

# Engineering Plastics from Lignin. XV. Polyurethane Films from Chain-Extended Hydroxypropyl Lignin

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## Synopsis

A series of polyurethane (PU) films was prepared from chain-extended hydroxypropyl lignins (CEHPL). In appearance, these films ranged from brittle and dark brown to rubbery and bronze. The thermal, mechanical, and network properties of these PUs were investigated by DMTA and DSC analysis. All films exhibited single  $T_g$ 's which varied between  $-53^\circ$  and  $101^\circ\text{C}$ , depending on lignin content. From swelling experiments, molecular weight between crosslinks ( $\bar{M}_c$ ) was determined and found to vary over 2.5 orders of magnitude. The  $\bar{M}_c$ 's were related to the change in  $T_g$  that accompanied network formation. Stress-strain experiments showed a variation in Young's modulus between 7 and 1300 MPa. Most of the variation in material properties was related to lignin content and to a lesser extent to diisocyanate type, hexamethylene diisocyanate, or toluene diisocyanate. The source of the CEHPL had no effect on the observed properties. From these results it was concluded that the properties of PUs can be controlled and engineered for a wide variety of practical uses.

## INTRODUCTION

Hydroxypropyl lignin (HPL) has been used for the preparation of polyurethane films with glass transition temperatures ( $T_g$ ) between  $63$  and  $198^\circ\text{C}$  and Young's moduli between  $1300$  and  $2400$  MPa.<sup>1</sup> These polyaromatic materials were homogeneous, rigid networks. Their major limitation was poor elongation, usually below 10%. In an effort to improve this behavior and provide for a wider range of thermal and mechanical properties, a series of polyethylene glycol (PEG)<sup>2</sup> or polybutadiene glycol (PBD)<sup>3</sup> extended lignin-based polyurethanes was prepared by mixing two polyol components prior to crosslinking. The addition of a flexible (soft) segment produced lignin-based PUs with a wide range of  $T_g$ 's ( $38$ – $158^\circ\text{C}$ ), Young's moduli ( $380$ – $1670$  MPa), and ultimate strain ( $6$ – $43\%$ ).<sup>2</sup> Addition of PEG was limited (by miscibility) to 17.8% of the polyol, and phase separation was not observed.<sup>2</sup> The molecular weight of the PEG also affected the properties of the PUs. These films contained between 35 and 45% lignin. There has also been research on lignin-PEG mixtures (and solutions) as raw materials for polyurethane film production.<sup>4</sup> PBD extended films<sup>3</sup> were phase-separated even at low levels of PBD addition. The elongation properties of the PBD films were poor until the

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HPL content dropped below 20% (ca. 12% lignin). The poor mechanical properties were attributed to macrophase separation.

In order to limit or eliminate phase separation, a polyether soft segment was attached directly to the lignin derivative by propylene oxide chain extension. This, in effect, yields a starlike copolymer with a rigid aromatic center and radiating flexible polyether arms. With an increase in the content of the soft-segment component, it was anticipated that toughness and elongation properties would improve. The chemical and thermal characteristics of these chain-extended hydroxypropyl lignin (CEHPL) prepolymers are described elsewhere.<sup>5</sup>

The current investigation deals with the effects of polyol composition on the thermal, mechanical, and network properties of solution-cast polyurethane films. In addition to the effects of soft segment content, differences in source of the lignin were also investigated.

## EXPERIMENTAL

### Materials

**Lignins.** An organosolv (ethanol) lignin (OSL) was supplied by Biological Energy Corp. of Valley Forge, PA; and two kraft lignins [KL(I) and KL(II)] were obtained from Westvaco Corp. of North Charleston, SC. The characteristics of these lignins have been described elsewhere.<sup>6</sup>

**Polyols.** Preparation and characterization of hydroxypropyl lignin (HPL)<sup>7,8</sup> and of chain-extended hydroxypropyl lignin (CEHPL)<sup>5</sup> polyols is described elsewhere.

**Diisocyanates.** 1,6-Hexamethylene diisocyanate (HDI) and 2,4-Toluene diisocyanate (TDI) (practical grade) Eastman Kodak Co., Rochester, NY, were used as purchased.

### Methods

**Film Preparation.** CEHPL (ca. 1 g) was dissolved in 1.5 mL of methyl-ethyl-ketone (MEK) with sodium sulfate added as a desiccant, and the solution was kept under nitrogen. The proper amount of diisocyanate was added to give an NCO/OH ratio of 1.8 (based on a hydroxyl content determined by titration). Three percent (total solids) dibutyl tin dilaurate (T-9 Catalyst, Union Carbide Corp.) was added, and the mixture (ca. 50% solids) was rapidly stirred for 1 min. The resin was poured through a glass wool plug onto a glass plate covered with a thin layer of silicone oil (L-520, Union Carbide Corp.). The plate was covered, to minimize evaporation of diisocyanate, and the resin was allowed to cure for 20 h. The cover was removed, and the films were post-cured in an air-circulation oven at 120°C for 2 h. The films were stored in a desiccator over P<sub>2</sub>O<sub>5</sub>. All films were prepared in duplicate.

