

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Poly(Vinyl Chloride)-Lignin Blends for Outdoor Application in Building

D. Feldman^a; D. Banu^a; S. El-Raghi^a

^a Centre for Building Studies, Concordia University, Montreal, Quebec, Canada

To cite this Article Feldman, D. , Banu, D. and El-Raghi, S.(1994) 'Poly(Vinyl Chloride)-Lignin Blends for Outdoor Application in Building', Journal of Macromolecular Science, Part A, 31: 5, 555 – 571

To link to this Article: DOI: 10.1080/10601329409349738

URL: <http://dx.doi.org/10.1080/10601329409349738>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

POLY(VINYL CHLORIDE)–LIGNIN BLENDS FOR OUTDOOR APPLICATION IN BUILDING

D. FELDMAN,* D. BANU, and S. EL-RAGHI

Centre for Building Studies
Concordia University
Montreal, Quebec H3G 1M8, Canada

ABSTRACT

The paper presents preliminary work carried out to prepare and evaluate the blends obtained from an unplasticized poly(vinyl chloride) (PVC) compound, formulated with several loadings of TiO_2 [between 0 and 10 parts per hundred parts (phr) PVC] and a kraft lignin (Tomlinite) in amounts up to 7.5 phr. A series of blends in which lignin (L) replaced partially or totally the TiO_2 filler were made on a laboratory scale. The potential utilization of this type of blend could be in the construction and building industry for outdoor application. The influence of L on the thermal stability and melt processing of the blends are discussed as well as on their stress-strain properties before weathering and after about a 2000 hour artificial weathering period in the presence of UV light, humidity, and moderate temperature. All the data are correlated with those of a PVC control loaded with 10 phr TiO_2 .

INTRODUCTION

Today, polymer blending has become one of the most commercially important and inexpensive ways of developing new materials from readily available base polymers. The main aim of polyblending is the production of good-performance materials at a reduced cost or the modification of some specific properties of polymers. This is achieved through the infinite blending possibilities, the ability to use existing

or more flexible processing equipment, and the capacity to combine expensive polymers with ordinary and abundant ones.

According to recent literature data, in 1989 United States sales of commodity blends represented 17% of total US plastics [1].

Today the amount of PVC produced worldwide represents about 30% of the total production of thermoplastics; this is second only to the production of all polyolefins [2]. Due to its commercial value, there are already established blends with PVC and other common or less common polymers whose practical benefits are improved processibility, improved impact strength, and increased glass transition temperature [1].

PVC is a polymer which is very sensitive to the weathering effects. Under UV irradiation and in the presence of oxygen and moisture, it undergoes a very fast dehydrochlorination and peroxidation process with the formation of polyenes and subsequent scission and/or crosslinking of the chains [3]. However, much practical experience is now available to provide guidance in the formulation of weather-resistant PVC compounds for outdoor service. Among the formulation factors affecting the outside performance of PVC compounds, the following are particularly important: PVC molecular weight (*K* value), the stabilizer system, the nature of the impact modifiers, and the presence of common pigments. One of these is titanium dioxide (TiO_2) which is often introduced at levels up to 10–12 phr [4, 5]. At these loadings TiO_2 can enhance the weathering properties of PVC products because of its ability to absorb to a certain degree UV radiation falling on the polymer [2b, 4].

TiO_2 is approximately 50% more costly than the unplasticized PVC (uPVC) used for outdoor service [4], and PVC producers are looking for ways to reduce their TiO_2 consumption [6].

The purpose of this paper is to present preliminary work carried out to prepare and evaluate the blends obtained from uPVC compounds, formulated with several loadings of TiO_2 (between 0 and 10 phr) and kraft lignin (L) in an amount up to 7.5 phr. A couple of blends were prepared in which L partially or totally replaced the TiO_2 .

The potential utilization of this type of blends could be in the construction and building industry for such outdoor applications as siding or window and door profiles.

The selection of L for these particular blends was justified by its low cost, i.e., about \$0.20–0.30/kg [6], and by some of its specific functions in plants such as:

- Response to mechanical stresses as a composite material component
- Response to chemical stresses by inhibiting atmospheric degradation and functioning as an oxidant and UV absorber [7]

The preliminary study includes the following evaluations:

- Processibility of PVC-L blends
- Effect of L on thermal stability of PVC-L blends
- Mechanical properties of PVC-L blends before and after artificial weathering period

Kraft L (Tomlinite) used in the present study is a technical product resulting from the alkaline delignification of a mixture of hardwoods. The basic chemical

components of L (primarily hydroxy and methoxy derivatives of phenyl propane units) are naturally bonded together by a set of linkages to form a very complex matrix. This matrix comprises a variety of functional groups such as hydroxyl, methoxyl, carbonyl, and carboxyl which impart a high polarity to the L macromolecules.

At first glance it appears likely that the PVC-L pairs meet the principal criteria for forming a miscible blend taking into account the criteria of miscibility of two polymers [10-12].

1. Their close solubility parameters, δ . δ PVC = $9.7 \text{ cal}^{1/2} \cdot [(\text{cm})^3]^{-1/2}$ [2c], estimated δ for Tomlinite = $\sim 10 \text{ cal}^{1/2} \cdot [(\text{cm})^3]^{-1/2}$ [8].
2. Their molecular weight. For PVC, \overline{M}_w = about 150,000 and \overline{M}_n = about 60,000 at $K = 67$; for L, \overline{M}_w = 2800 and \overline{M}_n = 650 [9]. The effect of molecular weight on miscibility is based on the Flory-Huggins theory. According to this theory, the entropy gained on mixing polymers is inversely related to their \overline{M}_n . Thus, a particular polymer mixture can be made more miscible by reducing the molecular weight of one or both components [11]. In our case the low molecular weight of L could assure the miscibility of the blend.
3. Their functionality, i.e., the possible interaction between the carbonyl groups of L and the α -hydrogen of PVC, or the possible interaction between the α -hydroxyl group of L and the chlorine of PVC.

