Liquefaction of Cornstalk Residue Using 5-Sulfosalicylic Acid as the Catalyst for the Production of Flexible Polyurethane Foams

Yanqiao Jin,* Chunmei Lai, Jiaqing Kang, Xianze Lu, Jin Liu, and Qiu-Feng Lü

Due to the huge demand for as well as the limited reserves of fossil resources, renewable biomass that can be converted into chemicals has become a global research focus. In this paper, cornstalk residue was liquefied using a mixture of polyethylene glycol with a molecular weight of 400 g/mol (PEG400) and ethylene carbonate (EC) as the liquefaction reagent and 5-sulfosalicylic acid (SSA) as the catalyst. The liquefaction product of the cornstalk residue (CRL) was used to replace petroleum polyols to prepare flexible polyurethane foams. The results showed that the optimum liquefaction conditions were as follows: PEG400/EC was 7.5:2.5 (w/w), the ratio of liquid/solid was 5:1 (w/w), the liquefaction temperature was 160 °C, the mass of SSA was 4 g, and the liquefaction time was 60 min. The hydroxyl number and residue content of the CRL at optimal conditions were 315.7 mg KOH/g and 4.5%, respectively. The compressive strength and apparent density of the polyurethane foam, which was prepared by 90 wt% CRL, 10 wt% commercial polyether GE-220, and methylene diphenyl diisocyanate, were 205.6 kPa and 0.075 g/cm^3, respectively.

Keywords: Cornstalk residue; Liquefaction; Biopolyol; Polyurethane foam

Contact information: Key Laboratory of Eco-Materials Advanced Technology, College of Materials Science and Engineering, Fuzhou University, Fuzhou 350108 China;
**Corresponding author: jinyanqiao@fzu.edu.cn*

INTRODUCTION

Polyurethane foam (PUF) is a type of engineering material that has a wide range of applications due to its light weight, durability, impact resistance, excellent heat resistance characteristics, *etc*. (Freire *et al*. 2015; Formela *et al*. 2018; Sawpan 2018). It is usually synthesized by reacting polyols with diisocyanates. However, both the polyols and diisocyanates are petroleum downstream products, and therefore the supply and cost have a strong dependence on petroleum. As a result, people are seeking suitable alternative resources due to the depletion of petroleum resources and increasing environmental concerns (Peterson *et al*. 2008; Cinelli *et al*. 2013; Gollakota *et al*. 2018).

Renewable, abundant, and environment-friendly biomass or biomass residue, such as stalk, rapeseed cake, corn stover residue, *etc*., have been attracting the attention of researchers in recent years (Tilman *et al*. 2009; Briones *et al*. 2011; Lu *et al*. 2014; Li *et al*. 2015). Chemicals can be obtained from biomass or biomass residue *via* chemical, physical, or biological methods (Durak and Aysu 2016; Hassan *et al*. 2017). Currently, a variety of biopolyols derived from biomass *via* liquefaction have been successfully developed for polyurethane (PU) preparation (Chen and Lu 2008; Hu *et al*. 2012; Amran *et al*. 2019). Liquefaction is a catalytic thermochemical conversion process in which biomass or biomass residue was converted into chemicals. The catalyst commonly used in the liquefaction process is concentrated sulfuric acid or alkali, which cause damage to the reactors and even the environment (Atabani *et al*. 2012; Yin and Tan 2012; Yue *et al*. 2017). In addition, the biopolyol percentage for preparing PU materials is generally lower, between 10% and 70% (Hu *et al*. 2012; Mahmood *et al*. 2016; Yue *et al*. 2017).

To avoid the disadvantages of the strong acid or base catalysts, a suitable organic acid, 5-sulfosalicylic acid (SSA), was used as the catalyst in this work to obtain high performance liquefaction products efficiently and improve the biopolyol percentage as much as possible. The raw material used in this work was cornstalk residue. It is the by-product of the cornstalk-bioethanol industry and mainly composed of 70.5 wt% lignin, 20.7 wt% cellulose, and 2.2 wt% hemicellulose. The cornstalk residue was liquefied using a mixture of polyethylene glycol with a molecular weight of 400 g/mol (PEG400) and ethylene carbonate (EC) as the liquefaction reagent and SSA as the catalyst. Liquefaction product of the cornstalk residue (CRL) was used as a substitute for petroleum polyols to synthesize PUFs. The influence factors of the liquefaction process and the properties of the CRL were investigated. The mechanical and thermal properties of the PUFs prepared from the CRL were also considered. Thus, the feasibility of producing PUFs from biopolyols generated from biomass residue was evaluated according to the research data.