**Differential Scanning Calorimetry (DSC).** A Perkin-Elmer DSC 4 equipped with a Thermal Analysis Data Station was used. The data was collected on the second scan of samples (ca. 20 mg) heated at 20°C/min under a helium atmosphere. The glass transition temperature ( $T_g$ ) was defined as one-half the change in heat capacity over the transition. The  $T_g$  was determined for two samples from each of two films.

**Dynamic Mechanical Thermal Analysis (DMTA).** A Polymer Laboratories DMTA was used to determine the viscoelastic properties of the polyurethane films. The test geometry was dual cantilever bending, and heating rate was 5°C/min at a strain of 1% and a frequency of 1 Hz. Care was taken to maintain sample dimensions of 0.1 mm thickness, 8 mm width, and 2 mm free length. The DMTA measurements were made on duplicate samples from each of two films. The sample chamber was purged with nitrogen. Activation energy ( $E_a$ ) for the  $T_g$  was calculated using

$$\log f = \log f_0 - E_a/RT \quad (1)$$

where  $f$  = frequency of vibration,  $f_0$  = pre-exponential factor,  $R$  = universal gas constant, and  $T$  =  $\tan \delta$  peak temperature (K). For these studies the geometry remained the same, but the heating rate was 1°C/min and five frequencies between 0.1 and 30 Hz were used.

**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).

**Swelling Studies.** The polyurethane films were swollen in DMF to allow determination of sol fraction and molecular weight between crosslinks ( $\bar{M}_c$ ). Each swelling experiment was run in triplicate on ca. 0.2 g of film swollen in 15 mL of DMF. The films were swollen for 3 days at room temperature, separated from the solvent and dried at 120°C to a constant weight. Film densities were determined in duplicate with a 25 mL pycnometer. The  $\bar{M}_c$  was found using the Flory-Rehner method<sup>9</sup>:

$$M_c = \frac{-V_s \rho_p (C^{0.33} - C/2)}{\ln(1 - C) + C + \chi C^2} \quad (2)$$

where  $M_c$  = molecular weight between crosslinks,  $V_s$  = molar volume of solvent (76.87 cc/mol for DMF),  $\rho_p$  = density of polymer,  $\chi$  = Flory-Huggins constant,  $C$  = relative concentration =  $W_D/\rho_p V_\infty$ ,  $W_D$  = dry weight of extracted film,  $V_\infty$  = final swollen volume =  $W_D/\rho_p + (W_\infty - W_D)/\rho_s$ ,  $W_\infty$  = weight of swollen polymer, and  $\rho_s$  = density of solvent (0.94 g/cc for DMF).

The percent sol fraction was calculated as follows:

$$\text{sol fraction (\%)} = \frac{W_0 - W_D}{W_0} \quad (3)$$

with  $W_0$  = initial weight of polymer and  $W_D$  = dry weight of extracted polymer. Percent swell was calculated with

$$\text{percent swell (\%)} = \frac{W_\infty - W_D}{W_D} \quad (4)$$

with  $W_\infty$  and  $W_D$  defined above.

## RESULTS AND DISCUSSION

The synthesis of HPL based polyurethane (PU) films by solution casting is well established.<sup>1,10</sup> An excess of diisocyanate has been found to be necessary to compensate for losses during solvent removal and curing. Limits on solvent evaporation are found to have a minor effect on the observed  $T_g$ , but this was not studied in depth. The use of excess diisocyanate also allows the occurrence of side reactions, i.e., allophanate and biuret linkages.<sup>11</sup> The procedure used for film preparation was not optimized. The films ranged in appearance between dark brown and light bronze. The physical properties varied between extremely brittle to very flexible and tacky. All the films appeared to be homogeneous to the unaided eye.

## Dynamic Mechanical and Thermal Behavior

A selected series of DMTA thermograms (Fig. 1) had as only difference between films the degree of chain extension with propylene oxide, i.e., the MS of the propyl ether chains attached to lignin. As MS increased and lignin content decreased correspondingly, the  $\tan \delta$  peak temperature and peak width decreased while magnitude of  $\log E'$  drop became more pronounced.

