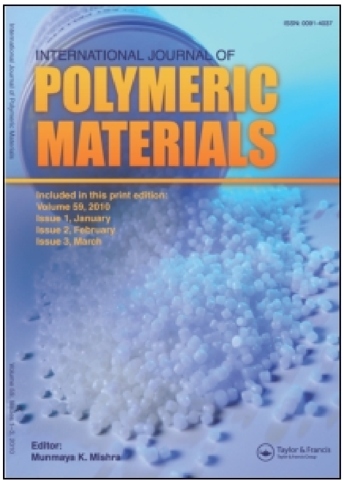

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MOLECULAR WEIGHT EFFECTS OF THE SOFT SEGMENT ON THE ULTIMATE PROPERTIES OF LIGNIN-DERIVED POLYURETHANES

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MOLECULAR WEIGHT EFFECTS OF THE SOFT SEGMENT ON THE ULTIMATE PROPERTIES OF LIGNIN-DERIVED POLYURETHANES

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Polyurethane (PU) films were prepared by solution casting using a three-component system, namely a novel semi-rigid solvolytic lignin, soft segment and a co-monomer. In the present study, the effects of varying the chain length of polyethylene glycol (as the soft segment) were investigated to produce lignin-based polyurethanes with variable thermal and mechanical properties. An important objective was to incorporate as much lignin as possible. The polyethylene glycol (PEG) studied included 5 different molecular weights (200, 400, 1000, 1500 and 2000 g/mol). The polyurethane films, prepared by solvent casting, were evaluated for crosslink density, and ultimate mechanical and thermal properties. Results showed that the films derived from the PEG 200 were either too weak or brittle to be tested. It was found that the PEG (400, 1000, and 1500) are better choices for producing polyurethanes from the solvolysis lignin studied. Crosslink densities of PU films using the 400, 1000 and 1500 were determined to be in the range of 0.8–2.6 mmol/cm^3, which is a lower range than those of films from PEG 2000, namely 2.4–2.8 mmol/cm^3. Also, the ultimate tensile strength decreased from about 50 MPa at high lignin content for PEG 400, 1000 and 1500 to about 18 MPa for PEG 2000 at low content of lignin. Ultimate strain also decreased from the

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30.9–62.7% range for the PEG 400 to 1500 series at low lignin content down to about 4% for PEG 2000 at high lignin content. Young's Modulus varied from a high of 2 GPa (PEG 400, lignin content = 30 wt%) down to 0.6 GPa (PEG 2000, lignin content = 20 wt%). The glass transition temperature was found to decrease from 108°C to about 45°C with increasing molecular weight of PEG for a lignin content of 30 wt% and an NCO/OH of 1.2. The data are consistent with the percolation theory approach to network formation, as well as the notion that the network itself consists of relatively large and stiff islands, each comprising many branch points, held together by a soft and pliable matrix.

Keywords: lignin-derived polyurethanes, molecular weight, crosslink density, mechanical and thermal properties

INTRODUCTION

Lignin is the most abundant natural aromatic polymer, found in all sorts of wood together with cellulose. It is a 3-dimensional, highly branched macromolecule that appears to be the polymerization product of several aralkyl alcohols that are present in the lignin in proportions that vary according to the plant species. The aralkyl alcohol constituents of lignin are characterized by having a double bond between the aliphatic carbons first and second away from the aromatic ring. The proximity of the stiff double bond to the aromatic ring, and the various aliphatic substituents farther away from the ring, as well as the various ring substitutions, all contribute to the backbone of the lignin macromolecule being rather crowded and far stiffer (less flexible) than the backbone of common flexible polymers such as poly (ethylene glycol) (PEG), polyethylene (PE), and even polystyrene (PS). The stiffness of the lignin backbone is reflected in its glass transition temperature, T_g, failing the range of 90–100°C, similar to PS, despite the fact that the aliphatic fraction of lignin far exceeds that of PS. Because of its backbone stiffness, the lignin macromolecule is far more extended in space and its end-to-end distance, as well as hydrodynamic volume, are substantially larger than the ones expected of fully flexible, randomly coiled macromolecules of equivalent chain length. Depending on the nature of the constituents, the lignin macromolecule is decorated by one or more hydroxyl groups per constituent unit, appearing as pendants at the end of the aliphatic and aromatic moieties. Lignin molecules are, hence, relatively stiff polyhydroxy macromolecules.

When a difunctional isocyanate molecule, such as 4,4-diphenylmethane diisocyanate (MDI), reacts with a difunctional diol, such as dihydroxy-terminated poly(ethylene glycol) (PEG), a linear polyurethane (PU) chain is created. The molar excess of isocyanate or hydroxyl groups is inversely reflected in the average chain length and the nature of the excess monomer is reflected in the nature of the chain's terminal groups. When the polyhydroxy lignin is used as the source of all or part of the hydroxyl groups, a highly branched, 3-dimensional polyurethane is created, in which the lignin residues serve as the crosslinking sites. Because of the stiffness of lignin relative to PEG-based PU chains, the resulting network maybe visualized as stiffer "islands" of lignin immersed in and covalently bonded with a more flexible and extensible matrix of PEG-based PU matrix.

