Engineering Plastics from Lignin. III. Structure Property Relationships in Solution Cast Polyurethane Films*

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Synopsis

Lignin-based polyurethane films were synthesized by solution casting from hydroxypropyl lignin derivatives and either an aliphatic or an aromatic isocyanate. Two lignins, kraft and steam explosion lignin, and two diisocyanates, hexamethylene diisocyanate (HDI) and tolylene diisocyanate (TDI), were chosen for the study. It was found necessary to use stoichiometric excess diisocyanate in the synthesis of the thermosetting polyurethanes. This part of the series addresses the effect of synthesis variables on film properties. The study examines the effect of lignin type, of diisocyanate type, and of composition in terms of NCO to OH stoichiometry on thermal and mechanical properties. Stoichiometric NCO-excess was found to cause a more significant increase in the glass transition temperature of TDI-based films than of films made with HDI. The films swelled less with increasing NCO/OH ratio. Use of aliphatic diisocyanate (HDI) resulted in films with lower moduli as compared to aromatic diisocyanate (TDI). Kraft-lignin-based polyurethanes had slightly inferior strength characteristics (Young's modulus and tensile strength) in comparison with those derived from steam explosion lignin. Variation in the NCO/OH stoichiometry had no noticeable effect on modulus or tensile strength, but did significantly influence glass transition temperature, swelling, and strain at break. It is observed that the properties of these thermosetting polyurethanes are very sensitive to their composition. The study illustrates that materials of satisfactory performance characteristics can be engineered by proper selection of synthesis variables and modification of network architecture.

INTRODUCTION

Polyurethanes are finding increasing applications in the field of fibers, elastomers, foams and coatings.[1] These are best known for their high tensile strength, load bearing capacity, and resistance to abrasion. With a wide range of structural variations, end products with diverse character and properties have been manufactured. Thermoplastic polyurethanes, moisture curing and two component solvent-based systems, blocked isocyanates, and prepolymers are some of the important industrial applications.

Various schemes to utilize lignin as a polyurethane base are available in the literature.[2–9] The primary impetus lies not only in its natural abundance and renewability, but also in its being one of the largest low value industrial bypro-

ducts. Isolated lignin has aliphatic and phenolic hydroxy functionality, and this creates reactivity towards isocyanates.[10] Reactions between lignin and isocyanates have been investigated, but most previous attempts have suffered from a lack of component characterization and an instability of the formulation. Most earlier studies viewed lignin as an inexpensive, inert filler and extender. In one example, Nichols[2] employed kraft lignin as a reinforcing agent in elastomeric compositions based on polyethers, polyester amides, and polyalkylene glycols. He reported improved properties for the final elastomeric product by using oxidized kraft lignin instead of lignin in the unmodified form. This observation indicates that functionalization by modification makes it possible to incorporate lignin into the matrix of a polymeric material. This concept was later used by Mills and Haxo[3] for abrasion-resistant rubber compositions. The method of producing such lignin-reinforced rubber vulcanizates involved coprecipitation of lignin with rubber latex and treatment with an organic polyisocyanate. Moorer et al.[5] and Santelli and Wallace[6] used glycols to improve the strength properties of lignin polyurethane foams. In these cases, however, lignin has been used as a coreactant rather than as the primary network component. These studies illustrate that the major limitation for the use of lignin in polymeric products concerns its polydisperse and multifunctional characteristics. The synthesis of a more uniformly functional derivative should therefore assist in the preparation of a lignin-based engineering plastic. It has previously been shown that the conversion of phenolic to aliphatic hydroxy groups enables macromolecular lignin to be used as a polyol component in polyurethane foams.[11] The synthesis of unifunctional hydroxyalkyl lignin derivatives, and their structural characterization, have been the subject of the earlier two papers in this series.[12,13] Hydroxypropylation, in particular, was identified as a promising modification reaction and this has been the subject of extensive investigation.[14–18] The incorporation of these types of isolated and purified lignin derivatives as a sole hydroxy component into polyurethanes remains to be demonstrated. Earlier work[11,15,16,19,20] was based on mixtures of hydroxyalkyl lignins and poly(oxyalkylene) ether homopolymers.

This study is aimed at illustrating some aspects of the structure–property relationships in lignin-derived polyurethanes. Solution casting with subsequent cure at elevated temperature was adopted as synthesis route since this was found to generate testable films. The variables in this study concerned types of materials (lignin and diisocyanate) and isocyanate to hydroxy (NCO:OH) stoichiometry. The study has examined the effect of these variables on thermal and mechanical film properties.

