

# Contributions to Characterization of Poly(vinyl chloride)–Lignin Blends

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**ABSTRACT:** The present study evaluates the impact of blending organosolv and kraft lignins, which are natural polymer by-products in the pulp and paper industry, with plasticized poly(vinyl chloride) (PVC) in flooring formulations. Also examined is the impact of replacing dioctyl phthalate, a PVC industry general-purpose plasticizer, with diethylene glycol dibenzoate (Benzoflex 2-45), tricresyl phosphate (Lindol), or alkyl sulfonic phenyl ester (Mesamoll) in these formulations. The influence of the different types of lignins and plasticizers on the processibility, thermal, and mechanical properties of the blends is discussed. These properties demonstrate that partial replacement of PVC (20 parts) with different lignins is feasible for some

formulations that can be successfully used as matrices for a high level of calcium carbonate filler in flooring products. In addition, the data demonstrate that the presence of certain plasticizers, which interfere with the intramolecular interactions existing in lignins, may allow the lignin molecules to have more molecular mobility. The morphology and the properties of PVC plasticized lignin blends are strongly influenced by the degree and mode of the lignin plasticization and its dispersion within the PVC matrix. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2732–2748, 2006

**Key words:** poly(vinyl chloride); lignin; poly(vinyl chloride)–lignin blends; plasticizers

## INTRODUCTION

Poly(vinyl chloride) (PVC) is the most commonly used member of the broad family of thermoplastics, and it is ranked second to polyethylene in terms of polymer consumption. It has become a very important bulk plastic worldwide over its 70-year history and is expected to increase because of its general properties, including mechanical properties that can be adjusted over a wide range because of the possibility of compounding PVC into rigid to flexible end products.<sup>1</sup>

The global sales of PVC before 2000 were approximately 23,500,000 metric tons, which reflects the high demand for PVC products. That could be translated into considerably more millions of metric tons of PVC additives as fillers, plasticizers, impact modifiers, and so forth.<sup>2</sup>

One of the major applications of PVC in the construction industry is as resilient flooring.<sup>3,4</sup> Diethylhexyl-phthalate (DEHP), commercially known as dioctyl phthalate (DOP), is normally used as a plasticizer in the manufacture of vinyl flooring to facilitate PVC processing as well as to improve the flexibility

and elongation. DOP is suspected to be an environmental pollutant when subjected to microbial degradation, especially when exposed to a humid environment.

Fungi have been shown to produce the enzymes capable of breaking the ester linkages present in this type of ester (alkyl phthalate) into more volatile components, which are subsequently released into the enclosed building environment. Inhabitants may thus be subjected to long-term exposure of low levels of volatile organic compounds.<sup>5</sup>

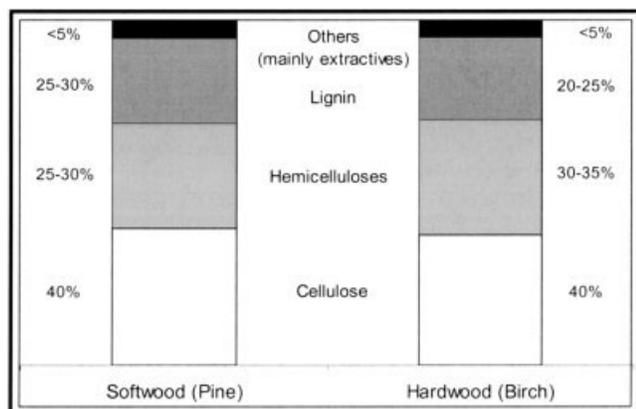
Considering this hazard, the objective of the study was the development of new vinyl flooring formulations with other plasticizers that have chemical compositions different than that of the common DOP plasticizer. After breaking the ester linkages both fungi and bacteria can metabolize the fragment molecules thus produced. Studies have shown that there are significant differences between plasticizers in their stability to microbial attack. The relative susceptibility to microbial attack is influenced, via their relative susceptibility to hydrolysis, by steric factors, which dictate the strength of the ester group. In general, linear structures are less resistant than branched structures.<sup>5</sup>

Having these observations in mind, the flooring compositions were formulated with the following plasticizers: diethylene glycol dibenzoate (Benzoflex 2-45, 2-45), tricresyl phosphate (Lindol), and alkyl sul-

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**Figure 1** The average chemical composition of soft wood and hard wood.<sup>6</sup>

fonic phenyl ester (Mesamoll). To also improve resistance to microbial degradation, the PVC was partially replaced by a natural polymer lignin, which results in high quantities, from wood delignification in the pulp and paper industry.

Although the proposed alternatives for DOP have different chemical structures, they are commercial products that are compatible with PVC and compatible or partially compatible with the lignins, as will be further discussed.

Lignins are natural organic materials, which together with cellulose and hemicelluloses form the structural components of trees and various plants, as shown in Figure 1. They are classified mainly into three major groups: soft wood lignin, hard wood lignin, and grass lignin. They impart rigidity to the cell walls, act as an intercellular binder, and are responsible for wood resistance to compression, impact, and bending. In addition, the presence of lignin renders the wood tissue resistant to the action of microorganisms.<sup>6</sup>

Lignin molecules are composed of phenyl propane units interconnected by about 10 different link-

ages in a complex matrix. This matrix consists of a variety of functional groups, including hydroxyl, methoxy, and carbonyl, which impart polarity to the lignin macromolecules.<sup>7</sup> Lignins represent a class of polymers that are quite different from most synthetic polymers because of the high degree of association between their macromolecules.<sup>8,9</sup> This high degree of association was demonstrated by analyzing the molecular weight distribution.<sup>8,10-12</sup> A thermal analysis of lignin also indicated high values of the glass-transition temperature ( $T_g$ ) of between 100 and 160°C, which is surprisingly high for a polymer with a molecular weight ranging from 1000 to 12000.<sup>13</sup> Studies done by Yoshida and al. on different molecular weight fractions of a kraft lignin obtained by successive extractions with organic solvents showed that the temperature range of the  $T_g$  increases significantly with increasing molecular weight.<sup>14</sup>

There are different kinds of technical lignins, depending on the chemical processes used for delignification of wood. Kraft lignin is obtained by treating wood with alkali, whereas organosolv lignins are obtained from the delignification of wood with organic solvents (mainly alcohols). In this study we used an organosolv lignin (Alcell lignin) and kraft lignins (Indulin and Tomlinitite), which are produced from softwood and hardwood, respectively.

This study evaluates the mechanical and thermal properties of PVC-Alcell, PVC-Indulin, and PVC-Tomlinitite blends prepared with the above-mentioned plasticizers in comparison to the respective controls without lignin.

## EXPERIMENTAL

### Materials

The synthetic polymer used in the study was PVC (OxyVinyls 185) supplied by OxyVinyls LP (Dallas, TX). It has the following characteristics: an equilib-

**TABLE I**  
Principal Properties of Lignins

Characteristics	Alcell	Indulin	Tomlinitite
Number-average molecular weight	800-900 <sup>a</sup>	1858 <sup>b</sup>	650 <sup>c</sup>
Weight-average molecular weight	>2000 <sup>a</sup>	7050 <sup>b</sup>	2800 <sup>c</sup>
Polydispersity	2.22	3.79	4.3
Specific gravity	1.27 <sup>a</sup>	1.3 <sup>a</sup>	1.3 <sup>d</sup>
Average particle size ( $\mu\text{m}$ )	16 <sup>a</sup>	8 <sup>d</sup>	16 <sup>d</sup>
pH value	4 <sup>a</sup>	6.5 <sup>a</sup>	6 <sup>a</sup>
Solubility parameter, $\delta$ ( $\text{cal}/\text{cm}^3$ ) <sup>1/2</sup>	13.7 <sup>e</sup>	$\cong 10$ <sup>f</sup>	$\cong 10$ <sup>f</sup>
Glass-transition temperature <sup>g</sup> ( $^{\circ}\text{C}$ )	97	142	133

<sup>a</sup> Data from producers.

<sup>b</sup> Data from ref. 10.

<sup>c</sup> Data from ref. 19.

<sup>d</sup> Data from ref. 18.

<sup>e</sup> Data from ref. 17.

<sup>f</sup> Data from ref. 13.

<sup>g</sup> Determined by DSC in our laboratory.

TABLE II  
Principal Properties of Plasticizers

Characteristics <sup>a</sup>	DOP	2-45	Lindol	Mesamoll
Molecular formula	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	(C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O	C <sub>21</sub> H <sub>21</sub> O <sub>4</sub> P	C <sub>15</sub> H <sub>31</sub> SO <sub>3</sub> C <sub>6</sub> H <sub>5</sub>
Molecular weight	390.57	314.4	368.4	368.06
Specific gravity	0.986	1.178	1.17	1.03-1.07
Viscosity (mPa.s at 25°C)	82	65-66	67	95-125/20°C
Boiling point (°C at 4 mmHg)	230	240/5 mmHg	248	200/9.75 mmHg
Pour point (°C)	-47	28	-28	≤ -15 (setting point)
Solubility parameter, <sup>b</sup> δ (cal/cm <sup>3</sup> ) <sup>1/2</sup>	8.23	10.1	9.86	~10
Solubility in water (mg/L)	0.23-0.34	<0.01	0.36	None
Glass-transition temperature <sup>c</sup> (°C)	-80.5	-52	-57.6	-68.2

<sup>a</sup> Data from producers.

<sup>b</sup> Data from ref. 20.

