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Synthesis and characterization of lignin–HTPB copolyurethane

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Abstract

Lignin–HTPB copolyurethanes have been synthesized from hydroxyl terminated polybutadiene (HTPB) and varied quantities of lignin and toluene diisocyanate. IR spectroscopy and estimation of isocyanate groups have established the formation of HTPB polyurethane and lignin–HTPB copolyurethane. The crosslink density, sol fraction, diffusion coefficient, mechanical properties and X-ray crystallinity of lignin–HTPB copolyurethane have been measured and compared with those of HTPB polyurethane. Tensile strength improvement of lignin–HTPB copolyurethane was observed up to 3-wt.% lignin incorporation. High hydroxyl value of lignin has been found responsible for the decrease in tensile strength with the increase in lignin content of lignin–HTPB copolyurethane. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Lignin; HTPB; Polyurethane; Copolyurethane; Tensile strength; Diffusion coefficient; Crosslink density

1. Introduction

The synthesis of polymers from renewable resource materials has attracted considerable attention of research workers. In this respect lignin is a source of different functional groups for polymer products. It is an aromatic amorphous biopolymer, which is deposited as a reinforcing agent in plants as mechanical support to the fibrous tissues [1–3]. Although the chemical structure of lignin is very complicated but the main repeat unit is simple 3-(4-hydroxy phenyl) prop-2-eneol [1,4]. Since lignin contains large number of aliphatic and aromatic hydroxyl groups in its structure most of the attempts are concentrated mainly on the preparation of lignin modified phenolic resin by replacing phenol with lignin [5–11], preparation of epoxy polymer [12–14] and also some polyurethanes [15–17]. Preparation of polyurethane from lignin is not an easy process because of the complex structure of lignin, which on direct reaction with diisocyanate gives brittle polyurethane. Glasser and coworkers [15–17] have prepared polyurethane from lignin by reacting different diisocyanates with liquefied lignin by the way of oxyalkylations. Although the basic lignin structure is rigid there is scope to develop flexible polyurethane from lignin by using hydroxy terminated polybutadiene (HTPB). Both the lignin and HTPB will act as polyol and react with a suitable diisocyanate to produce a segmented copolyurethane [18–23].

Polyurethane derived from HTPB has found wide use as solid fuel in rocket, as adhesive sealant and potting compounds [24–26]. These polyurethane binders not only provide better energetics, but it shows adequate mechanical strength. In addition these polyurethanes have excellent low temperature properties. Many researchers have prepared HTPB based polyurethanes and studied their properties like swelling value, crosslinking density, mechanical strength, thermal stability etc. [24–31]. Keeping this aspect in mind we have used hydroxyl terminated polybutadiene as a flexible agent and reacted with lignin and diisocyanate to produce flexible lignin HTPB copolyurethane. In this present work we have prepared different HTPB polyurethanes and lignin-HTPB copolyurethanes by varying the NCO/OH ratio and lignin content. The polyurethanes were characterized by the estimation of NCO groups and

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IR spectroscopy. The mechanical properties and crosslink density of lignin HTPB copolyurethane were measured and compared with those of HTPB polyurethane.

2. Experimental

2.1. Materials

Lignin was collected from the paper industry and used after purification [11]; 2,4-toluene diisocyanate (TDI) (E. Merck, India) and triethylamine (TEA) (S.D. Fine Chem. India) were used as received without purification. The solvents, tetrahydrofuran, dimethylformamide, chloroform and toluene were dried by standard methods [32]. HTPB, synthesized by free radical polymerization, was collected from Vikram Sarabhai Space Centre (VSSC), India. It has an average molecular weight ~2580; viscosity 4880 cp at 30°C; specific gravity 0.90; hydroxyl value 43.2 mg KOH per g and functionality 2.4 [33].

2.2. Synthesis of polyurethane and copolyurethane

The lignin HTPB copolyurethane and HTPB polyurethane were prepared using 2,4-TDI under dry nitrogen atmosphere in the presence of TEA as a catalyst.

2.2.1. HTPB polyurethane

A calculated amount (10 g, 3.88 mmol) of viscous HTPB was dissolved in 40 ml of dry THF in a three-necked flask. The one neck of the flask was fitted with a guard tube, one was used for pouring the reactant and through the third neck dry nitrogen gas was kept flowing continuously in order to maintain inert atmosphere. Then calculated amount of TDI, as per the composition of Table 1, was added dropwise to the HTPB solution at 15°C. After adding a catalytic amount of TEA, the reaction was continued for 25 min at 15°C. In order to get the HTPB polyurethane the reaction temperature was then raised to 45°C and continued for 10 min. A highly viscous solution was obtained and the THF was removed by applying vacuum. Then it was poured onto a flat aluminum mould pretreated with silicone spray for easy release of the HTPB polyurethane sheet.

2.2.2. Lignin–HTPB copolyurethane

In order to get lignin HTPB copolyurethane calculated amount of purified lignin with respect to HTPB in THF:DMF (80:20) solution (Table 1) was added into the HTPB prepolyurethane prepared at 15°C. The temperature was then raised to 45°C and the mixture was stirred well for 10 min. The highly viscous solution of lignin–HTPB copolyurethane was poured on to a flat aluminum mould to get a sheet. Both the sheets were then kept at a room temperature (25°C) for 24 h followed by heating at 80°C for 5 h.

2.3. Estimation of hydroxyl value of lignin

The hydroxyl value of purified lignin was estimated by standard process using acetic anhydride–pyridine mixture and back titration of the acetic acid by standard sodium hydroxide solution [34].

