

Kraft Lignin in Polyurethanes. III. Effects of the Molecular Weight of PEG on the Properties of Polyurethanes from a Kraft Lignin-PEG-MDI System

ANDERS REIMANN and ROLAND MÖRCK, *STFI, Box 5604, S-11486 Stockholm, Sweden*, HIROHISA YOSHIDA, *Tokyo Metropolitan University, Department of Industrial Chemistry, Fukazawa, Setagaya-ku, Tokyo 158, Japan*, HYOE HATAKEYAMA, *Industrial Products Research Institute, 1-1-4 Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan*, and KNUT P. KRINGSTAD, *STFI, Box 5604, S-11486 Stockholm, Sweden*

Synopsis

Polyurethane (PU) films were prepared by solution casting using a three-component system consisting of a low molecular weight fraction of softwood kraft lignin (KL), polyethylene glycol (PEG) of various molecular weights, and crude diphenylmethane diisocyanate (MDI) as starting materials. All films were prepared using a constant NCO/OH ratio. The effects of KL content, PEG content, and molecular weight of PEG on the tensile, thermal, and swelling properties of the PUs were studied. The results showed that the crosslink density T_g and tensile properties were essentially unaffected by variations in the sequence length of the soft segment at a given PEG content. The properties of the PUs were found to depend mainly on the soft/hard segment ratio. The behavior of the glass transition temperature upon changes in the PU composition indicated that the soft and hard segments were extensively mixed.

INTRODUCTION

The present work is part of an investigation carried out with the aim of studying the performance of nonderivatized softwood kraft lignin (KL) as a component in polyurethanes (PUs). Previous articles in this series^{1,2} describe the synthesis and characterization of PU films derived from a three-component system consisting of KL, a polyether triol, and polymeric MDI. In this PU system, KL was found to act both as a network former¹ (due to its comparatively high functionality) and as a part of the hard segment.^{1,2} The latter is due to the high content of aromatic rings in the lignin and to the generally stiff nature of its main chain.³ It was also found that low molecular weight KL fractions produced less crosslinked and more flexible PUs than KL fractions of medium and high molecular weight.² This was attributed to the increase in the functionality of KL with increasing molecular weight.

The present paper discusses the effects of the molecular weight (sequence length) of the soft polyether segment on tensile-, thermal-, and swelling properties of PU films prepared from a three-component system at a constant molar ratio between hydroxyl groups and isocyanate groups (NCO/OH ratio). The PU system chosen for this study consisted of crude 4,4'-diphenylmethane di-

isocyanate (MDI), poly(ethylene glycol) (PEG) of various molecular weights (300–4000), and a low molecular weight fraction of KL.

Saraf et al.⁴ have previously studied the effects of incorporation of PEG of different molecular weights into hydroxypropyl lignin-derived PUs. However, only PUs having low contents of PEG (< 18%) were studied. The isocyanate content was kept constant which resulted in an increase in the NCO/OH ratio with increasing molecular weight of PEG. As a consequence, effects of NCO/OH ratio-induced variations in crosslink density may have overlapped the effects of the molecular weight of PEG.

EXPERIMENTAL

Materials

Kraft Lignin

A softwood kraft lignin was isolated from a partly evaporated industrial kraft black liquor by precipitation with dilute sulphuric acid as described elsewhere,⁵ and was thereafter fractionated by successive extraction with organic solvents.⁵

A low molecular weight (propanol soluble-methylene chloride insoluble) fraction of this kraft lignin (KL) was used in the present investigation as starting material for synthesis of PUs.

Poly(ethylene Glycol) (PEG) and Diisocyanate

Poly(ethylene glycol) (PEG) of various molecular weights (300–4000) and crude MDI were obtained from MERCK, Darmstadt, West Germany. The crude MDI was a mixture of di- and triisocyanates in which 4,4'-diphenylmethane diisocyanate (MDI) was the main component.