MATERIALS AND METHODS

Materials

Kraft Lignin (KL). Commercial pine kraft lignin, isolated by acidification of kraft black liquor, was obtained from Westvaco, Charleston, S. C., under the trade name INDULIN ATR-Cl.

Steam Explosion Lignin (SEL). Steam explosion lignin was supplied by Iotech Corporation, Ottawa, Canada. The method of preparation involved extraction of steam exploded aspen chips with aqueous NaOH (0.4%), and this has been described by Marchessault et al.[21,22]

The chemical analysis on these two lignins indicated methoxy content of 13.7 and 18.2, phenolic hydroxy content of 5.5 and 4.3 and total hydroxy content of 11.9 and 9.6 for KL and SEL, respectively. Molecular weights and weight distributions by GPC showed weight average molecular weights M_w of 4300 and 2000 g/M with M_w/M_n values of about 5 and 3 for KL and SEL, respectively.

Hydroxypropyl Lignin (HPL). Solid lignins were reacted with propylene oxide according to a procedure reported earlier.[12,18] This involved a closed, mechanically stirred stainless steel reactor. Analysis results indicated that the HPLs had hydroxy contents of 4.3% and 9.3% for KL and SEL, respectively.

Isocyanates. Isocyanates used were hexamethylene diisocyanate (HDI) and 2,4-tolylene diisocyanate (TDI), practical grade by Eastman Kodak Company, Rochester, N.Y.

Methods

Film Preparation. Polyurethane films were prepared from the two diisocyanates and the two hydroxypropyl lignins (HPL's). Polyols were dried over P_2O_5 under vacuum prior to use. The polyol component, the isocyanate, and the catalyst were thoroughly mixed in tetrahydrofuran (THF) solution and allowed to stand for 5 min; the formulation was then poured onto glass plates coated with a thin layer of silicone oil L-520 (Union Carbide Corp.). The casting concentration of the polyurethane formulation was about 20% in all cases. Dibutyl tin dilaureate (T-9 Catalyst, Union Carbide Corp., South Charleston, W. Va) was used as catalyst in concentrations of 3% on total solids. The resin was allowed to stand for about 15 min at room temperature in a hood to evaporate part of the solvent, and set in the form of a uniform film. The film was cured in an air-circulated oven for 3 h at 105°C. The films were stored in a desiccator for at least 1 week before testing.

Differential Scanning Calorimetry (DSC). DSC was performed using a Perkin-Elmer Model DSC 4 equipped with scanning auto zero accessory. The heating rate was 10°C/min and sensitivity 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 the maximum value.

Stress–Strain Testing. Uniaxial stress–strain and ultimate property measurements were made using a standard Instron testing machine 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. Polyurethane films were swollen to equilibrium (120 h) in dimethyl formamide. The increase in weight due to swelling was expressed on unswollen weight.

RESULTS AND DISCUSSION

Synthesis

The synthesis of thermosetting polymer films from components which have the tendency to gel before completion of the reaction is best accomplished by solution casting. Formation of a film before the onset of gelation is necessary,

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TABLE I
Composition of Hydroxypropyl Lignin-Based Polyurethanes

| | HPL component | | Isocyanate | |
| | | Wt fraction | wt fraction | NCO/OH |
Designation	Type	(%)	(%)	ratio
HDI Series				
KH-1	kraft	50.0	50.0	4.7
KH-2		55.5	44.5	3.8
KH-3		62.5	37.5	2.8
KH-4		71.5	28.5	1.9
KH-5		83.3	16.7	0.9
IH-1	steam	50.0	50.0	2.2
IH-2	expln.	54.1	45.9	1.9
IH-3		57.0	43.0	1.6
TDI Series				
KT-1	kraft	50.0	50.0	4.6
KT-2		55.5	44.5	3.7
KT-3		62.5	37.5	2.7
KT-4		71.5	28.5	1.8
KT-5		83.3	16.7	0.9
KT-6		76.9	23.1	1.4
KT-7		87.0	13.0	0.7
IT-1	steam	42.9	57.1	2.8
IT-2	expln.	46.2	53.8	2.5
IT-3		50.0	50.0	2.1
IT-4		54.5	45.5	1.8
IT-5		60.0	40.0	1.4

and solvent removal and cure completion is subsequently carried out at higher temperature. However, this creates the risk that some of the (volatile) isocyanate is lost, thereby causing differences in the film composition in relation to that of its formulation. The use of higher than normal catalyst concentrations and the use of excess amounts of diisocyanate were found to yield most satisfying results.

