Engineering Plastics from Lignin. VII. Structure Property Relationships of Poly(butadiene Glycol)-Containing Polyurethane Networks

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Synopsis

Hydroxypropyl lignin-based thermosetting polyurethanes containing polybutadiene (PBD) glycol soft segments (M_n of 2800 g M^{-1}) were synthesized with excess hexamethylene diisocyanate (HDI) and tolylene diisocyanate (TDI) by solution casting. Miscibility of the glycol with the lignin derivative was found to be poor as expected, and phase separation between the two polyol components in polyurethanes was detected by thermal and mechanical analysis, and by electron microscopy. This study examines the effect of concentration of polybutadiene glycol on the thermal and mechanical properties of the polyurethanes. The two-phase network system displayed significantly different properties than either the poly(ethylene glycol)-containing polyurethanes or their soft segment-free counterparts described previously. Macrophase separation was observed at nearly all degrees of mixing and was found to affect thermal and mechanical properties. The glass transition temperature (T_g) of the lignin phase in the TDI-based networks increased with poly(butadiene glycol) content rising from 3.6 to 71.4% of polyurethane, and this was attributed to the employment of a constant diisocyanate weight fraction which gave rise to a variable NCO/OH ratio and crosslink density. Distinct phase separation was evidenced by scanning electron microscopy (SEM) at above 3.6 and 7.1% glycol content for HDI- and TDI-based films, respectively. The polyurethane films behaved like rubber-toughened lignin networks when PBD was the discrete phase, and like lignin-reinforced rubber when the lignin derivative was discrete. This behavior was evidenced by the Young's modulus decreasing from 2000 to 50 MPa and ultimate strain rising from 6 to greater than 150%, with soft segment content increasing from 0 to 71.4%.

INTRODUCTION

This study continues to explore opportunities for modifying macromolecular properties of lignin-based polyurethanes by mixing the polyol component prior to crosslinking with low modulus hydroxy-terminated soft segment constituents. Related investigations on the modification of the mechanical behavior of network epoxies[1-13] by the attachment of low molecular weight rubbery chains have demonstrated that properties can be influenced in a similar way as with polystyrene-modified rubbers.

In the previous study[14] polyurethanes synthesized from blends of hydroxypropyl lignin derivatives with poly(ethylene glycol)s were examined with regard to the effect of soft segment incorporation in relation to content

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and chain length (molecular weight), on thermal and mechanical network properties. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), and small angle X-ray analysis (SAXS), all failed to produce positive indications for the presence of a discrete soft segment phase in the network polymer. However, the network exhibited significant sensitivity to glycol content and molecular weight and to crosslink density. Uniform structure and improved mechanical properties with only minor additions of glycol demonstrated that these lignin-based thermosetting polyurethanes can be synthesized with a wide range of performance characteristics.

The objective of the present investigation was to study the effect of a less miscible polyol component in a mixture with lignin-derived polyester–ether polyol on polyurethane network properties. The specific polybutadiene glycol selected for the present study was based on the fact that (a) this system is rubbery at room temperature and has low secondary interchain forces and lower solubility parameter [$\delta = 8.6$ (cal/cm^3)$^{1/2}$], and (b) it has a functionality somewhat in excess of two and is thus capable of covalent network formation.

EXPERIMENTAL

Materials

Lignin. Commercial pine kraft lignin, isolated by acidification (with CO_2) of the spent pulping ("black") liquor of a kraft pulpmill, was obtained from Westvaco Corp., N. Charleston, SC, under the trade name INDULIN ATR-Cl. The chemical and molecular structure of this lignin in relation to other lignin preparations has been the subject of two prior reports.[15,16]

Hydroxypropyl Lignin. Solid kraft lignin was reacted with propylene oxide according to an earlier paper[17] in a closed, mechanically stirred stainless steel reactor. The hydroxy content of the isolated lignin derivative was found to be 4.3%.

Isocyanates. Hexamethylene diisocyanate (HDI) and 2,4-tolylene diisocyanate (TDI), practical grade, Eastman Kodak Co., Rochester, NY, were used throughout.

Polybutadiene Glycol. Polybutadiene (PBD) glycol ("Poly bd R45-HT", ARCO Chemical Comp., Philadelphia, PA) is a homopolymer of butadiene with an average molecular weight (M_n) of 2800 g M^{-1} and a hydroxy functionality of 2.4–2.6. The hydroxy groups amount to 0.83 meq/g and are predominantly allylic in character. The resin consists of 60% *trans*-1,4, 20% *cis*-1,4, and 20% vinyl-1,2 double bonds.

Methods

Film Preparation. Polyurethane films were prepared as described previously[18] by solution casting a mixture of polyol components (hydroxypropyl lignin and PBD glycol), diisocyanate, and catalyst (dibutyl tin dilaureate) in tetrahydrofuran (THF) on a glass plate coated with a thin layer of silicone oil. The casting concentration of the polyurethane formulation was about 20%. After allowing to stand for 5 min, the resin was cured in an air-circulated oven in 3 h at 105°C. The films were peeled from the glass plate

and stored in a desiccator for at least 1 week before testing.

Differential Scanning Calorimetry (DSC). DSC was performed using a Perkin-Elmer System 4 instrument. Heating rate was 10°C/min and sensitivity was 2 mcal/s. Dry nitrogen was used as purge gas. Samples were cut directly from vacuum-dried films to a weight of 18–22 mg. The glass transition temperatures were determined by the change in heat capacity of one half of its maximum value.

