

Engineering Plastics from Lignin. VI. Structure–Property Relationships of PEG-Containing Polyurethane Networks

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Synopsis

Hydroxypropyl lignin-based thermosetting polyurethanes were synthesized with excess hexamethylene diisocyanate (HDI) and tolylene diisocyanate (TDI) by solution casting. Four polyethylene glycols (PEG) of molecular weight 400, 600, 1000, and 4000 were mixed with lignin polyol to incorporate different proportions of soft segment into the network prior to crosslinking. Neither thermal nor mechanical and limited small angle x-ray scattering (SAXS) analysis provided distinct evidence for phase separation and microstructure formation. The study examines the effect of the soft segment in relation to chain length and weight contribution on the thermal and mechanical properties of the final networks. A significant sensitivity of glass transition temperature (T_g), of swelling in DMF, and of the mechanical properties to soft segment content was observed. Some of this sensitivity must, however, be attributed to differences in crosslink density since the polyol to diisocyanate weight ratio was kept constant throughout the synthesis series. The magnitude of the change of the different properties was found to be influenced by both glycol content and glycol molecular weight. The T_g of the network decreased from 105°C to as low as 38°C (HDI), and from 158°C to 70°C (TDI), with incorporation of up to 17.8% glycol, and it was greater with lower molecular weight glycols than with higher ones at any weight fraction. Swelling in DMF increased as expected with soft segment content. Mechanical properties were affected most if HDI and lower molecular weight glycols were used. The uniformity in structure, reduction in brittleness, and considerable improvement in mechanical properties with inclusion of minor PEG contents indicates that lignin-based network polyurethanes can be synthesized with controllable performance characteristics.

INTRODUCTION

The properties of thermosetting polymers depend on their network architecture. Understanding the structure–property relationships provides an important guide for engineering useful macromolecular materials. Structural modifications for the purpose of improving polymer performance are exemplified by the grafting of thermoplastic chains onto rubbery particles in rubber-modified elastomers, and this has proven effective for imparting energy-dissipative properties thereby reducing brittleness.¹ Much of the understanding about increasing toughness of elastomers has emerged with

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the advent of linear segmentation, particularly with thermoplastic polyurethanes.²⁻¹⁶ Many studies on the morphology of segmented copolymers have attributed the toughness in these materials to soft and hard segment architecture and the resulting microphase, "domain" texture that they produce.¹⁷ Evidence has been gathered with techniques such as small angle X-ray scattering (SAXS), infrared spectroscopy (especially FT-IR), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA).² Progress in the understanding of the variation in polymer structure on the molecular level has established that the combination of high modulus and strength originates from physically crosslinking or reinforcing a soft segment matrix with hard segment domains. Fewer studies have focused on the structure-property relationships of network systems based on urethane chemistry than on the linear thermoplastic polyurethanes.¹⁸⁻³³ However, epoxies have been studied more extensively than polyurethanes with regard to the effect of compositional variations and the morphology of rubber modified moieties. In some instances, these latter systems have been viewed as networks in which highly crosslinked regions are embedded in a less crosslinked matrix.³⁴ The existence of such heterogeneous textures has been inferred from the results of investigations using such techniques as electron and optical microscopy, DMA, differential swelling, and DSC, but controversy still exists with regard to this question of heterogeneous crosslink density.

In network polyurethanes, studies indicate that the existence of crosslinks can place restraint on the inducement of domain formation. In studying thermomechanical properties of linear thermoplastic elastomers in relation to crosslinking, Cooper and Tobolsky²¹ concluded that domain structures can be maintained or destroyed depending on the number and location of crosslinks. Related studies by Ophir and Wilkes²² and by Assink and Wilkes²³ concluded that covalent crosslinking of initially linear segmented urethanes can limit domain formation under certain conditions. Although advances in the characterization of network structures are not comparable to those of linear systems, improvements in the properties of rigid network polymers have sometimes been realized through the introduction (by blending) of polymers with greater chain flexibility.^{34,35}

Previous studies in this series examined the synthesis of hydroxypropyl lignin derivatives^{36,37} and their characterization.³⁸ Several structure-property relationships of lignin-based, solution-cast polyurethanes in relation to lignin type and composition³⁹ and crosslink density^{40,41} were determined. Results by thermal and mechanical testing indicated the network's sensitivity to variations in crosslink density and type of diisocyanate. This study addresses the effect of adding polyethylene glycol (PEG) in the molecular weight range of 400-4000 to lignin polyol in the synthesis of polyurethane networks.

EXPERIMENTAL

Materials

Lignins

Kraft Lignin (KL). Commercial pine kraft lignin, isolated by acidification of the spent pulping ("black") liquor of a kraft mill, was obtained from

Westvaco Corp., N. Charleston, S. C., under the trade name INDULIN ATR-C1.

Steam Explosion Lignin (SEL). Steam explosion lignin was supplied by Iotech Corp., Ottawa, Canada. This was extracted from steam exploded aspen chips with aqueous NaOH (0.4%) as has been described by Marchessault et al.⁴² and by Glasser et al.⁴³

The chemical analysis of these two lignins indicated methoxyl contents of 13.7% and 18.2%, phenolic hydroxyl contents of 5.5% and 4.3%, and total hydroxyl contents of 11.9% and 9.6% for KL and SEL, respectively. Molecular weights and molecular weight distributions (by GPC) indicated weight average molecular weights of 4300 and 2000 gM^{-1} at dispersion factors of nearly 10 and 3.5 for KL and SEL, respectively.

Hydroxypropyl Lignins. Solid lignins were reacted with propylene oxide according to a procedure described previously⁴⁴ in a closed, mechanically stirred stainless steel reactor. Hydroxyl contents were 4.3% and 9.3% for KL and SEL, respectively.

