Rigid Poly(vinyl chloride)–Organosolv Lignin Blends for Applications in Building

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SYNOPSIS

The article presents preliminary work carried out to prepare and evaluate the blends obtained from an unplasticized poly(vinyl chloride) (PVC) compound, formulated with several amounts of TiO_2 and an organosolv lignin. A series of blends in which lignin replaced partially or totally the TiO_2 were made on a laboratory scale. The influence of lignin on the melt processing of the blends and on their stress–strain properties was studied. Dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) were performed to examine the contribution of lignin to the properties of these blends. The possibility of a proton donor/proton acceptor interaction between lignin and PVC chains is discussed. This can arise due to the interaction between the carbonyl group of lignin and α hydrogen of PVC or between hydroxyl groups of lignin and chlorine of PVC. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Today the amount of poly(vinyl chloride) (PVC) produced worldwide represents about 30% of the total production of thermoplastics. It is now and probably will remain for some time the dominant resin used in building and construction. The cost and performance of rigid PVC (uPVC) make it among the most attractive replacements for wood and aluminum, particularly in window and door frames, house siding, and fences. Use of rigid PVC for all of these applications is expanding at 10–20% per year or higher, and this rate is expected to continue for several years.[1]

Due to the commercial value of PVC, there are already established blends with other common or less common polymers whose practical benefits are improved processibility, improved impact strength, and increased glass transition temperature (T_g).[2]

Very large quantities of the natural polymer lignin are produced annually by the pulp and paper industry. A very small amount is used around the world in thermosets, as antioxidants or fillers in rubber, and as a component in polyblends with thermoplastics.[3] The rest is used almost exclusively as fuel to generate energy.

Lignin is very stable in nature, and one of its functions in trees is to diminish the effect of chemical stress by inhibiting atmospheric degradation, acting as an antioxidant and ultraviolet (UV) light stabilizer.[4] Lignin as a macromolecule is composed of phenylpropane units tri or tetra substituted with hydroxyl and metoxyl groups. Phenylpropane units are interconnected by a set of linkages which result in a very complex matrix. This matrix comprises a variety of functional groups—mainly hydroxyl, methoxyl, carbonyl, and carboxy—which impart a high polarity to the lignin macromolecules.[5]

Taking into account the abundance of lignin, its functions in plants, and its functional groups as well as the commercial value and applications of PVC, it appeared reasonable to examine the contribution lignin can make to the properties of polyblends with PVC. The functional groups of both PVC and lignin make possible the proton donor/proton acceptor interactions (e.g., between carbonyl groups of lignin and α hydrogen of PVC or between hydroxyl groups of lignin and chlorine of PVC). These interactions are likely to contribute to the miscibility or partial miscibility of these polymers in a blend.[6,7]

The purpose of this article is to present the preliminary work carried out to prepare and evaluate blends obtained from uPVC compounds and an organosolv lignin. The research had a dual purpose: to develop dark-colored and cost-effective PVC–lignin blends for outdoor applications in the building industry and to aid in cultivating a market for lignin.

Although the delignification or pulping processes using aqueous organic solvents (organosolv processes) are relatively new and currently are being practiced only at the pilot and demonstration plant scale around the world, we chosed an organosolv lignin (L) from the ethanol-based ALCELL process for PVC–lignin blend preparation, taking into account the fact that this particular type of lignin is separated in much less unaltered form in comparison with the lignins resulting from kraft or sulfite pulping processes.[8,9] In addition, this type of delignification will probably represent the future of the pulp and paper industry due to the following advantages when compared with kraft and sulfite processes:

- A significantly lower degree of pollution by eliminating the use of polluting sulfur containing chemicals in the pulping process
- Lower capital costs
- Environmentally acceptable bleaching
- Higher pulp yields[8-11]

EXPERIMENTAL

Materials

PVC was a commercial unplasticized resin Geon 85862, supplied by BF Goodrich Technical Center, Avon Lake, Ohio. It is a suspension polymer of high molecular weight ($K = 67$). It was supplied already compounded, and its formulation, which is as follows, is designed for outdoor applications.

Ingredients	Level (phr)
PVC resin	100
Dimethyl tin dithioglycolate stabilizer	2
Acrylic processing aid	1.5
n-Butyl acrylate based impact modifier	6
Lubricants	3.75
TiO$_2$ (nonchalking silica coated)	Variable from 0 to 10

PVC specific gravity is 1.48 (when formulated with 10 phr TiO$_2$).

Lignin was an organosolv-type, ALCELL lignin (L) produced by ALCELL Technologies Inc., Miramichi, New Brunswick. Its molecular weight is M_w less than 2000, $M_n = 800$–900, specific gravity 1.27 and median size particles 16 μm. The blends were prepared from PVC compounds containing 7.5, 5.0, 2.5 TiO$_2$ and the corresponding quantity of L (i.e., 2.5, 5.0, and 7.5 phr) or from PVC compound without TiO$_2$ and 5.0, 7.5, 10, 15, and 20 phr L.

