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Liquefaction of Wood in the Presence of Polyol Using NaOH as a Catalyst and its Application to Polyurethane Foams

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The influences of various reaction parameters (e.g. temperature, time, type and concentration of polyol, and swelling agent) on the extent of liquefaction of the wood meal in polyol, and the properties of the liquefied wood-polyol mixtures have been evaluated. The residue % decreases significantly with the increase of reaction temperature. Similarly, residue % decreases with the increase in reaction time up to 1 h, and also with the increase in NaOH concentration from 0% to 2.5%. Moreover, a polyol:wood weight ratio of 4:6 offers lowest residue. The effects of various formulations for the preparation of polyurethane foams from the concentrated liquefied wood-polyol mixtures on the density, compressive strength and modulus of the resulting foams have also been evaluated. Both molecular weight and concentration of the polyols have profound influence on the residue %, acid and hydroxy values, and molecular weight of the liquefied wood-polyol mixtures as well as ultimate properties of the urethane foams. Once again, with the increase in concentration of blowing agent, e.g. water, both density and modulus of the foams increase, while compressive strength decreases. On the other hand, with the increase in isocyanate index both density and modulus decrease, but compressive strength increases.

KEY WORDS Liquefaction, wood dissolution, polyethylene glycol, glycerol, polyurethane, rigid foam, molecular weight, density, mechanical properties.

INTRODUCTION

Polyurethane foams which are generally produced by the combinations of two primary ingredients, e.g. polyisocyanates and polyols, show a wide range of applications due mainly to its rapid and easy processing, as well as some excellent chemical and physical properties.¹⁻³ However, in recent years there is a positive move towards the replacement of petroleum-based products by renewable resource-based materials. The

advantages of utilizing renewable resources, are multifold, e.g. to save the environment from pollution, to save the petroleum stock, low cost and abundant. Stanford *et al.*⁴ reported the feasibility of deriving liquid polyols and isocyanates from agricultural and wood wastes for polyurethane formation. Kurimoto *et al.*⁵ showed that wood can be partially liquefied (less than 33%) in polyol, and the liquefied wood-polyol concentrates can be combined with polyisocyanate to produce polyurethane foam with substantial strengths. As the resulting polyurethane foam contained a small lignocellulosic loading, this would limit the biomass characteristics in the foams. A mixture of corn starch and wood could be liquefied with polyols, but corn starch alone was easy to liquefy in same solvents.⁶⁻⁸ However, most of the liquefaction of biomass in polyols was studied in presence of acid which was used as the catalyst. Compared to weak acids, like phosphoric and oxalic acids, strong acids, like sulfuric and hydrochloric acids, were very effective catalyst as far as amount of dissolution of biomass were concerned. But, strong acids are highly corrosive and cause environmental pollution.⁹ No report has yet been published on the search of an alternative catalyst for the liquefaction of biomass, e.g. waste wood, in polyols.

In this study, the influences of various reaction parameters on the liquefaction of wood meal (birch) in two types of polyethylene glycol and glycerol, have been investigated. The physical, chemical and mechanical properties of the liquefied wood-polyols, and the polyurethane foams prepared from them have been evaluated.

EXPERIMENTAL

Material

Wood sample used in the liquefaction was 20–80 mesh wood meal of birch. Sodium hydroxide (NaOH), polyols, and other chemicals used in this study, were of reagent grade.

Method

A mixture of wood meal, polyols, aqueous NaOH, or water (70% based on oven-dry weight of wood meal) was heated in a closed pressure-proof tube at 150°C to 250°C for various length of time. The reaction was arrested by cooling in ice-cold water, and liquefied mixture was dissolved in dioxane:water (8:2) mixture. The pH of resulting mixture was measured and then filtered. The residue % was calculated from the oven-dried residue. For the further characterization of liquefied products, the undiluted mixtures were concentrated with an evaporator.

The amount of acid produced in the liquefied products was measured by titrating 1 g concentrated liquefied mixture in 100 ml dioxane:water (6:4) with 0.1 N KOH aqueous solution. The acid amount was expressed in terms of acid value, i.e. the value of milligrams of KOH required to neutralize the acid in one gram of sample.¹⁰ The hydroxy value of the concentrated liquefied mixture is defined as the milligram value of KOH equivalent to phthalic anhydride consumed in the phthalification of one gram of sample,¹⁰ and was measured according to the Japan Industrial Standard (JIS) K-1557. About 1 g sample was first esterified using 25 ml phthalic anhydride

solution in dioxane, and then the extra amount of phthalic anhydride was determined by back-titration with 1 N NaOH aqueous solution.