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

Poly(ethylene Glycols) (PEG). Poly(ethylene glycols) of molecular weight ($\langle M_N \rangle$) 400, 600, and 1000 (Carbowax PEG 400, 600, and 1000, by Fisher Scientific Co., Fair Lawn, N. J.), and of molecular weight 4000 (Carbowax PEG 4000 by Union Carbide Corp., New York, N. Y.) were used.

Methods

Film Preparation. Polyurethane films were prepared as described previously³⁹ by solution casting a mixture of polyol components (hydroxypropyl lignin and PEG), diisocyanate, and catalyst (dibutyltin dilaurate) in tetrahydrofuran (THF) on a glass plate coated with a thin layer of silicone release agent spray. The agent was necessary to permit film removal from the glass surface. The casting concentration of the polyurethane formulation was about 20%. Twenty minutes after mixing all components, at room temperature, and after most solvent had vaporized, the resin was cured in an air-circulated oven for 3 h at 105°C. The films were then peeled from the glass plate and stored at room temperature (ca. 23°C) in a desiccator for at least 1 week before testing.

Differential Scanning Calorimetry (DSC). DSC was performed using a Perkin-Elmer System 4 instrument equipped with a scanning auto zero accessory. The heating rate used was 10°C/min, while the sensitivity was 2 mcal/s. Dry nitrogen was used as purge gas. Samples were cut directly from vacuum dried solvent cast films to a weight of 18–22 mg. The glass transition temperatures was taken as that temperature corresponding to the point where the heat capacity had achieved one half of its change during the transition.

Stress-Strain Testing. Uniaxial stress-strain and ultimate property measurements were made using an 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.)

TABLE I
Composition of Kraft HPL-Polyethylene Glycol Urethane Systems^a

Designation	Hydroxy component (wt %)		Isocyanate component (wt %)	NCO/OH ratio at PEG molecular weight			
	HPL	PEG		400	600	1000	4000
HDI series							
KEH-MW-1	71.4	0.0	28.6	1.89	1.89	1.89	1.89
KEH-MW-2	67.9	3.5	28.6	1.80	1.86	1.91	1.97
KEH-MW-3	64.3	7.1	28.6	1.73	1.83	1.93	2.06
KEH-MW-4	60.7	10.7	28.6	1.65	1.80	1.95	2.15
KEH-MW-5	57.1	14.3	28.6	1.58	1.78	1.97	2.25
KEH-MW-6	53.6	17.8	28.6	1.52	1.75	1.99	2.36
TDI series							
KET-MW-1	71.4	0.0	28.6	1.83	1.83	1.83	1.83
KET-MW-2	67.9	3.5	28.6	1.74	1.80	1.85	1.90
KET-MW-3	64.3	7.1	28.6	1.66	1.77	1.87	1.99
KET-MW-4	60.7	10.7	28.6	1.59	1.74	1.89	2.08
KET-MW-5	57.1	14.3	28.6	1.53	1.72	1.91	2.18
KET-MW-6	53.6	17.8	28.6	1.47	1.69	1.93	2.28

^a Individual sample designations have numbers corresponding to molecular weight of glycol in place of MW.

Swelling. Polyurethane films were swollen to equilibrium (120 h) in dimethyl formamide. The weight increase was expressed in percent based on the unswollen weight.

RESULTS AND DISCUSSION

Synthesis

The synthesis of thermosetting polymer films from components which cannot conveniently be liquefied (hot-melted) and molded prior to reaction is best accomplished by solution casting. Films are formed by curing, following solvent removal, of unreacted polymer components. The limitations and uncertainties regarding polyurethane compositions prepared by this method have been discussed earlier.³⁹ Employment of a stoichiometric excess of diisocyanate and high catalyst concentration are requirements of the solution casting procedure which allow casting before completion of the reaction.

Table I summarizes the composition of the film preparations. Terminology of the polyurethanes is based on the components used for the synthesis as well as the molecular weight of the PEG. *Since the isocyanate content was kept constant at 28.6 wt %, the actual NCO/OH ratio changes, depending on the molecular weight of the PEG.* The ratio declines from KEH-400-1 to KEH-400-6 and increases from KEH-4000-1 to KEH-4000-6. Control of this molar ratio was found to be unnecessary in these polyurethanes since completion of the reaction required excess diisocyanate in all cases. The selection of a 28.6 wt % isocyanate content was based on the empirical observation that all polyurethanes produced apparent homogeneous films

under these conditions regardless of soft segment content or molecular weight. Higher isocyanate contents resulted in excessively brittle materials. Similar observations had been made earlier.³⁹ Lower isocyanate contents often resulted in incomplete reaction and visually inhomogeneous films.

Thermal Properties

The glass transition temperatures (T_g) of the polyurethanes are given in Table II. The data refer to the transition of the lignin phase; transitions originating from the PEG component were not detectable. This in turn implies that little or no phase separation of the PEG component occurs. The data were obtained with single samples, and thermal transitions frequently were subtle and broad. It should be noted that, even though multiple data were acquired to test the reproducibility of each glass transition temperature, all observations were done on a single film. Thus any experimental error in the synthesis of the film is reflected by the data (e.g., film with 17.8% glycol of 600 molecular weight). Because of this inherent var-

TABLE II
Experimental and Theoretical^a Glass Transition Temperatures of HDI-Based Kraft Polyurethane with Polyethylene Glycol Soft Segments

Glycol (wt %)	Glass transition temp (°C), PEG of molecular weight			
	400	600	1000	4000
HDI series				
0.0	105	105	105	105
3.5 Exp.	96	108 (98) ^b	99	110 (105) ^b
Th.	91	92	94	95
7.1 Exp.	87	94 (88) ^b	88	96
Th.	77	80	83	86
10.7 Exp.	66	66	67	84
Th.	65	69	72	77
14.3 Exp.	56	56	65	76
Th.	53	59	63	69
17.8 Exp.	38	96 (42) ^b	44	63
Th.	43	49	55	62
TDI series				
0.0	158	158	158	158
3.5 Exp.	120	148	157	131
Th.	139	142	144	145
7.1 Exp.	119	130	143	155
Th.	121	126	130	136
10.7 Exp.	86	128	131	120
Th.	105	111	116	125
14.3 Exp.	79	97	110	108
Th.	90	98	103	115
17.8 Exp.	70	41	95	95
Th.	77	85	94	105

^a Calculations based on the Gordon-Taylor equation with $k = 0.5$ (see text).