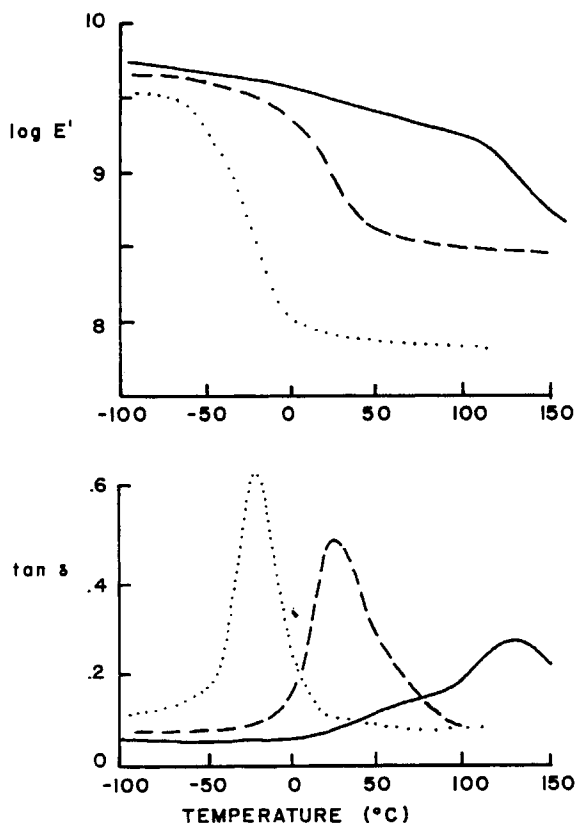


Fig. 1. Dynamic mechanical thermograms of three typical chain-extended hydroxypropyl lignins crosslinked with TDI: (—) sample KL(II)-A; (---) sample KL(II)-B; (···) sample KL(II)-C.

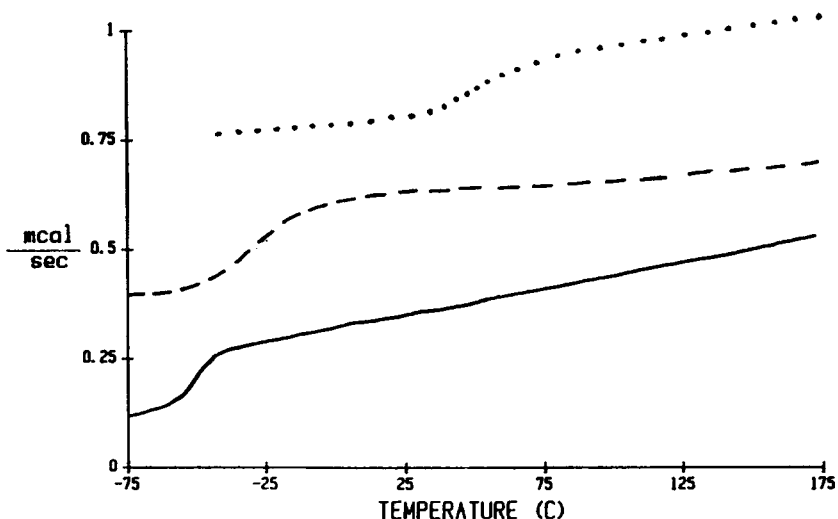


Fig. 2. DSC thermograms of chain-extended hydroxypropyl (organosolv) lignin crosslinked with TDI: (···) OS-B; (---) OS-C; (—) OS-D.

Thermal analysis by DSC (Fig. 2) of films with varying MS again revealed that  $T_g$  decreased as MS increased. Only one  $T_g$  was observed by both DSC and DMTA in all films over a wide temperature range ( $-75$ – $150^\circ\text{C}$ ). The results for all PU films are summarized in Table I. Six film types were prepared from three polyols differing in lignin source [OS, KL(I) and KL(II)], with two diisocyanates. The diisocyanates contained either a (rigid) aromatic ring (TDI) or a (flexible) aliphatic chain (HDI).

The  $\tan \delta$  peak temperature is related to glass transition temperature ( $T_g$ ) while peak width indicates the number and intensity of energy dissipative mechanisms.<sup>12,13</sup> The reduction of  $\log E'$  on heating is considered a reflection of network structure, particularly of the average molecular weight between crosslinks ( $\bar{M}_c$ ).

$T_g$  range by DSC and  $\tan \delta$  one-half peakheight by DMTA are also shown in Table I. Both of these parameters are indicators of energy dissipative mechanisms.<sup>12</sup> The differences between the  $T_g$  values obtained by the two methods are due to frequency effects and differences in heating rates.

