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Microwave-assisted liquefaction of wood with polyhydric alcohols and its application in preparation of polyurethane (PU) foams

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Abstract Microwave radiation was used as the heating source in southern pine wood liquefaction with PEG/glycerin binary solvent. It was found that microwave heating was more efficient than conventional oil bath heating for wood liquefaction. The wood residue content of the H_2SO_4 catalyzed liquefied wood dropped to zero within 5 min with microwave heating. The resulting liquefied wood polyols have suitable hydroxyl values for the preparation of rigid PU foams. Both the compressive strength and apparent modulus of the liquefied-wood-based PU foams increased as the isocyanate index increased from 80 to 120. The foams from H_3PO_4 catalyzed polyols had lower densities than those from H_2SO_4 and the petroleum-based controls. They also showed lower strength and modulus than those from H_2SO_4. Liquefied-wood-based PU foams generally have lower compressive strength and apparent modulus than the petroleum-based controls. However, they showed better restorability from deformation than the petroleum-based controls.

Mikrowellunterstützte Verflüssigung von Holz mit mehrwertigen Alkoholen und deren Anwendbarkeit zur Herstellung von Polyurethanschaumstoff

Zusammenfassung Mittels Mikrowellenstrahlung als Wärmequelle wurde Southern Pine Holz mit PEG/Glycerin als binärem Lösungsmittelsystem verflüssigt. Es zeigt sich, dass Holz mittels Mikrowellenerhitzung effizienter verflüssigt werden kann als mittels konventioneller Erhitzung im Ölbad. Der Restholzanteil des mit Katalysator H_2SO_4 verflüssigten Holzes fiel nach fünfminütiger Mikrowellenbeheizung auf Null. Die Hydroxylzahlen der so verflüssigten Holzpolyole sind für die Herstellung von PU-Hartschaumstoff geeignet. Sowohl die Druckfestigkeit als auch die Steifigkeit der PU-Schaumstoffe aus verflüssigtem Holz nahmen mit steigendem Isocyanatindex von 80 auf 120 zu. Die Schaumstoffe der mit Katalysator H_3PO_4 erzeugten Polyole wiesen geringere Dichten auf als diejenigen mit Katalysator H_2SO_4 und als Schaumstoffe auf Mineralölbasis. Die Festigkeit und der E-Modul waren ebenfall geringer. PU-Schaumstoffe auf Basis von verflüssigtem Holz wiesen generell eine niedrigere Druckfestigkeit und eine niedrigere Steifigkeit auf als die Kontrollproben auf Mineralölbasis. Allerdings zeigten sie ein besseres Rückverformungsverhalten als die Kontrollproben auf Mineralölbasis.

1 Introduction

Polyurethane (PU) foams are materials with great versatility and have been widely used for insulation, packaging, furniture cushioning, and much more. The pore size and density of these foams can be easily manipulated to meet their application needs. Polyols (polyether and polyester) and isocyanate are the two main raw materials for PU foam production and currently are obtained from fossil resources. The

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major drawback of petroleum-based products is that they are non-renewable and not-biodegradable. Due to increasing concerns over dwindling fossil resources and the environmental impact from petroleum-based products, obtaining polyols from renewable biomass has become an attractive alternative for the polyurethane industry. Most biomass consists of cellulose, hemicelluloses, and lignin that contain more than one hydroxyl group in the molecular chains, which in turn can be used as an alternative to petroleum-based polyols for preparing polyurethane materials.

Two different approaches have been attempted to apply biomass in polyurethane material production. One method was to directly incorporate biomass, such as starch, lignocellulose, lignin, coffee grounds, bark, and so forth, in polyurethane formulations (Hostettler 1979; Koch and Roper 1988; Yoshida et al. 1987). It was reported by Hatakeyama et al. (1995) that rigid polyurethane foams that contained as much as 50% biomass can be obtained by mixing biomass materials with petro-based polyols before foaming. However, most of this biomass only acted as solid filler rather than as reactive components in the foam structures, and as a result, foams with high densities were apt to be obtained. Another approach was to apply biomass via the hydroxyalkylation reaction. Different types of biomass such as sorbitol (Wilson and Fowler 1958), sucrose (Wismer et al. 1963), methyl glucoside (Hostettler et al. 1963), and lignin (Wu and Glasser 1984; Allan 1969) have been studied and polyols with desirable hydroxyl values and viscosities have been obtained by this method. These polyols have been used as the starting materials for the manufacture of rigid polyurethane foams with great functionalities (Ferrigno 1967).