^b Numbers in parentheses represent values obtained by interpolation from the obtained sample data. For example, the T_g 42°C value of the PEG 600/17.8% HDI sample was obtained by smoothing both the 17.8% HDI series data and the PEG 600 series data. These corrected values were employed for constructing the perspective plots of Figures 1, 3, 4, and 5.

iability, several outlying data points of Table II were smoothed by interpolation from neighboring sample data. These smoothed data are indicated in parentheses in Table II, and they were employed in the graph of Figure 1.

The T_g varied significantly only with PEG content; PEG molecular weight had a much less pronounced effect. It should, however, be stressed that the NCO/OH ratio and thus crosslink density varied at a constant lignin to PEG ratio and varying PEG molecular weight, since it was the weight ratio of polyol to isocyanate component that was kept constant throughout the series. The relationship between T_g and PEG content and molecular weight is shown as a surface plot in Figure 1. The apparent initial increase of T_g of the M_N 4000 sample at < 5% PEG content may not be significant or may be due to increased crosslink density (NCO/OH ratio, Table I). Occurrence of enthalpy relaxation effects during the initial DSC scan made it necessary to determine T_g from the second thermogram, which was always reproducible although subtle at times. The data of the HDI- and TDI-based films reflect similar trends although at different temperature levels. TDI-derived films generally displayed their glass transitions at around 50°C above those of their HDI counterparts. In summary, the polyurethanes show a steady drop in T_g with increasing PEG content and a less dramatic, but nevertheless significant, increase with rising molecular weights.

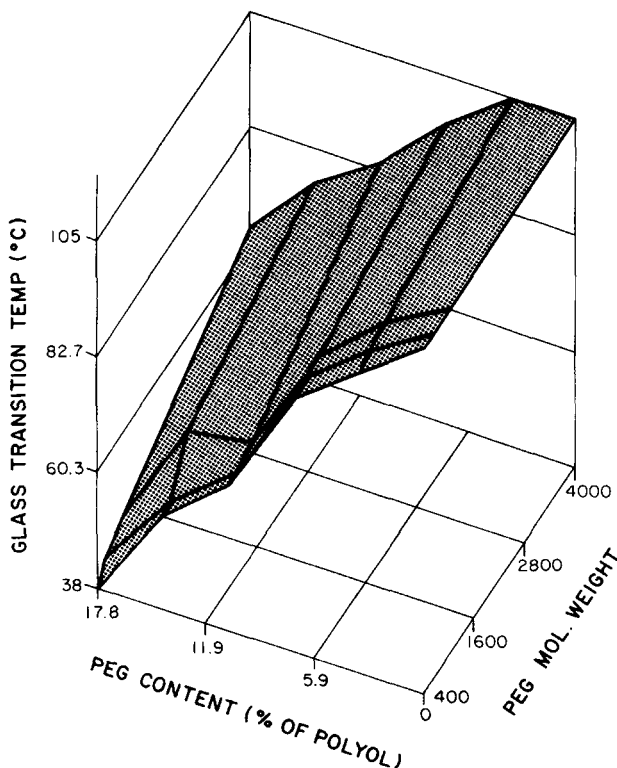


Fig. 1. Influence of PEG content and molecular weight on glass transition temperature of polyurethane films.

Glass-transition temperatures were calculated for the soft segment extended films according to the Gordon-Taylor⁴⁵ equation [eq (1)] of

$$T = \frac{kC_2T_2 + C_1T_1}{C_1 + kC_2} \quad (1)$$

where $T = T_g$ of composite, $C_{1,2}$ = weight fraction of PEG and of HPL-PU polymer, resp., $T_1 = T_g$ of PEG polymer, $T_2 = T_g$ of HPL-PU polymer, and k = adjustable constant. Unlike the usual application, however, where T_1 and T_2 are constant over the range, T_2 in this case (HPL-PU) was varied to reflect changes in the NCO/OH ratio (for reference, see Saraf and Glasser³⁹). This variation was $105 \pm 5^\circ\text{C}$ for the HDI-based films, and $158 \pm 10^\circ\text{C}$ for the TDI-based films. High weight percent of low molecular weight PEG constituted thereby the lower end, and the high weight percent of high molecular weight PEG the higher extreme on the temperature scale. T_1 was computed to be -92°C , -77°C , -64°C , and -51°C for the 400, 600, 1000, and 4000 molecular weight (M_n) PEG preparation, respectively, according to the Beaman-Boyer⁴⁶ rule [eq. (2)] of

$$T_g = \frac{2}{3}T_m \quad (2)$$

where T_m is the melting temperature of PEG (from Fig. 40 of Wunderlich⁴⁷).

C_1 was taken to be unreacted PEG, and C_2 only was considered to be polyurethane. Although this may represent an unrealistic oversimplification, the predicted glass transition temperatures were found to fit the experimental data reasonably well (Table II).

The absence of a detectable glass transition for the PEG phase suggests that both polyol components in these network polyurethanes are well mixed. This is also suggested by the rapid drop in T_g of the lignin phase. The absence of a PEG transition may also be the result of the generally low PEG content (< 20%).