Stress–Strain Testing. Uniaxial stress–strain and ultimate property measurements were made using a standard Instron testing machine (Model 1122) employing a crosshead speed of 1 mm/min. Samples were cut with a die in a dog-bone shape. Tensile characteristics were calculated on the basis of initial dimensions (gage length 10 mm and width 2.8 mm.)

Scanning Electron Microscopy. Scanning electron micrographs of the films were taken with an Advanced Metals Research Model 900 instrument. The samples were coated with gold–palladium alloy prior to scanning.

RESULTS AND DISCUSSION

Synthesis

Solution casting has been found to represent a convenient method for converting lignin-derived polyol components into polyurethane networks.[18] Limitations regarding this synthesis procedure have been discussed earlier.[18] This procedure is characterized by the employment of excess diisocyanate and by relatively high catalyst concentration. No tests were conducted to verify complete reaction of all special hydroxy functional groups of the immiscible PBD and lignin constituents with the crosslinking agent.

The use of PBD glycol as soft segment instead of polyethylene (PE) glycol[14] or no soft segment at all[18] caused differences in the polymerization behavior which relate to gelation and phase separation. Thermoset network polymers were synthesized when PBD glycol was the sole polyol component, but this was not possible when only PE glycol was present. In contrast to the synthesis of uniform films without visible nonuniformities with PE glycol, PBD glycol-containing polyurethanes were always found to possess inhomogeneities upon removal of solvent. Phase separation typical of networks with immiscible components resulted in the formation of polymers with either a discrete or continuous PBD glycol phase depending on composition. Similar phase-separated polymers have been described by Yu et al.[19] and Chen et al.[20] The nonpolar nature of the PBD glycol chains has the expected influence on the morphology of the resulting polyurethanes where miscibility of the two polyol components is poor. The composition of the PBD glycol (rubber) modified polyurethane formulations is summarized in Table I. Designations of the resulting film materials are based on the components used for the synthesis: hydroxypropyl lignin derivative (L), PBD glycol (B), and either HDI (H) or TDI (T).

Thermal Behavior

The glass transition temperature of the hard lignin phase of polyurethane films prepared from the polyol mixtures are given in Figure 1. Transition temperatures decline rapidly, by 36 and 73°C for TDI and HDI, respectively,

TABLE I
Composition of Polybutadiene Glycol (Rubber) Modified Polyurethane Films

| Sample designation	Polyol component		Isocyanate component (wt %)	NCO/OH ratio
	HPL (wt %)	Glycol (wt %)		
HDI Series				
LBH-2	83.3	0.0	16.7	0.95
LBH-10 (8)	71.4	0.0	28.6	1.89
LBH-6 (7)	67.8	3.6	28.6	1.92
LBH-5 (6)	64.3	7.1	28.6	2.03
LBH-7 (5)	53.6	17.8	28.6	2.27
LBH-11	35.7	35.7	28.6	2.85
LBH-8 (6)	17.8	53.6	28.6	3.81
LBH-12 (3)	7.1	64.3	28.6	4.78
LBH-13 (2)	3.6	67.8	28.6	5.21
LBH-9 (1)	0.0	71.4	28.6	5.74
LBH-1	0.0	80.0	20.0	3.58
LBH-4	0.0	83.3	16.7	2.87
TDI Series				
LBT-1	71.4	0.0	28.6	1.83
LBT-8	67.8	3.6	28.6	1.89
LBT-6	64.3	7.1	28.6	1.96
LBT-3	53.6	17.8	28.6	2.19
LBT-5	35.7	35.7	28.6	2.75
LBT-4	17.8	53.6	28.6	3.68
LBT-7	7.1	64.3	28.6	4.61
LBT-9	3.6	67.8	28.6	5.03
LBT-2	0.0	71.4	28.6	5.55
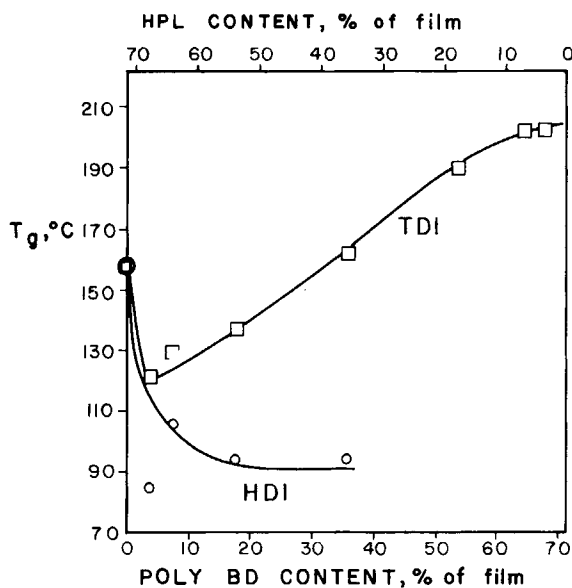
Fig. 1. Effect of poly(butadiene glycol) content on T_g of polyurethane films.

with films containing 3.6 wt % glycol (based on polyurethane), before pla-
teauing (HDI) or rising steadily with increasing glycol content (TDI). (The
detection of a distinct glass transition in for the lignin phase of HDI-based
films at high PBD glycol concentrations presented difficulties). The absence
of a continuous drop in T_g with rising soft segment content is opposite to
the results obtained with (miscible) PE glycol soft segments, which displayed
a constant decline in T_g with rising glycol content in reasonable accordance
with the Gordon–Taylor equation. The limitation of the T_g-reducing effect
of PBD glycol to very low levels of polyol mixing must be explained by a
minimal degree of miscibility of PBD in the lignin derivative network (i.e.,
<3.6% and <7.1% for HDI and TDI-based polyurethane, respectively). In
this context it is interesting to compare the rubber-modified polyurethane
films with the unmixed polyurethanes.

