Contribution to the Study of Rigid PVC Polyblends with Different Lignins

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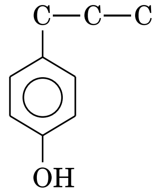
ABSTRACT: Evaluation of different types of lignins and lignin derivatives, representing a spectrum of significant differences in regard to delignification processes and the nature of wood, in blending with a rigid poly(vinyl chloride) (PVC) compound for outdoor application is discussed. The influence of lignins on the processability of the blends, as well as on their strength at yield, break, and impact before weathering, and after 7 days of artificial weathering period (in the presence of ultraviolet light, humidity, and moderate temperature) was investigated, and the data correlated with those of rigid PVC compound. Infrared and thermal analysis were performed to elucidate the morphology of the blends. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1731–1744, 1997

INTRODUCTION

The increasing utilization of rigid poly(vinyl chloride) (uPVC) in the building industry, for windows, siding, and other exterior profiles, is being driven by wood and metal replacement and demands for improved thermal efficiency.

Due to the commercial value of PVC, there are already established blends with other common or less common polymers whose practical benefit is well recognized.

Wood contains about 25 wt % of lignin, which together with cellulose, form the structural component of trees and other plants. Very large quantities of lignin are produced annually by the pulp and paper industry, where lignin is separated from cellulose fiber. A very small amount of lignin is used around the world as antioxidants or fillers in rubber or as a component in blends with thermoplastics or thermosets. The rest is used almost exclusively as fuel to generate energy. In contrast to cellulose, lignin has an aromatic structure. Its basic components are *p*-hydroxyphenyl propane units (1), guaiacyl units (2), and syringyl units (3), as shown:



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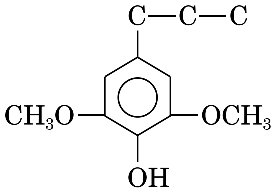

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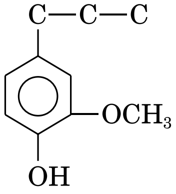

(3)

They are naturally bonded together by random coupling reactions resulting a three-dimensional amorphous polymer.

More than two-thirds of phenylpropane units

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in lignin are linked by ether bonds and the rest by carbon–carbon bonds. The chemical reactivity of lignin is largely determined by the presence of phenolic hydroxyl, benzylic hydroxyl, and carbonyl groups. Their frequency may vary according to the wood species and the method of isolation.[1]

Lignin is obtained as coproduct in pulp production by sulphite or sulphate processes. The sulphite process results in a lignosulphonate byproduct. The sulphate and soda pulping processes result in spent liquors, called black liquors, from which kraft lignin may be separated. In both processes, lignin undergoes significant chemical changes; and technical lignins are not identical in their structure to native lignins.

New delignification processes, based on aqueous–organic solvents or high-temperature wood steaming, were developed in the last decades around the world, especially due to environmental concerns related to conventional chemical pulp production. The lignin thus separated is in a much less unaltered form than lignins resulting from sulphate or sulphite pulping processes.[2–4] Taking into account the abundance of lignin (L), its function in plants, and its functional groups, as well as the commercial value and applications of PVC, it appeared reasonable to examine the contribution that lignin can make to the properties of polyblends with PVC. Previous articles[5,6] reported the evaluation of the blends (PVC–L) obtained from a PVC compound formulated with several amounts of TiO_2 and a hardwood kraft lignin or a hardwood organosolv lignin.

Although, in these blends, the two polymers are either not miscible or only partially miscible, their morphological structure up to 7.5% lignin loading does not affect their performance, as the mechanical properties have indicated. The possibility of a proton donor–proton acceptor interaction between lignin and PVC chains was postulated. This can arise due to the interaction between the hydroxyl or carbonyl groups of lignin and α hydrogen of PVC.

Weatherability of PVC–L blends with up to 10% hardwood kraft lignin indicated a lower weathering stability of these blends in comparison to PVC.

The present study is extended to different types of lignin; and as rigid PVC, a formulation for dark color products was selected. This particular formulation requires an inherently more weatherable thermal stabilizer and the addition of the appropriate ultraviolet (UV) stabilizers.[7]

By selecting a PVC compound with a more efficient thermal stabilizer and UV absorber, we expected to improve the weatherability of PVC–lignin blends.

Based on the previous results, all the blends for this study were formulated with 5% by weight lignin.

The care against pollution of our environment has opened up the interest in the utilization of renewable resources. The purpose of the research was to find new applications for lignin, an abundant inexpensive natural polymer for which there is, at present, only a small market.

EXPERIMENTAL

Materials

PVC was a powder compound for exterior window profile (Polycor D-7257) supplied by Les Industries Synergistic LTEE, St. Remi de Napierville, Quebec. It is formulated with 1% pigments, UV stabilizer, heat stabilizer, internal and external lubricant, processing aid, impact modifiers, and no titanium dioxide.

Five different lignins and lignin derivatives were selected for this study. They represent a spectrum of significant differences in regard to chemical functionality, thermal characteristics, and delignification processes. There are as follows.

1. A partially water soluble lignin (PWSL), isolated at the laboratory scale (Slovak Academy of Sciences) from water prehydrolizate of hardwood (170°C, 1 h), resulted from the company BUKOZA, Bratislava, Slovakia.
2. Softwood sodium lignosulfonate (SF NaLS).
3. Hardwood sodium lignosulfonate (HD NaLS). (Both lignasulfonates were provided by the company TEMBEC, Chemical Division, Temiscaming, Quebec. They were obtained from the ammonium sulphite liquors by treatment with sodium hydroxide. This treatment allows also the hydrolysis of carbohydrates to lower molecular weight compounds, which can be subsequently removed by evaporation. Thus, their content in carbohydrates in the final dry product is 1.6% in SF NaLS and 0.7% in HD NaLS).
4. Hardwood organosolv lignin (Alcell). This was provided by Alcell Technologies, Mira-

machi, New Brunswick, where it is produced at a pilot scale by digesting the wood chips with an aqueous ethanol liquor at appropriate temperatures, pH, and time. Lignin is recovered from the resulting black liquor by a patented technique.

5. Softwood kraft lignin (Indulin). This was obtained from Westvaco, Charleston, South Carolina. It is a purified pine lignin.

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 60 cm^3).

The Rheomix 600 was equipped with a torque rheometer, Haake Rheocord-M 300, for continuous measuring of the melt torque and with a thermocouple connected to a temperature recorder for continuous measuring of the melt temperature. Several batches were prepared for each formulation; 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 (8 min) at 195°C in a laboratory press equipped with temperature 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) or notched specimens (ASTM D 250) for mechanical testing.