The definitive interpretation of these observations is made difficult by the overlapping effects of PEG molecular weight and crosslink density resulting from variations in the NCO/OH ratio. A comparison at equivalent number of chains and constant crosslink density is complicated by the high average molecular weights and broad dispersities of the lignin derivatives. Two main factors have to be considered for assessing the impact of soft segment (PEG) addition on the thermal properties of rigid networks. For identical PEG content (by weight), the number of chains introduced into the network decreases with increasing molecular weight. And, since the stoichiometric isocyanate requirement decreases with increasing PEG molecular weight, use of constant amounts of diisocyanate possibly results in increased crosslink density through allophanate and biuret linkage formation (unless some isocyanate functionality is consumed by trace amounts of moisture). Both reduced chain number and increased crosslink density are expected to cause a rise in T_g of the network system. Thus, any effect of PEG molecular weight on the T_g of the lignin phase is probably masked by conflicting property effects.

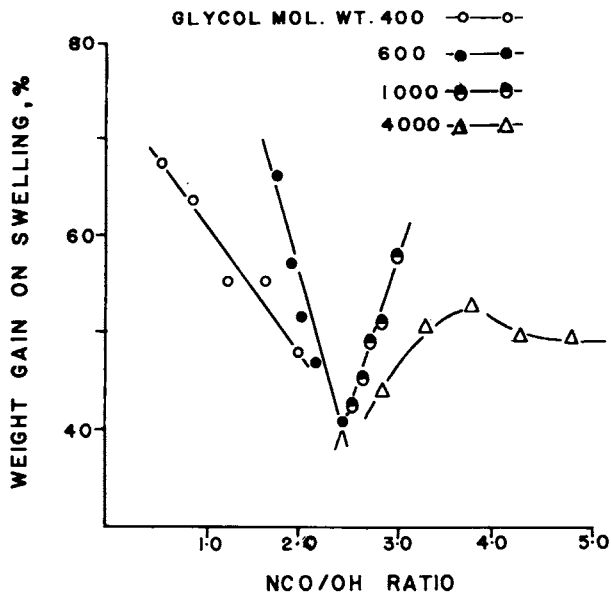


Fig. 2. Swelling behavior of HDI-based polyurethanes in relation to NCO/OH ratio; films. Glycol MW: (○) 400; (●) 600; (◐) 1000; (△) 4000.

Swelling

The effect of crosslink density, expressed as NCO/OH ratio, on swelling properties in DMF of HDI-based kraft polyurethane films is shown in Figure 2. Swelling increases with increasing PEG content of any molecular weight, but NCO/OH ratios of > 3 result in an apparent insensitivity towards DMF. It is to be noted that the NCO/OH ratio increases with increasing glycol content for the PEG 4000 series whereas it decreases for the lower molecular weight glycols. The results indicate that PEG of any molecular weight influences swelling in a predictable manner. This must account for why the degree of swelling is the same for the 1000 and the 4000 molecular weight PEG for the lowest NCO/OH ratios; however, with higher PEG 4000 content, swelling decreases, suggesting that crosslink density (via biuret and allophanate linkages) becomes a controlling factor. Near constant swelling properties at high NCO/OH ratios were also noted in PEG-free polyurethanes,³⁹ and this was attributed to insignificant changes in M_c with isocyanate-to-hydroxyl ratio rising beyond a critical value.

Stress-Strain Behavior

Ultimate strength properties of (kraft) lignin-based polyurethanes containing different types and amounts of PEG soft segments are given in Tables III and IV, and Young's modulus, tensile strength, and ultimate strain (of HDI-based films) are plotted vs. PEG content and PEG molecular weight in surface graphs (Figs. 3-5). Glycol content clearly has a more significant effect on modulus and tensile strength (but not on ultimate strain) than does molecular weight. It is evident that even minor percentages of PEG (especially $< 5\%$) significantly influence the tensile behavior

TABLE III
Tensile Properties of HDI Based Films

Sample	Kraft HPL (wt %)	Young's modulus (MPa)	Yield stress (MPa)	Yield strain (%)	Ultimate stress (MPa)	Ultimate strain (%)
KEH-400-1	71.4	1671±51			73.5	6.8
KEH-400-2	67.9	1042±38	48.6	8.1	46.4	9.4
KEH-400-3	64.3	1062±67	39.7	5.9	34.8	15.4
KEH-400-4	60.7	1618±42 (890) ^a	53.8	4.9	44.4 (32.2) ^a	11.0
KEH-400-5	57.1	707±112	30.8	7.2	31.2	24.9
KEH-400-6	53.6	384±38	19.2	9.3	26.0	43.0
KEH-600-1	71.4	1671±51			73.5	6.8
KEH-600-2	67.9	1034±33			47.1	7.3
KEH-600-3	64.3	965±30	47.3	7.0	46.7	8.0
KEH-600-4	60.7	965±60	40.2	7.1	39.2	10.0
KEH-600-5	57.1	716±49	31.9	6.8	33.4	26.5
KEH-600-6	53.6	1377±88 (500) ^a	52.9	5.4	47.3 (28.0) ^a	10.6 (37.0) ^a
KEH-1000-1	71.4	1671±51			73.5	6.8
KEH-1000-2	67.9	1221±59			51.5	5.8
KEH-1000-3	64.3	1085±50			50.2	6.2
KEH-1000-4	60.7	942±62	43.1	6.8	41.6	9.2
KEH-1000-5	57.1	745±28	35.8	7.0	35.0	9.6
KEH-1000-6	53.6	594±37	27.8	8.0	29.0	19.8
KEH-4000-1	71.4	1671±51			73.5	6.8
KEH-4000-2	67.9	1272±89	48.2	5.9	47.3	9.2
KEH-4000-3	64.3	1153±50	45.7	6.2	44.3	10.4
KEH-4000-4	60.7	962±75	39.7	6.5	39.1	11.0
KEH-4000-5	57.1	801±52	33.1	6.9	33.4	10.1 (12.0) ^a
KEH-4000-6	53.6	592±21	28.3	7.9	29.5	13.0

^a Numbers in parentheses represent values obtained by interpolation from the obtained sample data, as illustrated in Table II.