As is indicated in the Experimental Section below, we have dissolved the lignin in tetrahydrofuran (THF). Then, an excess amount of MDI was added and allowed to react with the lignin. As a result, at the end of this reaction each lignin molecule, on the average, will now contain urethane groups and will be decorated by reactable isocynate groups in a number equal to the number of hydroxyl groups initially present in the lignin macromolecule. Upon the addition of PEG to reach stoichiometry, these isocyanate groups, and all the previously unreacted MDI molecules, will react with the hydroxyls of the PEG to generate a 3-dimensional network in which the crosslinking lignin residues are connected to one another by linear polyurethane chains, each containing one or more PEG residues.

However, the efficiency of this latter reaction is strongly dependent on the initial concentration of the lignin in the THF, and on the chain length of the PEG employed. When a PEG chain reacts with an isocyanate group anchored on a lignin macromolecule, it becomes attached at one end as a tether. Because the PEG tether is highly flexible, its end-to-end distance is rather small. The pervaded volumes of the stiff lignin molecules, tumbling in the THF solution, are rather large, hindering their close approach to one another. Similarly, the hydroxyl-ends of the randomly coiled tethered PEG chains, with their very small radius of gyration, may be prevented by a neighboring tumbling stiff lignin molecule from approaching its pendant isocyanate groups sufficiently close, at the necessary angle and for sufficient duration to react and create a urethane bond. It is obvious that the shorter the PEG tethers on one lignin molecule are, the lower is the likelihood that their free hydroxyl ends will be able to react with an isocyanate group appended to another lignin macromolecule. Hence, it is expected that systems containing very short PEG chains will be the least efficient in creating 3-dimensional polyurethane networks, and that the efficiency will increase as the PEG chain length increases. One must note here that in the case of very long PEG chains this efficiency will decrease as a result of the increasing dilution of the hydroxyl chain-ends. The above picture makes it also obvious that when the amount of lignin in the reaction mixture is relatively small, tethered PEG chains will increasingly react with isocyanate groups on the same lignin molecule, making the network formation less efficient. Because the shorter PEG chains may at least reach other lignin molecules, the deleterious effect of lignin dilution on the efficiency of network creation is expected to be most noticeable in the case of the shortest PEG chains.

In light of the above, it is expected that the swelling and, especially, mechanical properties of the polyurethane products will reflect: (a) the degree of crosslinking efficiency (the lower the amount of unconsummated reactive groups, the more efficient the network formation); (b) the volume fraction of flexible chains in the polyurethane network; (c) the average chain length in the flexible portion of the polyurethane network.

Some progress has been made in studying newer approaches of using lignin, i.e. via its modification and/or fractionation [1,2]. Also, Saraf et al. [3] previously investigated the thermal properties of (kraft) lignin-based polyurethanes (PUs) containing different molecular weights and amounts of PEG soft segment. It was reported that the glass transition temperature (T_g) varied significantly only with PEG content; PEG molecular weight had a much less pronounced effect. In their study, only PU films containing low contents of PEG (less than 18 wt%) were investigated. Similarly, Reimann et al. [4] conducted work in the synthesis of polyurethanes from a kraft lignin to evaluate the effects of using different molecular weights of PEG on the crosslink density, tensile and thermal properties.

In the present work the effects of the molecular weight (sequence length) of PEG on the crosslink density, ultimate tensile properties and glass transition temperature of PU films prepared from a three-component system were investigated. The PU system chosen for this study consisted of solvolysis lignin, 4,4′-diphenylmethane diisocyanate (MDI) and polyethylene glycol (PEG) of various molecular weights. An important objective was to determine which PEG molecular weight is the most suitable for producing solvolysis lignin-based polyurethanes with acceptable and measurable mechanical and thermal properties.

EXPERIMENTAL

Materials and Methods

Materials

Solvolysis Lignin: The lignin was supplied by Alcell Technologies Inc., Newcastle, New Brunswick, Canada. Some typical but important characteristics of this lignin have been reported to be 17–19 wt% methoxyl content, $M_w = 2000$ g/mol, and $M_n = 900$ g/mol. Molecular weights were determined by size exclusion chromatography using polystyrene standards for calibration and should thus be taken as relative values. This lignin reportedly also has a median particle size range of 20–40 μm, and a glass transition temperature of 90–100°C [5]. In the present work it was used as received and without any premodification.

Polyethylene Glycol (PEG): Polyethylene glycol of molecular weight (M_n) 200, 400, 1000, 1500 and 2000 g/mol were purchased from Aldrich Chemical Co., Inc. (Canada) and used as received.

Methyl-Diisocyanate (MDI): 4,4-Diphenylmethane Diisocyanate (99%) of analytical grade was purchased from Aldrich Chemical Co., Inc. (Canada) and also used as received.

Dibutyltin Dilaurate: Purchased from Aldrich Chemical Co., Inc. (Canada) and used as received.

