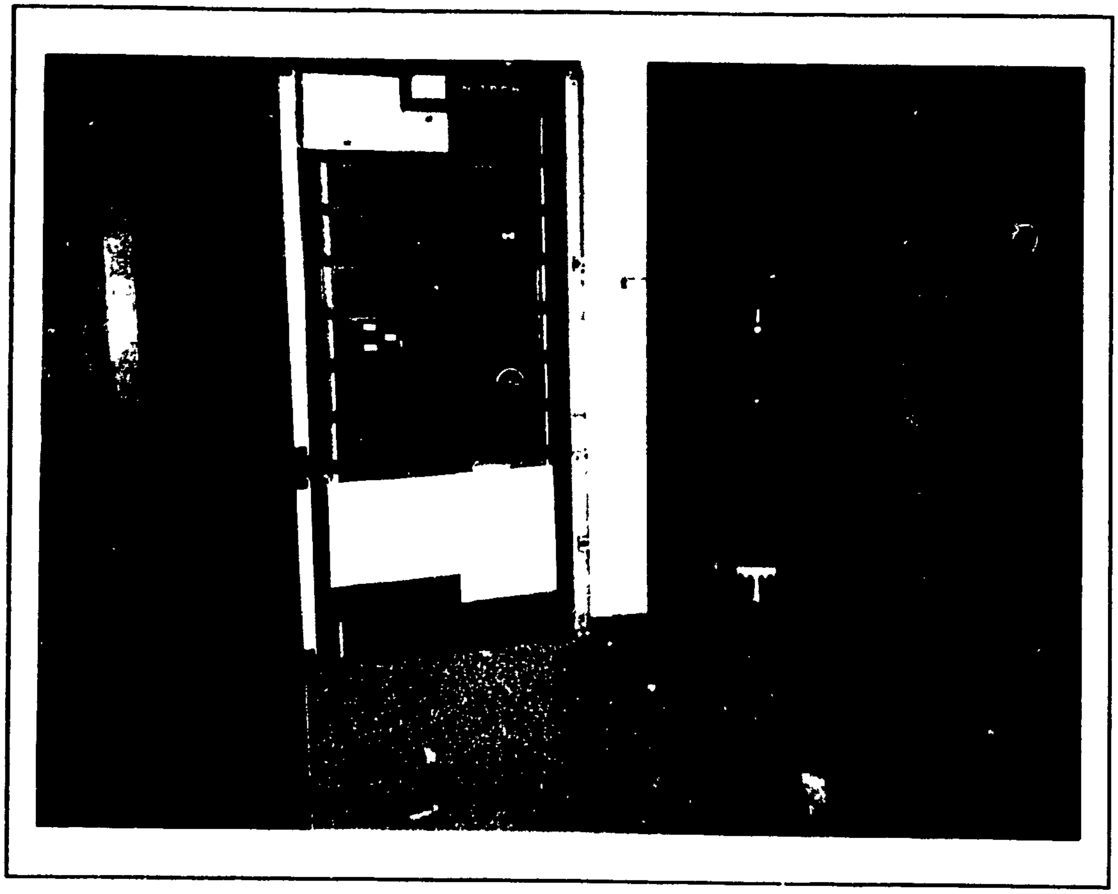


Figure 7 Mechanical testing, Instron universal machine

Percent elongation at yield was calculated by dividing the extension at yield from the chart (change in the gage length) by original gage length and multiply by 100; percent elongation at break was calculated by the same procedure, all the values presented in the following tables are average of 5 determinations. In all tests, the standard deviation was ± 0.1 MPa; less than the accepted ten percent in practice.

6.1.1 Results and Discussion:

Table 5 - Tensile strength at yield of blended and unblended PVC before and after weathering

Tensile strength (N/mm^2) after:	Formulation					
	With TiO_2				Without TiO_2	
	0L	2.5L	5L	7.5L	5L	7.5L
0 h Weathering	42.1	43.6	44.1	45.1	45.2	46
168 h Weathering	49.1	48	49.3	48	49.1	48
480 h Weathering	46.1	47	47.8	48	47.1	47.4
672 h Weathering	46.2	46.1	47.1	47	45.7	46.2
1512 h Weathering	47.8	47.1	47.5	48.2	48	46.8
2016 h Weathering	46.1	45.8	46.2	45.4	46	46

Table 6 - % Elongation at yield for blended and unblended PVC before and after weathering

% Elongation at yield after:	Formulation					
	With TiO_2				Without TiO_2	
	0L	2.5L	5L	7.5L	5L	7.5L
0 h Weathering	10	9.5	9.1	8.7	9.4	9.2
168 h Weathering	9.6	8.0	8.2	8.0	9.0	8.0
480 h Weathering	9.2	9.3	8.7	8.5	9.0	9.0
672 h Weathering	9.2	9.0	9.4	8.4	8.5	9.0
1512 h Weathering	9.5	8.9	8.7	8.7	9.2	9.4
2016 h Weathering	9.8	8.5	8.3	8.1	9.2	8.9

Table 7 - % Elongation at break for blended and unblended PVC before and after weathering

% Elongation at break after:	Formulation					
	With TiO_2				Without TiO_2	
	0L	2.5L	5L	7.5L	5L	7.5L
0 h Weathering	287	272	313	249	358	269
168 h Weathering	145	50	59	30.3	40	24
480 h Weathering	126	58	43	46.2	51	46
672 h Weathering	80	73	54	38.1	21.3	84
1512 h Weathering	61.7	53.2	32	30.1	28	34
2016 h Weathering	48.6	44.6	38	44.6	35	41

1) From figure 8 where the variation of tensile strength versus lignin loading is presented, it can be seen that polyblending of PVC with lignin led to an increase of tensile strength and from table 6 and 7 that there was a slight decrease in the elongation at yield and at break. The blends without TiO_2 showed a higher increase of tensile strength than that of the blends containing TiO_2. The tensile strength was in both cases higher than that of unblended PVC; this could be due to the interaction between lignin and PVC taking place

during melt mixing process.

When compared with unblended PVC the maximum tensile strength increase was of 7.4% for formulations containing TiO_2 and 9.3% for formulations without TiO_2. Blended PVC showed a decrease in elongation at yield from 4 to 13% in comparison with unblended PVC; elongation at break of blended PVC is lower than that of unblended PVC by 5.2% to 16% except for that of PVC - 5L - 5T and PVC - 5L - 0T which are higher than that of unblended PVC by 9% and 24.7% respectively as can be seen in tables 5,6 and 7.

2) During weathering there are simultaneous elimination of HCl, crosslinking and chain scission ...etc, but at a particular period one of this factors prevails on the other factors and this explains the changes in the mechanical properties associated with weathering action [48].

Figures 9 to 14 show the change of tensile properties with weathering periods. After 168 hour weathering the tensile strength increases and elongation decreases for both blended and unblended PVC and this may be due to the crosslinking occurring under the effect of weathering factors. From 168 hour to 672 hour there was a decrease of the tensile strength values and a slight increase of elongation, may be as an effect of the chain scission. At the end of weathering program (2016 hour), tensile strength decreased and elongation increased very slightly due to chain scission.

When comparing the tensile strength and elongation data of weathered specimens with those of unweathered unblended PVC (tables 5, 6, 7), it has been noticed that after weathering the tensile strength of blended and unblended PVC increased by ≈ 9.5%, and elongation at yield of unblended PVC decreased by 2%, while for blended PVC decreased by 8 - 19%; elongation at break of unblended PVC decreased by 83 % and blended PVC decreased by ≈ 85%

3) The effect of weathering on the appearance of all the specimens surfaces have been studied by visual and microscopic examination carried out for blended and unblended PVC after each period of weathering.

This examination showed that after 168 hour weathering, unblended PVC presented a slight change in the colour (from white to yellowish) due to the presence of chromophoric groups which were formed on PVC under the effect of UV light. For blended PVC the initial colour was grey and this colour changed gradually from grey to tan with chalking under the effect of UV light.

Micro cracks have been noticed also under microscope only for both blended and unblended PVC after different periods of weathering; the apparition of the cracks was detectable after 672 hour in the case of the blends, and only at the end of the weathering interval, i.e 2016 hour in the case of unblended PVC. The explanation regarding the formation of these cracks is the formation of aldehydes, ketones and alcohols from the peroxi radicals from the PVC surface as an effect of UV light and oxygen. These groups are sensitive to water and rain loosens these products and gradually erodes the PVC surface causing micro cracks [9].

Finally it can be said that both blended and unblended PVC showed discoloration after weathering and the comparison of the extent of this discoloration is difficult to be established between blended and unblended PVC due to the difference of the colour of the initial specimens (unblended PVC has white colour while the blended PVC has grey colour).

The faster apparition of cracks on blends could be due to hydrophillic character of lignin which increases the ability of the blends to take up water.

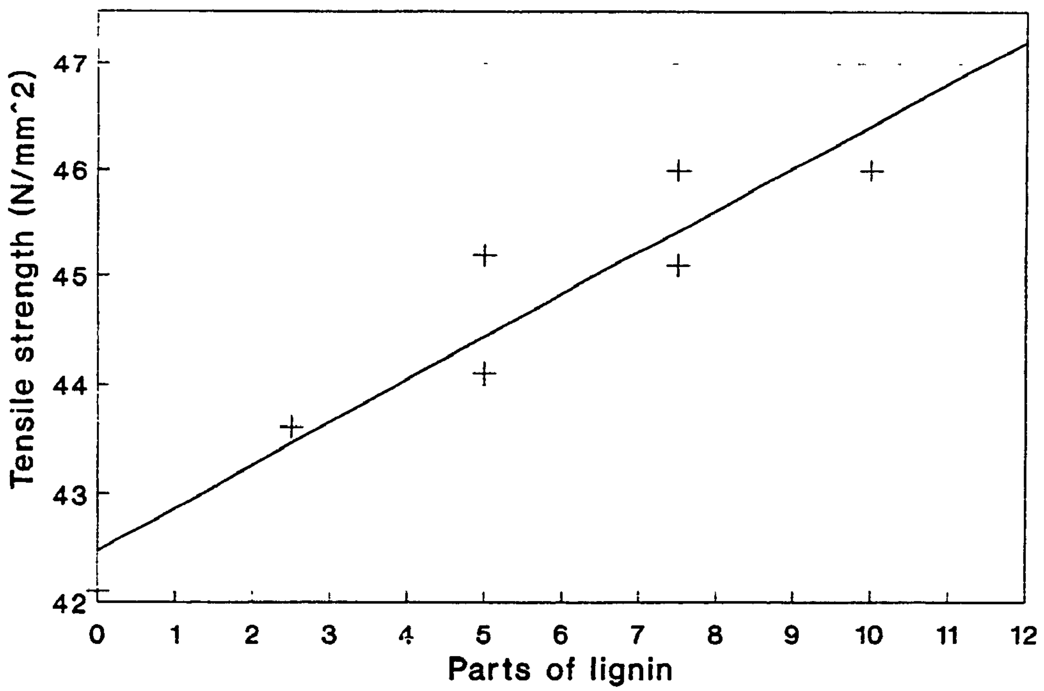


Figure 8 Variation of tensile strength at break with lignin loading before weathering

