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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1002/app.1988.070350118>

Journal of Applied Polymer Science, 35, 1, pp. 247-257, 1988-01-01

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Polyurethane-Based Sealants Modified by Blending with Kraft Lignin

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Synopsis

An investigation was conducted to establish the viability of blending Kraft lignin (L), a naturally occurring, readily available polymer resource, with polyurethane- (PU) based sealants. The sealants were tested in a detailed program where lignin-sealant blends, having blend ratios varying between 0 and 20 pbw L, were prepared on substrates of aluminum, mortar, and wood, and subjected to laboratory control (C), artificial weathering (AW), and natural weathering (NW) conditions. Results of tension testing showed that generally, lignin acts as a reinforcing agent which adds rigidity to the polymeric matrix, as indicated by the increase in toughness and modulus of blended sealants with the addition of lignin. In addition, the curing mode of PU, as determined by sequence hardness testing, was modified with the addition of lignin.

INTRODUCTION

The properties of polymer blends has become an area of major scientific research in the last 15 years due in large part to the intensified technological and economic interest in multicomponent macromolecular systems. The blending of two or more different polymers is carried out in order to enhance certain characteristics of the final product when compared with the initial polymers.

Most of the literature on polymer mixtures deals with mixing binary blends of synthetic polymers such as thermoplastics or elastomers with thermoplastics. Much less material has been published on the blending of synthetic and natural polymers and this is particularly true in the case of polyblends formulated with different types of lignin.

In this laboratory, previous research on polymer mixtures involved the study of properties of blends of polyurethane, epoxy, and silicone, respectively, with vinyl type polymers, polyorganosiloxane, or glass fiber reinforcement.¹⁻⁷ Subsequent papers reported results on acrylic terpolymer-based blends with improved mechanical properties.⁸⁻¹⁰

This paper reports results on the curing mode and mechanical performance of polyurethane-based sealants blended with Kraft lignin (L) to enhance the mechanical and curing behavior of these blends.

EXPERIMENTAL

Materials

The base polymer used was a one part self-curing, non-sag polyurethane-(PU) based sealant (MULCO-Maxiflex).

Kraft lignin (L), obtained from Domtar of Cornwall (Ontario), was the base polymer with which PU was blended. The lignin was extracted from black liquor (pulp residue from maple, beech, and elm hardwoods) by sulfuric acid precipitation. The pH of the precipitate was adjusted with carbon dioxide to a level between 6 and 7.¹¹ PU-based blends with 5, 10, 12.5, 15, and 20 parts by weight (pbw) L were prepared.

Procedure

The testing program consisted of establishing the curing mode of lignin-polyurethane (L-PU) blends as well as the mechanical properties in tension.

The curing of elastomeric sealants normally involves the formation of crosslinkages between the macromolecular chains; the cure process proceeds through the sealant, and may be detected by sequence hardness testing. The hardness of the various blends was determined according to ASTM C 661-70, using a Shore type A-2 durometer.

For the tension testing of lignin-polymeric blends, three series of six specimens were cast between aluminum, mortar (ASTM method C 719-79), and California redwood substrates in accordance with CAN2-19.6-M77, method 12.1 1978. After curing, each of the series was subjected to one of the following conditions:

1. Control (C); kept in the laboratory at 23°C and 35% relative humidity (RH).

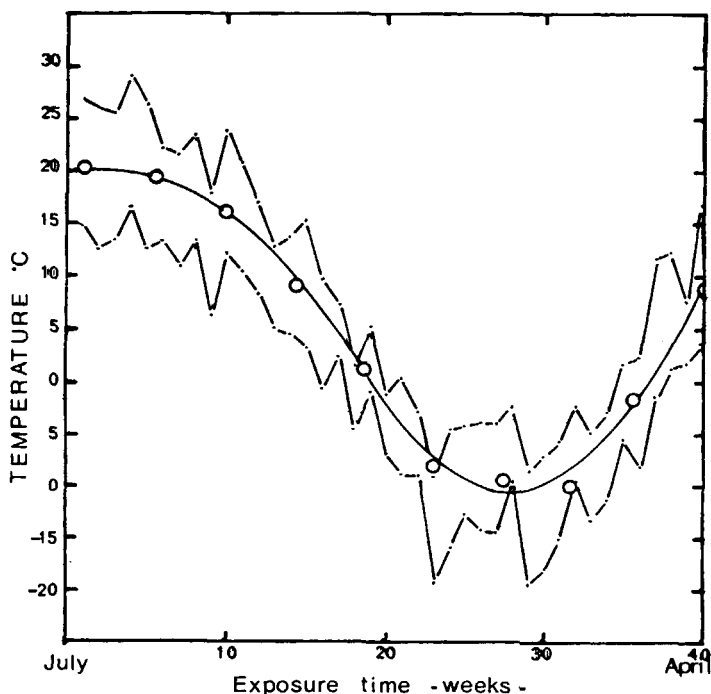


Fig. 1. NW exposure conditions: average weekly maximum and minimum temperatures, and average monthly temperatures.

2. Artificial weathering (AW); specimens were placed in an environmental chamber whose temperature was set to cycle between -30 and $+40^{\circ}\text{C}$ at 50% RH (4 times daily) for 180 days (i.e., 720 cycles); the specimens were concurrently subjected to ultraviolet radiation (wavelength 254 nm) for 12 of 24 hours.

3. Natural weathering (NW); specimens were placed outdoors in a relatively polluted area of central Montreal for 37 weeks, between July 1985 and April 1986. The temperature variation during the exposure period is shown in Figure 1.

Maximum and minimum temperatures recorded during this period were 32.6°C and -26.7°C , respectively.

Tensile stress-strain measurements were performed at 23°C with an Instron Model 1125 Universal Testing Machine, using a 500 kg load cell set at a full scale of 100 kg. A cross-head speed of 2 mm/min was used in conjunction with a 20 mm/min chart speed to produce a reasonably comprehensive plot of the stress-strain data.

Testing was conducted until there was a visible adhesive or cohesive failure or until the results recorded on the chart indicated a sharp decrease in load.

RESULTS AND DISCUSSION

Curing Characteristics

For the neat PU blends, the initial hardening test may be recorded after approximately 25 h have elapsed since the initial casting time. In the next 23 h, the sealant reaches 40% of the hardness obtained in one week and in the following 24 h, 70% of the one week hardness. The hardness after one week is 95% of the average hardness over 1519 h, indicating that most of the cure occurs in the first week after initial set. It should also be observed that a second hardening stage may occur after several months. It is not yet apparent what causes the subsequent hardening of the sealant after two months of curing.

For L-PU blends of 20 pbw of lignin, the initial hardness reading may be taken at 20 h, representing a 20% decrease in initial set time for this blended sealant in comparison to the neat sealant. The polyblend reaches 35% of its one week hardness after 24 h, 72% of its hardness in 48 h, and 85% of its hardness after 72 h from initial set. Generally, this is indicative of a more rapid cure for blended sealants in comparison to neat PU. This is all the more evident when considering the results shown in Figure 2 which shows curing tests for L-PU blend ratios of 0, 10, and 20 pbw L.

The curing time, as measured by sequence hardness testing, is affected by the amount of lignin blended with the base sealant. Furthermore, it can be shown that at any given time, the ratio of 10 sec (i.e., reading obtained 10 seconds after initial indentation) to 60 sec hardness decreases with increasing amounts of lignin, indicating a more rapid hardening process for blended vs. unblended sealants. Although the rate of curing appears to be similar for blended and unblended sealants, as indicated by the initial linear portion of the curves, overall, blended sealants harden more quickly than unblended