The compounds will be designated in the text as follows:

PVC control compound with 10 phr TiO$_2$:	PVC 10T–0L
PVC compound with 7.5 phr TiO$_2$ and 2.5 phr L:	PVC 7.5T–2.5L
PVC compound with 5.0 phr TiO$_2$ and 5.0 phr L:	PVC 5.0T–5.0L
PVC compound with 2.5 phr TiO$_2$ and 7.5 phr L:	PVC 2.5T–7.5L
PVC compound without TiO$_2$:	PVC 0T–0L
PVC compound without TiO$_2$ and 5.0 phr L:	PVC 0T–5.0L
PVC compound without TiO$_2$ and 7.5 phr L:	PVC 0T–7.5L
PVC compound without TiO$_2$ and 10 phr L:	PVC 0T–10L
PVC compound without TiO$_2$ and 15 phr L:	PVC 0T–15L
PVC compound without TiO$_2$ and 20 phr L:	PVC 0T–20L

Procedures

The blends were prepared by melt compounding in a Haake Rheomix 600 equipped with roller blades. Typical working conditions were as follows: temperature, 195°C; time of mixing, 8 min; speed of roller blades, 65 rpm; and filling coefficient, 67% (net chamber volume 69 cm^3).

The Rheomix 600 was equipped with a torque rheometer, Haake Rheocord-M, for continuous measuring of the melt torque and with a thermocouple connected to a temperature recorder for continuous measuring of the melt temperature. PVC was added first and L after 30 s. Several batches were prepared for each formulation, and after melt mixing the obtained blends were ground to a size of about 3–5 mm. Then sheets of 2 mm thickness were molded by compression at 195°C in a laboratory

press equipped with temperature and pressure controllers. After 20 min cooling with air and under pressure, the sheets were cut with a cutting die in shoulder-shaped specimens (ASTM D 638 type V) for mechanical testing.

The mechanical properties, tensile strength, and elongation at break were measured in 1 week's time after samples preparation and were correlated with the properties of PVC controls. They were measured in accordance with ASTM D 638 using an Instron universal testing machine at a cross head speed of 1 mm/min and at a temperature of 23 ± 2°C. All the indicated values are an average of at least five determinations. All the specimens were conditioned before testing at 23 ± 2°C and 50% relative humidity (RH) for 48 h.

The thermal analysis of PVC controls and PVC–L blends was carried out by means of a DuPont thermal analysis system consisting of a 2100 thermal analyst operating system and 912 differential scanning calorimeter or 982 dynamic mechanical analyzer.

All the results of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) represent the average of at least three determinations. For DMA measurements, samples of about 25 × 12 × 2 mm were run between 25 and 125°C at a heating rate of 5°C/min under nitrogen atmosphere. T_g, storage modulus at 30°C, and tan δ were determined. T_g was taken as the temperature of maximum peak in the loss modulus vs. temperature curve. For DSC measurements, samples of about 4–5 mg were run at a heating rate of 20°C/min under nitrogen atmosphere between −30°C and 195°C. The testing of the PVC controls and PVC–L blends samples was performed in 1 week's time after their preparations.

DSC measurements were carried out for measuring the relaxation energy of the blends in order to establish polymer–polymer phase behavior in time. The value of the endothermic peaks noticeable in the DSC curve in the T_g region is a measure of relaxation energy. These peaks appear as an effect of physical aging of the polymer. Physical aging of glassy polymers occurs after polymeric materials are processed at high temperature and then cooled below T_g. Quick cooling does not allow complete molecular relaxation, leading to a nonequilibrium state. During that time, even in solid state the "frozen-in" molecules have the tendency to approach the equilibrium state, which is characterized by a more molecular ordering. Consequently, the free volume of the material and its enthalpy will decrease. By heating, an energy consumption is needed to achieve molec-

ular disorder again. This energy is termed the relaxation energy or enthalpy relaxation.[12,13]

Morphological changes in polymers occur as an effect of physical aging, which causes changes in physical and mechanical properties. Physical aging, which takes place at a temperature below T_g, can influence only amorphous regions of polymers.[14]

The influence of L on the crystallinity of PVC in processed blends was examined in another set of DSC measurements. The specimens for testing were previously annealed for 5 min at 165°C and quench cooled with liquid nitrogen in order to erase the effects of physical aging. DSC analyses for determining the melting temperatures and latent heats of melting were performed between −30°C and 195°C, at a heating rate of 20°C/min, under nitrogen atmosphere. DSC cell calibration was carried out before the testing in accordance to manufacturer's specifications with indium etalon samples. Scanning electron microscopy (SEM) was performed using specimens that were broken in liquid nitrogen, on a Jeol JSM 820 instrument, following coating with gold palladium. Photographs were taken at 5000 and 10,000× magnification.

RESULTS AND DISCUSSION

Processibility of the Blends

The processibility or the fusion characteristics of PVC compounds are influenced principally by the type of resin and by the type of additives present. A change in formulation, especially in the case of rigid PVC composition, can affect the fusion characteristics of PVC compounds and consequently their processibility. Inadequate processibility may have a negative effect on the mechanical properties of PVC and its weatherability. The influence of L on the processibility of PVC–L blends is indicated in Table I. As can be seen from the data presented in this table, the fusion characteristics of both PVC controls (i.e., with 10 phr TiO_2 and 0 phr TiO_2) are different. Blends of PVC with L formulated with several parts of TiO_2 or without TiO_2 present almost the same characteristics as PVC controls. There is a slight tendency for fusion time and maximum torque to increase in relation to L content in blends with TiO_2 up to 7.5 phr L. For the blends without TiO_2, there is a slight tendency for fusion time to decrease and torque to increase in relation to L content.