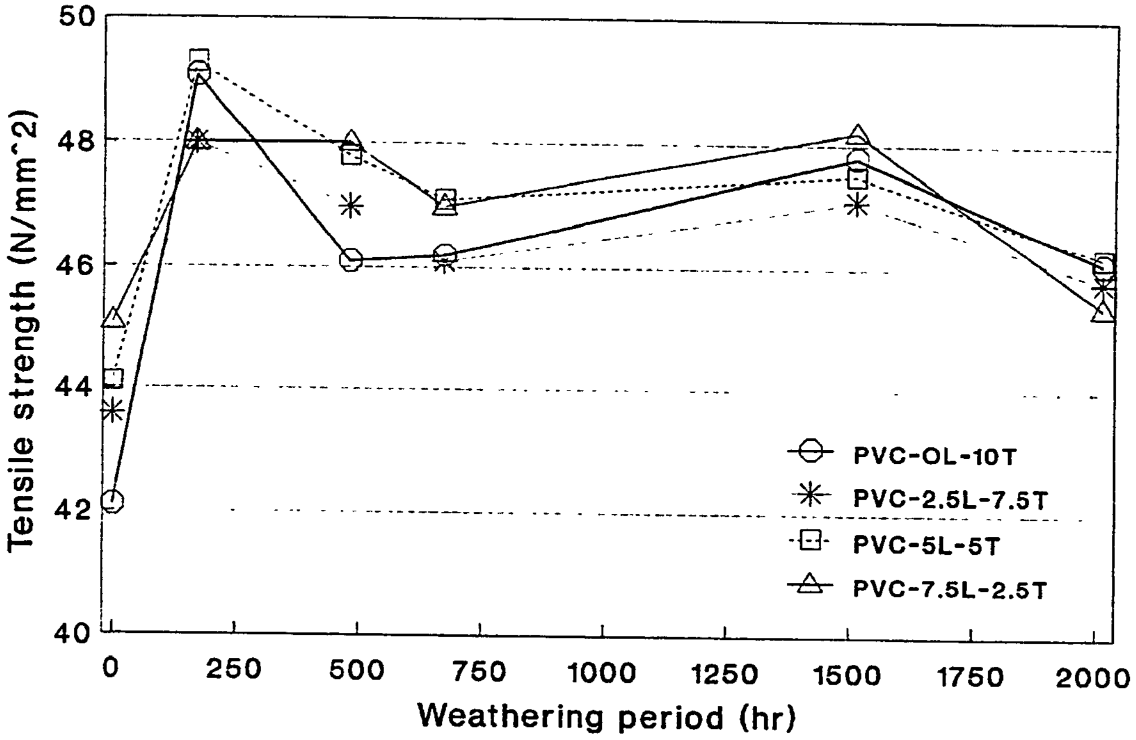


Figure 9 Variation of tensile strength of blended and unblended PVC with weathering period

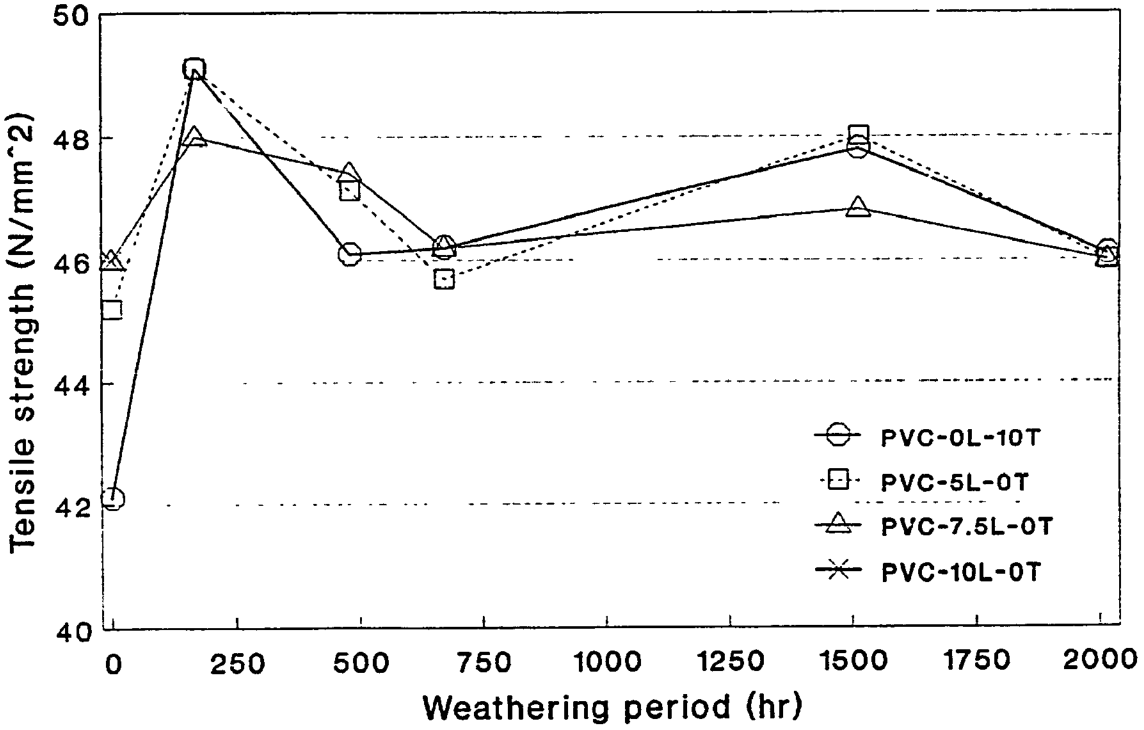


Figure 10 Variation of tensile strength of polyblends (no TiO2) and PVC with weathering period

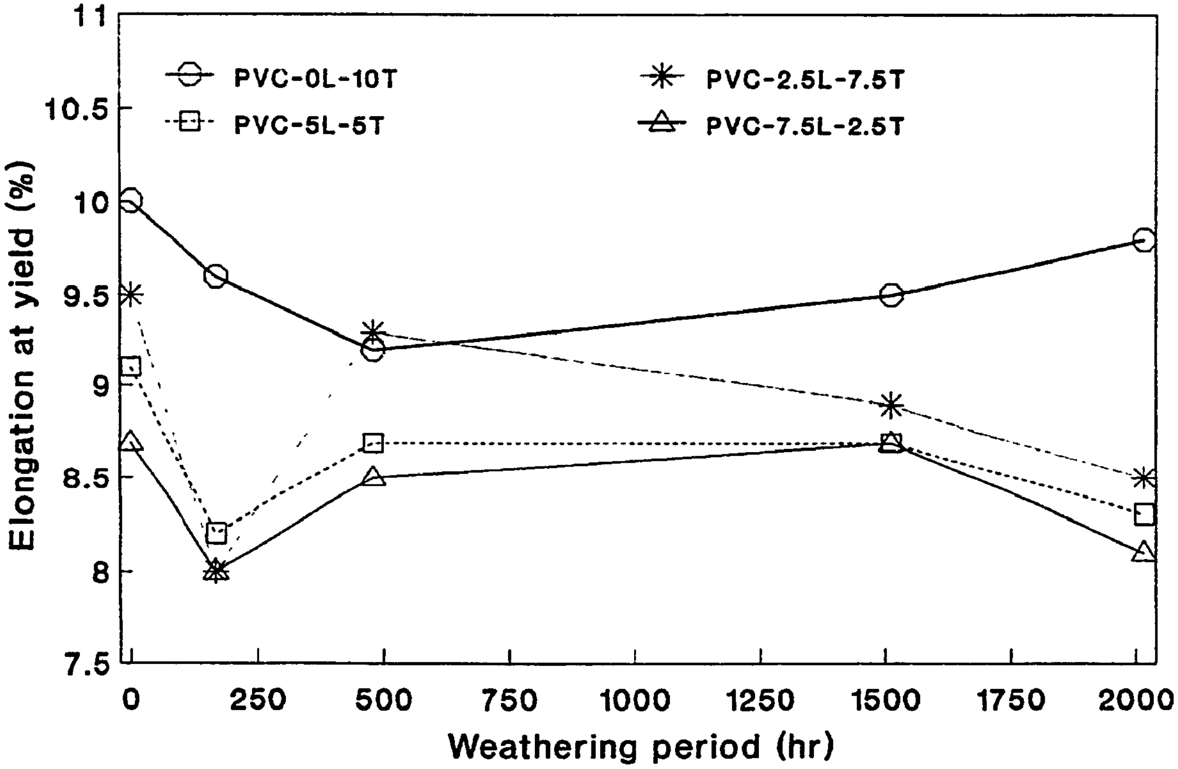


Figure 11 Variation of elongation at yield for blended and unblended PVC with weathering period

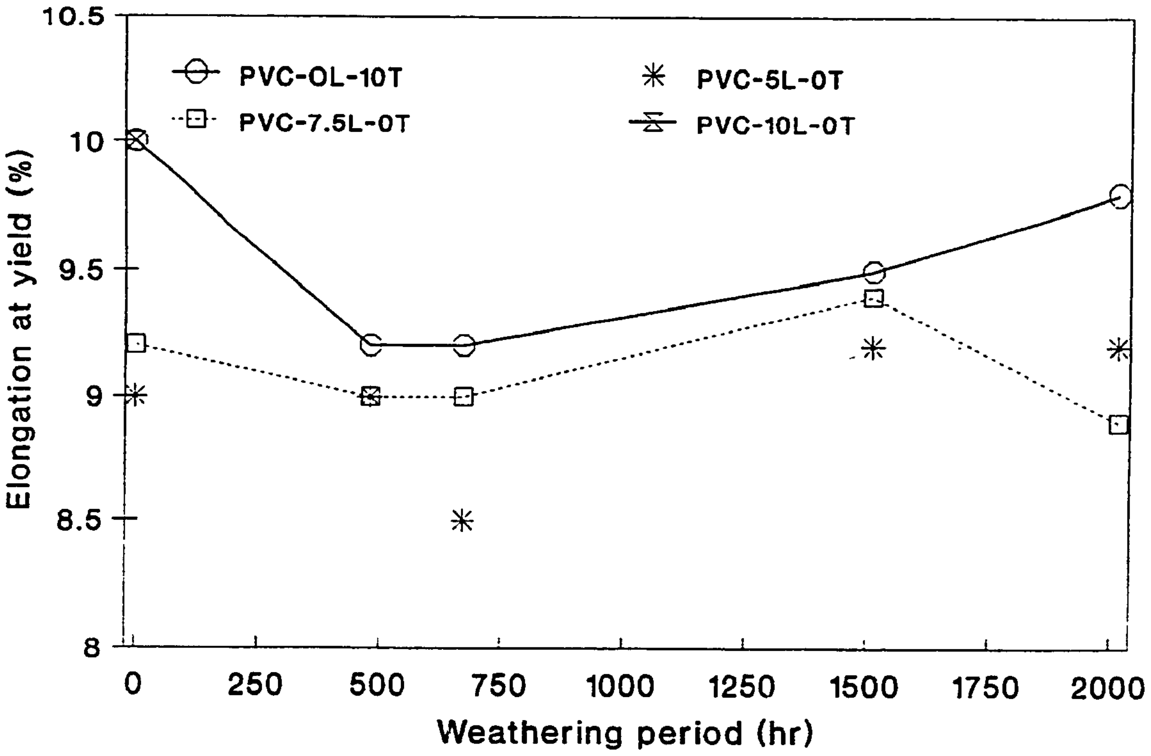


Figure 12 Variation of elongation at yield of polyblends (No TiO2) and PVC with weathering period

