Engineering Plastics from Lignin. XVII. Effect of Molecular Weight on Polyurethane Film Properties

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Synopsis

A series of five fractions with number average molecular weights ($\bar{M}_n$) between 1500 and 10,000 daltons were isolated from a Kraft hydroxypropyl lignin (HPL). From ^{1}H-NMR and UV analysis the chemical properties of the HPLs were found to vary slightly with molecular weight. The hydroxyl content decreased while the glass transition temperature (T_g) increased as the HPL molecular weight increased. The Fox–Flory equation adequately described the $\bar{M}_n$ vs. T_g relationship. The HPL fractions were used as polyols for the preparation of solvent-cast polyurethane networks (PU) in film form. The T_g of the PUs increased from 40° to 120°C as the $\bar{M}_n$ of the polyol rose from 1500 to 10,000 daltons. The molecular weight between crosslinks ($\bar{M}_c$) of the networks was determined by swelling. An observed decrease in $\bar{M}_c$ with an increase in $\bar{M}_n$ was related to the functionality of the system. The strength properties of films prepared from fractionated HPLs were superior to those prepared from nonfractionated HPLs.

INTRODUCTION

Considerable prior research has been devoted to characterizing lignin-based polyurethanes.[1-7] The effects of molar substitution (MS) of the hydroxypropyl chain length,[7] of polyurethane network density,[1-3,7] of added soft segment,[4,5] of lignin type,[6] and of diisocyanate type[1,7] have all been investigated. Molecular weight, however, has not been explored directly. This factor may be of great practical interest since lignins or lignin fractions from different sources will have different molecular weights and molecular weight distributions as well as different chemistry.[8,9]

The poor solubility of lignin has complicated attempts to fractionate lignins.[10-12] However, some success has been achieved with the fractionation of lignin derivatives.[13,14] A series of lignosulfonates have been fractionated, and several chemical characteristics were determined.[14] The molecular weights (determined by light scattering) of the fractions varied between 3000 and 55,000 daltons. Over this range the phenolic hydroxyl content decreased by 40% while the UV absorptivity increased by 10% as the molecular weight

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increased. A thermal transition of the dry lignosulfonate fractions was reported to be between 260 and 295°C. These values are considerably above the values typically reported for lignin in wood.[15-17]

Three other studies on changes in lignin chemistry with molecular weight noted differences in optical and chemical properties.[11-13] A liquid–solid extraction system, which provided five fractions varying in number average molecular weight ($\overline{M}_n$) between 400 and 3000 daltons, showed that UV absorptivity decreased by 10% and that phenolic hydroxyl content decreased as $\overline{M}_n$ increased.

Changes in material properties with molecular weight may impact network formation even if the chemical composition remains constant. For highly cured networks the molecular weight between crosslinks ($\overline{M}_c$) and the sol fraction generally decreases[18] as functionality (per molecular species) increases. Conversely, mono- and difunctional molecules greatly limit the ability of a prepolymer to form a network.

The current study deals with the isolation and characterization of HPL fractions of varying molecular weights, with the preparation of PU networks from them, and with the effect of molecular weight on mechanical and thermal properties.

EXPERIMENTAL

Materials

Hydroxypropyl Lignin (HPL). A pine Kraft lignin, INDULIN AT, was obtained from Westvaco Corp., Charleston, SC. The lignin was reacted with propylene oxide in a stainless steel reactor as described previously.[19,20]

Diisocyanate. Practical grade hexamethylene diisocyanate (HDI) was purchased from Eastman Kodak Co., Rochester, NY.

Methods

Fractionation of HPL. Fractional precipitation involved dissolving 17 g of HPL in 1250 mL of acetone. After 24 h (to insure complete dissolution) hexane, a nonsolvent, was added. The solution was allowed to precipitate for 2 h before the supernatant was removed. The solvent from both fractions was evaporated under vacuum and the yield of HPL determined. The precipitate was then redissolved for 24 h, in sufficient acetone to give a ca. 1% solution. Again, hexane was added as a nonsolvent and the process was repeated. Five fractions were prepared using hexane/acetone ratios of 5, 2.5, 1.1, and 0.5. The final precipitate was used as the fifth fraction. All fractions were stored over P_2O_5.