Two polymers are often termed miscible if they form a single, homogeneous phase as determined by an optical or thermal method and if intimate mixing is achieved on a molecular scale. However, by far the widest range of polymeric additives for PVC falls into a broad category that can be classified as partially miscible. Partially miscible blends display some phase separation (microscopically heterogeneous) but a significant degree of polymer mixing on a molecular scale occurs, producing mechanically compatible phases with useful properties [13].

EXPERIMENTAL

Materials

PVC Resin

A commercial unplasticized PVC resin, Geon 85862, was supplied by BFGoodrich 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 given in Table 1, is designed for outdoor applications. For the study of the effect of L on the thermal stability of PVC-L blends, the same PVC resin was used and the compound was formulated only with the heat stabilizer.

Lignin

L was a kraft-type extracted from a mixture of hardwoods. It was supplied by Domtar Research Centre, Senneville, Quebec. Its characteristics are reported elsewhere [9].

TABLE 1. Composition of PVC Compound

Ingredient	phr level
PVC resin	100
Dimethyl tin dithioglycolate stabilizer	2
Acrylic processing aid	1.5
<i>n</i> -Butyl acrylate-based impact modifier	6
Lubricants	3.75
Titanium dioxide (nonchalking silica coated)	Variable

Preparation of Blends

The blends were prepared from the PVC compounds containing 7.5, 5, and 2.5 phr TiO₂ and the corresponding quantity of L, i.e., 2.5, 5, and 7.5 phr, or from PVC compound without TiO₂ and 5 and 7.5 phr L.

They will be designated in the text as follows:

PVC control compound with 10 phr TiO₂: PVC-control

PVC compound with 7.5 phr TiO₂ and 2.5 phr L: PVC-2.5L/T

PVC compound with 5. phr TiO₂ and 5 phr L: PVC-5L/T

PVC compound with 2.5 phr TiO₂ and 7.5 phr L: PVC-7.5L/T

PVC compound without TiO₂ and 5 phr L: PVC-5L

PVC compound without TiO₂ and 7.5 phr L: PVC-7.5L

The parts of TiO₂ and L are referred as parts per hundred parts PVC resin (phr), and the term PVC compound describes the formulation containing all the additives as mentioned above.

PVC and the corresponding amount of L, both in the powder state, were first dry mixed under stirring for 5 minutes and thereafter the dry blends were mixed in the melt state at 195°C and 80 rpm for 8 minutes using a Brabender Batch Mixer Measuring Head equipped with roller blades. This equipment was electrically heated and operated under a fixed condition of temperature insured by temperature control channels. Several batches of 20.5 g each were prepared for each formulation. After melt mixing, the material was ground to a size of about 2–3 mm and molded by compression molding to sheets of about 3 mm thickness in a mold covered by metal plates on both sides. The mold was heated at 195°C in a laboratory press for 10 minutes under 6.9 MPa pressure. After 20 minutes cooling with air at room temperature, the resulting sheets were cut with a cutting die into shoulder-shaped specimens (ASTM D 638 Type V) for mechanical testing.

PVC-L blends for differential scanning calorimetry (DSC) investigation of the thermal stability were prepared by spraying a mixture of corresponding amounts of 2 wt% solutions of the two polymers in tetrahydrofuran into a 6-fold excess of hexane for precipitation. After filtration, the obtained samples of PVC-L blends were dried for 48 hours in vacuum at room temperature.

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-B lamps with a peak emission at 313 nm and spectral energy distributed between 280 to 390 nm.

In the view of many researchers, most of the photochemical changes suffered by plastics, including PVC, in natural weathering are attributable to the 290–315 nm UV band [2d]. Recent studies concerning the photodegradation of compounded, thermally processed rigid PVC formulations demonstrated photochemical yellowing due to wavelengths in the 280–340 nm region [5, 14].

Specimens of PVC-control and PVC-L blends were subjected to several cycles of 4 hours each of UV exposure at an equilibrium temperature of $60 \pm 1^\circ\text{C}$ alternating with condensation exposure at an equilibrium temperature of $50 \pm 1^\circ\text{C}$. The number of days of accelerated weathering was 7, 20, 28, 63, and 84, in accordance with ASTM G-53.

Physical Testing and Characterization

The influence of L on the melt processing characteristics of PVC-L blends was determined with a torque rheometer operated under fixed conditions of shear and temperature. A C.W. 1636 Brabender Plasticorder in conjunction with a Brabender Batch Mixer Measuring Head (described above) was used for measurements in the following conditions:

Temperature of the mixer measuring head: 195°C

Rotation of the roller blades: 80 rpm

Time of mixing: 8 minutes

The processing temperature was indicated by the PVC producer, and the rpm and time of mixing were experimentally determined.

The torque required to overcome the flow resistance of the melted blend was measured and recorded versus time. The maximum point of the curve obtained was identified as the fusion torque and represents an average of at least 5 determinations for each blend. The temperature of the melt in the Batch Mixer Measuring Head was measured by a thermocouple and continuously displayed. Temperature readings were taken every 30 seconds, and the maximum temperature reached by each blend was indicated as the maximum temperature of the melt. This also represents the average of at least 5 similar batches readings.

All the specimens were visually examined for changes in color and gloss, and microscopically examined for the presence of cracks or crazes using an Olympus model BHM reflected bright field incident light microscope with $100\times$ magnification.

The mechanical properties—tensile strength and elongation at break—were determined in accordance with ASTM D638 using an Instron 1125 universal testing machine at a crosshead speed of 1 mm/min and at a temperature of $23 \pm 2^\circ\text{C}$. All

the values plotted on the graphs are an average of 5–10 determinations. Testing of unweathered samples of the PVC-control and the PVC-L blends was performed after one week following specimen preparation and after each specified period of laboratory accelerated weathering. All the specimens were conditioned at $23 \pm 2^\circ\text{C}$ and 50% RH for 48 hours before testing.