However, one may conclude that the fusion characteristics of PVC–L blends in comparison with

PVC controls are very close, and the presence of L does not have a negative effect on the processibility of PVC–L blends. The specimens of PVC–L blends with TiO_2 were colored from beige to tan, and PVC–L blends without TiO_2 were dark brown.

Tensile Stress–Strain Tests

Table II shows the maximum tensile strength and the elongation at break data for PVC–L blends with and without TiO_2 as well as data for PVC controls also with and without TiO_2, as determined in accordance with ASTM D 638.

The presented data indicate a tensile strength increase correlated with L load without a major impact on the elongation up to 7.5 phr L in both compounds with or without TiO_2. At a higher content of L (i.e., 10 phr), in compounds without TiO_2 the tensile strength still increases, but the elongation declines from about 280% to about 180%. Blends with 15 and 20 phr L and without TiO_2 present unchanged values of tensile strength when compared with PVC control specimens, but they lost completely the elongation properties and were no longer investigated.

Similar data concerning an increase of tensile strength and a decrease of elongation for the blends of hydroxypropylcellulose and up to 10 wt % of an organosolv lignin were reported by Rails.[15]

DMA

For all the analyzed specimens, a one-step tensile storage modulus versus temperature curve and a related one-peak tensile loss modulus vs. temperature curve, both characteristics of miscible polymers, were observed.

Table II Tensile Properties of PVC–L Blends

Specimen Type	Tensile Strength Average (MPa)	(%)	Elongation at Break Average (%)	(%)
PVC 10T–0L	40.15	100.0	332	100.0
PVC 7.5T–2.5L	43.85	109.2	281	84.6
PVC 5.0T–5.0L	44.14	109.9	326	98.2
PVC 2.5T–7.5L	47.05	117.2	312	94.0
PVC 0T–0L	42.30	100.0	280	100.0
PVC 0T–5.0L	45.73	108.1	300	107.1
PVC 0T–7.5L	47.28	111.7	284	101.1
PVC 0T–10L	48.66	115.0	182	65.0
PVC 0T–15L	42.87	101.3	—	—
PVC 0T–20L	35.67	84.3	—	—

The results of DMA analyses are shown in Table III, where all the values represent the average of at least three runs with standard deviation within 0.1 GPa for storage modulus, 0.5°C for T_g, and 0.012 for max tan δ. When compared with data obtained for PVC controls, the results can be summarized as follows:

1. The values of storage modulus are very close and within the instrument limits of precision ($\pm 5\%$). Their fluctuation is quite erratic, and it is hard to correlate it with L content in blends.
2. The T_g values decrease roughly in order of increasing L loading in blends.
3. Although the data concerning the magnitude of tan δ are quite close, a slight increasing trend of their values, which can be correlated

Table I Influence of L on the Fusion Characteristics of PVC–L Blends

Specimen Type	Average Fusion Time (s)	Average Torque Value Max (fusion)	At the End of 8 Min	Average Temperature of the Melt (°C) At Max Torque	At the End of 8 Min
PVC 10T–0L	75	2500	1575	184	205
PVC 7.5T–2.5L	80	2530	1600	180	204
PVC 5.0T–5.0L	85	2570	1600	183	204
PVC 2.5T–7.5L	88	2425	1475	182	204
PVC 0T–0L	165	1960	1430	185	204
PVC 0T–5L	100	2280	1430	186	204
PVC 0T–7.5L	105	2350	1420	189	203
PVC 0T–10L	78	2370	1400	181	202

Table III   DMA Results for PVC Controls and Blends

| Specimen Type | Storage Modulus at 30°C | | T_g | | Max tan δ | |
	GPa	St. Dev. (GPa)	°C	St. Dev. (°C)	°C	St. Dev. (°C)
PVC 10T–0L	2.12	0.06	91.9	0.5	0.874	0.012
PVC 7.5T–2.5L	2.23	0.09	92.0	0.7	0.903	0.017
PVC 5.0T–5.0L	2.18	0.06	91.5	0.5	0.936	0.012
PVC 2.5T–7.5L	2.21	0.10	90.0	0.5	0.961	0.005
PVC 0T–0L	2.13	0.08	92.1	0.5	0.893	0.007
PVC 0T–5L	2.11	0.09	91.3	0.3	0.934	0.018
PVC 0T–7.5L	2.20	0.06	90.6	0.6	0.954	0.012
PVC 0T–10L	2.19	0.10	89.9	0.5	0.988	0.005

St. Dev. = standard deviation.

in all cases, with L loading is noticeable in all the blends.

It is known that loss modulus and tan δ, which is the ratio between loss and storage moduli, are particularly sensitive to molecular motions within a material. In the glass transition region, damping is high due to the onset of micro-Brownian motion within the molecular structure of the main chain, and so is the tan δ. Breaking intermolecular bonds allows greater chain mobility and results in a decrease of T_g as well as an increase in magnitude of tan δ.[16] The magnitude of tan δ, which is a characteristic of the rubbery state of the polymers, has little signification in the glassy state, where motion of molecular segments is practically inexistent.