Methods

Polyurethane Synthesis

PUs were synthesized by prepolymerization of all starting materials in tetrahydrofuran solution at room temperature for 6 h followed by preparation of films by solution casting as described previously.¹ The NCO/OH ratio was kept constant at 1.2 in all samples. No catalyst was used. The PU films obtained were cured to stable properties at 95°C (8 h).¹

Swelling Tests and Measurements of Tensile Properties

The crosslink densities of the various PUs were estimated from equilibrium swelling data using the Flory–Rehner equation.⁶ The tensile properties were measured at 23°C using an Instron instrument, Model 2412. Both procedures were described in detail in a previous paper.¹

Differential Scanning Calorimetry (DSC)

DSC analysis was carried out using a Perkin-Elmer differential scanning calorimeter, Model DSC-7. The glass transition temperature (T_g) was defined as the midpoint of the change in heat capacity occurring over the transition. The samples were first scanned from -50 to 95°C , thereafter cooled and scanned a second time. T_g was determined from the second scan. The measurements were made under an atmosphere of dry nitrogen at a heating rate of $10^\circ\text{C}/\text{min}$.

High Performance Size Exclusion Chromatography (HPSEC)

The number average (M_n) and weight average (M_w) molecular weights of the KL fraction used (relative values related to polystyrene) were measured by high performance size exclusion chromatography (HPSEC), as described previously.⁵

M_w and M_n of the PEGs were measured by HPSEC using Ultrastayragel (Waters Associates) columns (500 and 10^3 \AA) connected to an HPLC pump (Waters 590) and a refractive index detector (Waters 410). Tetrahydrofuran was used as mobile phase.

Determination of the Hydroxyl Group Content in KL

The content of phenolic hydroxyl groups in the KL fraction used was determined by selective aminolysis after acetylation of the sample.⁷ The total content of hydroxyl groups (phenolic and aliphatic) in the lignin fraction was estimated from an $^1\text{H-NMR}$ spectrum of an acetylated sample.

RESULTS AND DISCUSSION

The KL used in the present investigation was a low molecular weight fraction from an industrial softwood KL obtained as the second of five fractions (yield 22%) in fractionation of KL by successive extraction with organic solvents as described elsewhere.⁵ The weight average molecular weight (M_w) of this fraction was, as determined by HPSEC, 1090 (relative value related to polystyrene).⁵ The molecular weight distribution was relatively narrow ($M_w/M_n = 1.4$). The hydroxyl group content was 7.3 mmol/g , of which 5.0 mmol/g were found to be phenolic.⁵ The balance was a mixture of primary and secondary aliphatic hydroxyls. The average number of hydroxyl groups per molecule (functionality) was estimated to be 6–8.² This KL fraction was found in a previous study² to yield more flexible and less crosslinked PUs (at low and intermediate lignin contents) than the medium and high molecular weight fractions, as a result of its lower functionality.

The composition of starting materials for the various PUs produced in the present investigation are listed in Table I. Five series of PU films were prepared using PEG of different molecular weights (PEG 300, 400, 600, 1000, and 4000) as soft segment (M_w/M_n of the PEGs used were ≤ 1.1 as measured by HPSEC). The composition was varied systematically within each PU series. Since variations in the NCO/OH ratio normally leads to variations also in crosslink density, all films were prepared at a constant NCO/OH ratio (1.2).