The effect of lignin content and diisocyanate type on film  $T_g$  (DSC) (Fig. 3) reveals a strong, nearly linear dependence. Two underivatized lignin films (prepared for a separate study, Ref. 12) follow the same relationship. TDI crosslinked films have a consistently higher  $T_g$  than those crosslinked with HDI until the lignin content decreased to about 25%. This difference has been observed earlier.<sup>1</sup> The dependence of network physical properties on content of rigid structures in a polymer's backbone has been noted previously.<sup>14,15</sup> When the  $T_g$ 's of the CEHPL-based films are plotted against aromatic content (based on  $\text{C}_6\text{H}_6$  equivalent weight fraction) (Fig. 4), a significant relationship between aromaticity and  $T_g$  is noted. Surprisingly, the HDI-crosslinked films have a higher  $T_g$  than the TDI-based materials at the same aromatic content. This may be explained with differences in molecular weight between crosslinks

TABLE I  
 Dynamic Mechanical and Thermal Properties of Lignin-Based Polyurethanes (PU)

PU type	Lignin content of PU (%) <sup>a</sup>	DMTA		DSC	
		tan $\delta$ peak temp (°C)	1/2 peak width (°C)	$T_g$ (°C)	$T_g$ range (°C)
HDI series					
OS-HPL	40	90	38	72	40
OS-A	37	55	54	36	63
OS-B	30	14	38	-1	22
KL(I)-HPL	43	90	32	80	36
KL(I)-A	31	38	55	18	41
KL(I)-B	27	-1	34	-14	29
KL(I)-C	25	-20	31	-28	24
KL(I)-D	23	-24	27	-38	20
KL(II)-HPL	37	85	34	74	38
KL(II)-A	32	46	49	32	58
KL(II)-B	29	-10	27	-24	25
TDI series					
OS-B	30	84	49	61	62
OS-C	25	-20	35	-35	48
OS-D	20	-28	26	-42	40
KL(I)-A	31	79	69	56	64
KL(I)-B	27	46	68	25	58
KL(I)-C	25	32	63	1	50
KL(I)-D	23	22	52	-5	41
KL(I)-E	21	-33	30	-45	36
KL(I)-F	17	-36	26	-53	33
KL(II)-A	30	127	56	101	49
KL(II)-B	27	30	42	12	36
KL(II)-C	19	-23	28	-47	26

<sup>a</sup>Based on average MS values determined previously. Lignin contents of the films vary due to molecular weight differences between HDI and TDI.

( $\bar{M}_c$ ) due to steric reasons or differential reactivity of the second isocyanate group in TDI.<sup>16,17</sup>

Another measure of material properties is the activation energy ( $E_a$ ) of the  $T_g$ . This was determined by DMTA for one PU film series. The results (Table II) reveal that as  $T_g$  decreases with decreasing lignin content, the  $E_a$  of the transition also declines. This may be explained with the nature of the two polyol components. The flexible PPO chains contribute to small-scale local molecular motions more easily than does the aromatic lignin as the temperature rises from the glassy to the viscoelastic region. Thus the PPO facilitates an increase in free volume with heating, and this precedes the observed  $T_g$ . The magnitude of this effect would become more prominent as the PPO content increases. At high PPO contents, the increase in free volume would be sufficient to allow relatively unhindered motions of network chains resulting in reduced  $E_a$  values.

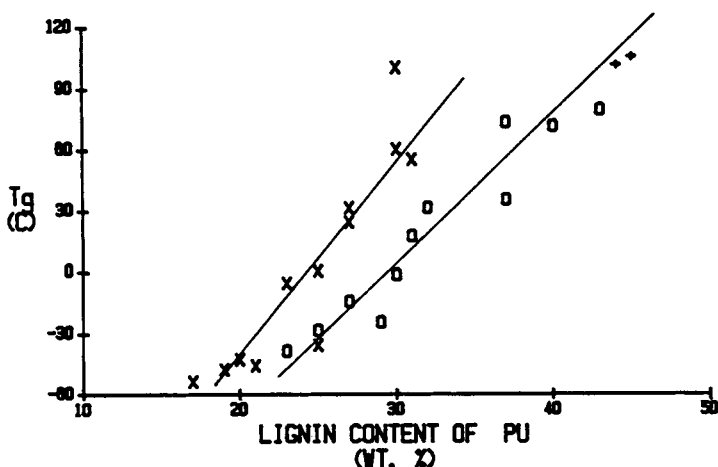


Fig. 3. Effect of lignin content and diisocyanate type on the  $T_g$  of PU prepared from chain-extended hydroxypropyl lignins crosslinked with HDI (○) and TDI (×). Two points (+) were taken from Ref. 12.

For polyols with a similar lignin content [KL(II)-A and KL(II)-B] the TDI films had a higher  $T_g$  and a higher  $E_a$  than the corresponding HDI films. This can be attributed to the flexibility of the crosslinker and possibly to differences in network  $\bar{M}_c$ .