HPL characterization. The characterization techniques applied to the HPL fractions have been described in detail elsewhere.[7] Gel permeation chromatography (GPC) was performed in THF on μ-spherogel columns with pore sizes of 100, 500, 1000, and 10,000 Å. Calibration was performed with polystyrene standards. Vapor pressure osmometry (VPO) was carried out in DMF on a Knauer instrument.

Film Preparation. Film preparation and analysis were described previously.[7]

RESULTS AND DISCUSSION

Properties of Fractions

Application of classical fractionation techniques[21] to lignin has been limited by problems with both solubility and intermolecular association.[10-12] Hydroxypropylation dramatically increases solubility and for both steric and electronic reasons should reduce association. Thus HPL was considered a suitable candidate for solution fractionation. Fractionation involves the collection of soluble material as fraction by varying the nonsolvent/solvent ratios.[21] For a hexane/acetone ratio (H/A) of 5, only the most soluble (low molecular weight) material remains in solution. This material (fraction 1) was collected while the precipitate was redissolved, and the process was repeated with a reduced H/A ratio. Five fractions were thus produced. Their GPC chromatograms are shown in Figure 1.

Molecular Weights. Yields and molecular weight characteristics of the five fractions and of the parent HPL (Table I) indicate that separation based on changes in molecular weight had been achieved. The molecular weight of the fractionated material increased as the amount of nonsolvent, hexane, decreased. Both the number average ($\overline{M}_n$) and weight average ($\overline{M}_w$) molecular weight increased in a consistent fashion as the H/A ratio decreased. From another view this means that the number average degree of polymerization for these fractions increased from ca. 4 to 40 lignin C_9 units. Linear polystyrene standards in conjunction with lignin model compounds of molecular weights between 94 and 784 daltons[22] provided calibration of the GPC columns. Molecular weight determinations of lignins[10,23,24] remain controversial owing to association phenomena[10] and column calibration.[23,24] It has been shown previously that the use of DMF with LiBr as well as the preparation of such lignin derivatives as acetates, silylates, and HPL reduce association[24,25] for both steric and electronic reasons. Since the $\overline{M}_n$ values (Table I) determined by both GPC and VPO provide good agreement, the increases in both $\overline{M}_n$ and $\overline{M}_w$ with decreasing H/A ratios was concluded to reflect real differences in molecular weight. The dispersity ratio DR ($\overline{M}_w/\overline{M}_n$) for the fractions was
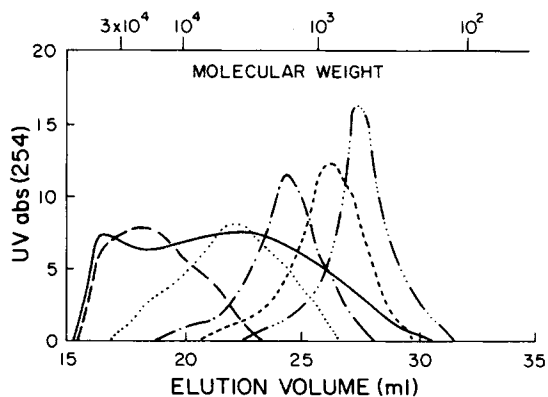

Fig. 1.   High pressure GPC chromatograms of the original (—) and fractionated HPLs: (– – –) fraction 5; (· · ·) fraction 4; (– ·) fraction 3; (- - -) fraction 2; (– · · ·) fraction 1.