Thermal analysis was carried out by means of a TA instrument (former DuPont) Thermal Analysis System consisting of a 2100 Thermal Analyst computer and a 912 Differential Scanning Calorimeter (DSC). For DSC measurements, samples for about 7–10 mg were run at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere between room temperature and 195°C .

RESULTS AND DISCUSSION

Thermal Degradation of PVC in PVC-L Blends

Thermal degradation of PVC is manifested by the evolution of hydrogen chloride. It is widely accepted that dehydrochlorination involves progressive “unzipping” of neighboring chlorine and hydrogen atoms along the polymer chain. Scission to a lower degree and crosslinking to a higher degree take place as degradation proceeds. All these effects contribute to the general deterioration of properties [15].

Blending of polymers usually results in reduction of thermal stability, especially when addition of the second polymer is quite large [16].

Braun et al. [17, 18] reported the negative influence of poly(styrene-*co*-acrylonitrile), poly(styrene-*g*-butadiene), and poly(styrene-*co*-acrylonitrile-butadiene) on the thermal stability of heterogeneous 1:1 blends of PVC with these polymers. In 1:1 blends of PVC with polystyrene, the thermal stability of PVC is not affected. The authors observed that the T_g of the PVC phase rises slower during annealing for increasing periods at 200°C in PVC-polystyrene blends (comparable with the rising of the T_g of PVC which is due to crosslinking) whereas in the other blends there is a stronger increase of T_g . The authors explained the large increase in T_g in the other blends by an accelerated crosslinking attributable to the negative influence of the double bonds and/or the nitrile group to the thermal stability of PVC. Braun et al. studied the thermal stability of the blends by DSC with samples stabilized with an organic tin stabilizer and compared the DSC results with those obtained by determining the amount of HCl evolved by conductivity measurements. All the data were well correlated.

As the DSC method appears to be a useful investigation tool for the thermal stability of PVC-polymer blends, we studied the thermal degradation of PVC-L blends (prepared from polymers solutions, see the Preparation of Blends Section) during annealing in the DSC at 195°C for up to 60 minutes. DSC samples were heated from room temperature to 195°C , kept at 195°C for 10 minutes, and then cooled to room temperature. This procedure was repeated up to 6 times, and T_g was determined after each cycle. The annealing temperature corresponds with the melt mixing temperature utilized for blends preparation. The curves in Fig. 1 show the variation of the T_g of PVC and PVC-L blends versus annealing time at 195°C . The T_g of PVC rose slowly during the annealing time, indicating a crosslinking reaction; the same trend was observed for the PVC-L blends. As can be seen, the T_g values

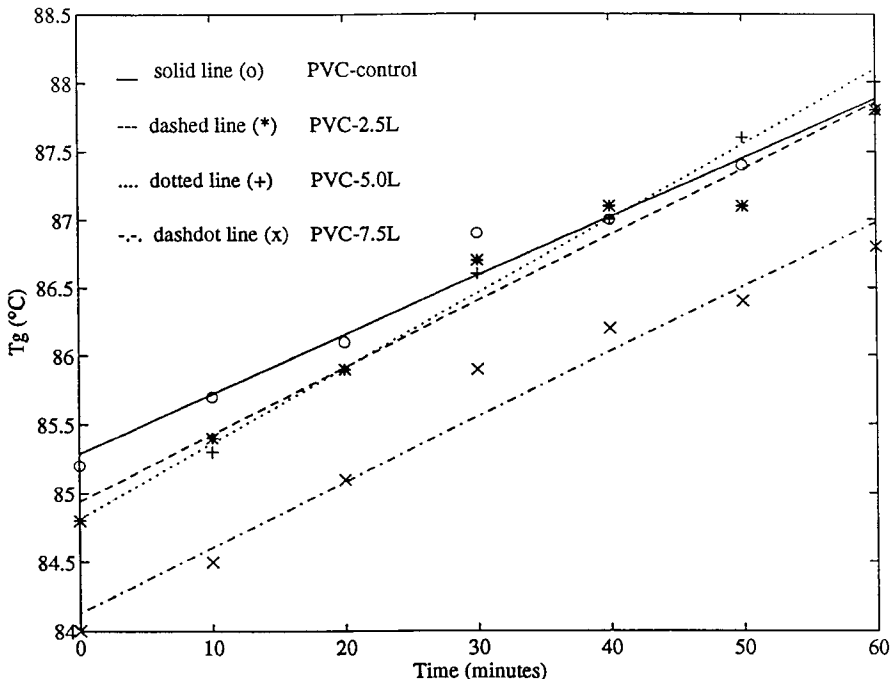


FIG. 1. Dependence of T_g on annealing time at 195°C for PVC and PVC-L blends.

are very close in all cases. Figure 2 shows the DSC thermograms after the first run (annealing time, 0 minutes) and the second run (annealing time, 10 minutes).

In the first DSC recordings, two T_g 's are easily recognizable for PVC-L blends; one at around 85°C, close to that of the PVC control, and the second at around 175°C, further than the L's T_g (which is around 131°C). The DSC thermogram after 10 minutes annealing time presents only one T_g , which is located at around 85°C for all the PVC-L blends, and slightly shifted in comparison with its location in the first run.

Figures 1 and 2 data suggest that:

1. The L presence in proportions from 2.5 to 7.5 phr does not affect the thermal stability of PVC in PVC-L blends.
2. The PVC-L blends prepared from solution and with any thermal treatment present two T_g 's. After 10 minutes annealing time at 195°C, the second T_g , located at high temperature, is no longer detectable. The presence of only one T_g in all the blends may be an indication of polymer miscibility occurring after thermal treatment.

All lignins are characterized by a broad molecular weight distribution. Several studies on kraft lignin fractionation showed that for the L's fractions, the T_g 's and temperature range of the T_g 's increase with an increase of molecular weight. The increasing T_g 's temperature range reflects an increased degree of branching and condensation in the high molecular weight fraction [19, 20].