Film Synthesis

Polyurethane films were made by varying the amounts of the components, the molecular weight of the PEG, and the NCO/OH molar ratio. Weighed quantities of lignin and MDI were initially each solubilized in THF. The solutions were then combined and stirred for another 10–20 minutes at room temperature until all the components had dissolved. Dibutyltin dilaurate catalyst, in concentrations of 3–4% on total solids, and PEG, whose amount was also determined by the desired lignin content and NCO/OH molar ratio, were added and the mixture stirred for another 40 minutes under nitrogen. The flask was opened and allowed to stand in the fumehood for about 5 minutes to partially evaporate the solvent as well as to quench any bubbles that may have formed during stirring. The solution was then poured onto a glass plate (14.50 × 7.55 cm) coated with Teflon lube spray. The typical casting concentration of the formulation was about 18–20% solids in all cases. If the concentration was lower, the casting liquid would overflow outside the glass plate, while in high concentration it would adhere to the glass plate, resulting in a non-uniform film. Also, it was necessary to do the casting outside the hood to avoid the presence of small voids caused by rapid solvent evaporation. After the solution gelled and became sufficiently rigid, the glass plate was placed back in the hood for slower evaporation overnight. In the case of the PU films containing lignin contents higher than 30 wt%, it was necessary to cover the film with another glass plate and place a heavy object on top to prevent the film from bending. The film was then peeled and dried in a vacuum desiccator over phosphorous pentoxide for five days followed by curing at 105 °C for 8 hours.

The procedures for swelling tests, stress-strain tests, and dynamic mechanical tests have all been described in detail elsewhere [6,7].

RESULTS AND DISCUSSION

For each of the PEG's used, several attempts were made in the present work to produce "good" films by varying the amounts of PEG, lignin and MDI. In our case, we designated "good" films as homogeneous (i.e. no visible separation of phases), not very brittle, and not too flimsy to be tested. The incorporated PEG would hopefully replace a portion of the hard segment in the crosslinked network and thereby reduce the stiffness. Therefore, only PEG having an appropriate chain length would assist in the preparation of good films of lignin-derived polyurethanes. Preliminary work revealed that the lignin-derived films produced from PEG 200 were either too weak at low lignin content, or too brittle at higher amounts of lignin, to be tested. This might be explained in terms of the chain length of PEG 200 as being too short to bridge in the network because of steric hindrance arising from the bulky chemical structure of lignin. Consequently, the PEG chain may become poorly incorporated into the network, with one or both ends swinging freely. Consequently, the network either became too brittle or too weak, and thus no further studies were conducted using PEG 200. Properties of the lignin-derived films produced from the 400, 1000, 1500 and 2000 g/mol of PEG only are discussed as follows.

Swelling Behavior

Figure 1 shows the crosslink density as a function of lignin content for each PEG used. As seen, for lignin contents lower than 30 wt%, the crosslink density increased, as expected, with increasing lignin content. This is primarily due to the particularly higher functionality of the solvolysis lignin used here in comparison with that of the polyethylene glycol. However, the crosslink density of the series containing PEG 1000, 1500 and 2000 decreased discernibly after 30 wt% lignin content, while that of PU films containing PEG 400 slightly increased. No explanation for this trend can be made at this time.

As seen in Figure 2, at a given lignin content the crosslink density increased with increasing chain length of PEG. This suggests that an increase in the molecular weight of PEG leads to more incorporation of

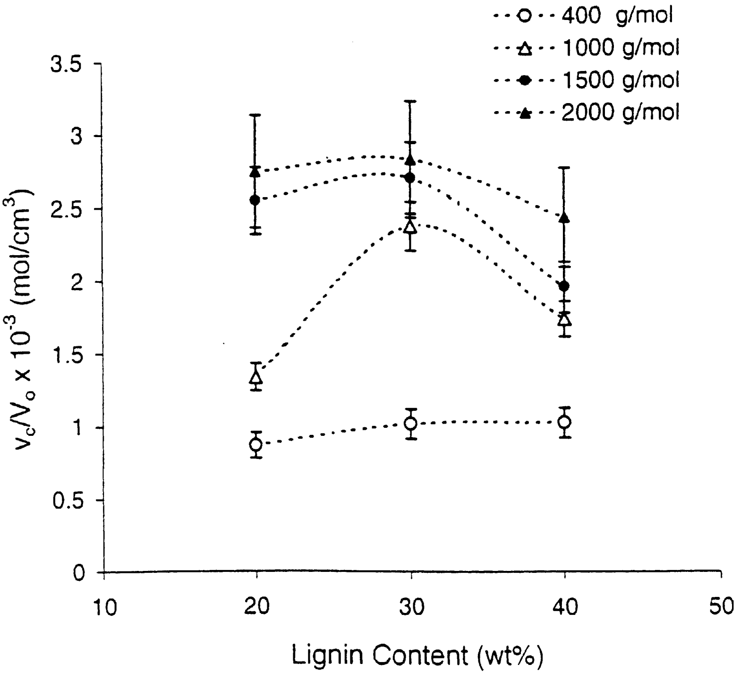

FIGURE 1 Crosslink density as a function of lignin content.

