Kraft Lignin in Polyurethanes. II. Effects of the Molecular Weight of Kraft Lignin on the Properties of Polyurethanes from a Kraft Lignin–Polyether Triol–Polymeric MDI System

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Synopsis

   Polyurethane films were prepared by solution casting using a three-component system consisting of polymeric MDI, a propylene oxide-based polyether triol and kraft lignin fractions of different molecular weights. The polyether triol was used as soft segment. The composition of the polyurethanes was varied whereas the NCO/OH ratio was kept constant. The crosslink density increased with increasing molecular weight of the kraft lignin fraction used, which is a result of an increase in functionality of the kraft lignin with increasing molecular weight. Polyurethanes prepared from low molecular weight kraft lignin were found to be more flexible than those prepared from medium and high molecular weight kraft lignin (at lignin contents below 30%). At kraft lignin contents higher than about 30% (which at the NCO/OH ratio used corresponds to a hard segment content of about 70%), rigid and glassy polyurethanes were obtained regardless of the molecular weight of the kraft lignin fraction used.

INTRODUCTION

   Lignin is a renewable, amorphous biopolymer consisting of phenylpropane units linked together through various types of ether- and carbon-carbon-bonds.[1-3] It is an important constituent of various plants and is, among the naturally occurring polymers, second in natural abundance only to cellulose.[2,3]

   Kraft lignin (KL) is a chemically degraded technical lignin,[4,5] produced in large quantities in the kraft pulping process. Its present use is almost exclusively as fuel in the recovery system of the kraft mills. KL and KL derivatives have, however, a potential to be utilized also in other applications.[3,6] One possible application area which has attracted a considerable interest is the use of KL or KL derivatives as polymeric components in thermosets like phenolic resins, polyurethanes, and epoxy resins.[3,6]

   The present work is part of an investigation on the performance of nonderivatized KL as a component in polyurethane (PU) systems. In the previous

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investigation of this series,[7] crosslink densities and the mechanical properties of solution-casted PU films prepared from a three-component system (KL-polyether triol-polymeric MDI) were studied using a prefractionated, nonderivatized kraft lignin as the KL component. Several isocyanate/hydroxyl group (NCO/OH) ratios were investigated. The results showed that KL acted as a crosslinking agent in this PU system and that the effective contribution of KL to the formation of a PU network was especially apparent at low NCO/OH ratios due to the comparatively high functionality of KL in the reaction towards isocyanates. It was also shown that PUs having a large variety of mechanical properties can be obtained from this three-component system at low and intermediate NCO/OH ratios by varying the lignin content while keeping the NCO/OH ratio constant.

It is, however, well known that kraft lignin is a heterogeneous material having a complex chemical structure[4,8] as well as a fairly broad molecular weight distribution.[9,10] The chemical structure of KL as well as the contents of certain functional groups have been found to vary to some degree with molecular weight.[9-11] These factors may influence the product properties when KL is used in polymer applications. As an example, Forss and Fuhrmann[12] found that high molecular weight fractions of KL performed considerably better than unfractionated KL as component in phenolic resin adhesives for plywood.

The objective of the present investigation was to clarify the effects of the molecular weight of KL on the swelling, thermal, and tensile properties of KL-derived PU films. The PU system chosen for this study consisted of polymeric MDI (PMDI), nonderivatized KL fractions of various molecular weights, and a propylene oxide-based polyether triol. The polyether triol was used as soft segment.

EXPERIMENTAL

Materials

Kraft Lignin

Softwood kraft lignin was isolated from an industrial kraft black liquor by acid precipitation.[10] The isolated kraft lignin was fractionated by successive extraction with organic solvents according to the scheme presented in Figure 1. A detailed description of the fractionation procedure is presented elsewhere.[10]

Polyether Triol

The propylene oxide-based polyether triol used (Bermodol-10), was supplied by Berol Kemi AB, Stenungsund, Sweden. According to the producer, the molecular weight and hydroxyl group content were 600 g/mol and 5.0 mmol/g, respectively.