TABLE IV
Tensile Properties of TDI-Based Films

Sample	Kraft HPL (wt %)	Young's modulus (MPa)	Yield stress (MPa)	Yield strain (%)	Ultimate stress (MPa)	Ultimate strain (%)
KET-400-1	71.4	2076±318			48.5	6.0
KET-400-3	64.3	1706±140			37.8	2.9
KET-400-4	60.7	2438±97			69.2	4.8
KET-400-5	57.1	1946±68			56.1	6.0
KET-400-6	53.6	1834±115			46.9	4.0
KET-600-1	71.4	2076±318			48.5	6.0
KET-600-2	67.9	1459±157			62.9	5.9
KET-600-3	64.3	1400±102			64.4	6.8
KET-600-4	60.7	1409±108			63.1	7.6
KET-600-5	57.1	1448±87	60.6	6.4	57.2	8.8
KET-600-6	53.6	592±71	30.0	7.7	33.7	31.0
KET-1000-1	71.4	2076±318			48.5	6.0
KET-1000-2	67.9	1590±57			50.5	3.3
KET-1000-3	64.3	1485±83			52.9	4.1
KET-1000-4	60.7	1531±150			55.5	4.6
KET-1000-5	57.1	1423±21			51.9	5.6
KET-1000-6	53.6	1317±38	50.7	5.3	45.8	10.2
KET-4000-1	71.4	2076±318			48.5	6.0
KET-4000-2	67.9	1508±115			60.9	5.3
KET-4000-3	64.3	1524±129			61.3	5.2
KET-4000-4	60.7	1459±158			59.6	5.2
KET-4000-5	57.1	1780±121			66.0	5.1
KET-4000-6	53.6	1931±110			63.1	4.7

of HDI-based films (Fig. 4). Young's modulus also decreases with increasing PEG content, albeit somewhat more slowly than tensile strength (Fig. 3). Whereas this phenomenon is pronounced with HDI-based polyurethanes, films made with TDI were often unaffected by soft segment addition. Changes are hardly observable with PEG 400, and only a modest decrease is noted at a high weight fraction of PEG 600. Moduli remain constant over the range tested for PEG 1000. PEG 4000, however, exhibits a different effect on the Young's modulus of TDI-based films, which increases (after an initial decline) with increasing PEG content.

Changes in film composition influence the strain at break more at the lower PEG molecular weights, and more at the higher PEG content (see Tables III and IV and Fig. 5). This behavior is again more pronounced with HDI- than with TDI-based networks. The HDI-derived materials have maximum extensibilities of up to five times that of lignin based polyurethane with no PEG. The effect of glycol content on this property diminishes noticeably with increasing molecular weight, at any particular weight contribution.

It is interesting to note that some of the lignin-based polyurethane films show distinct yield properties. This is illustrated for an HDI-based film

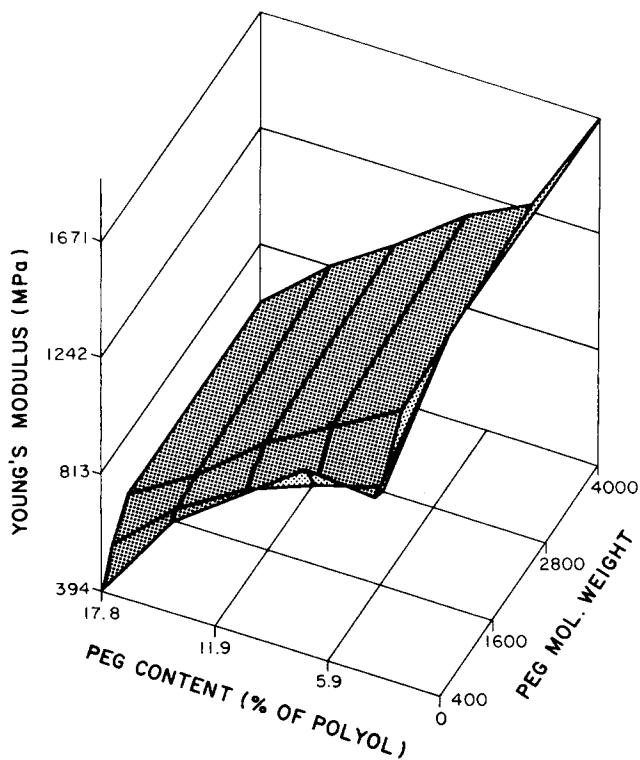


Fig. 3. Influence of PEG content and molecular weight on Young's modulus of HDI-based polyurethane films.

series (PEG 400) in Figure 6. TDI-based films, by contrast, do not exhibit this behavior at either molecular weight extreme (PEG 400 and PEG 4000). The occurrence of a yield point was typically found to shift to higher glycol contents with increasing glycol molecular weight (except for PEG 4000). Yield stress and tensile strength both show an expected decrease with glycol content (Fig. 4).

The sensitivity of material properties of lignin-based polyurethane films are greater towards HDI than towards TDI, and this must be attributed primarily to the aromatic nature of the latter. The observed increase in modulus with increasing glycol molecular weight at constant PEG content is similar to the results obtained on thermal properties and can again be interpreted with changes in both the actual number of chains and in the crosslink density accompanying molecular weight changes.