Figure 2 shows the T_g results of the two series in relation to the NCO/
OH ratio. A striking similarity between both film series is revealed with
the rubber-modified networks exhibiting transitions at a lower temperature
and with an apparent constancy in the decrease in T_g as a result of soft
segment incorporation. This likely reflects modification of the lignin phase
(i.e., by plasticization) due to a small amount of glycol reacted with the
lignin. It should be noted, however, that the increase in NCO/OH ratio in
the unmixed films was due to higher proportions of diisocyanate whereas
it resulted from differences in OH functionality and in stoichiometry for
the case of the mixed films. The rise in the lignin T_g of TDI-based films is
obviously due to differences in hard segment crosslink density with varying
glycol contents. Since the PBD glycol used has a much lower hydroxyl
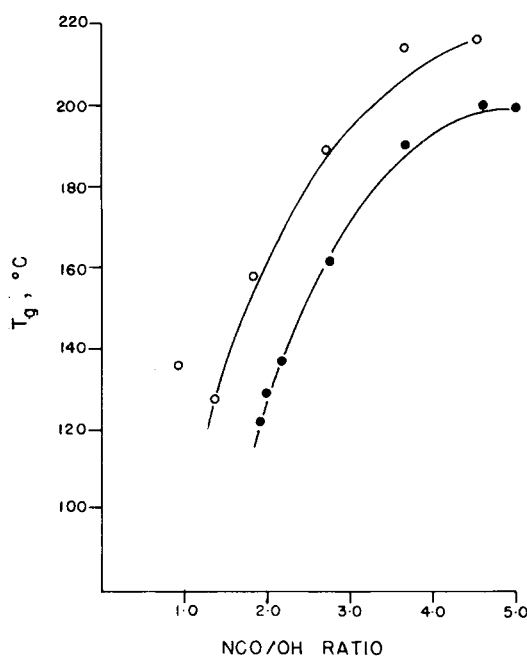

Fig. 2.   Glass transition temperatures of unmodified and poly(butadiene glycol)-modified
polyurethane films: (○) LT; (●) LBT.

content (0.83 meq/g) than the hydroxypropyl lignin (2.52 meq/g), the replacement of lignin with PBD glycol lowers the isocyanate requirement of the polyol component and increases considerably the crosslink density at constant isocyanate content. (This assumes complete consumption by reaction of all isocyanate groups, a reasonable assumption considering the high level of catalyst addition.) The comparative insensitivity towards crosslink density (NCO/OH ratio) variation of the HDI-based films is in agreement with soft segment-free lignin polyurethanes.[18]

Stress–Strain Behavior

Results from stress–strain tests of the polyurethane films are given in Table II, and, in part, in Figure 3. PBD glycol-modified lignin-based polyurethanes covering a range of 0–71.4% glycol content (0–71.4% lignin derivative content) at constant amount of diisocyanate (28.6%) were studied with regard to Young's modulus, ultimate stress, and ultimate strain. These two-phase soft-segment-containing network polymers had thus considerably greater glycol contents than the corresponding uniform thermosets discussed in the previous paper, which had miscible glycol contents of between 0 and 18% (of polyol).

Young's modulus is seen to decrease rapidly with PBD glycol content in the rubber-modified lignin films. The decrease from 1671 to 36 MPa is somewhat more gradual with HDI than with TDI-based films (Table II). Both types exhibit a corresponding increase in tensile strength as indicated by ultimate stress data and a significant loss of ultimate strain in relation to lignin content. Ultimate strain remains virtually unaffected by glycol content of the polyol rising from 0 to 75% of polyol (50% of polyurethane) when the films gain increasingly rubberlike behavior. Stress characteristics are much more drastically influenced by low glycol concentrations than are strain properties. As an example, two-thirds of the tensile strength is lost in HDI-derived films when only 25% of the polyol component is replaced by glycol; yet no extensibility is gained. Also, TDI-based networks generally have higher moduli than their HDI-derived counterparts, all other conditions being the same.

The decrease in modulus of both sets of films at relatively low glycol concentrations is evidently due to modifications of the highly rigid lignin-rich polyurethane system by the flexible chains of PBD glycol. Ultimate properties behave expectedly near either extreme of polyol mixing. This is apparent despite variations in crosslink density. That crosslink density does influence stress–strain behavior is apparent from the properties of the two pure PBD glycol networks LBH-1 and LBH-9, which differ only with regard to NCO/OH ratio and degree of crosslinking (Table II).

Scanning Electron Microscopy (SEM)

The polyurethane films were studied by SEM techniques (surface and freeze-fracture) because phase separation due to component immiscibility was evident at a macroscopic level. Both film surfaces and fracture surfaces were examined in relation to synthesis variables.

