Kraft Lignin in Polyurethanes I. Mechanical Properties of Polyurethanes from a Kraft Lignin–Polyether Triol–Polymeric MDI System

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Synopsis

Polyurethanes with various NCO/OH ratios and kraft lignin contents were synthesized by polymerization of kraft lignin (free of the low and high molecular weight fractions), a propylene–oxide-based polyether triol and polymeric MDI in tetrahydrofuran solution. Films were made by solvent casting and tested with respect to swelling behavior and tensile properties. The main findings were: At low NCO/OH ratios, kraft lignin contributed effectively to the formation of the three dimensional network; under particular conditions of NCO/OH ratio and kraft lignin content, polyurethanes of considerable toughness were obtained; at high kraft lignin contents, the obtained polyurethanes were hard and brittle regardless of the NCO/OH ratio used.

INTRODUCTION

Currently, about 750,000 tons of lignins are used annually worldwide for various industrial purposes.[1] Most of it is used in the form of water-soluble lignosulfonates utilizing the dispersing, binding, complexing, and emulsion-stabilizing properties of such lignins.[1-3]

In spite of extensive research, attempts to expand the use of lignins into other areas have not been very successful. One important reason for this is the frequent performance deficiencies shown by technical lignins.[1] To a large degree, this is believed to be a result of the heterogeneous and complex nature of lignin. Lack in the fundamental understanding of the structure–property relationship of lignin is also considered a contributing factor.

The present work is part of an investigation carried out with the aim of clarifying the performance of softwood kraft lignin as polyol component in polyurethane (PU) systems.

Saraf and Glasser[4] have studied some aspects of the structure–property relationship in lignin-derived polyurethane films using hydroxypropylated lignins (kraft lignin and steam explosion lignin) as the only polyol component

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in reactions with hexamethylene diisocyanate (HDI) and tolylene diisocyanate (TDI). The PUs obtained were generally stiff materials showing high values of Young's modulus and low ultimate strain upon tensile testing. The addition of up to 18% poly(ethylene glycol) to this system,[5] in order to introduce soft segments to the polymer, produced somewhat more flexible PUs with HDI, while the use of TDI still resulted in stiff PUs having high Young's modulus and low ultimate strain.

These investigations did, however, not clarify the effects of lignin contents lower than 25–30% (calculated as nonderivatized lignin) or the effects of increasing lignin content at a constant isocyanate/hydroxyl group (NCO/OH) ratio on the mechanical properties of lignin–polyether-derived polyurethanes.

In the present investigation, studies of the effects of lignin content on crosslink density and mechanical properties of solvent-cast, lignin–polyether-derived PU films were carried out at several NCO/OH ratio levels. The lignin contents used were generally lower than in the PUs studied by Saraf et al.[4,5]

The PU system chosen for the study consisted of a commercial polymeric isocyanate (polymeric MDI) using a prefractionated, nonderivatized kraft lignin and a commercial propylene-oxide-based polyether triol as polyol components.

EXPERIMENTAL

Materials

Softwood Kraft Lignin was precipitated from a partly evaporated industrial kraft black liquor by addition of dilute sulfuric acid at 80°C to pH 9.5. The precipitate was filtered, washed with acid and water, and spray-dried. Thirty grams of the isolated kraft lignin were suspended in 500 mL methylene chloride. The suspension was stirred at room temperature overnight. The undissolved material was filtered and washed repeatedly with methylene chloride until the filtrate was colorless. The material was thereafter dried in vacuum at room temperature, and suspended in 500 mL of methanol. The suspension was stirred at room temperature overnight. The methanol-insoluble material was thereafter filtered. The filtrate was evaporated to dryness under reduced pressure and kept in vacuum over phosphorus pentoxide for 3 days. The methanol-soluble–methylene-chloride-insoluble fraction of kraft lignin obtained (in the following denoted KL–F), was used in the synthesis of the various PUs. The yield was 45% of the starting material. The apparent weight average molecular weight (M_w) and the molecular weight distribution (M_w/M_n) were found to be 1700 and 2.0 respectively, as determined by gel permeation chromatography (GPC).

The Propylene-Oxide-Based Polyether Triol (Bermodol-10) used, was supplied by Berol Kemi AB, Stenungsund, Sweden. According to the producer, M_w and density of the polyol were 600 and 1.036 g/m^3 (20°C), respectively.