Liquefaction of biomass in the presence of organic solvents is an emerging research area to convert lignocellulosic materials such as forestry and agricultural residues into value-added products (Shiraishi et al. 1985; Shiraishi and Kishi 1986). Different organic solvents have been used in liquefaction reaction, and polyhydric alcohol is one of the most used solvents. Liquefied biomass prepared with polyhydric alcohols is rich in hydroxyl groups (Yao et al. 1993). One of the most promising applications of this liquefied biomass is to prepare polyurethane materials. It has been shown that liquefied wood using polyhydric alcohols as liquefaction solvents can be used directly as polyols to prepare PU foams without any additional treatment (Yao et al. 1995; Lee et al. 2000; Yan et al. 2008; Yao 1996).

Most biomass liquefactions in the past were carried out with conventional convective heating source such as oil bath, salt bath, fluidized sand bath, and electrical furnace. A few studies applied microwave as the heating method in wood liquefaction (Krzan and Kunaver 2006; Krzan and Zagar 2009). The use of microwave heating in organic synthesis was introduced in 1986 (Kappe 2008). Microwave irradiation directly couples microwave energy with the molecules that are present in the reaction mixture with dipolar polarization and ionic conduction (Kappe 2008). The main advantage of microwave heating over conventional heating is that the microwave irradiation penetrates and simultaneously heats the bulk of the material and therefore reduces reaction time from hours to minutes. Ethylene glycol, the monomer of polyethylene glycol (PEG), has a loss tangent ($\tan\delta$) value of 1.35, which is among the highest $\tan\delta$ value of common solvents (Kappe 2008). The higher the $\tan\delta$ value of a solvent, the better absorption and more efficient heating capability the solvent has under microwave irradiation. Therefore, wood liquefaction with PEG using microwave as the heating source has great potential to reduce reaction time and save energy.

The purposes of this study were to (1) compare wood liquefaction with PEG under microwave and conventional oil bath heating; (2) prepare and characterize the liquefied wood polyols obtained under microwave heating; and (3) evaluate the performances of the PU foam from the liquefied wood polyols.

2 Materials and methods

2.1 Materials

Wood meal (southern pine, *Pinus sp.*, 40 to 60 mesh) was oven-dried at 105°C for 24 hours before use. Polyethylene glycol #400 ($M_w = 400$), glycerin, diphenylmethane diisocyanate (MDI), dibutyltin dilaurate (DBTDL), and silicone surfactant SH193 were obtained from commercial sources and used as received. All other chemicals were of reagent grade.

2.2 Microwave-assisted liquefaction

PEG and glycerin were used as the liquefaction reagent at the ratio of 70/30 (w/w) and the solvent to wood ratio was 7/1 (w/w). Two different acid catalysts (sulfuric acid and phosphoric acid) were used in the liquefaction at 3% based on the weight of the PEG/glycerin mixture. The liquefactions were carried out in a microwave system (Ethos EX, Milestone, 25 Controls Drive, Shelton, CT, USA) equipped with an independent controller (Model 640 Terminal, Milestone) that has a temperature sensor inserted directly into the sealed 100 mL Teflon reaction vessels. A typical liquefaction procedure for the experiments was as follows: 2 g wood meal, 14 g PEG/glycerin, and 0.42 g acid catalyst were loaded into the Teflon reaction vessel, and pre-mixed thoroughly by stirring before liquefaction. The liquefaction temperature was increased from room temperature to 150°C at a heating rate of 65°C/min and then was kept at 150°C for 7 min. After the desired liquefaction time, the reaction vessel was immersed in cold water for at least 15 min before opening. Sodium hydroxide aqueous solution (48%) was added to neutralize the acid after liquefaction, and the neutralized liquefied wood was stored in refrigerator before use.

Conventional heating wood liquefaction was also conducted in an oil bath, and the experimental procedures were the same as the microwave heating other than using oil bath as the heating source.

2.3 Characterization of the liquefied wood polyols

2.3.1 Percentage of un-liquefied wood residues

Approximately 1 g liquefied wood polyols was dissolved in 20 mL methanol in a beaker and stirred for 4 hours. The diluted solution was then vacuum-filtered through a glassfiber filter. The solid residues were dried in an oven at 105°C to a constant weight. The percentage of un-liquefied wood residue content was calculated by (1):

$$R(\%) = (m_1/m_0) \times 100 \tag{1}$$

where R is the percentage of residue content (%), m_1 is the oven-dried weight of the solid residue, and m_0 is the oven-dried weight of the starting wood meal.

2.3.2 Viscosity

The viscosity of the liquefied-wood-based polyols was measured by a Viscosity Centipoise 98936 series viscometer (Cole-Parmer Co., 625 East Bunker Court, Vernon Hills, IL USA) in accordance with ASTM D 4878-08. All the tests were conducted at 25 ± 0.1°C.