longer PEG segments into the polyurethane network, resulting in a reduction of available PEG-derived hydroxyl groups due to increased distance between lignin-MDI segments and respective reactive sites. Although the NCO/OH molar ratio was kept constant, the MDI content was comparatively increased, providing more isocyanate groups to react with lignin hydroxyl groups. The effect of increasing the isocyanate functionality will be stronger than the increase in distance between lignin-MDI segments as well as the distance between the other sites where network formation can occur. On the other hand, a long chain length of PEG might entangle itself and make only one end available to react with isocyanate functionality while leaving the other end freely wrapped inside. This would cause a relative increase of available isocyanate groups. The excess isocyanate might even react with urethane groups to form allophanate bonds. Overall, this suggests that an increase in the molecular weight of the PEG component increases the crosslink density. This finding is contrary to that reported by Reimann et al. [4], who argued that the incorporation of longer PEG segments into the polyurethane would reduce the content

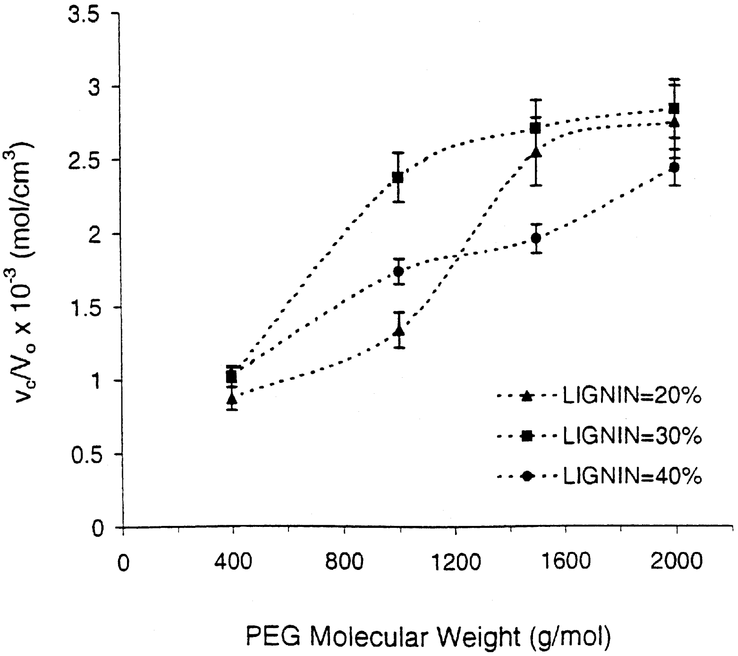

FIGURE 2 Crosslink density as a function of molecular weight of the soft segment.

of PEG-derived hydroxyl groups. As a result, the content of the MDI comonomer must, at a given lignin content, be reduced in order to keep the NCO/OH ratio constant. Altogether, this reduced the number of available reactive positions where chain growth can occur, i.e., leading to an increase in the unreactive chain length or average molecular weight between reactive sites. However, the increase in chain length might actually not cause much reduction in MDI content in order to keep the NCO/OH ratio constant.

Of the four series of PEG used in the present work, it is seen from Figure 2 that the crosslink density of PEG 400 was the lowest. However, when compared with the data reported by Reimann et al. [4], the crosslink densities determined here are about 40% higher. It must be noted that these authors did not employ a polymerization catalyst and also used a kraft lignin in the preparation of the lignin-derived polyurethanes. This trend strongly indicates that the polymerization catalyst does not only accelerate the reaction, but also helps it reach completion, thus increasing the formation of urethane bonds in the lignin polyurethane network.

Ultimate Tensile Properties

Ultimate Strength

Figure 3 shows the ultimate strength as a function of the content of solvolysis lignin used. As seen, the ultimate tensile strength in all the series of polyurethanes increased drastically with lignin content up to 30 wt%. This may be explained as follows. An increase in lignin content in the network results in additional crosslinking and more mechanical strength imparted to the polyurethane films. However, the higher amounts of hard segments in the components also provided more rigidity to the polyurethanes, making them more brittle, with a subsequent reduction in tensile strength. Therefore, as lignin content increased, even though this increased the tensile strength caused by the increase of hard to soft segment ratio, the inherent increase in the brittleness of the films led to a reduction in tensile strength. Also, as seen in Figure 3, there was only a small increase in strength when the lignin content was increased from 30 wt% to 40 wt%, when moderate to high molecular weight PEG was used. An exception is observed for low PEG, whereby a dramatic decrease in strength is observed after

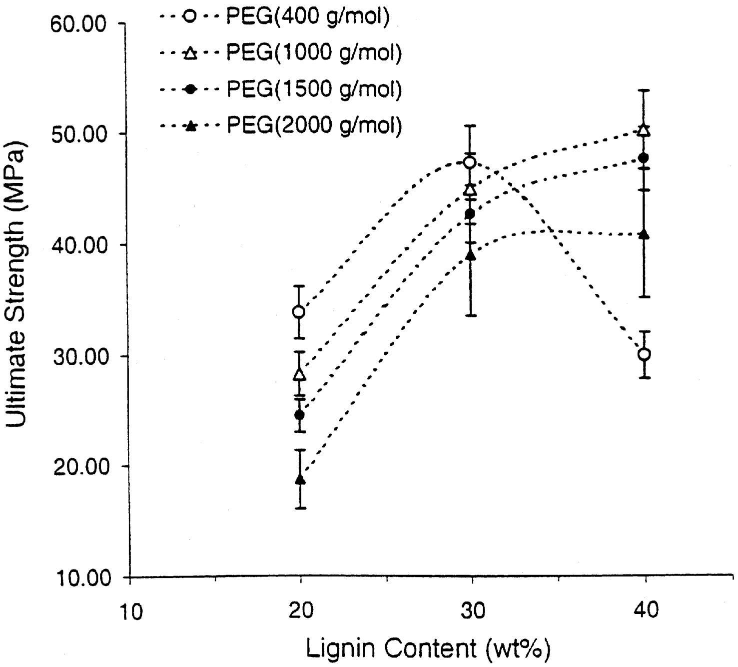

FIGURE 3 Ultimate tensile strength as a function of lignin content.