Keeping in mind these observations, the results presented in Table III suggest an increase in polymer chain mobility of PVC–L blends directly correlated with L content. It seems likely that in PVC–L blends the intermolecular bonds existing within the PVC structure are in some degree broken down due to the presence of L, as the T_g and tan δ values would indicate. However, breaking of the intermolecular bonds does not affect the stiffness of the material at room temperature, as the values of the storage modulus are practically unchanged in the PVC–L blends in comparison with PVC controls. Moreover, the tensile properties of the PVC–L blends in comparison with those of PVC controls (Table II) disclose an increase of tensile strength in relation to L loading.

DSC

DSC analyses were performed in order to obtain information regarding the influence of L on the relax-ation energy and T_g of the blends and on the crystallinity of the processed PVC in blends. The results of DSC analyses are shown in Table IV, where all the values represent the average of at least three runs. The standard deviation is within 0.4°C and in one case 1.2°C for T_g, within 0.09 J/g and in one case 0.17 J/g for relaxation energy, and within 0.04 J/g and in one case 0.09 J/g for latent heat of melting.

Figure 1 illustrates two typical DSC curves (second run) for PVC 10T control and PVC 2.5T—7.5L blend. The blend, representative for high L loading, exhibits a single T_g. In addition, in the DSC curves, melting endotherms are visible in the range of temperatures from 110 to 140°C, with a sharp peak located at around 128°C for PVC controls and around 120°C for blends. This is the range of temperatures that reflects part of the crystalline melting region of PVC.[16,17] Figure 2 illustrates typical DSC curves (first run) for PVC 10T—0L control and for PVC–L blends with different loadings of L.

By analyzing each DSC curve presented in Figure 2, one can see that their shape is different in the 40–70°C temperature interval. For the blends with L, a new small endotherm, which converges with the principal endothermic peak, appears in this region. It increases in magnitude and broadens by the presence of higher L loadings. One may conclude that the second endothermic peak is caused by L molecular relaxation, as it is not visible in the DSC curve of PVC control.

The fact that in the blend each polymer has its own aging behavior is an indication of the presence of two different phases.[13] This fact can be used as an argument for the likely immiscibility of the two polymers in the blend. On the other hand, the facts

Table IV   DSC Results for PVC Controls and Blends

| | T_g | | Relaxation Energy | | | PVC Crystallites Properties | | |
| | | | | | | $\Delta H_m{}^a$ | | |
Specimen Type	°C	St. Dev. (°C)	J/g	St. Dev. (J/g)	Peak Temp. (°C)	J/g	St. Dev. (J/g)	$T_m{}^b$ (°C)
PVC 10T–0L	82.7	0.3	1.12	0.09	86.9	1.28	0.07	128.5
PVC 7.5T–2.5L	80.4	0.4	1.65	0.06	85.3	0.94	0.02	127.1
PVC 5.0T–5.0L	79.8	1.2	1.71	0.09	85.2	0.84	0.04	124.0
PVC 2.5T–7.5L	79.6	0.1	1.84	0.10	84.9	0.93	0.04	122.5
PVC 0T–0L	82.0	0.1	1.38	0.09	86.2	0.55	0.09	126.0
PVC 0T–5L	80.0	0.2	1.97	0.17	85.6	0.87	0.03	—
PVC 0T–7.5L	79.4	0.6	—	—	85.2	0.67	0.03	122.6
PVC 0T–10L	78.7	0.2	2.08	0.13	83.7	0.47	0.04	120.5

^{a} ΔH_m: Latent heat of melting.
^{b} T_m: Melting temperature.

that the peaks are not perfectly separated and that the relaxation energy of the principal peak, which corresponds to PVC molecular relaxation, is higher in the blends than in PVC control (see Table IV) can be used as an argument for the likely miscibility of the two polymers in the blends. Consequently, they are probably partially miscible.

It is interesting to note that the peak temperatures of the relaxation energy endotherms of the

blends decrease roughly in order of increasing the L content. The same observation is valid for T_g values.