Table 1
Composition and physical properties of HTPB polyurethane and lignin–HTPB copolyurethane

Polymer code	NCO/OH mole ratio (TDI/HTPB)	Lignin (wt.%)[a]	%Hard block[b]	Appearance	Density (g/ml)
PU-I	1.5/1	0	8.82	Yellowish, soft	0.909
PU-I L-1	1.5/1	1	9.64	Brownish, hard	0.918
PU-I L-3	1.5/1	3	11.25	Dark, hard	0.915
PU-I L-5	1.5/1	5	12.80	Dark, hard	0.917
PU-II	2/1	0	11.74	Yellowish, soft	0.913
PU-II L-1	2/1	1	12.51	Brownish, hard	0.920
PU-II L-3	2/1	3	14.02	Dark, hard	0.921
PU-II L-5	2/1	5	15.47	Dark, hard	0.919
PU-II L-10	2/1	10	18.90	Dark, hard	0.928
PU-II L-15	2/1	15	22.06	Dark, hard	0.945
PU-III	2.5/1	0	14.48	Yellowish, hard	0.918
PU-III L-1	2.5/1	1	15.21	Brownish, hard	0.917
PU-III L-3	2.5/1	3	16.62	Dark, hard	0.913
PU-III L-5	2.5/1	5	17.99	Dark, hard	0.925
PU-III L-10	2.5/1	10	21.22	Dark, hard	0.935
PU-III L-15	2.5/1	15	24.20	Dark, hard	0.933

[a] With respect to HTPB.

[b] %Hard block = [wt. of (TDI + lignin)/total wt. of (TDI + lignin + HTPB)] × 100.

2.4. Estimation of free NCO group in prepolyurethane

The free NCO group of HTPB prepolyurethane was estimated immediately after 25 min reaction of HTPB and TDI at 15°C. After 25 min of reaction the residual NCO groups were reacted with a known excess amount of dibutylamine and trichlorobenzene mixture. Then the unreacted dibutylamine was titrated with alcoholic hydrochloric acid using bromocresol green indicator. The free NCO group was calculated using the following formula [35].

$$\%\text{Free NCO group} = [4.2 \times N \times (V_1 - V_2)/(1000W)] \times 100$$

where, V_1 and V_2 are the volumes in ml of HCl solution required for titration of the sample and the blank solutions respectively. W is the weight of the sample in g of the prepolyurethane and N is the normality of HCl.

2.5. IR spectroscopy

IR spectroscopy was used to examine the chemical structures of HTPB polyurethane and lignin HTPB copolyurethane. Thin films of these samples were directly cast from the viscous polymer solution onto the polished surface of potassium bromide disc [36]. Then the IR spectrum was taken in a Shimadzu IR 470 spectrophotometer.

2.6. Density of polyurethanes

The density of the solid cast HTPB polyurethane and lignin HTPB copolyurethane was measured using specific gravity bottle.

2.7. Measurement of swelling characteristics and crosslink density

Volume swelling and crosslink density of HTPB polyurethane and lignin HTPB copolyurethane were measured by immersing the polymer specimen in toluene at room temperature (25°C). In order to measure these properties circular test pieces of 20 mm diameter were die cut from the cast sheets. These were weighed and immersed in toluene at room temperature for 24 h. The specimens were then removed from the solvent, blotted and weighed in a stoppered weighing bottle. Also the thickness of the swollen samples was measured simultaneously. Volume swelling for a specimen was estimated using the Eq. (1).

$$q = \left[\frac{m_2}{m_1} - 1\right] \times \frac{\rho_c}{\rho_s} \tag{1}$$

where, q is swelled volume, m_1 and m_2 are specimen weights before and after swelling respectively. ρ_c and ρ_s are the densities of the specimen and solvent respectively.

Under equilibrium-swollen condition the crosslink density (V_c) and molecular weight between crosslink points (M_c), of the HTPB polyurethane and lignin–HTPB copolyurethane, were calculated by the Flory–Rhener equation (2) [37–39].

$$V_c = \frac{1}{M_c} = \frac{\ln(1 - V_2) + V_2 + \chi V_2^2}{V_s d_r \left(V_2^{1/3} - \frac{V_2}{2}\right)} \tag{2}$$

where, V_s is the molar volume of solvent, V_2 is the volume fraction of polymer in swollen sample, d_r is the density of the polymer and χ is the polymer–solvent interaction parameter.

2.8. Diffusion coefficient measurement

Diffusion coefficient of toluene at 10°C, 35°C and 70°C was calculated from the measurements of swelling of HTPB polyurethane and lignin HTPB copolyurethane as a function of time using Eq. (3) [40,41].

$$\frac{M_t}{M_\alpha} = 1 - \frac{8}{\pi^2} \mathrm{e}^{\left(-\pi^2 Dt/l^2\right)} \left[0.4 \leqslant \frac{M_t}{M_\alpha} \leqslant 1.0\right] \tag{3}$$

where, M_t and M_α are the weight fractions of solvent absorbed at time t and at equilibrium respectively. D is the diffusion coefficient of the solvent. As the thickness of the samples changed during swelling, M_t/M_α was plotted against $t^{1/2}/l$ to account for the thickness change. From the slope of the curve, the diffusion coefficient of the solvent was calculated.

To determine the activation energy of diffusion (E_D) of toluene in HTPB polyurethane and lignin HTPB copolyurethane the swelling in toluene was carried out at 10°C, 35°C and 70°C. E_D was calculated from the slope of the Arrheneous plot of $\ln D$ vs. $1/T$.

