Blends of Vinylic Copolymer with Plasticized Lignin: Thermal and Mechanical Properties

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ABSTRACT: The article presents an investigation into the use of plasticizers for reducing the degree of association existing within lignin molecules, in order to overcome adverse effects on the mechanical properties of its blends with a vinyl chloride–vinyl acetate (VC–VAc) copolymer. Infrared spectroscopy and differential scanning calorimetry were performed to examine the effect of the plasticizer type and concentration in plasticizing Alcell, an organosolv lignin. The results show that the compatibility and efficiency of a plasticizer are strongly influenced by the solubility parameter, which should be close to that of the lignin. Polyblends prepared with several plasticizers, Alcell lignin, and the VC–VAc copolymer were also investigated by thermal analysis and mechanical testing. Variations in the mechanical properties of these blends were found to correlate with the lignin dispersion quality and with the plasticizer efficiency in Alcell lignin. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 861–874, 2001

Key words: lignin; plasticizers; lignin–(VC–VAc) copolymer blends

INTRODUCTION

Wood contains about 25 wt % of lignin (L), which, together with hemicelluloses and cellulose, form the structural components of trees and various plants. L is a natural polymer, and its molecules are composed of phenyl propane units substituted with one or two methoxyl groups. The phenyl propane units are interconnected by about 10 different linkages in a complex matrix. This matrix comprises a variety of functional groups, including hydroxyl, methoxyl, and carbonyl units, which impart polarity to the L macromolecules.[1]

L is an amorphous polydisperse polymer, and its molecular weight ranges from 1000 to 12,000 depending on the conditions under which it is isolated. The glass transition temperature, T_g, is between 100 and 180°C, which is high compared to the T_g's of most synthetic polymers. The high T_g is probably due, in large part, to hydrogen bonding caused by the presence of phenolic hydroxyl groups in the main chain.[2] The chemical structure of L, particularly the aromatic ring present in the main chain, is also thought to contribute to the high T_g.[3]

The large quantities of L produced annually by the pulp and paper industry are used almost exclusively as fuel to generate energy. Considering this abundance of L, its chemical composition, and its functional characteristics in plants, it appears reasonable to examine the contribution L can make to the properties of polyblends with PVC. Previous work has reported on the evaluation of blends of rigid PVC with different types of L.[4–6] The data demonstrated an interaction between the two polymers occurring between the

Table I   Plasticizers Used in The Study

Plasticizer/Trade Name	Abbreviation	Supplier
Diethylhexyl phthalate	DOP	Fisher Scientific, Ottawa, ON
Butylbenzyl phthalate/Santicizer 160	160	Solutia, St. Louis, MO
Alkylbenzyl phthalate/Santicizer 261	ABP	Solutia, St. Louis, MO
Dibutyl sebacate	DBS	Fisher Scientific, Ottawa, ON
Diethylene glycol dibenzoate/Benzoflex 2-45	2-45	Velsicol, Rosemont, IL
Tricresyl phosphate/Lindol	Lindol	Akzo Nobel, Dobbs Ferry, NY

OH groups of L and the α hydrogen of PVC. The addition of L was possible up to 10 parts per 100 parts PVC (phr) and produced a matrix reinforcement as indicated by an increase in the Young's modulus. This increase, however, was accompanied by substantial losses in both strength and elongation at break, as well as in impact strength. Some decomposition of the lignin resulted from the high temperatures required to process the rigid PVC.

Technical grades of L have already been incorporated into a variety of thermoplastics and thermosets. However, these blends are typically characterized by a high degree of brittleness and by poor viscoelastic properties. Chemical modification of L by oxyalkylation or hydroxyalkylation has been proposed as a promising technique for overcoming the frequently adverse effects of L on the mechanical properties of polymers.[7] The aim of these modifications has been to block or eliminate various oxygen-containing functional groups, especially hydroxyl groups, responsible for the high degree of association of L molecules. Recently published data for a Kraft lignin–poly(vinyl acetate) blend, containing about 85% L, show that the mechanical properties are strongly influenced by the degree of association of the L molecules.[8]

Another possible method of decreasing this degree of association and, consequently, the T_g of L would be through the use of plasticizers. Plasticizers are materials which, when added to a polymer, cause an increase in flexibility and workability by reducing intermolecular forces and by decreasing the T_g. Plasticized PVC is probably the best example of their effectiveness, and most of the theoretical and practical aspects of plasticization follow the development of this polymer.

A good plasticizer should have the following general requirements: solvency and compatibility; efficiency in imparting a desirable property or properties (usually softness and flexibility); and permanence.[9] There are several theoretical techniques for assessing the compatibility of a plasticizer with a particular polymer. These include the Hildebrand solubility parameter, δ, and the Flory–Huggins interaction parameter. The solubility parameter is generally a useful guide to predicting compatibility. Frequently, a polymer will be compatible with a plasticizer when the two have solubility parameters that do not differ by more than ± 1.5 $(cal/cm^3)^{1/2}$. This relationship was developed based on the thermodynamic free energy of mixing. The square root of δ or the cohesive energy density (CED) is a measure of the

Table II   Characteristics of the Plasticizers

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

[a] Freezing point °C; two crystal forms.
[b] (10b).

Table III   Changes in T_g, ΔT_g, Hydroxyl, and Carbonyl Absorption Frequencies as Function of Plasticizer Content in AL–Plasticizers Blends

			Frequencies (cm^{-1})		
Sample Identification	T_g (°C)	ΔT_g (°C)	OH	C=O	C—O
AL control	97	22	3428	1706	1270
A1 treated at 140°C	97	22	3428	1706	1269
160	—	—	—	1720	1263
AL–160 (15 phr)	66	35	3421	1723	1286
AL–160 (30 phr)	38	31	3401	1723	1286
AL–160 (45 phr)	—	—	3401	1724	1286
2-45	—	—	—	1717	1272
AL-2-45 (15 phr)	65	34	3419	1717	1276
AL-2-45 (30 phr)	35	28	3412	1717	1276
AL-2-45 (45 phr)	—	—	3339	1717	1276
Lindol	—	—	—	—	—
AL–Lindol (15 phr)	69	34	3412	—	—
AL–Lindol (30 phr)	51	28	3408	—	—
AL–Lindol (45 phr)	—	—	3339	—	—
ABP	—	—	—	1732	1278
AL–ABP (15 phr)	66	40	3412	1723	1286