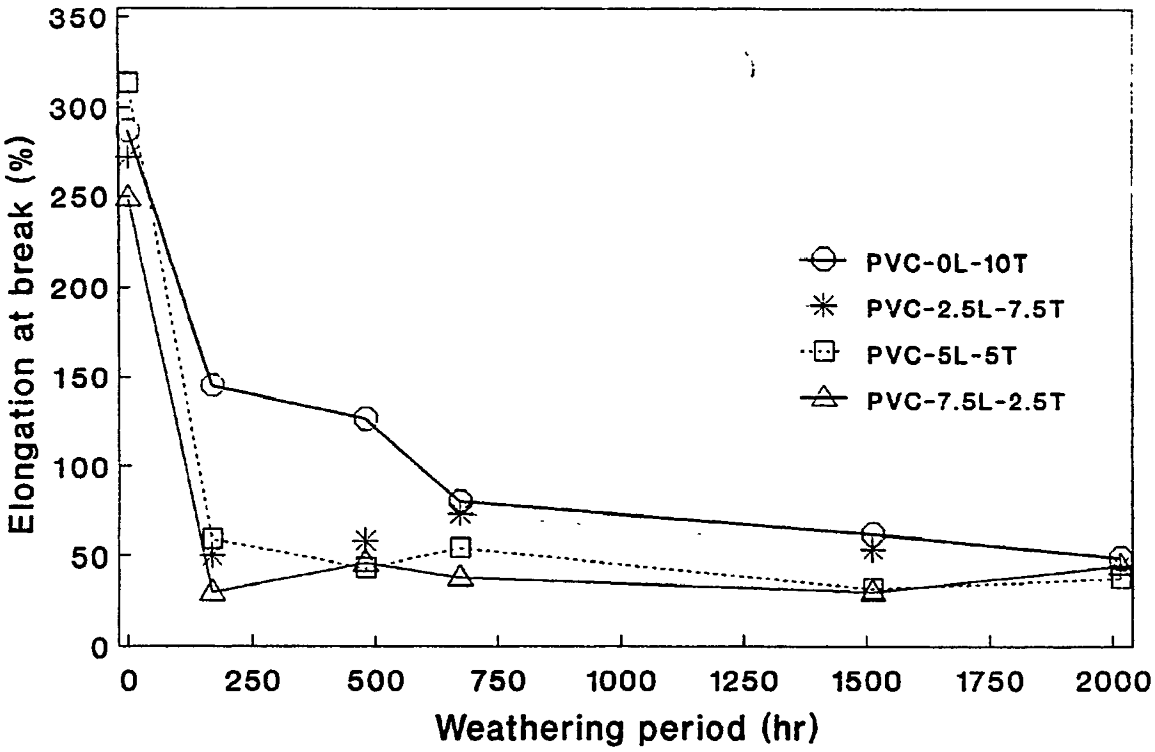


Figure 13 Variation of elongation at break for blended and unblended PVC with weathering period

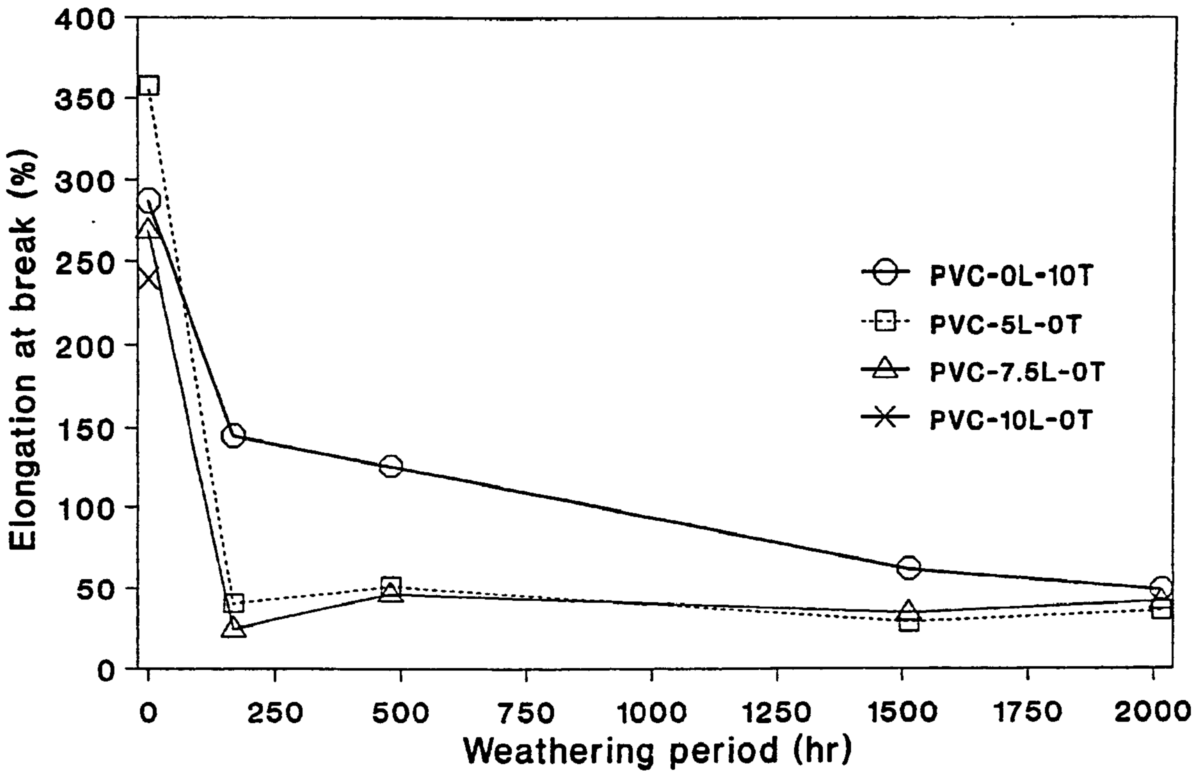


Figure 14 Variation of elongation at break of polyblends (No TiO2) and PVC with weathering period

6.2 Thermal Properties:

For amorphous polymers, the most important temperature dependent property is the glass transition temperature (Tg), i.e the temperature at which the polymer changes from a relative hard brittle material, to a more softer plastic material. This temperature represents a change of the arrangement of the macromolecules from more ordered to a less ordered one.

For two or more component systems, information about the compatibility of the components can be established through determination of the glass transition temperature of the blend versus the glass transition temperature of the unblended components. A single Tg between the component polymers Tg's is characteristic for miscible polymer blends. In cases of limited miscibility, two separate transitions between those of the constituents may exist [21].

The most common methods for determining Tg of polymers and polymer blends are the calorimetric methods, such as a differential scanning calorimetry (DSC), and mechanical methods such as dynamic mechanical analysis (DMA).

6.2.1 Differential Scanning Calorimetry (DSC) :

DSC is a technique in which the energy difference inputs into a substance and an inert reference material is measured as a function of a temperature variation while the substance and the reference material are subjected to a controlled - temperature program. A transition is noticed by absorption of energy by the specimen resulting in a corresponding endothermic peak in a heating curve.

A DuPont 910 Differential Scanning Calorimeter was used to analyze various L - PVC blends according to ASTM D 3418 [49]. Sample weighing 10 - 20 mg and the reference material were placed in an individual pans which sit on a thermoelectric disc as can be seen in figure 15.

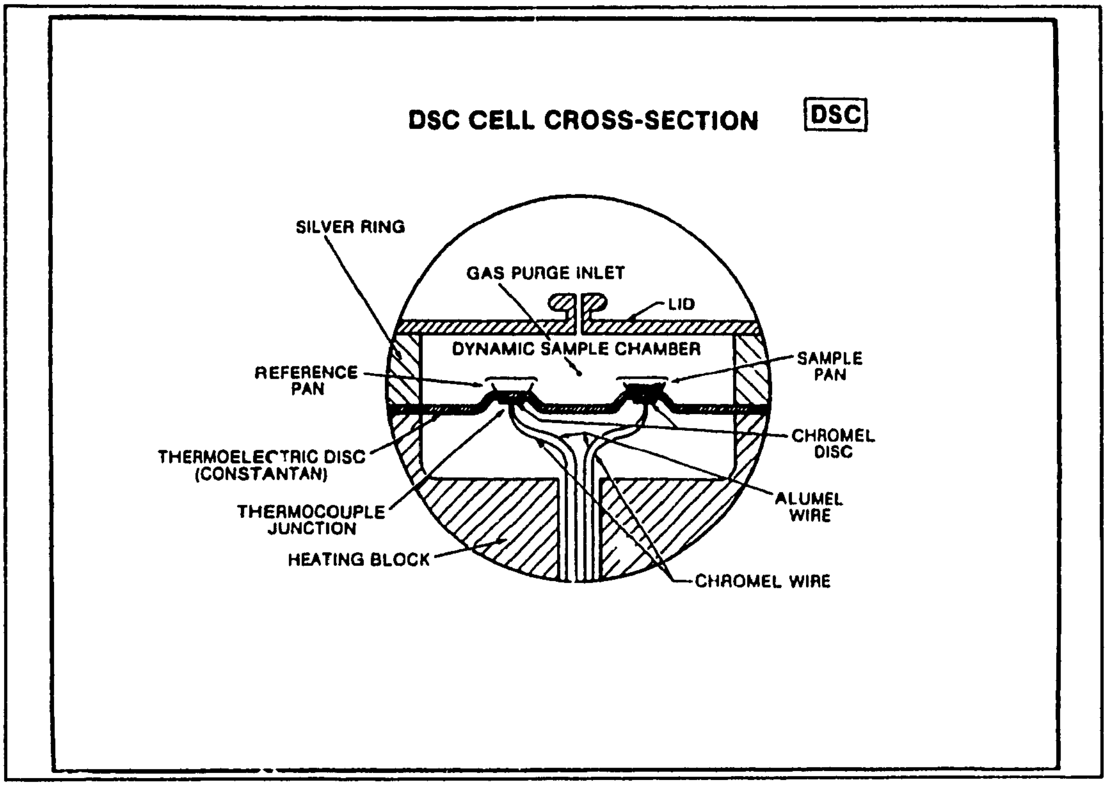


Figure 15 Thermal analysis (DSC) apparatus

Heat is transferred through the disc and into both reference and sample via the specimen pans. The difference in temperature of the specimen and reference is monitored by thermocouple connected to the underside of the disc beneath each pan. Since the thermal resistance to sample and reference is maintained constant, differential temperatures are directly proportional to differential heat flows. This differential heat flow is quantitatively measured and the resulted DSC curve is graphically plotted (the record is a DSC curve).

At Tg the heat required to change the sample from glassy to a rubbery matrix induces a difference in heat flow between sample and reference such that a negative heat flow is observed in this region.

Scans were started at a temperature of -30 ^{O}C at a rate of 20^{O}C/min to a final temperature of 185^{O}C. All scans were run under a dry nitrogen atmosphere by a gas flow of 20L/h; DSC analysis was carried out for both blended and unblended PVC before and after 2016 h weathering.

6.2.1.1 Results and Discussion:

Table 8 - Results of thermal analysis of blended and unblended PVC before and after weathering using DSC technique.

Formulation							
Property	**With TiO_2**				**Without TiO_2**		
	0L	2.5L	5L	7.5L	5L	7.5L	10L
Tg before weathering °C	85	86	86	85	86	85	86
Tg after weathering °C	86	85	86	83	85	85	85

Figure 16 and figure 17 show the DSC diagrams for the PVC and L - PVC polyblends respectively.

Figure 18 shows the DSC diagrams for blended and unblended PVC before weathering

Figure 19 shows the DSC diagrams for blended and unblended PVC after weathering.

The observations are:

1. The polyblends exhibit a single Tg, characteristic of monophasic systems (figure 18).
2. The Tg's of the polyblends were very close to that of PVC (table 8).
3. The slope of the transition is similar in all cases.

These observations are essential criteria for determining the miscibility of two polymers. In conclusion polyblending of Kraft lignin up to 7.5 phr with PVC produces compatible polyblends.

Figure 20 shows comparison between Tg's before and after weathering for blended and unblended PVC. It can be seen that there is a decrease in the glass transition temperature values for blended PVC after weathering and this could be due to the change in the crystallinity content of PVC with addition of lignin.