Figure 4 shows the film surface as well as the fracture surface as seen

TABLE II
Tensile Properties of Rubber Modified Kraft Polyurethanes

| Sample	HPL (wt %)	Young's modulus (MPa)	Ultimate stress (MPa)	Ultimate strain (%)
HDI Series				
LBH-10	71.4	1671 ± 51	73.5	6.8
LBH-6	67.8	1219 ± 70	43.7	5.1
LBH-5	64.3	1373 ± 70	34.5	3.1
LBH-7	53.6	1060 ± 93	24.5	2.6
LBH-8	17.8	208 ± 5	4.3	4.0
LBH-12	7.1	54 ± 4	6.3	62.4
LBH-13	3.6	45 ± 7	6.5	76.7
LBH-9	0.0	48 ± 8	8.1	140.0
LBH-1	0.0	36 ± 11	7.2	159.0
TDI Series				
LBT-1	71.4	2076 ± 318	48.5	6.0
LBT-8	67.8	1789 ± 46	62.9	4.7
LBT-6	64.3	1785 ± 134	43.5	3.7
LBT-5	35.7	634 ± 39	24.4	6.1
LBT-4	17.8	51 ± 4	5.1	38.0
LBT-7	7.1	36 ± 4	4.8	68.0
LBT-9	3.6	45 ± 6	8.6	130.0
LBT-2	0.0	52 ± 8	8.9	171.0
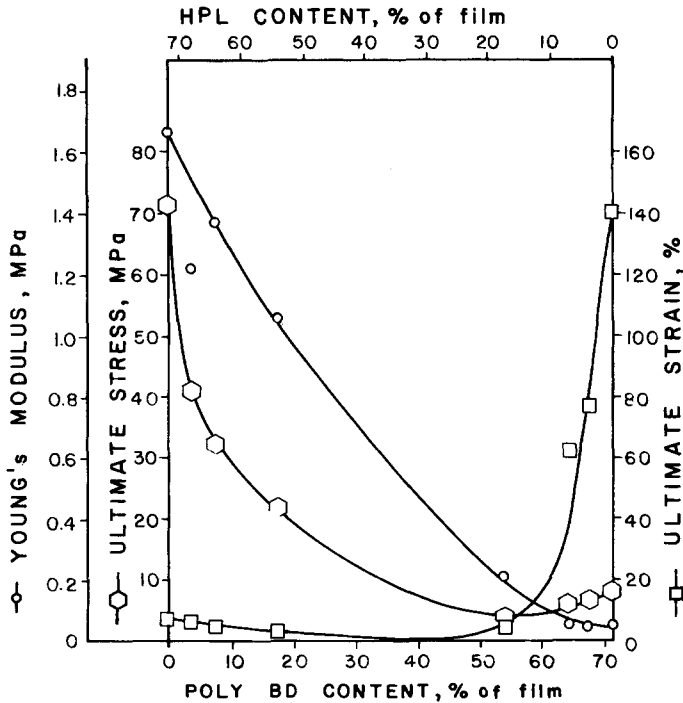
Fig. 3. Young's modulus, ultimate stress, and ultimate strain of HDI-based polyblended polyurethane films.
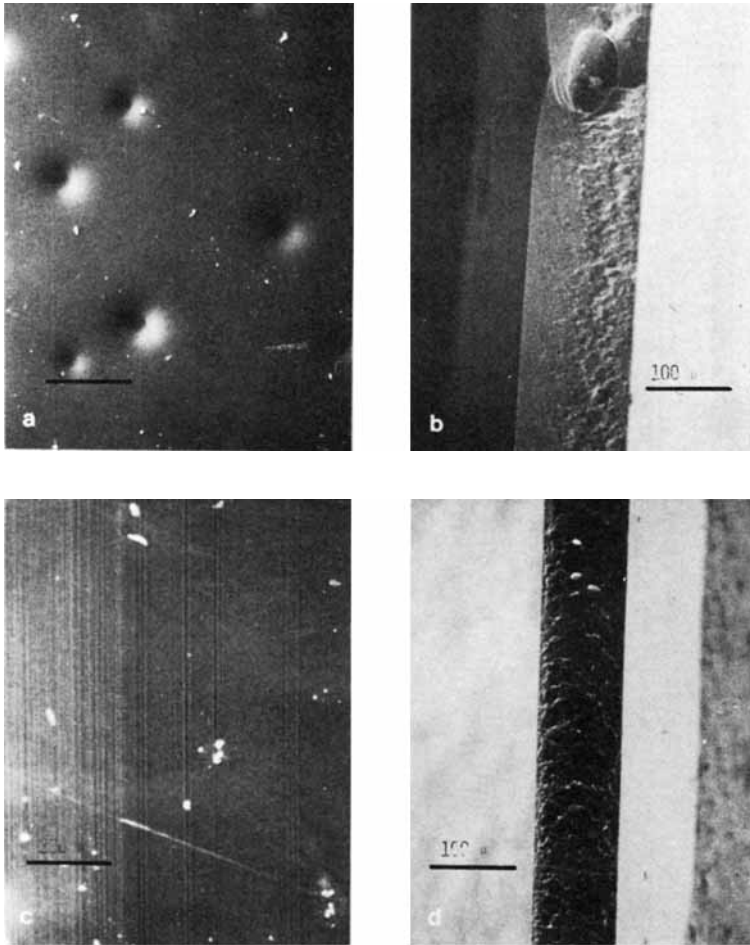
Fig. 4. SEMs of the surfaces and the fracture surfaces of HDI-based film LBH-6 (top, a and b) and TDI-based film LBT-8 (bottom, c and d) (both 3.6% PBD glycol content of film).

