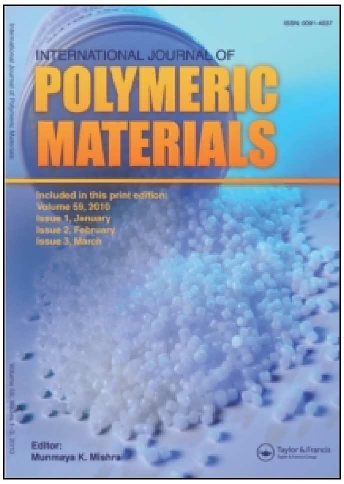


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Synthesis of polyurethanes from solvolysis lignin using a polymerization catalyst: Mechanical and thermal properties

Pei Ni[a]; Ronald W. Thring[a]
[a] Department of Chemical Engineering, University of New Brunswick, Fredericton, New Brunswick, Canada

To cite this Article Ni, Pei and Thring, Ronald W.(2003) 'Synthesis of polyurethanes from solvolysis lignin using a polymerization catalyst: Mechanical and thermal properties', International Journal of Polymeric Materials, 52: 8, 685 — 707

To link to this Article: DOI: 10.1080/00914030304931

URL: http://dx.doi.org/10.1080/00914030304931

International Journal of Polymeric Materials, 52:685–707, 2003
Copyright © Taylor & Francis Inc.
ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390198634

SYNTHESIS OF POLYURETHANES FROM SOLVOLYSIS LIGNIN USING A POLYMERIZATION CATALYST: MECHANICAL AND THERMAL PROPERTIES

Pei Ni and Ronald W. Thring
Department of Chemical Engineering, University of New Brunswick,
Fredericton, New Brunswick, Canada

Two methods of synthesis, namely, using a polymerization catalyst versus a non-catalytic route, were investigated to produce lignin-based polyurethanes. The films were characterized with respect to crosslink density, ultimate tensile behavior and glass transition temperature. The results indicated that use of the catalyst for polymerization is an effective way for producing films with consistent properties, even at lignin contents as high as 45 to 50 wt%. To illustrate the catalyst effectiveness, crosslink densities of catalyzed films with 20 wt% of lignin content increased drastically from 0.2–0.3 to 1.7–2.7 mmol/cm^3 *when the NCO/OH molar ratio increased from about 1.3 to 3.0, without much increase in the corresponding crosslink densities of the non-catalyzed films. Also, when the NCO/OH molar ratio increased from 1.2 to 3.2, the tensile strength increased from 1.9 MPa to a maximum of 55 MPa (NCO/OH = 2.6) before decreasing. Also, for same NCO/OH ratios, ultimate strain decreased drastically from 174.4% to 4.3%, with a corresponding increase in Young's Modulus from 0.03 GPa to 2.8 GPa. The glass transition temperatures of the catalyzed films also increased from 35 °C to 89 °C. Without the catalyst, only polyurethanes with low NCO/OH ratios, low lignin contents, and inferior mechanical properties, could be synthesized.*

Keywords: Lignin-derived polyurethanes, Polymerization catalyst, Mechanical and thermal properties

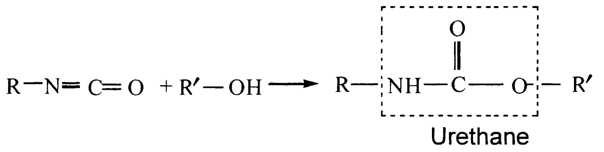
Received 31 March 2001; in final form 7 April 2001.

The authors would like to sincerely thank Alcell Technologies Inc., Miramichi, NB (Canada) for supplying us with samples of lignin. Financial support by the Natural Sciences and Engineering Council of Canada (NSERC) is greatly appreciated.

Address correspondence to Ronald W. Thring, Department of Chemistry, Environmental Science & Environmental Engineering, University of Northern British Columbia, 3333 University Way, Prince George, BC., V2N 4Z9, Canada. E-mail: thring@unbc.ca

INTRODUCTION

Lignin is formed between the wood fiber walls and mainly acts as a cementic material thus imparting structural rigidity to the wood. It is a three dimensional amorphous biopolymer comprised of phenylpropanoid units which are linked together by ether and carbon- carbon bonds. Lignin is considered to be one of the most promising future organic resources not only because it is renewable, but is second only to cellulose in abundance among the natural polymers. It is well known that lignin contains both aliphatic and phenolic hydroxyl groups, which can potentially act as reactive sites with isocyanate groups [1]. Consequently, a few attempts have already been made to use lignin as a component to manufacture polyurethanes. Generally, the reaction between isocyanate and hydroxyl compounds for the formation of urethane groups can be considered as the chain propagation reaction [2].

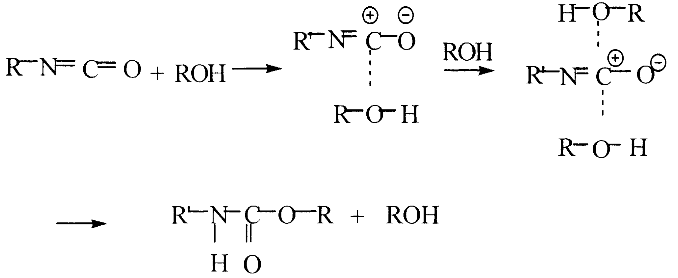


$$R{-}N{=}C{=}O + R'{-}OH \longrightarrow R{-}\boxed{NH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O}{-}R'$$

(1)

where: $R = (CH_2)_nNCO$ and $R' = (CH_2)_mOH$.

On the basis of studies by Baker and Gaunt [3], the non-catalyzed reaction can be visualized as proceeding via the following mechanism



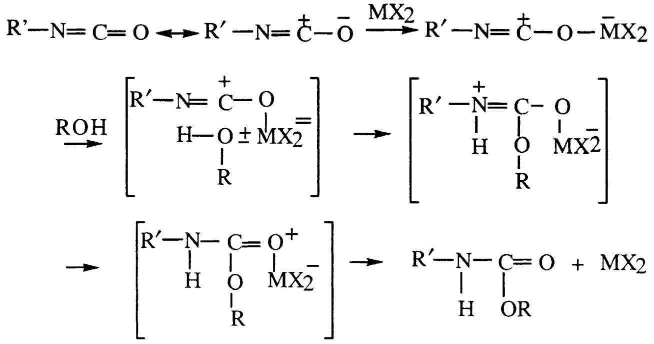
$$R{-}N{=}C{=}O + ROH \longrightarrow \underset{\displaystyle R{-}O{-}H}{\underset{\vdots}{R{-}N{=}\overset{\oplus}{C}{-}\overset{\ominus}{O}}} \xrightarrow{ROH} \underset{\displaystyle R{-}O{-}H}{\underset{\vdots}{\overset{\displaystyle H{-}O{-}R}{\overset{\vdots}{R{-}N{=}\overset{\oplus}{C}{-}\overset{\ominus}{O}}}}} \longrightarrow R{-}\underset{H}{\underset{|}{N}}{-}\underset{O}{\underset{\|}{C}}{-}O{-}R + ROH$$

(2)

where: $R = (CH_2)_nNCO$ and $R' = (CH_2)_mOH$.