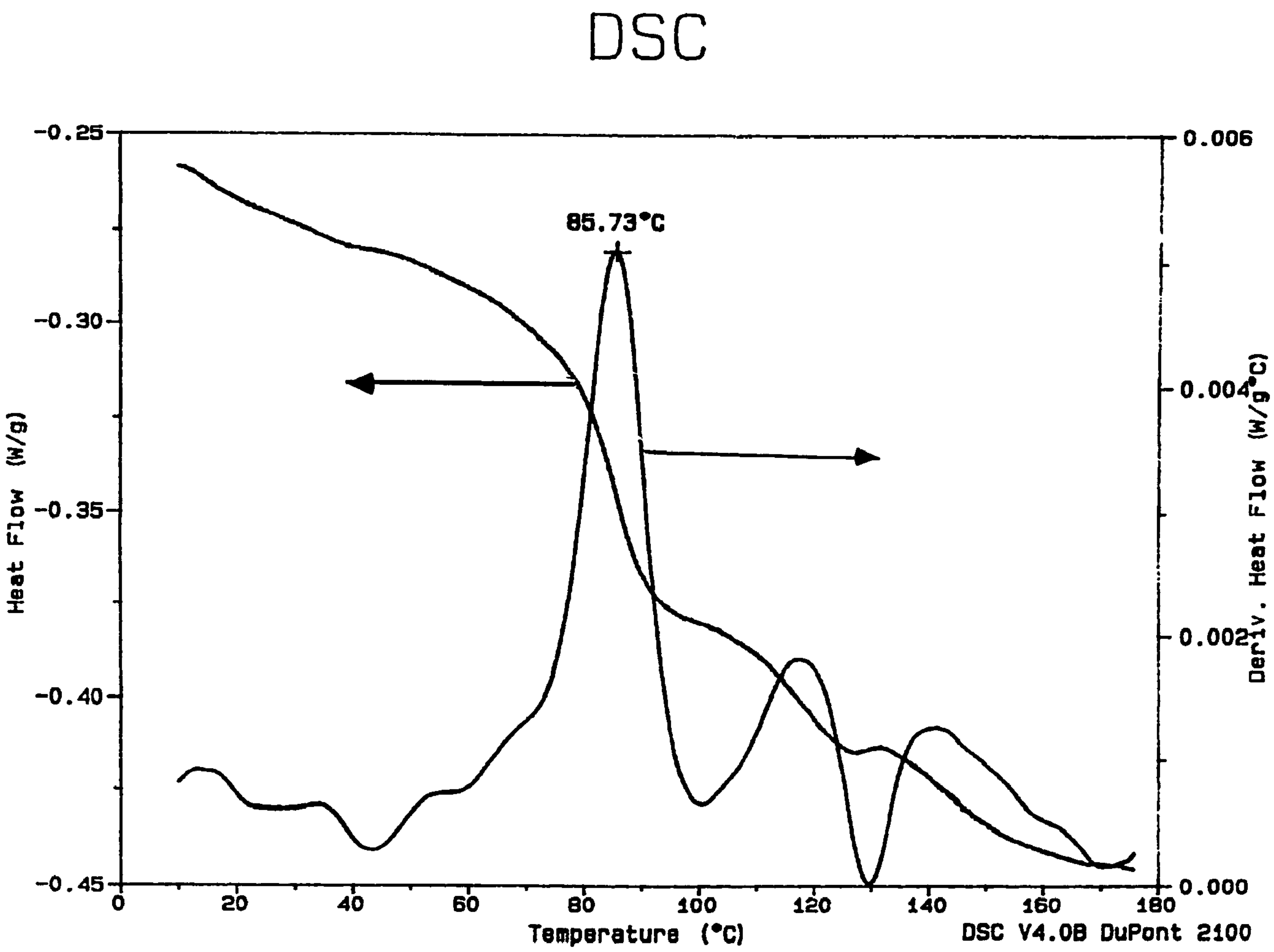


Figure 16 DSC diagram for PVC - 0L -10T

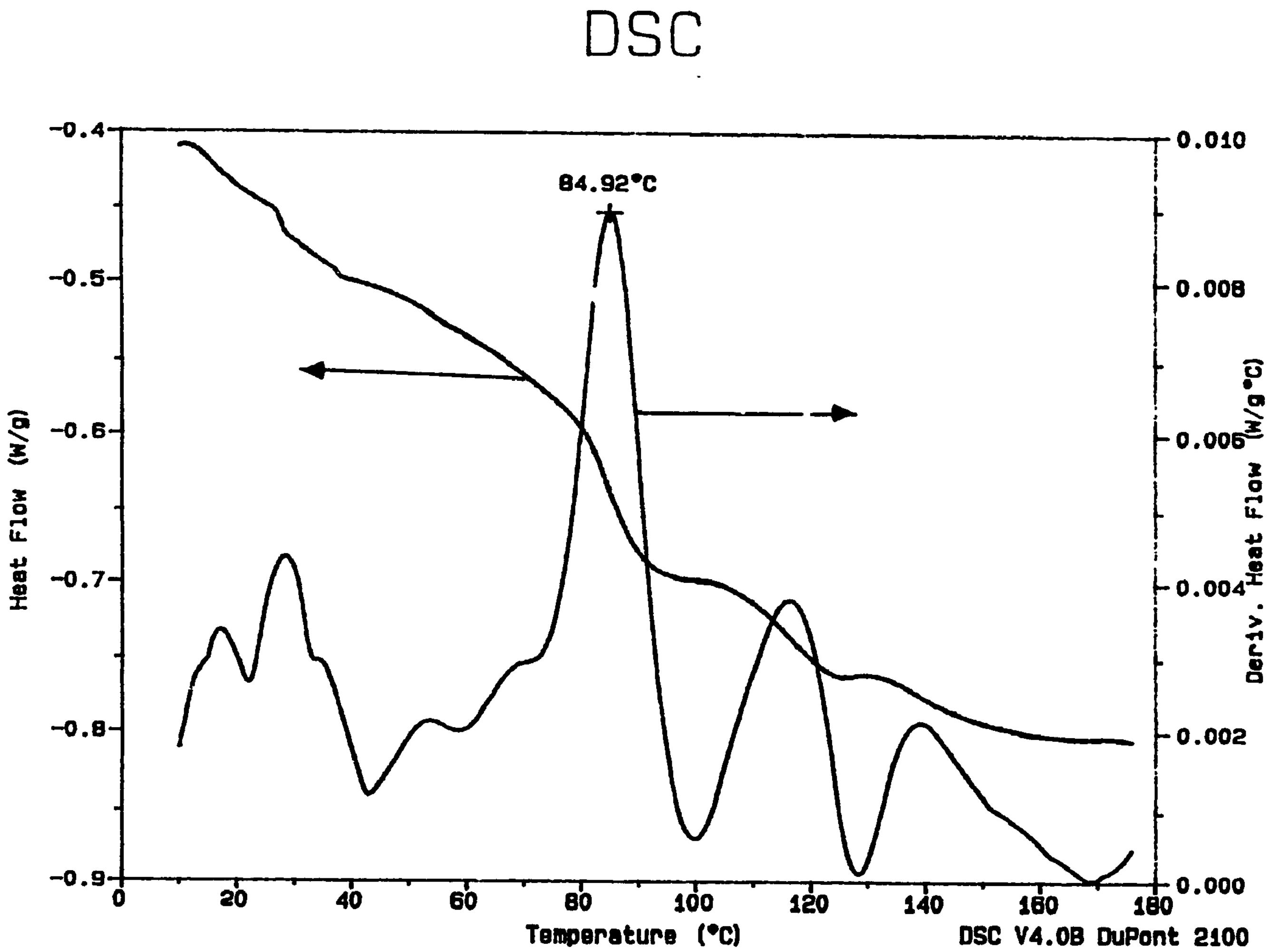


Figure 17 DSC diagram for PVC - 5L - 5T

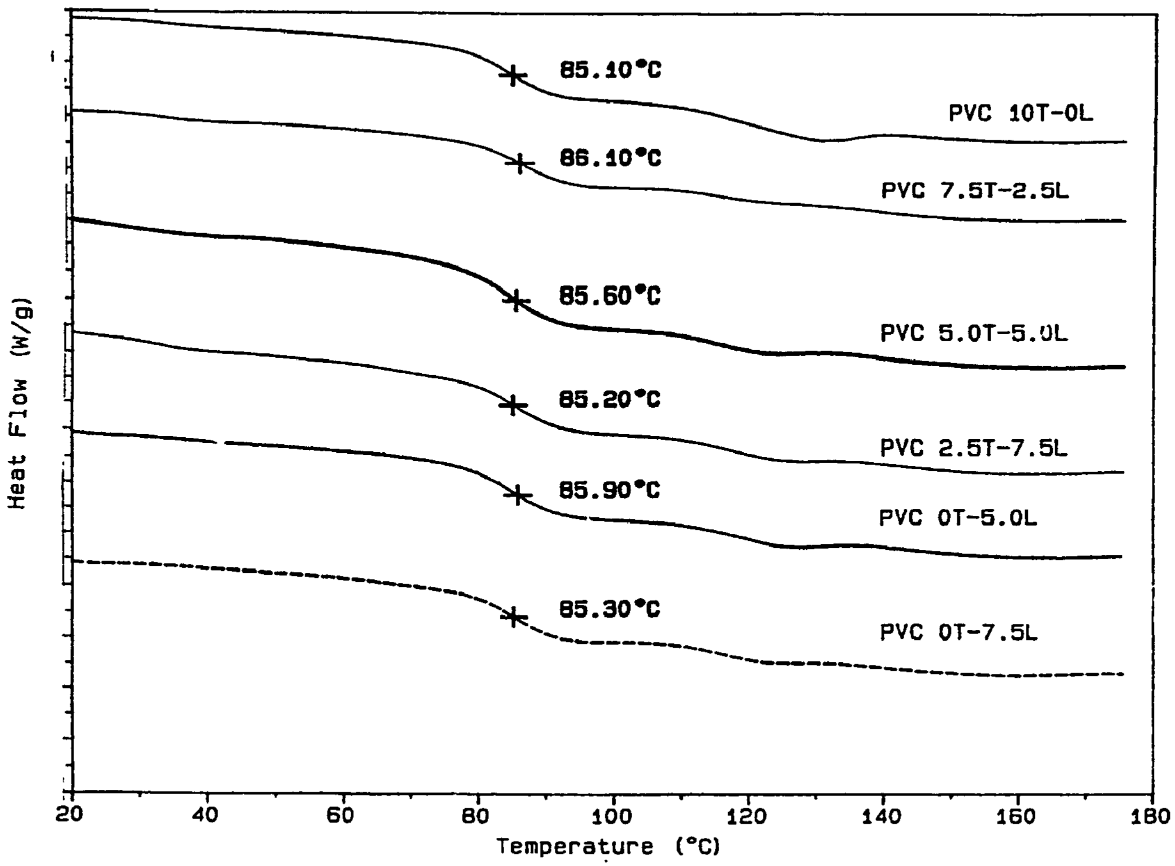


Figure 18 DSC diagram for blended and unblended PVC before weathering

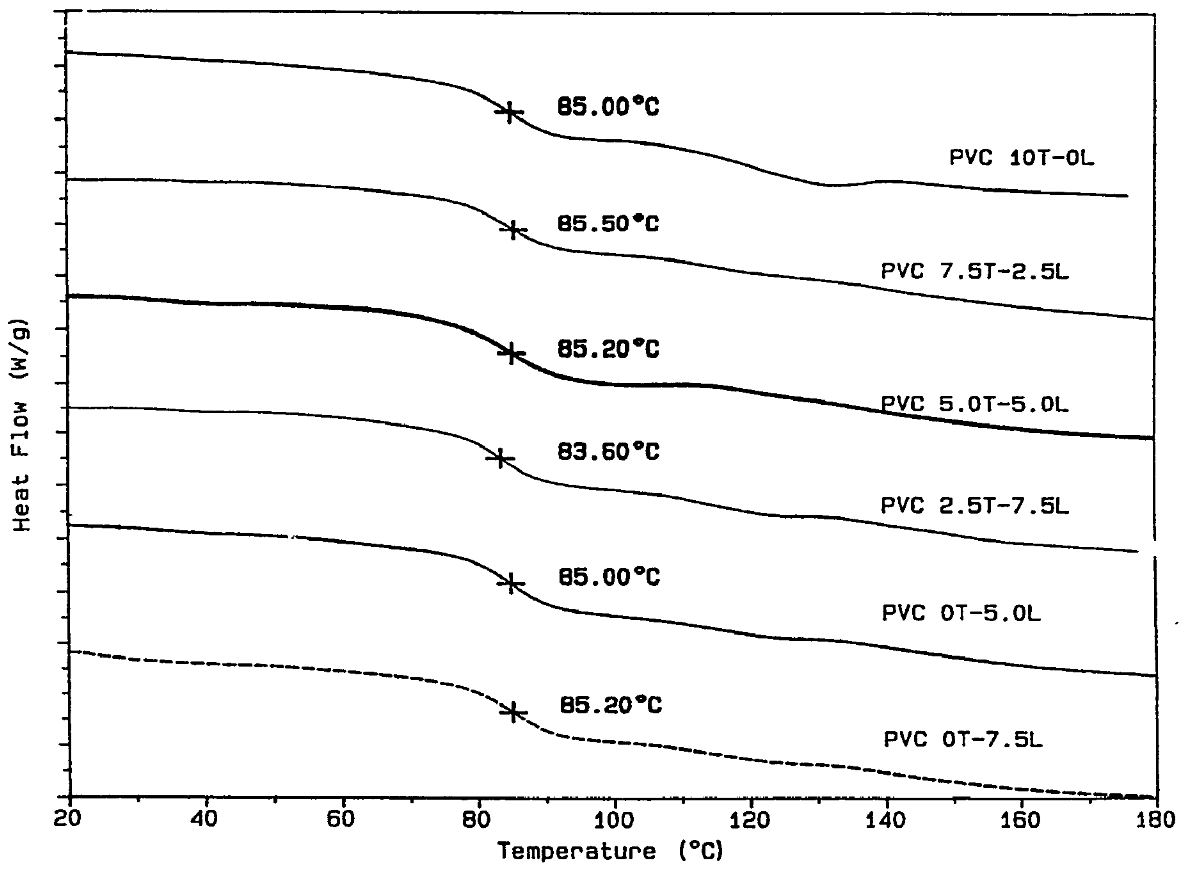


Figure 19 DSC diagram for blended and unblended PVC after weathering

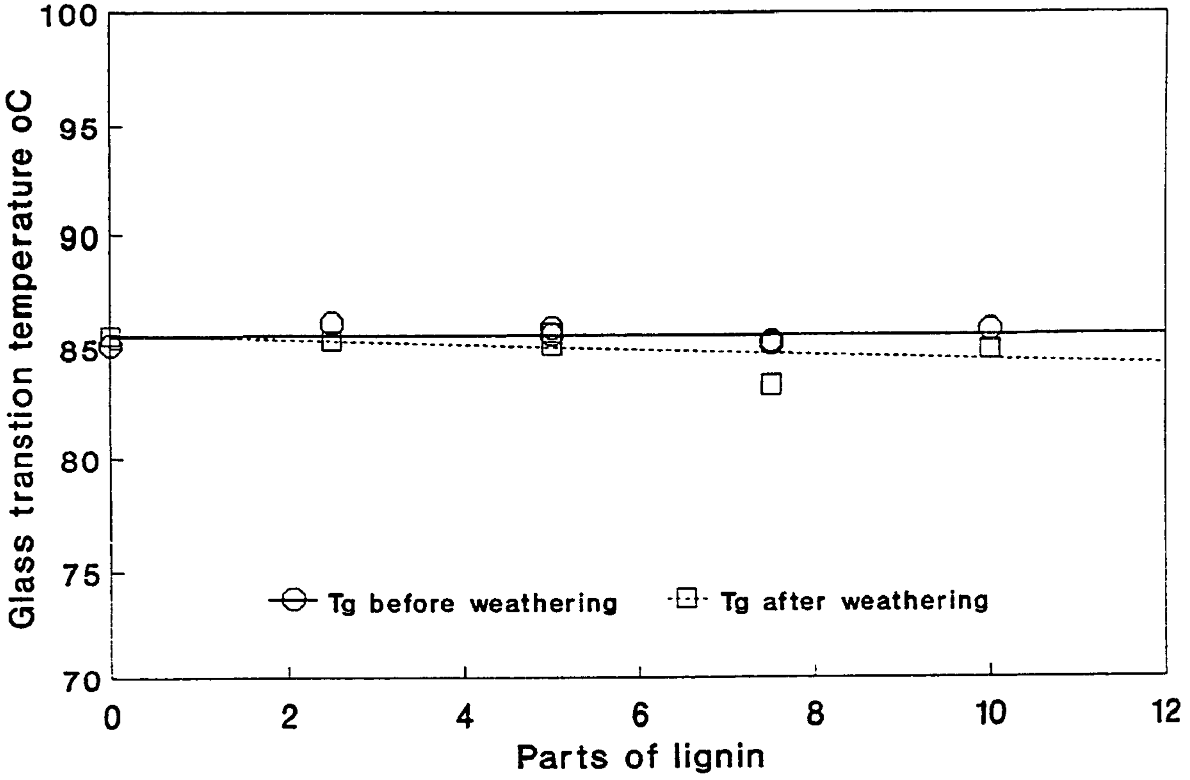


Figure 20 effect of weathering on the glass transition temperature of blended and unblended PVC (DSC)

6.2.2 Dynamic Mechanical Analysis (DMA):

Dynamic mechanical analysis (DMA) is a technique that measures stored and dissipated energy by a material with temperature change due to its viscoelastic properties. The stored energy represents the elastic modulus or stiffness of the material, while the dissipated energy represents the loss modulus or mechanical damping. Polymers are example of viscoelastic materials which have some of the characteristics of both viscous liquids and elastic solids; a solid material has a capacity to store energy, and a viscous fluid has a capacity for dissipating energy. When polymeric materials are deformed part of the energy is stored as potential energy and part is dissipated as heat [50].

The method is based on oscillating a sample mounted between two arms at a constant amplitude and detecting changes in the system's resonant frequency due the variation of the viscoelastic properties with temperature or time; electrical energy is used to maintain a constant amplitude throughout the test; the frequency of oscillation is a measure of modulus while the electrical energy is a measure of mechanical damping of the material.

DMA is used to determine glass transition temperature and provides information about compatibility of the constituents polymers of a blend. DMA was used to measure the Tg's and the variation of modulus and damping with the temperature of unblended and blended PVC. The specimens having the dimensions of about 25 x 12 x 3 mm; were clamped between two parallel arms of a DuPont 982 Dynamic Mechanical Analyzer (as shown in figure 21) and set into oscillation at a constant amplitude of 0.2 mm. The sample was then heated at a constant rate of 5 °C/min from 25°C to 180°C under a nitrogen atmosphere (ASTM D 4065) [51].