30 wt% lignin content. This behavior could be attributed to excessive crosslinking, mainly due to the higher amounts of lignin used.

Figure 4 shows that at a given lignin content, the ultimate strength decreased with increasing chain length of PEG. One exception to this trend occurs with the polyurethane containing 40 wt% lignin content and PEG 400, which has a lower tensile strength than the corresponding polyurethane of PEG 1000. This may be due to the increase in chain length provided by using longer soft segments as part of the polymer network, thereby reducing the strength. A similar finding was also reported by Reimann et al. [4] in their work on polyurethanes from kraft lignin. This is as expected, since the longer PEG chains (higher molecular weight) incorporated in the polymer network would lead to less stiffness or brittleness of polyurethane films and allow more lignin content. In the present study, it should also be noted that the tensile strength of PU films containing the PEG 400 was very low even when the lignin content reached 40 wt%, which could be interpreted as follows. When the lignin content was high enough, irrespective of the chain length in all four series of PEG, the lignin-derived films resulted in lower strength, but stiffer material. Figure 4 again illustrates that the 30 wt% lignin content is a pivotal amount in the

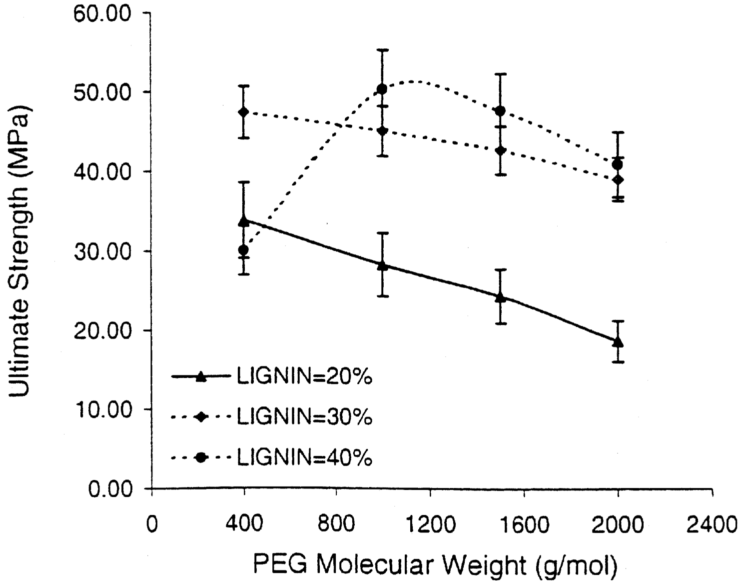

FIGURE 4 Ultimate tensile strength as a function of molecular weight of the soft segment.

production of these polyurethanes with acceptable mechanical properties. The data also suggest that PU films containing PEG 1000 and PEG 1500 can tolerate more lignin content before the mechanical properties become adversely affected.

Ultimate Strain

In Figure 5, the ultimate strain was plotted against lignin content for the four series of PU films containing PEG 400, PEG 1000, PEG 1500 and PEG 2000. For each series, as the lignin content increased from 20 wt% to 30 wt%, ultimate strain decreased dramatically before it leveled off after 30 wt% lignin. This must be primarily attributed to the increased rigidity of PU films as more lignin was incorporated with increased crosslink density. Also, at a given lignin content, increasing the PEG molecular weight results in an increase in ultimate strain for all series, except the PU films containing the PEG 2000 g/mol molecular weight, whose values were lowest. As explained before, when the longer chains of PEG are incorporated into the network, the stretching

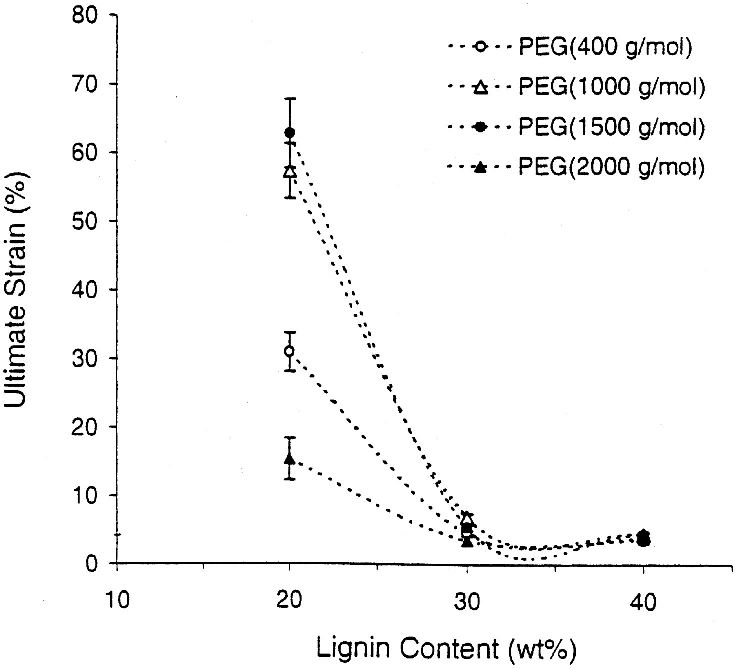

FIGURE 5 Ultimate strain as a function of lignin content.