Dynamic Mechanical Analysis

Dynamic mechanical spectra of three films with identical weight fraction of isocyanate representing (unmixed) polyurethane KEH-1, and two PEG-extended polyurethanes (constant PEG content), KEH-600-6 and KEH 4000-6, are given in Figures 7-9. Glass transition temperatures (measured at

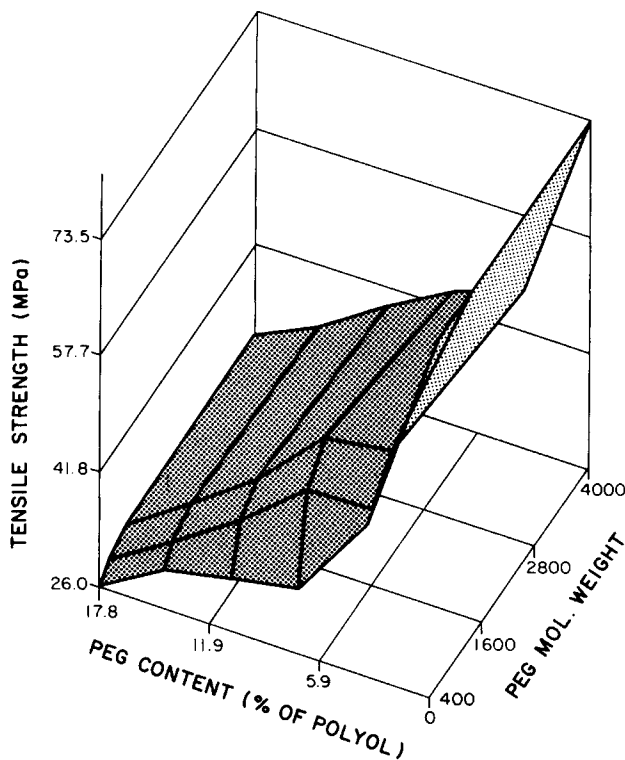


Fig. 4. Influence of PEG content and molecular weight on tensile strength of HDI-based polyurethane films.

maximum $\tan \delta$ -peak height) ranged between 120°C for KEH-400-6 and 142°C for KEH-600-6. Maximum damping ($\tan \delta$ peak) also differed in relation to PEG content and molecular weight, and was lowest with KEH-4000-6 (0.35) and highest with KEH-600-6 (0.66). Also the T_g of each PEG containing network was broader as compared to that from the unmixed network polymer, and it occurred at a lower onset temperature (95°C for KEH-1 and 55°C and 20°C for KEH-600-6 and KEH-4000-6, respectively). This significant broadening may arise in these systems for various reasons. For example, if some degree of inhomogeneity exists in terms of PEG, diisocyanate and lignin mixing, some degree of broadening might be expected. However, due to the fact that several variables are simultaneously changing in these systems as PEG molecular weight is altered, it is difficult to ascribe the broadening to any one factor.

The overall dynamic mechanical data are in basic agreement with the DSC results in that only one distinct T_g could be determined. This again indirectly supports the earlier hypothesis that these materials can be viewed as more homogeneous in nature than the often domain-forming linear segmented urethane systems.

The examination of the storage modulus reveals the thermosetting characteristics of these network polymers. In particular crosslinking generally

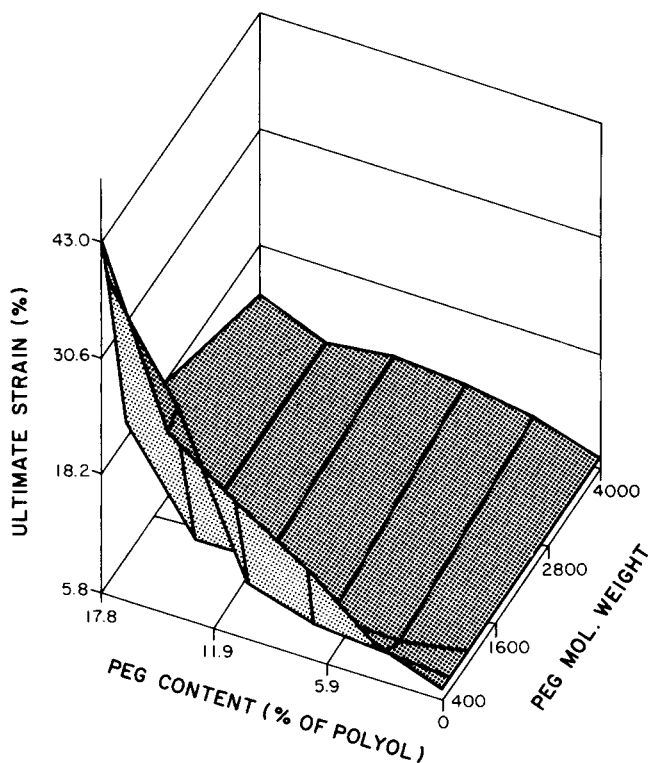


Fig. 5. Influence of PEG content and molecular weight on ultimate strain of HDI-based polyurethane films.

stabilizes the storage modulus (E') after the glass transition region is surpassed, and this happens at about 165°C in samples KEH-1 and KEH-4000-6. Sample KEH-600-6, on the other hand, seems to exhibit a continual loss in modulus with temperature following T_g . This is somewhat surprising in view of the nature of the chemistry discussed so far and in view of the swelling behavior which also implied network formation. In general it is clear from the storage modulus, at least for those two samples which tend to display a rubbery plateau region above T_g , that the modulus is above the typical rubbery plateau values for good elastomers, i.e., 10^5 – 10^6 Pa. As can be noted from Figures 7 and 9, these plateau values are of the order of about 10^8 – 10^9 Pa, which implies a higher than typical crosslink density for good elastomeric behavior. This is not necessarily surprising, however, in view of the nature of the excess diisocyanate that was used in preparing these materials.