Polymeric MDI (PMDI)

The PMDI used was also supplied by Berol Kemi AB. Size exclusion chromatography on a set of Ultrastyragel columns (styrene/divinylbenzene gels),
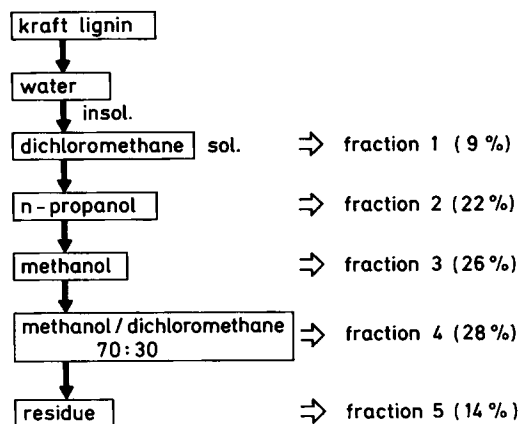
Fig. 1. Scheme for the fractionation of kraft lignin by successive extraction with organic solvents.

using tetrahydrofuran (THF) as eluent, showed that the PMDI consisted of 30% diisocyanates, 25% tri- and tetraisocyanates and 45% higher oligomers.

Methods

Preparation of Polyurethane Films

PU films were prepared by prepolymerization of a mixture of kraft lignin fraction, polyether triol, and PMDI in THF solution without catalyst followed by solution casting on glass plates as described previously.[7] The isocyanate-hydroxyl group (NCO/OH) ratio was defined as follows:

$$NCO/OH = \frac{W_I[NCO]}{W_{KL}[OH]_{KL} + W_p[OH]_p} \quad (1)$$

where [NCO] is the content of isocyanate groups in the PMDI (7.6 mmol/g) and where $[OH]_{KL}$ and $[OH]_P$ are the total contents of hydroxyl groups in the KL fractions (6.1–7.3 mmol/g) and in the polyether triol (5.0 mmol/g), respectively. W_{KL}, W_I and W_p are the weights of KL, PMDI, and polyether triol, respectively.

The KL content was defined as follows:

$$KL \text{ content} = \frac{W_{KL}}{W_{KL} + W_I + W_p} \times 100 \ (\%) \quad (2)$$

Characterization of the Kraft Lignin Fractions

The procedures for determination of hydroxyl group contents and for characterization of the KL fractions by high performance size exclusion chromatography (HPSEC) are reported elsewhere.[10]

Tensile and Swelling Tests

Tensile and swelling tests were carried out using the same procedures as described in the previous investigation of this series.[7]

Differential Scanning Calorimetry (DSC)

DSC analysis was carried out using a Perkin-Elmer differential scanning calorimeter DSC-7. The glass transition temperature (T_g) was defined as the midpoint of the change in heat capacity occurring over the transition. Glassy samples were first scanned through T_g to eliminate effects from enthalphy relaxation,[13] thereafter cooled and scanned a second time. In case of these samples, T_g was determined from the second scan. The measurements were made under an atmosphere of dry nitrogen at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Fractionation of KL by successive extraction with organic solvents according to the scheme presented in Fig. 1, yielded five fractions, including the undissolved residue after the fourth extraction step. This residue (fraction 5), which amounted to 14% of the unfractionated KL, could not be used in the polyurethane synthesis because of its low solubility in THF and other organic solvents.

Figure 2 shows high performance size exclusion chromatograms of fractions 1–4. As shown in this figure, fraction 1 consists of material having very low molecular weight. Fraction 2 is also composed of low molecular weight material,
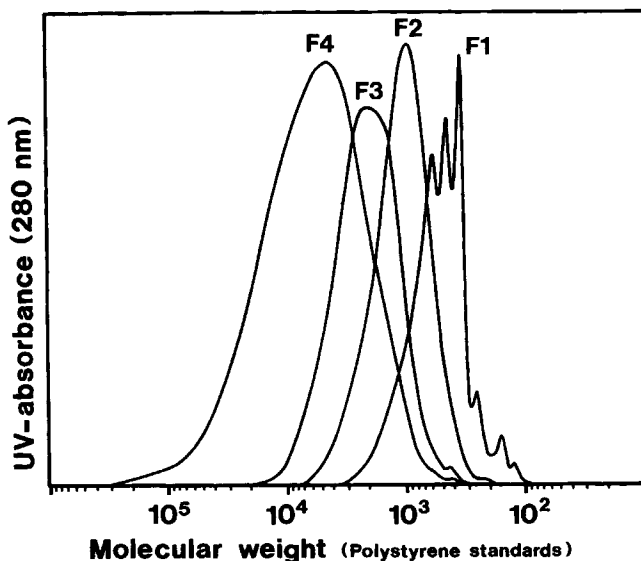

Fig. 2. Size exclusion chromatograms of kraft lignin fractions 1–4 (acetylated samples). The molecular weight scale is related to polystyrene.

whereas fraction 3 is of medium molecular weight.[10] Fraction 4 consists mainly of lignin from the high molecular weight part of the starting material.[10]

Molecular weight averages of the KL fractions, calculated from the size exclusion chromatograms (relative values related to polystyrene), are listed in Table I.