Artificial Weathering

The weathering of the samples was carried out using a Q–U–V accelerated weathering tester (Q-Panel Company, Cleveland, Ohio). Rain and dew are simulated in this tester by a condensation system. It contains a series of UV-A lamps with a peak emission at 340 nm and spectral energy distributed between 295 to 400 nm. Materials exposed to UV-A 340 lamps in this device receive an irradiance of 0.72 W m^{-2} nm^{-1} (±10%) at 340 nm. The UV irradiance from 295 to 400 nm is 39 W m^{-2} nm^{-1} (±10%).

Specimens of PVC–control and PVC–L blends were subjected to several cycles of four hours each of UV exposure at an equilibrium temperature of 60 ± 1°C, alternating with condensation exposure at an equilibrium temperature of 50 ± 1°C for a period of 7 days (168 h) according to ASTM D 5208.

For determining the effect of condensation exposure on the proportion of water absorbed by PVC control and blends, a water absorption test in conditions closed to those occurring during artificial weathering was conducted. ASTM D 570 was used as a guide line for the test. Three samples of 76.2 mm long (3 in.) by 25.4 mm wide (1 in.) by 2 mm thick were tested for each formulation. Before testing, they were dried in the oven at 50 ± 3°C, cooled in a desiccator, and immediately weighed with a precision of ±0.0001 g. The test specimens were thereafter immersed in distilled water and maintained at a temperature of 50 ± 2°C, for 84 h. These conditions correspond to the condensation exposure. After immersion, the specimens were reweighed, and the proportion of the absorbed water was calculated. Immediately after weighing, all the specimens were redried at 50 ± 2°C for 24 h, cooled in a desiccator, and reweighed to calculate the retention of water.

Testing

The tensile strength at yield and break were measured in accordance with ASTM D 638 using an Instron universal testing machine at a crosshead speed of 5 mm min^{-1} and at a temperature of 23 ± 2°C.

The impact strength (Izod) was measured in accordance with ASTM D 250 on notched specimens with a model 92T Tinus Olsen Impact Tester.

All the specimens for tensile and impact strength were tested one week after their preparation or after seven days of artificial weathering. They were conditioned at 23 ± 2°C and 50 ± 5% RH for 48 h prior testing. The indicated values are an average of at least five determinations. The coefficients of variations inferior to 10% were taken into account for each set of specimens tested.

The fluctuation of the elongation at break results was quite erratic for the blends with PWSL and both lignosulfonates; and, consequently, all these data were disregarded. TGA tests were performed in a 2000 DuPont TGA under nitrogen atmosphere. The temperature profiles were isothermal at 103°C for 10 min; ramp from 103 to 195°C at 100°C min^{-1}; and isothermal at 195°C for 16 min. The loss in weight during the drying period and the loss in weight during the degradation period were calculated. The first was reported to the weight of the humid sample and the second to the weight of the dry sample. Two specimens were tested for each lignin.

The infrared (IR) spectra were recorded with a Fourier transform IR (FTIR) spectrophotometer Magna 550 Nicolet. Samples of 0.0210 g PVC or PVC–L blends as resulted from melt compounding were precisely weighed (±0.001 g) and then pressed at a temperature of 190°C under a force of 0.75 t into a film of 13 mm diameter having a thickness of 50 μm, using a Spectra-Tech universal film maker. The thickness of the films was carefully controlled in order to ensure a uniform thickness for all the specimens.

The films were IR analyzed after the preparation and after 7 days of weathering. Prior to testing, the weathered films were kept in a vacuum oven for 72 h to ensure the complete removal of water.

Lignins were analyzed as KBr discs (3 mg/500 mg KBr). Pressing conditions and the weight ratio of lignins to KBr were carefully controlled.

RESULTS AND DISCUSSION

Thermal Stability of Lignins in the Processing Conditions

The thermal stability of lignins during processing conditions, i.e., 8 min melt mixing at 195°C and 8 min compression molding at 195°C, was determined by thermogravimetric analysis (TGA) (under nitrogen). In another set of experiments, a dry lignin sample of about 50 g weighed with a precision of ±0.0001 g was kept in the oven (air atmosphere) at 195°C for 16 min. After cooling in a desiccator for 1 h, the sample was reweighed, and the loss in weight was determined.

T_g of the dried samples and thermally treated samples were determined by differential scanning calorimetry (DSC) analysis. All the results are indicated in Table I. As can be seen from the data presented (Table I), the thermal stability, as expected, was higher for the hydrolytic and organosolv lignins and lower for the lignosulfonates and kraft lignin.

The T_g of all lignins increased after thermal treatment and T_gs of both lignosulfonates was no longer visible in the DSC curves up to 195°C. After thermal treatment, the lignosulfonates remained in the form of free flowing powder in contrast to other lignins, which were melted (Alcell and PWSL) or sintered (Indulin).

The IR spectra of dry and thermally treated lignins were recorded in the region from 4000 to 500 cm^{-1}. They are presented in Figure 1 for PWSL, Alcell, and Indulin, and in Figure 2 for lignosulfonates.

The main features of IR spectra of both dried and thermally treated lignin are practically similar in the case of Alcell and PWSL. A very small shift to lower frequencies in the OH stretch absorption occurred, i.e., 1 cm^{-1} for PWSL and 4 cm^{-1} for Alcell.

Table I Physical Characteristic of Lignins

					Characteristics after Thermal Treatment (16 min, 195°C)		
		Moisture (%)			Loss in Weight (%)		
Lignin Type	Specific Gravity	Oven (1 h, 105°C)	TGA (15 min, 103°C)	T_g (°C; Dried Samples)	Oven (Air)	TGA (N_2)	T_g (°C)
Hardwood partially soluble (PWSL)	1.31	3.62	3.20	110	2.31	2.14	126
Softwood Na lignosulfonate (SF NaLS)	1.22	2.28	2.30	138	5.16	4.66	—
Hardwood Na lignosulfonate (HD NaLS)	1.26	5.31	5.00	127	5.88	5.52	—
Hardwood organosolv (Alcell)	1.27	6.92	7.00	97	1.61	2.04	109
Softwood Kraft (Indulin)	1.24	5.84	5.65	141	4.55	4.21	175