2.3.3 Acid number

The acid number of the liquefied wood polyols was measured according to ASTM D 4662-08. Approximately 1 g of the liquefied mixture was diluted to 20 times its weight with methanol, and then titrated with 0.1 N potassium hydroxide (KOH) aqueous solution. The change in pH was monitored by a pH meter equipped with a composite glass electrode. The neutralization volume of the sample was obtained from the neutralization plot. The acid number (i.e., milligrams of KOH required to neutralize the acid in one gram of sample) was calculated as follows:

$$\textit{Acid number}\ (\text{mg KOH/g}) = \frac{56.1 \times V \times N}{W} \tag{2}$$

where the number 56.1 is the molecular weight of KOH, V is the amount of KOH solution consumed at the neutralization point, N is the equivalent concentration of KOH solution used, and W is the weight of the sample.

Table 1 Foam formulations for liquefied-wood-based polyols
Tab. 1 Schaumstoffformulierungen der auf verflüssigtem Holz basierten und mittels Schwefelsäure als Katalysator gewonnenen Polyole

	Ingredients	Parts by weight
A part:	1. Biomass-based polyol	100
	2. Catalyst (DBTDL)	1–1.5
	3. Surfactant (SH-193)	2–2.5
	4. Water (blowing agent)[a]	2–4.25
	5. PEG #400 (additive)	15
B part:	MDI (at isocyanate index from 80–120)	100–240 (H_2SO_4)[b] 160–300 (H_3PO_4)[c]

[a] Including the water from the NaOH solution using for neutralization after liquefaction

[b] Amount of MDI used for polyols from H_2SO_4 catalyzed liquefaction

[c] Amount of MDI used for polyols from H_3PO_4 catalyzed liquefaction

2.3.4 Hydroxyl number

The hydroxyl number of liquefied wood polyols was measured as the amount of KOH equivalent to the phthalic anhydride consumed in the phthalation of one gram sample. (ASTM D 4274-05) One gram (1 g) of liquefied wood sample was first esterified using 25 ml phthalic anhydride/pyridine mixture solution, and then the extra amount of phthalic anhydride was back-titrated with 0.5 N aqueous sodium hydroxide (NaOH) solution.

The hydroxyl number of a significant acidic sample should be corrected by the acid number of the sample. The hydroxyl number was then calculated as the following equation:

$$\textit{Hydroxyl number}\ (\text{mg KOH/g}) = [(B - C) \times N \times 56.1]/W + A \tag{3}$$

where B is the volume of the NaOH solution used for the blank titration of phthalic anhydride-pyridine reagent, C is the volume of the NaOH solution consumed in the back-titration of the sample, N is the equivalent concentration of NaOH solution, number 56.1 is molecular weight of KOH, W is the weight of the sample, and A is the acid number of the sample.

2.4 Preparation of rigid polyurethane foam

The formulations of the liquefied-wood-based polyurethane foam are listed in Table 1. As an initial step various amounts of biomass-based polyols, catalyst, surfactant, and water were pre-mixed thoroughly at a desired ratio in plastic cups. The calculated amount of MDI (based on an isocyanate index of 80 to 120) was then added and mixed quickly with a high speed (8,000 rpm) mixer for 10–15 seconds. The mixture was then immediately poured into a $17 \times 13 \times 13\ \text{cm}^3$

cardboard box and was allowed to rise freely at room conditions. Foam was removed from the box after one hour and was allowed to cure at room temperature for two days before cutting into test samples. The isocyanate index was calculated as follows:

$$Isocyanate\ index = \frac{M_{\mathrm{MDI}} \times W_{\mathrm{MDI}}}{M_{\mathrm{LB}} \times W_{\mathrm{LB}} + 2 \times W_W/18} \times 100 \quad (4)$$

where M_{MDI} is the amount of isocyanate groups per gram of MDI, W_{MDI} is the weight of MDI, M_{LB} is the hydroxyl number per gram of liquefied biomass-based polyol, W_{LB} is the weight of liquefied wood polyols, and W_W is the weight of water in the foam formulation.

A small amount of PEG #400 was added to improve the mixing efficiency and the foamability of the ingredients. Instead of using triethylene diamine, dibutyltin dilaurate, an organic tin catalyst, was used in the foam formulation.

2.5 Physical and mechanical properties of the rigid polyurethane foams

The foams were cut into 50 mm × 50 mm × 50 mm specimens for testing of the physical and mechanical properties. Approximately 15 to 20 specimens were cut from each $17 \times 13 \times 13\ \mathrm{cm}^3$ foam block. All specimens were conditioned for 48 hours at 23°C and 50% relative humidity before test. The foam specimens were callipered and weighted to determine the density (ASTM D 1622-08). Testing of mechanical properties of the foams was based on ASTM D 1621-04a. The compressive properties of the foams were tested by an INSTRON 4465 mechanical tester. The measurements were made in the direction perpendicular to the foam rise at a constant crosshead speed rate of 5 mm/min. The compressive strengths of the foams were determined as the stresses at the yield point of approximately 13% strain of the specimen deformation. Five replications were measured for every foam formulation.