However, the reaction between the isocyanate and hydroxyl groups, has been generally found to be too slow for practical purposes and usually does not reach completion [2].

Other workers have used catalysts to increase the reaction rate and complete the reaction. Several metal salts, organo-metallic compounds, and organic compounds have been found to catalyze the isocyanate–hydroxyl reaction. Mobay Chemical Company (USA) has studied many compounds, including tertiary amines, inorganic bases, organometallics and metal chelates, and concluded that certain organotin compounds possessed exceptionally high orders of catalytic activity, especially towards the urethane and chain extension reactions. This discovery also revealed that organotin catalysts having at least one carbon-to-tin bond were most active in accelerating the isocyanate–hydroxyl reaction [7]. Britain and Gemeinhardt [4] proposed a mechanism of the organometallic—catalyzed reaction of an isocyanate with an alcohol. Because of the exceptionally high catalytic activity, they proposed the formation of a ternary complex.



(3)

where: $R = (CH_2)_nNCO$, $R' = (CH_2)_mOH$, M = Metal ion (Sn) and $X = (CH_2)_p$ or $(CH_2)_qO$.

In reaction (3), a complex is formed by the combination of the catalyst MX_2 with the isocyanate. The complex then reacts with the alcohol through an intermediate, decomposing to give the urethane and a free catalyst molecule. Comparing reaction (2) and reaction (3), because of the extreme effectiveness of the catalyst, the isocyanate-hydroxyl reaction in (3) is much faster.

Saraf *et al.* [5] thus used dibutyltin dilaurate, an effective organotin catalyst in the preparation of lignin-derived polyurethanes. The lignin used was pre-modified through hydroxyl propylation to increase its reactivity by converting the phenolic hydroxyl groups to the more reactive aliphatic hydroxyl groups. This made it possible to produce polyurethanes using the modified lignin as a polyol component [6].

In the present work, a three-component system, namely, a novel solvolysis lignin, methyl-diisocyanate (MDI) and OH-terminated polyethylene glycol (PEG), was used to produce polyurethanes (PUs) with measurable properties. The solvolysis lignin, was a novel, semi-commercially produced organosolv lignin. Unlike other studies using lignin to produce polyurethanes, we used this lignin on an 'as received' basis with no pretreatment or modification. The objective was to compare the properties of lignin-derived polyurethanes prepared with dibutyltin dilaureate as catalyst, with those made without any catalyst.

The effects of lignin content and isocyanate to hydroxyl (NCO/OH) stoichiometry on the crosslink density, mechanical and thermal properties of the lignin-derived polyurethane films are therefore presented and discussed.

EXPERIMENTAL

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 [13]. In the present work it was used as received and without any pre-modification.

Polyethylene Glycol (PEG): Polyethylene glycol of molecular weight (M_n) 400 g/mol was 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.

METHODS

Film Preparation

With Catalyst

A quantity of lignin was dried over P_2O_5 under vacuum for 120 h then dissolved in tetrahydrofuran (THF). The flask was purged with nitrogen, then capped and magnetically stirred at a speed of about 200 rpm. MDI, whose amount was determined by the desired lignin content and NCO/OH molar ratio, was then added with more THF to rinse down the sides of the flask. The mixture was stirred for another 10–20 minutes at room temperature until all the MDI had dissolved. The NCO/OH molar ratio was calculated as follows:

$$\frac{\mathrm{NCO}}{\mathrm{OH}} = \frac{W_{\mathrm{MDI}}[\mathrm{NCO}]_{\mathrm{MDI}}}{W_{\mathrm{L}}[\mathrm{OH}] + W_{\mathrm{PEG}}[\mathrm{OH}]_{\mathrm{PEG}}} \tag{4}$$

where: W_{MDI}, W_L and W_{PEG} = weights (g) of MDI, lignin and PEG, respectively.

$[NCO]_{MDI}$ = molar content of isocyanate groups in MDI (8 mmol/g).

$[OH]_L$ and $[OH]_{PEG}$ = molar content of total hydroxyl groups in the solvolysis lignin (5.38 mmol/g) and PEG (5 mmol/g), respectively.

Dibutyltin dilaurate catalyst, in concentrations of $3 \sim 6\%$ 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 fume hood for about 5 minutes to partially evaporate the solvent as well as to quench any bubbles, which 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 casting concentration of the polyurethane 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 stick to the glass plate, resulting in a non-uniform film. It was necessary to do the casting outside of the hood to avoid the presence of small voids caused by rapid solvent evaporation. After the solution gelled and became sufficiently hard, the glass plate was placed back in the hood for solvent 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 warping. The film was then peeled and dried in a vacuum desiccator over phosphorus pentoxide for five days followed by curing at 105 °C for 8 hours.

Without Catalyst

The above procedure was used, except with no catalyst addition. Also, stirring was maintained under nitrogen in the water bath at a constant temperature of 60 °C for 2.5 hours.

Swelling Tests

Two sample specimens were cut into dimensions of about 5 mm × 5 mm (exact dimensions were measured by vernier calipers) and weighed. The samples were immersed in glass vials containing dimethyl formamide (DMF) solvent and allowed to stand in a controlled room kept at a constant temperature of 23 °C and 50% relative humidity. When the films reached equilibrium after 5 days, they were removed from the solvent, patted with lint-free tissue paper to remove the excess solvent on the surface, and the dimensions were measured again.

This had to be done quickly to minimize film shrinkage due to solvent evaporation. The crosslink density (mol/cm^3) of the NCO—OH bonds for each specimen was estimated using the following equation, which was introduced by Flory and Rehner [14].

$$\frac{\upsilon_c}{V_o}(\mathrm{mol/cm^3}) = \frac{-2[\upsilon + \chi\upsilon^2 + \ln(1-\upsilon)]}{V_1(2\upsilon^{1/3} - \upsilon)} \tag{6}$$

where: υ_c = effective number of moles of crosslinked chains, V_1 = molar volume of solvent, χ = the polymer-solvent interaction parameter, υ = volume fraction of polymer in swollen gel ($\upsilon = V_o/V$), V_o = volume of dry polymer, and V = volume of swollen gel at equilibrium.

In order to determine χ for our polyurethane-DMF system, swelling tests were carried out at 25, 30 and 35 °C. From the temperature dependency of the swelling volume, χ values were obtained from the following relationship [14].

$$\frac{\partial \ln \upsilon}{\partial \ln T} = \frac{-3\chi(1-\upsilon)}{5(1-\chi)} \tag{7}$$

In the present study, the polymer-solvent interaction parameter (χ) was determined to be 0.49. This value was calculated by using the above equation for several films with different NCO/OH molar ratios and solvolysis lignin contents [15].

Stress–Strain Tests

Tensile tests were performed in a controlled room maintained at 23 °C and 50% relative humidity. The dimensions of the film strips were: 130 mm length, 15 mm width and about 0.4 mm thickness. The samples were stored in the controlled room for 24 hours prior to testing. A Lorentzen & Wettre Tensile Strength Tester (CODE SE 060) operating at a crosshead speed of 10 mm/min was used. Ultimate strength, ultimate strain and Young's modulus were calculated from the stress-strain curves, on the basis of initial shape dimensions. For each film, three replicates were tested and the mean values calculated.

Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis was performed using a dynamic mechanical analyzer, the TA instrument DMA 2980, with a clamp type of dual cantilever. The heating rate was maintained at 3 °C/min from 30 °C to 150 °C. The oscillation amplitude and frequency were 50 µm and 1 Hz, respectively. The dimensions of the samples tested were approximately, 35 mm length, 15 mm width, and 0.4 mm thickness. The exact width and thickness were measured by using vernier calipers before testing. Glass transition temperatures (T_g) were determined on the peak of the loss modulus curve. For each film, three replicates were tested and average values taken.

RESULTS AND DISCUSSION

Since the catalyst route was much more efficient for polymerizing lignin-derived polyurethanes, most films in the present study were prepared in this manner. Therefore, unless it is specifically mentioned, the data presented and discussed is for the catalyzed polyurethanes.

Swelling Behavior

Films from the Catalyst Route

The degree of crosslinking was determined from swelling tests as described previously. It is well established that many network polymers, such as polyurethanes, can absorb large quantities of solvent without dissolving. The original shape is preserved and the swollen polymer will exhibit elastic rather than plastic behaviour. Since the dimethyl formamide is a very strong solvent for lignin, any lignin that is not incorporated into the network will be dissolved to produce a dark colored solution. It should be mentioned that when swelling tests were performed on the lignin-free polyurethane films, they became very gelatin-like, and any attempt to remove them from the vials was unsuccessful because they would fall apart, thus their dimensions could not be measured. The lack of a colored solution in the present work thus indicated that solvolysis lignin is an active ingredient in the polyurethanes system used in the present work.

Figure 1 shows the crosslink density increasing with the NCO/OH molar ratio for a given lignin content. As the NCO/OH molar ratio increases, there are more isocyanate groups available to crosslink with the hydroxyl groups, thus increasing the crosslink density. The data also illustrates that at a given NCO/OH molar ratio, crosslink density increases with increasing lignin content. This increase must contribute to more isocyanate groups being involved to crosslink with hydroxyl groups. As seen in Figure 1, when the NCO/OH molar

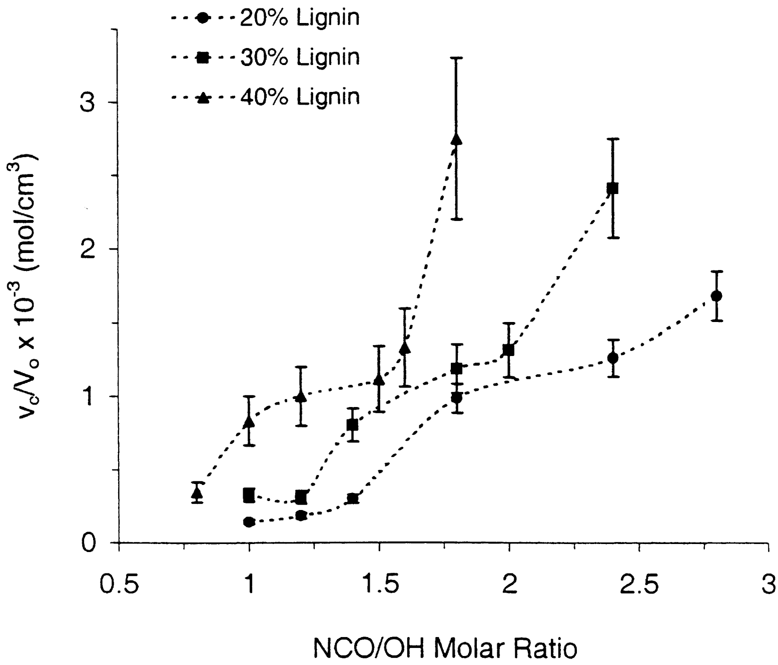


FIGURE 1 Crosslink density as a function of NCO/OH molar ratio.

ratio>1 (for 40 wt% lignin), >1.2 (for 30 wt% lignin) and >1.4 (for 20 wt% lignin), the crosslink density increases dramatically from 0.8 mmol/cm^3 to 2.8 mmol/cm^3, 0.3 mmol/cm^3 to 2.4 mmol/cm^3, and 0.3 mmol/cm^3 to 1.7 mmol/cm^3, respectively. This suggests that below these molar ratios, both isocyanate groups and hydroxyl groups are insufficient for producing a relatively complete network. Above these values, the network begins to build up well. Also, the rate increase of crosslink density for films with 40 wt% lignin content is higher than that with 30 wt% lignin, which in turn is higher than that of polyurethanes with 20 wt% lignin content. This suggests the hydroxyl groups of solvolysis lignin were more reactive than those in polyethylene glycol since at a given NCO/OH molar ratio, the increase in lignin content causes a concomitant decrease in PEG content inside the film sample.

In Figure 2, it can be seen that when the lignin content is over 30 wt% for most of the NCO/OH molar ratios used, crosslink density dramatically increases, suggesting that this amount of lignin is the minimum required for forming a well crosslinked network in the three-component system used here.

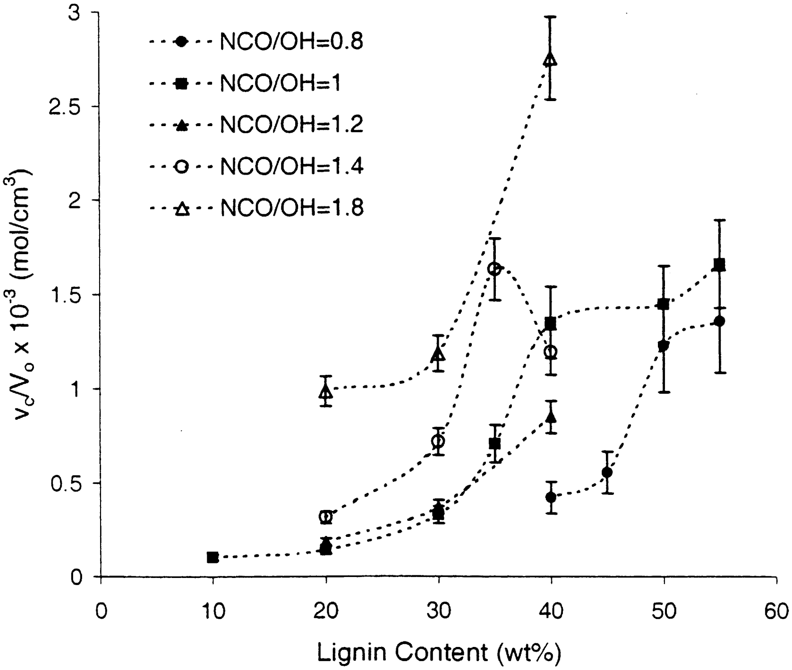


FIGURE 2 Crosslink density as a function of lignin content.