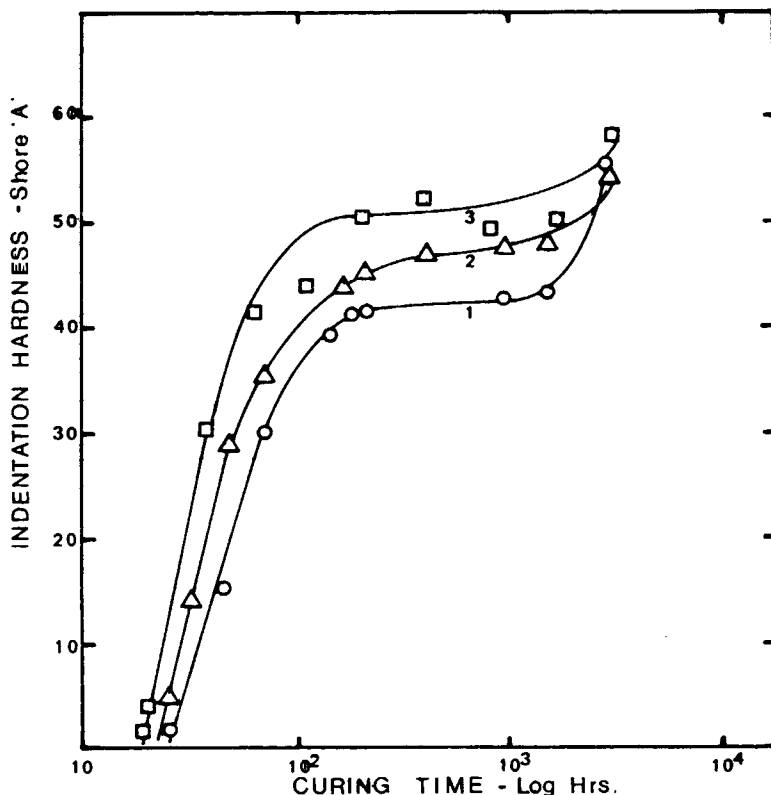
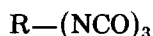
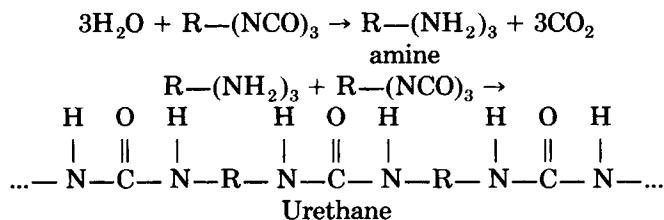


Fig. 2. Indentation hardness of L-PU polyblends in relation to curing time. Curve 1: L-PU; 0: 100; 2: L-PU; 10: 100; 3: L-PU; 20: 100.

sealants in direct proportion to the amount of lignin present in the blend. A discussion of the basic chemistry involved in the formation of PU, more specifically one component polyurethane sealants, is required to explain this phenomena. One component polyurethane sealants are produced by the reaction of moisture and an isocyanate-terminated prepolymer such as alkyl trimethyl triisocyanate, which here is referred to as:

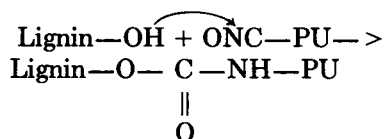


Combining 3 mol of water with the isocyanate yields an amine, which further reacts with the isocyanate to form urethane linkages, i.e.:



The rate of cure is affected by the activity of the functional end groups, and the presence of catalysts. The hardness of the cured products depends on the crosslinking density between molecular chains and the rigidity of the chains, which increases with a corresponding increase in the number of aromatic groups along the chain. Furthermore, the crosslink density is a function of the type of prepolymer used in the sealant formulation. It is thought that the incorporation of lignin into the PU matrix may be seen as adding to the crosslink density by increasing the concentration of aromatic groups within the polymeric network.

A possible mechanism might be based on the interaction of lignin hydroxyl groups with free isocyanate groups. That is,



An infrared (IR) spectroscopic study was carried out to determine the existence of chemical interaction between L and PU. Unfortunately, experimental difficulties encountered while establishing the spectra have so far made accurate conclusions impossible.

Tension Testing of (L-PU) Polyblends

L-PU blends on Aluminum Substrates

Figure 3 shows a series of typical stress-strain curves obtained from tension tests which, in this particular case, describe the behavior of specimens subjected to control conditions. Those specimens with 5 pbw lignin show the highest values (curve 2) for yield stress. All other blends tested (curves 3-5), with the exception of the 20 pbw L blend (curve 6), have higher yield stress than the neat PU sealant (curve 1).