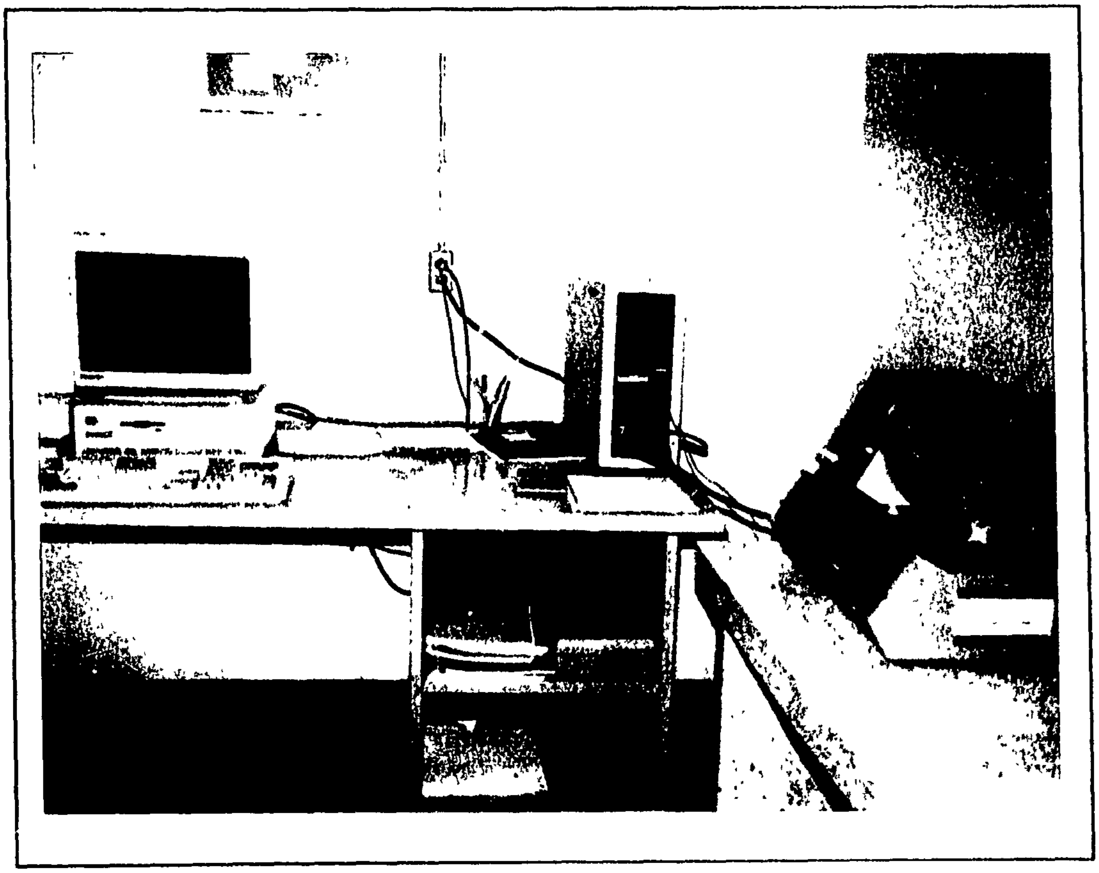


Figure 21 Thermal analysis (DMA) apparatus

6.2.2.1 Results And Discussion:

Table 9 - Results of thermal analysis of blended and unblended PVC before and after weathering using DMA technique.

Formulation						
Property	**With TiO_2**				**Without TiO_2**	
	0L	**2.5L**	**5L**	**7.5L**	**5L**	**7.5L**
Tg before weathering °C	94.9	94.2	94.9	94.8	94.6	93.5
Tg after weathering °C	95.8	96.8	96.7	96.9	98.7	97.6

DMA is very sensitive in detecting all changes in the state of molecular motion with temperature and is more accurate in determining Tg than DSC and DTA (differential thermal analysis).

Figure 22 shows the DMA diagram for PVC - 0L - 10T. Figure 23 shows the DMA diagram for PVC - 5L - 0T. Both figures show a one step tensile strength storage modulus versus temperature curve, a related one peak tensile loss modulus and tan δ versus temperature curves, characteristics of amorphous polymers and compatible polyblends. The Tg's were determined from the peak values in the loss modulus profile (ASTM D 4065).

Tg's for unblended and blended PVC before and after weathering are indicated in table 9 and figure 26, It has been noticed that Tg's raised for both blended and unblended PVC after weathering and this may be due to the crosslinking occurring during weathering.

It should be noted that the absolute values of tensile storage modulus are very sensitive to the stability of the sample dimension. As the thickness of the DMA samples was not uniform along each specimen, the modulus values are questionable and we prefer not to tabulate them . DMA was used only to prove the miscibility of the two polymers and detect possible changes in PVC morphology as effect of L presence.

The loss tangent or tan δ is the ratio of loss modulus (E") to the storage modulus (E'), tan δ = E"/E'. The loss modulus E" and tan δ are particularly sensitive to the morphology of multiphase systems.