<sup>c</sup> Determined by DSC in our laboratory.

rium constant of 56 (weight-average molecular weight = 38000), a solubility parameter (δ) of 9.7 (cal/cm<sup>3</sup>)<sup>1/2</sup>,<sup>15</sup> and a specific gravity of 1.4. The  $T_g$  as determined by differential scanning calorimetry (DSC) in our laboratory was 85.5°C.

The characteristics of the different lignins used in this study are presented in Table I. The plasticizer suppliers are provided elsewhere.<sup>16</sup> Mesamoll was supplied by Bayer Corp. (Pittsburgh, PA). Their principle characteristics are summarized in Table II.

Calcium carbonate (Pulpro 10, specific gravity = 2.71, mean particle size = 10 μm) was provided by Omya St. Armand Ltd. (Montreal). It contains 95% CaCO<sub>3</sub>, 2% MgCO<sub>3</sub>, and acid insoluble 3%.

### Formulations

All the composites were formulated with 100 parts polymer, 200 parts per 100 parts of resin polymer (phr) calcium carbonate (CaCO<sub>3</sub>), 35 phr plasticizer, 3 phr dibutyltin dilaurate as the heat stabilizer (Sigma-Aldrich Canada Ltd., Mississauga, ON), and 1.5 phr calcium stearate (lubricant grade L-155, Blachford Ltd., Mississauga, ON).

The PVC controls and PVC blends were prepared with each plasticizer at the specified concentrations. Lignin (i.e., Alcell, Indulin, or Tomlinite) replaced 20 parts of PVC in the PVC blends. In the PVC blends the two polymers represent 100 parts and the PVC/lignin

ratio was 80:20. The plasticizer loading (35 phr) was calculated for the 100 parts polymer. If the lignin loading is not taken into account, the quantity of plasticizer relative to PVC is only 42 phr. To establish if there is an interaction between the lignins and the plasticizers in the blends, parallel PVC controls with 42 phr plasticizer were prepared and their  $T_g$  tested by DSC.

### Procedures

The formulations of PVC controls and blends were prepared by melt mixing for 8 min at 145°C and a rotor speed of 65 rpm in a Haake Rheomix 600 equipped with roller blades, a torque rheometer for the measurement of the mix torque, as well as a thermocouple for continuous measurements of the melt temperature. The mixer was electrically heated and air cooled. For all mixes, the recorded torque showed that a plateau was reached about 2 min before the end of the mixing time.

After melt mixing, the batches were ground to a 2-3 mm size and compression molded at 155°C for 8 min under a pressure of 4 MPa in a Carver laboratory press equipped with temperature controllers. Then, they were cooled from molding temperature to room temperature at a cooling rate of 10°C/min under pressure.

TABLE III  
Equilibrium Torque of PVC Controls with 35 and 42 phr Plasticizers and Blends with 35 phr Plasticizer

Plasticizer type	Equilibrium torque at 148 ± 1°C (m.g)				
	PVC control		PVC-Alcell	PVC-Indulin	PVC-Tomlinite
35 phr	42 phr				
DOP	1200	1025	1025	1075	1075
2-45	1350	1100	1175	1200	1200
Lindol	1375	1150	1175	1325	1275
Mesamoll	1300	1050	1050	1200	1175

**TABLE IV**  
Glass-Transition Temperatures ( $T_g$ ) of PVC Controls and Blends and Differences Between Their  $T_g$ s ( $\Delta T_g$ )

Sample ident.	Lindol		2-45		Mesamoll		DOP	
	$T_g$ (°C)	$\Delta T_g$ (°C)						
Control 35 phr plasticizer	25.7	—	20.8	—	11.8	—	9.3	—
Control 42 phr plasticizer	21.1	4.6	10.9	9.9	3.6	8.2	1.1	8.2
Blend Alcell	22.1	3.5	16.9	3.9	9.7	2.1	2.2	7.1
Blend Indulin	21.8	3.8	15.1	5.7	2.5	9.3	1.8	7.5
Blend Tomlinite	22.5	3.1	13.1	7.7	4.6	7.2	2.3	7.0

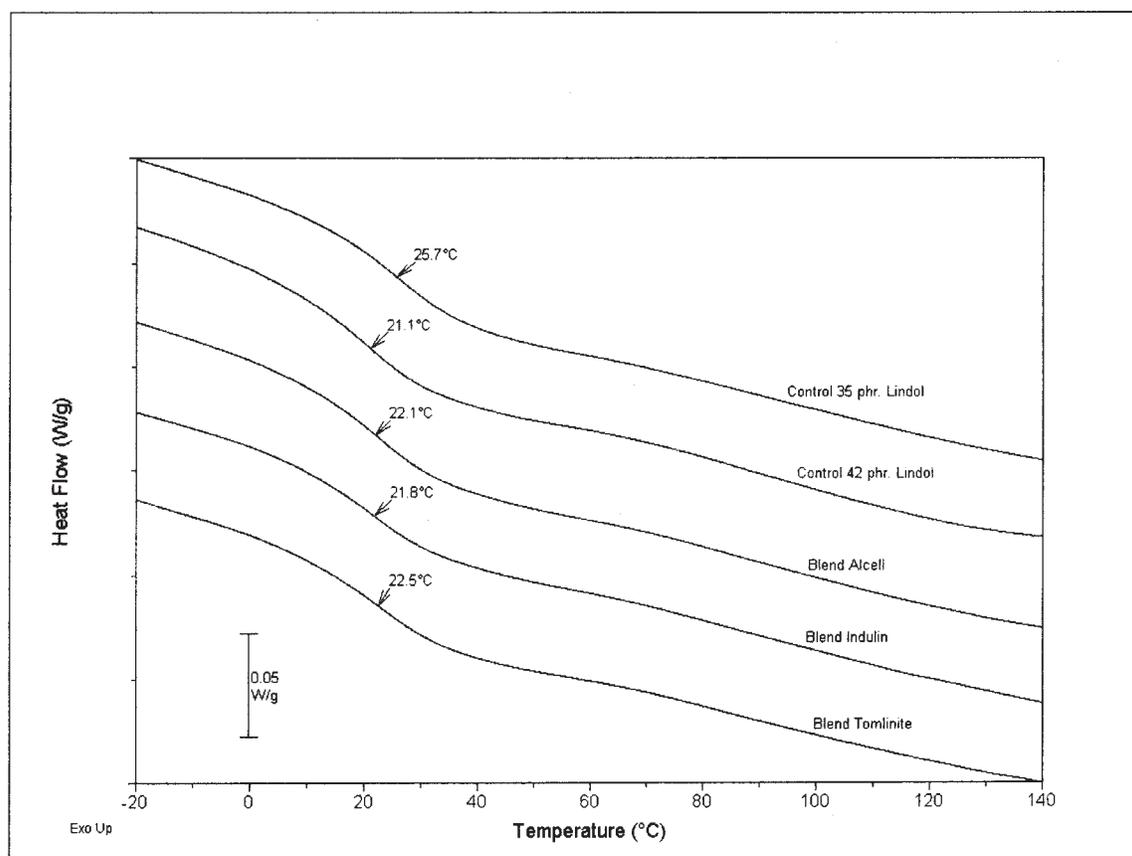
### Tensile testing

The 1.5 mm thick sheets were cut with a cutting die into shoulder-shaped specimens in accordance with ASTM D 638, and the tensile strength properties were measured using a universal tensile testing machine at a crosshead speed of 2 mm/min and a temperature of  $23 \pm 2^\circ\text{C}$ . All the specimens for mechanical testing were tested 1 week after their preparation. They were conditioned at  $23 \pm 2^\circ\text{C}$  and  $50 \pm 5\%$  relative humidity for 48 h prior to testing in accordance with ASTM D 618. The indicated values are an average of at least five determinations. The coefficients of variation infe-

rior to 10% were taken into consideration for each set of tested specimens.

### DSC testing

The thermal properties of raw materials and the blends were measured using a TA 2010 differential scanning calorimeter in accordance with ASTM 3418. For PVC controls and blends, at least two 20-mg samples weighed with an accuracy of  $\pm 0.002$  mg were punched from 1.5-mm sheets and tested. All samples were heated from  $-60$  to  $160^\circ\text{C}$  at a heating rate of