In a related study, Minoura et al.[23] synthesized solution-cast polyurethane films from a polybutadiene glycol with a functionality in excess of 2. The authors emphasize the complications arising from premature gelation, and stress the need for quick casting. Since efforts failed to prepare solution-cast films with stoichiometric quantities of diisocyanate and polyol, excess NCO-component had to be employed in order to assure complete reaction of the polyol. Thus, isocyanate (TDI or HDI) losses due to volatilization must be considered when solution-cast films are formulated.

Table I summarizes the composition of formulations used to synthesize the film test specimen. The films are designated with the letter K or I depending on whether they were prepared from kraft (KL) or steam explosion (SEL) (Iotech) lignin, and with the letter T or H depending on whether they were prepared with TDI or HDI. Film synthesis was found to be affected by lignin type and by NCO/OH stoichiometry. Between the two hydroxypropyl lignin derivatives (HPL), SEL proved to be the most sensitive to isocyanate content. At NCO/OH ratios of <1.5 in case of HDI and <1.1 in case of TDI, very brittle materials were obtained which were unsuitable for mechanical testing. No comparable problems were observed in case of hydroxypropyl KL. This difference may be attributed to differences in molecular weights, in molecular weight distributions,
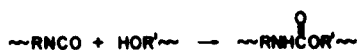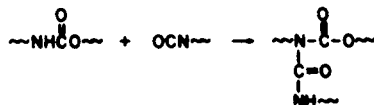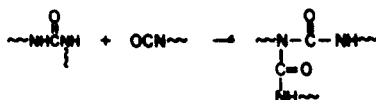
Fig. 1. Principal bonds producing crosslinks in thermosetting polyurethanes in relation to NCO:OH stoichiometry.

and in functionality between the two lignin preparations. The lower molecular weight (SEL) seemed to require a greater amount of crosslinking agent before films of sufficient mechanical strength were formed.

Polyurethanes are capable of forming three types of bonds in relation to NCO/OH ratio, and these are shown in Figure 1. In addition to normal urethane bonds, biuret linkages may be created by moisture, and allophanate linkages may result from the reaction of excess diisocyanate with urethane groups.[24]

Thermal and Swelling Behavior

Glass transition temperatures (T_g's) of the polyurethane films are given in Table II. The DSC thermograms show glass transitions at temperatures above

TABLE II
Thermal Properties of Hydroxypropyl Lignin-Based Polyurethanes

| Sample	NCO/OH ratio	Young's modulus (MPa)	Ultimate stress (MPa)	Ultimate strain (%)	T_g (°C)
KH-1	4.7	1398 ± 127	75.5	14.9	114
KH-2	3.8	1283 ± 95	79.2	12.7	126
KH-3	2.8	1327 ± 31	79.6	16.5	118
KH-4	1.9	1671 ± 51	73.5	6.8	105
KH-5	0.9	1591 ± 92	14.8	1.2	96
KT-3	2.7	1509 ± 400	54.4	7.0	189
KT-4	1.8	2076 ± 318	48.5	6.0	158
KT-6	1.4	1874 ± 168	49.2	3.8	136
KT-5	0.9	1975 ± 298	57.2	5.1	128
IH-1	2.2	1698 ± 168	80.5	12.1	94
IH-2	1.9	1597 ± 78	85.7	13.4	84
IH-3	1.6	1792 ± 140	70.5	7.0	74
IT-1	2.8	1915 ± 102	86.4	10.0	192
IT-2	2.5	2268 ± 355	86.2	7.4	174
IT-3	2.1	2387 ± 164	95.0	7.5	165
IT-4	1.8	2018 ± 127	80.9	7.8	146
IT-5	1.1	2086 ± 52	91.6	8.4	157
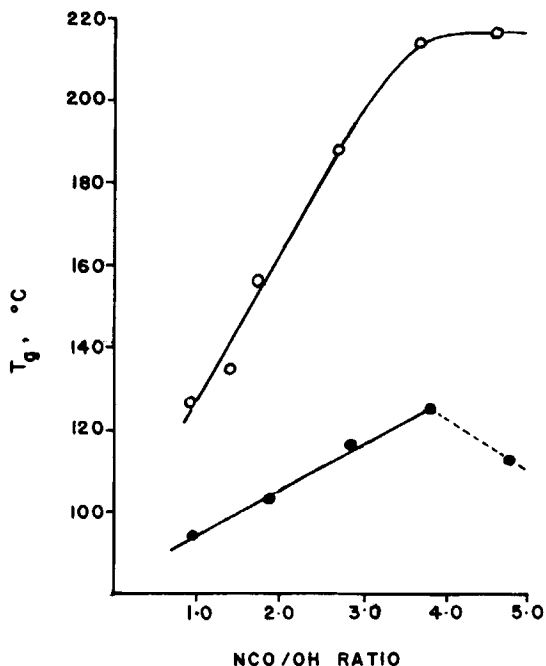
Fig. 2. Glass transition temperatures of HDI- and TDI-based kraft polyurethane films in relation to NCO:OH stoichiometry: (O) KT-series; (●) KH-series.