2.9. Measurement of sol content

The sol fractions of HTPB polyurethane and lignin HTPB copolyurethane were determined by refluxing the materials in THF for 24 h. After refluxing, the %sol was estimated in two ways. In one way it was obtained from the difference in weights of the polyurethane sample before and after refluxing using the following formula.

$$\%\text{sol} = \left[\frac{(W_1 - W_2)}{W_1}\right] \times 100$$

where W_1 and W_2 are the weights of the dry samples before and after reflux respectively. The %sol was also calculated directly after removing the solvent from the refluxed solution. The isolated sol was then dissolved in chloroform and IR spectrum was taken.

2.10. Mechanical properties

Tensile strength and %elongation at break of both the polyurethane and the lignin HTPB copolyurethane were determined according to ASTM D 638 by a tensile testing machine (KMI, India) at a grip separation speed of 5 cm/min. The dumb-bell shaped test specimens were cut from the cast sheet. Hardness of the specimens was measured by Hiroshima Shore A hardness tester.

2.11. XRD analysis

Wide angle X-ray diffraction study of the purified lignin, HTPB polyurethane and lignin HTPB copolyurethane was carried out using a Cu target in the angular range 10–50° (2θ) by a Phillips electronic X-ray diffractometer (model no. PW 1840).

3. Results and discussion

3.1. Synthesis of polyurethane and copolyurethane

Three different sets of HTPB polyurethane were prepared by varying the NCO/OH (TDI and HTPB) ratio of 1.5:1, 2:1 and 2.5:1. The NCO/OH ratio was calculated according to the hydroxyl value of HTPB. Lignin HTPB copolyurethanes were synthesized by incorporating 1, 3, 5, 10 and 15 wt.% of lignin (with respect to HTPB) into the above three different TDI/HTPB compositions. The composition and physical characteristics of these polyurethanes are given in Table 1. It may be noted from Table 1 that in PU-I series, upto 5 wt.% lignin could be incorporated whereas with higher than this amount of lignin, using 1.5 mol TDI, the copolyurethanes became weak and brittle. This is due to the high hydroxyl value of lignin ($\sim$3597 mgKOH per g), which indicates that 0.06 mol NCO group is required to react with all the hydroxyl groups of 1 g lignin. But in the PU-I set much less amount of TDI was used. Therefore, some quantity of lignin remains as filler in lignin–HTPB copolyurethane. Because of high molecular weight and giant structure, this filler causes poor packing of polymer chains into the network and ultimately the copolyurethanes became brittle. Also with the increase of lignin content the weight% hard block increases in the lignin–HTPB copolyurethane. It was reported that copolyurethanes containing higher weight % of hard block were of a "cheesy" consistency and possessed negligible physical strength [42]. Therefore, in PU-I series the strengths of copolyurethanes containing more than 5% lignin could not be measured.

The process of polyurethane and copolyurethane synthesis consists of two stages. In the first stage the reaction was carried out at 15°C for 25 min. This has been done in order to react only the *para* NCO group of TDI with the hydroxyl group of HTPB. It is reported that the NCO group in the *para* position of TDI is 8–10 times more reactive than that in the *ortho* position at 25°C [43]. With the increase of temperature the reactivity of the *ortho* NCO groups increases at a higher rate than that of the *para*, until at 100°C at which the *ortho* and *para* NCO groups are similar in reactivity. Dubois et al. [44] reported that the second order rate constant ratio of *para* and *ortho* NCO groups of TDI at 30°C is 88 whereas it is 22 at 70°C. Kothandaraman et al. [24] also studied the kinetics of TDI and HTPB prepolymer reaction and found that the activation energy for the reaction of the *ortho* NCO group is higher due to the inductive and steric effects provided by neighbouring methyl substituent in the 1 position than that of the *para* NCO group.

In order to establish this reaction sequence the free NCO groups in all the three prepolyurethanes were estimated after 25 min reaction at 15°C and results are shown in Table 2. It is seen that nearly 50% of total NCO groups of TDI remains unreacted. This result may indicate that after 25 min reaction at 15°C the *para* NCO group of TDI, due to higher reactivity, undergoes reaction with hydroxyl group of HTPB to form the HTPB prepolyurethane leaving unreacted *ortho* NCO terminal.

Simultaneously the IR spectra of all the three prepolyurethanes were taken. The three peaks of the IR spectrum are marked in Fig. 1. In Fig. 1(c), i.e. for NCO/OH ratio 2.5/1, a peak appeared at 3307 cm^{-1}, which corresponds to the N–H stretching of urethane linkage in prepolyurethane. Whereas in case of 1.5/1 and 2/1 NCO/OH ratios (Fig. 1(a) and (b)), instead of this sharp N–H stretching peak at 3307 cm^{-1}, two broad hydroxyl peaks appeared at 3460 and 3436 cm^{-1} respectively. This indicates that some OH groups of HTPB in PU-I and PU-II prepolyurethane remain unreacted because of 2.4 average functionality of HTPB. In this condition to react all the hydroxyl groups of HTPB with the *para* NCO

Table 2
Free NCO group remaining in HTPB prepolyurethane after 25 min reaction at 15°C

Polymer code	NCO/OH mole ratio	%Free NCO group
PU-I	1.5/1	49.83
PU-II	2/1	50.53
PU-III	2.5/1	52.07