The Polymeric Isocyanate used (polymeric MDI) was also supplied by Berol Kemi AB. After reaction with methanol, a GPC measurement was carried out, showing the M_w and M_w/M_n of the methanol-terminated polymeric isocyanate to be 1060 and 1.4, respectively.

Preparation of Polyurethane Films

PUs were produced in tetrahydrofuran (THF) solution by polymerizing KL–F, the polyether triol, and polymeric MDI without any catalyst. The isocyanate/hydroxyl group ratio (NCO/OH) and the KL–F content were defined as follows:

$$\frac{\mathrm{NCO}}{\mathrm{OH}} = \frac{W_{\mathrm{I}}[\mathrm{NCO}]}{W_{\mathrm{KL}}[\mathrm{OH}]_{\mathrm{KL}} + W_{\mathrm{p}}[\mathrm{OH}]_{\mathrm{p}}} \tag{1}$$

where [NCO] is the content of isocyanate groups in the polymeric isocyanate (7.6 mmol/g), $[\mathrm{OH}]_{\mathrm{KL}}$ is the total content of hydroxyl groups (phenolic and aliphatic) in KL–F (6.8 mmol/g),$[\mathrm{OH}]_{\mathrm{p}}$ is the content of hydroxyl groups in the polyether triol (5.0 mmol/g), and W_{KL}, W_{I}, and W_{p} are the weights of KL–F, polymeric isocyanate, and polyether triol, respectively:

$$\text{KL content} = \frac{W_{\mathrm{KL}}}{W_{\mathrm{KL}} + W_{\mathrm{I}} + W_{\mathrm{p}}} \times 100(\%) \tag{2}$$

A weighed quantity of KL–F ranging from 0.5 to 3.0 g was dissolved in 20 mL of THF in a reaction vessel under an atmosphere of dry nitrogen. A weighed quantity of polymeric isocyanate, ranging from 1.5 to 7.0 g, was then added. After the polymeric isocyanate had dissolved completely, a weighed quantity of the polyether triol ranging from 0.5 to 5.0 g, which had been dissolved in 10 mL of THF was added, and the polymerization carried out at room temperature for 8 h. The reactant solution was then concentrated to about 15 mL by evaporation under reduced pressure. PU films were obtained on glass plates by solvent casting. The films were dried in vacuum over phosphorus pentoxide for 1 week, and thereafter cured in an air-oven at 95 ± 1°C for 8 h.

Methods

Determination of Hydroxyl Group Content

The contents of phenolic hydroxyl groups in KL–F, the unfractionated kraft lignin, and the removed high and low molecular weight fractions were determined by selective aminolysis of acetylated samples.[6] The total contents of hydroxyl groups (phenolic + aliphatic) were estimated from ^{1}H-NMR spectra of acetylated samples.

GPC Analysis

Gel permeation chromatograms were recorded using a set of five polystyrene based columns (ultra-styragel 100, 500, 10^3, 10^4, and 10^5 Å) connected to a HPLC pump (Waters M 45) and a UV detector (Schoeffel GM 770) operating at 280 nm. Tetrahydrofuran (HPLC grade) was used as eluant (flow rate 0.7 mL/min). Twenty-microliter injections were made from 0.2–0.5% sample solutions. In the case of the unfractionated kraft lignin and the methanol-insoluble fraction of kraft lignin, acetylated samples were used. The column set was calibrated by the use of monodisperse polystyrene standards (Macherey-Nagel, Düren, West Germany). In the case of the polymeric isocyanate, the sample as such was used for the calibration. The apparent number average (M_n) and weight average (M_w) molecular weights were calculated from the GPC data by the aid of a laboratory computer (Trivector Trilab 2000).

Tensile Tests

Mechanical properties of the PU films were determined using an Instron instrument, Model 2412. The tensile tests were carried out at 23°C and 60% relative humidity. The crosshead speed and distance were 10 mm/min and 30 mm, respectively. In separate experiments it was found that Young's modulus, ultimate stress, and ultimate strain were in the case of the soft PU films studied rather insensitive to variations in crosshead speed (2–20 mm/min). This was also true for Young's modulus of the hard PU films. However, ultimate stress of the hard PUs was at 2 mm/min about 20% lower than at 10 mm/min while ultimate strain was about 30% higher. The dimensions of the test samples were: length 50 mm, width 5 mm and thickness below 1 mm. Young's modulus (E), ultimate stress (σ_b), and ultimate strain (ϵ_b) were calculated from the stress–strain curves, on the basis of initial sample dimensions. Five specimens were tested per sample and the mean values plotted in the figures. Also included in the figures are the minimum and maximum values found within each series of specimens.