by scanning electron microscopy for two PBD-glycol-modified polyurethane films, one based on HDI (LBH-6) and the other based on TDI (LBT-8). Both contain low levels of soft segment component (3.6%). It is noted in Figure 4(A) and (B), which extends from sample LBH-6, that distinct macroscopic islandlike regions exist and represent the macrophase separation of the PBD component. However, in Figure 4(C) and (D), which extends from the sample LBT-8, no distinct incompatibility is noted, possibly resulting from a somewhat greater solubility of the limited PBD in the TDI containing material. In fact, a modest amount of miscibility had already been suspected based on the earlier discussion of the thermal properties and the results presented in Figure 2. The phase structure of the two corresponding films with 7.1% glycol content is revealed by the micrographs of Figure 5. Here, again, inhomogeneties of a macrophase nature are denoted in both the HDI as well as the TDI-derived films. The trend of increasing sizes of these larger phase separated inclusions clearly arises from incompatibility as the glycol
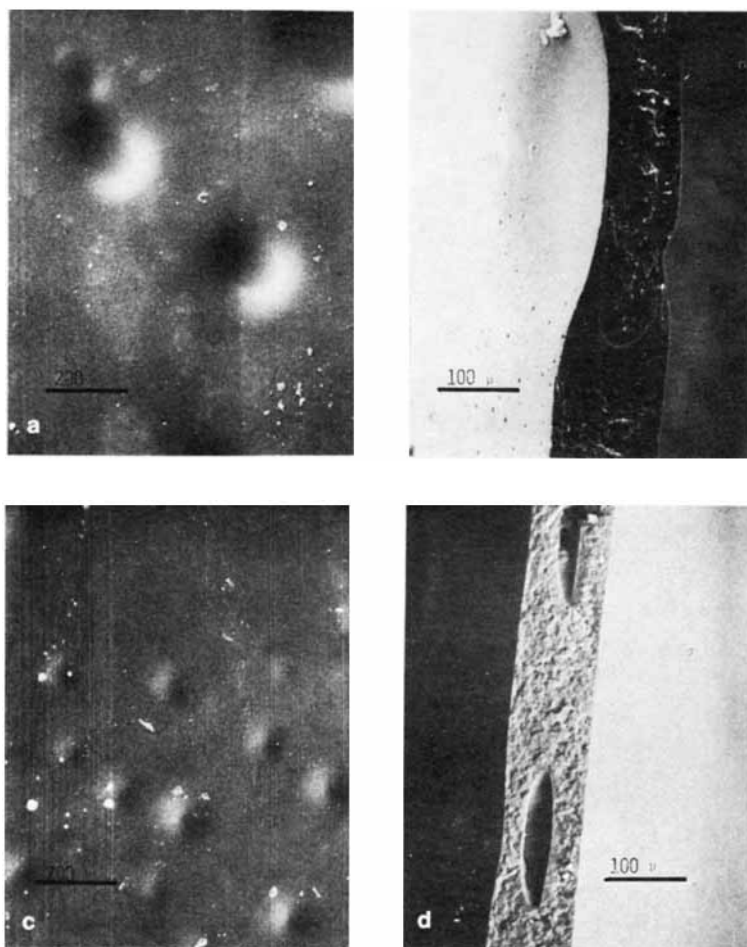
Fig. 5.   SEMs of the surfaces and the fracture surfaces of HDI-based film LBH-5 (top, a and b) and LBT-6 (bottom, c and d) (both 7.1% PBD glycol content of film).

content rises to 17.8% as denoted in Figure 6. It might be indicated that while some voids seem to be present within these materials, the large macrophase or islandlike behavior denoted in these latter micrographs are a consequence of the PBD glycol phase separation, as was confirmed by several microscopy investigations.