TABLE I
Yield, Molecular, Thermal, and Chemical Characteristics of the Original Kraft HPL
and Five Fractions of Varying Molecular Weight

	Parent HPL	Fraction				
		1	2	3	4	5
Hexane/acetone ratio	—	5.0	2.5	1.1	0.5	ppt
Soluble fraction (wt %)	—	12	12	23	24	26
$\overline{M}_n \times 10^3$ (VPO)	1.8	1.3	2.1	2.8	—	—
$\overline{M}_n \times 10^3$ (GPC)	2.8	1.5	2.3	3.2	8.0	10.0
$\overline{M}_w \times 10^3$ (GPC)	25.7	3.0	4.8	5.9	19.4	33.1
DR[a]	9.3	2.0	1.6	1.9	2.4	3.3
$S_n \times 10^3$	8.0	1.5	2.1	2.9	9.6	15.2
T_g (°C)	50	−5	24	40	66	86
T_g range (°C)	36	22	28	34	40	39
^{1}H-NMR range (% total signal)[b]						
2/3	12	10	13	12	10	7
4/5	40	36	35	41	38	39
6/7	24	26	28	24	28	44
8	24	28	24	23	26	22
UV absorptivity (L mol^{-1} cm^{-1})	22.1	20.2	22.6	21.6	20.7	19.4
Total OH[c]	6.5	6.3	7.1	6.4	6.0	4.7

[a] $\overline{M}_w / \overline{M}_n$ from GPC.
[b] In accordance with Ref. 29.
[c] By chemical titration.

substantially less than that of the parent HPL. The final precipitate (i.e., fraction 5) had (expectedly) a higher DR than the other fractions. The presence of a small percentage of very high molecular weight material has a substantial impact on $\overline{M}_w$ and thus on DR. A low DR reflects a uniform molecular weight distribution.

Thermal Properties. Variations in molecular weight of low molecular weight polymers may result in a variation of a material's glass transition temperature (T_g) for both synthetic polymers and lignin.[26, 27] The T_g of the HPL fractions increased as the molecular weight of the fraction rose (Table I). This relationship follows the Fox–Flory relationship

$$T_g = T_{g\infty} - k/\overline{M}_n \qquad (1)$$

where $T_g = T_g$ of a specific fraction, $\overline{M}_n$ = the number average molecular weight of that fraction, $T_{g\infty} = T_g$ of the material at infinite molecular weight, and k = const, which is related to the degree of branching for the system.[27]

The fit for the five fractions (Fig. 2) indicated a $T_{g\infty}$ of 92°C and a k of 1.5×10^5. The T_g of the parent HPL did not fit onto the same line. The large differences in T_g support the molecular weight differences observed by GPC. The $T_{g\infty}$ of 92°C was higher (by 24°C) than that predicted** from one of the simple copolymer equations.[28]

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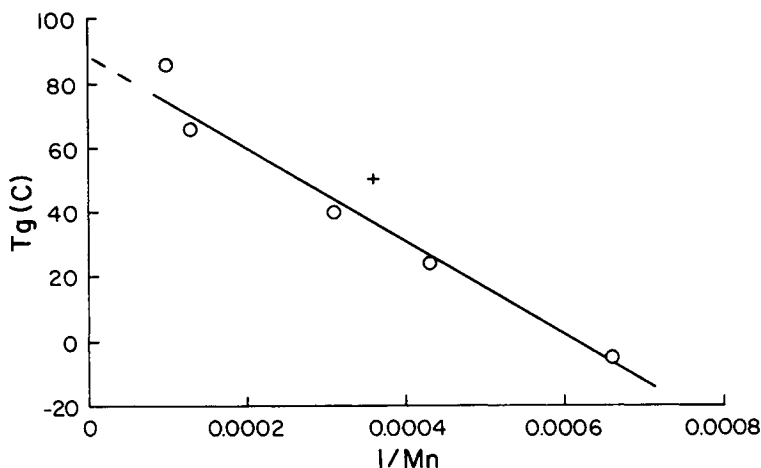**The T_g predicted with eq. (3) using 180 and −75°C as the T_g for lignin and PPO, respectively, was 68°C.