A more comprehensive characterization of these KL fractions is presented elsewhere.[10,14]

Polyurethane Composition and Preparation

Four series of PU films were prepared by solution casting using a three-component system in which KL fractions 1–4, PMDI, and a propylene oxide-based polyether triol were used as starting materials. The compositions of the PUs studied are listed in Table II. All PU films were prepared using a constant molar ratio between isocyanate groups and hydroxyl groups (NCO/OH ratio) of 0.9. This somewhat low NCO/OH ratio was chosen, since previous results[7] indicated that the mechanical properties of PUs derived from this three-component system are more sensitive to variations in KL content at low NCO/OH ratios than at high. As can be seen from Table II, the KL content was varied from 0% to 35–36% in each PU series. The content of the polyether triol thereby ranged from about 21–25% to 63%, as a consequence of the constant NCO/OH ratio. Another consequence of the constant NCO/OH ratio, is that variations in the ratio between soft (polyether triol) and hard (KL + PMDI) segments are mainly due to variations in the contents of KL and polyether triol.

The KL fractions 1, 2, and 3 were completely soluble in THF and the PU films prepared from these fractions were clear and transparent.

KL fraction no. 4 contained about 20% THF-insoluble material. Dispersed, undissolved lignin particles were therefore present in the PU films prepared from this fraction.

TABLE I
Fractionation Yields, Molecular Weight Averages and Hydroxyl Groups Contents
for Kraft Lignin Fractions 1–4 and Unfractionated Kraft Lignin

Fraction no.	Yield (% of starting material)	Nonderivatized*			Acetylated*			Total hydroxyls mmol/g
		M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n	
1	9	420	580	1.4	450	620	1.4	6.1
2	22	790	1090	1.4	900	1290	1.4	7.3
3	26	1270	2140	1.7	1710	2890	1.7	6.4
4	28	—	—	—	3800	10500	2.8	.6.3
Starting material	—	—	—	—	1360	5410	4.0	6.5

* M_n and M_w were calculated from size exclusion chromatograms calibrated with monodisperse polystyrene standards.

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TABLE II
Polyurethane Composition and Amount of Sol Fraction

KL fraction ——— Sample no.	Kraft lignin* (%)	Polyether triol* (%)	PMDI (%)	NCO/OH ratio	Sol fraction** (%)
1–1	4.0	58.5	37.5	0.9	16.3
1–2	9.3	52.7	38.0	0.9	14.0
1–3	18.1	43.2	38.7	0.9	17.2
1–4	26.9	33.9	39.2	0.9	15.8
1–5	35.3	24.7	40.0	0.9	21.9
2–1	3.5	58.7	37.8	0.9	15.2
2–2	8.0	53.5	38.5	0.9	12.8
2–3	16.1	44.3	39.6	0.9	12.2
2–4	26.5	31.7	41.8	0.9	13.4
2–5	35.8	21.0	43.2	0.9	13.2
3–1	4.0	58.5	37.5	0.9	9.4
3–2	9.2	52.9	37.9	0.9	7.0
3–3	17.4	43.6	39.0	0.9	6.2
3–4	27.0	33.0	40.0	0.9	2.8
3–5	29.0	30.8	40.2	0.9	3.2
3–6	35.0	24.2	40.8	0.9	1.7
4–1	3.6	58.9	37.5	0.9	7.9
4–2	8.0	54.0	38.0	0.9	8.3
4–3	17.4	43.9	38.7	0.9	9.6
4–4	26.9	33.5	39.6	0.9	3.9
4–5	35.2	24.6	40.2	0.9	2.4
0–1	0.0	62.8	37.2	0.9	16.1

* Calculated as percentage of the total weight of the starting materials.
** Acetone-soluble material in cured polyurethanes calculated as percentage of dry polyurethane film.