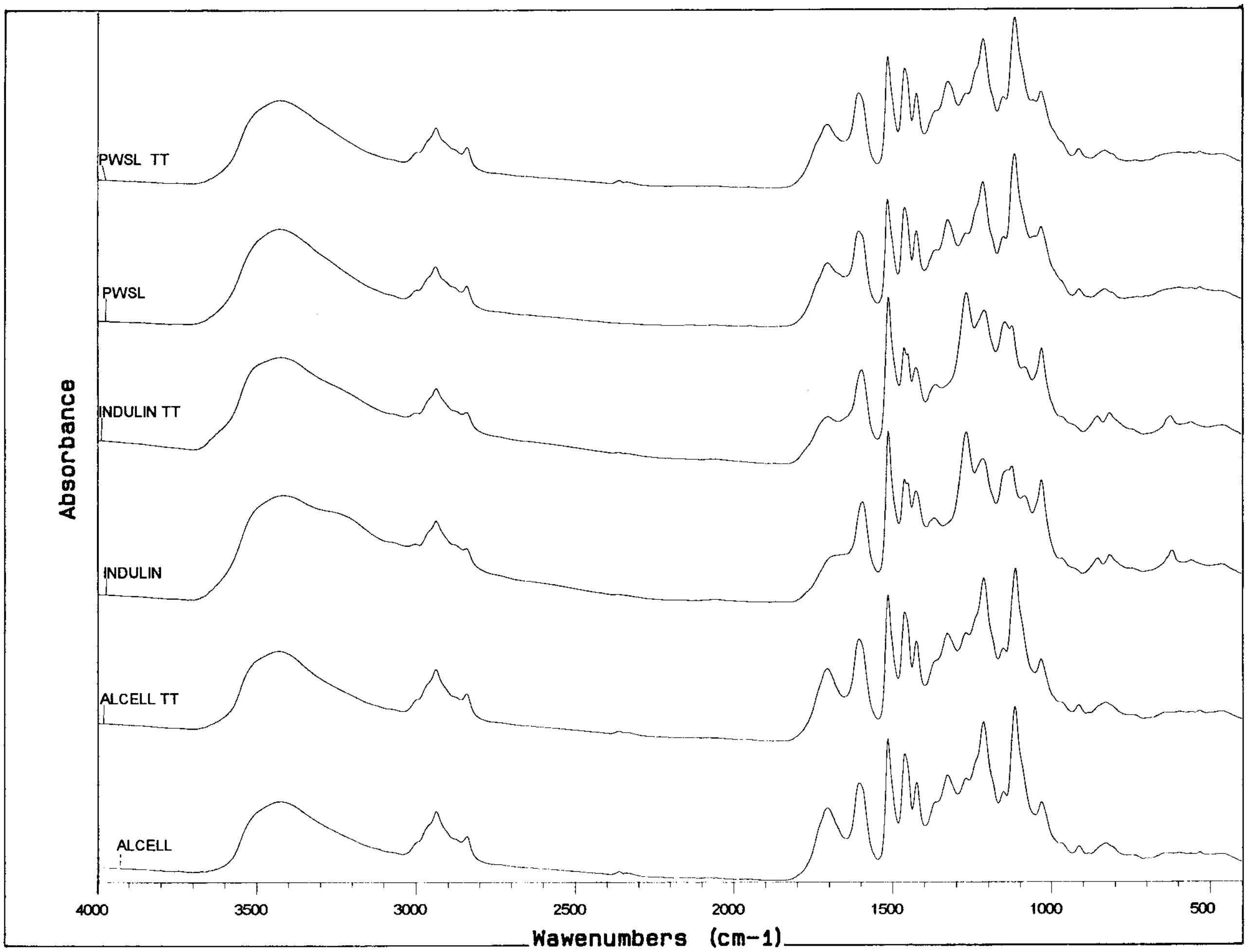


Figure 1 FTIR spectra of PWSL, Alcell, and Indulin dried and thermally treated.

The spectra of thermally treated Indulin presents a modification of the OH peak at 3400 cm^{-1}, albeit its maxima is in the same position. The weak shoulder at about 1685 cm^{-1} representing C=O stretching vibrations shows a detectable increase in intensity; it becomes a peak located at 1705 cm^{-1} in the thermally treated sample.

The main characteristic of IR spectra of thermally treated SF and HD NaLS in comparison with the spectra of the untreated samples is a shift in the position of the OH stretching band from 3396 to 3419 cm^{-1}. This shift to lower frequency is characteristic for intermolecular hydrogen bonding. This bonding effects a weakening of the O—H bond; consequently, its frequency is shifting to lower frequencies.[8]

According to the data presented in Table I and IR spectra, it looks likely that hydrolytic (PWSL) and organosolv (Alcell) lignins have the highest thermal stability in comparison with the other lignins. As effect of thermal treatment, their loss in weight is about 2% in either nitrogen or oxygen atmosphere; the increase in T_g was of 16°C for PWSL and 12°C for Alcell, and no visible changes occurred in IR Spectra.

As an effect of thermal treatment, the loss in weight of Indulin is more than 4%, its T_g increased with about 35°C, and modification in OH and C=O stretching absorption bands of the IR spectra are visible.

Both lignosulphonates are affected the most by thermal treatment, as can be seen from their loss in weight of more than 5% (5.9% in air and 5.5% in nitrogen for HD NaLS and 5.2% in air and 4.7% in nitrogen for SF NaLS), their increase in T_g beyond the limits, and their high degree of association through hydrogen bonding.