As denoted in Figure 7, which represents the fracture surfaces obtained from sample LBT-4, one clearly sees that there is a very distinct two phase character where the size of the dispersed phase is in the order of 5–10 μm on the average. While fracture leads to some dilatation effects from the fracturing process, the principal point to observe is that one would have to classify the degree of adhesion of the dispersed phase to the matrix component (the lignin-rich phase) as being intermediate. That is, there are several indications in the micrographs that suggest a relatively poor interfacing of the particles with the matrix whereas other regions seem to show no distinct failure at the boundary regions. A surprisingly extensive
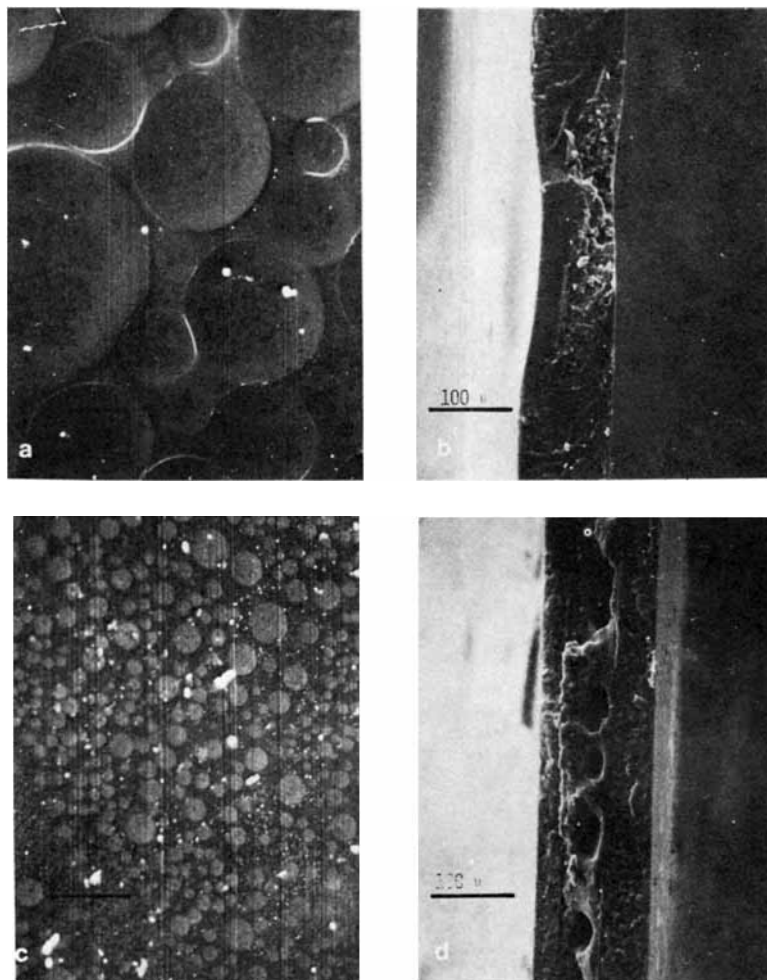
Fig. 6. SEMS of the surfaces and the fracture surfaces of HDI-based film LBH-7 (top, a and b) and LBT-3 (bottom, c and d) (both 17.8% PBD glycol content of film).

porous structure was denoted in the PBD-glycol-rich urethanes (53.8 and 64.3%) when fractured, as shown in the micrographs given in Figure 8. The exact cause of this porous texture is not particularly clear to the authors, for it results from the film casting technique rather than from the fracture process as has previously been confirmed with other microscopy studies.

In summary of these qualitative microscopy investigations, it can be concluded that the PBD glycol exhibits a high degree of immiscibility with the hydroxypropyl lignin phase in these polyurethane systems. This, of course, had already been expected based on the initial thermal results as well as the nonpolar character of the polybutadiene oligomers.

Stress–strain properties were significantly different in films with low soft segment content (up to 50% of the polyol component) as compared to those with high PBD glycol content. This is in striking contrast to the compatible soft segment-containing PE glycol chains[14] for which no signs of inhomogeneity were found, and where properties changed more gradual
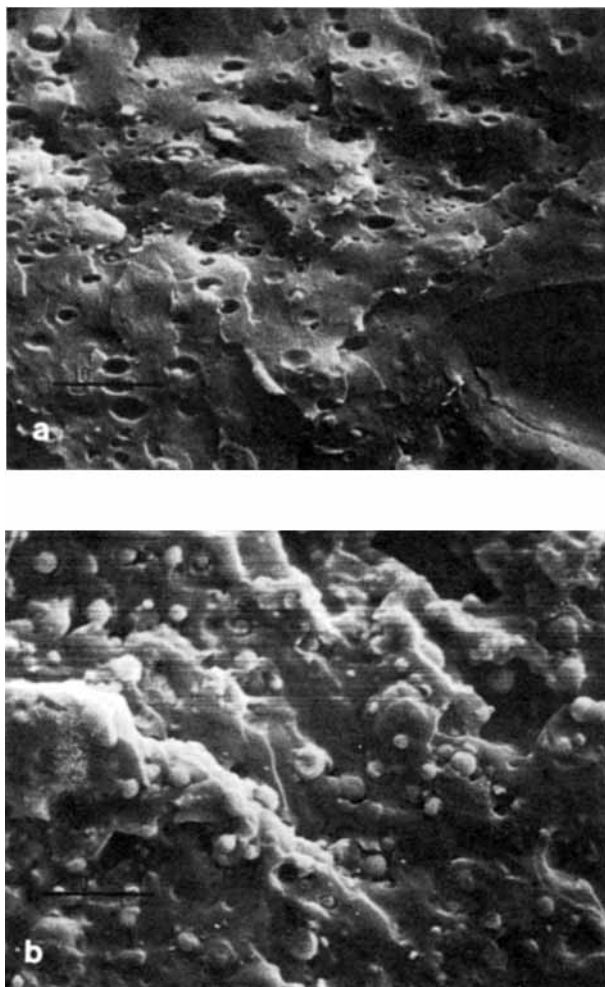
Fig. 7. SEMs of fracture surfaces of film LBT-6 (above) and LBT-4 (below) illustrating fracture behavior of rubber-toughened lignin polyurethane (a, top) and lignin-reinforced PBD polyurethane (b, bottom).

in response to soft segment incorporation. (An overlapping effect of crosslink density variation had been pointed out as a consequence of NCO/OH ratio differences.) It is likely that the polyether chains of PE glycol are more uniformly distributed throughout the network than are the PBD glycol chains because (a) hydrogen bonds are formed between urethane bonds and the polyether oxygen and (b) the solubility properties of the two polyol components are more similar. Other work[21] on this aspect of component miscibility and on domain structure formation in thermoplastic polyurethanes tends to support this hypothesis.