TABLE I
Polyurethane Composition

Sample	KL (%)	PEG (%)	MDI (%)	NCO/OH
PEG 300				
1	0.0	50.1	49.9	1.2
2	5.0	44.9	50.1	1.2
3	10.0	39.6	50.4	1.2
4	17.0	32.1	50.9	1.2
5	24.9	24.2	50.9	1.2
PEG 400				
6	0.0	57.3	42.7	1.2
7	5.0	51.1	43.9	1.2
8	10.0	45.2	44.8	1.2
9	17.1	36.7	46.2	1.2
10	25.0	27.2	47.8	1.2
11 ^a	32.0	19.1	48.9	1.2
PEG 600				
12 ^b	0.0	66.9	33.1	1.2
13 ^b	5.0	60.5	34.5	1.2
14	10.0	53.0	37.0	1.2
15	17.0	43.5	39.5	1.2
16	25.0	31.9	43.1	1.2
17	31.9	22.3	45.8	1.2
PEG 1000				
18 ^b	0.0	77.0	23.0	1.2
19 ^b	4.9	69.1	26.0	1.2
20	10.0	60.9	29.1	1.2
21	17.0	49.6	33.4	1.2
22	25.0	36.6	38.4	1.2
23	32.0	25.3	42.7	1.2
PEG 4000				
24	17.0	60.0	23.0	1.2
25	25.0	44.5	30.5	1.2
26	32.1	30.6	37.3	1.2
27	34.9	25.0	40.1	1.2
28	37.9	19.0	43.1	1.2

^a Too brittle for tensile testing.

^b Too soft for tensile testing.

Crosslink Density

The PUs studied in the present investigation are to be considered as cross-linked, thermosetting polymers. The relatively high functionality of KL can be expected to favour the formation of urethane crosslinks^{8,9} especially at high KL contents, whereas the excess isocyanate groups may react with urethane groups to give allophanate crosslinks.^{8,9} Minor amounts of biuret crosslinks may be formed in a reaction between moisture-induced urea groups and isocyanate groups.^{8,9}

The crosslink densities of the PUs studied were estimated from equilibrium swelling tests in dimethylformamide¹ using the Flory–Rehner equation.⁶ The procedure used is described in detail in the first paper of this series.¹

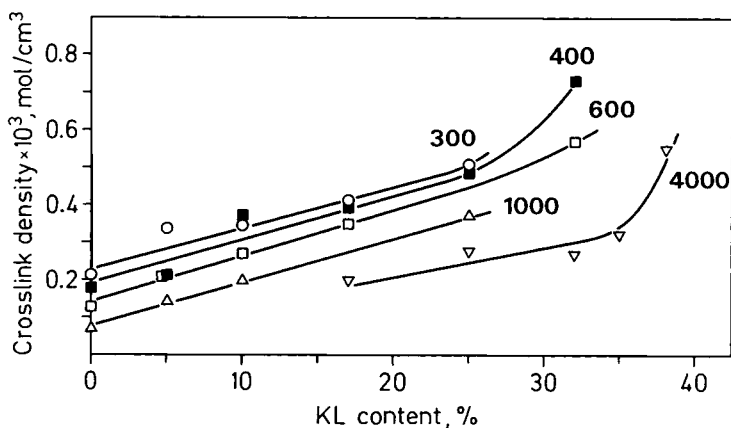


Fig. 1. Crosslink density as a function of KL content. The numbers in the figure indicate different molecular weights of PEG.

In Figure 1, the crosslink densities obtained in the present study are plotted against KL content. The crosslink density increases, as expected with increasing KL content in all five PU series studied. Clearly, this is mainly a result of the relatively high functionality of KL. As can be seen from the figure, crosslink density decreases with increasing molecular weight of PEG at any given KL content. This is also to be expected since an increase in the molecular weight of PEG, leading to the incorporation of longer PEG segments into the PU, will result in a reduction in the content of PEG-derived hydroxyl groups. As a consequence, the content of MDI must, at a given KL content, be reduced in order to keep the NCO/OH ratio constant. Altogether this results in a reduced number of positions where crosslinking can occur, i.e., in an increase in the average molecular weight between crosslinks.