Crosslink Density

In Figure 3, the crosslink densities of films prepared with and without the catalyst are plotted against the NCO/OH molar ratio. As seen, both series show that the crosslink density increases as the NCO/OH molar ratio increases. It can be seen that when the NCO/OH molar ratio was below 1.6, the crosslink density of the catalyzed films was lower than that of those prepared without the catalyst. This may be explained as follows. In this study, the total weight of film remained constant. Therefore, when the lignin content was fixed at 20 wt% in the lower range of the NCO/OH molar ratio, the PEG content was higher than that of lignin. Although the functionality of PEG is less reactive than that of lignin, because of the high catalyst efficiency, the PEG (soft segment) reacted to completion with MDI and was therefore fully incorporated into the polyurethane network in the catalyzed films. Since the PEG has fewer hydroxyl groups in a unit than does the lignin, this leads to a lower crosslink density. In the non-catalyst route, although there were enough hydroxyl groups from PEG, they usually did not react well with the isocyanate due to their lower

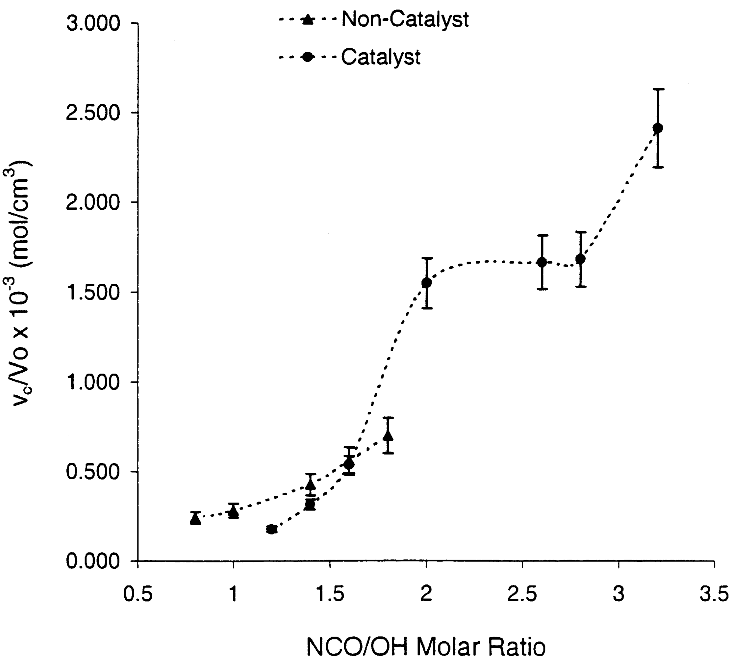


FIGURE 3 Crosslink density as a function of NCO/OH molar ratio for both series of films.

reactivity. Thus in a unit network, more lignin, whose hydroxyl groups are more reactive than those of PEG, crosslinked with MDI, thereby leading to a higher crosslink density.

TENSILE PROPERTIES

Ultimate Strength of Catalyzed Films

Figure 4 shows that the ultimate strength reached a maximum before decreasing with increasing NCO/OH molar ratio. This maximum point shifted further to the right at higher NCO/OH molar ratios with decreasing lignin content. This might be explained by the fact that at the low NCO/OH molar ratio, there were insufficient isocyanate groups to react with hydroxyl groups. Therefore, the number of available sites for crosslinking in the polyurethane is insufficient, and only a partial network was established. However, as the NCO/OH molar ratio increased, more isocyanate groups participated in the reaction with lignin hydroxyl groups and the network became

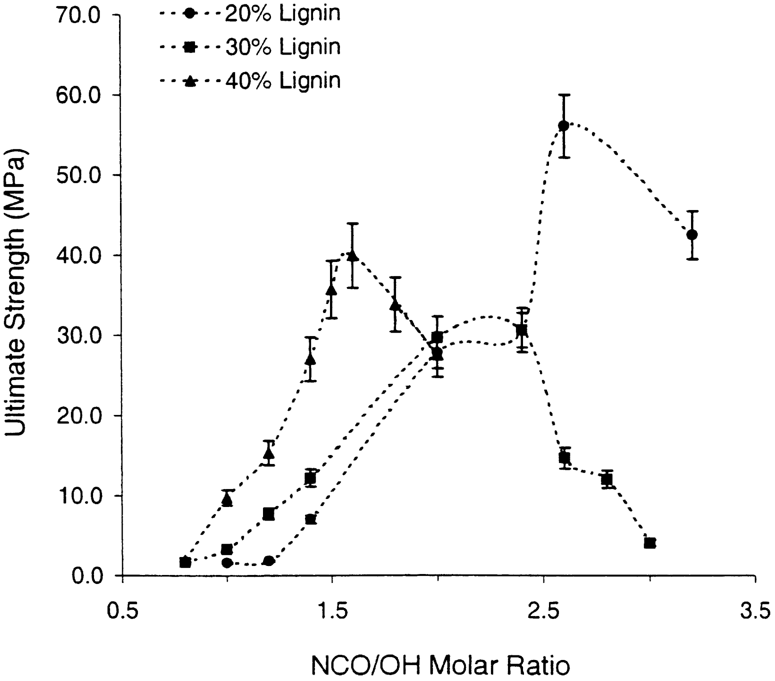


FIGURE 4 Ultimate strength as a function of NCO/OH molar ratio.

increasingly well formed and more uniform. Finally, the network reached its optimum degree of crosslinking, thus exhibiting a maximum tensile strength. With a further increase in the NCO/OH molar ratio, at a given lignin content, more isocyanate groups participated in network formation. However, an excess of isocyanate groups caused the network to over-crosslink, resulting in the films becoming more brittle, which lead to inferior strength properties.

It can be seen in Figure 5 that the ultimate tensile strength increased with increasing lignin content for all NCO/OH molar ratios used. This must be attributed to the rigidity imparted by the lignin to the polyurethane network. Figure 5 also indicates that for higher NCO/OH molar ratios, (e.g., 1.4, 1.8 and 2), the ultimate strength decreases after attaining a maximum value. Since the NCO/OH molar ratio was fixed, at high lignin content, excess hydroxyl groups of lignin caused the network to randomly crosslink with isocyanate groups, resulting in high stiffness and lower strength. For the successful production of these films, a proper balance of the components is therefore required. Also shown in Figure 5, when the lignin content is

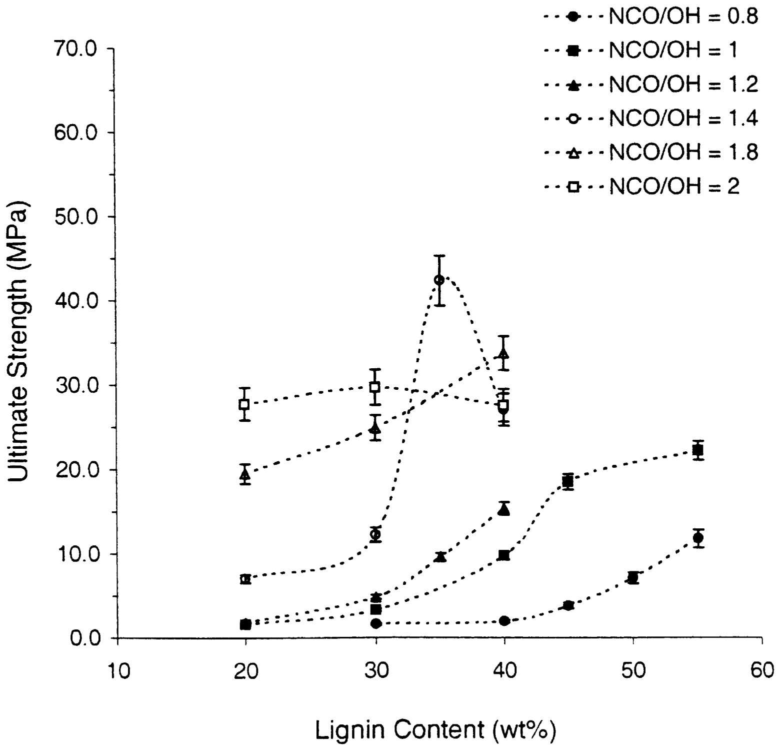


FIGURE 5 Ultimate strength as a function of lignin content.