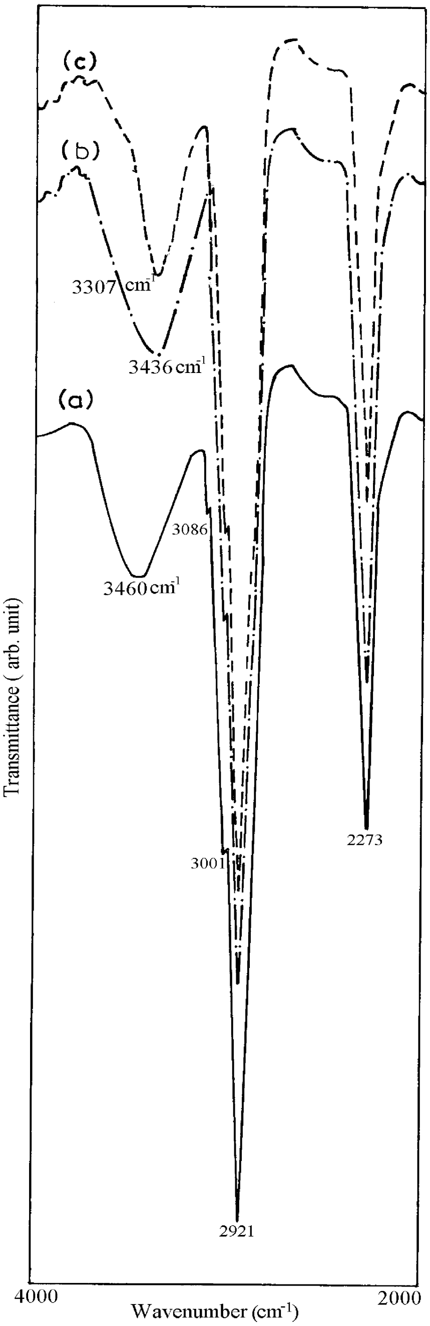


Fig. 1. IR spectrum of HTPB prepolyurethanes taken immediately after 25 min reaction at 15°C, (a) PU-I, (b) PU-II and (c) PU-III.

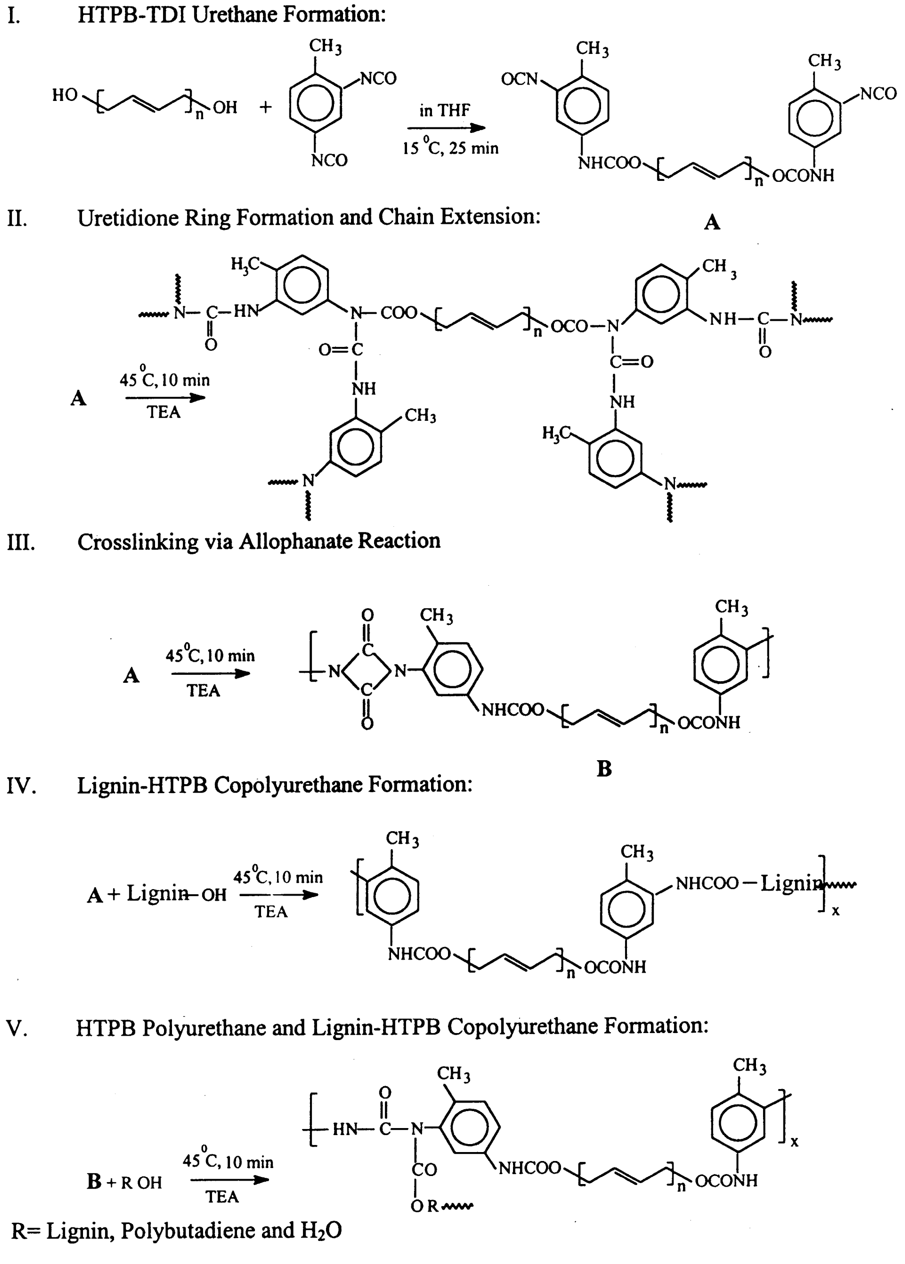
group of TDI, minimum 2.4 mol of TDI is required. This condition is only fulfilled in case of 2.5/1 NCO/OH ratio. Therefore, from these experimental results it can be assumed that the reaction between HTPB and TDI at 15°C for 25 min leads to the formation of *ortho* NCO terminated HTPB prepolyurethane. A reaction scheme is proposed for the polyurethane and copolyurethane synthesis (Scheme 1).