The temperature range over which the  $T_g$  occurs reflects the complexity and magnitude of molecular motions present in a network material.<sup>13</sup> This can be determined as  $\tan \delta$  peak width, at one-half of peak height. Results (Table I and Fig. 5) show that as lignin content declines, so does  $T_g$  range. The initial rise in  $T_g$  range with chain extension (i.e., from HPL to A-type polyols, Table I, and from  $> 35$  to  $< 35\%$  lignin content, Fig. 5) must be explained with the

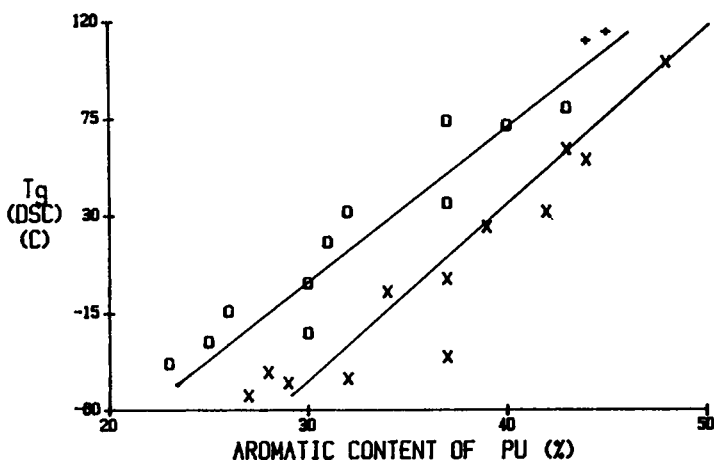


Fig. 4. Glass transition temperatures of PU films normalized for aromatic content ( $C_6H_6$  equiv. wt %) of both lignin and diisocyanate. The films were crosslinked with HDI (○) and TDI (×). Two points (+) were taken from Ref. 12.

TABLE II  
Effect of Lignin Content and Diisocyanate Type on the Activation Energy of the Film  $T_g$

Film type	Lignin content of PU (%) <sup>a</sup>	PU $T_g$ (°C)	$E_a$ of $T_g$ (kJ/mol)
HDI series			
KL(II)-HPL	37	85	212
KL(II)-A	32	46	156
KL(II)-B	29	-10	107
TDI series			
KL(II)-A	30	127	352
KL(II)-B	27	30	315
KL(II)-C	19	-23	271

<sup>a</sup>Based on the average MS as determined previously.<sup>5</sup> Lignin contents of the films may vary due to molecular weight differences between HDI and TDI.

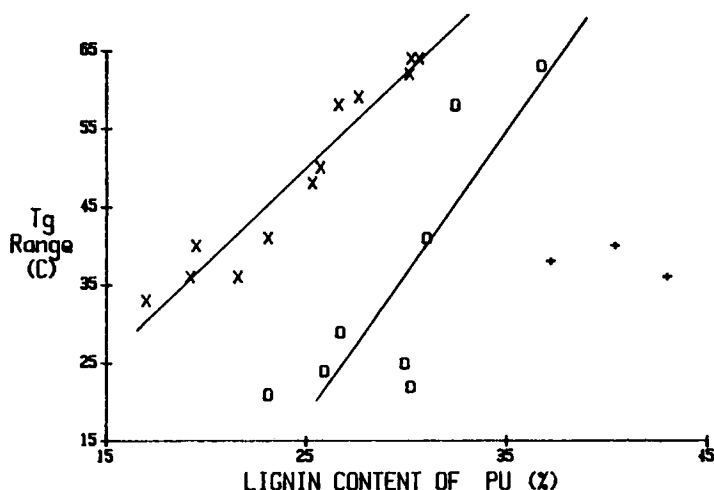


Fig. 5. Effect of lignin content and diisocyanate type on the  $T_g$  range of PU films crosslinked with HDI (○) and TDI (×). Networks formed from the original hydroxypropyl lignins and crosslinked with HDI are shown separately (+).

introduction of a new type of ether linkage. The original arylalkyl linkage between lignin and the first PO unit can be expected to have a different rotational energy barrier than the dialkyl ether linkage between subsequent PO units. Thus the  $T_g$  range for the PU films prepared from CEHPL with an MS of 2.0 can be expected to be greater than that with an MS of 1.0 (i.e., the HPL-films).

### Mechanical Properties

Preparation of PU films allowed control of  $T_g$  over a wide range of temperatures. This affects mechanical properties (i.e., load vs. elongation behavior) dramatically (Fig. 6). The observed differences were related to both MS and diisocyanate type. Breaking strength was as high as 66.5 MPa (H-OS-HPL) and elongation at break reached 95% (T-OS-C) (Table III).