3 Results and discussion

3.1 Residue content and apparent viscosity of liquefied wood polyols

The wood residue contents of the liquefied wood using two different acid catalysts and two heating methods at various reaction times are shown in Fig. 1. As can be seen, liquefied wood using sulfuric acid (H_2SO_4) as the catalyst had substantially lower residue content than that using phosphoric acid (H_3PO_4). Wood meal was almost completely liquefied within 2 min by microwave heating at 150°C. With conventional oil bath heating, however, the residue contents dropped rapidly to 32% in the initial 5 min, and then decreased gradually as the reaction time increased to 30 min, where it reached almost zero. The residue content with phosphoric acid as the catalyst also exhibited similar trend as that with H_2SO_4 when using microwave heating. It dropped to 41% within 5 min at the initial stage of the liquefaction, and then leveled off as the reaction time increased. However, with conventional oil bath heating, more than 90% of the wood meal had not been liquefied in the first 30 min. Then the residue content decreased very slowly with the increasing reaction time. The residue contents remained as high as 78% at 120 min of reaction.

The most interesting and significant point of the result is the drastic decrease in residue contents with microwave liquefaction during the initial period for both sulfuric and phosphoric acid catalysts. Traditional heating depends on convection currents and the thermal conductivity of the materials that must be penetrated, and often results in the temperature of the reaction vessel being higher than that of the reaction mixture (Krzan and Zagar 2009). In contrast, microwave irradiation heats the bulk of the materials simultaneously by dipolar polarization and ionic conduction. The ability of a specific material or solvent to convert microwave

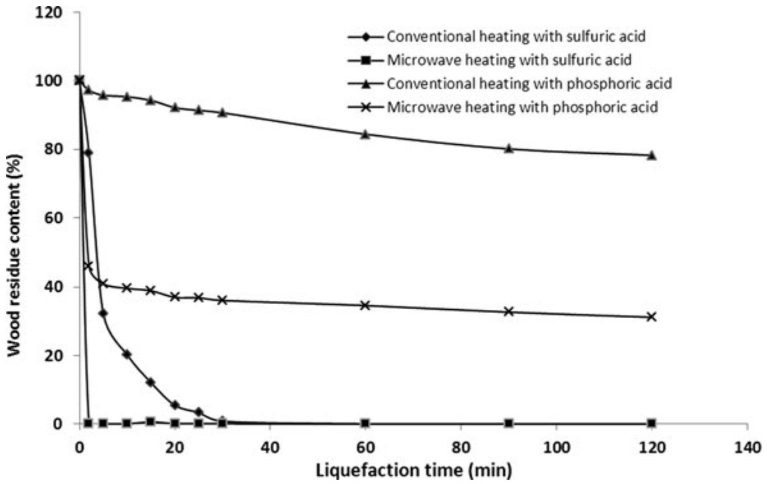


Fig. 1 Wood residue content as a function of reaction time of the liquefied wood with two heating methods and two catalysts
Abb. 1 Restholzanteil in Abhängigkeit der Reaktionszeit und in Abhängigkeit von zwei Heizverfahren und zwei Katalysatoren

Table 2 Some physical properties of the biomass-based polyols obtained under microwave heating

Tab. 2 Verschiedene physikalische Eigenschaften der Polyole, erzeugt aus Biomasse mittels Mikrowellenerhitzung

Liquefaction conditions[a]		Apparent viscosity (cP)	Residue content[b] (%)
Acid catalyst	Reaction time (min)		
H_2SO_4	5	1420	0
	30	1450	0
	60	1480	0
	120	1720	0
H_3PO_4	30	7500	4.53
	60	5900	4.33
	120	4200	3.94
PEG #400		140	–
PEG #400/glycerin (70/30, w/w)		360	–

[a] Liquefaction conditions: PEG # 400/glycerol/acid = 70/30/3 (w/w/w) Wood/Solvent = 1/7 (w/w); Reaction temperature, 150°C

[b] Based on the weight of whole mixtures (wood + solvent)