The crosslink density decreases, as expected, with increasing PEG content over the total composition range studied as shown in Figure 2. This correlation

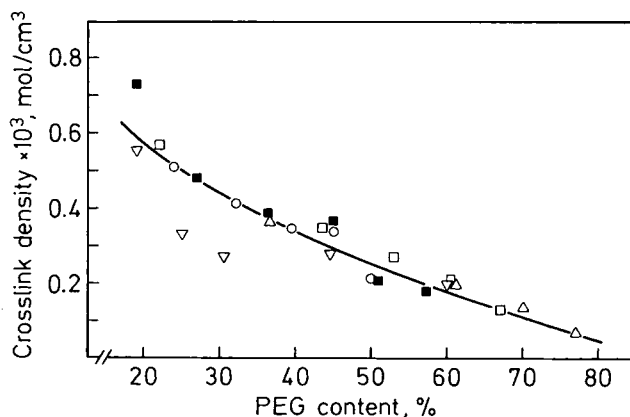


Fig. 2. Crosslink density as a function of PEG content. The symbols indicate PUs from the PEG 300 (○), PEG 400 (■), PEG 600 (□), PEG 1000 (△), and PEG 4000 (▽) series.

is relatively independent of the molecular weight of PEG, which is somewhat surprising since an increase in the sequence length of the PEG segments results in a lower number of reactive positions as discussed above. However, since the KL content increases with increasing molecular weight of PEG (at a given PEG content), the higher functionality of KL may perhaps compensate for the lower number of reactive positions and keep crosslink density on roughly the same level regardless of the chain length of the PEG segments.

The crosslink densities of the PUs studied in the present investigation are generally somewhat lower than those found in a previous study² in which the same lignin fraction was used. This divergence very likely originates from the higher functionalities of the polyether triol and the polymeric MDI used in the previous investigation.

Glass Transition Temperatures

The samples from three of the PU series studied (PEG 400, 600, and 4000) were analyzed by DSC. The PUs were cured to stable properties at 95°C (8 h). The samples were, however, somewhat unstable at higher temperatures, probably due to additional curing. All samples subjected to DSC analysis were therefore initially scanned through T_g up to 95°C, where the first scan was interrupted. Upon cooling, the samples were rescanned. The second scan was necessary in order to avoid effects from enthalpy relaxation,¹⁰ overlapping with the glass transition in the first scan of samples having a glassy character. T_g was, for all samples, determined from the second scan.

The results of the T_g determinations are summarized in Table II and Figures 3 and 4. Most samples display a quite broad transition region, as indicated in

TABLE II
Glass Transition Temperature and Width of Glass Transition Region Obtained
from Second DSC Scan

Sample	Hard segment (wt %)	T_g (°C)	Width of glass transition (°C)
6	42.7	-15	30
7	48.9	0	30
8	54.8	18	25
9	63.3	30	30
10	72.8	38	30
11	80.9	50	40
13	33.1	-25	35
14	39.5	-6	35
15	47.0	10	40
16	56.5	32	40
17	77.7	42	50
24	40.0	-33	25
25	55.5	10	50
26	69.4	32	50
27	75.0	36	45
28	81.0	47	35

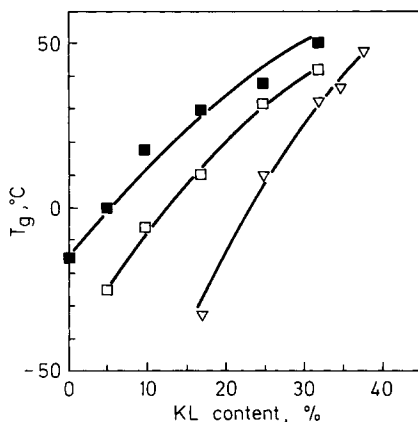


Fig. 3. T_g as a function of KL content. The symbols indicate PUs from the PEG 400 (■), the PEG 600 (□), and the PEG 4000 (▽) series.

Table II. Table II also shows that the T_g , defined as the midpoint of the change in heat capacity occurring over the glass transition, increases with increasing weight fraction of hard segment (and, as a consequence, decreases with increasing weight fraction of soft segment) in each of the three PU series studied. This effect, which is discussed more in detail below, is reflected also in Figure 3, showing that T_g increases with increasing KL content in each PU series.