The molecular weight of the concentrated liquefied mixture was determined in a gel permeation chromatography (GPC: Model 6000A, Waters liquid chromatography) equipped with a differential refractometer R401 detector, and a set of two shodex GPC KF-802 and KF-803 columns (8 mm i.d. \times 300 mm L). THF was used as the mobile phase at a flow rate of 1 ml/min, and molecular weight was determined according to monodispersed polystyrene standards.

For the preparation of foam, a definite amount of concentrated liquefied mixture, surfactant (silicon oil) and catalyst (triethylene diamine) and water were premixed thoroughly in a paper cup, and then prescript amount of polymethylene polyphenyl isocyanate (MDI), at an isocyanate index of 95 to 125, was added and mixed at a stirring speed of 8000 rpm for 10–15 s.⁵ The mixture was immediately poured into a 12 \times 12 \times 10 cm cardboard box. After 1 h, foam was removed from the box and was allowed to cure at room temperature for two days before cutting into 5 \times 5 \times 5 cm test specimens. The compressive properties of the foams were measured in a Shimadzu Autograph DCS-500R. The measurements were done in the direction perpendicular to foam rise at a cross-head speed of 5 mm/min, according to the Japan Industrial Standard (JIS) K-7220 for foam. The compressive strength of the foams were determined as the stress at 10% strain.

RESULTS AND DISCUSSION

Figure 1 shows the effect of residue % on liquefaction temperature for the liquefaction of wood meal birch in polyethylene glycol-400 (PEG-400) using NaOH as a catalyst. It is evident from this figure that residue % decreases significantly with the increase in reaction temperature. For example, the residue % decreases from about 90% to 0% with the increase in temperature from 150°C to 250°C. It is generally accepted that cellulose is a semicrystalline and linear condensation polymer consisting of D-anhydroglucopyranose units joined together by β -1,4-glycosidic bonds.¹¹ Due to its semicrystalline structure, highly hydrogen bonded cellulose cannot be dissolved easily in conventional solvents, unless intracrystalline swelling is established in presence of solvents.¹² Sodium hydroxide is the most often used by industry as a swelling agent. In fact, when alkali ions interact with the cellulose, the water molecules of hydration remain with ions. Thus, the cellulose chains are forced apart and swelling occurs.¹³ Moreover, Vanase *et al.*¹⁴ reported that the liquefaction mechanisms of lignocellulosics, e.g. wood, in organic solvents depend upon the solvent-substrate interaction. The solvent-substrate interactions are more likely to be based on polar interaction complexes perhaps induced via hydrogen bonding. One hypothesis is that the glycol molecules cross-link adjacent cellulosic chains with the diol —OH groups H-bonding with —OH groups of the cellulose. The cellulose matrix then swells, and the cellulosic chains moved enough apart to avoid dehydration and carbonization, which are believed to be processes that occur intramolecularly between the chains.

However, at temperature below about 170°C the glycosidic bonds in cellulose are

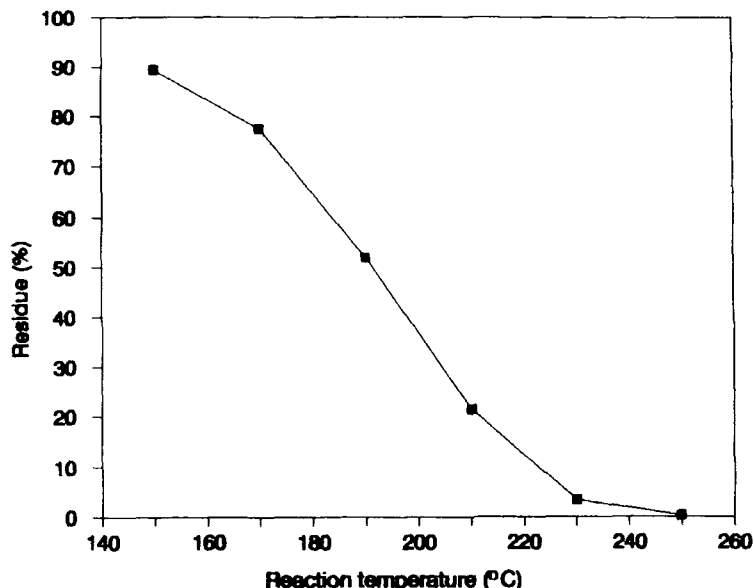


FIGURE 1 The variation of residue (%) with the reaction temperature ($^{\circ}\text{C}$) for the liquefaction of wood meal (birch) in presence of polyethylene glycol-400 using NaOH as a catalyst. Reaction conditions: reaction time, 1 h; polyol:wood, 4:6 (wt. ratio); catalyst concentration, 5 (wt. %).