**Figure 2** DSC thermograms of a PVC control and blends with Lindol as the plasticizer.

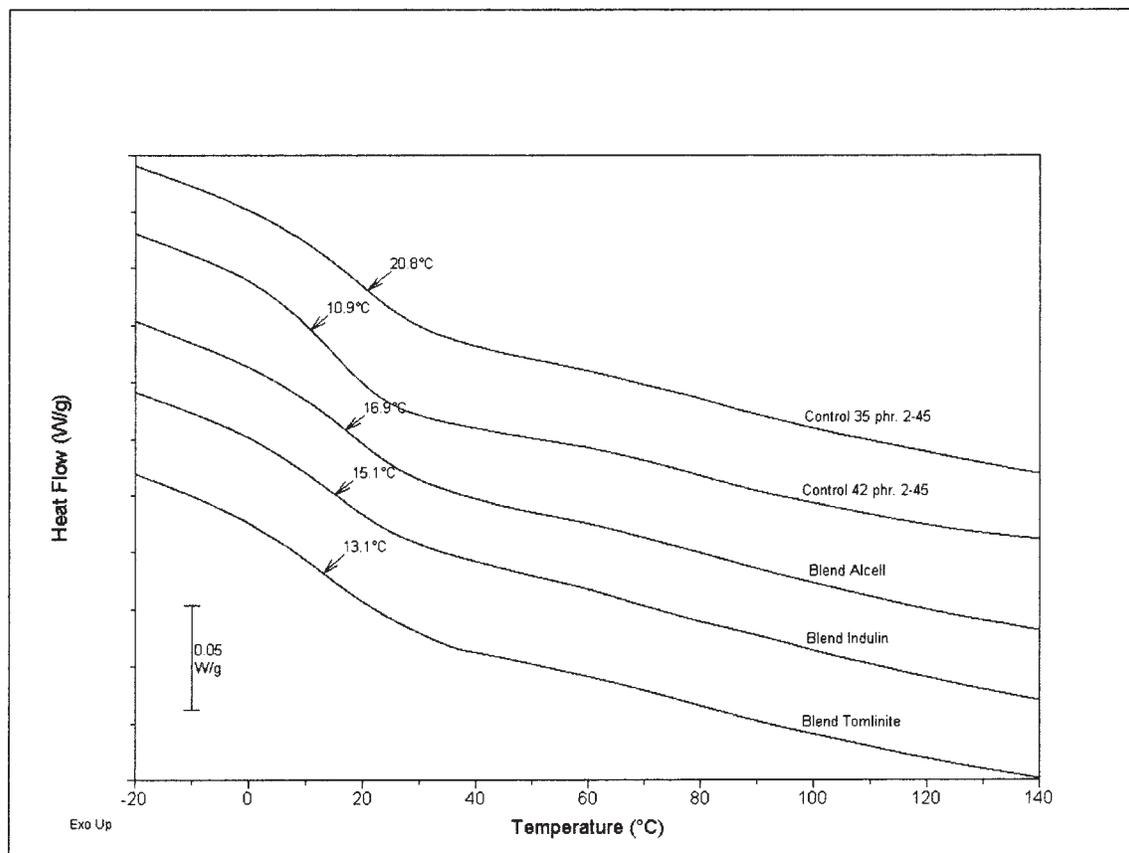


Figure 3 DSC thermograms of a PVC control and blends with 2-45 as the plasticizer.

20°C/min. The scans were performed under a nitrogen atmosphere at a flow rate of 20 mL/min. The reported  $T_g$  values were estimated from the second run.

As shown earlier, in order to make certain that some interaction between the plasticizer and lignin took place in the blends, controls with 42 phr plasticizer were also tested in similar conditions.

In addition, mixtures of each lignin with 35 phr plasticizer were obtained by a method described elsewhere.<sup>16</sup> They were tested from  $-40$  to  $160^\circ\text{C}$  to establish the efficiency of each plasticizer for the respective lignins, knowing that one of the criteria for measuring plasticizer efficiency is the extent to which the  $T_g$  of a polymer is lowered by the introduction of a given amount of plasticizer.<sup>15</sup>

### Morphology

The extent of the dispersion of lignins in the various blends was examined by taking photomicrographs of razor-cut samples at  $100\times$  magnification. These micrographs allowed a comparative determination of the dispersion quality by visual inspection of the lignin agglomerate size and distribution through the polymer matrix in each blend.

## RESULTS AND DISCUSSION

### Processibility

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

### Thermal properties

The  $T_g$  values of the PVC controls with 35 phr plasticizer, the respective blends, and the controls with 42 phr plasticizer are shown in Table IV. The table also provides the differences in degrees Centigrade between the  $T_g$  of the controls and the respective blends ( $T_g$ ), as well as the differences be-

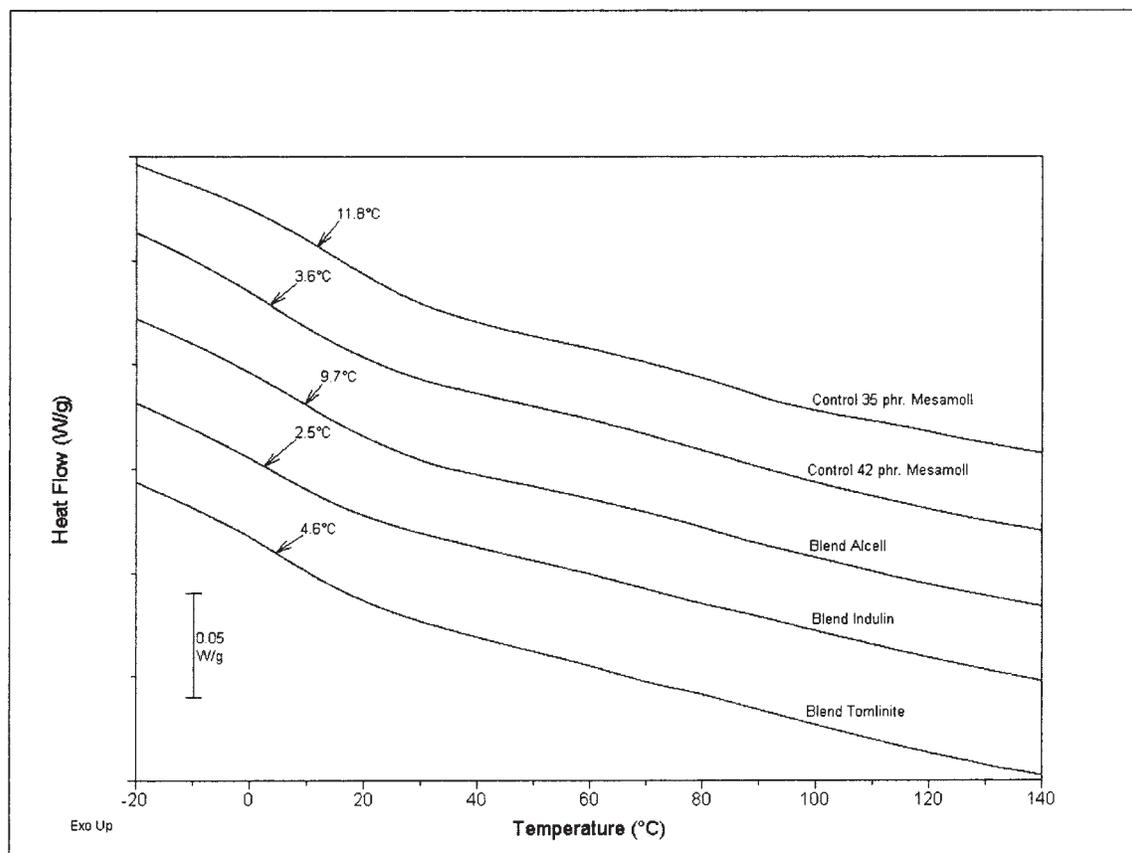


Figure 4 DSC thermograms of a PVC control and blends with Mesamoll as the plasticizer.

tween the  $T_g$ s of the controls with 42 and 35 phr plasticizer. DSC thermograms in the temperature interval between  $-20$  and  $140^\circ\text{C}$  (Figs. 2–5) reveal single  $T_g$ s for all the blends, which indicate a relatively homogenous structure. Unlike the quite sharp and narrow glass-transition range for the blends plasticized with 2-45, Lindol, and to a lesser extent with Mesamoll, the  $T_g$  region of DOP plasticized blends was broad and less sharp, indicating a certain degree of inhomogeneity on the molecular scale. It is interesting to note that, compared to all plasticizers, DOP has the lowest solubility parameter (see Table II) and thus the lowest efficiency in plasticizing lignins.

The solubility parameter is generally a useful guide to predict compatibility. Frequently, a polymer will be compatible with a plasticizer when the two have solubility parameters that do not differ by more than  $\pm 1.5$   $(\text{cal}/\text{cm}^3)^{1/2}$ .<sup>20</sup>

The data presented in Table IV point out that, in comparison to the respective controls, the  $T_g$ s of all the blends ( $\Delta T_g$ ) decreased a few degrees Centigrade. In most of the cases the blends' decreased  $T_g$  values are not comparable with the differences between the  $T_g$ s of the controls plasticized with 35 and 42 phr plasticizer, depicting interactions between

the plasticizers and lignins. However, the degree of interactions varies as a function of the plasticizer and lignin type as the  $\Delta T_g$  data suggest. A correlation between the  $T_g$  decrease of the blends and their mechanical property variations is further discussed.

The effect of the plasticizer efficiency on the lignins used in the study (i.e., the extent of lowering their  $T_g$ s) was also determined by DSC. The mixtures of lignins with 35 phr plasticizer were homogenous powders. However, some of them were really "dry blends" whereas others were "slightly wet powders," indicating in the latter case the presence of traces of the plasticizer liquid phase. The only pair that presented two distinct phases was the Alcell–DOP mixture. The  $T_g$  of the lignin and 35 phr plasticizer mixtures as determined in the second run, the differences between the  $T_g$ s of lignins and those of the respective lignin–plasticizer mixtures ( $\Delta T_g$ ), and their physical aspects are presented in Table V. Figures 6–9 represent their thermograms for the first and second DSC scans.