The greatest percentage increase in toughness, tangent modulus (5% offset), and stress and strain at yield is observed for blends having 5 pbw of lignin in the matrix (Tables I and II). In other blends in this series, additional lignin decreases both the toughness and the strain at yield. However up to a limiting value of 15 pbw L, there are increases in stress at yield, in comparison to the values obtained for the neat sealant, but not as significant as those for specimens blended with 5 pbw of lignin. It is also observed that the modulus of control specimens increases progressively with the addition of lignin.

Similarly for AW specimens, the maximum values for toughness, and stress and strain at yield are obtained in blends with 5 pbw L; additional L beyond 5 pbw decreases these values. It may also be shown that, in general terms there is an increase in modulus with the addition of L.

For the NW test series, the highest value of yield stress was achieved in blends having 12.5 pbw L (as opposed to 5 pbw L observed in the C & AW series). Furthermore, the addition of L enhanced the yield stress in all sealants blended with up to 15 pbw of L in comparison to neat PU sealant (Table II).

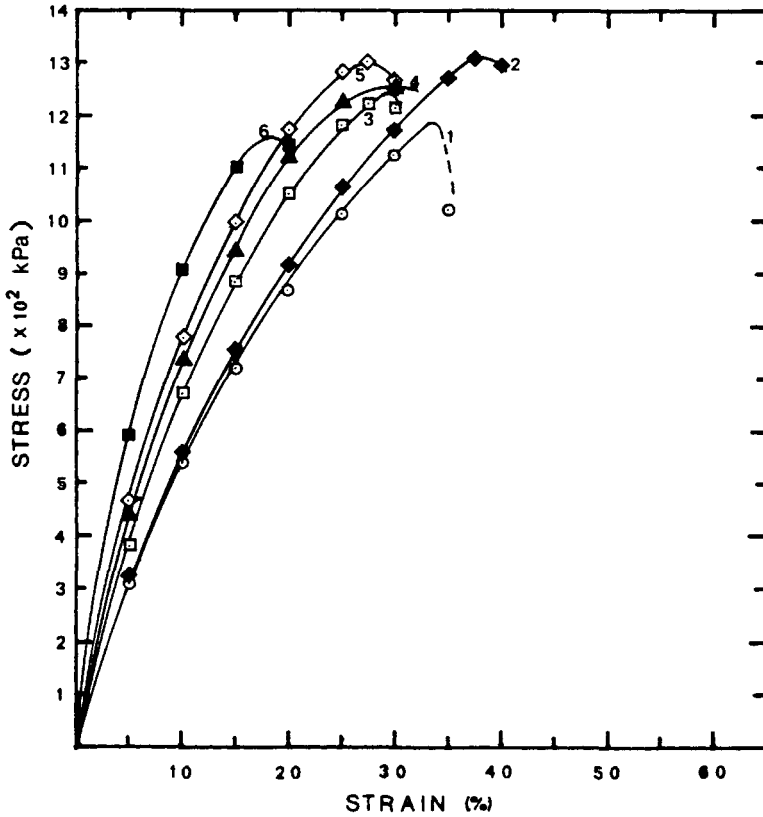


Fig. 3. Tensile stress-strain curve obtained from control, L-PU polyblends on aluminum substrates. Curve 1: L-PU, 0:100; 2: L-PU, 5:100; 3: L-PU, 10:100; 4: L-PU, 12.5:100; 5: L-PU, 15:100; 6: L-PU, 20:100.

TABLE I
Toughness and Tangent Modulus (at 5% strain) of Lignin-Polyurethane
Polyblends on Aluminum Substrates

Polyblend	Toughness (KPa)			Tangent modulus (KPa)		
	Exposure Condition			Exposure Condition		
L:PU	C	AW	NW	C	AW	NW
0:100	284	297	267	310	269	202
5:100	345	370	315	324	246	239
10:100	241	241	263	385	337	309
12.5:100	247	182	246	436	365	327
15:100	239	177	162	469	433	363
20:100	149	167	178	595	509	465

In this test series, as in all other tests on aluminum substrates, the maximum toughness was observed in blends having 5 pbw L.