distance between the lignin and isocyanate functionalities will be increased as will the distance between the chain growth sites. For the PU films containing the PEG of 2000 g/mol molecular weight of PEG, this chain length was probably too long to entangle with one end to form a network while leaving the other end free. This could be one reason for the high chain growth and brittle nature of polyurethanes from PEG 2000, thereby giving rise to very low ultimate strain. This can be seen more clearly from the series curve for 20 wt% lignin content in Figure 6, where the ultimate strain decreases after reaching a maximum value. Also, with increasing lignin content, a maximum value in ultimate strain was also reported by Reimann et al. [4] in their work on polyurethanes from kraft lignin.

Young's Modulus

Young's moduli of PU films containing PEG of the four sequence lengths with increasing lignin content are shown in Figure 7. As seen,

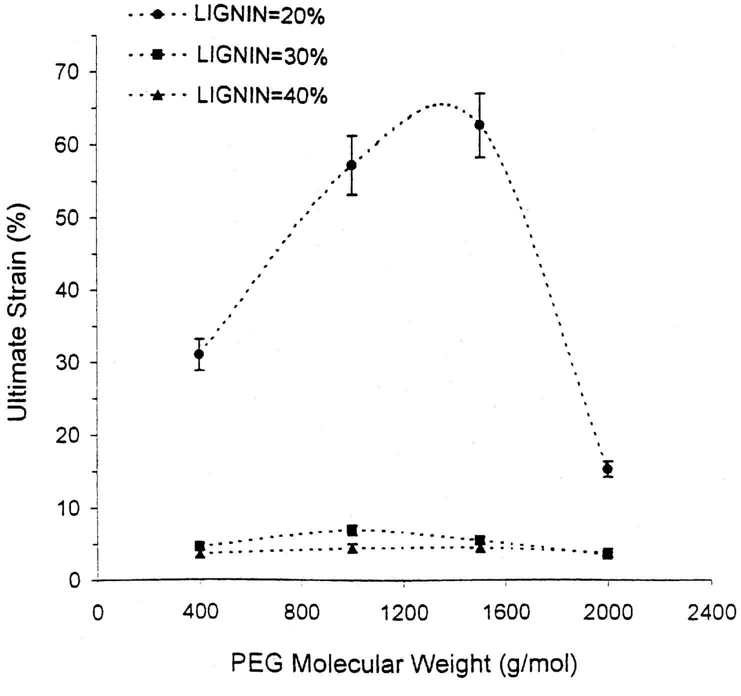

FIGURE 6 Ultimate strain as a function of molecular weight of the soft segment.

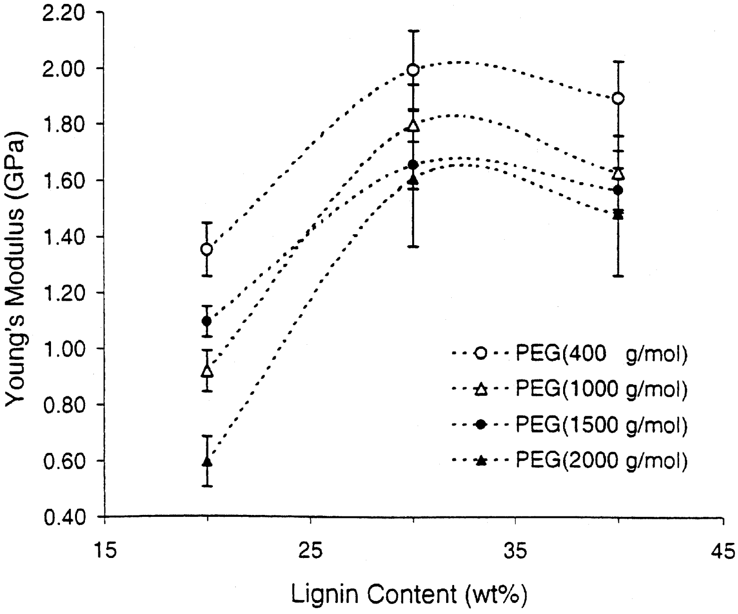

FIGURE 7 Young's modulus as a function of lignin content.

as the lignin content increased, Young's modulus increased too for PU films containing less than 30 wt% of lignin for all series. These trends share similar characteristics to those previously discussed for crosslink density and ultimate strength versus lignin content. However, the small decrease in Young's modulus, with continual increase in lignin content, was not expected since the stiffness of the polymer should increase as well with increasing hard to soft segment ratio. For a given lignin content, Young's modulus of derived polyurethane films decreased (see Figure 8) with increasing chain length of the soft segment. Again, this might be due to the longer chains provided by the increased molecular weight of PEG, which increased the flexibility to polyurethane films with no further crosslinking occurring due to the same amount of lignin used.