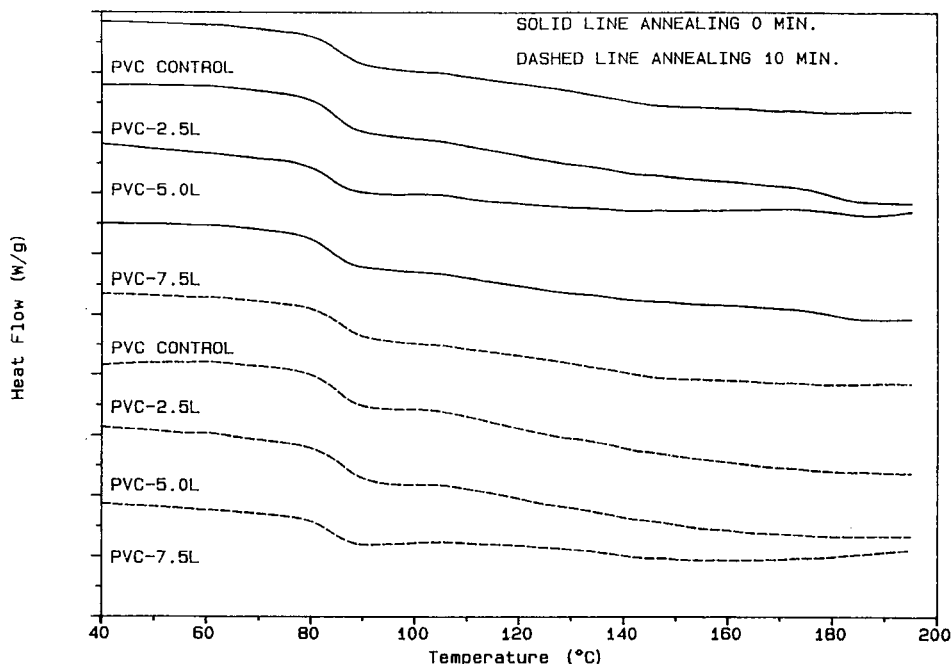


FIG. 2. DSC curves of PVC and PVC-L blends prepared from solution.

In the case of Tomlinite L, three fractions of increasing molecular weight and T_g 's were obtained by successive extractions with organic solvents as described in a previous paper [21] depicting the similarities between Tomlinite L and other kraft lignins.

From the data presented in Fig. 2 (annealing time = 0 minutes), where two T_g 's are detectable in the blends prepared from solution, it appears likely that the interaction between the low molecular weight fractions of L and PVC took place at room temperature in solution. The second T_g in the DSC curve, located in the temperature interval of T_g of the high molecular weight L fraction, indicates immiscibility at room temperature in a solution of these fractions with PVC.

The interaction between the high molecular weight fraction of L and PVC seems to take place only at elevated temperatures which are superior to their T_g , as can be seen in Fig. 2 (10 minutes annealing time), when the second T_g characteristic of the high molecular weight fraction of L is no longer present.

Processibility of PVC-L Blends

The fusion characteristics of PVC compound 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. Improper processibility may have a negative effect on the mechanical properties of PVC and its weatherability [2e]. The influence of L on the fusion characteristics of PVC-L blends is indi-

TABLE 2. Influence of L on the Fusion Characteristics of PVC-L Blends

Fusion characteristics	Composition					
	PVC-C	PVC-2.5L/T	PVC-5.0L/T	PVC-7.5L/T	PVC-5.0L	PVC-7.5L
Fusion torque (m·g)	3830	3510	3770	3950	3830	4100
Maximum temperature of the melt (°C)	196	198	197	195	195	195

cated in Table 2. As can be seen, the data are close to each other and also close to PVC control characteristics, suggesting that the presence of L did not have a negative effect on the processibility of PVC-L blends.

Visual and Microscopic Examination of PVC-Control and PVC-L Blends Exposed for Different Weathering Periods

For exterior PVC applications, in addition to the effect of artificial weathering on the mechanical properties, the durability test should also include color and gloss changes, chalking, and the development of cracks and crazes.

Consequently, specimens of PVC control and specimens of blends were examined periodically for changes in color, and a microscopic examination was undertaken for assessing the development of cracks and crazes. The results of the examination are indicated in Table 3. Changes in aspect, visually or microscopically

TABLE 3. Changes in Aspect of PVC Control and PVC-L Blend Specimens during the Weathering Period (side exposed to UV light and water vapor)

Specimen	Change in color	Appearance of crazes
PVC-control	From white to yellow reddish white	Perceptible at the end of the test (84 days)
PVC-2.5L/T	From dull beige to white gray	Barely perceptible at 28 days examination
PVC-5.0L/T	From beige to light gray	Slightly perceptible at 28 days examination
PVC-7.5L/T	From brown to light gray	Slightly perceptible at 28 days examination
PVC-5.0L	From tan to dull tan; chalking at the end of the test (84 days) examination	Slightly perceptible at 28 days examination
PVC-7.5L	From tan to dull tan; chalking at the end of the test (84 days) examination	Slightly perceptible at 28 days examination

detected, were ascertained only on the exposed side of the specimens. As can be seen from Table 3, the color of the PVC control, which was initially white, changed gradually during the weathering period due to HCl loss. In the case of blend specimens which were initially colored from light beige to tan, the color changed gradually to lighter tones due to L discoloration as an effect of UV light. This effect will be further discussed. Crazes were detected only by microscope and during the specified weathering period; they appeared earlier in PVC-L blend specimens than in PVC-control.

Several hypotheses have been advanced to explain the origin and mechanism of the cracks and crazes appearing on PVC surfaces as an effect of weathering. One hypothesis suggests the appearance of water-sensitive structures according to the following stages:

1. Formation of free radicals through light initiation
2. Formation of peroxides from free radicals and oxygen
3. Formation of peroxi-radicals from unstable peroxide structures
4. Formation of compounds such as alcohols, aldehydes, or ketones from peroxi-radicals

These water-sensitive structures are washed from the surface when it rains, leaving very small cracks or crazes behind [25, 26].