An inspection of the data tabulated in Table V shows that there are appreciable differences in the efficiency of each plasticizer on the three lignins. Plasticizers 2-45 and Lindol perceptibly reduce the  $T_g$  of all the lignins, and in the meantime all the mixtures

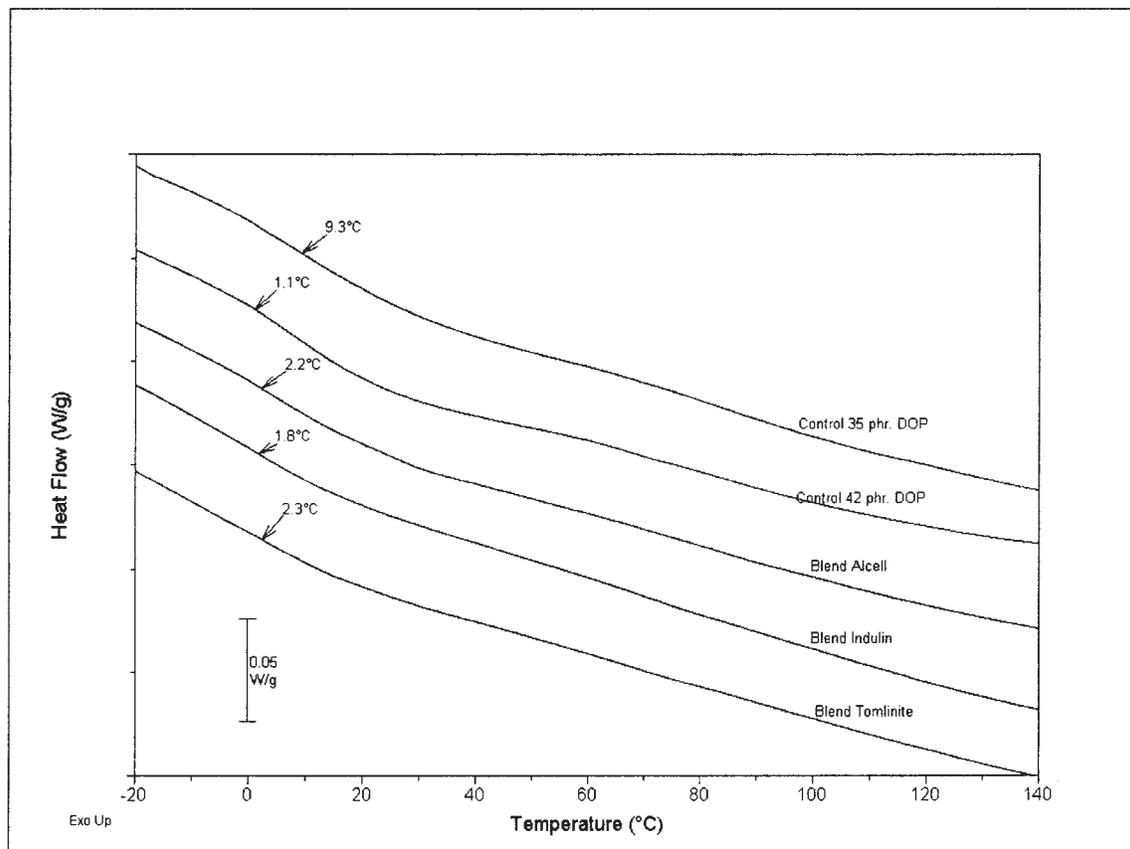


Figure 5 DSC thermograms of a PVC control and blends with DOP as the plasticizer.

present only one solid phase. The results are not surprising when taking into account their high and close solubility parameter.

Mesamoll and DOP seem to be poorer plasticizers for lignins than 2-45 and Lindol. They effect a modest reduction in the  $T_g$  and traces of the liquid phase were observed in their mixtures with lignins.

The sensible differences in the extent of  $T_g$  reduction of the different pairs of lignin-plasticizer suggest that the magnitude and mode of changes in the lignins' chain mobility are different and are strongly influenced by the type of plasticizer.

Although each plasticizer-lignin mixture presents apparently a single  $T_g$ , as can be seen from Figures

7-9, the transitions are very broad, indicating a somewhat less than homogenous blend.

According to the literature data, a sharp transition ( $T_g$  interval  $< 15^\circ\text{C}$ ) is typical for a material that is homogenous on the scale of thermal measurements, with a resolution scale of 100-500 nm. In contrast, a broad transition is characteristic for a less homogenous blend.<sup>21</sup>

In order to elucidate the phase behavior and morphology of these lignin-plasticizer blends, the enthalpy relaxations appearing in the first DSC scan were also studied.

The appearance of multiple enthalpy relaxations in the first DSC scan is symptomatic of heterogeneous

TABLE V  
Glass-Transition Temperatures ( $T_g$ ) of Lignin and 35 phr Plasticizer Mixtures and Differences Between  $T_g$  of Lignin and  $T_g$  of Lignin and 35 phr Plasticizer Mixtures ( $\Delta T_g$ )

Plasticizer type	Alcell			Indulin			Tomlinite		
	Aspect	$T_g$ ( $^\circ\text{C}$ )	$\Delta T_g$ ( $^\circ\text{C}$ )	Aspect	$T_g$ ( $^\circ\text{C}$ )	$\Delta T_g$ ( $^\circ\text{C}$ )	Aspect	$T_g$ ( $^\circ\text{C}$ )	$\Delta T_g$ ( $^\circ\text{C}$ )
2-45	Dry powder	32	65	Dry powder	62	80	Dry powder	47	86
Mesamoll	Wet powder	83	14	Wet powder	121	21	Wet powder	130	3
DOP	Two phases	—	—	Wet powder	126	16	Wet powder	123	10
Lindol	Dry powder	42	55	Dry powder	114	28	Dry powder	55	78

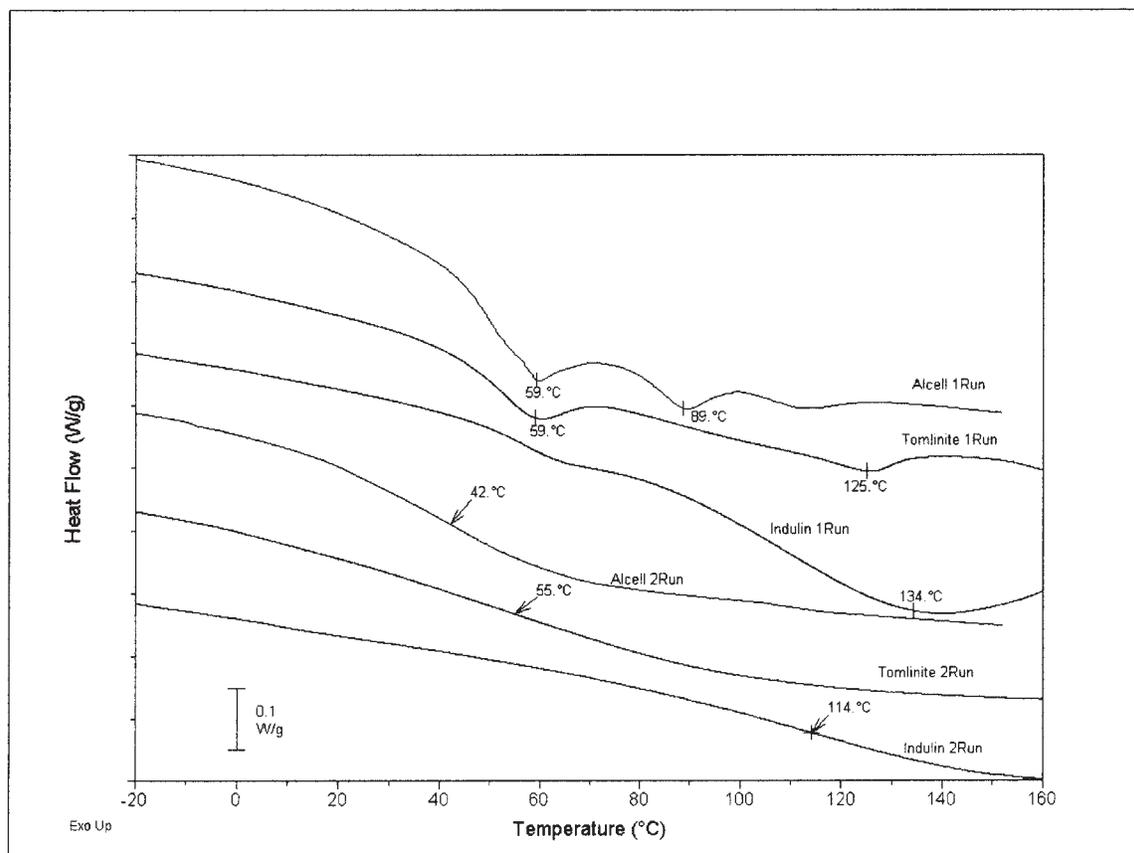


Figure 6 DSC thermograms of mixtures of different lignins with 35 phr Lindol as the plasticizer.

blends. If mixing is homogenous on a molecular level, then the cooperative nature of the relaxation process implies that a single enthalpy relaxation will be observed whose position and magnitude now reflects the mixture and not the pure components.<sup>22</sup> The enthalpy relaxation, which is a time-related phenomenon, is due to the relaxation of the polymer chains eliminating the excess free volume in an effort to approach the preferred or true equilibrium state of the system. This behavior is manifested through a slow decrease in volume (densification), decrease in enthalpy (enthalpy relaxation), or other state function variables. The excess free volume is quenched in the system when the respective system is cooled from the melt. The rapid rise in viscosity that occurs as the  $T_g$  is approached freezes the polymer chains in a nonequilibrium conformation and configuration.<sup>23</sup>

The first scan of the DSC thermograms (Figs. 7–9) shows that each pair of plasticizer–lignin mixtures exhibit a specific relaxation behavior comprising in most of the cases two distinct relaxation peaks located at quite different temperatures, confirming the heterogeneity of the mixtures. The apparently single broad transition observed in the second scan could be the result of two or more separate overlapping transitions that occur in a large temperature range.

As can be seen from Table I, the molecular weight distribution of lignins is very broad. In addition, be-

cause of the presence of many phenolic OH groups, strong intermolecular bonds are formed between the lignin fractions of different molecular weights.