intensity of the intermolecular interactions in a pure liquid or solid. The strength of the solvent–solvent bonds and polymer–polymer bonds are thus related to the CED.[10] Another criterion for plasticizer efficiency is the extent to which the T_g of the polymer is lowered by the introduction of a given amount of the plasticizer. The extent of T_g reduction can be related to the magnitude and mode of changes in the polymer chain mobility.[11,12]
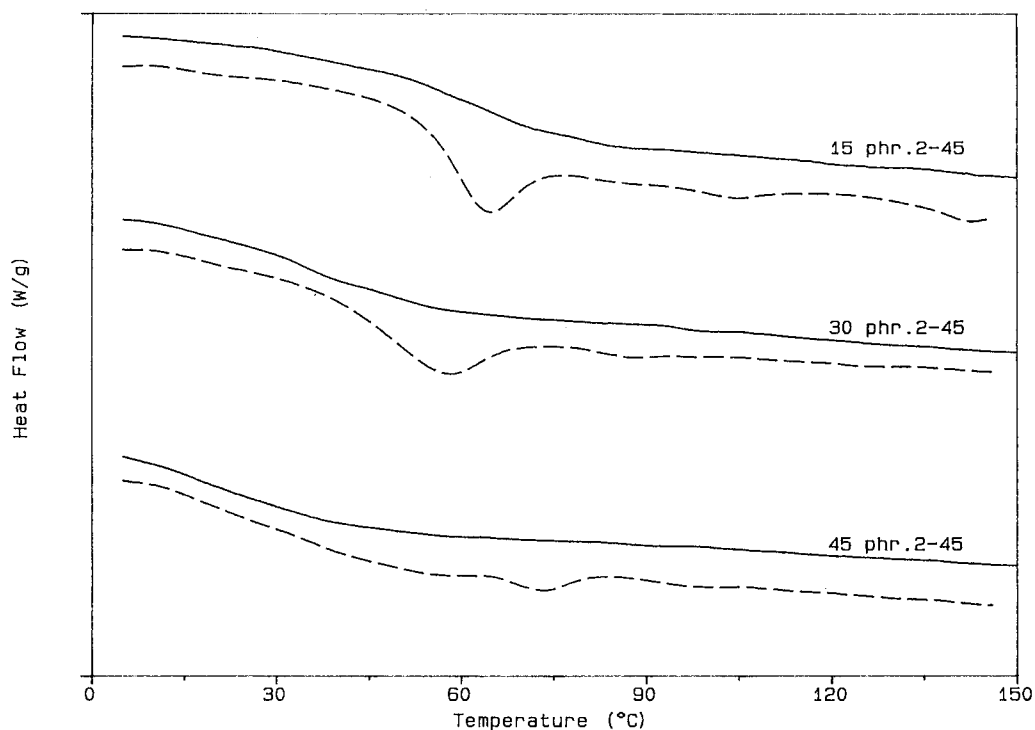
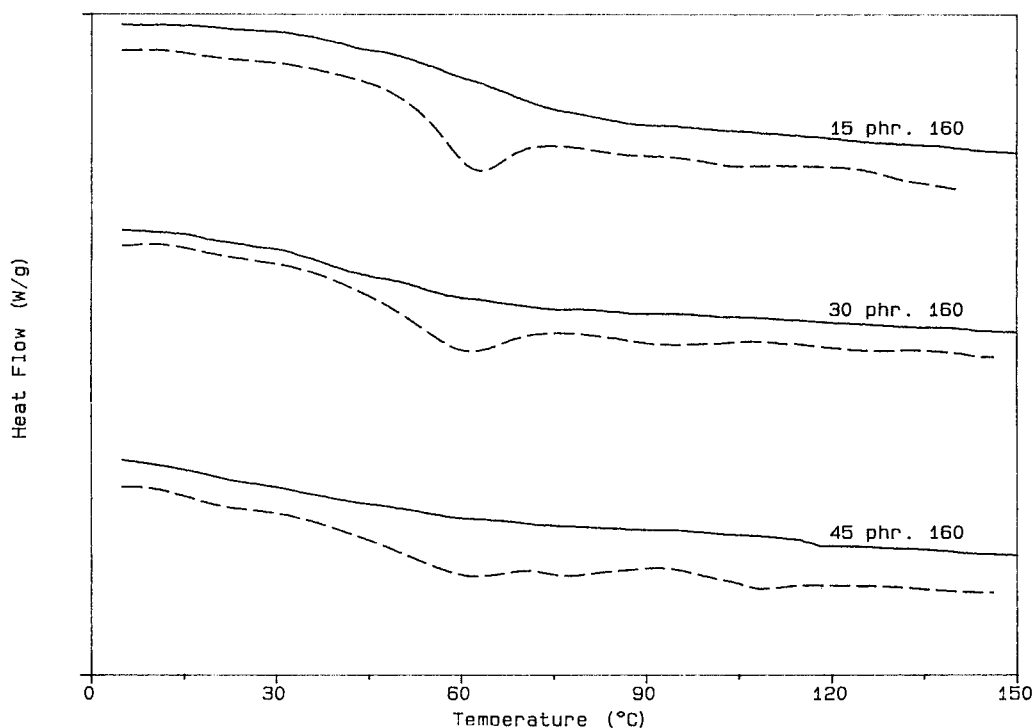**Figure 1**   DSC thermogram of AL–2-45 blends.

Figure 2 DSC thermogram of AL–160 blends.

In the present work, an organosolv lignin, Alcell L (AL), was tested with several common plasticizers to determine compatibility. AL is obtained through a new delignification process, which is milder and less polluting than are traditional sulfite or sulfate processes. The effect of the plasticizer type and level on the T_g of AL was determined by differential scanning calorimetry (DSC). The molecular interactions between AL and the plasticizers were studied by infrared spectroscopy.

Selected AL–plasticizer blends were compounded with a vinyl chloride–vinyl acetate (VC–VAc) copolymer in a batch mixer. The copolymer has a 9.7 % VAc content and a low processing temperature. Plasticizers, which are found to be compatible with AL, are compared to a plasticizer determined to be incompatible with AL in these blends. Results from thermal and mechanical tests on the composites are presented and discussed.

EXPERIMENTAL

Materials

L is an organosolv-type AL produced at the pilot scale by Alcell Technologies Inc. (Miramachi, NB). This grade is obtained through a new, more efficient and less polluting delignification process.

The characteristics of AL as determined by the manufacturer are the following: M_w less than 2000, M_n between 800 and 900, specific gravity of 1.27, softening temperature (ring and ball, ASTM E28) of 145°C, and median particle size between 20 and 40 μm. The T_g as determined by DSC in our laboratory is 97°C. The solubility parameter δ is 13.7 $(cal/cm^3)^{1/2}$.[13]

The plasticizers used in this study are presented in Table I. Their principal characteristics are summarized in Table II.