Fig. 2.   Plot of Fox–Flory relationship for the fractions (○) and for parent HPL (+).

The k value from eq. (1) may be used to estimate branching.[27] Since k depends, however, on chemical composition and secondary interactions, the significance of k for a single lignin (derivative) system remains limited.

Chemical Composition. Proton NMR and UV spectroscopy were used to characterize the chemical structure of the HPL fractions (Table I). Integration of the ^{1}H-NMR signal provides information on the relative abundance of different types of functional groups. Specifically, the ^{1}H-NMR spectra were divided into four regions with characteristic protons which have been previously assigned.[29,30]

The signal distribution was similar for the parent HPL and the fractions, except the highest molecular weight material (i.e., fraction 5). This showed a reduced response for aromatic (range 2/3) and methyl protons (range 8), and an increase in acetoxy methyl protons (range 6/7). No explanation for this difference can be given at present. The reduction in the aromatic signal is reflected by a reduced UV absorptivity coefficient at 280 nm. Hydroxyl content of the fractions averaged 6.5% (with a 10% error margin) with the exception of fraction 5, which was lower.

Polyurethane Networks

Effects of Molecular Weight on Dynamic Mechanical and Thermal Properties. Lignin-based polyurethane (PU) films were prepared from fractionated HPL at a constant NCO/OH ratio of 1.6. This ratio is below that of films described earlier.[7] DMTA spectra of the PU networks from HPL fractions are shown in Figure 3. The molecular weight of the polyol component influenced the observed T_g, measured by both DMTA and DSC, as well as the range over which the transition occurred (Table II). Dynamic mechanical and thermal properties are influenced by molecular weight and molecular weight distribution. As the molecular weight of the HPL fraction increased, the T_g of the PU film increased in a consistent fashion. This may be visualized by considering that both the difunctional HDI and the grafted propylene
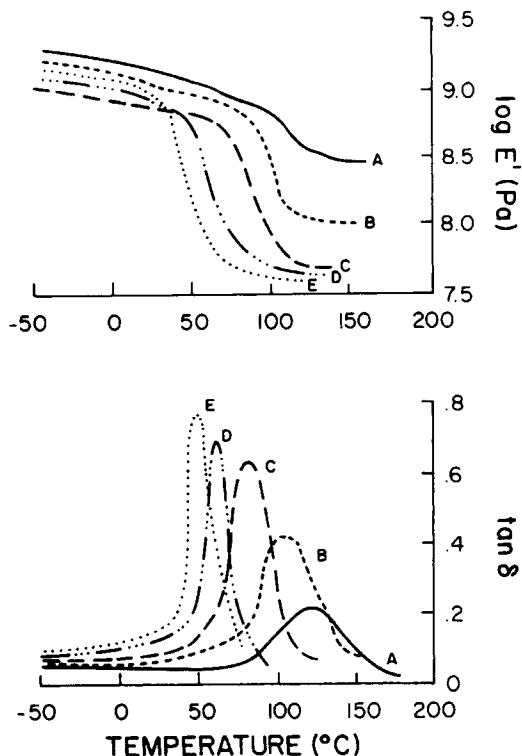
Fig. 3. Tan δ and log E' response for PU films prepared from HPL fractions: (A) fraction 5; (B) fraction 4; (C) fraction 3; (D) fraction 2; (E) fraction 1.

TABLE II
Thermal Properties of PU Films Prepared with Fractionated HPL

Fraction	$\overline{M}_n$	DMTA		DSC	
		Tan δ peak (°C)	1/2 Peak Width (°C)	T_g (°C)	T_g range (°C)
Parent HPL	2800	90	32	80	36
1	1500	48	18	40	18
2	2300	70	17	64	20
3	3200	94	21	81	28
4	8000	108	33	102	32
5	10,000	126	36	120	36

oxide chain have low T_g values, 20[††] and $-75°C$, respectively.[31-33] These two network components were connected in the curing reaction to produce a low T_g material around a lignin molecule of varying T_g. Motion in the low T_g material begins at a temperature well below that required for motion of the lignin component. Since the PU films are homogeneous, the lignin component must participate in the observed T_g. Segmental motion of a large lignin molecule (with higher T_g) would be restricted by both size and branching.