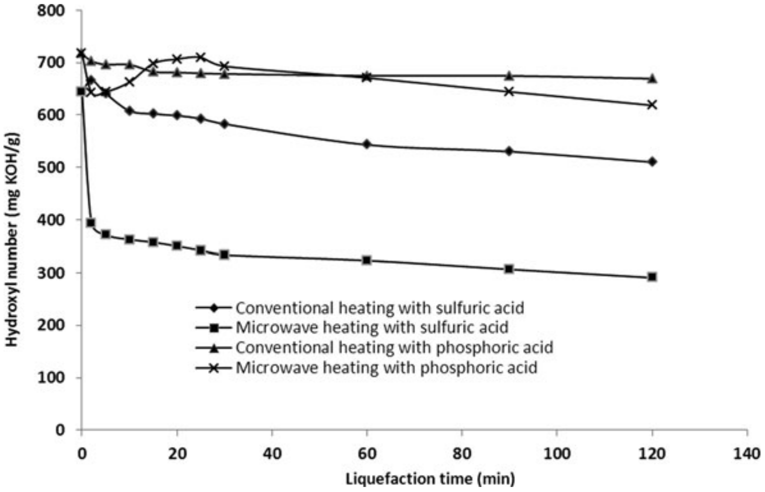
energy into heat at a given frequency and temperature is determined by the $\tan\delta$ of that material. In general, a reaction medium with a high $\tan\delta$ has a good absorption of microwave energy and results in efficient heat. Ethylene glycol has a high $\tan\delta$ value of 1.35, compared to that is 0.123 of water (Kappe 2008). When PEG, the polymer form of ethylene glycol, was used as the liquefaction solvent and subjected to microwave heating, the temperature of the reaction system increased very quickly to the required temperature, and the liquefaction reaction likely reached an equilibrium stage within 3 to 5 min. The reaction could then be controlled by some other factors, such as the efficiency of the catalyst, rather than liquefaction temperature.

As can be seen in Fig. 1, the liquefaction quickly reached zero residue content with sulfuric acid as the catalyst. This result implied that the potential benefit of the microwave enhancement is to require using a lesser amount of concentrated acid, or to lower the acid concentration to attain a satisfactory liquefaction, as in using much higher catalyst contents with conventional heating. In addition, a fast liquefaction time is an important factor contributing to the process flexibility to achieve process improvements, such as for the development of a continuous liquefaction reactor. It is well recognized that the use of H_2SO_4 will lead to many negative effects, such as the serious corrosion of equipment as well as environmental pollution. Thus, these positive enhancement effects with microwave heating seem to provide a mean to ameliorate the negative aspects of using the sulfuric acid in the liquefaction process.

In the case of phosphoric acid, the enhanced catalytic effects with microwave also promote the liquefaction reaction and attain the minimum wood residue contents faster than in conventional heating. It should be noted that, in addition to a catalytic effect, the use of phosphoric acid is also known to chemically activate lignocellulosic materials (Hsisiheng et al. 1998; Diao et al. 2002). Studies have shown that during thermal treatment, phosphoric acid pretreated lignocellulosics begin to lose carbonyl and methyl groups in hemicelluloses at 50°C; the composition of lignin started to change at 100°C; substantial oxidation of cellulose to form ketones occurred at 150°C (Jagtoyen and Derbyshire 1989); and the bond cleavage reactions of the biopolymer chains occurred around 150°C (Solum et al. 1995). Thus, it is likely that these chemical activation reactions by phosphoric acid might all be involved in the wood liquefaction reaction over this temperature range. A study to evaluate the effect of these chemical activation reactions with H_3PO_4 on the reaction of wood liquefaction is in progress.

The apparent viscosities of the liquefied wood polyols obtained from liquefactions with microwave heating are listed in Table 2. On average, the liquefied wood polyols with H_2SO_4 catalyst yielded consistently lower viscosity than that with H_3PO_4 catalyst. This is to be expected, due to the stronger acidity of H_2SO_4 than H_3PO_4, sulfuric acid catalyzed liquefied wood resulted in complete wood liquefaction without wood residue, which in turn yielded lower viscosity. However, it is interesting to note that the effects of the reaction time are different on the apparent viscosities of those polyols catalyzed with H_2SO_4 and H_3PO_4. The apparent viscosity of the polyols catalyzed by H_2SO_4 increased while it decreased with polyols catalyzed by H_3PO_4 as the reaction time increased. It is likely that the increase in viscosity with H_2SO_4 was mainly due to the recondensation of degraded lignocellulosic materials, because a tar-type substance was observed in the liquefied wood catalyzed by sulfuric acid with microwave heating. The occurrence of recondensation liquefied wood between decomposed wood components and/or liquefaction solvent has been reported previously (Kobayashi et al. 2004). As for the H_3PO_4 catalyst, the decrease in viscosity may appear to relate to the decrease in residue contents with increasing reaction time as shown in Table 2, yet the minute difference in residue contents is not expected to exert such a significant effect on the viscosities. The chemical activation of woody component of liquefied wood by H_3PO_4 as mentioned earlier could likely be a factor for the observed result. As indicated previously,

Fig. 2 Hydroxyl number as a function of reaction time of the liquefied wood polyols with two heating methods and two catalysts
Abb. 2 Hydroxylzahl in Abhängigkeit der Reaktionszeit und in Abhängigkeit von zwei Heizverfahren und zwei Katalysatoren



a study to evaluate the effect of these chemical activation reactions with phosphoric acid on the reaction of the wood liquefaction is in progress and the result will be published separately.