Crack formation is explained in another hypothesis by penetration of water vapor inside the material and subsequent plasticization of the polymer. This process reduces T_g as well as the modulus of a polymer when it operates locally at the tip of a forming crack or craze. This effect should make the polymer yield more easily under the high concentration of stress occurring at that point. However, because the degree of plasticization is still relatively low, the critical strain is not substantially increased. The net result is that propagation of a crack is facilitated and promoted [2f].

According to a third point of view, water or water vapors reduce "by wetting" the surface energy for crack or craze formation and thus facilitate and promote the growth of holes (craze cells and cracks) from extremely small voids in the polymer which serve as nuclei [2f].

It is probable that all the factors on which the aforementioned hypotheses are based are contributory to the formation and development of cracks and crazes on a PVC surface during weathering.

Electron spin resonance spectroscopy had disclosed the formation of free radicals during the degradation of L by UV light. It was demonstrated that phenoxy radicals are intermediates in the degradation and discoloration processes of L. The phenoxy radicals are formed as an effect of UV light, mainly from the aryl α -carbonyl structures and structures containing double bonds in conjunction with aromatic rings, either by a direct hydrogen abstraction mechanism, from free phenolic units, or by generation of singlet oxygen which is able to create phenoxy radicals in turn [27, 28].

In analogy with PVC photodegradation, phenoxy radicals resulting from the effect of UV light on L may lead to the formation of such water-sensitive compounds as alcohols, aldehydes, and ketones. These compounds can be "washed" from the surface when it rains, forming very small cracks and crazes.

In conclusion, several factors may contribute to the early development of crazes on the UV light and condensation exposed surfaces of PVC-L blends.

1. The hydrophilic character of L creates preferential sites for water vapor penetration, thus favoring plasticization and/or reducing the surface energy for craze formation.
2. There is a possibility that UV stabilizer present in PVC compounds does not deactivate the phenoxy radical of L formed by the action of UV light. This would also explain the discoloration of PVC-L blends since the α -carbonyl structures conjugated with aromatic double bonds, as well as phenolic hydroxy groups, are the principal chromophoric groups in L. As was pointed out, these two structures participate in the formation of the phenoxy radicals, and a reduction in their concentration will consequently result in discoloration.

Tensile Properties of PVC-L Blends

The tensile properties of PVC-L blends were measured before and after several artificial weathering periods and were correlated with the properties of PVC-control. The tensile properties of the blends before weathering may indicate whether the L acts in blends as an "inert" filler or if there is a specific interaction between the two polymers. For the weathered specimens the tensile strength results can indicate changes in the bulk material properties of PVC-control and PVC-L blends and may illustrate whether crosslinking or chain scission of the polymer has occurred.

Tensile Properties before Weathering

Figure 3(a) shows the tensile strength at break and Fig. 4(a) the elongation at break data for PVC-control and blends depending on L content. These results can be summarized as follows:

1. The tensile strength increases with L load; the tensile strength of the blends without TiO_2 are slightly higher than that of the blends with TiO_2 . The maximum tensile strength (for PVC-7.5L/T and PVC-7.5L blends) is of about 9% higher when compared with the value of PVC-control. If L acts as an "inert" filler in the system, then taking into account the simple theory of stress-strain properties of filled polymers elaborated by Nielsen [22], particularly the case of perfect adhesion between filler and polymer, the presence of small amounts of filler (less than 10% volume, as in our case) should drastically decrease the tensile strength (at least 20–30% of the value of unfilled polymer). The data from Fig. 3(a) indicate exactly the contrary.
2. The elongation at break decrease of all PVC-L blends in comparison to the PVC-control can be correlated with L loading too; it shows a maximum decrease of -13% (Fig. 4a). Again, according to stress-strain theory, the elongation at break for maximum L loading (7.5 phr, i.e., 6.6 vol%) should be around 40% of the value of unfilled polymer if L acts as a filler, much lower than the experimental data presented in Fig. 4(a).

The lack of correlation between the values of the tensile stress-strain data predicted by the theoretical model and the experimental values obtained for PVC-L

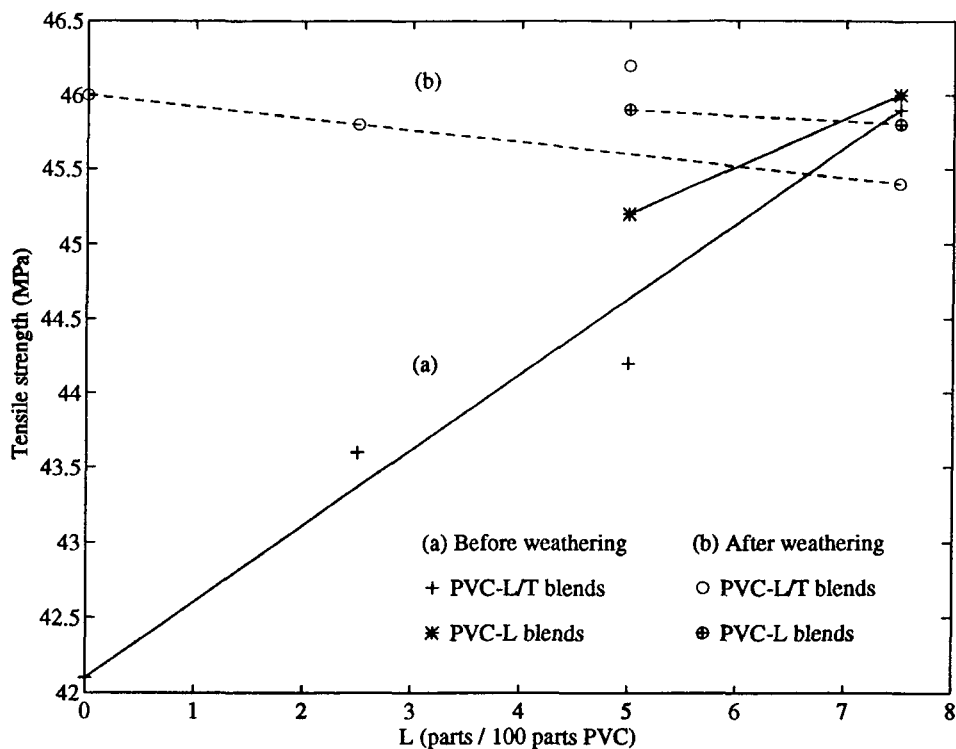


FIG. 3. Variation of the tensile strength at break vs L content. (a) Before weathering. (b) At maximum weathering time (84 days).

blends is an indication of some degree of interaction between the two polymers in the blends.