Overall, the addition of lignin stiffens the PU matrix such that with 20 pbw of lignin incorporated in the blend, an average increase of 100% in modulus is achieved for all specimens adhered to aluminum substrates.

TABLE II
Yield Stress and Yield Strain of Lignin-Polyurethane Polyblends on Aluminum Substrates

Polyblend	Yield stress (KPa)			Yield strain (%)		
	Exposure Condition			Exposure Condition		
L : PU	C	AW	NW	C	AW	NW
0 : 100	1191	1191	1038	35.8	37.5	38.5
5 : 100	1315	1281	1183	39.4	43.0	40.0
10 : 100	1225	1174	1186	29.6	30.8	33.3
12.5 : 100	1255	1059	1214	29.6	25.8	30.4
15 : 100	1283	1140	1078	27.9	23.3	22.5
20 : 100	1146	1183	1167	19.6	21.3	22.9

L-PU Polyblends on Mortar Substrates

For control specimens, the failure mode was dominantly adhesive in nature, placing a limit on the amount of stress induced in the sealant.

For mortar specimens subject to AW conditions, it was observed that a considerable number of substrates had extensive microcracking visible on their surfaces, and the failure mode of these specimens was dominantly initiated in the substrate, being localized at the interface with the sealant where the highest stress concentrations in the sealant occur. The results obtained were inconsistent and this precludes any valid conclusions being made.

L-PU Blends on Wood Substrates

Lignin-polyurethane blends on wood substrates exhibit lower values for toughness, modulus, and stress and strain at yield (Tables III and IV), in comparison to values obtained from specimens adhered to aluminum (Tables I and II) and mortar substrates. This is due to the initiation of failure in the substrates, which limits the strain to which the sealant may be subjected, and consequently reduces the ultimate stress and toughness of these specimens.

The tangent modulus of control specimens (Table III) is observed to increase 12, 37, 62, and 70% for lignin loadings of 5, 10, 15, and 20 pbw, respectively. There is a similar progressive increase in modulus with the addition of lignin, shown for both AW and NW specimens; for lignin loadings

TABLE III
Toughness and Tangent Modulus (at 5% strain) of Lignin-Polyurethane Polyblends on Wood Substrates

Polyblend	Toughness (KPa)			Tangent modulus (KPa)		
	Exposure Condition			Exposure Condition		
L : PU	C	AW	NW	C	AW	NW
0 : 100	127	73	118	253	192	173
5 : 100	132	164	99	282	214	184
10 : 100	93	121	114	347	286	234
12.5 : 100	59	77	91	374	322	231
15 : 100	67	83	144	410	372	300
20 : 100	29	33	136	431	428	342

TABLE IV
Yield Stress and Yield Strain of Lignin-Polyurethane Polyblends on Wood Substrates

Polyblend	Yield stress (KPa)			Yield strain (%)		
	Exposure Condition			Exposure Condition		
	C	AW	NW	C	AW	NW
L:PU						
0:100	801	550	674	23.8	20.0	26.5
5:100	833	893	682	23.8	27.5	21.7
10:100	800	906	761	17.5	20.0	22.5
12.5:100	715	766	724	12.5	15.0	18.8
15:100	802	826	917	12.5	15.0	23.5
20:100	575	674	943	7.5	7.5	21.7

of 5, 10, 15, and 20 pbw there are increases in modulus of 11, 49, 94, and 123%, respectively, for AW specimens, and increases in modulus of 6, 35, 73, and 98%, respectively, for NW specimens. The increased modulus is due to the stiffening of the L-PU matrix, which causes higher yield stress to develop, as observed by the increase of up to 62% in stress at yield for AW specimens of 5 pbw loading (Table IV). An increase of 5 pbw of lignin loading increases the yield stress from 1 to 12% for AW and NW specimens, respectively, whereas there is a decrease in stress at yield for all subsequent lignin addition in the case of control specimens.