stable towards alkali, but, when cellulose was heated with sodium hydroxide at temperatures of 170°C and above a considerable fall of DP due to random scission of glycosidic bonds takes place.¹⁵ Therefore, it might be considered that the fragmented cellulose molecules may form new chemical reaction complexes or soluble cellulose derivatives with polyethylene glycol. Wayman and Lora¹⁶ also showed the autohydrolysis and delignification of wood in presence of organic solvents at 175°C and 195°C . In the IOTEC explosion process of wood it was found that hemicellulose and lignin are very easily to degrade compared to cellulose.¹⁷ However, all these types of reactions can enhance the solubility of wood into polyol. Consequently, the residue % decreases sharply with the increase of temperature.

Figure 2 shows that similar to temperature, residue % decreases with the reaction time up to 1 h, and after that the amount of residue increases once again. This phenomenon is similar to what has been observed by Wayman and Lora during the autohydrolysis of aspen which was attributed to the recondensation of the lignins.¹⁶ The same Figure 2, indicates that the pH of the liquefied mixture changes slightly with the increase of reaction time from 15 min to 30 min, and then it levels off with reaction time.

Figure 3 illustrates that in comparison with non-catalytic process, aqueous alkali has a profound effect on liquefaction of wood in presence of polyethylene glycol. For example, with the increase in NaOH concentration from 0% to 2.5%, the residue % decreases and pH increases significantly. On the other hand, with the increase of NaOH concentration from 2.5% to 5% both residue % and pH change, but very slowly. Cellulose swells more in aqueous alkali, like sodium hydroxide, than it does in water, once the alkali concentration reaches a threshold value.¹⁸ It is also obvious

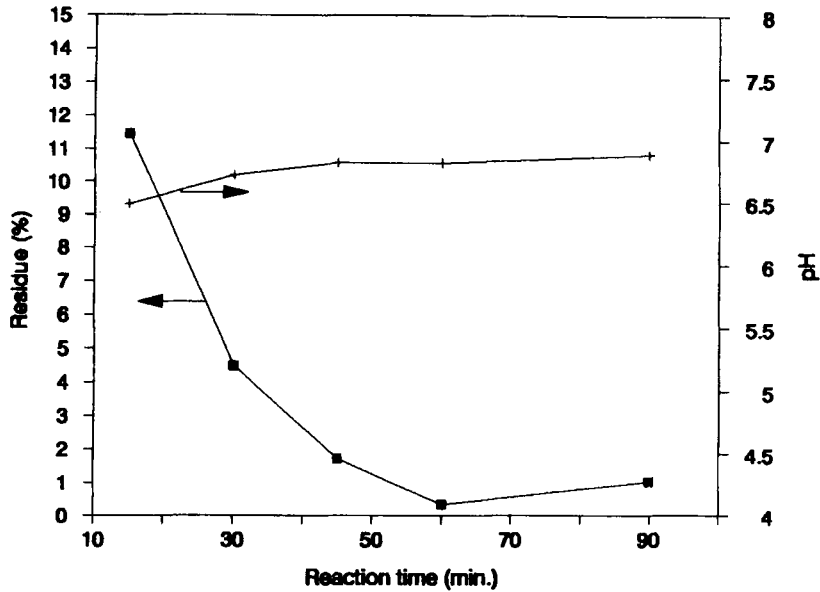


FIGURE 2 The variations of residue (%) and pH of liquefied mixture with the reaction time (min) for the liquefaction of wood meal (birch) in presence of polyethylene glycol-400 using NaOH as a catalyst. Reaction conditions: reaction temperature, 250°C; polyol:wood, 4:6 (wt. ratio); catalyst concentration, 5 (wt. %).