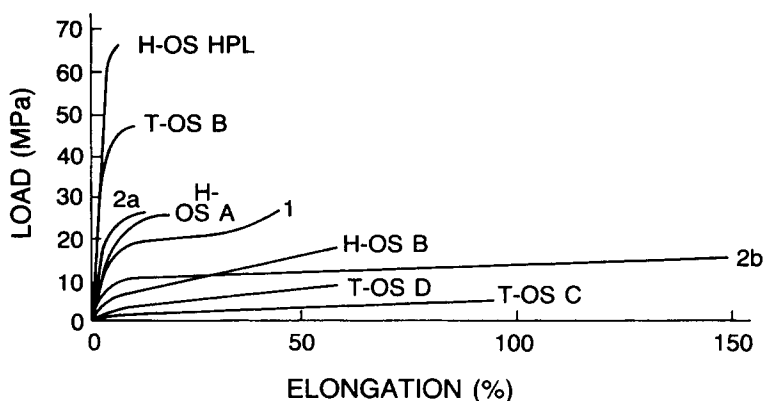


Fig. 6. Load-elongation response of OS polyols crosslinked with HDI and TDI. The first letter represents the type of diisocyanate HDI (H) or TDI (T) and the second set of letters represents the polyol (s, Table I). Response 1 is that of a HDI crosslinked PU prepared from a mixture of a HPL and PEG (taken from Ref. 15). Responses 2a and 2b are polypropylene glycol-based polyurethanes prepared with a molecular weight between crosslinks ( $M_c$ ), which is similar to the PU films (taken from Ref. 18).

The modulus of elasticity (MOE) decreased dramatically as the lignin content of the films decreased. Since MOE is related to the stiffness of the polymer backbone,<sup>14</sup> lignin is recognized as the stiffening component (i.e., modulus builder) of the PU networks (Fig. 6). MOE varied by almost 3 orders of magnitude with lignin content rising from 23 to 43%. MOE varied by 1 order of magnitude in relation to diisocyanate type. Mixtures of HPL and PEG<sup>2</sup> were not found to influence MOE as dramatically as did chain extension (Fig 7). Networks prepared from CEHPL allowed for greater control over MOE.

When MOE is plotted against the aromatic content of the network (based on  $C_6H_6$ -equivalent wt %) the HDI and TDI networks were not substantially different (Fig. 8). This parallels the  $T_g$  data. The minor differences observed between the MOE of HDI and TDI networks (Fig. 8) might be due to differences in  $\bar{M}_c$ . A low  $\bar{M}_c$  could limit chain mobility and lead to an elevated MOE.<sup>19</sup>

As the lignin content of the PU films increased, MOE and breaking strength increased while elongation at break decreased (Table III). However, the greater amount of scatter as compared to the MOE results prevented distinction between TDI and HDI network data. An inverse relationship between strength and strain is typical of many polymer networks,<sup>20</sup> and this reflects chain mobility. This can be determined by both the chemical nature of the polymer backbone (aromatic vs. polyether content) and the crosslink density of the network.<sup>19</sup>

While the PU film (mechanical) properties depended on the chemical nature of the network, the source of the lignin (OS vs. KL) did not influence MOE. Networks prepared from OS and KL HPL were previously found to be similar.<sup>12</sup> In the current study, small differences in lignin chemistry were overshadowed by the effect of chain extension. Lignin origin did not influence breaking strength or elongation at break. Chain stiffness and  $\bar{M}_c$  influenced molecular motion, and this is reflected by the  $T_g$  and MOE data. Ultimate

TABLE III  
 Mechanical Properties of PU Films

Film type	Lignin content (%) <sup>a</sup>	Youngs modulus (MPa)	Ultimate strength (MPa)	Ultimate strain (%)
<b>HDI series</b>				
OS-HPL	40	1,300	66.5	6.6
OS-A	37	171	28.1	21.1
OS-B	30	97	14.7	55.0
KL(I)-HPL	43	1,270	53.9	7.9
KL(I)-A	31	146	16.1	12.1
KL(I)-B	27	10	10.3	43.0
KL(I)-C	25	6	2.9	39.6
KL(I)-D	23	8	2.7	36.2
KL(II)-HPL	37	1,410	65.0	8.1
KL(II)-A	32	126	19.2	40.0
KL(II)-B	29	25	3.4	59.0
<b>TDI series</b>				
OS-B	30	451	46.9	8.4
OS-C	25	85	15.0	95.0
OS-D	20	7	7.4	56.8
KL(I)-A	31	950	52.7	6.8
KL(I)-B	27	221	21.8	21.5
KL(I)-C	25	140	15.5	68.0
KL(I)-D	23	79	12.2	63.0
KL(I)-E	21	13	2.4	47.4
KL(I)-F	17	13	2.3	44.6
KL(II)-A	30	975	34.0	5.1
KL(II)-B	27	127	17.3	99.0
KL(II)-C	19	15	3.6	55.7

<sup>a</sup>Based on the average MS as determined previously. Lignin contents of the films vary due to molecular weight differences between HDI and TDI.

properties were typically more sensitive to defects than to differences in network density.