Swelling Tests

All three starting materials used in the present investigation have an average functionality larger than 2.0. A certain degree of crosslinking must therefore be expected in these PUs.

Crosslink density values were estimated from equilibrium swelling data using a modified version of the Flory-Rehner equation[15] which for cross-linked polymers relates crosslink density (ν_e/V_o) to the measured volume fraction of polymer (v) in a sample that has reached its equilibrium swollen state:

$$\frac{\nu_e}{V_o} = \frac{-2[v + \chi v^2 + \ln(1-v)]}{V_1(2v^{1/3} - v)} \tag{3}$$

where ν_e = effective number of moles of cross-linked chains, V_o = volume of dry polymer, χ = polymer-solvent interaction parameter, and V_1 = molar volume of solvent.

χ for the PU-DMF system used here was in the previous investigation of this series[7] determined to 0.40. Figure 3 shows that the crosslink density in-
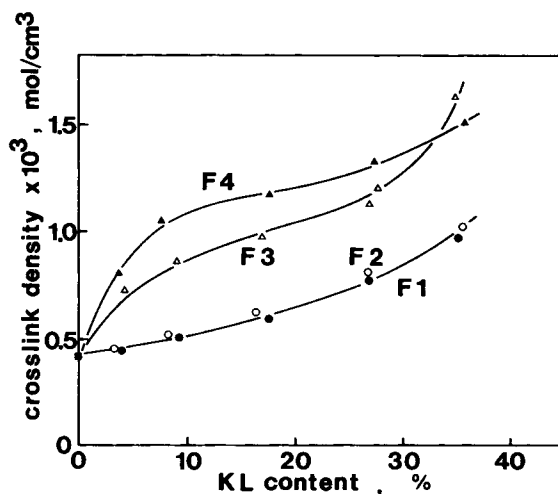
Fig. 3.   Crosslink density as a function of kraft lignin content.

creases in each PU series with increasing KL content. This is a result of the larger average number of hydroxyl groups per molecule (higher functionality) in KL compared to the polyether triol. From the data presented in Table I and Ref. 10, the average number of hydroxyl groups per molecule in the KL fractions were estimated to 2.5–3.5, 6–8, 8–14, and > 20 for fractions 1, 2, 3, and 4, respectively.

Figure 3 also shows that the crosslink density increases, at a given KL content, with increasing molecular weight of the lignin fraction used. The PUs prepared from medium and high molecular weight KL (fractions 3 and 4) show a steep increase in crosslink density at low KL contents (< 10%), whereas the crosslink density of the PUs derived from low molecular weight KL (fractions 1 and 2) increases only slightly at low KL contents. Also this is most likely an effect of the increase in the functionality of KL with increasing molecular weight. These observations suggest that medium and high molecular weight KL act as crosslink points in the PU system studied, whereas low molecular weight, nonderivatized KL acts more like a chain extender.

The KL-free PU and the PUs prepared from low molecular weight KL contain more soluble material (sol fraction) than the PUs prepared from medium and high molecular weight KL (Table II). This fact most probably reflects the differences in crosslink density between the four PU series studied. The existence of a relationship between the degree of crosslinking and the amount of sol is not unexpected,[13,16] and Figure 4, in which the weight fraction of sol is plotted against crosslink density for all samples studied, confirms that there is a general tendency of a decrease in the weight fraction of sol as the crosslink density increases.

^{13}C-NMR spectra of the sol fractions from several KL-containing PUs (derived from KL fractions 1–3) showed that the sols were composed of all three starting materials.
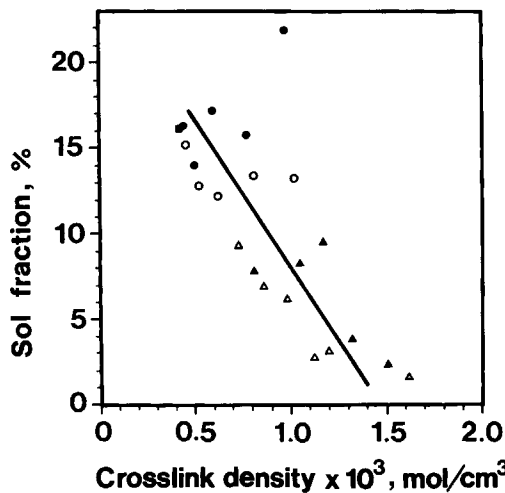
Fig. 4. Sol fraction as a function of crosslink density.