[††] Estimated from group contribution theory.[33]

TABLE III
Network Properties of PU Films Prepared with Fractionated HPL

Fraction	$\overline{M}_n$	Sol content (%)	Swell (%)	$\overline{M}_c{}^a$
Parent HPL	2800	10.6	286	2,000
1	1500	17.1	363	2,500
2	2300	11.5	249	1,400
3	3200	8.0	173	800
4	8000	5.9	145	700
5	10,000	3.7	132	400

ᵃCalculated from the Flory–Huggins equation. The χ value was calculated from group contribution theory.

Range of Energy Dissipative Mechanisms. Tan δ peak width, measured at one-half peak height, and T_g range may both be used as expressions of network heterogeneity by indicating complex energy dispersions.[30] A broad tan δ peak or a wide T_g range is typical of a chemically or morphologically heterogeneous material. Polypropylene oxide (PPO) possesses a simple mode of molecular motion that contributes to a narrow T_g. The observed increase in tan δ peak width and T_g range with increasing molecular weight (Table II) may contribute to an increase in molecular weight distribution. A broad distribution provides for a wide range of chemical features (i.e., functionality and intermonomer bonds) and reactive sites on a molecule, and this is expected to increase the complexity of molecular events as the polymer passes through T_g.

Swelling Properties. Swelling experiments allow for the characterization of network materials through the application of gel theory.[18] Swelling data permit the determination of molecular weight between crosslinks ($\overline{M}_c$) according to the Flory–Huggins equation. Flory's χ parameter needed for this equation was estimated through calculation of a PU solubility parameter from group contribution theory.[31] This approach has been discussed elsewhere.[2,7] Experimental results (Table III) indicate that sol fraction, swelling, and $\overline{M}_c$ decreased as the polyol molecular weight increased. The $\overline{M}_c$ value of the film from parent HPL was high compared to that predicted for a hypothetical PU with the same $\overline{M}_n$. These results may be explained by considering the functionality of the polyol and how it changes with molecular weight.

A network is formed by a system of molecules having a functionality of greater than two.[18] Molecules which react at only one site will not significantly contribute to mechanical strength (i.e., they do not assist in resisting an applied mechanical force). A molecule which is connected to the network at two points acts as a chain extender but not as a junction point. Only molecules which are incorporated into the network with three or more sites contribute as crosslink points. In the current study the HPL molecules must provide the junction points for network formation. Since the number of reactive sites per HPL molecule increases as the molecular weight increases, there are relatively few molecules with only one or two reactive sites, and more molecules that contribute to the network as junction points. $\overline{M}_c$ thus decreases. Conversely, low molecular weight fractions have a relatively higher

concentration of mono- and difunctional molecules, and networks formed from these materials have a higher $\overline{M}_c$. Low molecular weight components in the unfractionated HPL contribute to a higher $\overline{M}_c$ than expected on the basis of molecular weight alone.

Application of a Network Model

Networks may be conceptualized as having two components, a backbone and a crosslinking component.[18] The backbone of the HPL-based PU networks may be represented by an idealized linear HPL–HDI copolymer. The crosslinking component may be visualized as additional HDI chains connecting the linear HPL–HDI copolymer. This concept has been used by Chan et al.[34] as the basis for modeling the difference between the T_g of an uncured thermoset and that of a network:

$$\Delta T_g = \Delta_c T_g + \Delta_p T_g \qquad (2)$$

where $\Delta T_g = T_g$ of PU film $- T_g$ of HPL fraction, $\Delta_c T_g =$ copolymer effect, i.e., T_g of a comparable linear copolymer, and $\Delta_p T_g =$ crosslinking effect.