The influence of L on the crystalline region of processed PVC blends (100–140°C) was examined in another set of DSC measurements. It is generally accepted now that PVC is partly crystalline.[17,18] All PVC processes involve the melting or partial melting of primary crystallites and the formation of second-
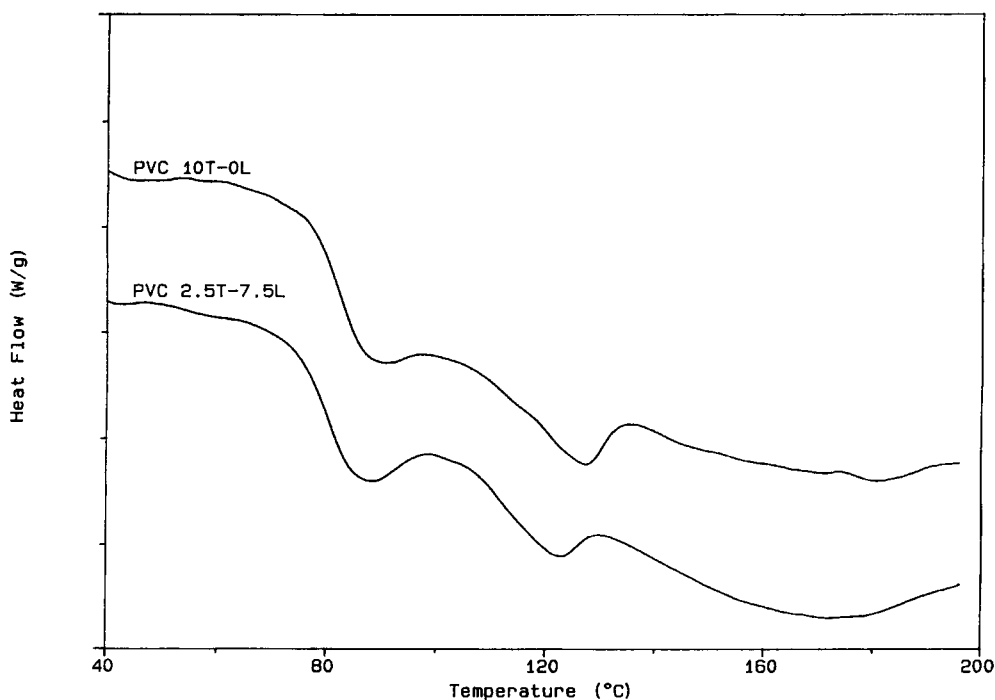

Figure 1   Illustrative DSC curves—second run: PVC 10T—0L (control) and PVC 2.5T—7.5L.
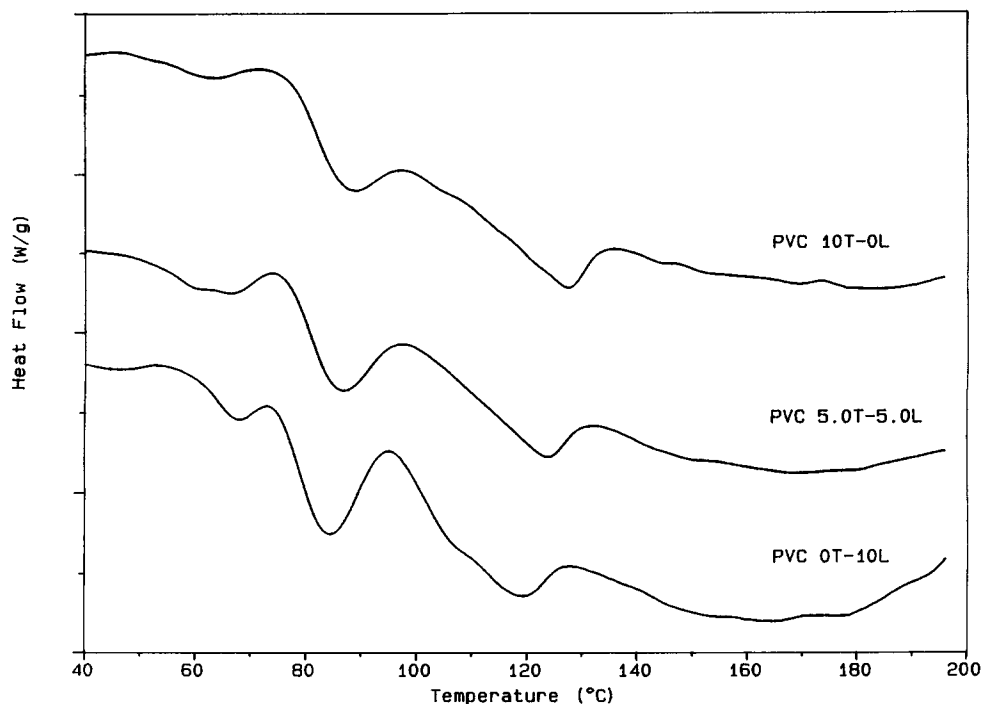
Figure 2   Typical DSC Curves, first run, for PVC 10T–0L (control) and PVC–L Blends with different L loadings.

ary crystallinity on subsequent cooling. The newly formed crystallites will have various sizes and degree of perfection and will melt on a wide melting range. They will act as ties or crosslinks in a three-dimensional network, giving a tough product.[19]

The specimens for testing were annealed for 5 min at 165°C and quench cooled in order to erase completely the effects of physical aging and thus increase the resolution of melting peaks. The latent heat of melting of the PVC crystals is indicated in Table IV. As can be seen from this table, there is a gradual reduction of the magnitude of their latent heat of melting, which reflects a diminution of these particular crystallites in relation to the amount of L present in blends, with a discontinuity at 7.5 phr L in the blends with TiO_2.

For the blend without TiO_2, the latent heats are smaller than the blends with TiO_2. Some observation is applicable for PVC–OT control. Experimental results published in the literature led us to the hypothesis that the presence of filler is needed to act as nucleating centers for PVC crystallite growth.[20]

As stated earlier, the crystallites in PVC act as crosslinks in a three-dimensional network. If part of the crystallites diminish, as was observed in PVC–L blends, the toughness of the material will be affected. The storage moduli and especially the tensile properties of PVC–L blends demonstrated the con-

trary. A reduction of free volume, probably due to polar–polar interactions between PVC and L chains, could be a possible explanation for the contradictory results observed concerning mechanical properties of the blends and the degree of PVC crystallinity. Higher relaxation energy data of the blends in comparison with PVC controls, as shown in Table IV, suggest a reduction of the free volume. The polar–polar interaction between carbonyl groups of L and α hydrogen of PVC or between hydroxyl groups of L and the chlorine of PVC could be responsible for the relaxation energies increasing or free volumes decreasing, which in turn could be responsible for an increase of tensile strength.