Swelling Tests

The crosslink density of the various PUs was determined by swelling tests. Prior to testing, the PU films were freed from soluble material by extraction with acetone. Three film samples having a weight of approximately 0.2 g each were placed in 20 mL of reagent grade dimenthyl formamide (DMF) and allowed to stand for 1 week at 22°C. In separate experiments, it was found that the films reached equilibrium swelling after 2–4 days, depending on the nature of the sample. After swelling, the samples were removed from the DMF and weighed (after removing excess DMF using a filter paper).

The crosslink density was obtained using the following equation:[7]

$$\frac{\nu_c}{V_0}\,(\mathrm{mol/cm^3}) = \frac{-2[v + \chi v^2 + \ln(1 - v)]}{V_1(2v^{1/3} - v)}$$

where ν_c = effective number of moles of crosslinked chains, V_1 = molar volume of solvent, χ = polymer–solvent interaction parameter, v = volume fraction of polymer in swollen gel ($v = V_0/V$), V_0 = volume of dry polymer, and V = volume of swollen gel at equilibrium.

In order to determine χ for the PU–DMF system, swelling tests were carried out at 22, 26, 32, and 36°C. From the temperature dependency of the swelling volume, χ values were obtained as follows:[7]

$$d \ln v/d \ln T = -3\chi(1 - v)/5(1 - \chi) \qquad (4)$$

where T = temperature (K).

The density of PU at 22°C was determined by the use of a density gradient column containing reagent grade *n*-heptane and tetrachloromethane. Densities at 26, 32, and 36°C were determined using a pycnometer.

RESULTS AND DISCUSSION

The kraft lignin used was, as described in the experimental section, fractionated in such a way that a low molecular weight fraction (methylene-chloride-soluble) and a high molecular weight fraction (insoluble in methanol) were removed. The low molecular weight fraction was removed since a number of the compounds in the monomer fraction of kraft lignin are known to contain only one hydroxyl group per molecule[8] and therefore cannot participate in the formation of 3-dimensional PU networks. The high molecular weight fraction was removed because of its low solubility in organic solvents and its tendency to form heterogenities and phase separations in the PU system.[9]

Results from the characterization of the kraft lignin fraction (KL–F) used in the present investigation are listed in Table I together with the corresponding results for the removed low and high molecular weight fractions and the unfractionated kraft lignin. These results show that the molecular weight distribution of KL–F is much narrower than those of the unfractionated kraft lignin and the higher molecular weight methanol-insoluble part of the kraft lignin. The molecular weight averages (M_n and M_w) listed in the table were calculated from gel permeation chromatograms calibrated with monodisperse polystyrene standards and should therefore be considered as relative.[10] M_n and M_w for the unfractionated kraft lignin and the methanol-insoluble part of kraft lignin were obtained from acetylated samples. Table I furthermore shows that phenolic hydroxyl groups dominate over aliphatic hydroxyl groups in all lignin samples. It is also obvious from M_w and the total hydroxyl group content that KL–F has a markedly higher polyol functionality than the polyether triol.

Film Formation

All PU films obtained were optically clear and appeared to be homogeneous. No evidence of phase separation was observed upon curing. Only small

TABLE I
Characterization of the Kraft Lignin and Kraft Lignin Fractions[a]

	M_n	M_w	M_w/M_n	Phenolic OH (mmol/g)	Total OH (mmol/g)
KL–F	850	1700	2.0	4.6	6.8
Unfractionated kraft lignin	1400	39,000	28	4.3	6.5
Methylene chloride, soluble part	420	580	1.4	5.1	6.1
Methanol, insoluble part	> 3000	> 50,000	> 20	—	—

[a] M_n and M_w are relative values obtained from gel permeation chromatograms calibrated with polystyrene standards.

amounts of starting materials could be extracted from the films with acetone after curing.

From KL–F-free PUs with NCO/OH ratios below 0.5, only waxlike materials were obtained upon casting. The KL–F-free PU with a NCO/OH ratio of 0.5 did form a film, but the film was too weak for tensile testing. Films with sufficient strength for tensile testing could be obtained at a NCO/OH ratio of 0.5 when the KL–F content was 5% or higher.