The synthetic polymer used in all the experiments is Oxy 1810, a VC–VAc copolymer supplied by the Occidental Chemical Corp. (Dallas, Texas). It has the following characteristics: a K value of 57 (M_w 54,000 and M_n 26,000), specific gravity of 1.37, and a VA content of 9.7%. For convenience, this copolymer will be referred to as PVC.

The PVC controls and PVC–AL blends are formulated with 33 or 44 phr of the plasticizer, 3 phr dibutyltin dilaurate (DBTL) as the heat stabilizer, obtained from Sigma–Aldrich Canada Ltd. (Mississauga, ON), and 1.5 phr calcium stearate (CaS) lubricant grade L-155, obtained from Blachford Ltd. (Mississauga, ON). The AL content in all blends is 30 phr.
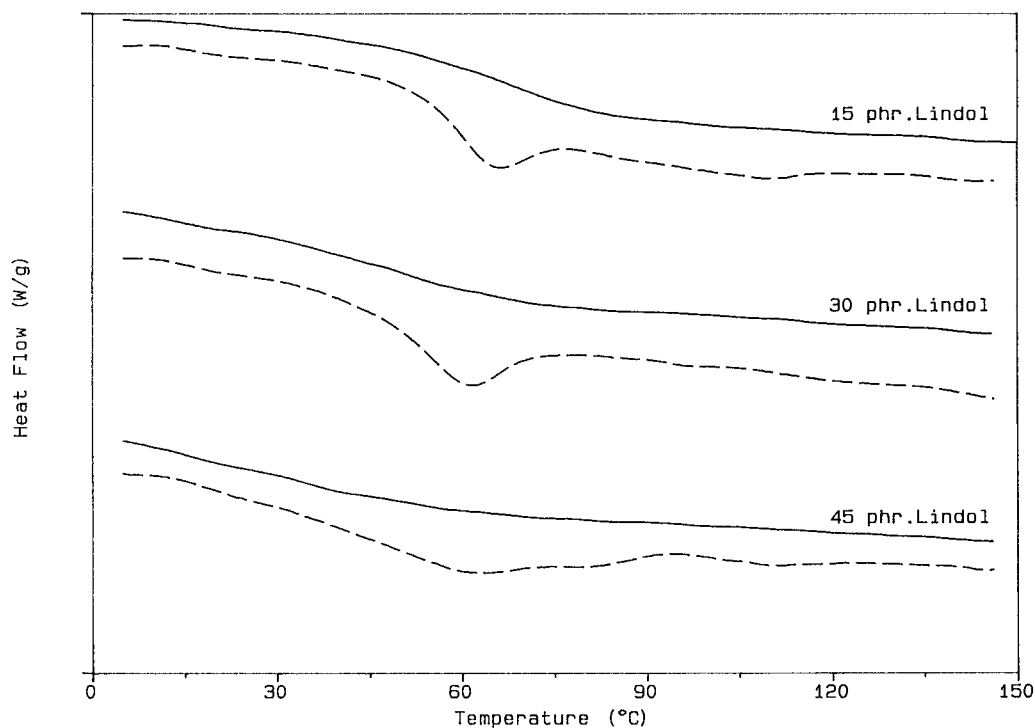
Figure 3 DSC thermograms of AL–Lindol blends.

Procedures

Blends of AL with 15, 30, and 45 phr of the plasticizer were prepared by mixing for 8 min in an open bowl in order to obtain a reasonably uniform blend, followed by a period of 8 min heating at 145 ± 1°C in a forced-air oven. This oven temperature corresponds to the softening temperature of AL. At the end of the heating period, the resultant melts were examined for homogeneity and subsequently cooled at room temperature in a desiccator. After cooling for 2 h, the blends were ground to a fine powder in an agate mortar. A control AL sample containing no plasticizer was prepared in the same manner.

Plasticized PVC controls and PVC–AL blends were prepared by melt mixing for 8 min at 141°C, at a rotor speed of 65 rpm in a Haake Rheomix 600, equipped with roller blades. The Rheomix 600 was equipped with a torque rheometer, the Haake Rheocord-M 300, for continuous measurement of the mixing torque, and with a thermocouple for continuous measurement of the melt temperature. In all mixes, the recorded torque showed that a plateau was reached about 2 min before the end of the mixing time.

Several batches were prepared for each formulation. After melt mixing, the product was ground to a size of 2–3 mm. Subsequently, sheets of 1.5 mm thickness were molded by compression at 155°C and 4.37 MPa pressure. The molded sheets were cooled from the molding temperature to room temperature at a cooling rate of 10°C/min under pressure. After cooling, specimens were cut with a cutting die into dog-bone specimens (ASTM D638) for tensile testing.

The T_g's of the AL–plasticizer blends and the PVC–AL blends were measured using a 912 DuPont differential scanning calorimeter connected to a DuPont 2100 thermal analyzer operating system. At least two specimens of about 5–6 mg for the AL–plasticizer blends and of about 14–15 mg for PVC–AL blends were run at a heating rate of 20°C/min, under a nitrogen atmosphere, between 40 and 160°C for 15 and 30 phr formulations and from 80 to 160°C for 45 phr formulations. The reported T_g represents the inflection point of the heat flow versus the temperature curve. It was measured in the second scan. In addition, the width of the T_g peak, or ΔT_g, which represents the difference between the final and onset glass transition temperature, was also measured in the case of the AL–plasticizer blends. The T_g's were measured after the blends had been aged 24 and 336 h at room temperature. For the blends aged for 336 h, the first DSC thermograms were also re-

Table IV   Properties of PVC Blends as Function of Type and Amount of Plasticizer

Sample ID	Torque (mg)	T_g (°C)	Modulus at 100% Elongation (MPa)	Tensile Strength		Elongation at Break (%)
				Yield (MPa)	Break (MPa)	
35 phr Plasticizer (27 Parts/100 Parts PVC + AL)						
DOP control	780	16.0	4.13		15.89	775
DOP/PVC–AL blend	650	19.4	5.32	11.06	11.56	557
Lindol control	819	33.1	7.73		22.90	730
Lindol/PVC–AL blend	620	35.3		11.76	17.76	572
160 control	685	25.0	3.10		15.71	764
160/PVC–AL blend	550	27.2	6.61	10.77	13.34	685
2-45 control	700	18.1	2.78	14.71	14.77	852
2-45/PVC–AL blend	500	25.5	8.73	11.57	16.04	715
44 phr Plasticizer (34 Parts/100 Parts PVC + AL)						
DOP control		15.5	1.92		9.65	800
DOP/PVC–AL blend	531	17.6	3.16	7.42	7.64	580
Lindol control	508	23.3	2.88	13.84	14.69	852
Lindol/PVC–AL blend	459	28.3	5.94	10.91	12.51	656
160 control	454	16.3	1.44		9.57	788
160/PVC–AL blend	401	18.1	2.58	8.32	8.88	733
2-45 control	380	14.4	1.5		9.60	937
2-45/PVC–AL blend	331	21.8	3.03	9.33	11.68	823

corded in order to obtain information about blend relaxation after aging. The presence of two separate enthalpy recovery peaks in an aged blend serves as an indication of heterogeneity in the blend. Five different specimens of an AL–160 blend (30 phr) were scanned to determine the method's precision. The average T_g was 36.2°C with a standard deviation of 1.4°C and the ΔT_g was 31°C with a standard deviation of 2.1°C. The T_g of the PVC–AL blends was determined after aging for 1 week.