30 wt% or higher, the rate of increase of ultimate strength increased dramatically in all series of NCO/OH molar ratio except 0.8 and 2. Again this suggested that for this particular system, the 30 wt% lignin content is a pivotal amount from which there were just enough hydroxyl groups available to crosslink with the isocyanate functionality to establish enough bonds to form a stable polymer network.

It was observed during the experiments that when the films were peeled off the glass plate, they spontaneously shrunk and curled up in all cases except for those films with a lignin content of 20 wt% and an NCO/OH molar ratio of 0.8. In this case the film stuck very tightly to the glass plate. More shrinking and curling occurred at either higher lignin contents or higher NCO/OH molar ratios. Thus, in the case of excess crosslinking, bond rupture would be initiated by stress concentrations and stress cracking due to film shrinkage, resulting in weakened films. This might be part of the reason why it was not possible to cut and test the brittle films that were produced at

NCO/OH molar ratios greater than 1.4, 2, 3, and 3.2 for lignin contents of 50, 40, 30, and 20 wt% respectively in the present work.

Ultimate Strength of Catalyzed and Non-Catalyzed Films

Figure 6 shows that for both series of polyurethanes prepared from the catalyst and non-catalyst routes, the ultimate tensile strength increased as the NCO/OH molar ratio increased. However, at NCO/OH molar ratios lower than 1.8, the strength of films prepared without the catalyst is higher than that of catalyzed PU films. This is to be expected since the crosslink density of non-catalyzed PU films was seen to be greater than that of PU films prepared with the catalyst. Due to the absence of the catalyst and the availability of less reactive hydroxyl groups from PEG, isocyanate groups would mostly crosslink with lignin hydroxyl groups, giving more rigidity to the PU films. On the other hand, when the catalyst was used, PEG was also

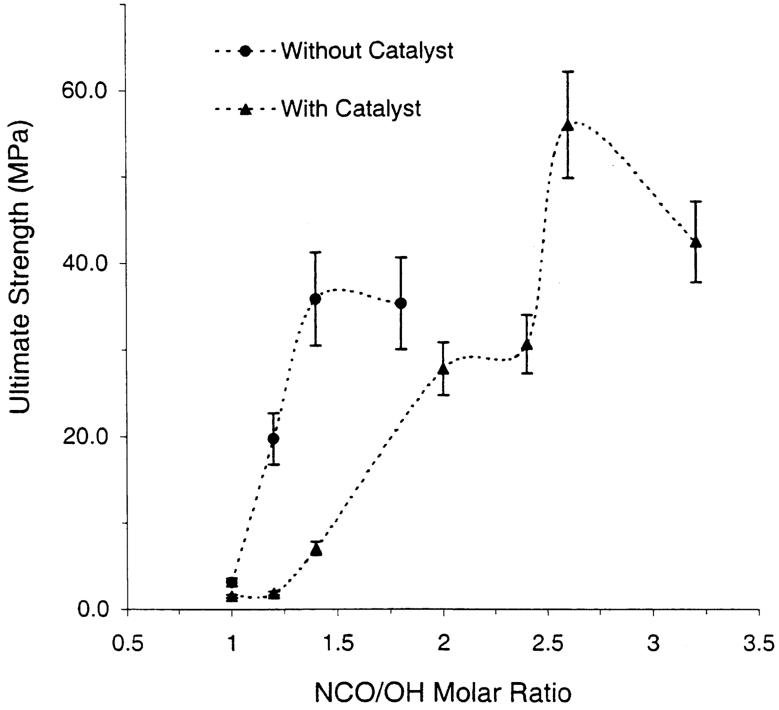


FIGURE 6 Ultimate strength as a function of NCO/OH molar ratio for both series of films.

incorporated into the network and softened the PU films, resulting in lower ultimate tensile strengths at the same NCO/OH ratios. When the NCO/OH molar ratio was further increased at a fixed lignin content of 20 wt%, the PEG content had to be decreased to keep the total weight of the film constant. This resulted in more lignin participating in the PU network, thereby imparting strength and rigidity to the films. It was also observed that the maximum strength of catalyzed PU films shifted further right at NCO/OH molar ratios greater than 2.6.

Ultimate Strain of Catalyzed PU Films

In Figure 7, it can be seen that the ultimate strain generally decreased as the NCO/OH molar ratio increased. As the NCO/OH molar ratio increased, there is increased crosslinking between the isocyanate and hydroxyl groups, causing the polyurethane network to bond more strongly, resulting in low elongation. Discrepancies can be seen at the points of NCO/OH = 1 for 20 wt% lignin, and NCO/OH = 0.8 for

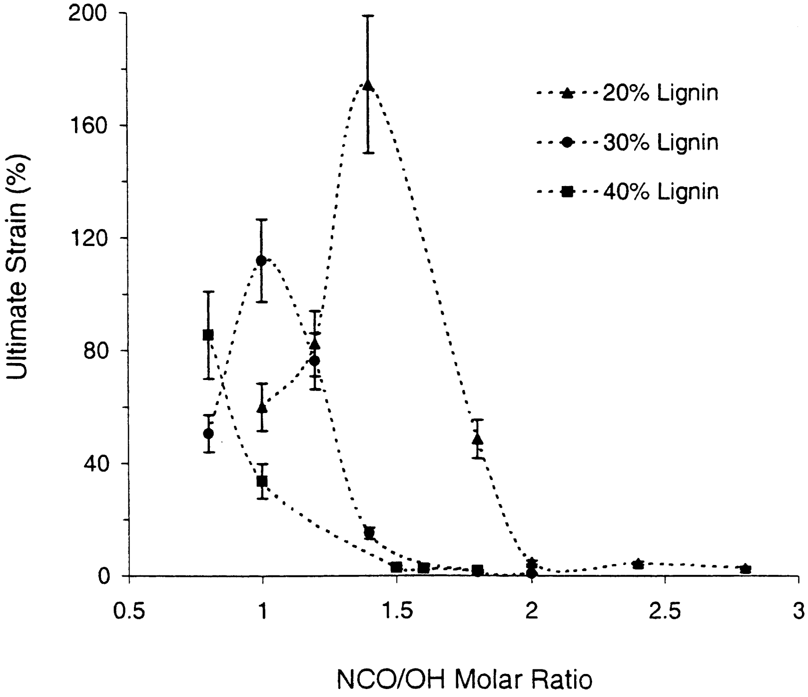


FIGURE 7 Ultimate strain as a function of NCO/OH molar ratio.