It has been noted that during the thermolysis,

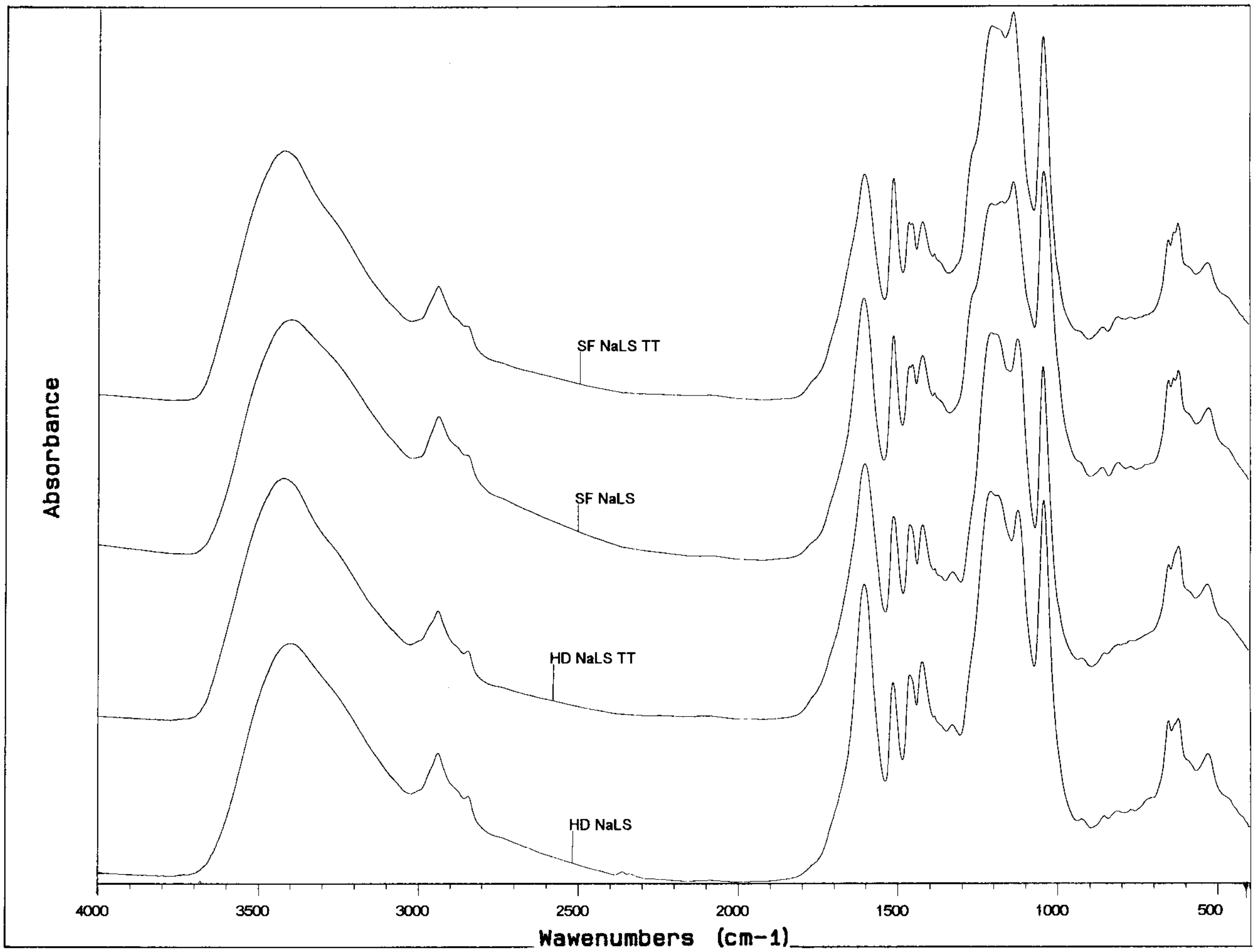


Figure 2 FTIR spectra of lignosulfonates dried and thermally treated.

the thermal decomposition of lignins takes place in two stages. The first stage, which occurs at comparatively low temperatures (100–250°C), involves dehydration and a very minor hydrolytic cleavage occasioned by the formed water.[9,10]

The T_g increasing, as well as changes in IR spectra of all the thermally treated lignins, suggest an intermolecular dehydration process.

Processibility of the Blends

The fusion characteristics of PVC compounds are influenced principally by the type of resin as well as 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. In turn, improper processibility may have a negative effect on the mechanical properties of PVC and its weatherability.[11]

The influence of different lignins on the processibility of PVC–L blends is indicated in Table II. The data presented in this table were obtained from torque vs time curves generated by the torque-rheometer.

The fusion torque and fusion time correspond to the end of the melting process. Beyond this point, torque is decreasing gradually, caused by frictional heating, until an equilibrium torque which corresponds to an equilibrium viscosity.

As can be seen from the data presented in Table II, a decrease in fusion time and a higher torque are noticeable in all the blends in comparison with PVC control. It looks likely that on the first stage of processing, the lignin acts as a rigid body, which enhances the shear force suffered by PVC grains. Consequently, the PVC agglomerates are broken

Table II Fusion Characteristics of PVC–Control and PVC–L Blends

	Fusion		Equilibrium	
Specimen Identification	Torque (m g)	Time (min)	Torque (m g)	Temp (°C)
PVC–Control	3270	1.30	2070	203
PVC–PWSL	3900	0.75	1900	202
PVC–SF NaLS	3780	0.92	2175	203
PVC–HD NaLS	3790	0.93	2200	203
PVC–Alcell	4240	0.65	1990	202
PVC–Indulin	4070	0.70	1970	202

down to primary particles more rapidly in blends, and fusion time decreases. In addition, the presence of rigid lignin will increase the external friction between melt and the contact surfaces around it, and the maximum torque will increase.

The presence of lignin influences, in a lower measure, the equilibrium torques and temperatures. The equilibrium torques are slightly lower for the blends with PWSL, Indulin, and Alcell in comparison with the equilibrium torque of PVC control. This, in fact, represents a beneficial effect of lignins because a lower equilibrium torque reflects a lower viscosity of the melt. The opposite is noticeable for lignosulfonates due probably to their higher content of inorganic materials, rendering them more rigid, even in the molten state.

Mechanical Properties of PVC–L Blends

The mechanical properties of PVC–L blends, such as tensile strength at yield and break and impact strength, were measured before and after seven days of artificial weathering and were correlated with the properties of PVC control. The results of the tests are shown in Table III.

Unweathered Blends

From Table III, it is apparent that all lignins except SF and HD ligno-sulfonates afford an reinforcement of the blends, as expressed by the increase in tensile strength at yield. The matrix reinforcement is accompanied by substantial losses of the strength at break. The influence of the lignins on the strength at yield increasing and strength at break decreasing in relation to the respective data of PVC control can be summarized as follows.

Yield Strength Increasing (%)		Breaking Strength Decreasing (%)	
Alcell	+7	Alcell	−12
Indulin	+5	Indulin	−18
PWSL	+4	PWSL	−21
HD NaLS	−5	HD NaLS	−23
SF NaLS	−11	SF NaLS	−26

All the specimens of the blends do not fail at the point of highest stress but rather gradually. From these data, one may conclude that the inter-

Table III Mechanical Properties of PVC–Control and PVC–L Blends

	Unweathered Specimens			7-Day Weathered Specimens		
	Tensile Strength (MPa)			Tensile Strength (MPa)		
Specimen Identification	Yield	Break	Impact Strength (Jm^{-1})	Yield	Break	Impact Strength (Jm^{-1})
PVC–Control	51.63	48.25	87.01	55.76	47.49	82.02
PVC–PWSL	53.90	36.70	44.84	57.70	—	35.21
PVC–SF NaLS	45.93	34.65	42.70	48.16	35.21	41.10
PVC–HD NaLS	48.83	35.80	42.70	49.36	—	45.66
PVC–Alcell	55.38	41.14	40.02	59.53	38.08	31.37
PVC–Indulin	54.45	38.15	39.90	58.76	38.44	32.56

action between lignin and PVC, which probably produces a sort of network between the two polymers[6] and consequently improves their mutual adherence, decreases in the following order: Alcell > Indulin > PWSL > HD NaLS > SF NaLS.