those of the glass transition temperatures of the HPL's, but generally below those of the corresponding lignins. An increase of T_g with increasing NCO/OH ratio is observed in all four series. Between the two isocyanates selected, TDI-based films had T_g's higher than those of the corresponding HDI films for the same NCO/OH ratio. This is illustrated in Figure 2 for the K-series films. Similar results were reported for HDI- and TDI-derived polyurethane elastomers from poly(oxypropylene) glycols,[24] and for poly(ϵ-caprolactone) diol-based polyurethanes.[25] It is also observed that the T_g of TDI-based films rises more steeply with NCO/OH stoichiometry than that of their HDI equivalents. At very high isocyanate contents, in excess of ca 3.5 NCO/OH ratio, the T_g of both film types begins to level off or decline. While it is possible that the crosslink density is still increasing at this point, the probable reason for this drop is that the segmental contribution by HDI through the hexamethylene "soft segments" has an overriding influence on thermal properties.

The swelling behavior of HDI-based films in dimethyl formamide (DMF) is shown in Figure 3. Swelling decreases expectedly with NCO/OH ratio. No apparent decrease in swelling is, however, observed at NCO/OH ratios in excess of about 3. These two observations, on thermal and swelling behavior in relation to NCO/OH ratio, thus suggest that crosslink density remains constant or even declines with NCO/OH ratio rising beyond 3–3.5.

Hydroxypropyl SEL-based polyurethane films were studied over a smaller NCO/OH ratio range than kraft HPL. T_g's of these films were lower than those obtained from kraft HPL at the same molar NCO/OH ratio, which is not surprising considering that the T_g of hydroxypropyl SEL is lower than that of the KL derivative. However, it is interesting that the IT films have T_g's very close
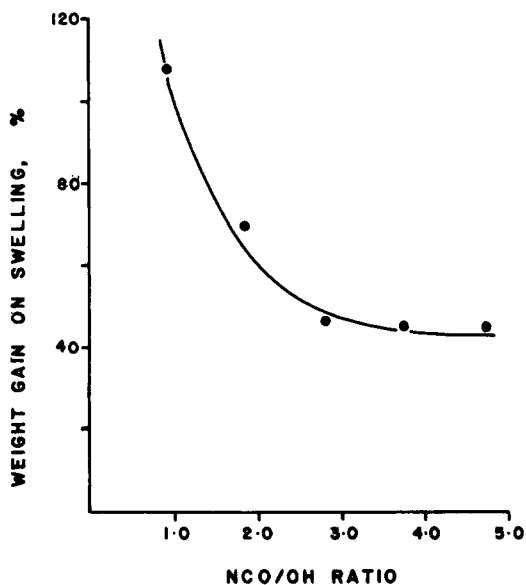
Fig. 3. Swelling behavior of HDI-based kraft polyurethane films in relation to NCO:OH stoichiometry.

to those of the KT films at the same NCO/OH stoichiometry. These results are not included in Figure 2 because of the very limited NCO/OH range; they are, however, listed in Table II.