Thermal Properties

Figure 9 shows the glass transition temperature, Tg, based on loss modulus, of polyurethane films containing sequence lengths of PEG, decreasing with increasing PEG content. This might be interpreted that increasing the PEG content results in more soft segments being incorporated into the polymer network, reducing the hard to soft

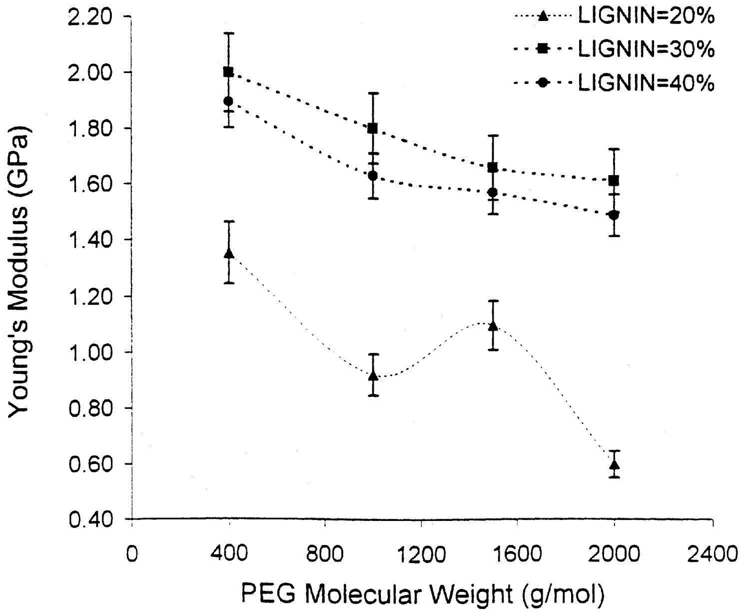

FIGURE 8 Young's modulus as a function of molecular weight of the soft segment.

segment ratio and thus decreasing the glass transition temperature. It should be noted that the rate of decline of Tg is higher at PEG contents higher than about 25 wt%. This phenomenon has also been previously reported in separate studies by Saraf et al. [3] and Reimann et al. [4], in their respective studies on kraft lignin. This strongly suggests that the PEG content is a major factor in controlling the Tg of lignin-derived polyurethanes. Figure 9 also reveals that the Tg of films containing the PEG 400 was the highest in all the series of PEG studies here at a PEG content of about 15 wt%, but decreased dramatically to its lowest value at a PEG content of approximately 37 wt%. This indicates that a distinctive feature of PEG 400, perhaps its chain length, is responsible for the nearly linear decrease in Tg. An important conclusion from this finding is that PEG 400 might be the best choice for preparing polyurethanes with acceptable mechanical and thermal properties from the type of solvoloysis lignin studied here.

It has been previously reported that phase separation between the soft and hard segments usually results in the glass transition of the soft segment occurring at a low temperature and is relatively insensitive to variations in the soft/hard segment ratio [8–11]. The Tg data from the present work may therefore not necessarily give the

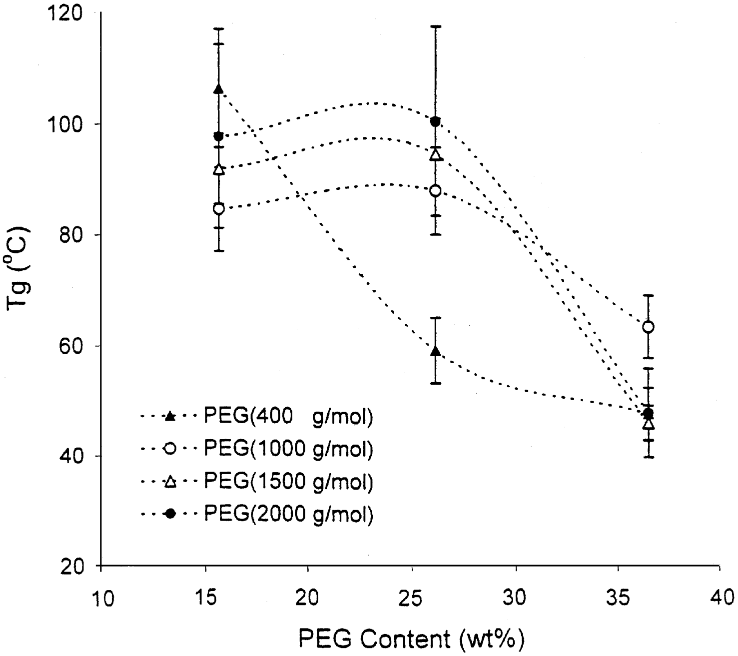

FIGURE 9 Glass transition temperature (based on loss modulus) as a function of PEG content.

conclusion that the polyurethanes studied are completely homogeneous. However, it does indicate that phase separation, if present, occurs only to a limited extent. Experimental evidence was provided by the fact that when the swelling tests were carried out on the polyurethanes, no discoloration of the DMF solvent occurred due to lignin dissolution.