Figure 3 also shows that T_g decreases at a given KL content, with increasing sequence length of the PEG segment. This can be attributed to the reduction in crosslink density discussed above and to the increase in PEG content that follows with increasing molecular weight of PEG at a given KL content and NCO/OH ratio.

Phase separation between the soft and hard segments is a well-recognized phenomenon in the case of linear, thermoplastic PU elastomers.¹¹ The hard segments are considered to associate through urethane-urethane hydrogen

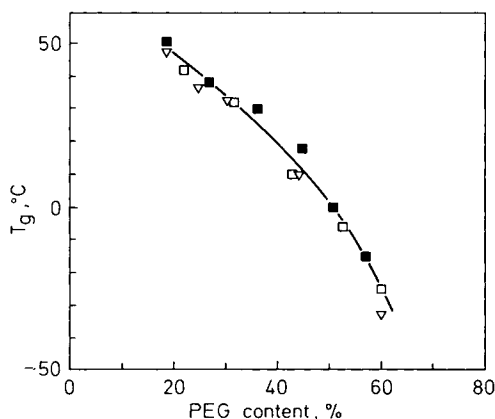


Fig. 4. T_g as a function of PEG content. The symbols indicate PUs from the PEG 400 (■), the PEG 600 (□), and the PEG 4000 (▽) series.

bonds and/or incompatibility of polymer components and form domains which are dispersed in the continuous soft phase, thereby reinforcing the elastomeric matrix.¹¹ In crosslinked PUs, however, the crosslinks may immobilize the chains to some extent and thereby prevent or considerably reduce the aggregation of the hard segments into domains.¹¹⁻¹⁴ In the present study, a gradual decrease in T_g is observed as the weight fraction of soft segment increases (Fig. 4). This correlation, which appears to be independent of the sequence length of the soft segment, is found over the total composition range studied and can be considered as a strong indication of phase mixing.¹⁵⁻¹⁸ 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.¹⁵⁻¹⁸ The behavior of T_g shown in Figure 4 and Table II does not necessarily imply that the PUs studied in the present investigation are completely homogeneous. These results do, however, indicate that phase separation, if present, occurs only to a limited extent.

All PU films studied in the present investigation were clear and transparent except PU no. 24, which displayed a certain degree of turbidity. The first DSC scan of this PU showed a melting endotherm at 29°C (Fig. 5), indicating the presence of soft segment crystallization in this sample. None of the other samples analyzed by DSC showed any evidence of soft segment crystallinity.

According to Slowikowska and Daniewska,¹⁹ short polyether soft segments do not crystallize, due to their relatively limited mobility, whereas the capacity of soft segment crystallization in PUs having longer polyether segments depends largely upon the degree of crosslinking. In the present study the PEG segments of the PUs from the PEG 4000 series could be expected to crystallize. However, since indications of soft segment crystallinity were found only in PU no. 24 (17% KL content), it is probable that the increase in crosslink density and/or hard segment content that accompanies further raises in KL content may reduce the possibilities for chain orientation and thereby inhibit crystallization of the PEG segments.

Tensile Properties

The tensile properties (Young's modulus, ultimate stress, and ultimate strain) of the PUs studied are plotted as functions of KL content in Figures 6-8. The tensile tests were carried out at 23°C, which means that some of the samples

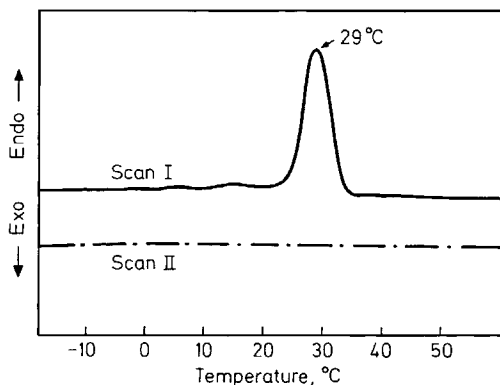


Fig. 5. DSC scans of PU No. 24.