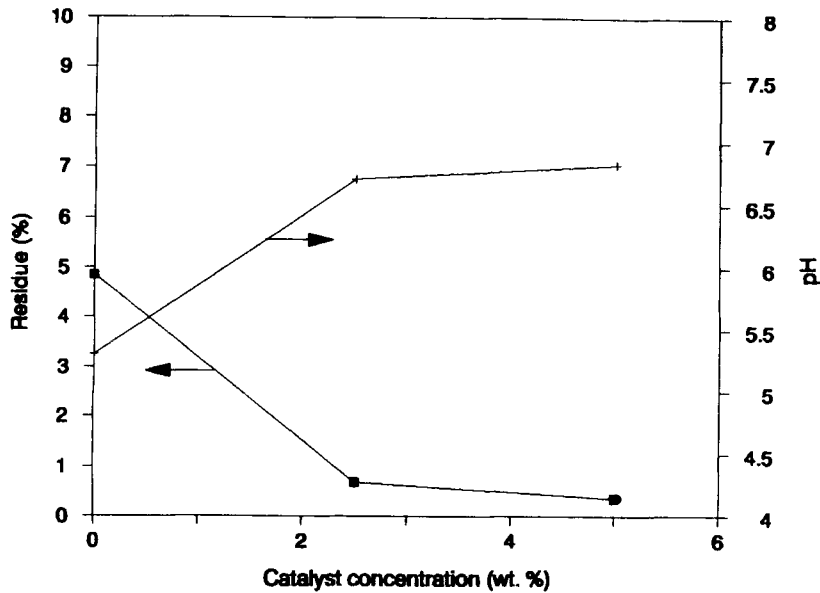


FIGURE 3 The variations of residue (%) and pH of liquefied mixture with the catalyst (NaOH) concentration (wt. %) for the liquefaction of wood meal (birch) in the presence of polyethylene glycol-400. Reaction conditions: reaction temperature, 250°C; reaction time, 1 h; polyol:wood, 4:6 (wt. ratio).

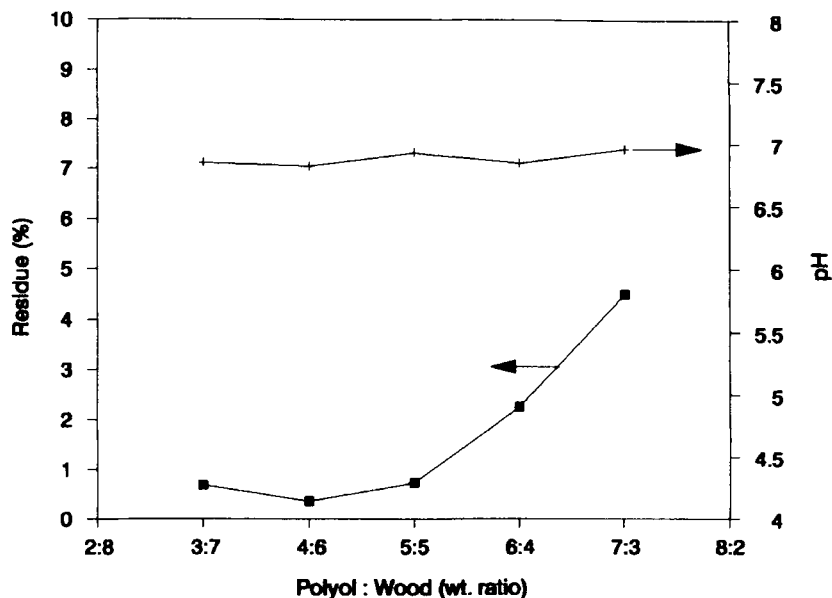


FIGURE 4 The variations of residue (%) and pH of liquefied mixture with the polyol:wood (wt. ratio) for the liquefaction of wood meal (birch) in presence of polyethylene glycol-400 using NaOH as a catalyst. Reaction conditions: reaction temperature, 250°C; reaction time, 1 h; catalyst concentration, 5 (wt. %).

from this figure that the pH of the resulting liquefied mixture is acidic when water was used as a swelling agent, while pH is around neutral (i.e. ≈ 7) for aqueous NaOH used as the swelling agent. Furthermore, the initial pH of liquefaction for the former case was acidic, and for the latter case it was alkaline. As it is mentioned earlier, the glycosidic linkage in cellulose is susceptible to acid-catalyzed hydrolysis similar to those of aqueous alkali.¹¹ Although both acids and alkalies cause degradation under certain conditions, their mode of action and efficiencies are entirely different.¹⁹ As a result, the extents of wood dissolution are different in presence of water and in aqueous NaOH.