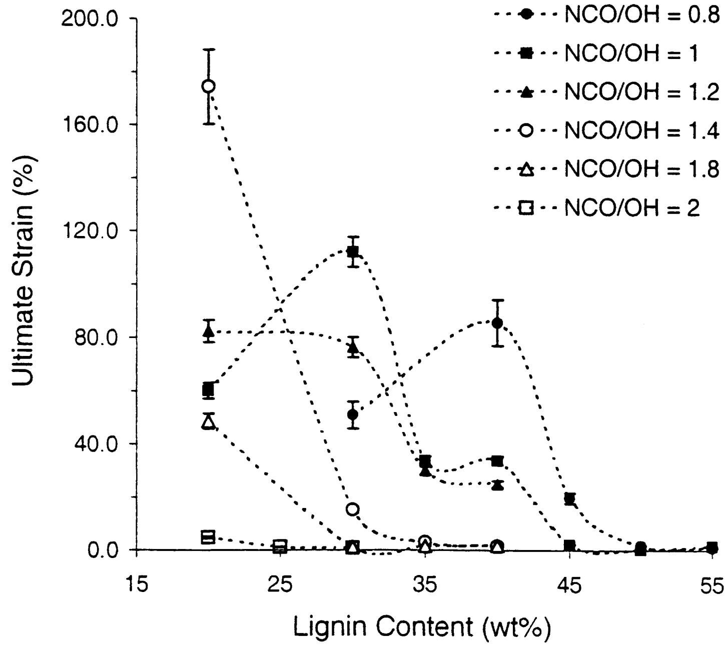


FIGURE 8 Ultimate strain as a function of lignin content.

30 wt% lignin content. At these values, the ultimate strain was lower than maximum value, even though the NCO/OH molar ratio was lower. This may be explained by the lack of isocyanate functionality due to an insufficient number of crosslink sites in the network in which case the PU films were too weak to elongate.

Figure 8 shows that for a given NCO/OH molar ratio, ultimate strain decreased with increasing lignin content. When the NCO/OH molar ratio was kept constant with decreasing lignin content, the PEG (soft segment) content in the PU film network had to be necessarily increased. The more the content of the softer segment, the more flexible the ensuing polyurethane film became. For instance, the PU film with 20 wt% lignin at an NCO/OH molar ratio of 1.4 exhibited an ultimate strain as high as 180%.

Ultimate Strain of Catalyzed and Non-Catalyzed Films

Figure 9 shows the strain of catalyzed PU films as being substantially higher than those films prepared using no catalyst. As previously mentioned, the network formed in the catalyzed PU films was

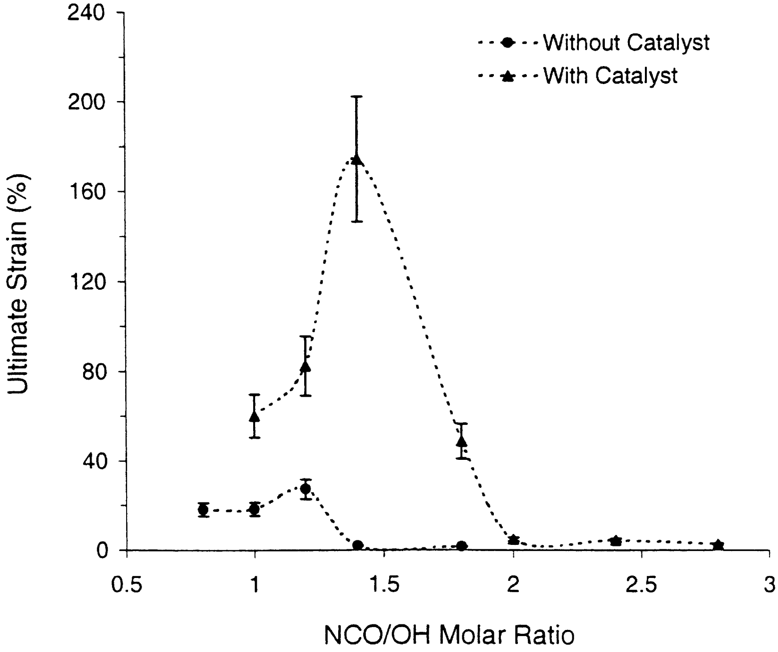


FIGURE 9 Ultimate strain as a function of NCO/OH molar ratio for both series of films.

dominated by PEG, which has high elongation. With the assistance of the catalyst, there is essentially no difference between the reactivities of the functional hydroxyl groups of lignin and those of PEG, although the latter would normally be much less reactive than the former. This again reflects that the catalyst does have a significant impact on the ultimate properties of lignin-derived PU films.

Young's Modulus of the Catalyzed PU Films

As seen in Figure 10, Young's modulus increased, reached a maximum and then decreased with increasing NCO/OH molar ratio. This may be due to the fact that by increasing the NCO/OH molar ratio, more isocyanate groups are available to crosslink with hydroxyl groups, thus bonding the polyurethane network more strongly. However, a further increase in the NCO/OH molar ratio, at a given lignin content, resulted in improper and non-uniform crosslinking in the network due to excess isocyanate groups. PU films then became more brittle, leading to a low modulus.

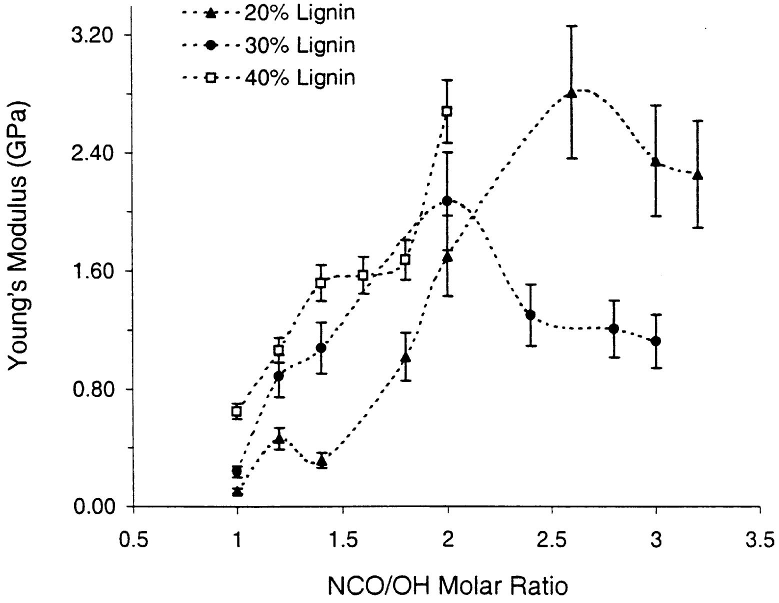


FIGURE 10 Young's modulus as a function of NCO/OH molar ratio.

At a constant NCO/OH molar ratio, Young's modulus is seen to also increase with lignin content. This is not only due to an increase of stiff segment, namely the lignin, which contains many phenylpropane units, but also because of the decrease in content of PEG, the soft segment, in the film. The same conclusion is also reflected in Figure 11, in which Young's modulus is plotted against lignin content for different NCO/OH molar ratios. It can be seen that Young's modulus increased sharply when the lignin content was greater than 30 wt%, again indicating that this lignin content is pivotal towards the formation of uniformly crosslinked networks of solvolysis lignin-derived polyurethanes.