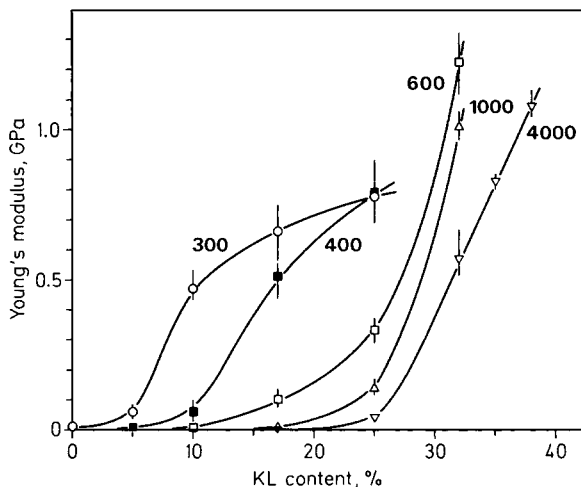


Fig. 6. Young's modulus as a function of KL content. The numbers in the figure indicate different molecular weights of PEG.

were tested below their T_g and others above. This will, of course, as discussed below, have a considerable influence on the tensile properties of the PUs.

Our previous studies on the properties of PUs derived from a KL-polyether triol-polymeric MDI system^{1,2} have shown that these types of PU increase in strength and modulus as the amount of lignin increases. This behavior is to be expected since both crosslink density and the content of hard segments increases with increasing KL content. Also the presently studied PUs are thus very weak at low KL contents but increase in strength and modulus as the KL content rises. Figure 6 shows that the point where the more steep increase in Young's modulus (E) is initiated shifts to higher KL contents as the sequence length of the soft segment increases. This point corresponds in each PU series studied, to the transition from the rubbery state to the glassy state. The effects of KL content and molecular weight of PEG on ultimate stress (σ_b) are similar to the effects on E (Fig. 7).

All PU series studied, except the PEG 300 series, display a maximum in ultimate strain (ϵ_b) as a function of KL content, as shown in Figure 8. The maximum shifts to higher KL contents as the sequence length of the PEG

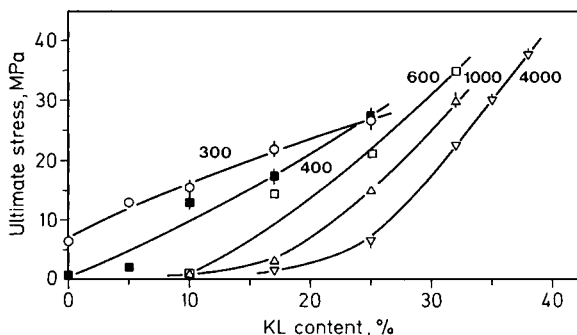


Fig. 7. Ultimate stress as a function of KL content. The numbers in the figure indicate different molecular weights of PEG.

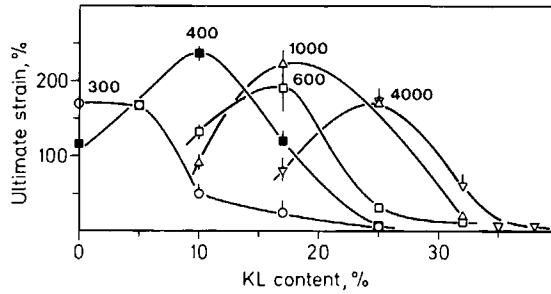


Fig. 8. Ultimate strain as a function of KL content. The numbers in the figure indicate different molecular weights of PEG.

segment increases. The increase in ϵ_b before the maximum appears is contrary to the generally expected behavior,⁹ where an increase in crosslink density and hard/soft segment ratio normally results in a reduction in ϵ_b .