Reduction of the free volume as an effect of polar–polar interaction between PVC chains and plasticizer molecules is cited as a possible reason for the PVC embrittlement (i.e., tensile strength increasing and elongation decreasing), which occurs in presence of low levels of plasticizer.[17]

SEM

SEM was employed to characterize further the morphology of the blends. Due to the complexity of the PVC compound itself, the analysis was undertaken in the following order:
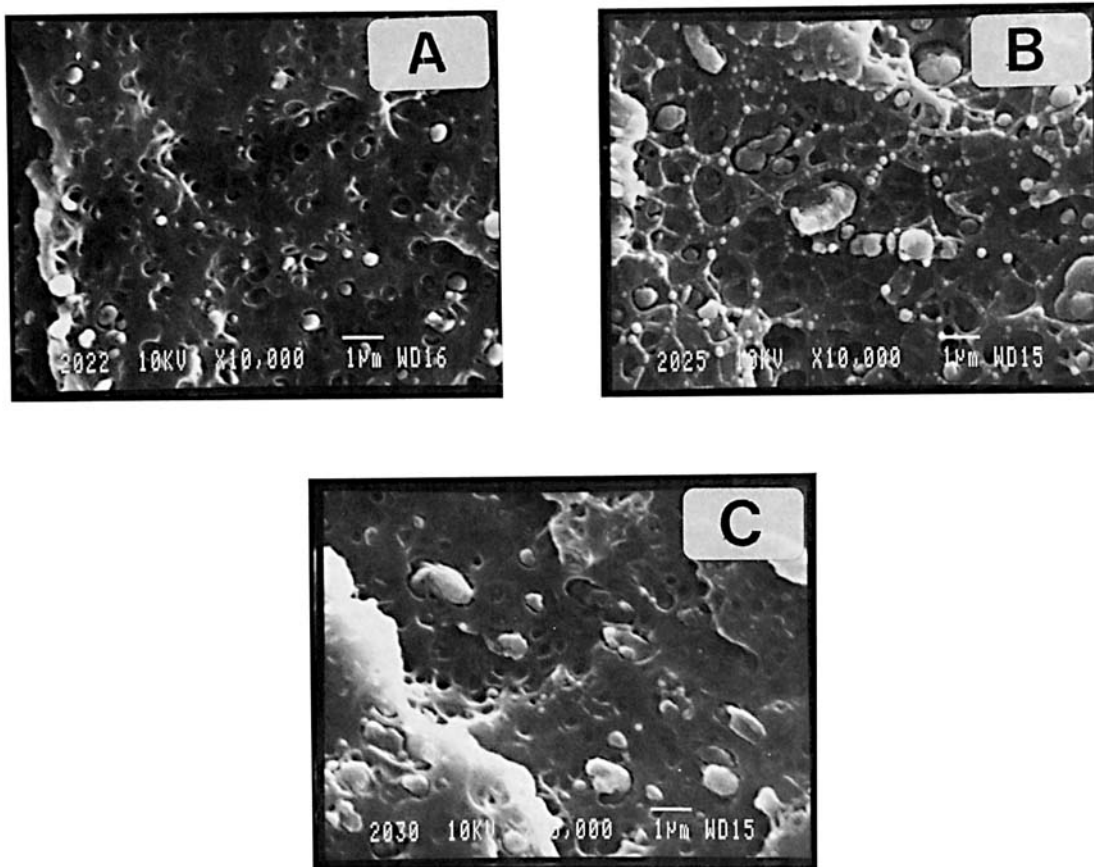
Figure 3 Scanning electron photomicrographs (×10,000) for PVC 0T–0L (control) and PVC–L blends. (A) PVC 0T–0L; (B) PVC 0T–5L; (C) PVC 0T–10L.

1. *PVC control 0T–0L (photomicrograph A).* One may observe a fine dispersion of spheres having a diameter of less than 0.5 μm. This can be attributed to the impact modifier (IM). As was shown earlier, beside TiO₂, IM is the ingredient with the highest level in the PVC compound. It can be seen that IM is evenly distributed in the PVC matrix.

2. *PVC 0T–5L (photomicrograph B).* The fine dispersion of IM is observable, and in addition one may notice irregular particles having a diameter up to 2 μm, confirming the L presence. The morphology of these specimens is different from the morphology of the ensemble of the other specimens. This is probably due to a plastic deformation during freeze breaking.

3. *PVC 0T–7.5L to PVC 0T–20L.* All these blends present an identical morphology. This can be seen in the photomicrograph C for PVC 0T–10L. L particles size vary up to 2 μm, as in the case of the PVC 0T–5L blend. They have an irregular shape, and any co-

alescence is observable. It is likely that no adhesion took place between the PVC matrix and L dispersed phase.