Young's Modulus of Catalyzed and Non-Catalyzed Films

It can be seen from Figure 12 that the Young's modulus of non-catalyzed films was much higher than that of the catalyzed ones when NCO/OH molar ratios were below 2. As before, this suggests that the PEG in the catalyzed films also participated more extensively in network formation due to the high activity of the catalyst, thus producing more flexible films.

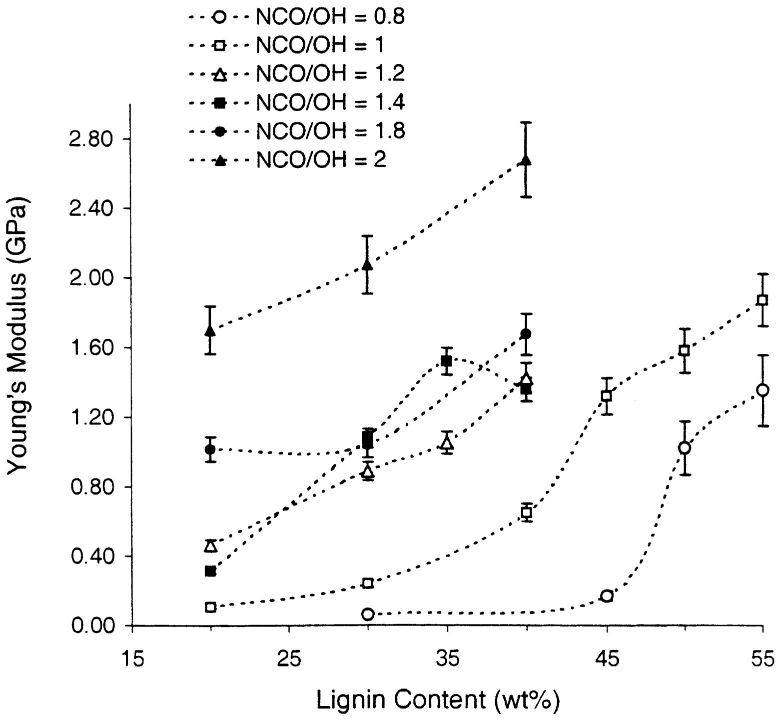


FIGURE 11 Young's modulus as a function of lignin content.

Thermal Properties

The glass transition temperature (T_g) is a very important property of any polymer. When the surrounding temperature of a polymer is lower than T_g, the molecular chains are usually in an entangled, immobile state. When the transition occurs, the chains become more mobile and may slip against each other.

In the present work, the glass transition temperature was measured by dynamic mechanical analysis (DMA) using a TA instrument (DMA 2980) with a clamp type of dual cantilever. In the present work the glass transition temperature was determined based on the loss modulus (E″) peak.

T_g of Catalyzed and Non-Catalyzed Films

As indicated in Figure 13, there is a linear decrease in T_g with increasing PEG content, which can be attributed to participation of

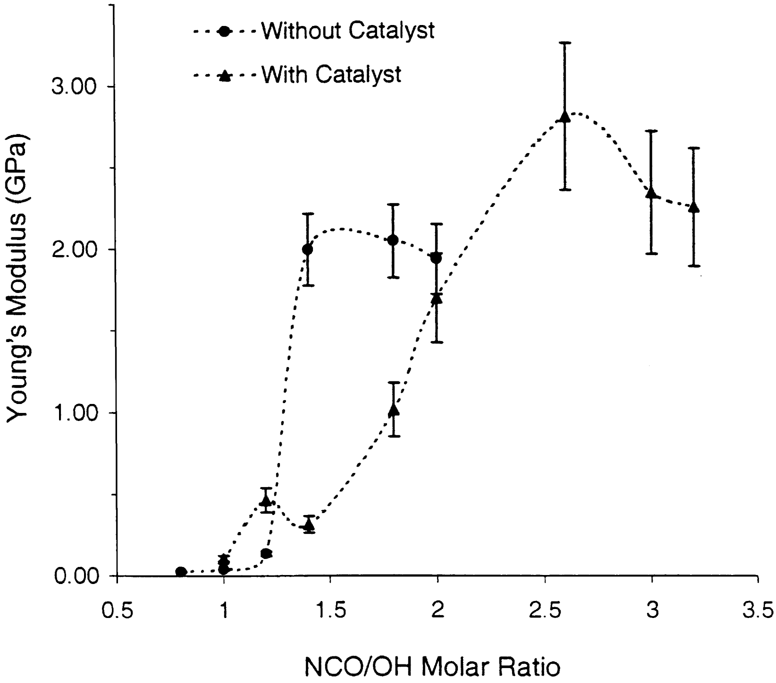


FIGURE 12 Young's modulus as a function of NCO/OH molar ratio for both series of films.

the increased amounts of the soft segment added in the polymer network. It might be interpreted that since the PEG is a long and linear chain which interweaves inside the network, once there is enough energy, it will begin to turn and cause the whole structure to change from a glassy to leathery state. As seen before, an increase in PEG decreased the crosslink density and Young's modulus. Saraf *et al.* [7] and Reimann *et al.* [1] have reported similar results in separate studies. Also, both authors noted that T_g only varied significantly with PEG content but was essentially independent of the chemical structure and functionality of the lignin component. In our case, as shown in Figure 13, at a given PEG content, increasing the lignin content seemed to lower the T_g. This is an unexpected result since lignin acts as the stiffening segment, and therefore should increase T_g. Figure 14 shows that for a given PEG content, the glass transition temperature increased with NCO/OH molar ratio. The higher the crosslink density, the more restricted the main chain motion becomes, resulting in a higher T_g. As shown in Figure 15, for both series, as the

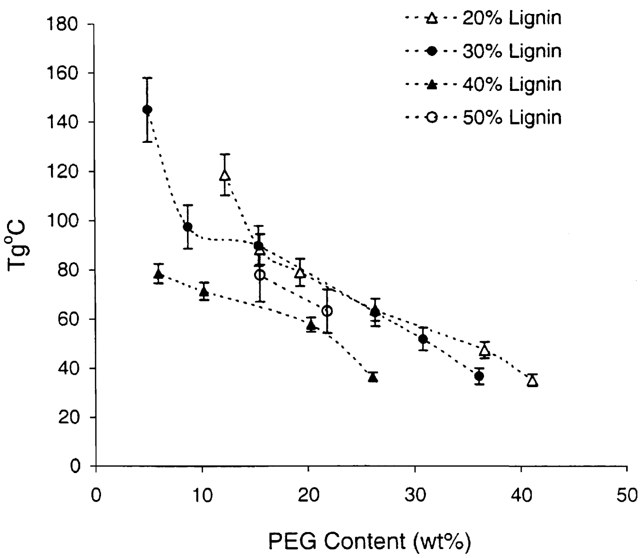


FIGURE 13 Glass transition temperature (T_g) as a function of PEG content for different lignin contents.