The effects of compositions of polyol:wood on the extent of dissolution of wood meal in polyethylene glycol, as well as pH of the liquefied mixtures are presented in Figure 4. From Figure 4, when one compares various polyol:wood weight ratios it appears that a ratio of 4:6 offers lowest residue. However, polyol:wood composition has a negligible effect on pH of the liquefied mixtures. Therefore, the optimum liquefaction conditions of wood meal in polyol can be considered as: temperature, 250°C; time, 1 h; NaOH concentration, 5%; and polyol:wood, 4:6 (wt. ratio).

The extent of liquefaction of wood meal in various polyols (e.g. glycerol, and polyethylene glycols, PEG, -200 and -400) alone and their mixtures is compared in Table I. Table I reveals that residue % for glycerol and PEG-200 are same, but the residue % for higher molecular weight polyol, i.e. PEG-400 is lower compared to those of lower molecular weight polyols. When the residue % for mixtures of PEG-400 and glycerol are compared, it appears that, except for 8:2 and 5:5 wt. ratio of PEG-400 and glycerol which have similar residue, the residue % increases with the

TABLE I

Effect of nature of polyol on the liquefaction of wood meal using NaOH used as a catalyst

Nature of polyol ^a	Residue (%)	pH of liquefied solution
Glycerol	1.39	6.84
Polyethylene glycol - 200	1.39	6.92
Polyethylene glycol - 400	0.35	6.82
Polyethylene glycol - 400 : Glycerol (8:2)	0.69	6.84
Polyethylene glycol - 400 : Glycerol (5:5)	0.69	6.90
Polyethylene glycol - 400 : Glycerol (2:8)	1.04	6.74
Phenol	1.04	4.96

^aReaction conditions: polyol:wood meal (birch), 4:6 (wt. ratio); catalyst, 5 (wt. %); temperature, 250°C; reaction time, 1h.

increase in glycerol content in the mixtures. This fact also indicates that low molecular weight polyols are less efficient solvent for wood dissolution compared to those of higher ones. Once again, the same Table 1 shows that the residue % for phenol is lower than those of glycerol and PEG-200, but higher compared to those of PEG-400. Similarly, Vanasse *et al.*¹⁴ reported that in the presence of creosote oil as a solvent about 97% wood converted to oil, while in presence of ethylene glycol the wood conversions levelled off at values of 60–66%. However, the pH of the liquefied mixtures does not change much with the change in type of polyol.

As it is mentioned earlier in the case of alkali-catalyzed liquefaction the starting pH of liquefaction was alkaline (i.e. pH \approx 9). However, the pH becomes close to neutral (i.e. pH \approx 7) at the end of liquefaction. Therefore, during the course of reaction the pH changes around 2 units. Incidentally, Richards reported²⁰ when cellulose is heated with aqueous alkali in an autoclave at elevated temperatures it breaks down to numerous substances of low molecular weight, mostly acids. The identity of such substances varies with the alkali as well as with the temperature. As a result, in order to calculate the hydroxy value of the liquefied wood-polyol mixtures, the acid value should be measured. In fact, the actual hydroxy value is the sum of acid value and measured hydroxy value (i.e. apparent hydroxy value). The variations of acid value and hydroxy value of liquefied wood-polyol mixtures with the change in compositions of polyol:wood, nature of polyol are listed in Table II. It is obvious from this table that acid value decreases with the decrease in wood content in the mixtures, or with the increase in polyol content. It is quite natural that production of acidic products is proportional to the concentration of wood. On the other hand, both apparent and actual hydroxy values increase along with the concentration of polyol. It is also evident from this table that acid value increases, while hydroxy values decrease with the increase in molecular weight of the polyol. This fact is also

TABLE II

Hydroxy value of liquefied wood meal prepared in the presence of various polyols using NaOH used as a catalyst

Nature of polyol*	Polyol: wood meal (wt. ratio)	Acid value (mgKOH/g) [A]	Hydroxy value (mgKOH/g)	
			Apparent [B]	Actual [A+B]
Glycerol	4:6	20.35	628.55	648.90
Polyethylene glycol - 200	4:6	26.78	284.14	310.92
Polyethylene glycol - 400	3:7	41.04	112.00	153.04
Polyethylene glycol - 400	4:6	34.04	169.99	204.03
Polyethylene glycol - 400	5:5	24.44	193.16	217.60
Polyethylene glycol - 400 : Glycerol (5:5)	4:6	23.30	391.21	414.51

*Liquefaction conditions: reaction temperature, 250°C; reaction time, 1h; catalyst, 5 (wt. %).