As can be seen from Table III, all the lignins contribute to a drastic decrease of the resistance to impact of the blends. The values of the impact strength data for all PVC–L blends are closer than the values of the yield strength increasing or break strength decreasing. Their variation is between 52 and 46% of the impact strength of PVC control.

Because PVC resin is a brittle material, the formulations of rigid PVC compounds always include 5–10% impact modifiers. They interfere with crack development in the matrix and can act as internal energy absorbers. As a general rule, the more effective impact modifiers are those with a more rubbery nature.

Lignin can be considered to be a highly brittle polymer,[12] and the drastic reduction of the impact strength of the blends is a consequence of the lignins' brittleness. In addition a slight decomposition of lignins caused by the elevated processing temperature imposed by rigid PVC processing, as well as quite long processing time imposed by batch laboratory conditions, could also explain the impact strength reduction of the blends.

Weathered Blends

Table III shows mechanical properties retention of the PVC control and PVC–L blends after 7 days of artificial weathering. This has as an effect an embrittlement of the PVC control and blends, which is expressed by the increase of the tensile strength at yield and a decrease of the tensile strength at break.

The influence of weathering on the strength at yield increasing and the strength at break decreasing in correlation with the corresponding data for unweathered specimens can be summarized as follows.

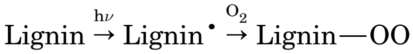
Yield Strength Increasing		Breaking Strength Decreasing	
PVC–control	+2%	PVC–control	−2%
PVC–Indulin	+8%	PVC–Indulin	+1%
PVC–Alcell	+8%	PVC–Alcell	−5%
PVC–SF NaLS	+7%	PVC–SF NaLS	+2%
PVC–PWSL	+7%	PVC–PWSL	brittle fracture
PVC–HD NaLS	+1%	PVC–HD NaLS	brittle fracture

These data illustrate, at a macroscopic scale, that due to the exposure to artificial weathering conditions (UV light, moderate temperature, and humidity), the initially developed networks between lignins and PVC resin are modified in different ways (i.e., brittle fracture, as in the case of PWSL and HD NaLS; moderate decrease in strength at break, as in the case of Alcell; or increase in strength at break, as in the case of SF NaLS and Indulin).

It looks likely that the blends with Indulin and SF NaLS are affected by the weathering exposure to a lesser degree than the other blends.

It is important to note that both Indulin and SF NaLS are softwood lignins, with a predominance of guaiacyl units. According to data in the literature, the softwood lignins are more cross-linked and therefore more resistant to degradation than hardwood lignins.[13]

On the other hand, in the structure of softwood lignin, guaiacyl units with a sterically hindered phenol structure prevail. As an effect of UV light and atmospheric oxygen, many of the chemical bonds of lignin (C—C, C—O, etc.) are broken with the formation of free radicals, as follows:



$$\text{Lignin} \xrightarrow{h\nu} \underset{\text{R}\bullet}{\text{Lignin}^{\bullet}} \xrightarrow{\text{O}_2} \underset{\text{ROO}\bullet}{\text{Lignin—OO}^{\bullet}}$$

The hindered phenolic structures in softwood lignin represent potential radical scavengers (antioxidants) by terminating chain reactions induced by oxygen.[14]

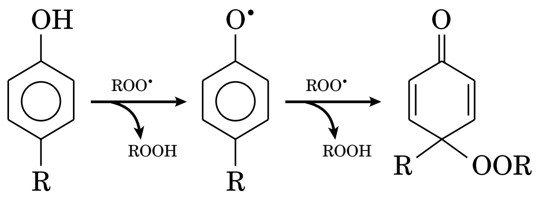


Table IV Water Absorbtion and Water Retention of PVC–Control and PVC–L Blends

Specimen Identification	Water Absorbed During 84 h Immersion at 50 ± 2°C (%)	Retention of Water after 24 h Drying at 50 ± 2°C (%)
PVC–Control	0.358	—
PVC–PWSL	0.365	—
PVC–SF NaLS	1.043	0.191
PVC–HD NaLS	1.545	0.448
PVC–Alcell	0.323	0.027
PVC–Indulin	0.423	0.050

It is interesting to note that sterically hindered phenols are currently used in PVC compounds as primary antioxidants, i.e., to trap free radicals formed during PVC autooxidation.[15] The changes of the impact strength for the control and blends as an effect of artificial weathering in correlation with the corresponding data for unweathered specimens are as follows: PVC–control, −6%; PVC–HD NaLS +7%; PVC–SF NaLS, <0.1%; PVC–Indulin, −15%; PVC–PWSL, −21%; PVC–Allcel, −24%.

The increase of the impact strength of HD NaLS and practically unchanged value of SF NaLS blends after weathering was very surprising, and it was suspected that presence of water could be at the origin of these values. Some hygroscopic thermoplastics behave similarly. For example, at room temperature, dry nylon has a notched impact strength of about 4 KJ m^{-2}, and wet nylon has an impact strength greater than 20 kJ m^{-2}.[16] The results of the water absorption test (Table IV), particularly the retention of water after drying of the immersed specimens, indicate that these two blends have the highest degree of water retention, which correlates well with their impact strength increasing.

In conclusion, the results of the mechanical test obtained before and after weathering for PVC–L blends and correlated with the results for PVC control indicated the following.

1. All lignins except lignosulfonates afford a reinforcement of the blends, as expressed by the increase in the strength at yield. This reinforcement is accompanied by losses in the strength at break. Lignosulfonates blends are characterized by the decrease of both strength of yield and strength at break.
2. As an effect of artificial weathering, the blends' toughness, as expressed in strength at break, declines dramatically for the blends with PWSL and HD NaLS, declines for the blends with Alcell, and increases very slightly for the blends with Indulin and SF NaLS.
3. All the lignins contribute to a drastic decrease of blends' impact resistance. When compared with data for PVC control for the unweathered blends, impact strength reduction is higher, in relative terms, than that of weathered blends.

It should be mentioned that owing to our batch processing conditions, the processing times were longer than those utilized usually in the rigid PVC extrusion, and even the impact strength of PVC–control was lower than the strength of extruded profiles. However, the effect of processing is reflected in the same manner for both the control and the blends.

Thermal Properties and Infrared Spectra

Thermal Properties

The possible changes occurring in the morphology of the PVC matrix at a molecular scale as the effect of lignin presence were correlated with values of T_g and tan δ (ratio between damping or loss modulus and storage modulus) of blends because it is known that both those properties are particularly sensitive to the molecular motions within a viscoelastic material.