The temperature range of the glass transition of the different molecular weight fractions increases significantly when increasing their molecular weight.<sup>14</sup> By analyzing the position and intensity of the relaxation peaks in the first scans (Figs. 6–9), one may conclude that each plasticizer, depending on its characteristics and chemical configuration, solvates the low and medium molecular weight fractions within a particular lignin and partially swells some high molecular weight fractions. Depending on the lignin's degree of solvation and swelling, the size and the position of the transitions occurring at different temperature intervals will be different and will be reflected in the values of overlapping transitions. Moreover, the degree of solvation and swelling of lignin by a particular plasticizer will influence the mechanical properties of the respective blends as will be further discussed.

## Mechanical properties

### General considerations

The mechanical properties data of PVC controls and blends as a function of plasticizer type are presented

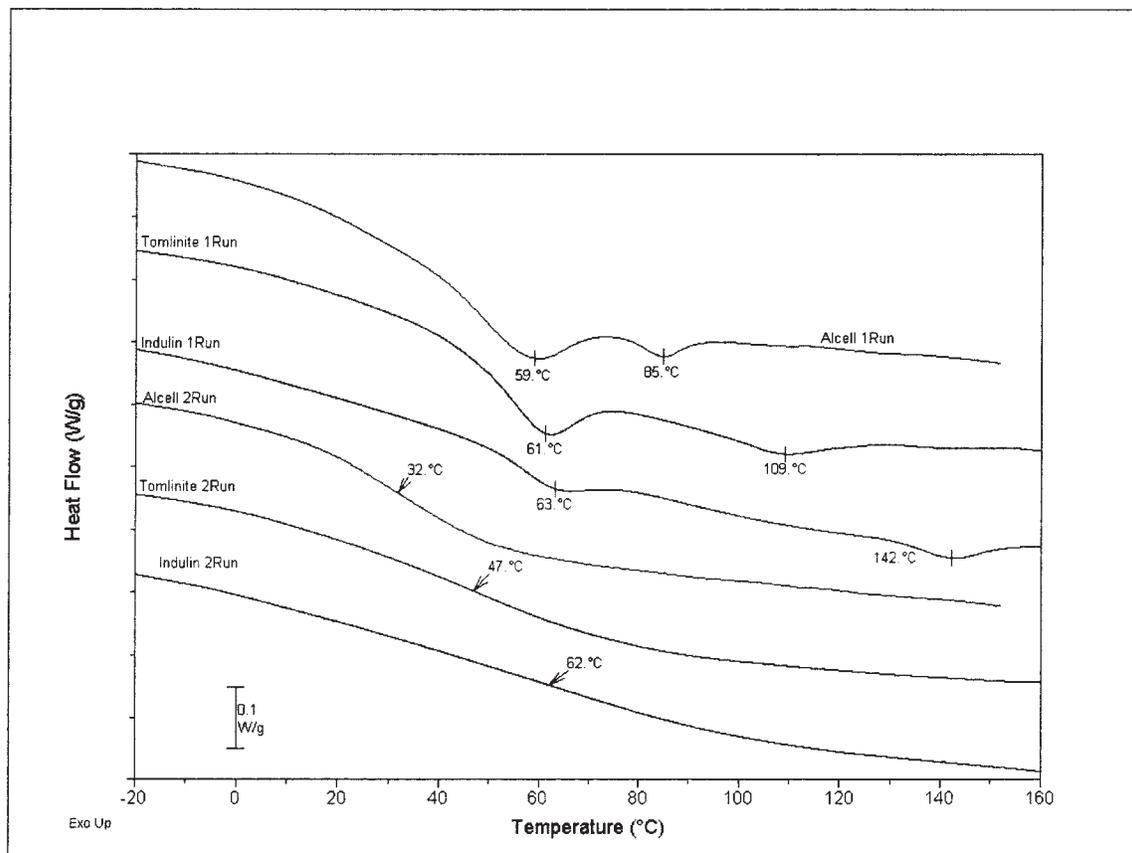


Figure 7 DSC thermograms of mixtures of different lignins with 35 phr 2-45 as the plasticizer.

in Table VI and the respective stress-strain curves in Figures 10–13. Table VII indicates the variation in the percentages of the mechanical properties of the blends relative to respective PVC controls. Because of the fact that the mechanical properties of the formulations are strongly influenced by the  $T_g$ , the decrease in the  $T_g$  values of the blends ( $\Delta T_g$ ) versus the respective controls are provided in Table VII.

All specimens were tested at room temperature ( $\cong 23^\circ\text{C}$ ). As can be seen from Table IV, the testing temperature was in all cases above or very close to the specimens'  $T_g$ s.

Figures 10–13 indicate that the stress-strain curves are representative for ductile materials. They exhibit a distinct yield and the failure is ductile with neck propagation and strain hardening for all the controls and for a few blends.

By analyzing the data presented in Table VII, one may discern two extremes in the PVC-lignin blends. In one extreme there are the blends plasticized with Lindol that are characterized by similar  $T_g$  values of about  $22^\circ\text{C}$  and that are about  $3^\circ\text{C}$  lower than those of the respective controls. In the other extreme there are the blends plasticized with DOP that are characterized by  $T_g$  values of about  $2^\circ\text{C}$  and that are about  $7^\circ\text{C}$  lower than those of the respective controls. For all these

blends the modulus values are reduced by about 50% in comparison with the respective controls, a fact that is quite surprising when considering that the  $\Delta T_g$  of Lindol plasticized blends is about only  $3^\circ\text{C}$  and the  $\Delta T_g$  of DOP plasticized blends is about  $7^\circ\text{C}$ .

The tensile properties are highly dependent on intermolecular PVC-PVC, lignin-lignin, PVC-lignin, PVC-plasticizer, lignin-plasticizer, and matrix-filler interactions. Above the  $T_g$ , increasing molecular mobility leads to diminished bond strength by interchain or intermolecular separation.<sup>24</sup>

Consequently, the decrease of the modulus values for DOP plasticized blends should be higher than that of Lindol plasticized blends. Increasing the molecular mobility at room temperature, which is the testing temperature (and which is higher than the  $T_g$  values of the DOP blends and close to that of Lindol blends), should also produce an increase in elongation and a decrease in tensile strength at yield and break. Indeed, Lindol plasticized blends generally present these features, whereas DOP plasticized blends are characterized by much more modest increases in elongation or even a decrease (as for Indulin blend) and comparable decreases in tensile strength at break. The tensile strength at yield values decrease less than those of Lindol plasticized blends. All these results suggest

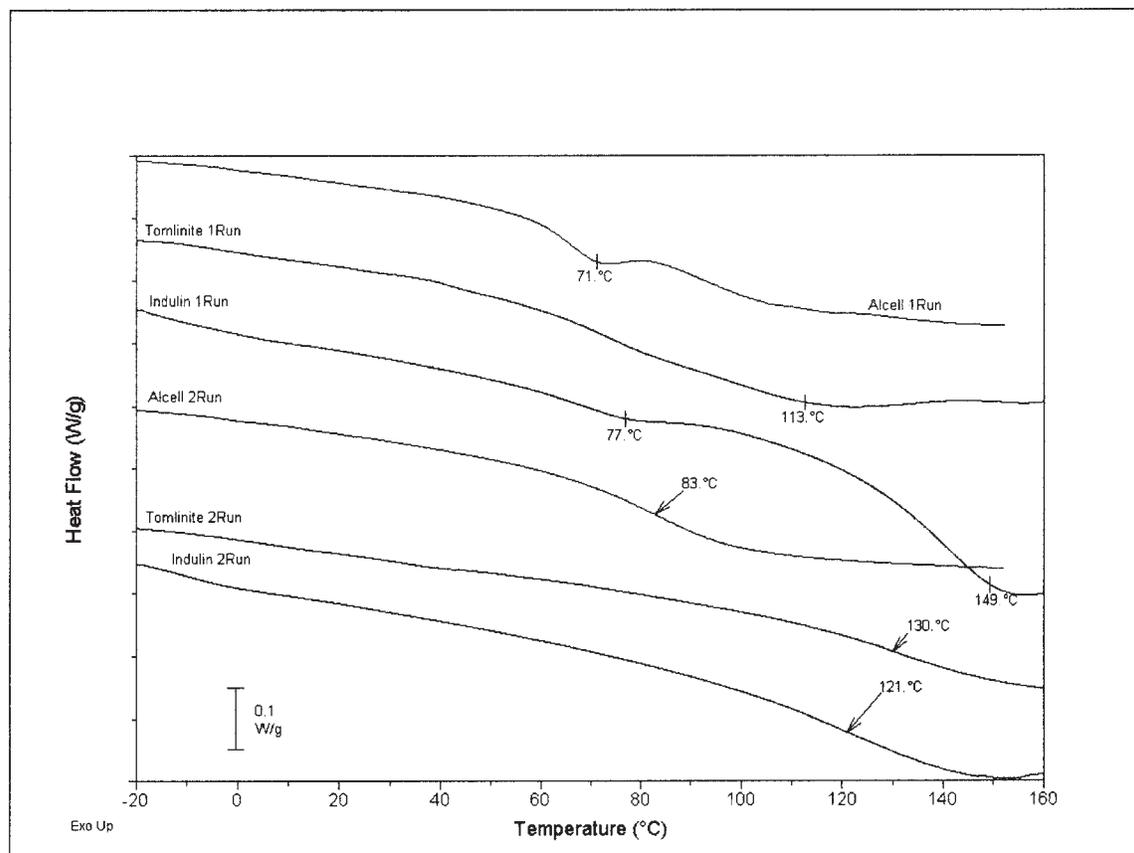


Figure 8 DSC thermograms of mixtures of different lignins with 35 phr Mesamoll as the plasticizer.

that different factors affect the mechanical properties of the Lindol and DOP plasticized blends.