The infrared spectra were obtained with a Nicolet Magna 550 Fourier transform infrared (FTIR) spectrophotometer. AL and AL–plasticizer blends were analyzed as KBr discs (3-mg sample/300 mg KBr).

Mechanical properties (modulus, yield and break strength, elongation at break) were measured in accordance with ASTM D638 using an Instron universal testing machine at a crosshead speed of 5 mm/min and at a temperature of 23 ± 2 °C. All specimens were tested 1 week after preparation. They were conditioned at 23 ± 2°C and 50 ± 5% RH for 48 h prior to testing. The indicated values are an average of at least five determinations. The coefficients of variation inferior to 10% were taken into account for each set of specimen tested.

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

RESULTS AND DISCUSSION

AL–Plasticizer Blends

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

Table III gives the positions of hydroxyl and carbonyl absorption stretching bands in AL (control and thermally treated), as well as the position of C=O bands in the plasticizers. The tabulated positions of hydroxyl and carbonyl bands in the
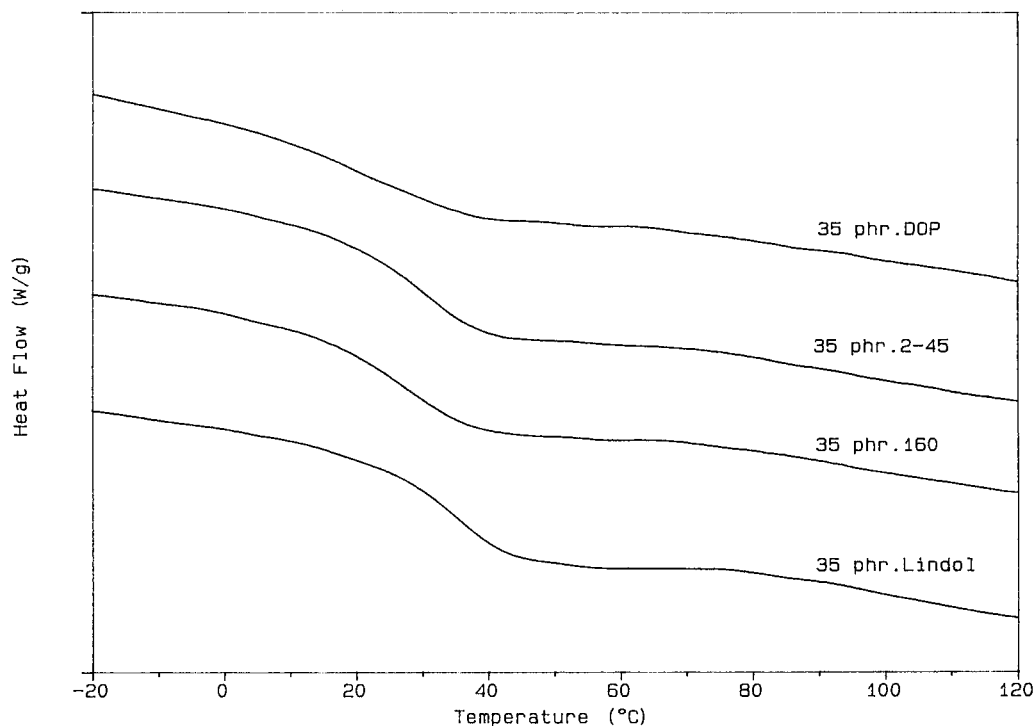
Figure 4 DSC thermograms of PVC–AL blends with 35 phr of the plasticizer.

blends were obtained by difference spectra (i.e., the spectra of either AL or plasticizer subtracted from the spectra of the blends). The subtraction is required to account for the presence of carbonyl groups in AL and for the presence of water (typically 0.1%) in the plasticizers. The assignment of hydroxyl and carbonyl bands in AL correlates well with recent literature data,[14] along with the assignment of carbonyl bands in all plasticizers except Lindol.[15,16]

The data in Table III show a number of interesting results: The appearance of a single transition in the DSC thermograms of the blends is a first indication of a homogeneous structure. The tabulated T_g's of the AL–plasticizer blends decrease markedly with the plasticizer content. Moreover, it seems that the magnitude of the decrease in T_g is insensitive to plasticizer chemical structure, with the exception of the relatively bulky Lindol. At the 45-phr plasticizer level, all the blends exhibit a very broad transition range and the precise location of T_g is very difficult to assign. ΔT_g is quite high in all the blends, indicating a certain degree of heterogeneity, especially at the 15 phr plasticizer content. According to the literature, a sharp transition ($\Delta T_g < 15°C$) is typical for a material that is homogeneous on

the scale of thermal measurement. A broad transition, on the other hand, suggests a somewhat less than homogeneous blend.[17] The ΔT_g values correlate quite well with the plasticizer solubility parameters, demonstrating the influence of δ on the homogeneity of the blends.

The first scan of the blends aged for 335 h with different plasticizer contents are shown as dashed lines in Figures 1–3. These figures show that the least homogeneous blends are those containing 45 phr of the plasticizer, which exhibit at least two broad peaks in the dashed DSC curve. According to the literature, the presence of multiple enthalpy recovery peaks in aged blends can be used as an indication of the heterogeneity of the blends.[18]