These observations indicate that KL–F contributes actively to the film formation.

Curing

Curing at elevated temperature is required to obtain PU films with stable physical properties. Thermogravimetric analysis of kraft lignin fractions of different molecular weights showed that the thermal stability of kraft lignin decreases with decreasing molecular weight.[11] The initial temperature of weight loss was, in the case of the fraction of lowest molecular weight, as low as 112°C. The lignin-derived PUs studied in this investigation were therefore cured at 95°C in order to avoid thermal decomposition and/or evaporation of volatile components from the lignin.

In Figures 1 and 2, the effect of curing time at 95°C on Young's modulus and crosslink density is shown for two PU films, i.e., one containing 24.7% KL–F, and one without KL–F. The NCO/OH ratio was 1.2. As can be seen, Young's modulus (E) and crosslink density increase and reach constant levels as curing time increases. For the KL–F-free PU, a constant level is reached after 4 h of curing, whereas the KL–F-derived PU requires 8 h.

These results suggest that curing at 95°C for 8 h is adequate for obtaining stable physical properties in the PU system studied.

Effect of NCO/OH Ratio and KL Content on Crosslink Density. It is well known that the mechanical properties of 3-dimensional network polymers

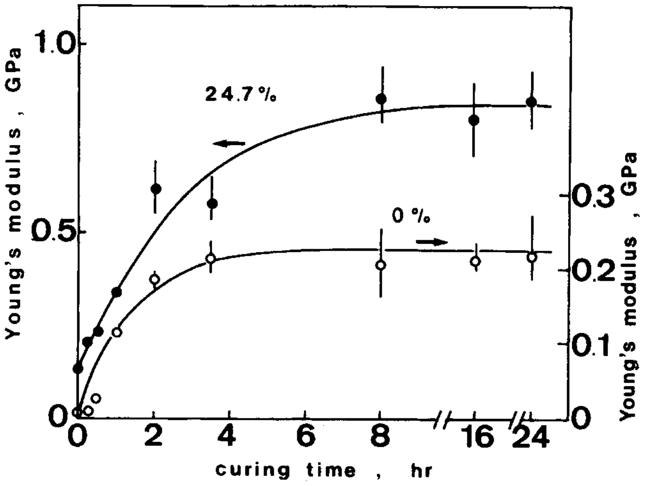

Fig. 1. Young's modulus of KL–F-free (○) and KL–F-containing (●) PUs as a function of curing time. The curing temperature was 95 ± 1°C. The numbers in the figure indicate KL–F contents.

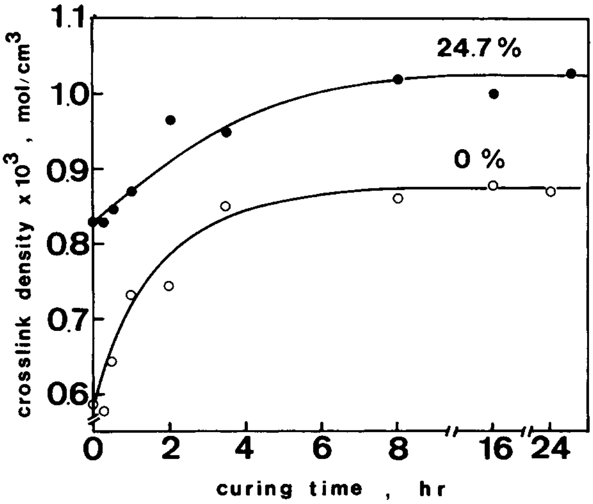

Fig. 2. Crosslink density of KL–F-free (○) and KL–F-containing (●) PUs as a function of curing time. The curing temperature was 95 ± 1°C. The numbers in the figure indicate KL–F contents.

are highly dependent on the crosslink density. In the present investigation, the crosslink densities of the various PU samples were studied by the use of swelling tests.

The estimation of crosslink density from swelling data requires access to the polymer–solvent interaction parameter χ. Brown[12] reported a χ value of 0.44 for the kraft lignin–DMF system. However, since this value does not necessarily apply to kraft lignin-derived PUs, swelling tests were carried out in DMF at different temperatures and χ values for PUs having different NCO/OH ratios and KL–F contents were calculated according to eq. (4) as described in the experimental section. The results obtained are presented in Table II. From these, a χ value of 0.40 was selected for the estimation of crosslink densities.