Finally, in viewing the dynamic mechanical data it is noted that no distinct glass transition peak is observed for the PEG component. In addition, no melting point transition is indicated for this same component which might have been expected if distinct phase separation of the PEG had occurred, particularly for the high molecular weight PEG segments where crystallization would be more likely. As indicated above, the lack of

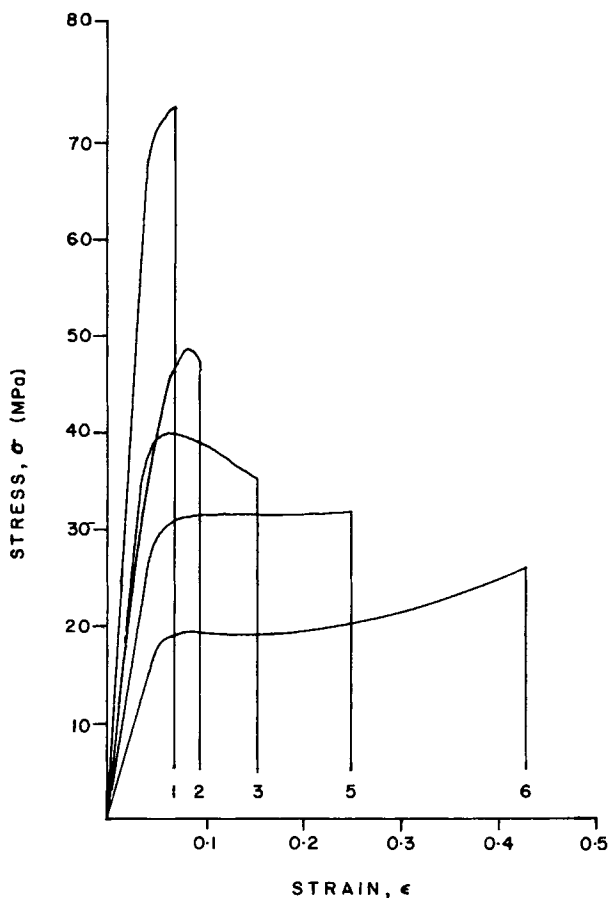


Fig. 6. Influence of PEG 400 content on stress-strain properties of polyurethane films.

the observation of two distinct transitions suggests a more homogeneous material than is typically observed for the linear segmented urethanes. However, due to the fact that the PEG component was of relatively low content, < 17.8%, some additional investigations were made via small angle X-ray scattering for purposes of trying to denote whether microphase separation was present or not. While only a limited number of samples were investigated, no success was obtained in identifying such phase separation by use of a Krakty camera technique discussed elsewhere by one of the authors,⁴⁸ and hence it can again be concluded that a reasonably homogeneous system is generated using the chemical reaction schemes discussed above. Additional support for the homogeneity of these materials is derived by the display of high optical transparency, which is in line with general homogeneity at least at the level somewhat below that of the dimensions of the wavelength of light. Homogeneity is further supported by the fact that when the very nonpolar soft segment polybutadiene glycol is used in synthesizing similar urethane systems, the resulting materials produce turbid and inhomogeneous solids in contrast to their PEG counterparts, despite the use of identical reaction conditions.⁴⁹

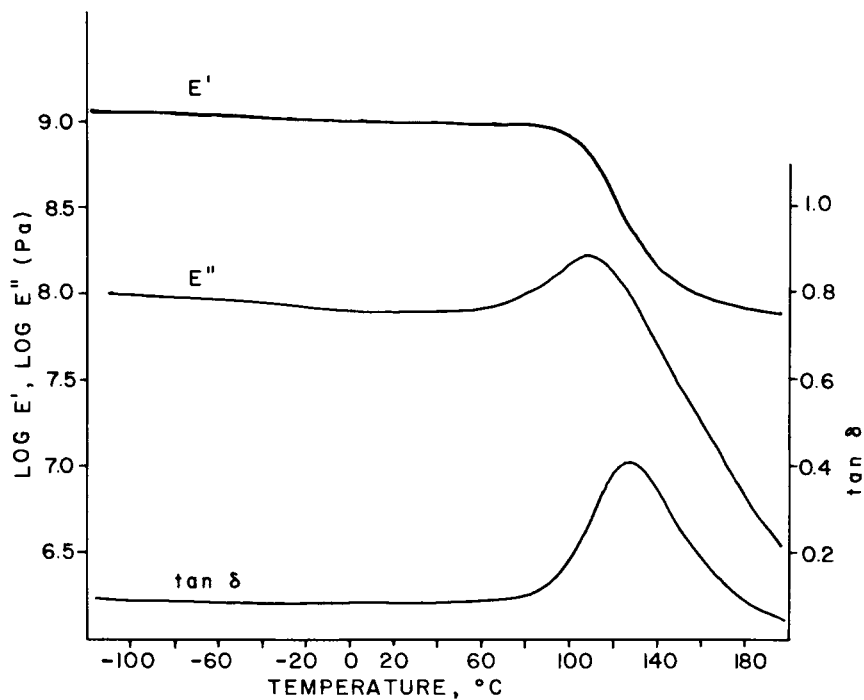


Fig. 7. Dynamic mechanical spectrum of unblended polyurethane KH-4.