Tensile Properties after Weathering

Figure 3(b) presents the tensile strength at break and Fig. 4(b) the elongation at break for the PVC-control and PVC-L blends versus L content at maximum weathering period, i.e., 84 days. Figures 5 and 6 show the variation of the tensile strength properties of PVC-control and blends at different periods of exposure to artificial weathering. The trend of the curves is the same for PVC-control and blends, and the shape of the curves broadly suggest the predominant process at a particular period of weathering, which controls the overall degradation. After the first 8 days of weathering exposure, it is likely that the tensile strength increase and the elongation decrease are caused by chemical crosslinking. This may be followed by a dominant chain scission process in the 8–24 days period, which leads to a decrease of the tensile strength and a slightly increase in elongation.

The next moderate increase in tensile strength and slight decrease of elongation after 63 days exposure could be caused by a physical aging which is time and temperature dependent process. The physical aging phenomenon results from the

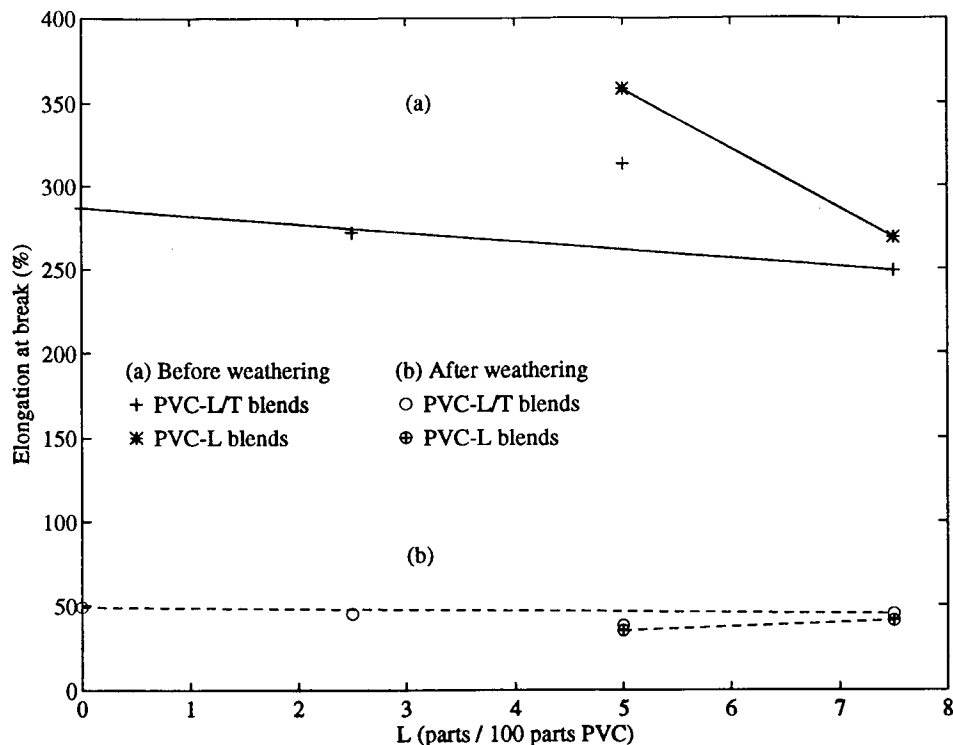


FIG. 4. Variation of the elongation at break vs L content. (a) Before weathering. (b) At maximum weathering time (84 days).

relaxation of the polymer chains, frozen in a nonequilibrium state during the transformation from melt to glass, with the elimination of excess free volume in an effort to approach the preferred or true equilibrium state of glass. Changes in elongation at break, stress relaxation, and enthalpy relaxation are caused by the physical aging process [23, 24].

In the last period of artificial weathering (between 63 and 84 days), the tensile strength decreased again and elongation increased very slightly for all PVC-L blends except PVC-control and PVC-2.5L/T, suggesting a predominance of changes in the chemical structure (chain scission, elimination of HCl, etc.). The shape of the tensile strength and elongation at break curves as obtained from data at several periods of weathering suggests the predominance of one of the degradation processes at a particular time period along the weathering interval. However, it is important to point out that during weathering, physical aging and changes in chemical structure (e.g., chain breaking, crosslinking, elimination of HCl resulting in the formation of polyene sequences) occur simultaneously, so that while one of these processes is predominant at a certain time period, the others are not excluded.