Dynamic Mechanical Analysis

Dynamic mechanical spectra of three lignin-based polyurethane films representing increasing degrees of rubber modification are shown in Figures 9–11. Film LH-4 is unmodified (Fig. 9), and films LBH-6 (Fig. 10) and LBH-
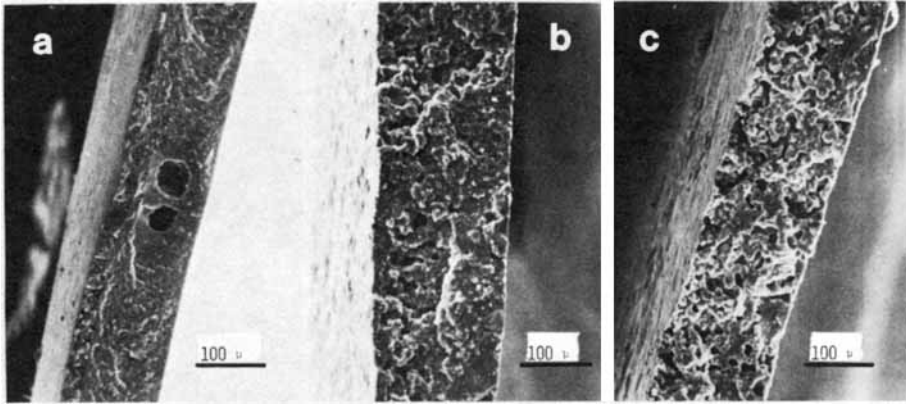
Fig. 8.   SEMs of polyurethanes with high PBD content illustrating pronounced pore structure; (a) rubber-modified lignin polyurethane (17.8% PBD glycol, 53.6% HPL); (b,c) lignin-reinforced (17.8% in b and 7.1% in c) PBD polyurethane.

8 (Fig. 11) contain 3.6 and 53.6 wt % PBD glycol, respectively, amounting to nearly 5 and 75% of the polyol fraction. This type of composition represents two extremes where one represents lignin (rigid matrix) as the continuous phase, and the other where the rubber (soft component) is continuous. Where LBH-8 contains a distinct PBD glycol transition at $-60°C$ (Fig. 11) (which is close to the transition of the homopolymer), no such transitions can be detected in LBH-6 (with 3.6% PBD glycol content). The peak value of the loss tangent, tan δ, for the low glycol content film (LBH-6) occurs at about 120°C (Fig. 10) and is slightly larger in magnitude and
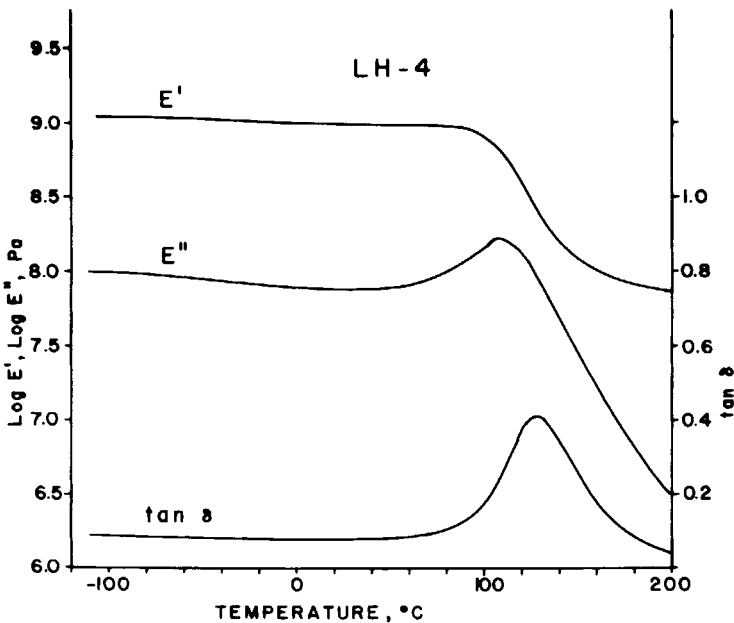

Fig. 9.   Dynamic mechanical spectrum of polyurethane film LH-4 without glycol content.
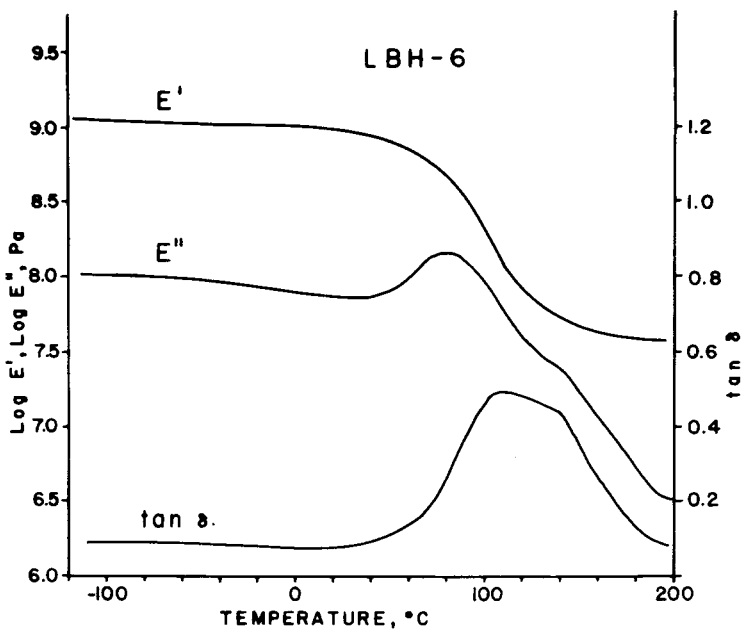
Fig. 10. Dynamic mechanical spectrum of polyurethane film LBH-6 with 3.6% glycol content (on film substance).