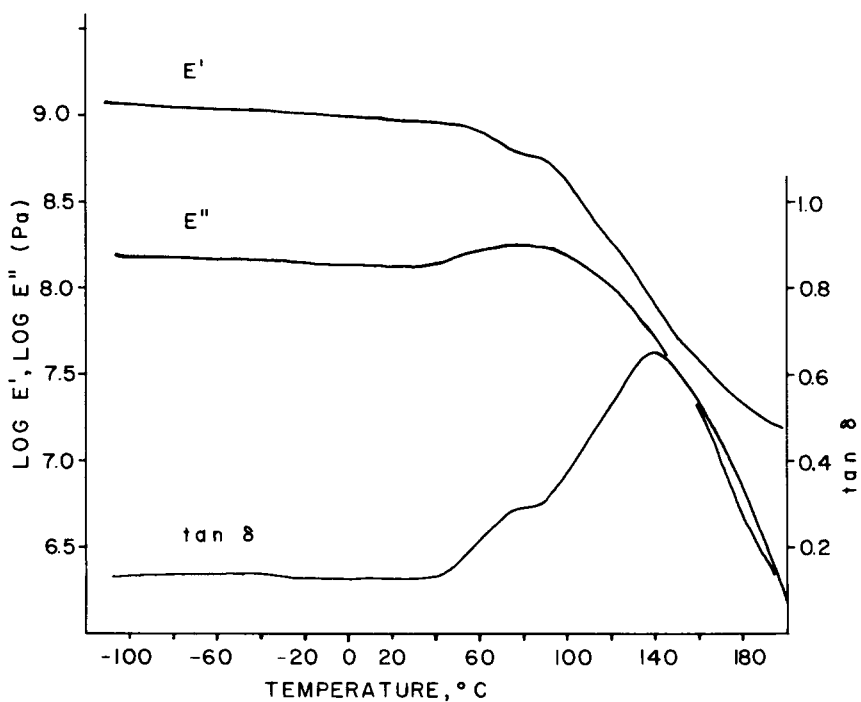


Fig. 8. Dynamic mechanical spectrum of PEG 600-blended polyurethane KEH-600-6.

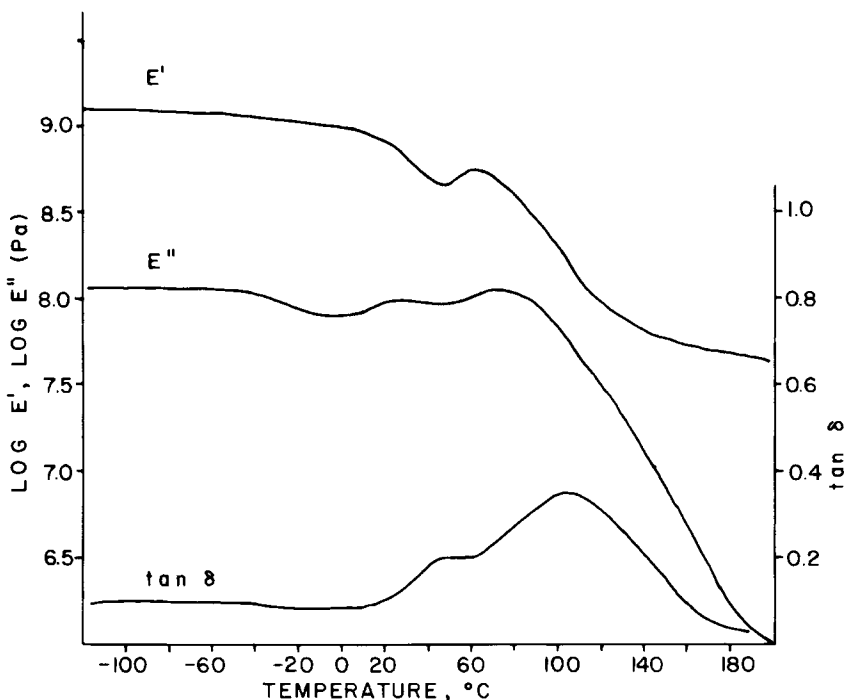


Fig. 9. Dynamic mechanical spectrum of PEG 4000-blended polyurethane KEH-4000-6.

CONCLUSIONS

(1) Extending hydroxypropyl lignin derivatives with poly(ethylene glycol)s of molecular weights ranging from 400 to 4000 was found to result in the synthesis of uniform polyurethane films. The soft segment introduces increased chain mobility and results in lower mechanical relaxation and thermal transition temperatures.

(2) The reduction in glass transition temperatures was proportionate to the PEG content of the PEG-containing network. The effect of different PEG molecular weights overlapped with differences in crosslink density as a consequence of constant NCO/OH weight ratios during synthesis. They were apparently responsible for differences in the swelling (in DMF) behavior and for ultimate strain properties at high PEG content.

(3) Most film properties, especially thermal transitions, were influenced by the type of diisocyanate (aromatic vs. aliphatic). Glass transition temperature and modulus were higher with TDI- than with HDI-based polyurethanes of otherwise identical composition.

(4) A three- to fourfold decrease in modulus and an up to fivefold increase in elongation was observed as a result of adding up to 17.8% of PEG to the polyol component. The degree of change was a combined effect of PEG content and molecular weight, crosslink density, and diisocyanate type.

(5) The energy dissipation characteristics (damping) and their dependence on temperature, as measured by dynamic mechanical analysis are a function

of both the contribution to weight by the soft segment as well as the crosslink density of the polyurethane network.

(6) Dynamic mechanical spectra of PEG-containing polyurethanes failed to exhibit clear transitions which could be assigned to a distinct soft segment phase. This is probably the result of the absence of organization into microstructural entities (domains). Homogeneity and absence of phase organization was further supported by limited small angle X-ray scattering experiments.

(7) The crosslink density effects associated with differences in PEG molecular weights (because of constant diisocyanate:polyol weight ratios during synthesis) make it difficult to distinguish the specific influence of each factor. However, the results suggest that it is possible to introduce a considerable measure of thermoplasticity into these thermosetting lignin-based polyurethanes by judicious choice of the PEG component in terms of amount and molecular weight.

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