Stress–Strain Behavior

The four thermosetting film series were examined for the effect of crosslink density on mechanical properties. Table II summarizes ultimate film properties, and these are generally characteristic of rigid (glassy) materials. Ultimate stress
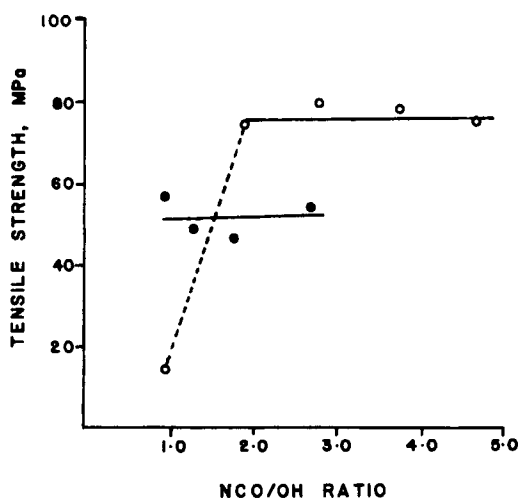

Fig. 4. Tensile strengths of KH- (O) and KT-series (●) polyurethane films in relation to NCO:OH stoichiometry.
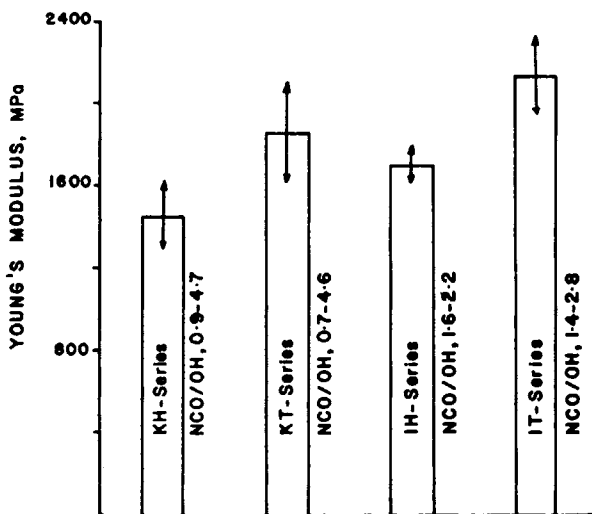
Fig. 5. Average Young's modulus values of polyurethane films from two lignins in relation to NCO/OH stoichiometry.

(tensile strength) is shown in Figure 4 in relation to NCO/OH ratio. A straight-line relationship without dependence on NCO/OH ratio is found for all films except for the KT-film with NCO/OH < 1.0. HDI produced stronger films with the kraft lignin derivative than did TDI; and no significant difference was noticed for the SEL-based films.

Average modulus values for the four film series are shown in Figure 5. The moduli of the polyurethanes ranged between 1500 and 2100 MPa, and this is similar to the 2000 MPa value reported for pine kraft lignin by Falkehag.[26] With TDI as diisocyanate, the polyurethanes generally had higher modulus values than when HDI was used. This was expected because of the introduction of rigid aromatic rings into the system. At very high NCO/OH ratios (in excess of 3), films with acceptable strength properties were obtained only from the KH-series. The corresponding KT-series films produced very brittle materials unsuited for testing. Similarly, film KT-7, with a NCO/OH ratio of 0.7, failed to produce testable material apparently by reason of incomplete network formation.

Young's modulus values exhibited a surprising insensitivity towards variation in NCO/OH stoichiometry. Increasing NCO/OH ratios should theoretically result in more frequent allophanate crosslinks and lower average molecular weights between crosslinks (M_c). The experienced insensitivity of the moduli towards crosslink density must be interpreted with the behavior of glassy network systems. In studying the effect of crosslink density on the engineering behavior of epoxies, Misra et al.[27] found that although the T_g's decreased expectedly with increasing M_c, the modulus remained nearly constant and independent of M_c. This result was attributed to the glassy nature of the system at room temperature, at which the long range segmental motion of the chains is frozen. However, the authors note that the effect of M_c cannot be observed even above the T_g of the system, as is evidenced by results from creep experiments. The general explanation of this behavior of bisphenol-A-based epoxies is that the bulky aromatic groups restrict the motion of the main chains.
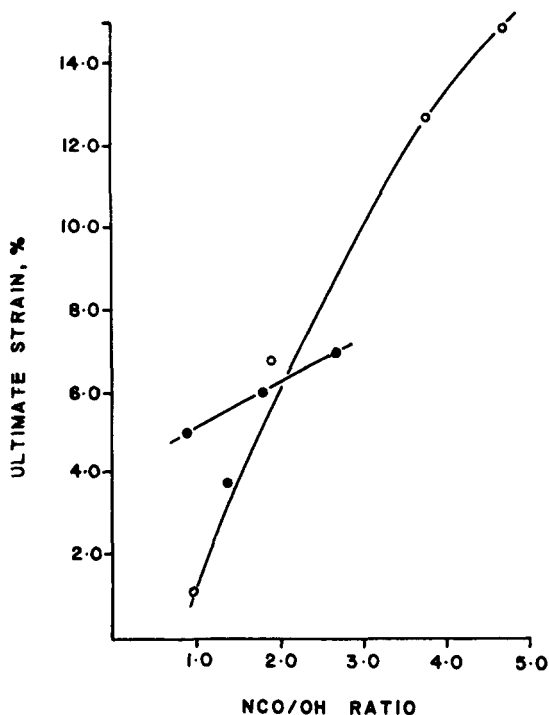
Fig. 6. Ultimate strain values of kraft-lignin-based polyurethane films in relation to NCO:OH stoichiometry: (●) KT-series; (○) KH-series.