In the second stage the reaction temperature was raised to 45°C and the prepolyurethane solution was stirred continuously for 10 min before casting. At this condition the free *ortho* NCO groups of prepolyurethane undergo various crosslinking/chain extension reactions to result a crosslinked three-dimensional polyurethane structure (Scheme 1, III). After heating at 45°C, the IR spectra of PU-I and PU-II were taken again and it showed no peak for OH group although a peak for urethane N–H stretching was present. This indicates that the unreacted hydroxyl groups of PU-I and PU-II prepolyurethane participated in the crosslinking reaction as shown in Scheme 1 (V). The lignin HTPB copolyurethane was prepared by adding the lignin solution into the HTPB prepolyurethane and the reaction was carried out at 45°C for 10 min. The formation of lignin–HTPB copolyurethane is shown in Scheme 1 (IV) and (V).

3.2. IR spectroscopy

IR spectrum of HTPB was reported elsewhere [27,33]. IR spectra of HTPB polyurethanes have been taken at three different time intervals of the reaction progress. The first spectrum was taken immediately after 25 min of the reaction at 15°C i.e. for prepolyurethane. Fig. 2 shows a representative spectrum of PU-III sample. The second spectrum was taken after heating the polyurethane at 45°C for 10 min and the third spectrum was taken after 5 h heating the sample at 80°C. The spectra have shown a gradual decrease of NCO peak intensities at 2273 cm^{-1}, which ultimately disappeared in the third spectrum taken after heating the sample at 80°C. This indicates that the NCO group of TDI undergoes complete reaction to form three-dimensional crosslinked HTPB polyurethane. Appearance of a strong peak for aliphatic tertiary N–C stretching at 1220 cm^{-1} (Fig. 2) corroborates the crosslink formation as shown in Scheme 1.

The IR spectrum of lignin–HTPB copolyurethane (PU-III L-1) is given in Fig. 3. Comparing the spectra in Figs. 2 and 3 it is seen that the NCO peak intensity at 2273 cm^{-1} has decreased to a large extent. Also a broad peak has appeared at 3460 cm^{-1} for lignin OH group (Fig. 3) whereas the N–H str. peak at 3307 cm^{-1} (Fig. 2) has disappeared in the spectrum of PU-III L-1 (Fig. 3) after the addition of lignin solution. This indicates the formation of urethane linkage between lignin hydroxyl group and NCO group of prepolyurethane. The OH peak at 3460 cm^{-1} (Fig. 3) may be attributed to the higher hydroxyl value of lignin compared to the insufficient NCO groups in PU-III prepolyurethane.



Scheme 1. Reaction scheme for synthesis of HTPB polyurethane and lignin–HTPB copolyurethane.

3.3. Volume swelling

The %volume swelling of the polyurethane and copolyurethane was measured at different time intervals in toluene at room temperature. The results are shown in Fig. 4. Fig. 4 indicates that the %volume swelling steadily increases upto 10 h and after that it nearly remains constant in all the cases. Fig. 4 also indicates that for a specific NCO/OH ratio, the %volume swelling gradually decreases with increasing lignin incorporation. This is due to the higher crosslinking in case of lignin copolyurethane than that of HTPB polyurethane.

Equilibrium volume swelling of the polyurethanes and copolyurethanes in toluene at room temperature was also determined according to Eq. (1) and it is plotted against the amount of lignin incorporation in Fig. 5. The dashed line connecting the two ends represents the average swelling characteristics of the hypo-

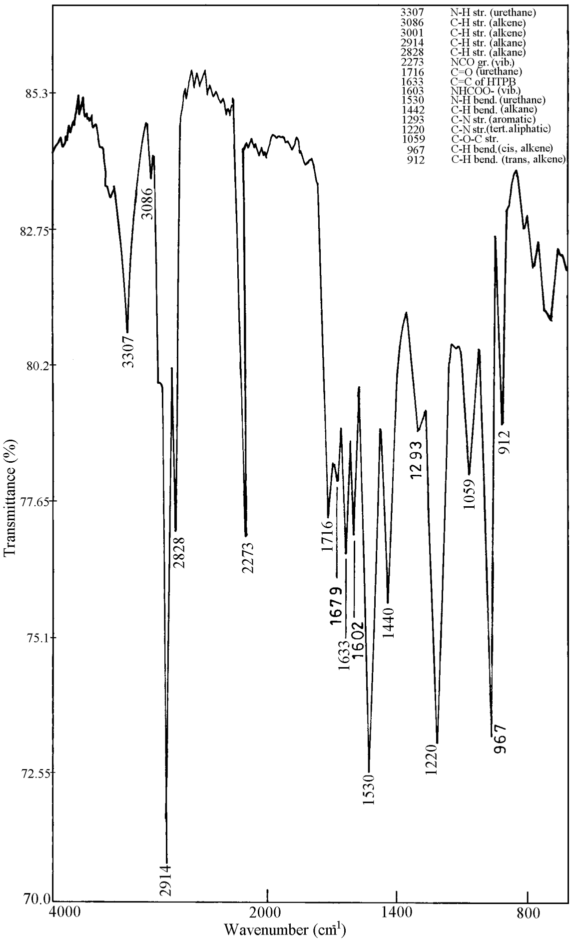


Fig. 2. IR spectrum of HTPB prepolyurethane (PU-III).