#### DOP plasticized blends

An inspection of Table V and Figure 9 shows that DOP is a poor plasticizer for lignins. Consequently, quite large size lignin particles are present in the blends and probably more plasticizer is available for the PVC matrix, which will become softer as the  $T_g$  data indicate (see also Fig. 14). The presence of the poorly plasticized lignin with a quite high  $T_g$ , and consequently in the glassy state, will act as a reinforcing filler and enhance the modulus of the PVC matrix in blends. Moreover, the quite large size particles of lignin will impede the PVC matrix from undergoing cold drawing and therefore the material will elongate less. These facts may explain why the reduction in the modulus values for a  $\Delta T_g$  of 7°C in DOP plasticized blends are of the same order of magnitude as in Lindol plasticized blends where the  $\Delta T_g$  was only 3°C and why the elongation increases less in DOP plasticized blends.

#### Lindol plasticized blends

The data in Table V and Figure 6 show that Lindol is generally a good plasticizer for lignins. It reduces the

$T_g$ s of Alcell and Tomlinite and to a lesser extent that of Indulin. The relaxation peaks from Figure 6 suggest that Lindol plasticizes both the low and high molecular weight fractions of Alcell and Tomlinite, whereas Indulin seems to be only partially plasticized. The morphology of the blends plasticized with Lindol well illustrates its effectiveness in plasticizing different lignins. Thus, the morphology of Alcell and Tomlinite blends is quite different from that of Indulin blends, where large lignin domains are evident (Fig. 15). The presence of these large Indulin domains may indicate that more plasticizer is available for the PVC matrix, which will become softer as can be seen from the data presented in Table 6 and Figure 10. In contrast, the well-plasticized Alcell and Tomlinite may have a plasticizing effect on the PVC matrix, as can be seen from Figure 10 and Table VII.

#### 2-45 plasticized blends

Table V shows that 2-45 seems to be a good plasticizer for all the lignins. In addition, all the blends have a comparable morphology, all lignins being evenly distributed through the PVC matrix (Fig. 16). The mechanical properties of these blends display some interesting characteristics. When compared with the respective data of the control, the Alcell blend's  $T_g$  is

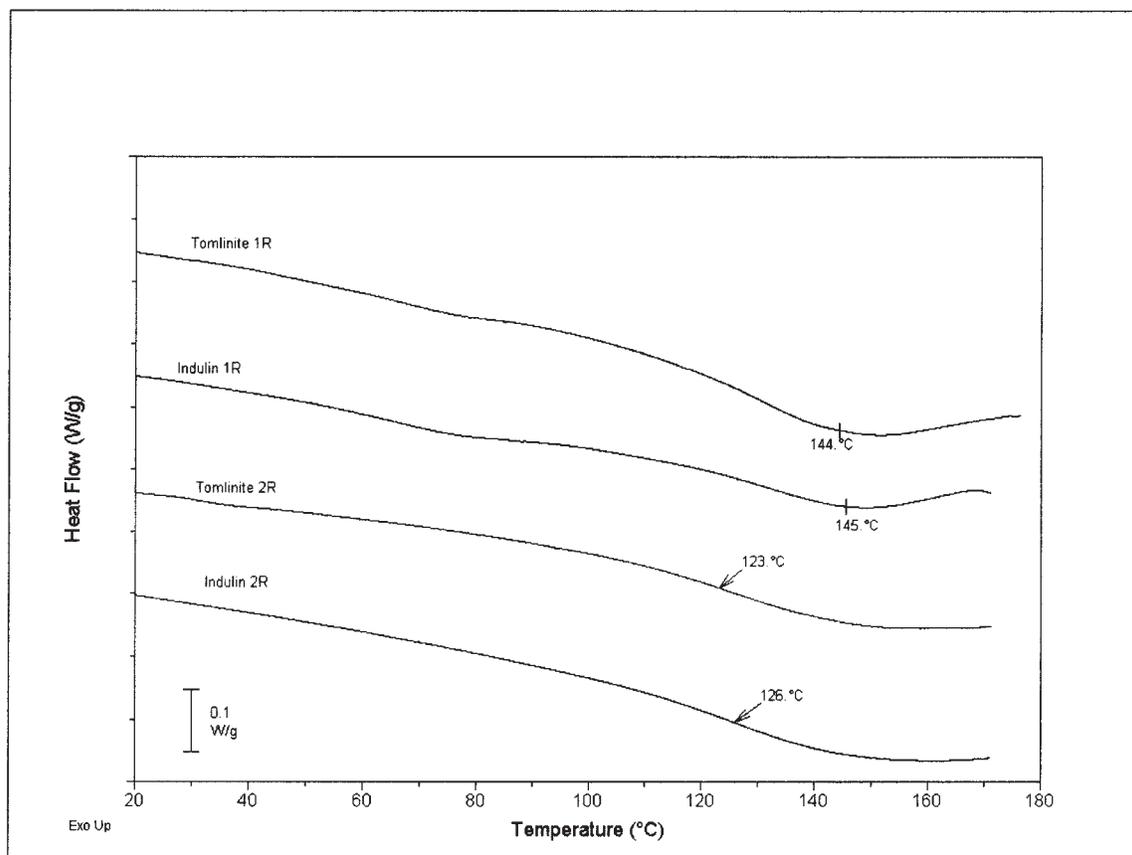


Figure 9 DSC thermograms of mixtures of different lignins with 35 phr DOP as the plasticizer.

3.9°C lower, the elongation value is higher, and the strength at yield and break values are lower. In addition, a slight increase of strain is noticeable, depicting a higher degree of plasticization in relation to the control. However, the blend modulus, which should be lower, is higher. This is surprising because of the fact that modulus values are very sensitive to temperature. DSC data of an Alcell and 2-45 mixture (Table V, Fig. 7) indicate that 2-45 is a good plasticizer for Alcell, reducing its  $T_g$  from 97 to 32°C. However, the relaxation peaks located at relatively low temperature suggest that 2-45 plasticizes mostly the low molecular weight fractions. The remaining high molecular weight fractions, in the glassy state and evenly distributed through the plasticized PVC matrix, will act as a reinforcing filler, thus enhancing its modulus. In contrast, the low molecular weight plasticized Alcell fractions will act as a plasticizer, pushing the already plasticized PVC chains apart more and thus enhancing the elongation.

When compared with the control's  $T_g$ , the  $T_g$ s of Indulin and Tomlinite blends are 5.7 and 7.7°C lower, respectively, and the modulus decreases in the same order. The tensile strengths at yield are higher than that of the Alcell blend and both elongate less than the Alcell blend and than the PVC control (Tables VI, VII).

The DSC thermograms indicate that 2-45 plasticizes the high molecular fractions of these two lignins to a certain degree. These partially plasticized fractions probably develop some interactions with PVC chains and, because of their high molecular weight, a high force is needed for the chain segments to be able to slip past each other at the yield. In addition, they are less evenly distributed through the PVC matrix than Alcell (Fig. 16), which explains why their blends elongate less.

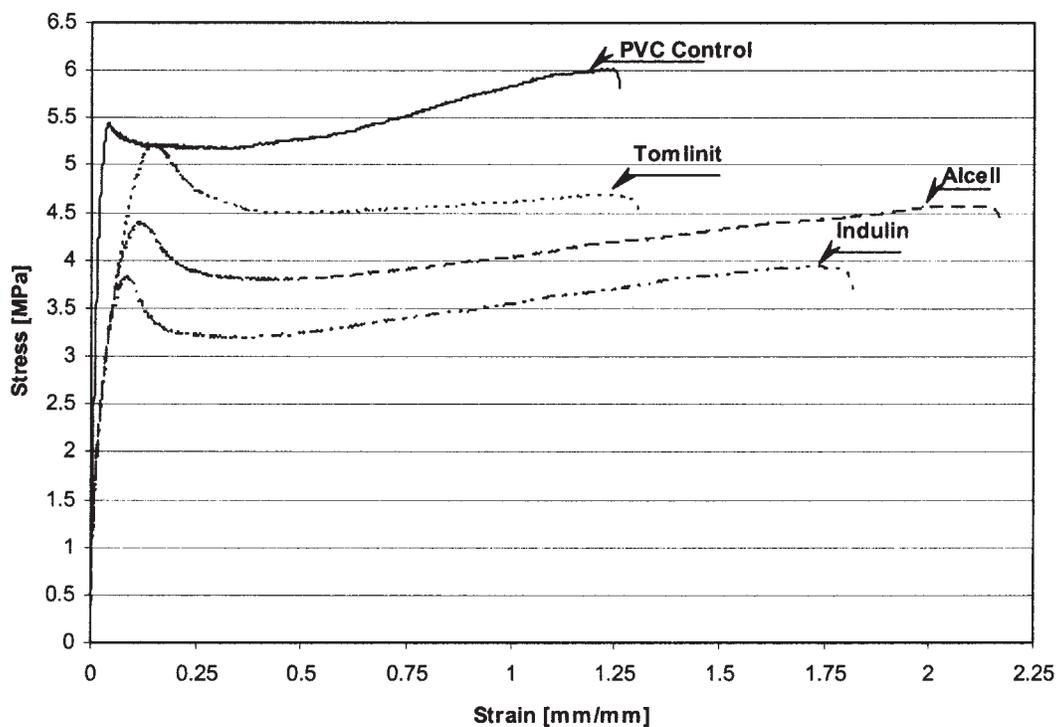
#### Mesamoll plasticized blends

The properties of PVC–lignin blends plasticized with Mesamoll can also be quite well correlated with the degree of plasticization of each lignin by this plasticizer (Fig. 17). Data presented in Table V show that Mesamoll is a rather poor plasticizer for all three lignins. It modestly reduces their  $T_g$  and all plasticizer–lignin mixtures are rather wet powders. However, their DSC thermograms (Fig. 8) are characteristic for a quite homogenous mixture, judging from the aspect of the first runs, which suggest that all the molecular weight fractions of Tomlinite and Indulin, and to a lesser extent those of Alcell, are participating in the transition. This fact may explain the higher  $T_g$ s of

**TABLE VI**  
**Mechanical Properties of PVC Controls and Blends Relative to Plasticizer Type**

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

<sup>a</sup> At 2% elongation.