4. *PVC 10T–0L (photomicrographs D and E).* In this case, especially at a magnification of 10,000× (E), one may easily distinguish the particles of IM as in PVC 0T–0L and the crystallike TiO₂ particles. The latter have an irregular shape different from that of IM and L.

5. *PVC 5T–5L (photomicrograph F) and PVC 2.5T–7.5L (photomicrograph G).* Although the composition of these blends is very complex (PVC, IM, TiO₂, and L) the L particles' inclusion is detectable. These L inclusions, with a diameter of 1.5–2 μm, are similar to those in the blends without TiO₂. Again, it seems likely that no adhesion took place between the PVC matrix and L dispersed phase.

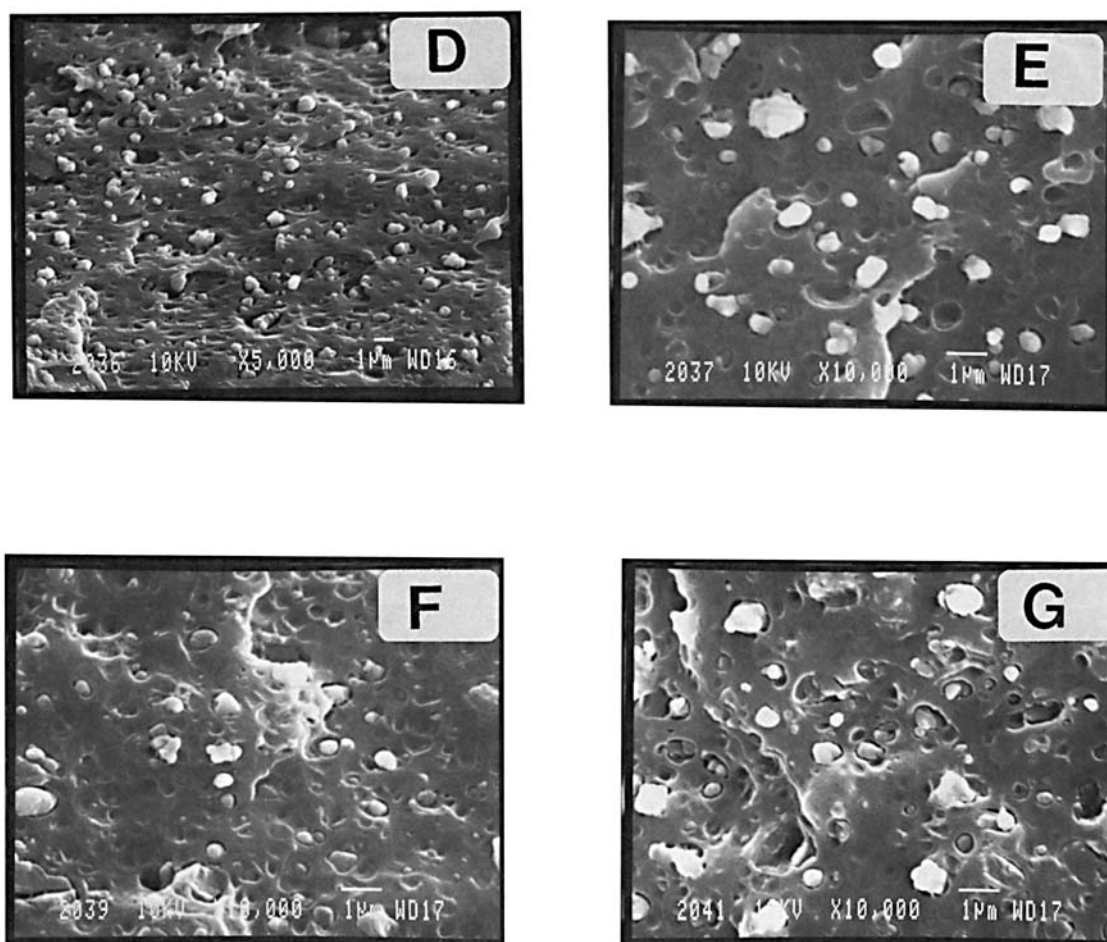The examination of SEM photomicrographs leads to the following conclusions:

Figure 4 Scanning electron photomicrographs (×10,000) for PVC 10T–0L (control) and PVC–L blends. (D) PVC 10T–0L (×5,000), (E) PVC 10T–0L; (F) PVC 5T–5L; (G) PVC 2.5T–7.5L.

- The size of L particles in PVC–L blends does not increase with the gradual increase of L content.
- Any sign of coalescence between L particles is noticeable.

These two conclusions prove that the PVC–L blends are not typically miscible thermoplastic blends. Generally, the thermoplastic blends present an increase of the particle size of the dispersed phase and usually coalescence signs.[21]

CONCLUSIONS

Blends of uPVC formulated with several loadings of TiO$_2$—from 0 to 10 phr—and an organosolv lignin—in amounts up to 10 phr—were prepared by melt mixing and compression molding. The mechanical

properties of the PVC–L blends were ascertained by tensile stress–strain, and their morphology was studied by DMA, DSC, and SEM analyses.

Mechanical data indicated a tensile strength increase correlated with L load, without a major impact on the elongation up to 7.5 phr L in both compounds with or without TiO$_2$. At higher than 7.5 phr L in the blends, their strength still increased but the elongation declined.