In figures 24 and 25 are illustrated the tan δ curves for blended and unblended PVC before and after weathering respectively. As can be seen in figure 24 the peak heights of tan δ are practically unchanged and the temperatures interval of tan δ increased with few degrees as an effect of L loading depicting the increased stiffness of the polyblends. The data from the figure 25 which represents the tan δ of weathered unblended and blended PVC indicate also almost the same peak height for all the tan δ. The tan δ temperature interval for the PVC - L blends after weathering are very close to the tan δ temperature interval of unblended PVC.

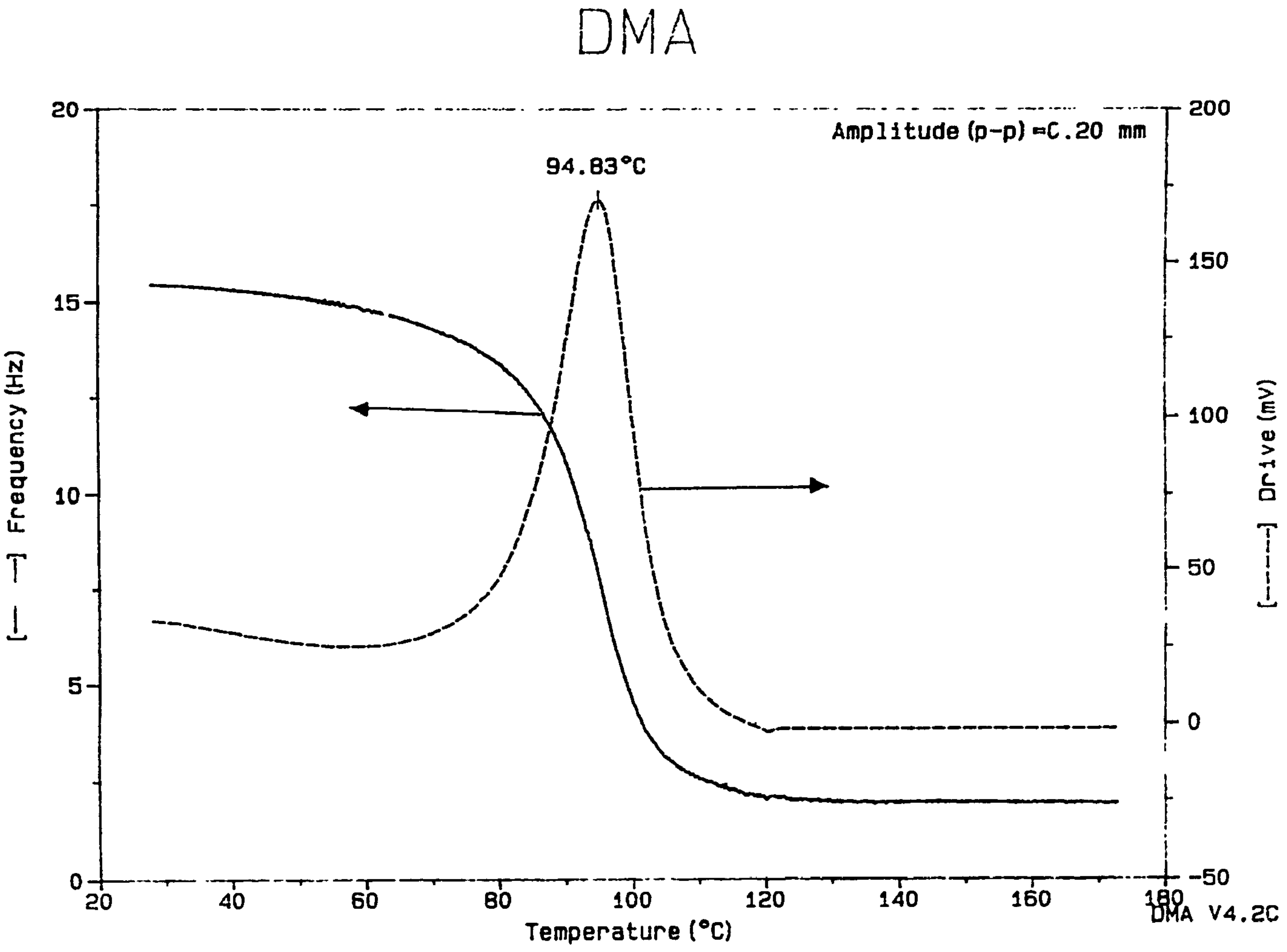


Figure 22   DMA diagram for PVC - 0L - 10T

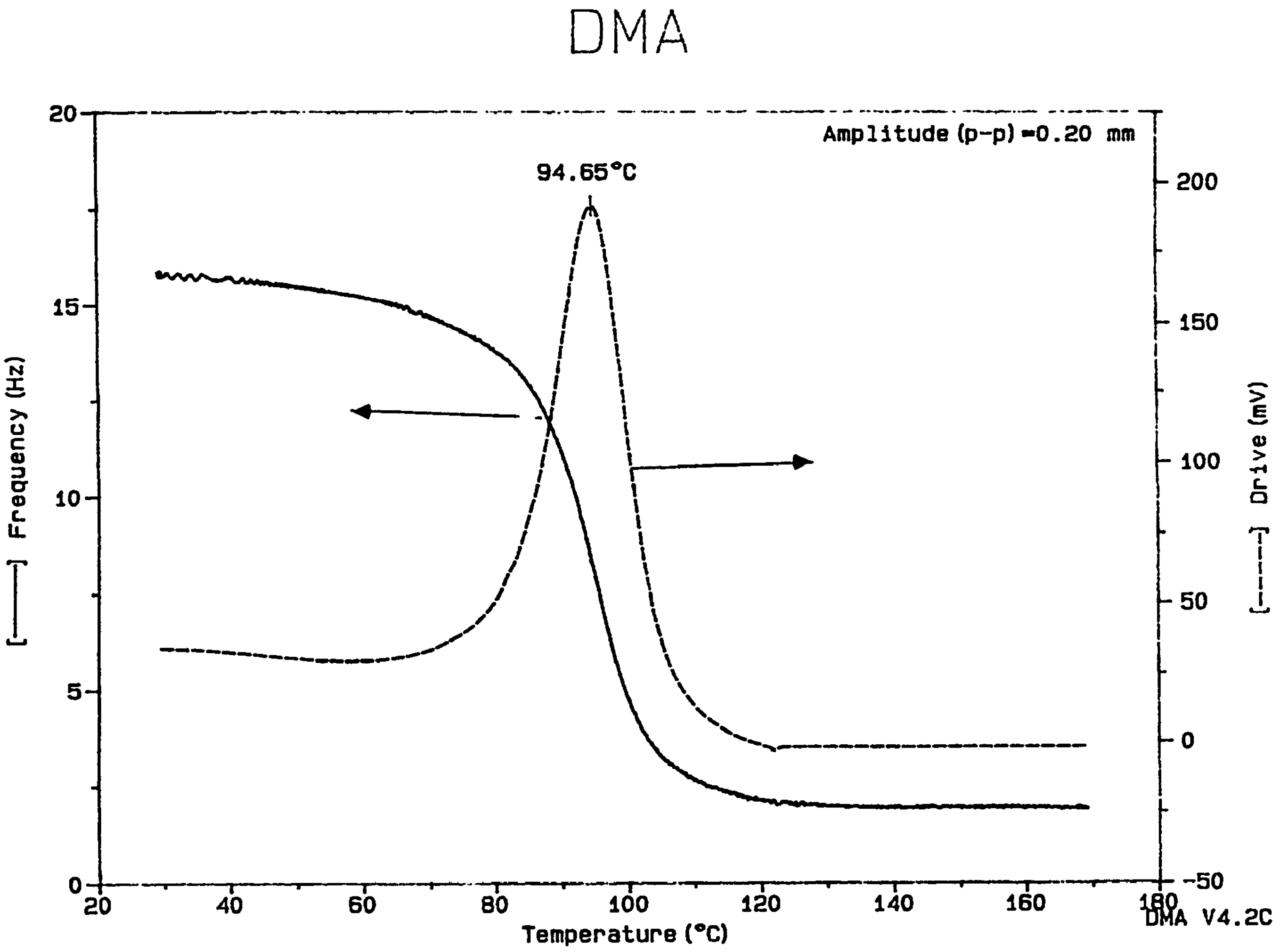


Figure 23 DMA diagram for PVC - 5L - 0T

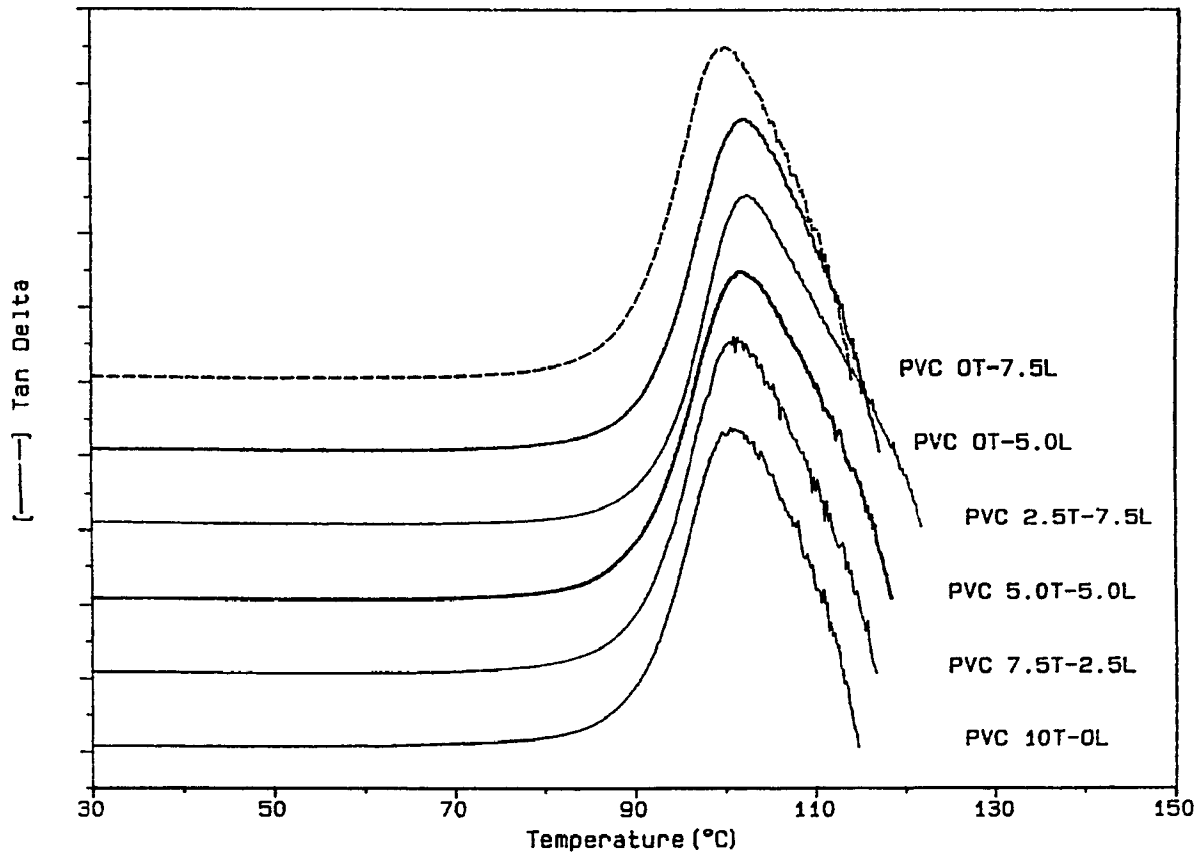


Figure 24 DMA diagram for blended and unblended PVC before weathering

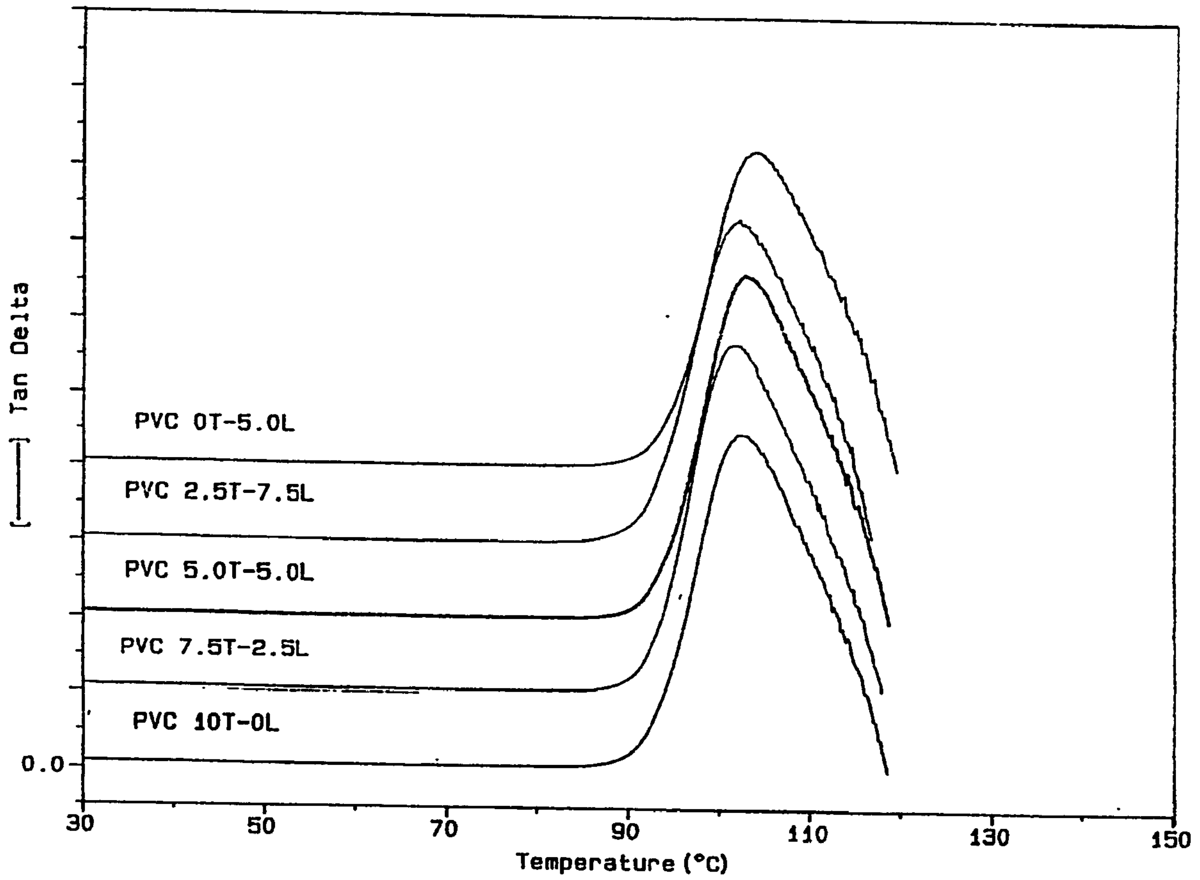


Figure 25 DMA diagram for blended and unblended PVC after weathering

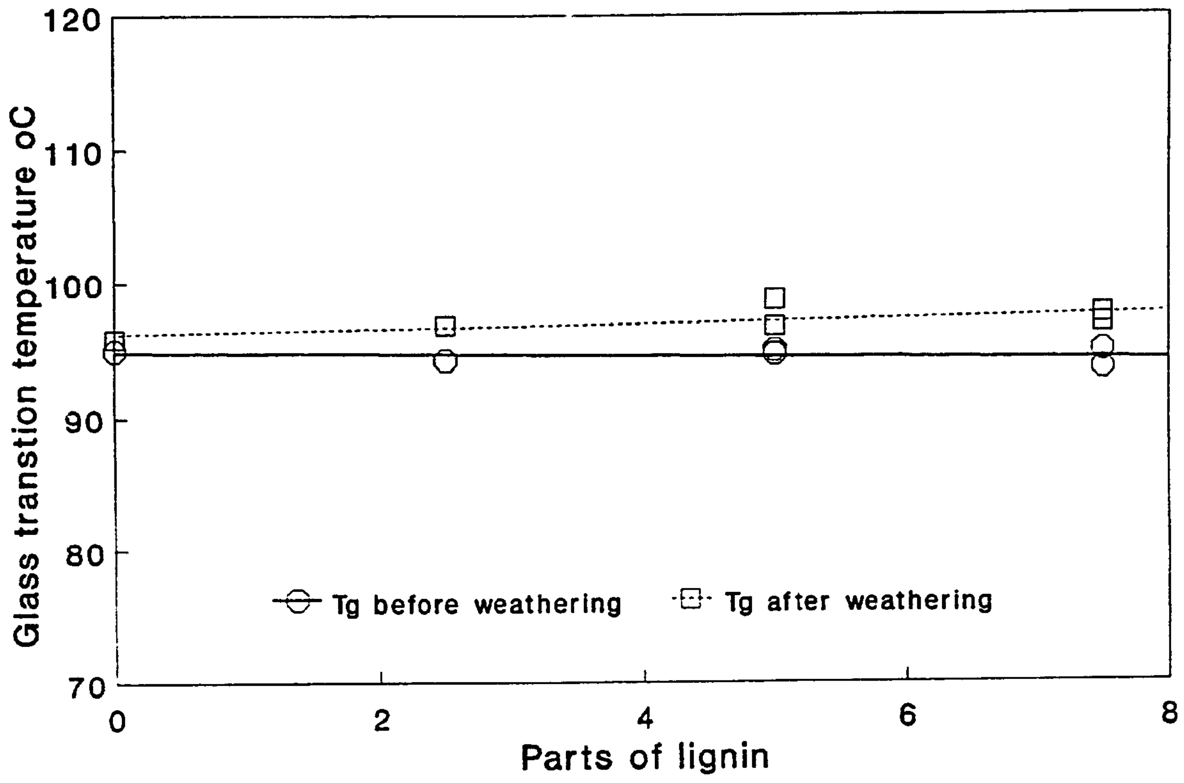


Figure 26 Effect of weathering on the glass transition temperature of blended and unblended PVC (DMA)

6.2.3 **Heat Distortion Temperature:**

The distortion temperature represents the temperature at which a specimen softens sufficiently to produce a 0.25 mm deflection under an external load. The test was carried out according to ASTM D 648 [52].