If one compares the values of the tensile strength and elongation at break before weathering and at the end of the exposure period (Figs. 3, 4a and 4b), the results can be summarized as follows:

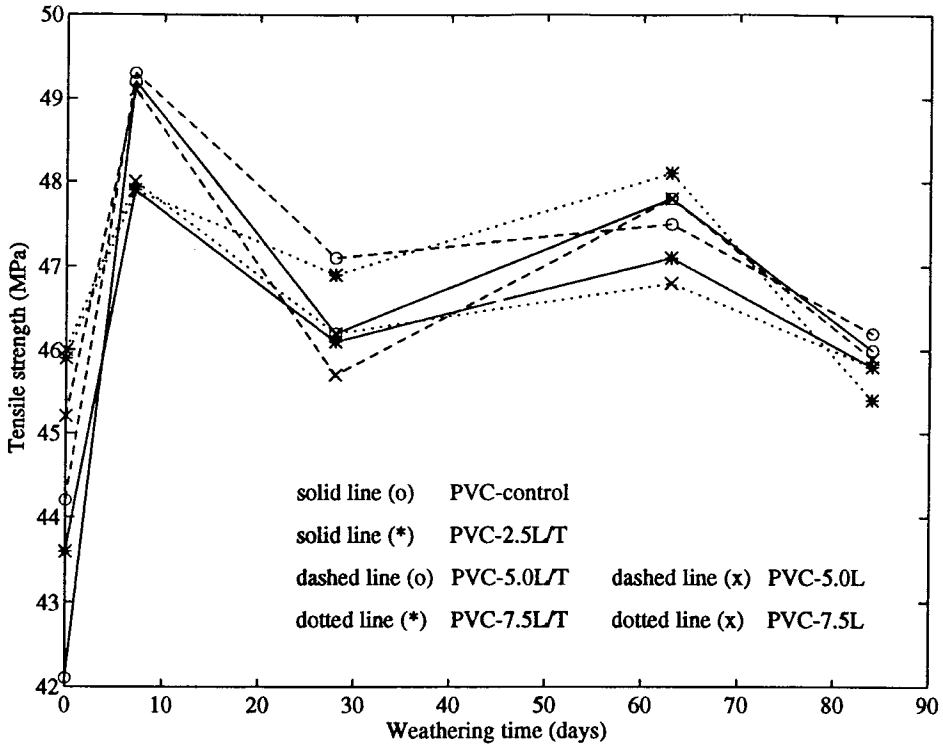


FIG. 5. Variation of the tensile strength at break vs weathering time.

1. Tensile strength at break increases after weathering are 9.3% for PVC-control, 5.2% for PVC-2.5L/T, 4.5% for PVC-5L/T, and 1.4% for PVC-5L. The data for PVC-7.5L/T presents a decrease of 1.1% whereas at the same L loading without TiO₂, i.e., PVC-7.5L, the tensile strength at break did not change after weathering.
2. The elongation at break after weathering decreased in equal measure, i.e., 83% for the PVC-control and almost all PVC-L blends except for the case of PVC-5L blends where the decrease was 88% for the blend with TiO₂ and 90% for the blend without TiO₂.

The tensile strength increase and elongation decrease for PVC-control and blends as an effect of 84 days of artificial weathering are an indication of an overall process of crosslinking. It is interesting to note that lowering the TiO₂ level or its total replacement with L did not affect the tensile properties of PVC-L blends to any considerable degree in comparison with those of PVC-control where TiO₂ loading is 10 phr. This observation encourages further research into this subject. The PVC compound without TiO₂ was blended with 5 and 7.5 phr L. The reason was that only 2.5 phr L would not be sufficient to insure good weathering properties. However, analysis of the results led to the conclusion that blends with 2.5 phr L should be considered in future research.

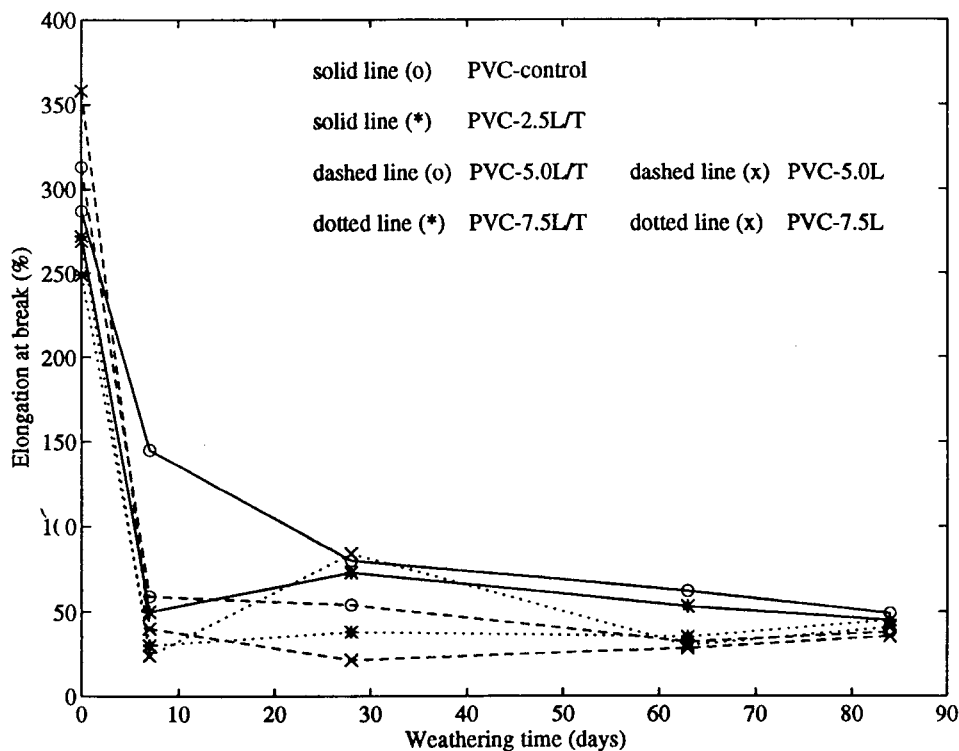


FIG. 6. Variation of the elongation at break vs weathering time.

Color changes caused by artificial weathering as well as earlier development of crazes on the exposed surface of PVC-L blends disclose a quite modest (in comparison with PVC-control) weathering stability as an effect of L presence.

Both phenomena, color changes and development of crazes, seem to be generated by the formation of free radicals of L as an effect of UV light. Consequently, further research should find an effective UV stabilizer that either absorbs more light than L itself or is able to deactivate the phenoxy radicals.