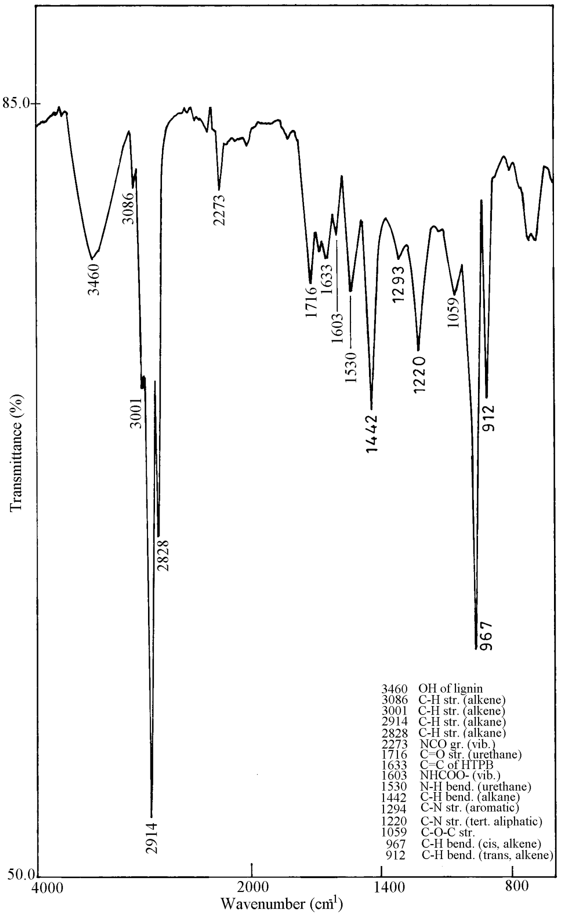


Fig. 3. IR spectrum of lignin–HTPB copolyurethane (PU-III L-1).

thetical copolyurethane of HTPB and lignin having constraints arising out of chain entanglement and chemical bonding between the components. The shape of the experimental curve definitely indicates extreme constraint on the equilibrium swelling. As pure lignin does not swell in toluene the aforesaid constraint suggests the formation of bonding between lignin and HTPB via urethane linkage, which restricts the swelling of the HTPB soft phase in toluene. Therefore, the equilibrium volume swelling decreases as the amount of lignin increases in the copolyurethanes.

3.4. Crosslinking density

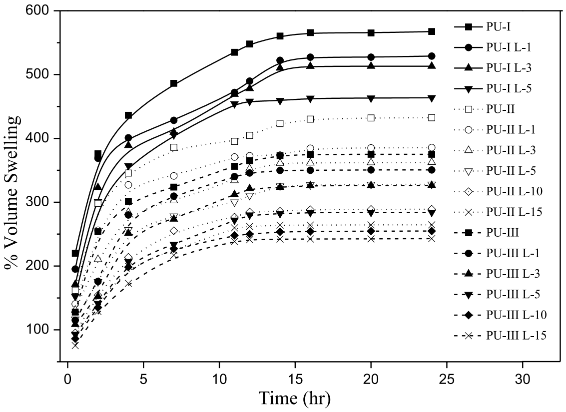


Fig. 4. Percent volume swelling of HTPB polyurethane and lignin–HTPB copolyurethane.

The crosslink density (V_c) of the HTPB polyurethane and lignin–HTPB copolyurethane has been calculated by using Eq. (2) and it is plotted against the amount of lignin present in the copolyurethane in Fig. 6. Fig. 6 shows that the crosslink density increases with increasing NCO/OH ratio of TDI and HTPB. This is due to the presence of more number of reactive NCO groups, which participate into crosslinking reaction. Fig. 6 also

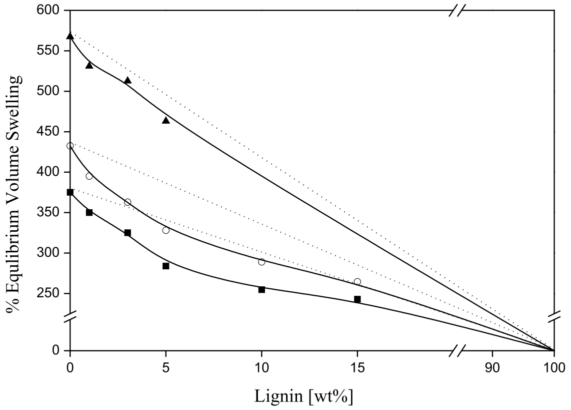


Fig. 5. Percent equilibrium volume swelling of HTPB polyurethane and lignin–HTPB copolyurethane.

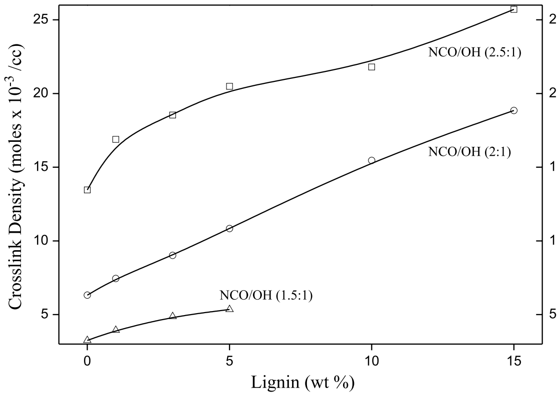


Fig. 6. Crosslink density of HTPB polyurethane and lignin–HTPB copolyurethane.

shows that the crosslink densities of lignin copolyurethanes are significantly higher than that of HTPB polyurethane for a particular NCO/OH ratio. The crosslinking reactions of the lignin copolyurethanes occur according to the proposed reaction paths IV and V in Scheme 1.

3.5. Diffusion coefficient

The diffusion coefficient of toluene at 35°C in HTPB polyurethane and lignin HTPB copolyurethane is calculated according to Eq. (3). Fig. 7 shows the variation of diffusion coefficient with the %lignin incorporation. From Fig. 7 it is evident that the diffusion coefficient decreases with the increase of NCO/OH ratio as well as with the increase of lignin content. In both the cases the crosslink density of the polyurethanes increases. Hence it is apparent that the diffusing species shows higher diffusivity in a lightly crosslinked medium than that in highly crosslinked system.