When the FTIR spectra of the blends are compared with those of the pure plasticizers and AL alone, a modification in the frequency of the hydroxyl stretching mode is readily detected (see Table III). The OH absorption bands shift to lower frequencies. This shift may be attributed to a weakening of the intermolecular hydrogen bonding within the AL molecules and suggests an association between the OH group of AL and the C=O group of the plasticizer. Interestingly, a small increase in the frequency of the carbonyl
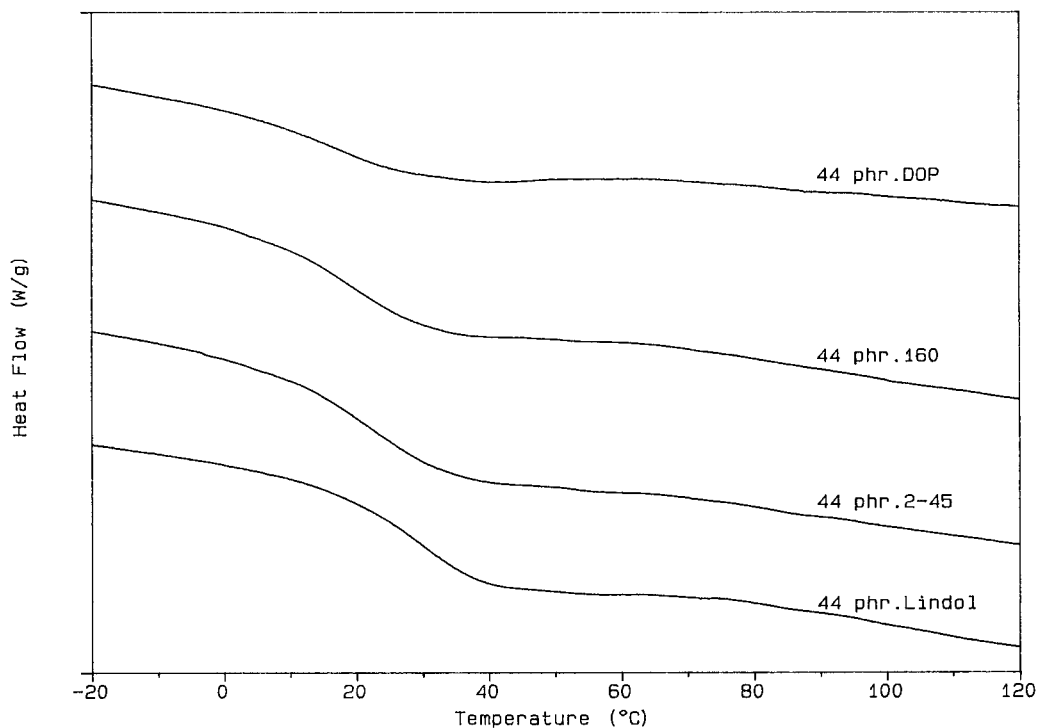
Figure 5 DSC thermograms of PVC–AL blends with 44 phr of the plasticizer.

absorption peaks is observed in all blends. This may arise from the association of C=O with other functional groups of AL. The literature contains evidence of an increase in the frequency of the carbonyl stretching peak due to association of the carbonyl group with functional groups in the same polymer other than OH.[19]

In summary, the DSC and FTIR results discussed above show the effectiveness of plasticizers in decreasing the high degree of association occurring within the AL molecules. The compatibility of a given plasticizer with AL is strongly influenced by both the concentration in the blend and by the solubility parameter. For the compatible plasticizers studied in this work, concentrations near 30 phr appear to give the best results.

PVC–AL Blends

The extensive literature concerned with PVC plasticization reveals that when plasticizers are compared at equal efficiency, that is, using amounts that produce similar reductions in the T_g, the final blend properties can be similar. However, properties of the compounds containing the same amounts of the plasticizer can show significant variations.[11,20,21] With this in mind, it was

decided to determine whether AL plasticization would overcome the adverse effects on the mechanical properties of its blends with other polymers. Blends of AL with PVC and several plasticizers were prepared and tested, and the results were compared with similar data obtained for PVC controls.

Blends and controls were formulated with the following plasticizers: 2-45, 160, and Lindol. DOP is not compatible with AL; however, it was also chosen as a plasticizer for comparative purposes. Another reason for its selection was its importance as a "reference" plasticizer for PVC.[22]

The blends were formulated with 35 and 44 phr of the plasticizer, which represents 27 and 34 parts per hundred parts polymers, that is, PVC and AL together. This concentration range seems to represent the optimal level from the AL plasticization results discussed earlier.

The processibility, steady-state torque, T_g, and tensile properties of the plasticized PVC–AL blends were compared with the same data obtained for the PVC controls. All the results are presented in Table IV. The stress–strain curves for the PVC controls with 35 phr of the plasticizer and blends with 35 and 44 phr of the plasticizer are presented in Figures 4–6.
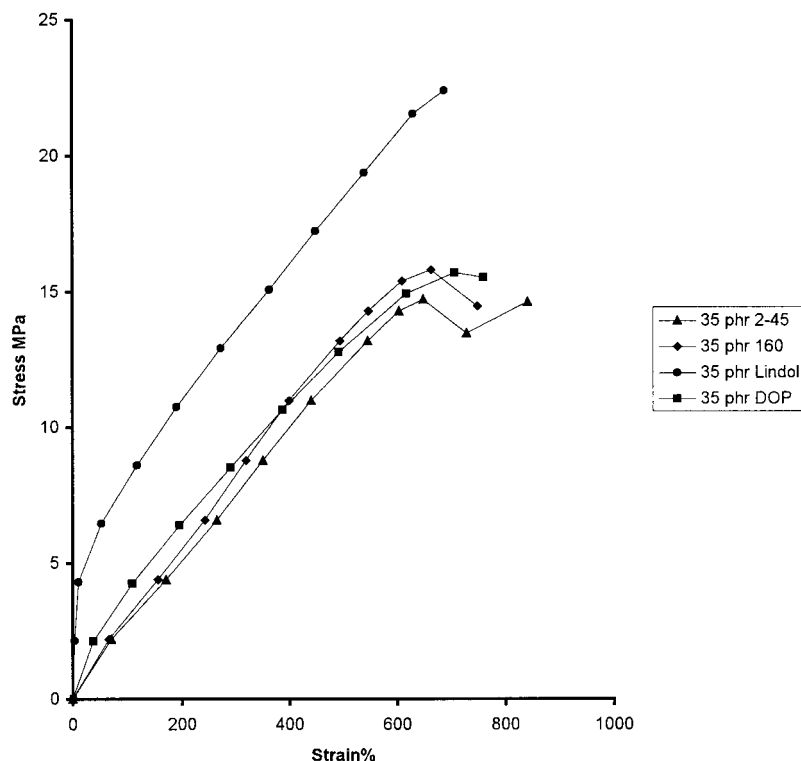
Figure 6   Stress–strain data for PVC control with 35 phr plasticizer.

Processibility

From the data shown in Table IV, it can be seen that both the type and level of the plasticizer have a distinct influence on the control and blend mixing torque. It has long been known that the forces involved in mixing a highly viscous melt, which are measured as the torque acting on the rotors, can be correlated with the melt viscosity.[23] PVC–AL blends all exhibit a decreased torque value in relation to their respective controls, indicating a decreased melt viscosity. The decrease in the mixing torque is also seen to be a function of the plasticizer type. According to the experimental results shown in Table IV, the melt viscosity of the blends decreases in the following order: DOP > Lindol > 160 > 2-45. It is interesting to note that this order corresponds to the effective lowering of AL T_g by the same plasticizers as shown in Table III.