For the PU films ΔT_g was determined from experiment. The $\Delta_c T_g$ was calculated from the Fox relationship

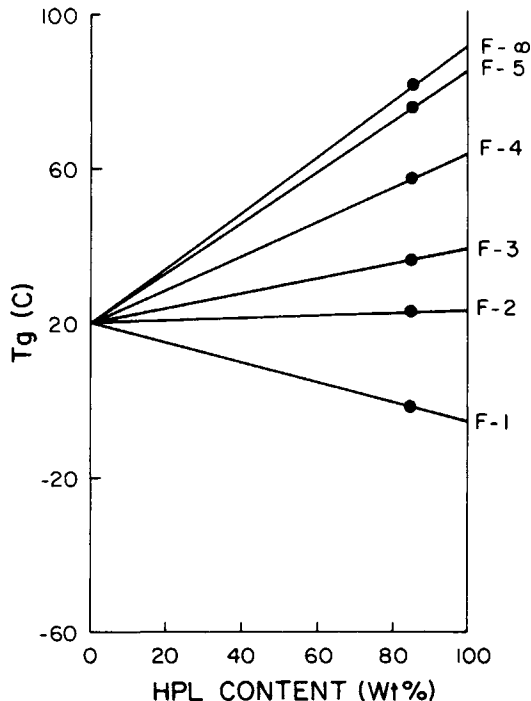$$1/T_g = W_A/T_{gA} + W_B/T_{gB} \qquad (3)$$

Fig. 4.   Fox relationship used to determine $\Delta_c T_g$. The T_g of a hypothetical HDI polymer was calculated from group contribution theory, Ref. 33; and T_g of the HPL was determined with the Fox–Flory relationship [eq. (1) in text].

TABLE IV
Determination of Copolymer Effect, $\Delta_c T_g$; Crosslinking Effect, $\Delta_\rho T_g$; and ΔT_g of PU Films
Prepared from Fractionated HPL

Fraction	$\Delta T_g{}^a$ (C)	$\Delta_c T_g{}^b$ (C)	$\Delta_\rho T_g{}^c$ (C)
Parent HPL	33	−5	38
1	45	4	41
2	40	−1	41
3	41	−3	44
4	36	−7	43
5	34	−10	44
Theoretical[d]	32	−11	43

[a] From experiment (T_g film − T_g polyol).
[b] From Fox equation, Figure 4.
[c] By difference, eq. (2) in text.
[d] From Fox–Flory plots, eq. (1) in text.

where T_g = the T_g of the copolymer (K), T_{gA} and T_{gB} = the T_g of the respective homopolymers (K), and W_A and W_B = the weight fractions of the homopolymers.

The calculated $\Delta_c T_g$ for the five HPL fractions and an idealized high molecular weight HPL [from eq. (1)] are shown as single points in Figure 4. The T_g of a hypothetical HDI homopolymer was computed to be 20°C and the Fox relationship predicted that the T_g of an ideal HPL–HDI copolymer ($\Delta_c T_g$) would be somewhere between 20°C and the T_g of the HPL in relation to the weight fraction of the respective components [eq. (3)]. The calculated $\Delta_c T_g$, the experimental ΔT_g (i.e., difference between the T_g of the cured PU film and the T_g of the polyol), and the calculated $\Delta_\rho T_g$ values are given in Table IV.

All $\Delta_\rho T_g$ values (Table IV) were positive and large. The differences in $\Delta_\rho T_g$ were not substantial over this $\overline{M}_c$ range, since all of the systems were highly crosslinked. However, compared to the linear copolymer, the $\Delta_\rho T_g$ was substantial. Thus it appears that crosslinking, as indicated by $\Delta_\rho T_g$, dominates the chain in the T_g observed with curing the HPL–HDI networks.