ϵ_b of the PUs from the PEG 400, PEG 600, and PEG 4000 series is, in Figure 9, plotted against the temperature difference between the test temperature and T_g . This plot superimposes the ϵ_b data from these three PU series to a common curve. The exact position of the ϵ_b maximum is difficult to determine since the number of measurements in the region where the maximum appears (around $T - T_g = 0^\circ\text{C}$) are too limited. Figure 9 does, however, clearly indicate that the maximum in ϵ_b is, in all PU series studied, related to the transition from the rubbery state to the glassy state. Smith and Magnusson^{20,21} have previously observed ϵ_b maxima in PU elastomers at test temperatures somewhat above T_g .

In Figures 10 and 11, σ_b and ϵ_b of all PUs studied are plotted as functions of PEG content. As can be seen, σ_b shows an almost linear relationship with PEG content (and as a consequence also with the combined contents of KL and MDI) whereas the maximum in ϵ_b appears at 45–50% PEG content, regardless of the sequence length of the soft segment. The exact positions of the ϵ_b maxima are also here difficult to determine due to the limited number of measurements

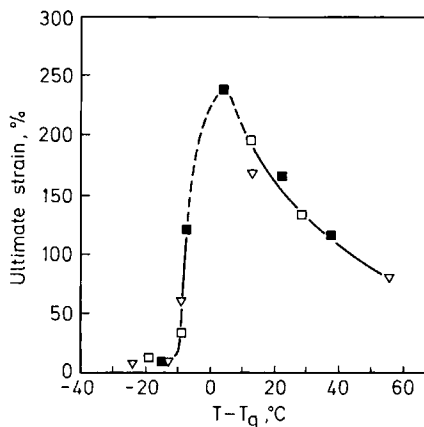


Fig. 9. Ultimate strain as a function of the temperature difference between the test temperature (T) and T_g . The symbols indicate PUs from the PEG 400 (■), PEG 600 (□), and PEG 4000 (▽) series.

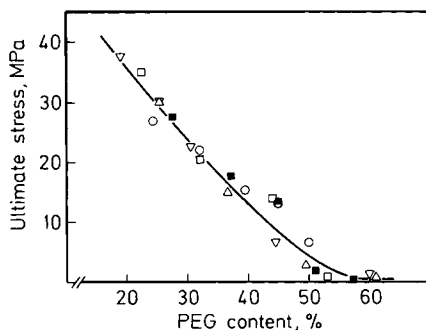


Fig. 10. Ultimate stress as a function of PEG content. The symbols indicate PUs from the PEG 300 (○), PEG 400 (■), PEG 600 (□), PEG 1000 (△), and PEG 4000 (▽) series.

in each PU series. These figures as well as Figures 2 and 4 show that the ratio between the soft (PEG) and hard (MDI + KL) segments has an important bearing on the properties of the PUs studied here.

In our previous studies of KL-polyether-derived PUs, high contents of KL (> 30–35%) resulted in rigid and glassy PUs at room temperature regardless of the NCO/OH ratio used¹ and regardless of the molecular weight of KL.² The results of the present investigation clearly show that the KL content at which the PU becomes rigid and glassy at room temperature strongly depends upon the sequence length of the soft segment. Thus, PUs containing long PEG segments will, at a given NCO/OH ratio, tolerate more lignin than PUs having shorter PEG segment.

In order to fulfill the requirements of a constant NCO/OH ratio, an increase in the sequence length of the PEG segments will, at any given PEG content, result in an increase in KL content and in a decrease in the content of MDI. Thus, the KL content increases whereas the ratio between the soft and hard segments remains unchanged.

CONCLUSIONS

The kraft lignin-PEG-MDI system studied was found to be capable of producing different types of polyurethanes having large differences in mechanical properties.

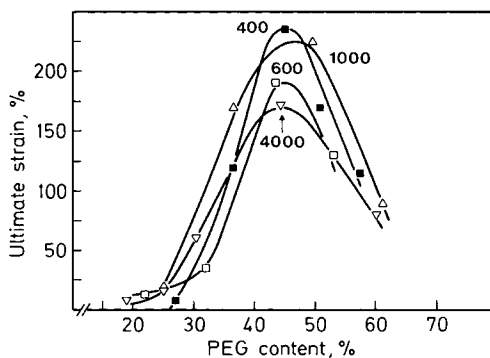


Fig. 11. Ultimate strain as a function of PEG content. The symbols indicate PUs from the PEG 400 (■), PEG 600 (□), PEG 1000 (△), and PEG 4000 (▽) series.