TABLE III

Molecular weight of liquefied wood meal prepared in the presence of various polyols using NaOH used as a catalyst

Nature of polyol*	Polyol: wood meal (wt. ratio)	Molecular weight		Polydis- persity
		Number average	Weight average	
Glycerol	4:6	26012	45957	1.76
Polyethylene glycol - 200	4:6	1926	10114	5.25
Polyethylene glycol - 400	3:7	1569	6687	4.26
Polyethylene glycol - 400	4:6	3175	12999	4.09
Polyethylene glycol - 400	5:5	7826	21126	2.69
Polyethylene glycol - 400 : Glycerol (5:5)	4:6	22121	45599	2.06

*Same as Table 2.

true whether polyol alone or a mixture of lower and higher molecular weight polyols are considered.

The effects of concentration and nature of polyol on the molecular weight of the liquefied mixtures are illustrated in Table III. This table reveals that both number and weight average molecular weights increase with the decrease in molecular weight

TABLE IV
Physico-mechanical properties of liquefied wood-based polyurethane foam

Polyol ^a	Polyol: Wood meal (wt. ratio)	Water (wt.%)	Isocya- nate index	Density (g/cc)	Mechanical proper- ties ^b (MPa)	
					Strength X10 ⁻²	Modulus X10 ⁻¹
PEG - 400	4:6	1.5	1.05	0.032	7.63	24.68
PEG - 400	4:6	2.0	0.95	0.041	-	-
PEG - 400	4:6	2.0	1.05	0.029	6.92	38.19
PEG - 400	4:6	2.0	1.15	0.026	6.93	34.58
PEG - 400	4:6	2.0	1.05	0.032	7.06	33.28
PEG - 400	5:5	2.0	1.15	0.029	8.18	36.05
PEG - 200	4:6	2.0	1.15	0.057	10.01	30.01

^aSame as Table 2.

^bCompressive strength at 10% strain.

PEG = Polyethylene glycol.

of the polyol, but increase with the increase in amount of polyol in the mixture. Comparing the molecular weight data with those of residue % (Table I) and both acid and hydroxy values (Table II), it is clear that degradation of wood components by aqueous alkali into low molecular weight fragments enhances with the increase in molecular weight of the polyol or lowering the concentration of polyol. Higher acid value at lower concentration of polyol as well as for higher molecular weight polyol (see Table II) also supports this fact. Although the mechanism of this type of alkaline degradation is unknown higher molecular weight and lower concentration of the same polyol is beneficial to use as a solvent as far as alkali-catalyzed liquefaction of wood is concerned.

The effects of various formulations for the preparation of polyurethane foams from the concentrated liquefied wood-polyol mixtures on the density, compressive strength and modulus of the resulting foams are presented in Table IV. This table shows that with the increase in concentration of blowing agent, e.g. water, both density and modulus of the foams increase, while compressive strength decreases. As a result, the concentration of blowing agent was kept constant for further foam preparations. However, with the increase in isocyanate index both density and modulus decrease, but compressive strength increases. In fact, isocyanate index, i.e. [NCO]/[OH] ratio, is closely related to crosslink density.⁵ When the [NCO]/[OH] ratio is less than 1.0, there will exist untreated hydroxyl group and/or water molecules, which result defect in shell structure and shrinkage. On the other hand, at higher [NCO]/[OH] ratio, excessive —NCO groups may further involve in cross-linking reactions with urethane and urea to produce allophanate linkage and biurate, respectively.¹ As a result, the compressive strength increases along with isocyanate index. When one compares

the properties of the foam prepared from two different polyol content in the liquefied wood-polyol mixtures, it appears that all properties are higher for higher polyol content. This can be attributed to the higher molecular weight and higher residue content for liquefied wood-polyol mixture comparing higher polyol content to those of lower ones. Once again, compared to higher molecular weight polyol, the lower molecular weight polyol results foam with very high density and compressive strength, but lower in modulus. Lower molecular weight, but higher residue content and hydroxy value for the low molecular weight polyol in comparison with those of higher ones, may be the reason for such differences in properties.

CONCLUSION

From the above-mentioned discussions, the optimum liquefaction conditions of wood meal in polyol were found as: temperature, 250°C; time, 1 h; NaOH concentration, 5%; and polyol:wood, 4:6 (wt. ratio). Rigid polyurethane foams could be prepared from concentrated liquefied wood-polyol mixtures and polymeric isocyanate (e.g. MDI). The polyurethane foams thus prepared showed excellent density and mechanical properties. Since the cost of waste wood is inexpensive, the liquefied wood in polyol could be a promising source for a primary ingredient for rigid polyurethane foams.

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