Thermal Properties

The T_g values of the PVC controls and the PVC–AL blends are shown in Table IV. The DSC thermograms of the blends, in the temperature interval between −40 and 120°C, at both 35 and 44 phr of the plasticizer concentration levels are shown in Figures 4 and 5, respectively. At both levels, a single T_g is observed which indicates a relatively homogeneous structure. However, for the DOP blends, the endotherm is much less pronounced, which may signify a certain degree of heterogeneity for this particular blend in comparison with the others.

When compared with the PVC controls, all blends exhibit a slightly higher T_g except for those containing 2-45, where the differences are more remarkable. The differences in the T_g between the PVC–AL blends and the respective controls are shown in Table V.

If we correlate the values of the T_g increases in the PVC–AL blends with the values of the T_g in the plasticized AL samples (Table III), the data shown for the PVC–AL blends with 2-45 in Table V seem to be too high. This result may be due to different conformations adopted by the plasticizer molecules in the polymer blend matrix of the final product. Conformation is important because it determines how much free volume is created.[12] Another reason may be the low melt viscosities of these particular blends. Further discussion is pre-

Table V Increase in T_g for the PVC–AL Blends Relative to the Controls

Plasticizer Type	Plasticizer Content (phr)	
	35	44
DOP	3.4	2.1
Lindol	2.2	5.0
160	2.2	1.8
2-45	7.4	7.4

sented later in relation to the mechanical properties.

Mechanical Properties

The mechanical properties of the PVC controls are shown in Table IV and the stress–strain curves in Figures 6–8. From the data presented in Table IV and Figure 6, it can be seen that most of the PVC control samples behave as soft elastic materials undergoing ductile failure with uniform yielding. The PVC control with Lindol has a relatively elevated T_g in comparison with the other controls due to the bulky structure of Lindol. Consequently, its modulus at the testing temperature is high with a discrete yield point.

The PVC–AL blends are rather tough elastic materials. All present a distinct yield point, and the failure mode is ductile with neck propagation and strain hardening as can be seen in Figures 7 and 8.

For both plasticization levels studied, the mechanical properties of the PVC–AL blends determined at room temperature are not dependent, as expected, on the T_g. When the blends are ordered with respect to increasing T_g, certain trends are evident in the tensile properties relative to the PVC controls. These trends are summarized in Table VI.

A tensile force acting on a specimen below the T_g introduces the energy necessary for the chains to overcome secondary forces due to intermolecular bonding and slip past each other. The second-
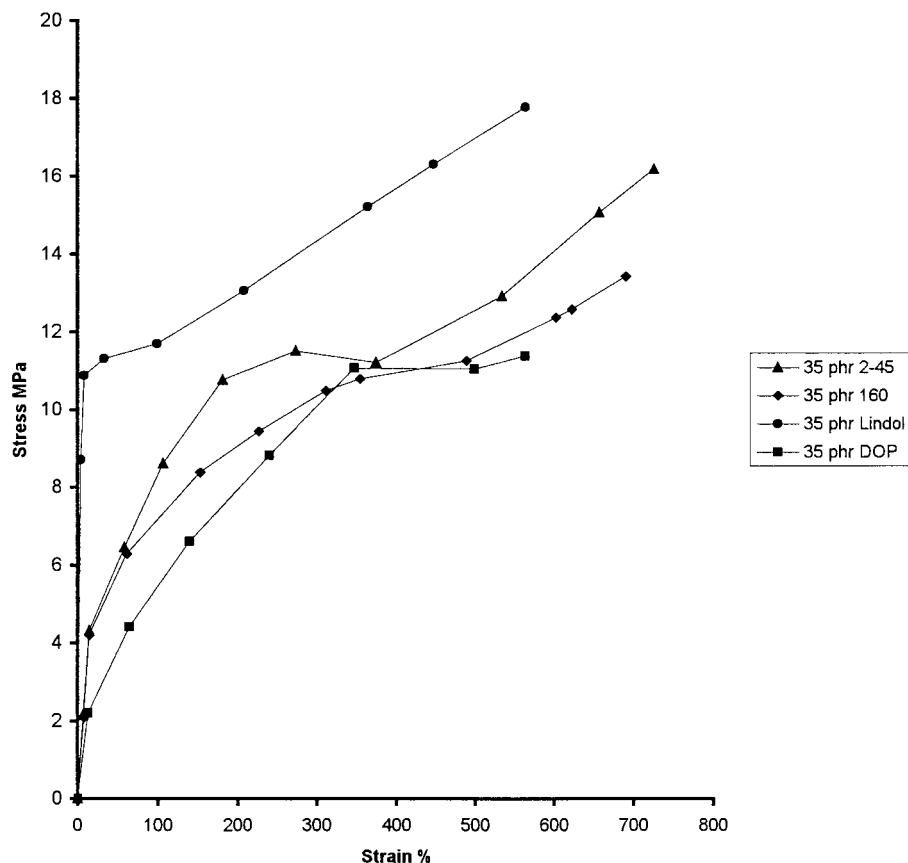

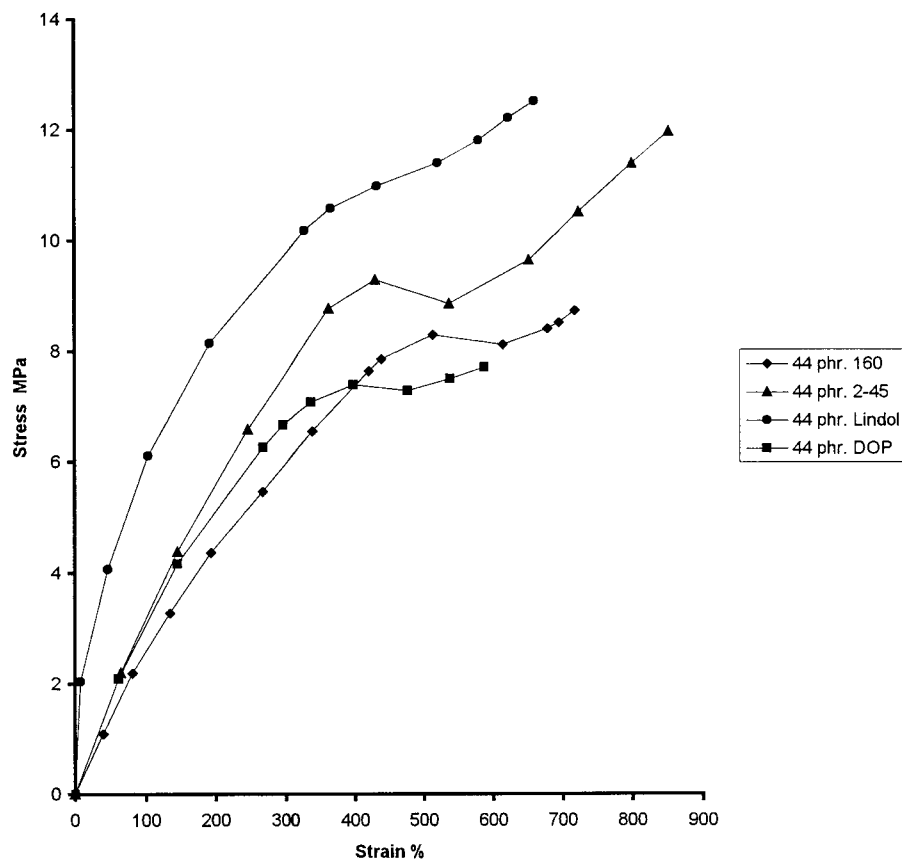**Figure 7** Stress–strain data for PVC–AL blends with 35 phr of the plasticizer.