Network polymers can be characterized by swelling.<sup>10,21</sup> This allows one to distinguish components which are covalently bonded into the network from entrapped sol molecules. Swelling data often become the basis for  $\bar{M}_c$  determination if the respective Flory-Huggins chi parameter ( $\chi$ ) is known.  $\bar{M}_c$  may also be determined using the modulus in the rubbery region.<sup>13</sup> In this study, however, the absolute value of  $\log E'$  was not considered to be reliable (due to the design of the DMTA instrument), and thus  $\bar{M}_c$  was determined by swelling.

If the CEHPL molecules are viewed as multifunctional stars, then, as the MS increases, so does the average length of the radial arms. These radial arms are reactive at their terminus, so that, as MS increases, so does the distance between the lignin centers. Thus the tightness of the network decreases and its ability to swell increases. If equilibrium swelling is assumed, the density of

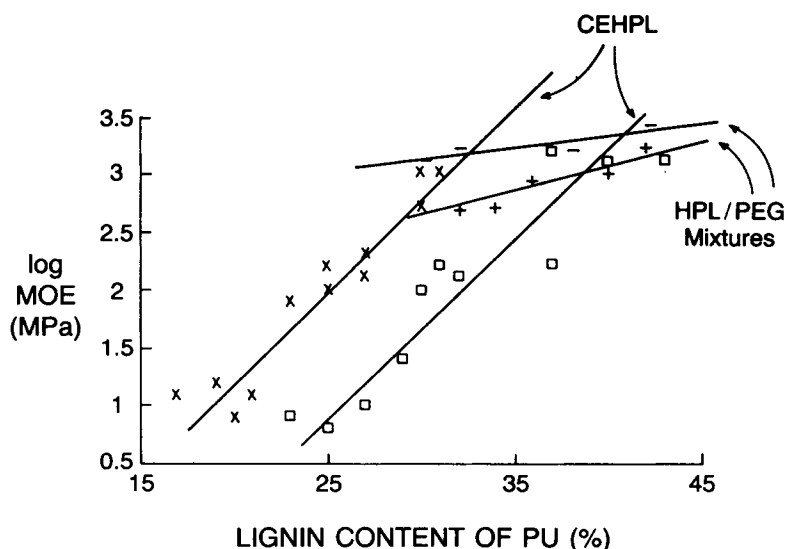


Fig. 7. Effect of lignin content and diisocyanate type on the Young's modulus (MOE) of PU films crosslinked with HDI ( $\circ$ ) and TDI ( $\times$ ). Also included are the MOE values for films prepared from blends of HPL and PEG and crosslinked with HDI ( $+$ ) and TDI ( $-$ ) (Ref. 2).

a network can be quantified through use of eq. (2) on the basis of  $\chi$  and weight gain during swelling.<sup>5</sup>

Swelling data and sol fraction contents are given in Table IV. As lignin content decreased, sol fraction and percent swell increased. Values for  $\chi$  increased constantly as lignin content declined owing to the relationship between network composition and  $\delta_p$  (Table IV).

$\bar{M}_c$  values were calculated from equation 2, and they were related to both  $\chi$  and percent swell (Table IV). There was a consistent increase in  $\bar{M}_c$  as lignin content decreased. While  $\bar{M}_c$  was expected to increase in relation to the length of the polyether arms, the magnitude of change was surprising. The large  $\bar{M}_c$  values were consistent with the high sol fractions observed. Both of these

<sup>5</sup> $\chi$  of the network polymer may be computed from the solubility parameters and the volume fraction of each component by use of eq. (6).<sup>22</sup> The solubility parameter of each component, PPO,<sup>23</sup> lignin,<sup>24</sup> and HDI<sup>23</sup> or TDI,<sup>23</sup> was known or calculated from group contribution theory [eq. (5)],<sup>20</sup>

$$\delta = \rho_p \sum V_i \delta_i \quad (5)$$

where  $\rho_p$  = density of the network,  $V_i$  = volume fraction of component  $i$ , and  $\delta_i$  = solubility parameter of component  $i$ :

$$\chi = \frac{V_s (\delta_s - \delta_p)^{1/2}}{RT} \quad (6)$$

where  $\chi$  = Flory-Huggins constant,  $V_s$  = molar volume of solvent (DMF),  $R$  = universal gas constant,  $T$  = absolute temperature, and  $\delta_s$  and  $\delta_p$  = solubility parameter of solvent and network, respectively.