In the glass transition region, damping is high, due to the onset of microbrownian motion within the molecular structure of the main chain, and so

Table V Thermal Properties of PVC–Control and PVC–L Blends

	Unweathered Specimens		7-Day Weathered Specimens	
Specimen Identification	T_g (°C)	Tan δ	T_g (°C)	Tan δ
PVC–Control	87.4	0.922	88.1	0.930
PVC–PWSL	87.3	0.941	88.6	0.930
PVC–SF NaLS	86.7	0.891	88.0	0.871
PVC–HD NaLS	86.4	0.936	87.6	0.889
PVC–Alcell	87.6	0.955	89.3	0.936
PVC–Indulin	86.8	0.892	88.5	0.915

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. The magnitude of tan δ, which is a characteristic of the rubbery state of the polymers, has little meaning in the glassy state, where molecular motion is practically nonexistent.[17]

The results of the dynamic mechanical analysis (DMA) test are shown in Table V. When compared with data for PVC control they can be summarized as follows. The T_g's of the blends are very close to that of PVC control. For all the blends with hardwood lignin, the values of tan δ increase slightly, suggesting an increase in molecular mobility in the rubbery state. For the blends with softwood lignin, the slightly lower values of tan δ suggest a decrease in polymer chain segments mobility in the rubbery state.

The lower values of tan δ and an unchanged magnitude of T_g suggest that the chain molecular mobility in the rubbery state is lowered by the presence of some restraints. It is known that the initiation of microbrownian motions within the molecular chains in the transition region occur gradually. The presence of only a few still frozen-in segments will impose some restraint in chain mobility, and, consequently, tan δ will decrease. Higher values of T_g, as well as a higher degree of crosslinking of softwood lignins in comparison with hardwood lignin, could be responsible for the presence of such kind of segments in the rubber state of the respective blends.

By analyzing the T_g and tan δ data obtained for weathered specimens, a slight increase of T_g, accompanied by a slight decrease of tan δ, is noticeable for all the specimens except the PVC control and PVC–Indulin blends.

The T_g increasing and the corresponding tan δ decreasing suggest that the artificial weathering yields to a certain degree of crosslinking within the polymer chains in most of the blends. The slightly increase of T_g, as well as a slight increase of tan δ in the case of PVC control and PVC–Indulin blends, reflect both a certain degree of crosslinking (T_g increasing) and a certain degree of chain scission (tan δ increasing). Information in the literature regarding changes in properties of rigid PVC during weathering indicates that chain scission rather than crosslinking reaction is the predominant mechanism in the degradation of the exterior exposed rigid PVC compounds.[18,19] Also, information in the literature regarding photodegradation of lignin in presence of oxygen clearly indicates that UV light in the presence of oxygen yields low-molecular-weight degradation products.[20,21]

It looks likely that our results are, in most of the cases, in contradiction with data in the literature. However, when assessing the characteristics of weathered specimens, the effect of physical aging should be also taken into consideration. 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 the aging time, even in the solid state, the macromolecules have tendency to approach the equilibrium state, which is characterized by more molecular ordering. Morphological changes in polymers occur as an effect of physical aging, which causes changes in physical and mechanical properties.[22] The embrittlement of most of the weathered specimens, as well as the increase in T_g as determined by DMA, are mostly the effects of physical aging. The differences between other properties, such as

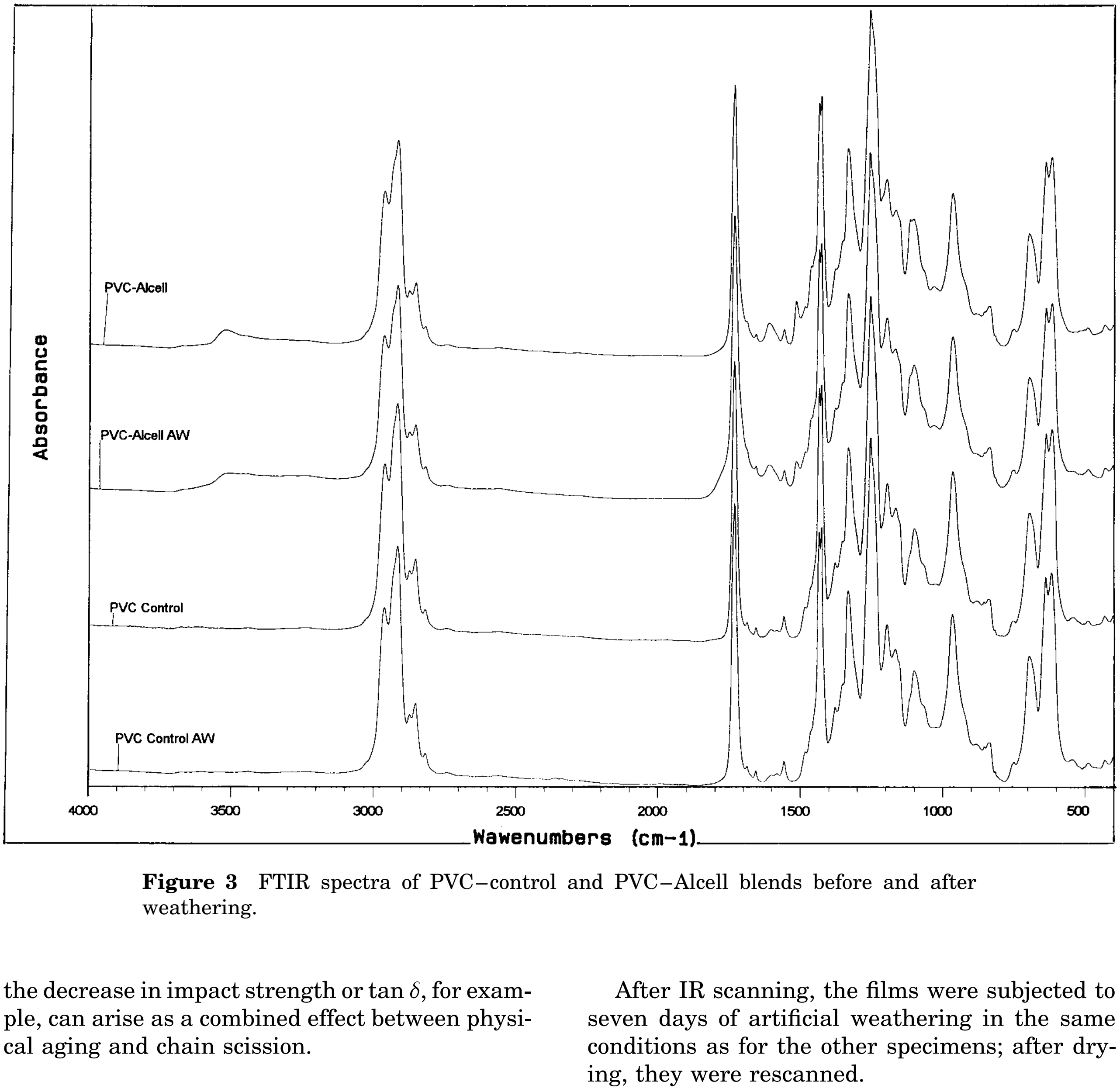


Figure 3 FTIR spectra of PVC–control and PVC–Alcell blends before and after weathering.

the decrease in impact strength or tan δ, for example, can arise as a combined effect between physical aging and chain scission.