CONCLUSIONS

The preliminary work which was carried out in order to prepare and evaluate PVC-L blends in which L partially or totally replaced TiO_2 led to the following conclusions:

The presence of L did not affect the thermal stability of PVC and its rheological properties during the melt mixing process.

The interaction of L and PVC for forming miscible blends can take place at temperatures which are superior to the T_g of the high molecular weight fraction of L.

The increase in tensile strength and the decrease in elongation at break of unweathered PVC-L blends depends on the L load. The maximum tensile strength (at break) is about 9% higher and the elongation at break is about 13% lower than the respective values of PVC-control for PVC-7.5L/T. The PVC-7.5L presents the same increase in the tensile strength (i.e., 9%) whereas the elongation at break is reduced by only 6%.

The lack of correlation between the PVC-L blends values of tensile stress-strain data predicted by the theoretical model and the experimental values are an indication of some degree of interaction between the polymers in the blends.

After a weathering period of 84 days, the tensile stress-strain data reflect an overall crosslinking process occurring in PVC-control as well as in blends. The partial or total replacement of TiO_2 by L in different blends did not greatly affect the tensile stress-strain properties of the blends in comparison to PVC-control. However, changes in color as well as the development of crazes on the surfaces exposed to UV light and water for PVC-L blends indicate a lower weathering stability of the blends in comparison to PVC-control.

These preliminary data encourage further research for PVC blending with L, including

1. Studies concerning the stabilization of L (Tomlinite) or other type of lignins (or lignins fractions) toward UV light
2. Preparation, testing, and weatherability of PVC compounds-L blends with new types of lignins (or lignin fractions) in the presence of a particular UV stabilizer or UV stabilizer system for L

Further research will have a dual purpose: to help develop durable and cost-effective PVC-L blends for outdoor applications, and to aid in cultivating a market for L.

ACKNOWLEDGMENTS

The authors wish to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support. Thanks are extended to BFGoodrich Company, Technical Center, Avon Lake, Ohio, USA, for providing us the PVC compounds used in this study, as well as to Dr. J. Summers for his recommendations.

REFERENCES

- [1] R. D. Deanin, IUPAC International Symposium on Macromolecules, Montreal, July 13, 1990.
- [2] (a) W. V. Titow, *PVC Technology*, 4th ed., Elsevier Applied Science, New York, 1984, pp. 10-11; (b) pp. 469-482; (c) p. 127; (d) pp. 260-261; (e) pp. 359-371; (f) pp. 466-469.
- [3] L. I. Nass, *Encyclopedia of PVC*, Dekker, New York, 1976, pp. 272-276.

- [4] L. S. Burn, *Polym. Degrad. Stab.*, **36**, 155 (1992).
- [5] A. L. Andrady, A. Torikai, and K. Fueki, *J. Appl. Polym. Sci.*, **37**, 935 (1989).
- [6] D. Feldman, D. Banu, M. Lacasse, and J. Wang, in *Materials Relevant to Recycling of Wood Based Materials* (R. M. Rowel, T. L. Laufenberg, and J. K. Rowed, Eds.), *M.R.S. Symp. Proc.*, **226**, 1776 (1992).
- [7] S. Falkenhag, *Appl. Polym. Symp.*, **28**, 247 (1975).
- [8] C. Schuerch, *J. Am. Chem. Soc.*, **74**, 5061 (1952).
- [9] D. Feldman, D. Banu, C. Luchian, and J. Wang, *J. Appl. Polym. Sci.*, **42**, 1307 (1991).
- [10] S. Krause, *J. Macromol. Sci.—Rev. Macromol. Chem.*, **7**, 251 (1972).
- [11] A. Rudin, *The Elements of Polymer Science and Engineering*, Academic Press, New York, 1982, pp. 428–465.
- [12] D. R. Paul, in *Polymer Blends and Mixtures* (D. J. Walsh, J. S. Higgins, and A. Maconnachie, Eds.), Nato ASI Series E No. 89, 1985, pp. 1–23.
- [13] G. H. Hofmann, pp. 117–148 in Ref. 12.
- [14] A. L. Andrady and N. D. Searle, *J. Appl. Polym. Sci.*, **37**, 2789 (1989).
- [15] J. Wypych, *Polyvinyl Chloride Stabilization*, Elsevier, New York, 1986, pp. 3–26.
- [16] J. Wypych, *Polym. Networks Blend*, **2**, 53 (1992).
- [17] D. Braun and S. Kömmerling, *Angew. Makromol Chem.*, **195**, 205 (1992).
- [18] D. Braun, N. Eidam, and S. Kömmerling, *Ibid.*, **184**, 197 (1991).
- [19] R. Mörck, H. Yoshida, and K. P. Kringstad, *Holzforschung*, **40**(Supplement), 41 (1986).
- [20] J. H. Yoshida, R. Mörck, and K. P. Kringstad, *Ibid.*, **41**, 171 (1987).
- [21] J. Wang, D. Banu, and D. Feldman, *J. Adhes. Sci. Technol.*, **6**, 587 (1982).
- [22] L. E. Nielsen, *J. Appl. Polym. Sci.*, **10**, 97 (1966).
- [23] S. E. Petrie, in *Polymeric Materials—Relationship between Structure and Mechanical Behavior* (E. Baer and S. Radcliffe, Eds.), American Society for Metals, Metals Park, Ohio, 1975, pp. 55–117.
- [24] H. U. Hoppler and W. Surer, *Thermochim. Acta*, **206**, 251 (1992).
- [25] J. W. Summers, *J. Vinyl Technol.*, **5**, 43 (1983).
- [26] J. W. Summers and E. B. Rabinovitch, *Ibid.*, **5**, 91 (1983).
- [27] J. Gierer and S. T. Lin, *Sven. Papperstidn.*, **75**, 234 (1972).
- [28] G. Gellerstedt and E. L. Petterson, *Ibid.*, **80**, 15 (1977).

Received June 18, 1993

Revision received August 20, 1993