SEL-derived films have a higher range of moduli as compared to those based on KL (Fig. 5). Tensile strength values are also significantly higher, and this must be attributed to both differences in functionality and molecular weight of the starting polyol components. SEL's are known for their very low molecular weights, which correspond on the average to oligomers containing 2–3 phenyl-propane units.[22] By contrast, KL has molecular weights (M_N) about 2–3 times as large. The hydroxy content of the hydroxypropyl SEL was about twice that of the corresponding KL preparation. This can be considered as being responsible for the increased internal bond strength and, consequently, higher stress levels at break of the SEL-based films. Increasing crosslink density increases the moduli of SEL-films more quickly in comparison to KL-derived films.

Ultimate strain values (strain at break) are plotted in Figure 6 against NCO/OH ratio. No distinct trend is recognized for films of the KT-series. Films of the KH-series, however, show a surprising increase in maximum extensibility with NCO/OH ratio rising from 0.9 to 4.7. This is opposite to what was expected, because increasing crosslink density theoretically gives rise to a more rigid material. Other factors than crosslink density may contribute to this observation. One possible explanation is internal bond strength, which refers to a property that is influenced more by chain breakage than by chain slippage. Increasing isocyanate content serves to bridge lignin moieties with more urethane bonds, and, if the failure is dependent on the bonds produced in polyurethane synthesis, then the fracture may not occur till much higher elongations. If this explanation

is valid, then film KH-4, having higher stress at break as compared to KH-5, can be understood as the result of complete reaction of hydroxy groups; and the higher elongation at break of film KH-1 as compared to KH-4 is a result of the influence of a larger concentration of hexamethylene "soft segments" in film KH-1 (Table II). The swelling data, showing hardly any effect of increased crosslink density at very high NCO/OH ratios, and T_g plateauing, or even decreasing, can be considered as supporting evidence for this explanation.

CONCLUSIONS

1. Hydroxypropylation serves as a useful chemical modification procedure which improves the solubility characteristics of lignins, reduces the differences in reactivity of different functional groups, and converts lignins into polyester–ether polyols suitable for the synthesis of thermosetting polyurethane films.

2. This investigation of polyurethane films synthesized from monomeric diisocyanates and hydroxypropyl lignins by solution casting demonstrates that engineering plastics which are suitable for mechanical testing can be prepared from lignin. The limitations regarding the testing of mechanical properties of lignins are circumvented by synthesizing network polymers of sufficient size by crosslinking reactions.

3. The thermosetting characteristics of lignin-based polyurethane films originate not only from the multifunctionality of the HPL's, but also from NCO:OH stoichiometry. Excess NCO over OH component produces crosslinks with allophanate bonds which are seen to have a predominant effect on glass transition temperature and swelling.

4. Rigidity characteristics depend on the diisocyanate type used. A comparison of materials produced with hexamethylene diisocyanate (HDI) and with tolylene diisocyanate (TDI) shows that straight chain characteristics of the diisocyanate have a controlling influence on thermal and mechanical properties.

5. Glass transition temperatures of the polyurethanes increase generally with NCO/OH ratio. This trend is more pronounced with TDI-based polyurethanes than with HDI-based films, for which the glass transition temperature declines at very high NCO/OH ratio. This may be attributed to the incorporation of straight chain isocyanate molecules, and their segmental motion probably overrides their contribution to crosslink density.

6. Use of excess diisocyanate has apparently no detrimental effect on the properties of the films produced with HDI. Problems were, however, encountered with TDI-based films having either very high (>3) or very low (<1) NCO/OH ratios.

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