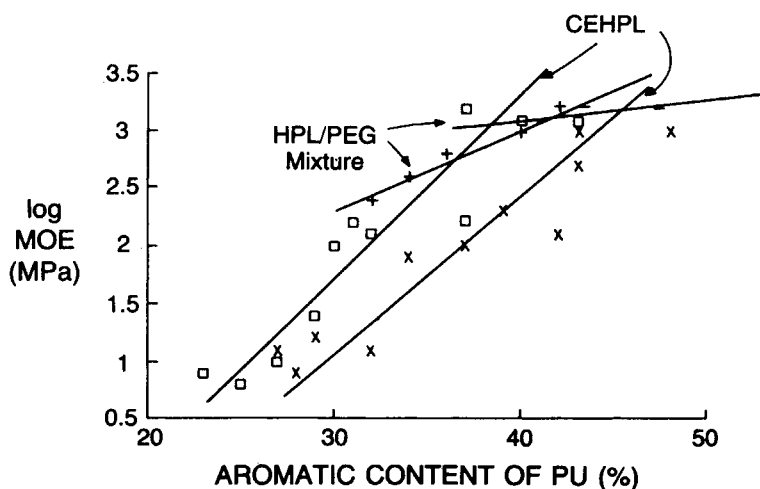


Fig. 8. Young's modulus of PU films prepared from CEHPL, normalized for the aromatic content (wt % of  $C_6H_6$  equivalents) of both the lignin and diisocyanate. The films were crosslinked with HDI ( $\circ$ ) and TDI ( $\times$ ). Also included are the MOE values for films prepared from blends of HPL and PEG and crosslinked with HDI (+) and TDI (-) (Ref. 2).

TABLE IV  
Network Properties of PU Films as Determined from Swelling Experiments

Film type	Sol fraction (%)	Swell (%)	$\chi^a$	$M_c^b$
<b>HDI series</b>				
OS-HPL	2.6	69	0.01	250
OS-A	6.9	57	0.06	180
OS-B	3.6	42	0.14	320
KL(I)-HPL	10.6	154	0.01	420
KL(I)-A	7.0	51	0.10	400
KL(I)-B	8.5	73	0.18	800
KL(I)-C	38.9	69	0.26	710
KL(I)-D	22.0	125	0.27	1070
KL(II)-HPL	20.4	100	0.04	560
KL(II)-A	11.9	81	0.19	450
KL(II)-B	20.2	70	0.40	620
<b>TDI series</b>				
OS-B	8.6	98	0.02	410
OS-C	34.8	279	0.18	3400
OS-D	50.9	390	0.47	25,600
KL(I)-A	12.5	92	0.03	510
KL(I)-B	12.8	152	0.12	730
KL(I)-C	9.0	147	0.20	960
KL(I)-D	14.2	177	0.24	1320
KL(I)-E	53.6	372	0.48	27,900
KL(I)-F	38.4	396	0.49	30,500
KL(II)-A	11.3	137	0.01	670
KL(II)-B	30.8	264	0.14	2320
KL(II)-C	40.6	376	0.43	19,480

<sup>a</sup> Calculated from group contribution theory using eqs. (5) and (6) in the text.

<sup>b</sup> Calculated using eq. (2) in the text.

observations indicate that an incomplete network was formed from the highly chain-extended polyols. Incomplete networks may be the result of intramolecular cyclization or the presence of small amounts of hydroxyl containing impurities that prevent crosslinking.

The  $\bar{M}_c$  values were typically lower for the polyols crosslinked with HDI compared to TDI. This can again be attributed to steric and chemical differences between the isocyanate groups.

## CONCLUSIONS

A series of homogeneous PU films with a wide range of thermal and mechanical properties was prepared from CEHPLs. The  $T_g$  and  $T_g$  range of the films which could be measured by both DMTA and DSC were related to both the lignin content and diisocyanate type. At a constant NCO/OH ratio the PU networks crosslinked with TDI possessed a higher  $T_g$  and greater  $T_g$  range than those crosslinked with HDI. But, if the  $T_g$  was expressed as a function of the aromatic content of the network, the HDI crosslinked networks yielded a higher  $T_g$  than TDI networks. This was seen as an indication that HDI networks were more highly crosslinked than TDI networks.

The MOE and ultimate strength decreased while the ultimate strain increased as the lignin content decreased. The PU networks prepared from CEHPL were more sensitive to lignin content than were networks which used polyethylene glycol as a soft segment. The MOE was also found to vary depending on the type of diisocyanate used, with TDI providing a higher MOE than HDI at a similar lignin content.

The CEHPL networks were characterized by swelling experiments. High sol fractions (< 54%) and large  $\bar{M}_c$  values indicated that the films were not completely crosslinked.  $\bar{M}_c$  increased with chain extension as expected.

The source of the lignin (OS vs. KL) did not affect network properties. These properties were dominated by lignin content and diisocyanate type. PU networks could be prepared in a controlled manner.

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