In Figure 3, the crosslink densities of the PU films are plotted as a function of NCO/OH ratio. Also the crosslink density of KL–F-free, uncured PU is shown. The numbers in the figure indicate the various KL–F contents. Upon

TABLE II
Polymer–Solvent Interaction Parameter (χ) in the Polyurethane–Dimethylformamide System

NCO/OH	KL–F(%)	χ
0.5	0	0.38
	8.6	0.41
	17.3	0.42
	25.7	0.41
2.1	0	0.39
	3.9	0.38
	18.0	0.41

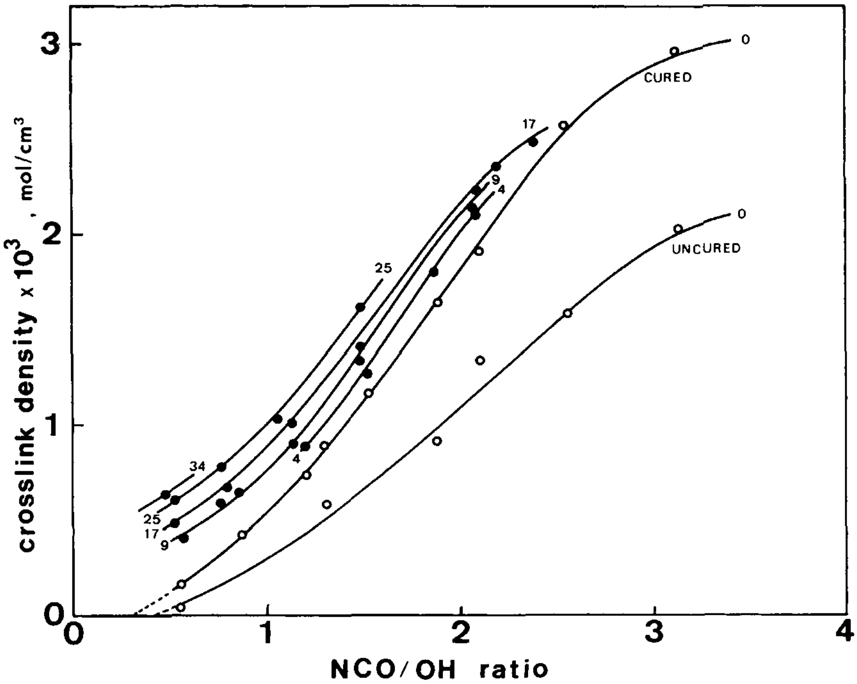

Fig. 3. Crosslink density as a function of NCO/OH ratio for KL–F-free (○) and cured KL–F-containing (●) PUs. The numbers in the figure indicate KL–F contents (%).

extrapolation of the crosslink density of the uncured KL–F-free PU to zero, a NCO/OH ratio of 0.44 is obtained. This value is in good agreement with the NCO/OH ratio at which the KL–F-free PU no longer forms films, as discussed above.

From the figure, it can furthermore be concluded that upon curing the crosslink density of the KL–F-free PU increases about 1.5 times at any given NCO/OH ratio. It can also be seen that the crosslink density of the KL–F-free, cured PU increases linearly with increasing NCO/OH ratio in the NCO/OH range 1–2.5 and approaches what appears to be a constant level at 3–3.5. Low NCO/OH ratios (1 or lower) favor the formation of urethane linkages while, at higher NCO/OH ratios, the excess isocyanate can react with urethane groups to form allophanate linkages,[13] which leads to an increase in crosslink density. Biuret crosslinks may also be formed from a reaction between excess isocyanate and moisture-induced substituted urea groups.[13]

Figure 3 furthermore shows that the crosslink density of cured KL–F-derived PUs is higher than that of the KL–F-free cured PUs at any given NCO/OH ratio. The relative contribution of KL–F to the crosslink density is, however, much larger at low NCO/OH ratios than at high. Altogether these observations show that lignin participate actively as a crosslinking agent in the studied PU system. This is most likely a result of the higher functionality of KL–F, compared to the polyether triol, leading to an increased formation of urethane crosslinks.