The apparatus consists of a rigid chassis which is supplied with three stations, each with its own dial gauge, weights and two types of indentor foot; the chassis stands freely in common heating chamber as shown in figure 27. The heating bath (which is filled with paraffin oil) is temperature - controlled and is provided with heater, stirrer, contact thermometer thermostat to control the rate of temperature rise.

The test specimen is a rectangular bar 125 mm long, 12.5 mm wide and 3mm thick, three specimens from each polyblend were placed on the supports; the test was started at 23^{o}C and then the temperature of the bath was raised at the rate of 120 ^{o}C per hour. The temperature in degrees C at which the deflection of the test specimen reaches the value of (0.25 mm) is noted. The mean of the results of 3 specimen testing gives the deflection temperature under load at 1.8 MPa.

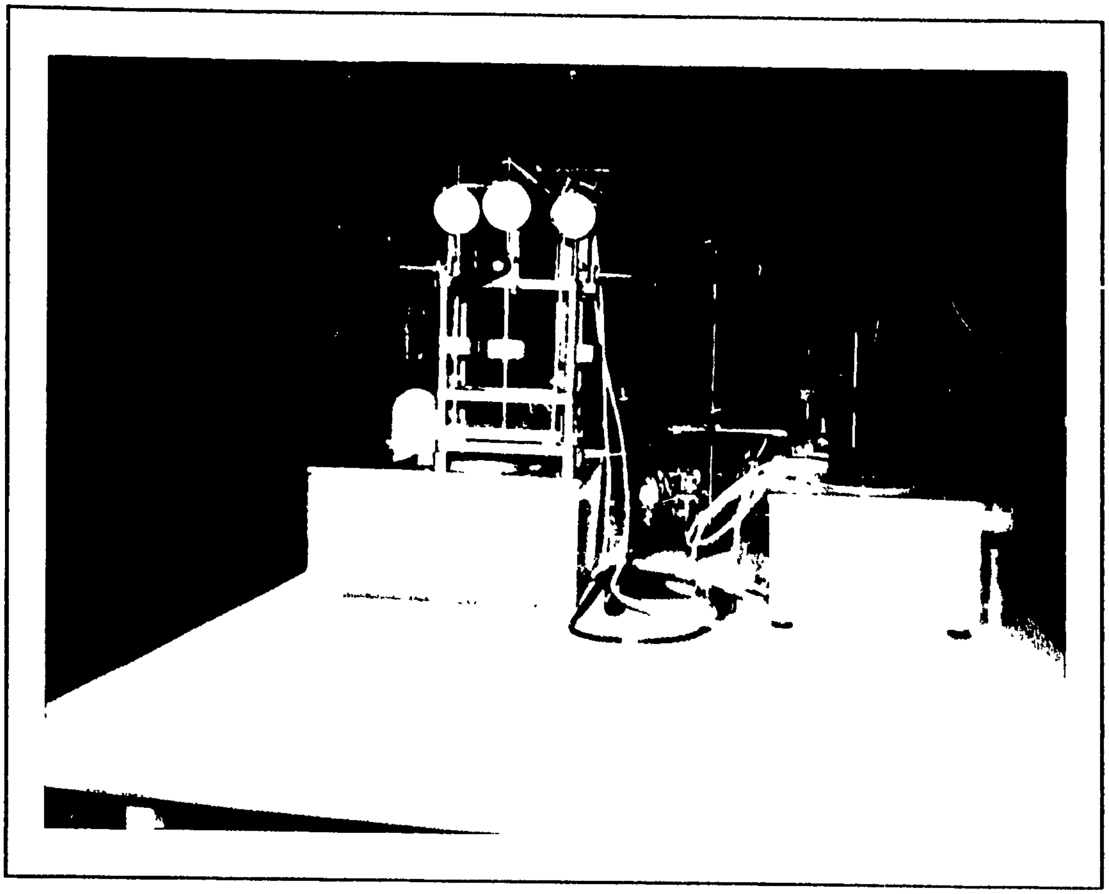


Figure 27 Heat deflection temperature determination apparatus

6.2.3.1 Results And Discussion:

Table 10 - Heat distortion temperatures of blended and unblended PVC

Formulation	**0L**	**2.5L**	**5L**	**7.5L**
Temperature °C.	70.2	70.5	69.9	70

Table 10 and figure 28 show that the addition of lignin to PVC did not affect the heat distortion temperature of the polymer.