Figure 8 Stress–strain data for PVC–AL blends with 44 phr of the plasticizer.

ary forces become greater as temperature decreases below the T_g.[24,25] This temperature dependence of the intermolecular forces leads to the expectation that the modulus of the blends would be an ordered function of the T_g, that is, the modulus should be highest for Lindol and lowest

Table VI   Mechanical Properties of PVC–AL Blends Relative to the PVC Controls

T_g (°C)	Plasticizer	Increase in Modulus (%)	Decrease in Breaking Strength (%)	Decrease in Elongation (%)
		PVC–AL Blends with 35 phr Plasticizer		
19.4	DOP	28.8	27.2	28.1
25.5	2-45	214	(8.6)	16.1
27.2	160	113	15.9	10.0
35.3	Lindol	—	22.4	21.6
		PVC–AL Blends with 44 phr Plasticizer		
17.6	DOP	64	20.8	27.5
18.1	160	79	7.2	7.0
21.3	2-45	102	(21.7)	12.2
28.3	Lindol	106	14.8	23

Values in parentheses represent increases in breaking strength relative to the controls.

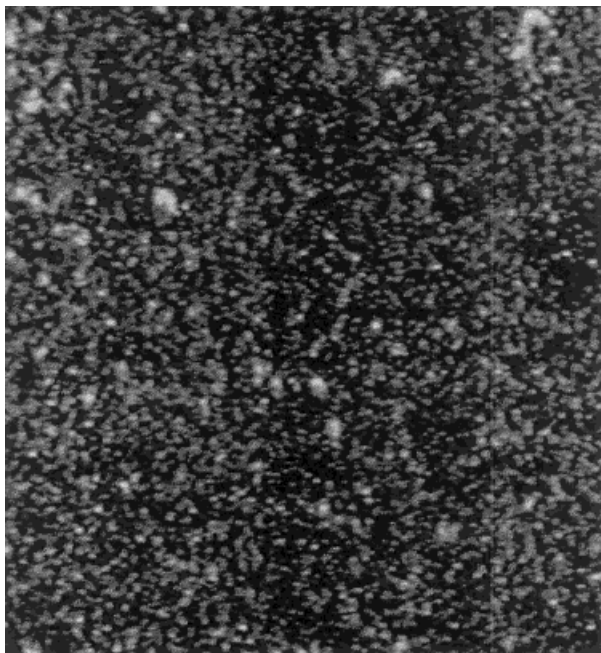**Figure 9** Photomicrograph of PVC–AL blends with 35 phr of the DOP plasticizer; 100× magnification.

Figure 10 Photomicrograph of PVC–AL blends with 35 phr of the 2-45 plasticizer, 100× magnification.

for DOP. The same trend should be noted for the tensile strength at break and for the decrease in elongation.

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

Photomicrographs at 100× magnification were obtained to examine the morphology of the samples. These micrographs are shown in Figures 9–12 for the 35 phr samples. The morphology of the 2-45 and Lindol blends is seen to be quite different from that of the DOP and 160 samples, where large lignin domains are evident. There are thus significant differences in the dispersion quality among the four 35 phr samples. DOP and 160 clearly give the poorest lignin dispersion, while Lindol and 2-45 both give excellent dispersions. It has long been known that the toughness of a polymer composite is strongly influenced by filler size and dispersion quality.[26] The toughness
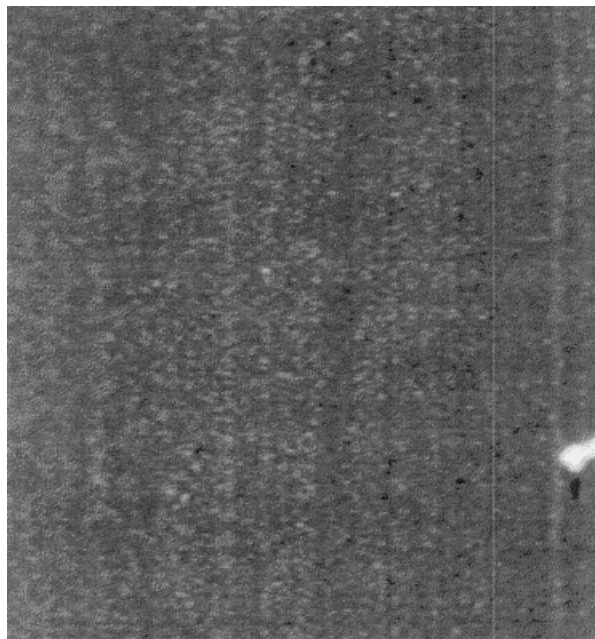
of the samples tested here can be estimated by calculating the areas under the stress–strain curves in Figures 7 and 8. The exercise reveals that Lindol and 2-45 give tougher composites than do DOP and 160. This result is not surprising given the lignin dispersion quality in the four
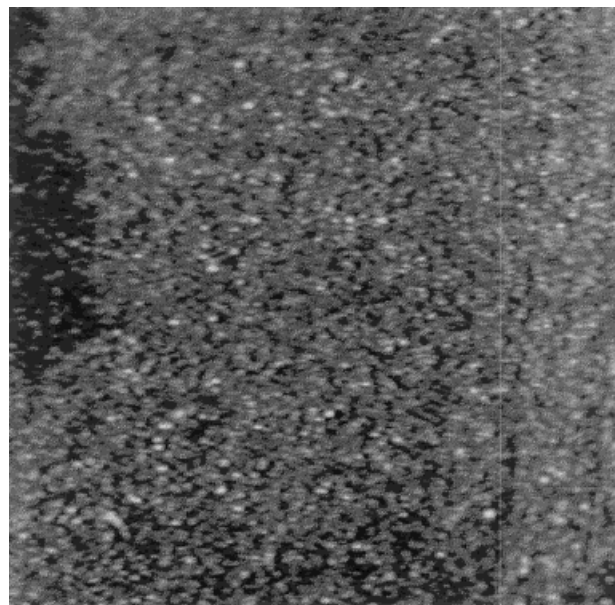