Differential Scanning Calorimetry

The results of the DSC analysis are summarized in Table III. Representative DSC scans for the PUs originating from KL fraction 2 are shown as examples in Figure 5.

The glass transitions are rather indistinct and occur over wide temperature ranges (Fig. 5). The latter observation may reflect structural inhomogeneties in the network, e.g., a broad distribution of molecular weights between crosslinks.[17] Figure 6 shows that the T_g increases, in each PU series studied, with

TABLE III
DSC Analysis

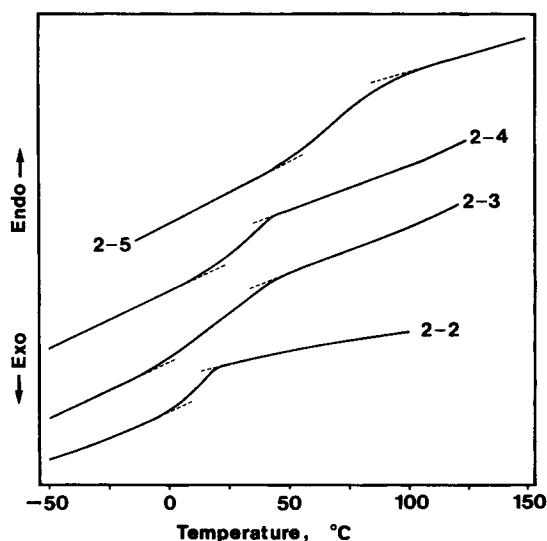| Sample	T_g, °C	Width of glass transition, °C
1–2	8	50
1–3	11	55
1–4	34	65
2–2	11	30
2–3	18	60
2–4	30	40
2–5	70	65
3–1	4	40
3–2	13	55
3–3	34	40
3–4	81	45
3–6	92	45
4–2	5	55
4–3	42	40
4–4	96	70
4–5	104	60
0–1	2	55

Fig. 5. DSC scans for PUs 2-2, 2-3, 2-4, and 2-5.

decreasing weight fraction of soft segments (or with increasing weight fraction of hard segment). The increase in T_g is found over the total composition range studied even though it is less apparent below 50–55% polyether content. This is partly a copolymer effect due to the gradual change in composition[18,19] and partly an effect of the accompanying increase in crosslink density.[18,19]

The gradual change in T_g with increasing weight fraction of hard segments is also a strong indication of phase mixing.[20–23] In case of perfect phase separation between the soft and hard segments, the glass transition of the soft segment should occur at low temperature and be relatively insensitive to variations in the soft/hard segment ratio.[20–23] It is, however, reasonable to expect that the presence of chemical crosslinks in the PUs studied here should decrease the mobility of the chains and thereby prevent or considerably reduce the aggregation of the hard segments into domains. In a previous study, Saraf et al.[24] could not detect any evidence of phase separation in cross-linked, lignin-poly-
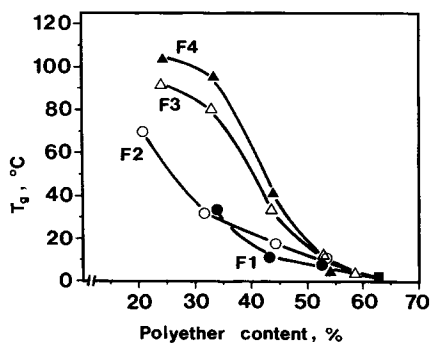

Fig. 6. Glass transition temperature (T_g) as a function of polyether triol content.
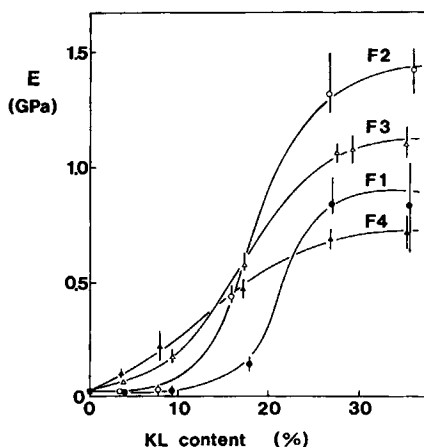
Fig. 7. Young's modulus (E) as a function of kraft lignin content.

ether derived PU films when using small angle X-ray scattering. The polyether content was, however, quite low ($\leq 18\%$).