As shown above, small amounts of lignin blended with a polyurethane sealant increase the toughness, modulus, and stress and strain at yield of the polyblend. Additional quantities of lignin incorporated in the PU matrix are not seen as beneficial for the toughness of the sealant since too stiff a blend causes higher stresses in the zones located along the edges and extremities of the sealant-substrate interface. A stiffer blend is characterized by an increase in modulus with increased polymer loading. Incidence of higher stresses in failure zones are borne by the decrease in strain at yield with lignin loadings above 5 pbw.

The tangent modulus of L-PU blends increases progressively with a corresponding increase in lignin loading for all specimens tested (Figs. 4 and 5). Furthermore, at any given L loading, the modulus of specimens adhered to aluminum substrates is generally greater than that of either mortar or wood substrates, and in this respect, the modulus of specimens adhered to mortar is greater than those adhered to wood.

The increase in modulus is to be expected since the lignin acts as a reinforcing filler, which, as mentioned previously, stiffens the blend. Lower values of modulus obtained for specimens adhered to mortar and wood substrates is indicative of the mode of failure of these specimens, which primarily failed in the substrate. Hence, the type and condition of the substrate affected the test results, as can be demonstrated clearly in the case of AW mortar specimens. The considerable deterioration of these substrates due to the aging process rendered them unsuitable for proper testing and evaluation of the blends.

Figure 5 clearly shows a loss of modulus with aging: there is a 20% loss of modulus in AW specimens, and a 30% loss of modulus for NW specimens in comparison to C specimens. This indicates that the effects of NW are more

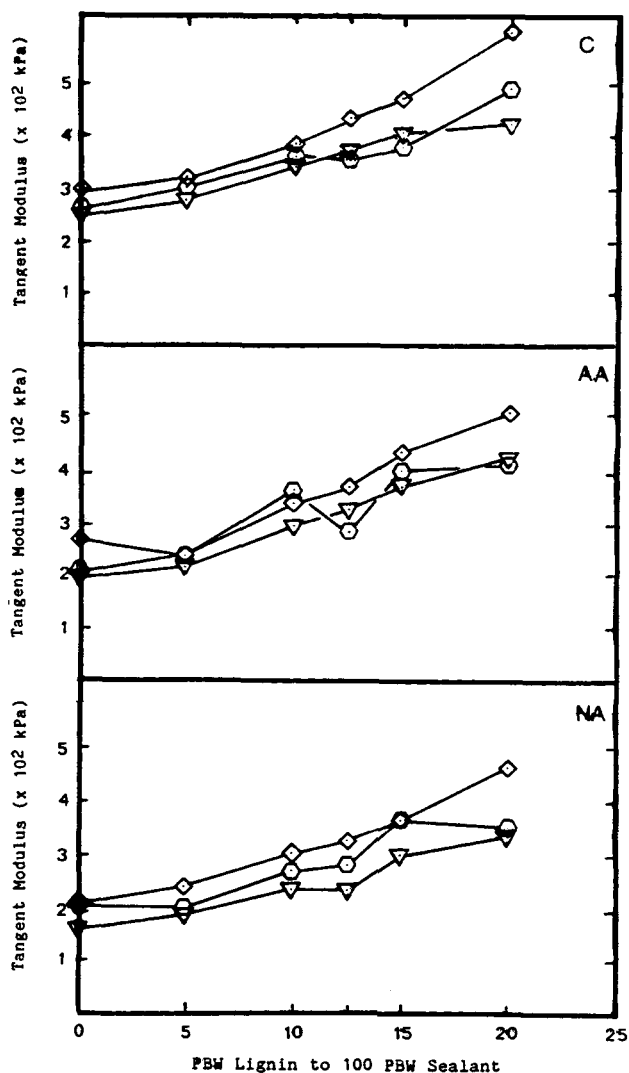


Fig. 4. Tangent modulus of L-PU polyblends as a function of L loading in: C, AW, and NW conditions. Substrates: (∇) wood; (\circ) mortar; (\diamond) aluminum.

severe than that of AW conditions. The loss in modulus observed from the AW and NW test series is caused by the action of ultraviolet radiation in conjunction with the effect of temperature fluctuations. These temperature variations may lead to a cryolysis, a process which has been discussed in previous papers.^{4,5} Furthermore, the AW process does not subject the specimens to the effects of moisture, pollutants, or other environmental factors, hence these combined elements may in part account for the differing results between aging methods.