When compared with the PVC controls, the torque rheometer data indicated that the presence of L does not have a negative effect on the processibility of PVC–L blends. SEM results indicated the immiscibility of the two polymers in blends. Immiscibility was also confirmed by the DSC analyses, which disclosed the existence of two endothermic relaxation peaks in the T_g region. The fact that these two peaks are not perfectly separated and that the relaxation energy of the principal peak, which cor-

responds to PVC molecular relaxation, is higher in the blends than in the PVC control is an argument for the likely miscibility of the two polymers in blends.

Part of the results of DMA analyses (i.e., a gradual decrease of T_g and especially a gradual increase of tan δ of the blends as function of L loading) suggested that the presence of L led to a certain degree of breaking of the intermolecular bonds existing within PVC structures. The same conclusion can be drawn from the diminution, due to the L presence, of the latent heat of melting of the PVC crystallites, as determined by DSC. It was demonstrated that these crystallites act as ties or crosslinks in the PVC matrix.

The fact that the toughness of the blends is not affected by the diminution of these particular crystallites, as was demonstrated by the values of blend storage moduli at room temperature and especially by the values of tensile strength, might be explained by a reduction of the free volume of the blends, probably due to polar–polar interaction between PVC and L chains. This polar–polar interaction can be expected, taking into account the functionality of both polymers.

Although the PVC–L blends are not miscible or only partially miscible, their morphological structure up to a 7.5 phr L loading does not affect their performance, as the mechanical properties have indicated. Consequently, mechanical and processing properties of this type of blends, as well as the fact that PVC is now and probably will remain for some time the dominant resin used in construction, encourage further research for PVC blending with lignins. The research would comprise blending of lignins with PVC compounded for dark colors, blend testing according to all existing standards for evaluation of PVC for exterior building products (i.e., flexural and impact strength), coefficient of linear expansion, as well as retention of physical properties after long-term weathering.

REFERENCES

1. R. D. Leaversuch, *Mod. Plastics,* November, 46 (1994).
2. R. D. Deanin, IUPAC International Symposium on Macromolecules, Montreal, Canada, July 13–18, 1990.
3. A. Gandini, in *Comprehensive Polymer Science—First Supplement,* A. Allen and S. L. Aggrawal, Eds., Pergamon Press, Oxford, 1992, pp. 534–549.
4. S. F. Falkehag, *Appl. Polym. Symp.,* **28,** 247 (1975).
5. K. V. Sarkanen and C. H. Ludwig, Eds., *Lignin, Occurrence, Formation, Structure and Reactions,* Wiley Interscience, New York, 1971.
6. H. G. Hofmann, "Polymer Blend Modification of PVC," in *Polymer Blends and Mixtures,* D. J. Walsh, J. S. Higgins, and A. Maconnachie, Eds., Martinus Nijhoff Publ., Dordrecht, 1985, pp. 117–148.
7. L. M. Robenson, *J. Vinyl Technol.,* **12,** pp. 89 (1992).
8. J. H. Lora, C. F. Wu, E. K. Pye, and J. J. Balatinecz, "Characteristics and Potential Applications of Lignin Produced by an Organosolv Pulping Process," in *Lignin—Properties and Materials,* W. E. Glasser and S. Sarkanen, Eds., ACS Symposium Series 397, ACS, Washington, DC, 1989, pp. 302–323.
9. O. Faix, *Das Papier,* **46,** 733 (1992).
10. A. Linder and G. J. Wegener, *Wood Chem. Tech.,* **8,** 323 (1988).
11. A. K. Varshney and D. P. Patel, *J. Sci. Ind. Res.,* **47,** 315 (1989).
12. S. E. B. Petrie, "The Problem of Thermodynamic Equilibrium in Glassy Polymers," in *Polymeric Materials: Relations between Structure and Mechanical Properties,* E. Ber and S. V. Raddcliffe, Eds., Am. Soc. Metals, Metals Park, OH, 1974, pp. 55–117.
13. M. Bosma, G. Len Brinke, and T. S. Ellis, *Macromolecules,* **21,** 1465 (1988).
14. K. H. Illers, *J. Macromol. Sci. Phys.,* **B14,** 471 (1977).
15. T. G. Rials and W. G. Glasser, "Phase Morphology of Hydroxypropylcellulose Blends with Lignin," in *Lignin Properties and Materials,* W. E. Glasser and S. Sarkanen, Eds., ACS Symposium Series 397, ACS, Washington, DC, 1989, pp. 464–485.
16. S. V. Wolfe, *J. Macromol. Sci. Chem.,* **A26,** 249 (1989).
17. M. Gilbert, *J. Macromol. Sci.—Rev. Macromol. Chem. Phys.,* **C34,** 77 (1994).
18. E. Rabinovitch and J. Summers, *J. Vinyl Tech.,* **14,** 126 (1992).
19. J. Summers, *J. Vinyl Tech.,* **3,** 107 (1981).
20. P. Choi, M. Lynch, A. Rudin, and J. W. Tech, *J. Vinyl Tech.,* **14,** 156 (1992).
21. B. D. Favis and J. P. Chalifoux, *Polymer,* **28,** 1761 (1988).