broader compared to unmodified polyurethane (LH-4) (Fig. 9). The storage modulus (E') begins to decline at ca. 30°C for LBH-6 (Fig. 10) whereas it is virtually stable to ca. 90°C for LH-4 (Fig. 9). The modulus behavior beyond the glass transition, however, is similar in both cases and approaches a
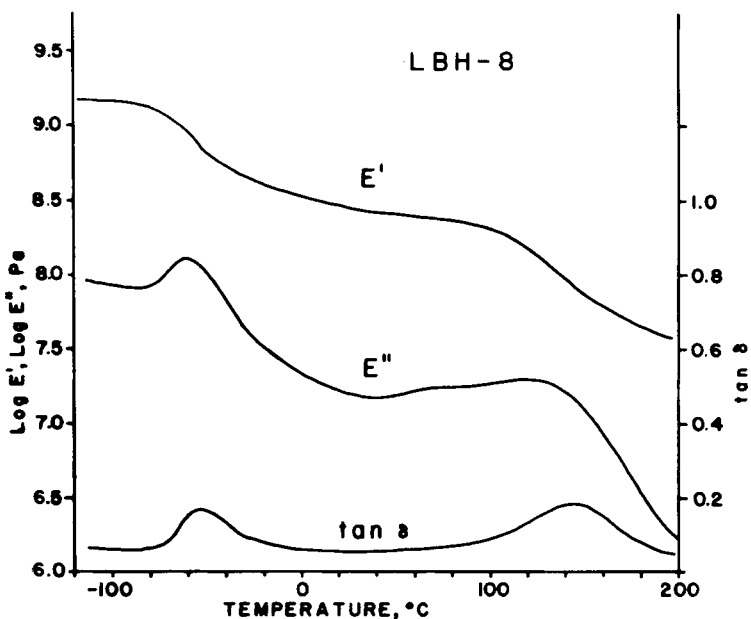

Fig. 11. Dynamic mechanical spectrum of polyurethane film LBH-8 with 53.6% glycol content (on film substance).

plateau value above 150°C. The film with the higher glycol content (LBH-8, Fig. 11), on the other hand, has a storage modulus typical of rubber networks. Specifically, storage (E') and loss modulus (E'') are considerably lower than corresponding moduli for LBH-6, and two distinct transitions are observed for the two separate phases. The PBD glycol phase has a tan δ transition at ca. −50°C, and the lignin phase at ca. 140°C. A rubbery pleateau exists between the two transitions. The lignin transition occurs at a somewhat higher temperature than that of the LBH-6 film, and E' continues to decline without reaching a plateau value. Modulus stabilization beyond the glass transition, as in the case of film LH-4 and LBH-6, indicates network structure. The existence of discrete rubber-rich regions in the lignin phase of LBH-6 was determined by scanning electron microscopy (Fig. 4). No clear transition was revealed for this rubbery phase, probably due to the very low magnitude of the modulus change at the transition. Assuming that the specific magnitude of tan δ for rubber and lignin are similar, the 15-fold difference in weight fraction between the two phases would make it difficult to detect the transition arising from the rubber phase by dynamic mechanical (or even thermal) analysis.

CONCLUSIONS

1. Hydroxypropyl lignin derivatives form phase-separated soft-segment-containing polyurethane films by solution casting (from THF) with PBD glycol by crosslinking with diisocyanates. As expected, the hydrophobic nature of the butadiene chains produces nonuniform polyurethanes in which macrophase separation occurs at low soft segment contents. Non-uniformity in morphological textures increases with PBD glycol content, and at high glycol content the rubber phase becomes continuous as expected.

2. The glass transition temperatures of rubber-modified (with PBD glycol) lignin polyurethanes drop sharply up to ca. 5% glycol content, but then increase with increasing rubber component. This is contrary to results obtained with (compatible) PE glycol. Low hydroxy functionality and low stoichiometric requirement of the glycol as compared to lignin, in conjunction with immiscibility and separation of segments between lignin structures, produces a more highly crosslinked lignin phase and a lightly crosslinked PBD glycol phase.

3. The mechanical properties of PBD glycol-modified lignin polyurethanes are sensitive to mixing ratios, especially at either extreme of blending. Whereas ultimate strain declines sharply with lignin content rising to ca. 20% of film weight, tensile strength and Young's modulus are rapidly reduced at high PBD glycol concentrations.

4. Incompatibility between the PBD glycol soft segment component and the lignin-rich rigid matrix is revealed by scanning electron microscopy, at essentially any composition.

5. Incompatibility between polyol components further enlarges the menu of plastics formulation on the basis of lignin derivatives.

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