It has also been observed that the addition of lignin in progressively increasing amounts reduces the loss of modulus in L-PU blends. Hence, it may be concluded that, in general, the addition of small quantities of lignin to the

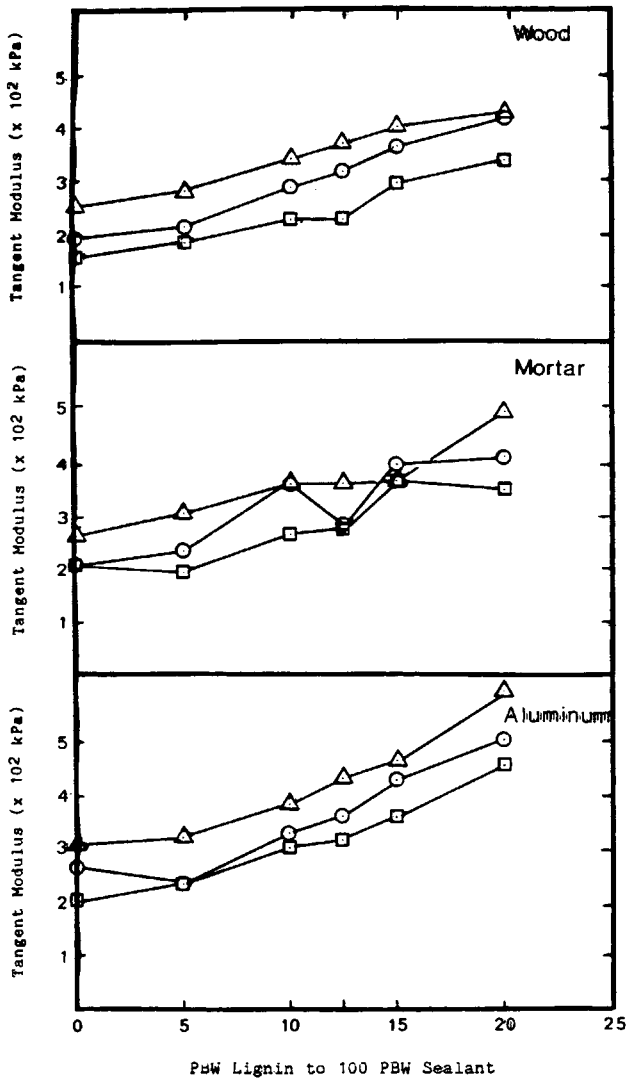


Fig. 5. Tangent modulus of L-PU polyblends as a function of L loading on: wood, mortar, and aluminum. Aging conditions: (Δ) C; (\circ) AW; (\square) NW.

L-PU matrix is beneficial in terms of both strength and durability, in spite of the incompatibility of PU and L reported elsewhere.¹²

CONCLUSIONS

The curing mode of L-PU sealants is modified with the addition of lignin. Thus the initial setting time is reduced with the addition of lignin, but the rate of curing remains constant, indicating that the matrix is hardened in direct proportion to the amount of lignin present in the blend. It is surmised that incorporation of lignin may contribute to an increase in the degree of crosslinking of PU.

The tangent modulus of L-PU blends increases progressively with the amount of L added to the blend. In terms of tensile strength of sealant blends, the values obtained vary according to the amount of lignin present in the matrix and to the type of substrate to which it is adhered. The best strength results, in the majority of tests, were obtained with sealants blended with 5 pbw lignin. In certain blend quantities, lignin may be considered as an active filler capable of reacting with PU groups. Difficulties encountered in a preliminary IR study of this polyblend did not permit the type of interaction between blend components to be established.

The durability of the blended sealants, as measured by the change in mechanical properties of specimens subjected to natural and artificial weathering programs, is generally neither hindered nor improved with the addition of lignin.

The authors wish to thank the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR) and the Natural Sciences and Engineering Research Council (NSERC), Ottawa, Canada, for partial support for the first two authors. Thanks are also extended to D. Banu for assistance and advice concerning this study.

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Received April 8, 1987

Accepted April 30, 1987