**Figure 10** Stress-strain curves of a PVC control and blends with Lindol as the plasticizer.

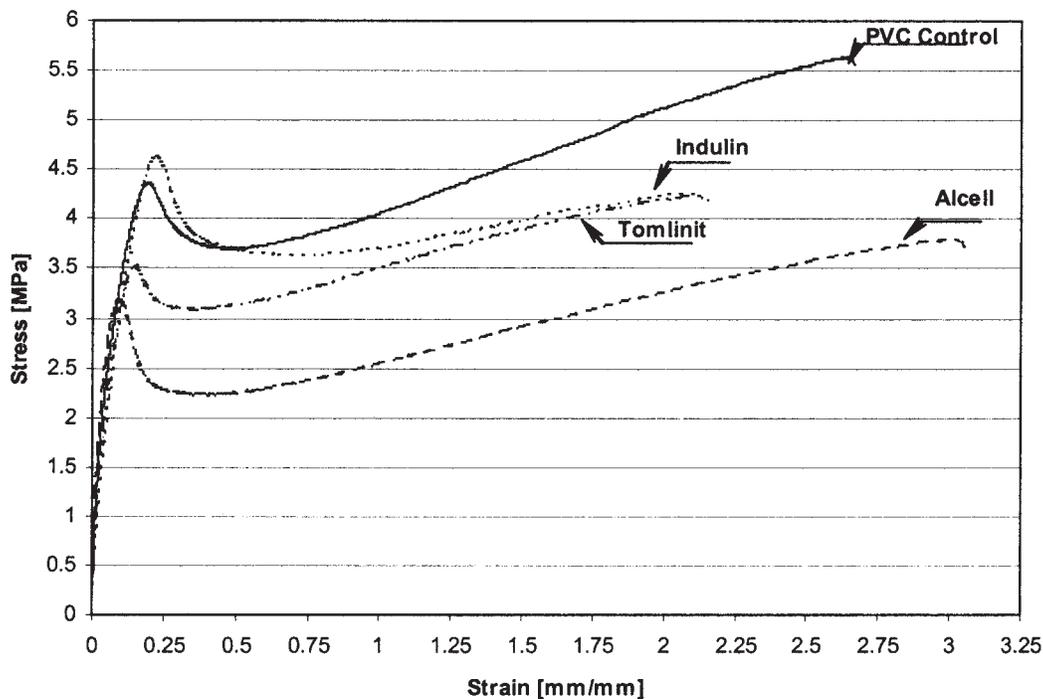


Figure 11 Stress-strain curves of a PVC control and blends with 2-45 as the plasticizer.

these mixtures in comparison with other plasticizer-lignin mixtures.

When compared with the  $T_g$  value of the PVC control plasticized with Mesamoll, the blends'  $T_g$  values are 2.1, 7.2, and 9.3°C lower for Alcell, Tomlinit, and

Indulin blends, respectively, with a modest decrease in moduli for such decreases in the  $T_g$ s. Surprisingly, their tensile strength at yield and the elongation at break do not vary much in relation to the respective properties of the control, except the Indulin blend

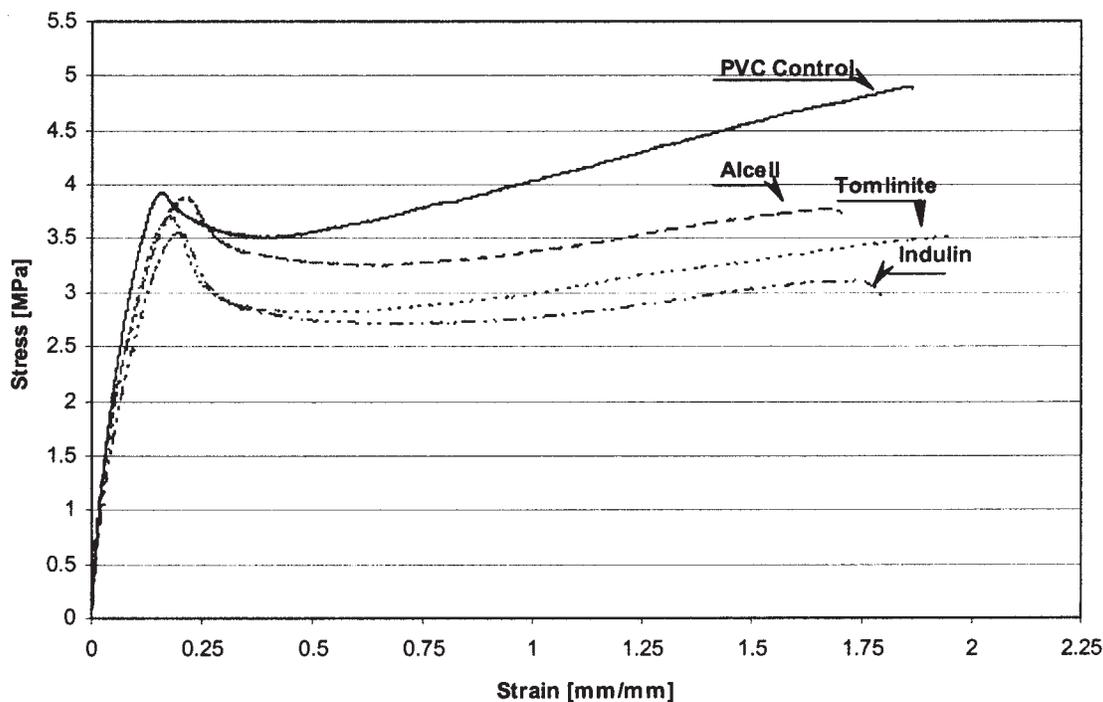


Figure 12 Stress-strain curves of a PVC control and blends with Mesamoll as the plasticizer.

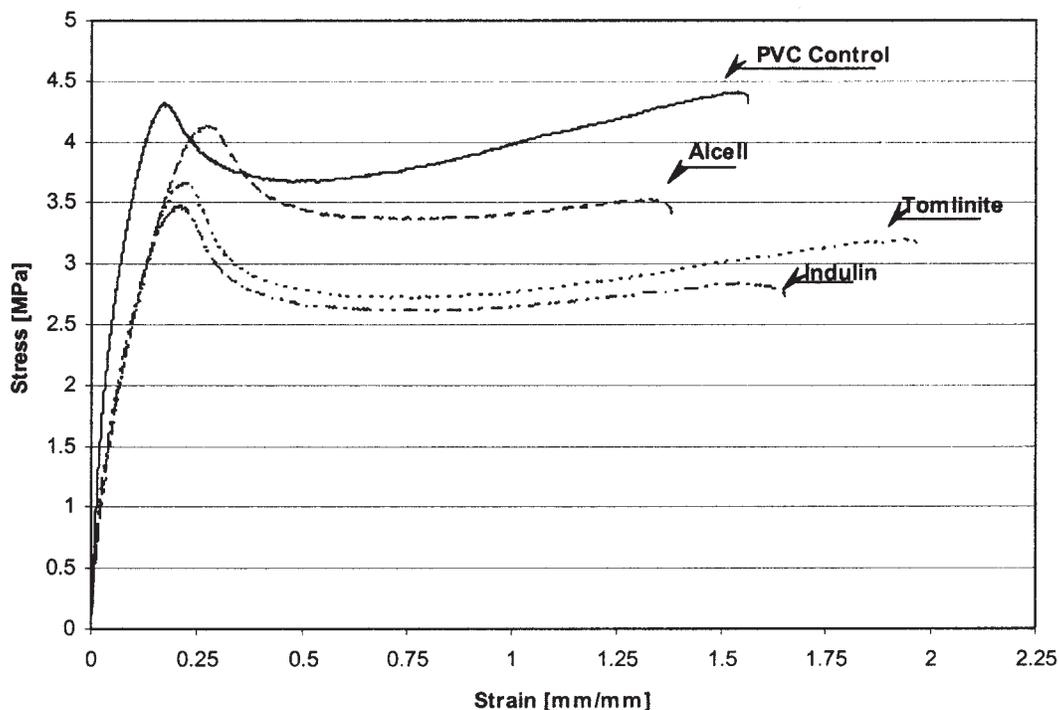


Figure 13 Stress-strain curves of a PVC control and blends with DOP as the plasticizer.