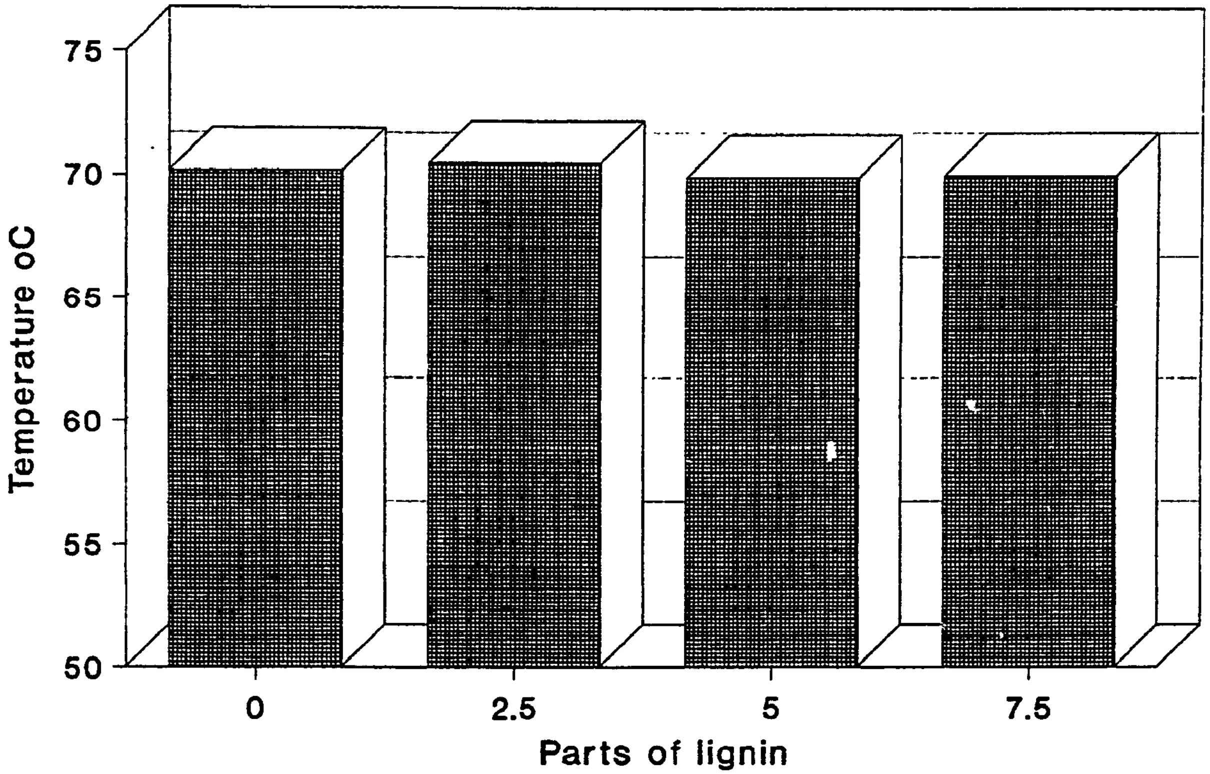


Figure 28 effect of polyblending on heat deflection of PVC

6.3 Water Absorption:

The moisture content of a plastic material has an adverse effect on its mechanical strength, appearance and dimension stability.

The water absorbtion test was done according to ASTM D 570 [53] and carried out in order to find out if the presence of L, which is highly hydrophillic due to its OH groups, leads at a higher water absorbtion of polyblends.

The apparatus used were an analytical balance capable of reading 0.0001 g and an oven, capable of maintaining uniform temperature of 50 ± 3^{o}C. Rectangular test specimen 76.6 mm long by 25.4 mm wide and 3 mm thick with smooth edges and free from cracks was used for the test.

The specimens were dried in an oven for 24 h at 50 ± 3^{o}C, cooled in a desicator and immediately weighed to the nearest 0.001 g. The conditioned specimens were placed in a container of distilled water maintained at a temperature of 23 ± 1^{o}C. At the end of each 24 h period the specimens were removed from the water once at a time, all the surface water whipped off and weighed immediately to the nearest 0.001 g.

The test was repeated for serval periods of immersion. Percentage increase in weight during immersion was calculated in the nearest 0.01 % as follows:

$$Increase\ of\ weight, \% = \frac{wet\ weight - conditioned\ weight}{conditioned\ weight}$$

6.3.1 Results and Discussion:

Table 11 - Percentage water absorption of blended and unblended PVC

Water absorption (%) after:	Formulation			
	0L	2.5L	5L	7.5L
24 h	0.07	0.07	0.07	0.08
48 h	0.13	0.10	0.13	0.13
96 h	0.17	0.15	0.16	0.18
144 h	0.24	0.21	0.24	0.27
192 h	0.24	0.20	0.24	0.26
216 h	0.28	0.23	0.27	0.29
240 h	0.30	0.30	0.30	0.34
336 h	0.37	0.33	0.33	0.36

Percentage water absorption values after 336 hour immersion for blended and unblended PVC are close to each other as shown in figure 29. In conclusion, addition of lignin to PVC did not affect its water absorption.

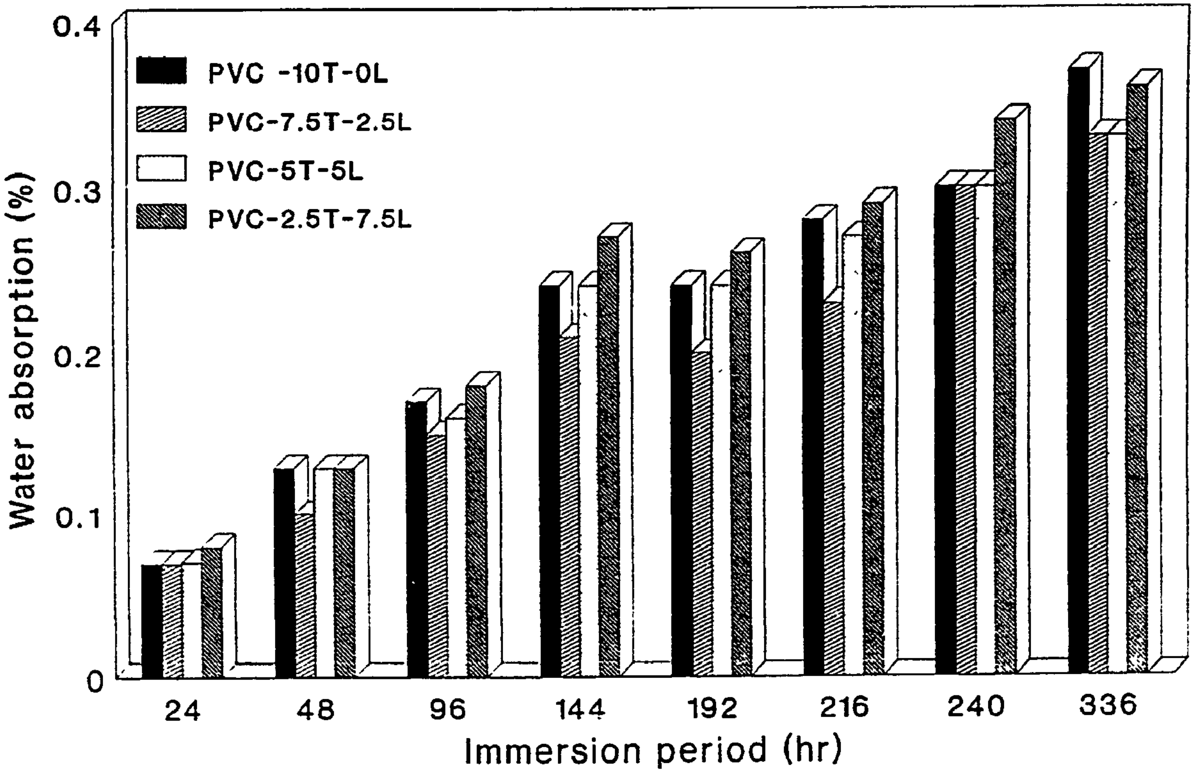


Figure 29 Effect of polyblending on the percentage water absorption of PVC

6.4 Laboratory Flammability Test:

Rigid PVC is one of the less combustible of all the thermoplastic manufactured on a large scale. Its LOI is about 50.

The rate of burning was determined according to ASTM D 635 [5] in order to find out in which extent the presence of L affects the flammability of PVC.

Specimens 125 ± 5 mm in length by 12.5 ± 0.2 mm in width (3mm thickness) from each mixture were used. Each specimen was marked by scribing two lines at 25 mm and 100 mm from one end of the specimen. The specimen was clamped at the end nearest to the 100 mm mark in a support with its longitudinal axis horizontal and its transverse axis inclined at 45^o to the horizontal. A screen of wire gauze was clamped in a horizontal position under the test specimen and a pan of water was placed on the floor of the hood in a position to catch any burning materials that may drop during the test. The burner is adjusted to produce a blue flame ($\approx$ 25 mm long) and it was placed so that the flame contacts the end of the specimen. The stop watch is started when the flame contacted the specimen, and the burner was removed at 30 second or when the flame front reached the 25 mm mark whichever came first. The test was carried out in a laboratory hood totally closed with a heat resistant glass window for observing the test.

6.4.1 Results And Discussion:

$$Average\ Time\ of\ Burning\ (ATB) = \frac{\sum(t - 30s)}{number\ of\ specimens}$$

Where,

t = burning time

$$Average\ Extent\ of\ Burning\ (AEB) = \frac{\sum(100\ mm - unburned\ length)}{number\ of\ specimens}$$

It was found that:

1) Average time of burning (ATB) is less than 5 seconds for blended and unblended PVC.

2) Average extent of burning (AEB) is less than 5 mm for blended and unblended PVC.

In conclusion the obtained results demonstrate that the presence of lignin did not affect PVC burning rate in spite of the high content of carbon and oxygen in the lignin composition; this may be due to the small quantities of lignin introduced in PVC compound.

7. Cost Evaluation:

Partial or total replacement of TiO_2 (1.56 - 2.76 \$/Kg) with lignin (0.2 - 0.4 \$/Kg) will lead to a reduction in the cost of rigid PVC compounding as shown in the table below:

Table - 12 Cost evaluation of polyblends

Formulation	Cost
PVC - 0L - 10T	100%
PVC - 2.5L - 7.5T	78.2%
PVC - 5L - 5T	56.4%
PVC - 7.5L - 2.5T	34.6%
PVC - 10L - 0T	12.8%

8. Conclusions And Recommendations

This research was carried out to prepare and evaluate PVC - L polyblends in which TiO_2 was partially or totally replaced with lignin.

From the obtained results in this preliminary study, the following conclusions may be drawn:

1) Addition of lignin to PVC does not affect its processability.

2) Partial replacement of TiO_2 with kraft lignin leads to an increase in tensile strength and a slight decrease in elongation at yield and at break for unweathered blends.

3) Total replacement of TiO_2 with kraft lignin leads to higher.increase in the tensile strength and a decrease in the elongation at yield and at break.

4) After weathering, the tensile strength of blended and unblended PVC are almost the same.

5) Addition of kraft lignin to PVC decreases elongation at yield after weathering.

6) The artificial weathering action (UV and humidity) has the same effect on the elongation at break for both blended and unblended PVC.

7) Both blended and unblended PVC showed discoloration and micro cracks after artificial weathering exposure only on the exposed sides of specimens. Even though the apparition of micro cracks on PVC - L blends took place earlier than unblended PVC,

the mechanical and thermal analysis indicated that L addition has no negative effect on the weatherability of PVC.

8) Kraft lignin interacts with PVC forming miscible blends, as resulted from glass transition temperature determination before and after weathering. The glass transtion temperature of the polyblends are close to that of PVC.

9) Kraft lignin addition to PVC has no negative influence on its burning rate or the percentage of water absorption.

In conclusion lignin could replace TiO_2 in PVC compositions with improvements in some properties and reduction of the cost of compounding. However more research is needed for the stabilization of some lignins toward UV light.

Recommendations:

1) The study of the PVC blends processing using different parameters and other techniques (as extrusion or injection) to find the most suitable laboratory production procedures.
2) Studies on PVC polyblends with other kinds of lignin which are already available as a by - product of the pulp and paper industry.
3) Use of stabilized lignin to obtain a more durable PVC for siding, door and window frames.
4) Production and evaluation of polyblends using PVC with lower K value or with

plasticized PVC.

5) Studies concerning the effect of addition of lignin on the impact strength of PVC.

6) Studies on the effect of weathering action on the polyblends by surface examination using the electronic microscopy technique.

7) Evaluation of the durability (natural weathering) of PVC - L blends during outside applications.

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