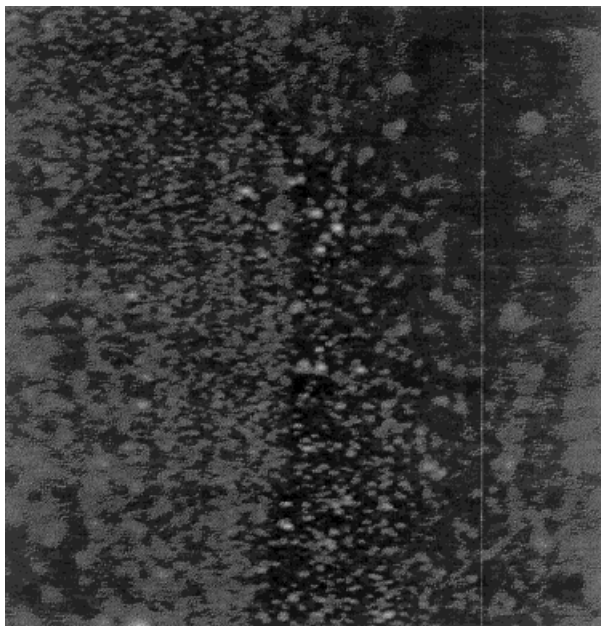**Figure 11** Photomicrograph of PVC–AL blends with 35 phr of the 160 plasticizer, 100× magnification.

Figure 12 Photomicrograph of PVC–AL blends with 35 phr of the Lindol plasticizer; 100× magnification.

samples. The same result can be obtained for the 45 phr samples.

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

CONCLUSIONS

The study examined the possibility of using plasticizers for reducing the degree of association existing between L molecules. The effect of the plasticizer type and concentration on AL plasticiza-

tion for a number of commercial plasticizers leads to the following conclusions:

1. Plasticization does, in fact, diminish the high degree of association occurring within AL molecules, as confirmed by DSC determination of T_g and through FTIR spectroscopy.
2. The compatibility and efficiency of an AL plasticizer is strongly influenced by the solubility parameter of the plasticizer. High values of the solubility parameter imply good compatibility.
3. For all the plasticizers studied, a concentration level of 30 parts per hundred parts AL is sufficient for optimal efficiency.
4. Compatible plasticizer–AL blends exhibit only one T_g, which is an indication of a homogeneous structure.
5. Blends of AL and a VC–VAc copolymer (9.3% VAc) with plasticizers having varying efficiencies in AL (but commonly used in PVC) are mostly homogeneous, exhibiting one sharp T_g with values close to room temperature. In relation to the PVC controls, the blends exhibit a slight increase in stiffness accompanied by moderate losses in strength and elongation at break, especially at the 35 phr plasticizer level. The mechanical properties are also influenced strongly by the morphology of the polymers, especially by the lignin particle size and distribution.

REFERENCES

1. Gandini, A In Comprehensive Polymer Science, 1st supplement; Allen, G.; Aggrawat, S. L.; Russe, S., Eds.; Pergamon: Oxford, 1992; pp 535–550.
2. Yoshida, H.; Morck, R.; Kringstad, K. P. Holzforshung 1987, 41, 171.
3. Hatakeyama, T.; Nakamura, K.; Hatakeyama, H. Polymer 1978, 19, 593.
4. Feldman, D.; Banu, D.; El-Raghi, S. JMS Pure Appl Chem A 1994, 31, 555.
5. Feldman, D.; Banu, D.; Lora, J.; El-Raghi, S. J Appl Polym Sci 1994, 61, 2119.
6. Feldman, D.; Banu, D. J Appl Polym Sci 1997, 66, 1731.
7. Wu, L. C. F.; Glasser, W. G. J Appl Polym Sci 1984, 29, 1111.

8. Li, Y.; Mlynar, J.; Sarkanen, S. J Polym Sci Polym Phys Ed 1997, 35, 1899.

9. Krauskoph, L. G. J Vinyl Tech 1993, 15, 140.

10. Sears, J. K.; Darby, J. R. The Technology of Plasticizers; Wiley: New York, 1982; (a) pp 79–144; (b) pp 983–1062.

11. Buszard, D. L. In PVC Technology, 4th ed.; Titow, W. W., Ed.; Elsevier: London, 1984; pp 120–138.

12. Pizzoli, M.; Scandola, M. In Polymeric Material Encyclopedia; Salamone, J. C., Ed.; CRC: Boca Raton, FL, 1996; Vol. 7, pp 5301–5303.

13. In, Y.; Hu, Q. J Appl Polym Sci 1995, 57, 1441.

14. Faix, O. In Methods in Lignin Chemistry; Lin, S. Y.; Dence, C. W., Eds.; Springer-Verlag: Berlin, 1992; pp 91–97.

15. Haslam, J. Identification Analysis of Plastics, 2nd ed.; Heyden: London, 1981; pp 574–585.

16. Beltran, M.; Garcia, J. C.; Marcila, A. Eur Polym J 1997, 33, 453.

17. Bair, H. E. In Thermal Characterization of Polymeric Materials; Turi, E. A., Ed.; Academic: New York, 1981; pp 878–892.

18. Bosma, M.; Len Brinke, G.; Ellis, T. S. Macromolecules 1988, 21, 1465.

19. Graton, A. Infrared Spectroscopy of Polymer Blends, Composites and Surfaces; Hanser: Berlin, 1992; pp 181–195.

20. deValle, L. R.; Gilbert, M. Plast Rubb Process Appl 1990, 13, 151.

21. Patel, S. V.; Gilbert, M. Plast Rubb Process Appl 1986, 6, 321.

22. Krauskoph, L. G. In Plastic Additives Modifiers Handbook; Edelbaum, J., Ed.; Van Nostrand: New York, 1992; pp 359–378.

23. Mc Kinney, P. V. J Appl Polym Sci 1965, 9, 3359.

24. Birley, A.; Haworth, B.; Batchler, J. Physics of Plastics; Hanser, Oxford University: New York, 1995; pp 253–258.

25. Powel, P.; Housz, J. I. Engineering with Plastics, 2nd ed.; Stanley Thornes: Cheltenham, UK, 1998; pp 137–147.

26. Suetsugu, Y. In Mixing Compounding of Polymers; Manas-Zloczower, I.; Tadmor, Z., Eds.; Hanser: Munich, 1994; pp 521–548.