Figure 10 shows the relationship of the range over which the Tg occurred from the lowest to the highest values for increasing PEG content. It can be seen that the difference value leveled off at as much as 60°C in the area of 15 wt% and 25 wt% of PEG content, before decreasing sharply and linearly after the PEG content was larger than about 25 wt%, except for PEG 400. This might be interpreted that as the NCO/OH molar ratio was a constant value, decreasing the PEG content necessarily increased the lignin content, leading to the addition for a crosslinking agent and bulky chemical structure in the polyurethane network. Since it is well known that the lignin is a three–dimensionally structured material, its further addition resulted in more energy being required to overcome the barrier caused by steric

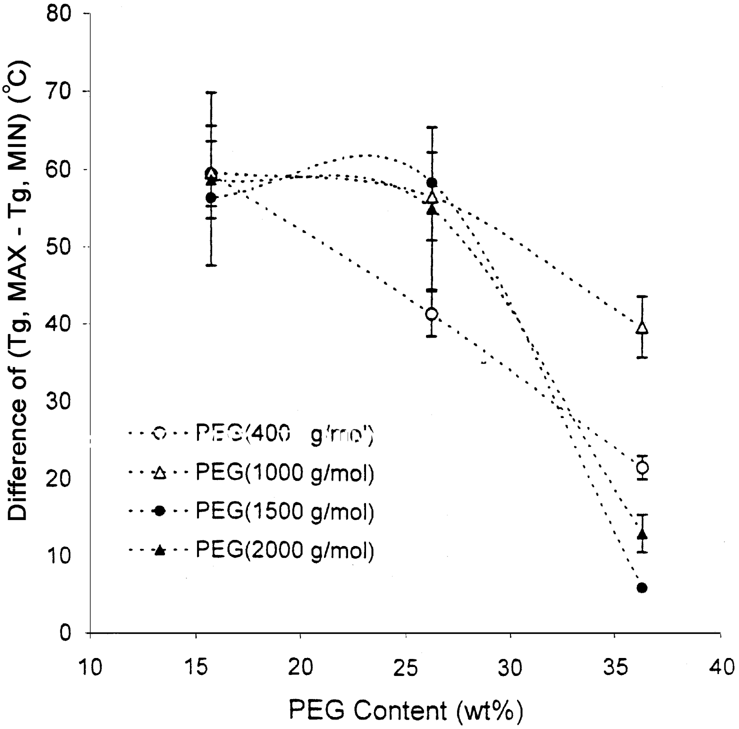

FIGURE 10 Glass transition temperature difference (T_g, MAX − T_g, MIN) as a function of PEG content.

hindrance for chain mobility. In the case of PEG 400, the difference value decreased linearly with increasing PEG content. This again may reflect the high effectiveness of the addition of PEG 400 in the network. It again shows that the PEG 400 might be the best choice for the solvolysis lignin-derived polyurethane films in the present work.

CONCLUSIONS

In the present research, polyurethanes were prepared from a three-component system, namely solvolytic lignin, MDI comonomer and PEG. An important motivation for this study was to assess which was the optimal sequence length or molecular weight of PEG to be used from 200, 400, 1000, 1500 and 2000 g/mol in terms of producing polyurethanes with measurable mechanical and thermal properties. These properties of the resultant films were determined and compared, and the following conclusions can be made.

The lignin-derived polyurethane films produced from the PEG 200 were too weak or brittle to be tested. It is therefore not recommended to use this molecular weight of PEG to prepare such polyurethanes.

For the films whose properties could be determined, it was found that the crosslink density increased, as expected, with increasing content of solvolysis lignin, which acted as the crosslinking agent. At a given lignin content, the crosslink density also increased with increasing chain length of PEG.

With increasing lignin content, the ultimate strength and Young's modulus of all the series of polyurethane films studied increased rapidly before reaching a maximum at 30 wt% lignin content, then leveled off to a constant. Also, for a given lignin content, the ultimate strength increased with decreasing chain length of PEG for all four series investigated.

When the lignin content increased from 20 wt% to 30 wt%, the ultimate strain was found to dramatically decrease to very low values before leveling off after 30 wt% in all the series of films. Also, at a given lignin content, increasing the PEG molecular weight resulted in an increase of ultimate strain for all series, except for polyurethanes containing PEG 2000, which had the lowest values.

In each series, the glass transition temperature decreased with increasing content of PEG. Polyurethanes from PEG 400 showed a distinctive character in the variation of glass transition temperature, which decreased markedly as the PEG content increased from about 15 wt% to 25 wt%.

The data obtained in the present work are consistent with the percolation theory approach to network formation, as well as the notion that the network itself consists of relatively large and stiff islands, each comprising many branch points, held together by a soft and pliable matrix.

From this study, it can be concluded that PEG 400 is the best choice for synthesizing lignin-derived polyurethanes with moderate mechanical and thermal properties. The next best selection was found to be PEG 1000 and 1500, respectively, with molecular weights above the latter possibly resulting in either inferior mechanical or thermal properties, or both.

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