Variations in the sequence length (molecular weight) of the soft PEG segment at a given PEG content and NCO/OH ratio does not cause any significant changes in crosslink density, T_g , or tensile properties. Provided that the NCO/OH ratio is constant, the results obtained indicate that the PEG content (soft/hard segment ratio) rather than the sequence length of the soft segment determines the properties of the PUs derived from the three-component system studied here.

An increase in the molecular weight of PEG does, however, alter the composition of the hard segment (at a given PEG content and NCO/OH ratio) in such a way that the KL content increases and the content of MDI decreases. As a consequence, the sequence length of the soft segment determines the amount of KL that can be incorporated without obtaining a rigid and glassy PU at room temperature.

The T_g data for the PUs investigated here indicate that the soft and hard segments are extensively mixed at all sequence lengths of the soft segment studied.

The authors wish to express their sincere gratitude to the Swedish National Board for Technical Development for financial support to this investigation.

References

1. H. Yoshida, R. Mörck, K. P. Kringstad, and H. Hatakeyama, *J. Appl. Polym. Sci.*, **34**, 1187 (1987).
2. H. Yoshida, R. Mörck, K. P. Kringstad, and H. Hatakeyama, *J. Appl. Polym. Sci.*, to appear.
3. H. Yoshida, R. Mörck, K. P. Kringstad, and H. Hatakeyama, *Holzforschung*, **41**, 171 (1987).
4. V. P. Saraf, W. G. Glasser, G. L. Wilkes, and J. E. McGrath, *J. Appl. Polym. Sci.*, **30**, 2207 (1985).
5. R. Mörck, H. Yoshida, K. P. Kringstad, and H. Hatakeyama, *Holzforschung (Suppl.)*, **40**, 51 (1986).
6. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 521 (1943).
7. P. Månsson, *Holzforschung*, **37**, 143 (1983).
8. J. H. Saunders, *Rubber Chem. Technol.*, **33**, 1259 (1960).
9. K. C. Frisch, in *Polyurethane Technology*, P. F. Bruins, Ed., Wiley-Interscience, New York, 1969.
10. T. G. Rials and W. G. Glasser, *Holzforschung*, **38**, 191 (1984).
11. S. Abouzahr and G. L. Wilkes, in *Processing, Structure and Properties of Block Copolymers*, M. J. Folkes, Ed., Elsevier Applied Science, London, 1985, Chap. 5.
12. S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **11**, 1361 (1967).
13. R. Bonart, L. Morbitzer, and G. Hentze, *J. Macromol. Sci. Phys.*, **B3**, 337 (1969).
14. K. U. Fulcher and G. E. Corbett, *Br. Polym. J.*, **7**, 225 (1975).
15. C. G. Seefried, J. V. Koleske, and F. E. Critchfield, *J. Appl. Polym. Sci.*, **19**, 2503 (1975).
16. N. S. Schneider, C. S. Paik Sung, R. W. Matton, and J. L. Illinger, *Macromolecules*, **8**, 62 (1975).
17. N. S. Schneider and C. S. Paik Sung, *Polym. Eng. Sci.*, **17**, 73 (1977).
18. R. R. Aitken and G. M. F. Jeffs, *Polymer*, **18**, 197 (1977).
19. I. Slowikowska and I. Daniewska, *J. Polym. Sci. Polym. Symp.*, **53**, 187 (1975).
20. T. L. Smith and A. B. Magnusson, *J. Polym. Sci.*, **42**, 391 (1960).
21. T. L. Smith and A. B. Magnusson, *J. Appl. Polym. Sci.*, **5**, 218 (1961).

Received January 30, 1989

Accepted October 2, 1989