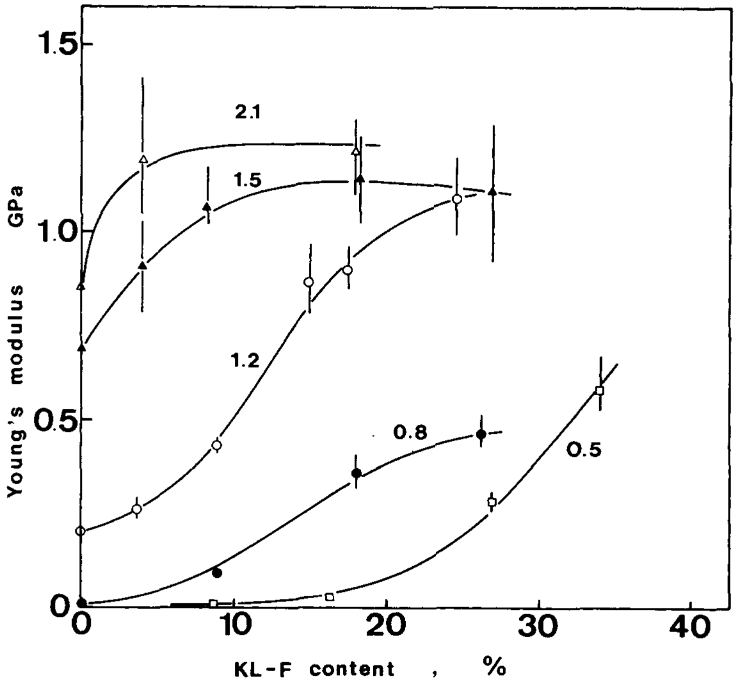

Fig. 4. Young's modulus of cured PUs as a function of KL-F content. The numbers in the figure indicate NCO/OH ratios.

Mechanical Properties

Tensile properties (Young's modulus, ultimate stress, and ultimate strain) of the PU films studied in the present investigation are shown as functions of KL-F content in Figures 4-6. The various property values plotted in the figures are average values obtained from measurements of five specimens. The minimum and maximum values in each series of specimens are also indicated.

Figure 4 shows that at low and intermediate NCO/OH ratios, Young's modulus (E) increases with increasing KL-F content over the total range studied. This can be attributed to the introduction of more aromatic rings into the system which leads to an increase in chain stiffness[14] and to the increase in crosslink density with increasing KL-F content. At higher NCO/OH ratios (1.5-2.1), E levels off at about 5-10% KL-F content which is unexpected from the point of view that more aromatic rings are introduced into the PU system and since crosslink density increases with increasing KL-F content also at these NCO/OH ratios.

Ultimate stress (σ_b) shows a similar KL-F content dependency as E (Fig. 5), although a small maximum in σ_b can be observed at NCO/OH ratios of 1.5 and 2.1 and at 5-10% KL-F content.

At the lowest NCO/OH ratio studied (0.5), ultimate strain (ϵ_b) shows a maximum at a KL-F content of 15-20%, as can be seen from Figure 6. A maximum in ϵ_b can be found also at the NCO/OH ratio of 1.2 but now at

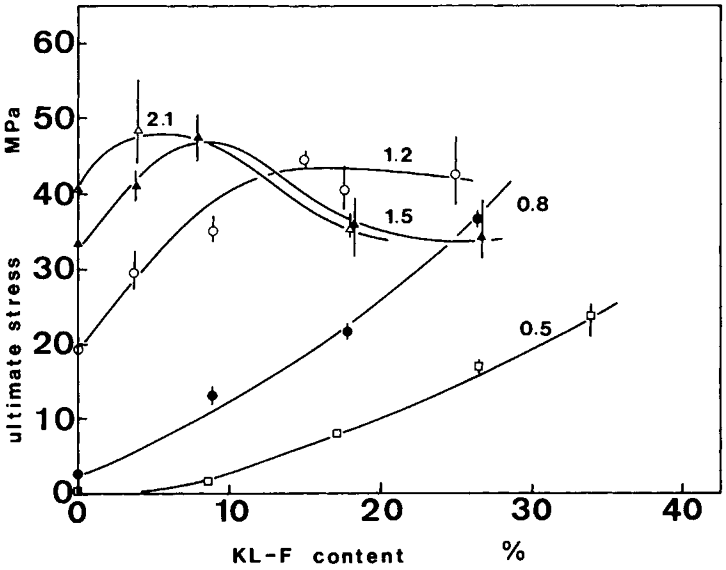

Fig. 5. Ultimate stress of cured PUs as a function of KL-F content. The numbers in the figure indicate NCO/OH ratios.