Infrared Spectra

Presence of strong spectral contribution of the several additives of PVC control results in a complex IR spectra for both PVC and PVC–L blends, restricting the amount of information that can be gained concerning the changes that have occurred as effect of PVC blending with lignin and as an effect of weathering. Most of the prominent lignin absorption peaks are barely detectable in the blend spectra except the absorption band of hydroxyl group. To illustrate, spectra of PVC control and PVC–Alcell blend films before and after weathering are presented in Figure 3.

After IR scanning, the films were subjected to seven days of artificial weathering in the same conditions as for the other specimens; after drying, they were rescanned.

The main variation in the blends spectra before and after weathering occurs in the domain of OH stretch absorption; their spectra in this region are presented in Figure 4 for the blends with PWSL, Alcell, and Indulin and in Figure 5 for the blends with lignosulfonates.

Table VI shows the position of OH stretching absorption maxima in lignins and in PVC–L blends before and after weathering.

As can be seen from the data presented in Table VI, mixing of PVC with lignins produces large shifts to lower frequencies in the OH stretching absorption band. As discussed earlier, when hydrogen bonding occurs, the force constant for

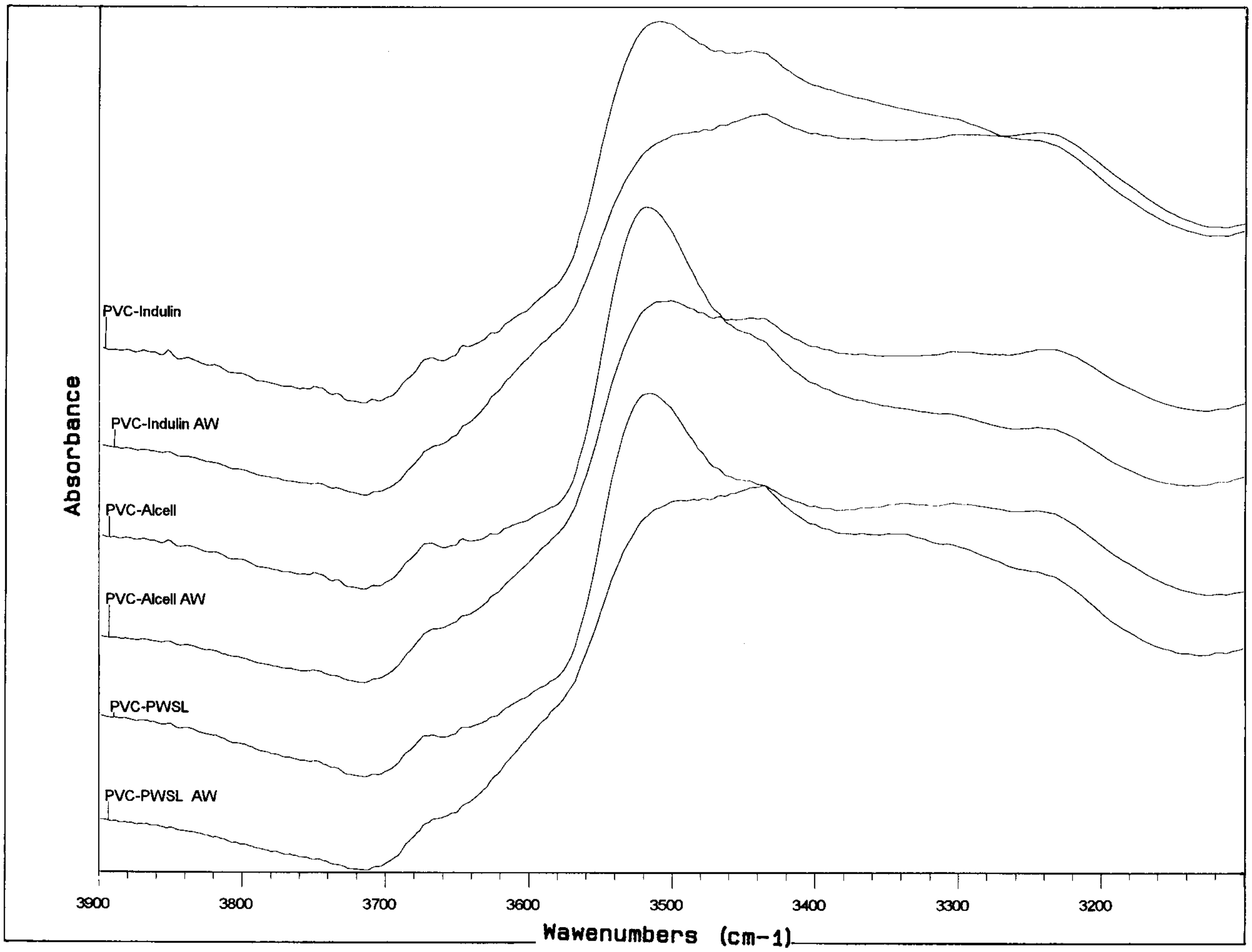


Figure 4 FTIR spectra of PVC blends with PWSL, Alcell, and indulin before and after weathering.

stretching of the H—O bond will be reduced, as well as the frequency of OH stretch absorption. The shifts in the OH stretching frequency to lower frequencies are by 39 cm^{-1} for blends with HD and SF lignosulfonates, 90 cm^{-1} for those with PWSL, 92 cm^{-1} for blends with Alcell, and 95 cm^{-1} for blends with Indulin for the unweathered blends. If one compares the OH absorption band in lignin spectra (Figs. 1 and 2) with OH absorption band in blends spectra (Figs. 4 and 5), the band broadening is visible in all the blends. OH band broadening and shifts in frequencies are interpreted as evidence for interactions between hydroxyl groups of lignins and α hydrogen of PVC. According to these results, the hydrogen bonding between lignins and PVC in the blends would increase in the following order: Indulin > Alcell > PWSL > HD NaLS > SF NaLS. This sequence is practically in agreement with the results of mechanical tests for the unweathered specimens. From the examination of IR spectra of weathered specimens, it is apparent that seven days of artificial weathering do not affect the PVC control spectra (see Fig. 3). For all the lignin blends, the main variations in the spectra are evident in the domain of hydroxyl stretching absorption. Figures 4 and 5 clearly show the broadening of this band, and Table VI shows its shifting to higher frequencies for PWSL, Indulin, and Alcell blends. Based on the OH frequencies increasing in these blends, one may assume a weakening of the interaction between PVC and the respective lignins. On the other hand, the OH frequencies values in the artificially weathered HD and SF NaLS blends yield