In the study, the viscosity of the polyols with conventional oil bath heating was not measured. It has been reported that the viscosity of the liquefied wood obtained by traditional heating is as high as 270,000 cP and is much higher than the values in this study (Kurimoto et al. 1999). However, the values listed in Table 2 are somewhat larger than those of the fossil-based polyols, but are still suitable for the preparation of polyurethane foam.

3.2 Hydroxyl and acid number of liquefied wood polyols

The hydroxyl number is a measure of the concentration of the hydroxyl groups on the polyol. It is an important parameter that needs to be monitored during polyol production. The time-dependent changes in hydroxyl number of the liquefied wood polyols are shown in Fig. 2. It can be seen that microwave heating had a more profound effect on the hydroxyl number of the liquefied wood polyols catalyzed by H_2SO_4 than that by H_3PO_4. For liquefied wood catalyzed by H_2SO_4 with microwave heating liquefaction, the hydroxyl number dropped almost 45% compared to the starting value, within 2 min, and leveled off thereafter with the prolongation of reaction time. In conventional oil bath heating, it first increased at the early stage of the liquefaction and then decreased slowly with the increase of reaction time. Microwave heating showed less significant effect on the hydroxyl number of polyols obtained from phosphoric acid catalyzed liquefaction. However, the changes of the hydroxyl number followed a more complicated pattern under microwave heating than that of conventional oil bath heating. It decreased at the first 2 min of the reaction and then gradually increased in the following 30 min and again decreased when the reaction time further increased to 120 min. With conventional heating, it simply decreased slowly during the whole investigated liquefaction time.

Other than the substantial decrease of the hydroxyl number of H_2SO_4 catalyzed and microwave heated liquefied wood polyol, all other liquefied wood polyols showed little changes in the value of hydroxyl numbers compared to the starting point. They generally decreased slowly with the increasing liquefaction time. In addition, all significant changes of the hydroxyl numbers occurred within the 2 to 30 minutes of the liquefaction. The hydroxyl number of liquefied solvent (i.e., PEG and glycerin) was used as the starting point in the plot because the hydroxyl groups in solid wood were inaccessible (Yao et al. 1996). It would assume that the hydroxyl groups will be liberated with the progress of liquefaction, which will increase the hydroxyl number of the liquefied wood polyols at the early stage of liquefaction as reported by Yao and co-workers (Yao et al. 1996). However, most polyols in this study had decreased hydroxyl number at the early stage of the liquefaction except for the polyols with sulfuric acid as catalyst under conventional heating. This result might be due to the oxidation and recondensation reactions among the liquefaction solvent and decomposed wood components that took place immediately after the beginning of the liquefaction and consumed plenty of hydroxyl groups (Hassan and Shukry 2008; Wang and Chen 2007). In this experiment, a tar-type substance was observed in the liquefied wood catalyzed by H_2SO_4 with microwave heating, which indicated the occurrence of recondensation between decomposed wood components and/or liquefaction solvent and wood components. In addition, liquefied wood polyols obtained at this condition showed the lowest value of hydroxyl numbers among all investigated polyols in this study. Apart from the recondensation reaction, the dehydration reaction between the acid substances derived from the decomposed wood components and the polyhydric alcohol (i.e., liquefaction solvent) could

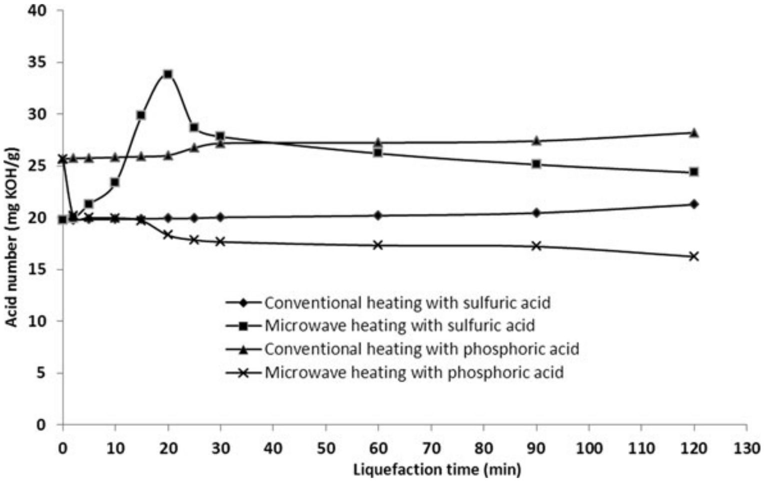


Fig. 3 Acid number as a function of reaction time of the liquefied wood polyols with two heating methods and two catalysts

Abb. 3 Säurezahl in Abhängigkeit der Reaktionszeit und in Abhängigkeit von zwei Heizverfahren und zwei Katalysatoren

also cause the decrease of the hydroxyl number of the liquefied wood polyols (Hassan and Shukry 2008).