Figure 6 also shows that the T_g increases with increasing molecular weight of KL at a given PU composition (at KL contents higher than 10% or at polyether contents lower than 50%). This effect is probably to some degree due to the fact that the T_g of KL itself increases with increasing molecular weight,[14] which can be expected to influence the T_g also of the PUs.[18,25] A significant contribution to the observed effect is, however, expected to arise also from the increase in crosslink density that follows with increasing molecular weight or KL, since it is well known that crosslinking introduces restrictions on the molecular motion thereby increasing the T_g.[18,19,26]

Tensile Tests

The tensile properties of the PUs studied are plotted as functions of KL content in Figures 7–10. All measurements were carried out at 23°C, which means that some of the samples were tested below their T_g and others above. This will of course, as discussed below, have a strong influence on the results.
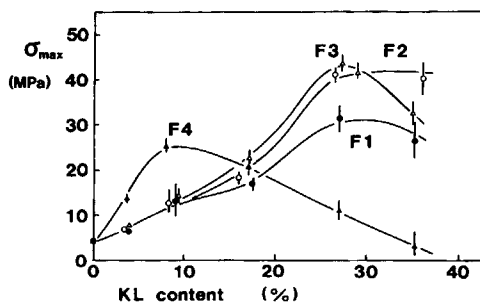

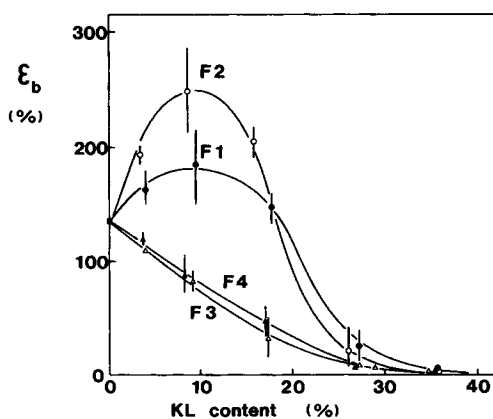Fig. 8. Tensile strength (σ_{max}) as a function of kraft lignin content.

Fig. 9. Ultimate strain (ϵ_b) as a function of kraft lignin content.

Figures 7 and 8 show that Young's modulus (E) and the tensile strength (σ_{max}) of the PUs gradually increase with increasing KL content until they level off or decrease somewhat when the KL content reaches 25–30%. σ_{max} of the PUs derived from high molecular weight KL (KL fraction 4) does, however, display a behaviour that differs from this pattern. In this PU series, σ_{max} goes through a maximum at about 10% KL content, which is followed by a substantial decrease at higher KL contents. This decrease was in separate experiments found to be a result of the presence of increasing amounts of undissolved lignin particles in the PUs, since no decrease in σ_{max} appeared when only the THF-soluble part of fraction 4 was used. This indicates that undissolved particles may act as the origin of cracking rather than as a reinforcing filler in this PU system.

The relationship between ultimate strain (ϵ_b) and KL content is shown in Fig. 9. ϵ_b of the PUs prepared from KL fractions 3 and 4 decreases with increasing KL content over the total composition range studied. This is expected since the polyether content decreases and crosslink density increases with rising KL content. These factors cause a gradual increase in T_g, as discussed above, which gradually changes the room temperature character of the PUs from rubber-like to rigid and glassy.

For the PUs prepared from KL fractions 1 and 2, an unexpected maximum in ϵ_b is observed at about 10% KL content. The maximum which occurs in
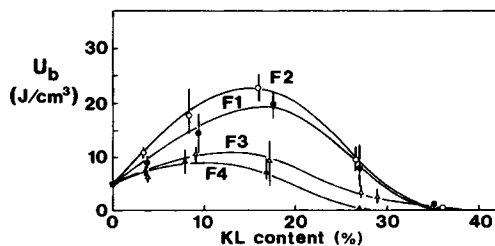
Fig. 10. Tensile energy absorption (U_b) as a function of kraft lignin content.

samples (PUs 1–2 and 2–2) having their T_g located 10–15°C below the test temperature, is probably related to the fact that some of the samples in each PU series were tested below their T_g and others above. Smith and Magnusson[27,28] have previously found ϵ_b-maxima in PU elastomers at test temperatures located somewhat above T_g.