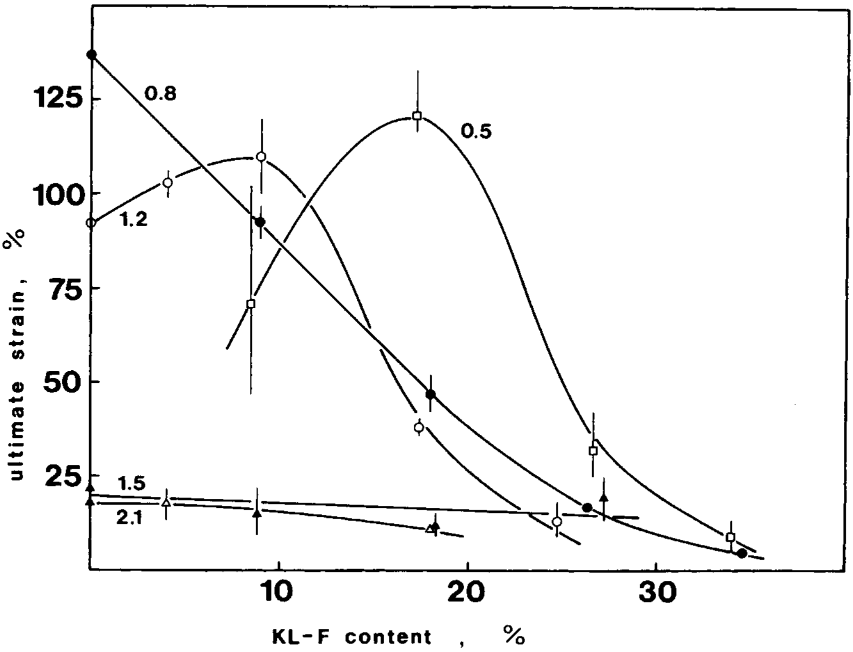

Fig. 6. Ultimate strain of cured PUs as a function of KL–F content. The numbers in the figure indicate NCO/OH ratios.

lower KL–F content (ca. 10%). The presence of these ϵ_b maxima is surprising because any increase in KL–F content results in an increased crosslink density. Thus, normally an increase in crosslink density leads to a decrease in ϵ_b.[14] At higher NCO/OH ratios (1.5–2.1), low values of ϵ_b are found ($<$ 25%), showing only a small KL–F content dependency. This is to be expected, since the contribution from KL–F to the crosslink density is comparatively small at these NCO/OH ratios.

CONCLUSIONS

In the PU system studied, kraft lignin acts as a network former due to its higher functionality compared to the polyether triol used for the introduction of soft segments into the polymer. The effective contribution of kraft lignin to the formation of a crosslinked polyurethane network is especially apparent at low NCO/OH ratios ($<$ 1).

At low and intermediate NCO/OH ratios (0.5–1.2), PUs having mechanical properties ranging from soft to hard can be synthesized by varying the kraft lignin content while keeping the NCO/OH ratio constant. This is very likely a combined effect of increases in crosslink density and chain stiffness with increasing kraft lignin content. At higher NCO/OH ratios (1.5 and higher) the PUs obtained are generally hard and brittle. The main effect from the kraft lignin at these NCO/OH ratios is a moderate increase in E. At the intermediate NCO/OH ratio of 1.2 and at kraft lignin contents of up to 10–15%, tough materials can be obtained. Flexible but rather weak PUs are obtained at kraft lignin contents ranging from 10 to about 20% at the lowest NCO/OH ratio studied (0.5).

The results from the present investigation further show that when an optimum quantity of kraft lignin (5–20% depending on the NCO/OH ratio used) is used, the resulting PUs show improved mechanical properties compared to the PUs synthesized with the polyether triol as the only polyol component. This effect can be found at all NCO/OH ratios studied, but is, however, comparatively small at higher NCO/OH ratios.

High contents of kraft lignin ($>$ 30–35%) results in hard and brittle PUs regardless of the NCO/OH ratio used. This must also be attributed to a combined effect of the increased crosslink density (caused by the high functionality of the lignin) and of an increase in chain stiffness.

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