Liquefied wood polyols were acidic due to the acid catalyst used during liquefaction as well as the acidic substances generated from decomposed wood components, mainly cellulose and hemicelluloses. Figure 3 shows the changes of acid number of liquefied wood polyols as a function of reaction time. A distinct difference in the relationship of acid number and liquefaction time existed as affected by two heating methods and two acids. While the sulfuric acid catalyzed polyols with microwave heating showing consistently greater acid number than that with conventional heating, the phosphoric acid catalyzed polyols yielded greater acid number with conventional heating as compared to that of microwave heating. Furthermore, similar as the changes in hydroxyl number, most of the variations in acid number were shown in the initial stage of the liquefaction between 0 and 30 min, which is designated as the active region. And the acid number remained relatively unchanged between liquefaction times of 30 to 120 min, which is designated as the equilibrium region.

In the active region, the liquefied wood polyols obtained from microwave heating liquefaction with sulfuric acid catalyst displayed the greatest variation in acid-number-versus-time relationship. It increased rapidly from 19 to 34 mg KOH/g from 2 to 20 min and then dropped to 27 mg KOH/g at 30 min of the liquefaction. To the contrary, the acid number of the liquefied polyols obtained from conventional heating remained unchanged at around 19 mg KOH/g along the whole investigated liquefaction time of 120 min. Similarly, the acid number of the polyols from H_3PO_4 catalyzed liquefaction changed in a more complicated pattern with microwave heating than that with the conventional heating. It dropped from its initial value of 25 mg KOH/g to around 19 mg KOH/g within 2 min and then decreased very slowly with the increase of liquefaction time. With the convention heating liquefaction, the acid number of liquefied wood polyols did not change drastically compared to that with microwave heating.

In the equilibrium region, the only noticeable change in acid number is shown with liquefied wood polyols obtained by microwave heating liquefaction with sulfuric acid catalyst. It dropped gradually from 27 mg KOH/g to 24 mg KOH/g during the liquefaction time of 30 min to 120 min. Liquefied wood polyols obtained from conventional heating with phosphoric acid catalyst yielded the highest average acid number and the liquefied wood polyols obtained from microwave heating with phosphoric acid catalyst resulted in the lowest average acid number.

The increase of acid number could be attributed to either the increasing of organic acid generated from decomposed wood components or the oxidation of alcohols and the decomposed wood components (Yao et al. 1995; Kurimoto et al. 1999; Lee et al. 2002). In the case of microwave heating liquefactions, there may be an esterification reaction between the resulted acidic substances and alcohols that caused the decrease of the acid number (Wade 2006). In addition, the various chemically activated reactions between phosphoric acid and lignocelluloses, as described earlier, may also be involved.

3.3 Physical and mechanical properties of liquefied wood based PU foams

The physical and mechanical properties of the liquefied-wood-based PU foams are shown in Table 3. Petroleum-based PU foams (i.e., PEG400 and PEG400/glycerin) were also prepared as the control. The isocyanate index used in the foaming fabrication had significant effect on both the compressive strength and the apparent modulus of the liquefied-wood-based PU foams. In general, the strength and modulus of the foams increased as the isocyanate index increased from 80 to 120, mainly due to the increase of the crosslink density of urethane bond in cured PU foam (Wang

Table 3 Influence of liquefaction reaction time and isocyanate index on the mechanical properties of the foams
Tab. 3 Einfluss der Reaktionszeit und des Isocyanatindexes auf die mechanischen Eigenschaften der Schaumstoffe