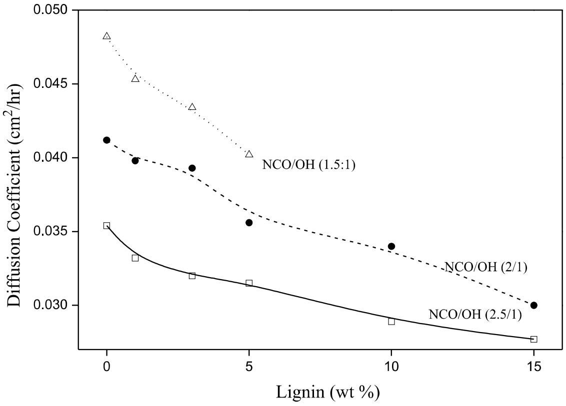


Fig. 7. Diffusion coefficient of toluene in HTPB polyurethane and lignin–HTPB copolyurethane.

In order to measure the activation energy of diffusion (E_D), the swelling experiment was carried out at different temperatures. It is measured only in case of PU-II, PU-II L-15, PU-III, and PU-III L-15 samples. The results show that the activation energies of diffusion of HTPB polyurethanes are less (9.64 kJ/mol for PU-II, 10.27 kJ/mol for PU-III) than those of lignin HTPB copolyurethanes (18.24 kJ/mol for PU-II L-15 and 20.39 kJ/mol for PU-III L-15). These results also correlate well with the results of swelling experiment. The high value of activation energy of diffusion of lignin copolyurethane indicates that it is more resistant to toluene.

3.6. Sol fraction

The soluble fractions of different polyurethanes and copolyurethanes were extracted with THF and the results are shown in Fig. 8. Fig. 8 shows that the %sol fraction gradually decreases with the increase of %lignin in the polyurethane. The %sol also decreases with the increase of NCO/OH ratio. From the structure of HTPB it is known that out of three different OH groups, viz., geraniol (G), 2-hexene 1-ol (H) and vinyl (V), the geraniol OH groups participate in crosslinking and the other two (H and V) act as chain extender. The chain-extended HTPB polyurethane forms cyclic inelastic loops, which do not participate in the crosslink network and remain as the sol fraction [45–49]. In both the HTPB polyurethane and lignin–HTPB copolyurethane the variation in sol content with the increasing lignin quantity is supposed to be dependent on the number of inelastic cyclic loops.

It is to be mentioned that the sol fractions obtained from both the HTPB polyurethane and lignin–HTPB copolyurethane have shown identical IR spectra. The

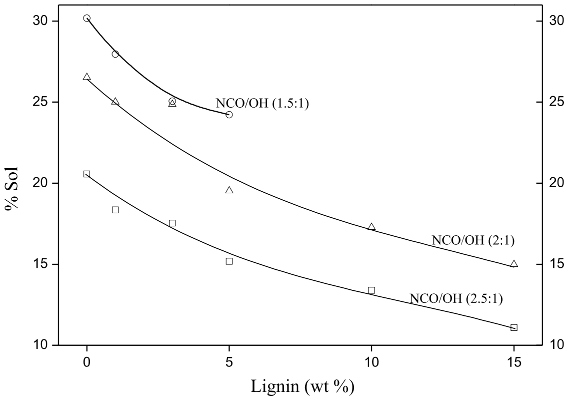


Fig. 8. Variation of sol with lignin content of HTPB polyurethane and lignin–HTPB copolyurethane.

presence of C═O stretching peak at 1717 cm^{-1}, N–H stretching vibration at 3307 cm^{-1}, aromatic C–N vibration at 1530 cm^{-1} and C–O–C vibration at 1220 cm^{-1} indicates that the sol fraction is the low molecular weight HTPB polyurethane which is also reported earlier [27].

3.7. Mechanical properties

The tensile strengths of HTPB polyurethane and lignin HTPB copolyurethane are shown in Fig. 9. Similarly, the hardness and elongation at break of these polyurethanes are shown in Fig. 10. Fig. 9 indicates that these polyurethanes possess lower tensile strength compared with other elastomer [50]. This is because of the lack of rigidity in the soft backbone chain of HTPB in polyurethanes and copolyurethanes. Many workers synthesized the HTPB polyurethanes by varying the different parameters but they achieved maximum tensile strength of 25 kgf/cm^2 only. However, it is reported that HTPB polyurethanes are generally used in products where the requirement of tensile strength and elongation at break are ~8 kgf/cm^2 and 40–50% respectively [26]. From Fig. 9 it is also found that the tensile strength of the polyurethanes increases with the increase in NCO/OH ratio. This higher tensile strength is due to the higher rigidity imparted by the higher crosslink density and intermolecular interaction of the hard domain through hydrogen bonding. Consequently, the hardness of these polyurethanes increases which in turn decreases the % elongation at break (Fig. 10).

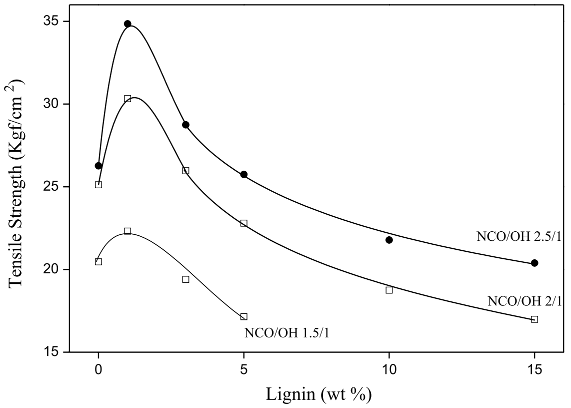


Fig. 9. Tensile strength of HTPB polyurethane and lignin–HTPB copolyurethane.