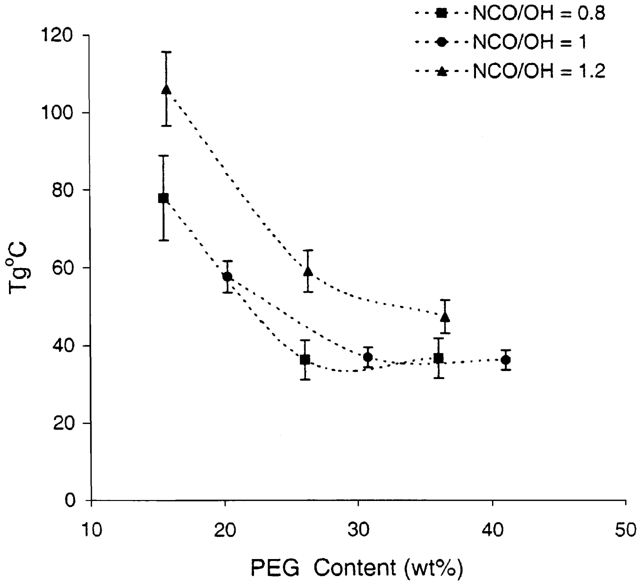


FIGURE 14 Glass transition temperature (T_g) as a function of PEG content for different NCO/OH molar ratios.

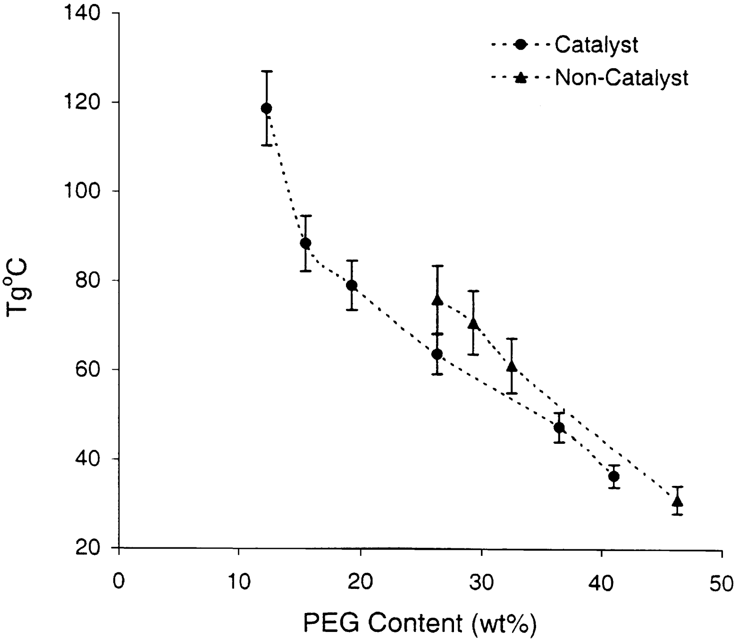


FIGURE 15 Glass transition temperature (T_g) as a function of PEG content (at 20 wt% lignin) for catalyzed and uncatalyzed polyurethanes.

content of PEG soft segment increased, the T_g decreased almost linearly. When the PEG content ranged between 25 wt% to 40 wt%, all T_g's of catalyzed polyurethanes are seen to be approximately 10 °C lower than those of the uncatalyzed ones, possibly due to the chemical structural differences between the films. As stated before, more hydroxyl groups of PEG, and therefore more PEG in the catalyzed films were activated due to the catalyst and its high efficiency, when compared to the uncatalyzed films using the same component amounts. Thus, the catalyzed films were dominated by the long soft PEG segment activated by the highly efficient catalyst, which caused a decrease in T_g.

CONCLUSIONS

In the present work, lignin-derived polyurethanes were synthesized using two procedures, namely, with and without a polymerization catalyst. The following important conclusions can be made from a comparison of their properties.

(i) PU films containing solvolysis lignin, MDI and PEG can be prepared by solution casting. The films can have various desirable properties tailored by changing the content of any one of the three components.

(ii) PU films containing up to 50 wt% lignin and NCO/OH molar ratio of 3.2 could be prepared with the catalyst. For the catalyzed PU films containing 30 wt% lignin or higher, their properties changed quite dramatically at NCO/OH molar ratios between 1.2 and 1.4 or higher. The crosslink density was found to generally increase with lignin content and NCO/OH molar ratio. However, crosslink densities for catalyzed PU films were lower than the corresponding values from films prepared with no catalyst.

(iii) For both series of PU films, the ultimate strength and Young's modulus increased as the NCO/OH molar ratio and lignin content increased whereas the ultimate strain decreased. However, the ultimate strength and Young's modulus of non-catalyzed PU films were higher than the corresponding values from the catalyzed films. Ultimate strains of the catalyzed films were found to be much higher than those of non-catalyzed samples.

(iv) The glass transition temperature (based on the loss modulus) of PU films from both series decreased linearly when the PEG content and/or NCO/OH molar ratio increased. Also, other changes in the chemical structure of the films due to the different routes affected the glass transition temperature. Generally, T_g's of catalyzed PU films were lower than those of PU films prepared by the non-catalyst route.

REFERENCES

[1] Reimann, A., Morck, R., Hatakeyama, H. and Kringstad, K. P. (1991). *Sixth International Symposium on Wood and Pulping Chemistry*, p. 523.

[2] Benning, C. J. (1969). "*Plastic Foams*", **1**(2), 119.

[3] Baker, J. W. and Gaunt, J. (1949). *J. Chem. Sci.*, **9**, 19.

[4] Britain, H. (1960). *J. Appl. Polymer Sci.*, **4**, 207.

[5] Saraf, V. P. and Glasser, W. G. (1984). *J. Appl. Polymer Sci.*, **29**, 1831.

[6] Hsu, O. H. and Glasser, W. G. (1988). *J. Appl. Poly. Symp.*, Chap. 28, p. 72.

[7] Smith, W. M. (1964). "*Manufacture of Plastics*", **1**, 467.

[8] Ferrigno, T. H. (1967). "*Rigid Plastics Foams*", p. 29.

[9] Vanderlaan, M. N. (1995). *MSc Thesis*, University of New Brunswick (Canada).

[10] Rials, T. G. and Glasser, W. G. (1986). *Holzforschung*, **40**, 353.

[11] Saraf, V. P., Glasser, W. G., Wilkes, G. L. and McGrath, J. E. (1985). *J. Appl. Polym. Sci.*, **30**, 2203.

[12] Saraf, V. P., Glasser, W. G. and Wilkes, G. L. (1985). *J. Appl. Polym. Sci.*, **30**, 3809.

[13] Lora, J. H., Creamer, A. W., Wu, L. C. F. and Goyal, G. C., *Polymers for Advanced Technologies*, **2**, 41–47, John Wiley, New York, 1990.

[14] Flory, P. J. and Rehner, R. (1943). *J. Chem. Phys.*, **11**, 521.

[15] Thring, R. W. and Vanderlaan, M. N. (1997). *Biomass and Bioenergy*, **13**, 125.

[16] Saraf, V. P. and Glasser, W. G. (1985). *J. Appl. Poly. Sci.*, **30**, 2207.