Liquefaction condition		Isocyanate index	Density (g/cm^3)	Compressive strength (kPa)	Apparent modulus (MPa)	Permanent deformation[a] (%)
Catalyst	Reaction time (min)					
H_2SO_4	5	80	0.035	8.04	0.21	0.63
		100	0.035	69.92	2.25	1.36
		120	0.035	105.88	2.93	1.46
	30	80	0.034	6.68	0.16	0.83
		100	0.037	61.00	1.35	1.46
		120	0.035	90.08	2.47	2.91
	60	80	0.036	8.13	0.14	1.02
		100	0.035	55.54	0.91	1.24
		120	0.035	85.84	1.86	1.99
	120	80	0.036	8.76	0.22	1.13
		100	0.037	49.54	1.35	1.59
		120	0.035	69.65	1.66	1.79
H_3PO_4	30	80	0.021	32.79	1.12	3.03
		100	0.022	45.80	1.31	2.56
		120	0.020	57.89	2.30	1.49
	60	80	0.021	27.10	0.83	3.23
		100	0.021	41.35	1.42	3.56
		120	0.021	56.26	1.69	2.23
	120	80	0.022	49.51	1.07	4.04
		100	0.021	50.74	1.22	4.03
		120	0.022	53.22	2.12	1.09
PEG #400		80	0.035	7.65	0.16	1.92
		100	0.035	52.44	1.21	2.14
		120	–	–	–	–
PEG #400/glycerin (70/30, w/w)		80	0.034	88.28	2.78	7.12
		100	0.034	95.62	2.48	10.01
		120	0.037	102.53	2.18	9.10

[a] The permanent deformations of the foams after compression tests (20% strain)

and Chen 2007). The deformation of the foams made from H_2SO_4- and H_3PO_4 catalyzed liquefied wood polyols exhibited different trends with regard to the influence of the isocyanate index. Deformation increased with the isocyanate index when H_2SO_4 was used in the liquefaction while it decreased when H_3PO_4 was used. The microwave heating liquefaction reaction with H_2SO_4 and H_3PO_4 could undergo different mechanisms by virtue of the PU foams made from H_2SO_4 and H_3PO_4 catalyzed polyols displayed different physical mechanical properties. The foams from H_3PO_4 catalyzed polyols had lower densities than those from H_2SO_4 and the petroleum-based controls, indicating that the cell size in this type of foam was larger than those from H_2SO_4 catalyzed polyols. However, the blowing agent used in the foam formulation was the same. The lower density could cause the lower compressive strength of the foams made from H_3PO_4 catalyzed polyols. In addition, they also have higher values in permanent deformation than those made from H_2SO_4 catalyzed polyols.

Liquefaction time showed a more profound influence on the properties of the PU foams made from H_2SO_4 catalyzed polyols than those from H_3PO_4. Both the compressive strength and apparent modulus of the foam decreased with the increase in liquefaction time when H_2SO_4 was used as the catalyst during liquefaction. This could be attributed to the extensive degradation of wood natural polymers to less reactive fragments and/or smaller molecules that can not provide sufficient strength of the resulting foam products when liquefaction time was prolonged. Liquefaction time did not show a significant effect on the mechanical properties of the foams from H_3PO_4 catalyzed polyols. As can be seen in Table 3, the biomass-based PU foams generally have lower compressive strength and apparent modulus than the petroleum-based controls. However, they showed better restorability from deformation than the petroleum based controls. The foams made from liquefied polyols with only 5 min liquefaction time, isocyanate index of 120, and H_2SO_4 as the catalyst provide the best mechanical properties, and they were even somewhat superior to the petroleum-based controls. This result indicated the advantage of microwave heating over conventional heating by substantially shortening reaction time during liquefaction. It also suggested a potential for obtaining economically feasible products via microwave-assisted wood liquefaction.

4 Conclusion

Microwave was used as the heating source in wood liquefaction with PEG/glycerin binary solvent. PU foams were prepared from the resulting liquefied wood, and the mechanical properties of the liquefied-wood-based PU foams were evaluated. It was found that microwave heating was more efficient than conventional oil bath heating for wood liquefaction. The wood residue content of the H_2SO_4 catalyzed liquefied wood dropped to zero within 5 min with microwave heating, while it took 30 min for the wood residue content to decrease to zero with the oil bath heating at the same temperature. The viscosities of the liquefied wood using H_3PO_4 as the catalyst in the liquefaction were higher than those using H_2SO_4. The resulting liquefied wood polyols have suitable hydroxyl number values for the preparation of rigid PU foams. Both the compressive strength and apparent modulus of the liquefied wood based PU foams increased as the isocyanate index increased from 80 to 120. The liquefaction reactions using H_2SO_4 and H_3PO_4 as the catalyst could undergo different mechanisms with microwave heating. The foams from H_3PO_4 catalyzed polyols had lower densities than those from H_2SO_4 and the petroleum-based controls. They also showed lower strength and modulus than those from H_2SO_4. Liquefied-wood-based PU foams generally have lower compressive strength and apparent modulus than the petroleum-based controls. However, they showed better restorability from deformation than the petroleum-based controls. The foam made from liquefied wood polyols with 5 min liquefaction time, isocyanate index of 120, and H_2SO_4 as the catalyst showed somewhat superior mechanical properties than the petroleum based controls. The foam from liquefied wood polyols could potentially be developed to a marketable product.

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