Mechanical Properties

Tensile samples were used to obtain the mechanical properties of the PU films at room temperature. The Young's modulus (MOE), ultimate strength and ultimate strain of all films from fractionated HPL (Table V) indicate a significant increase in MOE over that of the parent HPL, a slight increase in ultimate strength, and no consistent change in ultimate strain. However, the change in MOE was not consistently related to variations in $\overline{M}_c$. The MOE of the PU films reached a maximum for fraction 2 and then decreased. The relationship between MOE and $\overline{M}_c$ was surprising. The low MOE value for the network based on fraction 1 polyol could be due to that network being close to its T_g at ambient temperature. The consistent decrease in MOE with decreasing $\overline{M}_c$, however, was opposite to expected behavior and cannot be explained at this time.

TABLE V
Mechanical Properties of PU Films Prepared from Fractionated HPL

Fraction	$\overline{M}_c$	Young's modulus (MPa)	Ultimate strength (MPa)	Ultimate strain (%)
Parent HPL	2000	1050	48.7	5.7
1	2500	1520	43.5	4.2
2	1400	2030	44.5	1.5
3	800	1550	49.3	1.9
4	700	1200	56.7	2.6
5[a]	400	—	—	—

[a]Samples were too fragile to be reliably tested.

The increase in ultimate strength was strongly correlated with $\overline{M}_c$ (Table V). A similar trend had been noted earlier for lignin-based PU films in which the strength of the network was seen to increase with a decrease in the hydroxypropyl chain length.[7] However, in the previous study, the change in network $\overline{M}_c$ was related to changes in chemical composition (specifically the lignin content of the network) while for the present investigation the change in strength is related to molecular weight.

The variation of the ultimate strain characteristics of the PU films from fractionated lignin may be related to the ability to form a uniform network. A relatively high ultimate strain for the network based on fraction 1 supported the attribution of a low MOE to a ductile-type failure.

CONCLUSIONS

A series of fractionated HPL polyols were prepared from dilute solution with molecular weight increasing as expected. The $\overline{M}_n$ of the fractions varied between 1500 and 10,000 daltons, and the dispersity ratio was reduced to 1.6–3.3. The chemical composition of the fractions varied insignificantly while the T_g of the fractions varied inversely with molecular weight as predicted by the Fox–Flory relationship.

A series of polyurethane networks (PU films) was prepared from the HPL fractions which displayed rising tan δ peak temperature and T_g as the molecular weight of the HPL fraction increased. The increase in T_g was related to the $\overline{M}_n$ of the fractions. The tan δ at one-half peak width and the T_g range both increased with $\overline{M}_n$, which was indicative of a variety of different molecular motions contributing to the transition.

Swelling studies were used to characterize network properties. Both sol content and swelling decreased as the molecular weight of the polyol increased. This was explained with functionality differences between the fractions. Small molecules with low functionality act more as chain ends or chain extenders and less as network junction points. Swelling experiments allowed the determination of $\overline{M}_c$. Network $\overline{M}_c$ decreased as the molecular weight of the fractions increased. This was related to the average functionality of polyol molecules.

The difference in T_g between prepolymer and film was attributed to two separate effects according to Chan et al. These two effects were related to the T_g of the modified (by copolymerization) starting polyol and a crosslinking

effect. The first effect ($\Delta_c T_g$) could be modeled with the Fox equation which predicted that hypothetical (linear) HPL–HDI copolymer would have a T_g of between -1 and 80°C. The second effect ($\Delta_p T_g$) showed a large increase in the T_g of the HPL–HDI network due to crosslinking. The T_g increase ranged from 38 to 44°C depending on the level of crosslinking.

The mechanical properties of PU films generally improved as the molecular weight of the HPL increased. At a comparable molecular weight, networks prepared from fractionated HPLs possessed better mechanical properties than networks prepared from nonfractionated HPL.

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