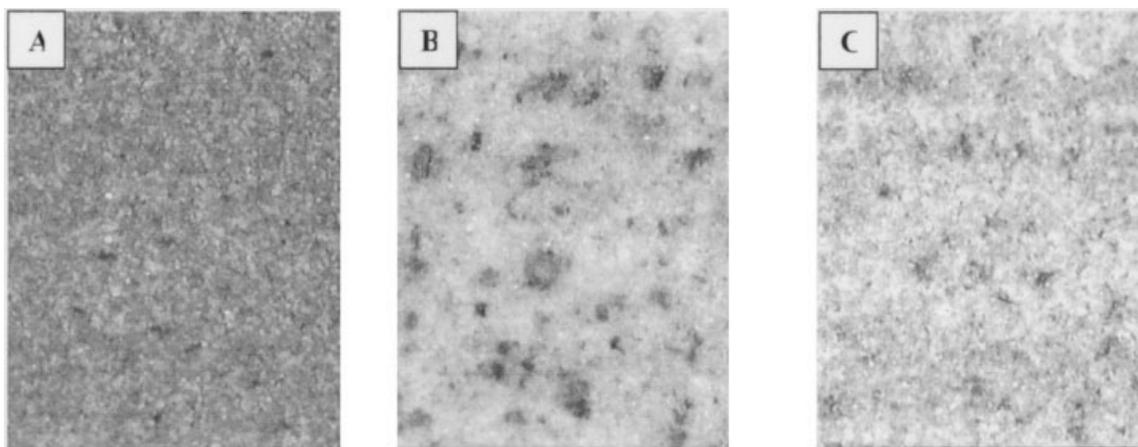
whose decrease of yield strength is below the average decrease and the Tomlinite blend whose elongation at break is above the average decrease.

As in the DOP plasticized blends, a lack of correlation can be observed between the blends'  $T_g$  decrease and their modulus and elongation values. Probably in

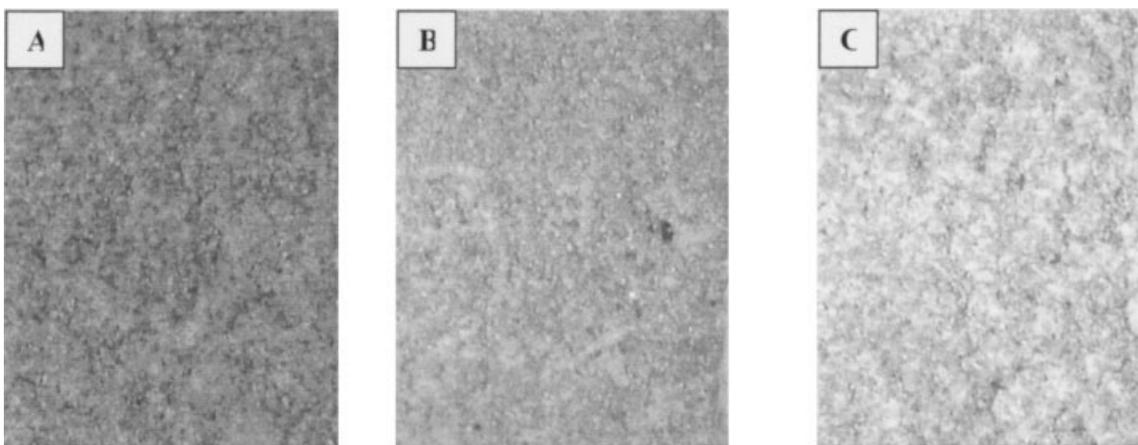
TABLE VII  
Mechanical Properties Variations of PVC-Lignin Blends as Percentage of Respective Values of Controls and Differences Between  $T_g$ s of Control and  $T_g$  of Blends

Sample ident.	$\Delta T_g$ (°C)	Young's modulus <sup>a</sup> (%)	Tensile strength (%)		Elongation (%)
			Yield	Break	
Lindol plasticizer					
Blend Tomlinite	3.1	51.4	89.1	79.7	106
Blend Alcell	3.5	56.1	75.3	76.7	167
Blend Indulin	3.8	50.5	63.8	65.1	141
2-45 plasticizer					
Blend Alcell	3.9	115.6	74.0	71.0	113
Blend Indulin	5.7	88.8	84.5	78.2	76.0
Blend Tomlinite	7.7	68.5	109.0	78.4	77.2
Mesamoll plasticizer					
Blend Alcell	2.1	95.1	99.5	80.2	95.0
Blend Tomlinite	7.2	86.7	95.6	71.5	107
Blend Indulin	9.3	82.6	86.5	62.4	95.8
DOP plasticizer					
Blend Tomlinite	7.0	54.9	86.7	71.8	102
Blend Alcell	7.1	55.1	96.5	77.5	126
Blend Indulin	7.5	56.9	79.1	61.3	85.0

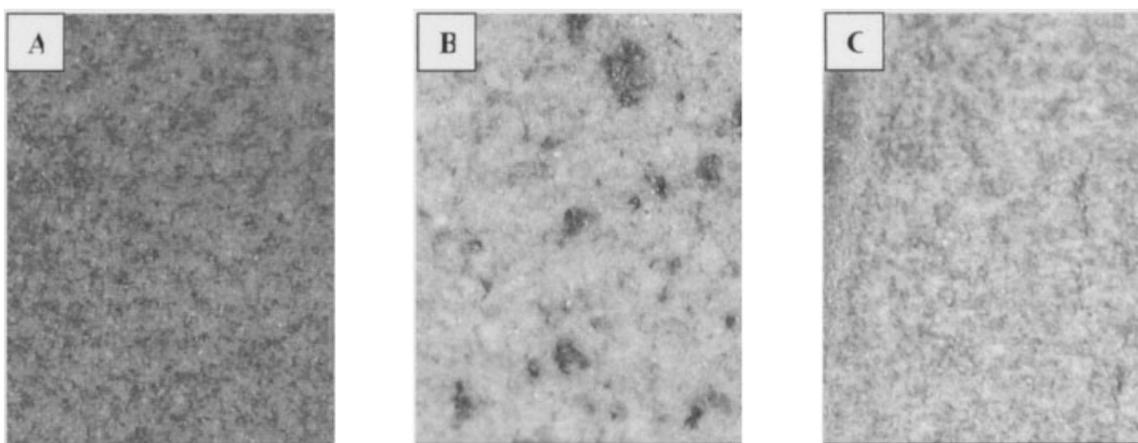
<sup>a</sup> At 2% elongation.



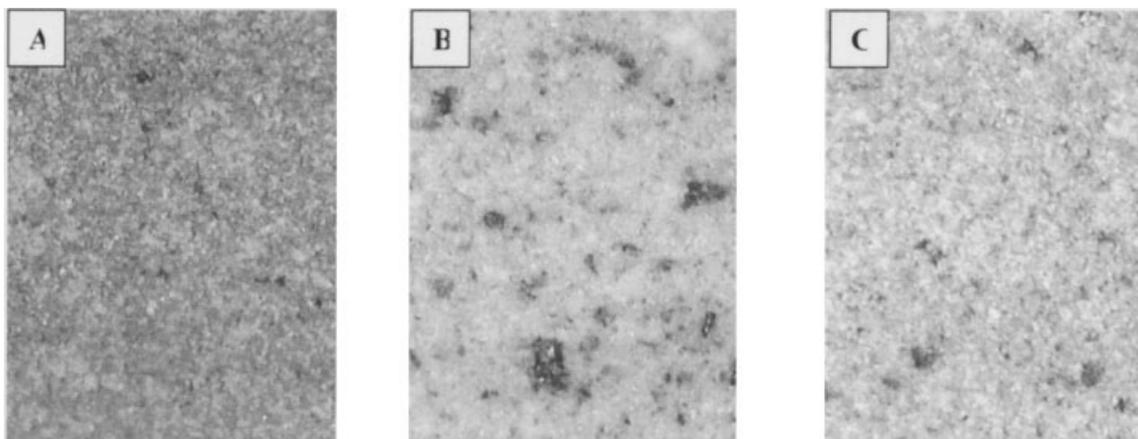
**Figure 14** Photomicrographs (original magnification  $\times 100$ ) of a PVC control and blends with DOP as the plasticizer; (A) Alcell, (B) Indulin, and (C) Tomlinite.



**Figure 15** Photomicrographs (original magnification  $\times 100$ ) of a PVC control and blends with Lindol as the plasticizer; (A) Alcell, (B) Indulin, and (C) Tomlinite.



**Figure 16** Photomicrographs (original magnification  $\times 100$ ) of a PVC control and blends with 2-45 as the plasticizer; (A) Alcell, (B) Indulin, and (C) Tomlinite.



**Figure 17** Photomicrographs (original magnification  $\times 100$ ) of a PVC control and blends with Mesamoll as the plasticizer; (A) Alcell, (B) Indulin, and (C) Tomlinite.

this case (Mesamoll plasticizer) more plasticizer is available for the PVC matrix, which becomes softer as the  $T_g$  data and Figure 12 indicate. The presence of only partially plasticized lignins with a high  $T_g$  will act as a reinforcing filler and will enhance the modulus but in the meantime will impede the PVC matrix from normal elongation.

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

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

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

### CONCLUSIONS

In conclusion, the thermal and mechanical properties demonstrated that the partial replacement of PVC (20 parts) with different lignins is feasible in some formu-

lations plasticized with 35 phr plasticizer. Some plasticized PVC-lignin blends were successfully used as matrices for a high level (200 phr) of calcium carbonate filler in a vinyl tile composition.

The blends of Alcell, Tomlinite, or Indulin plasticized with Lindol; those of Alcell and Indulin plasticized with 2-45; and those of Alcell and Tomlinite plasticized with Mesamoll exhibit mechanical properties comparable to those of a PVC control plasticized with DOP, which represents the typical formulation for PVC floor tile. By analyzing the presented data we concluded that in some PVC-lignin blends the level of plasticizer could be reduced to 30 phr. More work will be undertaken in this respect.

These new formulations will be tested further for resistance to fungi and bacteria.

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