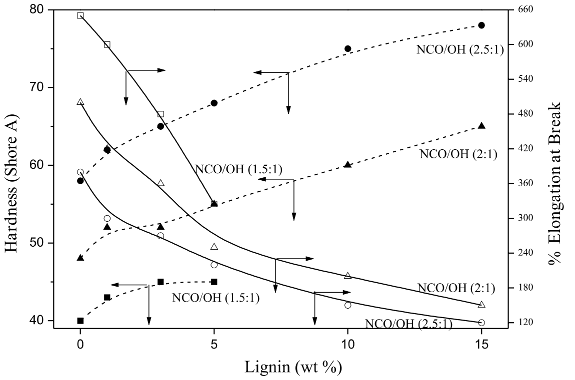


Fig. 10. Hardness (Shore A) and %elongation at break of HTPB polyurethane and lignin–HTPB copolyurethane.

Fig. 9 also indicates that the tensile strength of lignin–HTPB copolyurethane is highest in case of 1 wt.% lignin incorporation and beyond that it gradually decreases. It is also seen from the figure that the tensile strengths of PU-II L-3 and PU-III L-3 containing 3 wt.% lignin are higher than those of HTPB polyurethanes (PU-II and PU-III). The decrease of tensile strength with the increase in lignin content can be explained on the basis of hydroxyl value of purified lignin (~3597 mgKOH per g), which suggests that 60 mmol NCO group is required to react all the hydroxyl groups of 1 g lignin. But in the HTPB prepolyurethane series, PU-I, PU-II and PU-III 5.82, 7.76 and 9.70 mmol NCO groups respectively are available for reaction with lignin hydroxyl groups. So some unreacted lignin remains as filler, which causes the irregularity in the three-dimensional network structure, and consequently the tensile strength of lignin–HTPB copolyurethane decreases. On the other hand, since the crosslink density and the hard segment of the lignin–HTPB copolyurethanes increase with the increase in lignin content, the hardness of these polyurethanes gradually increases with the corresponding decrease in elongation at break (Fig. 10).

3.8. X-ray diffraction study

Wide angle X-ray diffraction study of the purified lignin, HTPB polyurethane and lignin HTPB copolyurethane was carried out using Cu target in the angular range 10–50° (2θ). The X-ray diffractograms in Fig. 11 show broad peaks in the range 14–32° having maxima at 20.3° for PU-I, PU-II and PU-III. These diffractograms indicate that the synthesized polyurethanes are amorphous in nature although there must be some amount of crystalline phase due to the presence of hard segments. This small amount of crystallinity is overshadowed by the presence of long aliphatic hydrocarbon chain of HTPB and the hydrogen bonding between –OCONH–groups of polyurethane. As a result the polyurethanes exhibit overall amorphous character [51].

The wide angle X-ray diffraction of purified lignin (Fig. 11) also shows its amorphous character [52,53]. The inclusion of amorphous lignin has decreased the peak intensity in all the copolyurethanes than that of corresponding HTPB polyurethane (Fig. 11), which was observed by others also [52,53].

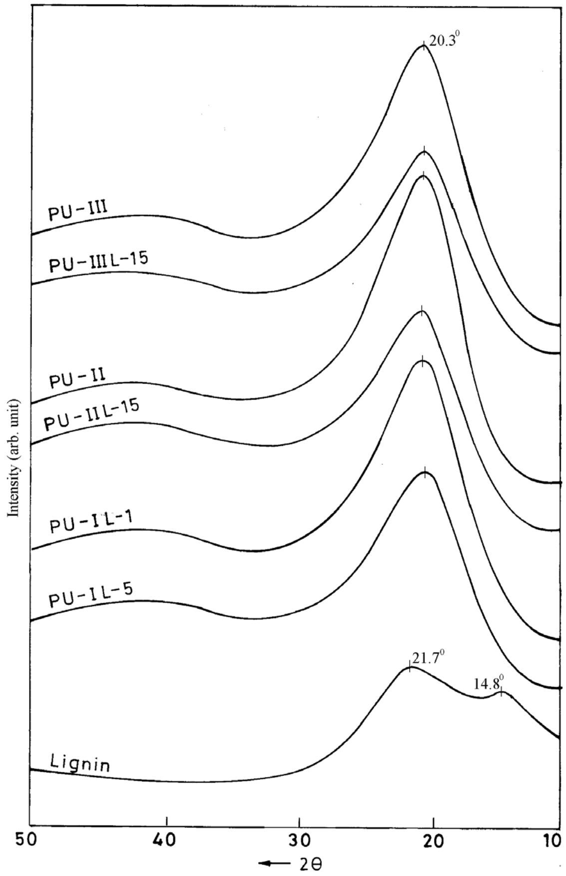


Fig. 11. X-ray diffraction of HTPB polyurethane and lignin–HTPB copolyurethane.

4. Conclusion

The lignin–HTPB flexible copolyurethane has been synthesized by a simple method without oxyalkylation. The differential reactivity of *ortho* and *para* isocyanate groups of TDI helps to form a bridge between HTPB and lignin. Although lignin has been found to form flexible copolyurethane with HTPB but its high hydroxyl value limits its higher loading in the polyurethane structure. With higher amount of lignin crosslink density of the polyurethane becomes high and mechanical properties becomes poor. However, upto 3% lignin incorporation the copolyurethane has shown better properties. Increase in lignin content in the copolyurethane has decreased both the swelling performance in toluene and activation energy of diffusion. Percent sol has also decreased with the increase in lignin content.

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