It is evident from Fig. 9 that the PUs derived from low molecular weight KL show considerably higher values of ϵ_b than the PUs derived from medium and high molecular weight KL. This difference is observed over the total composition range studied, except at KL contents of about 30% or higher (corresponding to a hard segment content of about 70% or higher), where all PUs are of a rigid and glassy character at room temperature regardless of the molecular weight of KL.

Below 30% KL content, the PUs prepared from KL fractions 1 and 2 show higher values of tensile energy absorption (U_b) than those prepared from KL fractions 3 and 4 (Fig. 10). This is a consequence of the considerably higher levels of ϵ_b found at low and intermediate KL contents in the two former PU series. All four PU series studied display a broad maximum in U_b appearing at about 15–20% KL content for the PUs derived from KL fractions 1 and 2, and at about 10–15% for the PUs originating from KL fractions 3 and 4.

The glass transition of the PUs studied here cover wide temperature regions (35–70°C) and only seven samples, having KL contents of about 30% or more (PUs 1–5, 2–5, 3–4, 3–5, 3–6, 4–4, and 4–5), display transition regions located entirely above the temperature at which the tensile tests were performed. Three of these glassy samples (PUs 3–4, 3–5, and 3–6) belong to the series of PUs prepared from KL fraction 3. The other three samples in this PUs series (PUs 3–1, 3–2, and 3–3) have glass transition regions located partly above and partly below the temperature used during tensile testing. These samples can therefore be considered to display a greater or lesser degree of rubbery character. In Figure 11, σ_{max}, E, and ϵ_b of the PU series derived from KL fraction 3 are plotted against crosslink density. The properties of samples 3–1, 3–2, 3–3, and 3–4 follow the expected behaviour (σ_{max} and E increases and ϵ_b decreases with increasing crosslink density). However, in the glassy state (PUs 3–4, 3–5, and 3–6) E and ϵ_b are only slightly influenced by further increases in crosslink
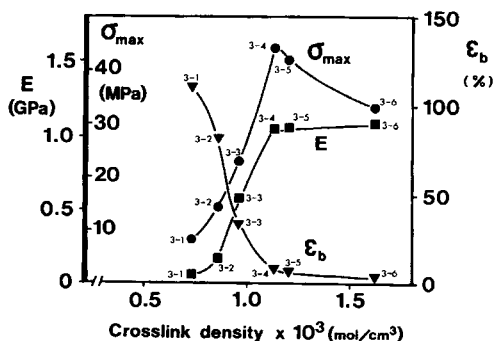

Fig. 11. Young's modulus (E), tensile strength (σ_{max}), and ultimate strain (ϵ_b) as functions of crosslink density (PUs 3–1, 3–2, 3–3, 3–4, 3–5, and 3–6).

density, whereas σ_{max} decreases somewhat. A similar insensitivity of tensile properties towards increases in crosslink density in the glassy state has previously been reported for high T_g epoxies[29-31] and for glassy, lignin-derived PUs.[32] This behavior was attributed to the fact that the segmental motion is strongly restricted in the glassy state.[29-32] Deformation of glassy, amorphous polymers are therefore thought to be predominantly due to stretching of covalent bonds and van der Waal's bonds[29] and the degree of crosslinking may thus have relatively little influence on the tensile properties in the glassy state.

CONCLUSIONS

The crosslink density of kraft lignin-derived polyurethanes increases with the molecular weight of the kraft lignin. This is due to an increase in functionality with increasing molecular weight of kraft lignin.

At lignin contents lower than about 30%, the three-component polyurethane system studied here produces tougher and more flexible polyurethanes with low molecular weight kraft lignin than with lignin of medium or high molecular weight.

At kraft lignin contents of about 30% and higher, rigid, and glassy PUs are obtained regardless of the molecular weight of the kraft lignin. This can partly be attributed to the high content of hard segment ($\geq 70\%$) in these PUs and partly to the raise in crosslink density with increasing lignin content.

Undissolved lignin particles may form mechanically weak points in polyurethanes.

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