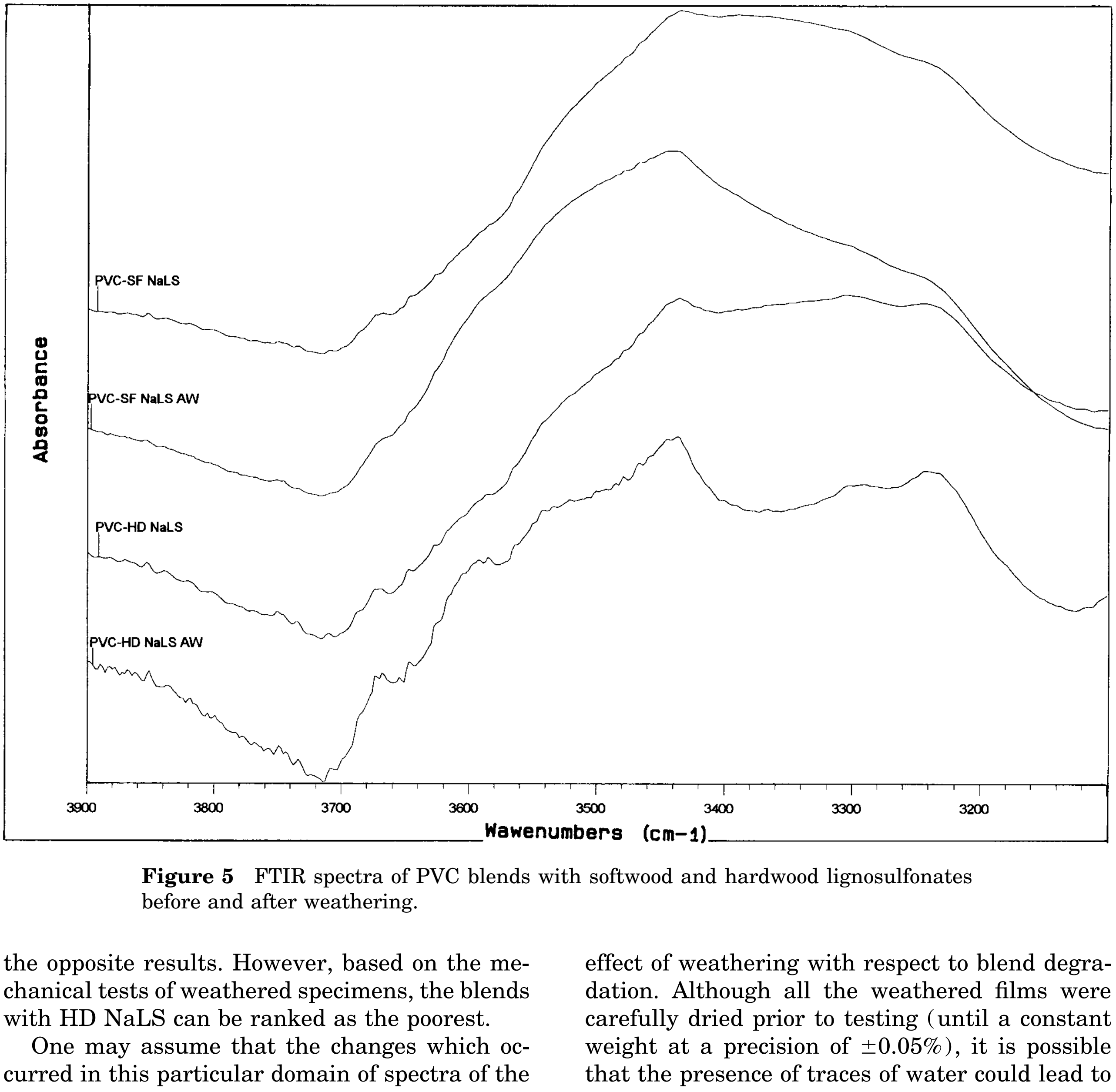


Figure 5 FTIR spectra of PVC blends with softwood and hardwood lignosulfonates before and after weathering.

the opposite results. However, based on the mechanical tests of weathered specimens, the blends with HD NaLS can be ranked as the poorest.

One may assume that the changes which occurred in this particular domain of spectra of the weathered specimens do not accurately reflect the effect of weathering with respect to blend degradation. Although all the weathered films were carefully dried prior to testing (until a constant weight at a precision of ±0.05%), it is possible that the presence of traces of water could lead to these contradictory results, taking into account

Table VI Positions of the Hydroxyl Stretching Absorption Maxima in Lignins and in PVC–L Blends Before and After Weathering

Specimen Identification	Unblended Lignin (cm^{-1})	Blend Before Weathering (cm^{-1})	Blend After Weathering (cm^{-1})
PVC–PWSL	3426	3516	3436
PVC–SF NaLS	3396	3435	3436
PVC–HD NaLS	3396	3435	3438
PVC–Allcel	3427	3519	3502
PVC–Indulin	3416	3511	3436

that the hydroxyl stretch region is susceptible to interference from water, either through overlap with the absorptions of hydrogen-bonded water or by the presence of water changing the nature and extent of hydrogen bonding in the specimens.[23]

CONCLUSION

Examination of different lignins and lignin derivatives representing a range of significant differences in regard to delignification processes, chemical functionality, and thermal stability in polyblending with a commercial formulation of rigid PVC compound discloses differences in their influence on the mechanical, thermal, and weathering properties.

The mechanical properties, particularly strength at yield and break of the polyblends, as well as IR spectra, demonstrated an interaction between the two polymers occurring between OH groups of lignin and α hydrogen of PVC. This interaction decreases in the following order: Indulin $>$ Alcell $>$ PWSL $>$ SF and HD NaLS.

A major drawback of all the lignins is that they diminish the impact strength of the blends in comparison with that of PVC control. In addition, the weathering stability of the blends is lower than that of PVC control.

A slight decomposition of lignins caused by the high temperature imposed by rigid PVC processing could partially explain their effect on the impact strength and weathering stability of the blends.

If all the obtained results are taken into account, a tentative rating would rank the softwood lignins above hardwood lignins. Blending a softwood lignin with a plasticized PVC, which requires a lower processing temperature, could lead to better results. A further study should be done to verify if this supposition is correct.

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