EXPERIMENTAL

Materials

The cornstalk residue was supplied by COFCO Biochemical Co., Ltd. (Inner Mongolia Province, China). It was dried at 80 °C for 24 h, and then ground and screened to obtain a geometrical size of 200-mesh before use. The reagents PEG400, SSA, phosphotungstic acid (PTA), H_2SO_4 (98 wt%), phthalic anhydride, stannous octoate (SO), triethylamine (TEA), pyridine, sodium hydroxide, and 1,4-dioxane were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). EC was obtained from Aladdin Chemical Co., Ltd. (Shanghai, China). All the mentioned reagents were analytically pure and used without further treatment. Commercial polyether polyol GE-220 (hydroxyl number: 56 mg KOH/g, viscosity: 350 mPa × s) and diphenylmethane diisocyanate (MDI) were provided by INOV Polyurethane Co., Ltd. (Shandong Province, China).

Methods

Liquefaction of cornstalk residue

The solvent mixture of PEG400 and EC (the mass ratio of PEG400:EC was 8.5:1.5, 8:2, 7.5:2.5, 7:3, and 6.5:3.5) and the catalyst SSA (1 g, 2 g, 3 g, 4 g, and 5 g) were placed into a dried flask with magnetic stirring and equipped with a condenser and a thermometer. When the reactor was heated to 130 °C to 170 °C under a nitrogen atmosphere in an oil bath, a certain amount of cornstalk residue was added into the flask and reacted for 30 min to 90 min. The mass ratio of liquid:solid (mixed solvents:cornstalk residue) was 3:1, 4:1, 5:1, 6:1, and 7:1. The final, dark brown product was rapidly cooled to room temperature and the biopolyol (denoted as CRL) was obtained.

Preparation of PUFs

The PUFs in this work were prepared using a single-step method. First, the polyols (mixture of CRL and GE-220) were mixed with deionized water (0.35 g), SO (0.2 g), and

TEA (0.25 g) in a beaker, and then stirred until smooth. The mass percentage of CRL was 0 wt%, 50 wt%, 90 wt%, and 100 wt%. Secondly, MDI was added into the beaker, and the mixture was vigorously stirred for 16 s to 20 s. Then, the mixture was rapidly placed into a self-made mold and left for free foaming at room temperature for 30 min. Finally, the mold was kept in an oven at 80 °C for 1 h and then the PUF was obtained. The mass of MDI was measured according to the following Eq. 1,

$$M_{\mathrm{MDI}} = \left(M_{\mathrm{GE-200}} \times W_{\mathrm{GE-200}} + M_{\mathrm{CRL}} \times W_{\mathrm{CRL}} + \frac{W_0}{9}\right) \times \frac{R}{W_{\mathrm{MDI}}} \tag{1}$$

where M_{MDI}, $M_{\mathrm{GE\text{-}220}}$, and M_{CRL} are the mole numbers of isocyanate groups per gram of MDI, hydroxyl groups per gram of GE-220, hydroxyl groups per gram of CRL, respectively (mol), W_{MDI}, $W_{\mathrm{GE\text{-}220}}$, W_{CRL}, and W_0 are the masses of MDI, GE-220, CRL, and water, respectively (g), and R is the index of isocyanate (R = 1.2).

Characterization

The Fourier transform infrared (FT-IR) spectroscopy spectra of the cornstalk residue, CRL, and PUFs were recorded in the spectral range of 4000 $\mathrm{cm^{-1}}$ to 400 $\mathrm{cm^{-1}}$ using a Nicolet FT-IR 5700 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The hydroxyl number and acid number of the CRL were measured according to the Chinese national standards GB 12008.5 (1989) (Feng *et al.* 2007) and GB 12008.3 (1989) (Cui *et al.* 2017), respectively. The hydroxyl number mentioned in the text was corrected by the acid number. The determination of residue content was calculated according to the following Eq. 2,

$$R = \frac{w_1}{w_0} \times 100 \tag{2}$$

where R is the residue content (%), w_0 is the mass of CRL (g), and w_1 is the mass of the solid residue after filtration (g).

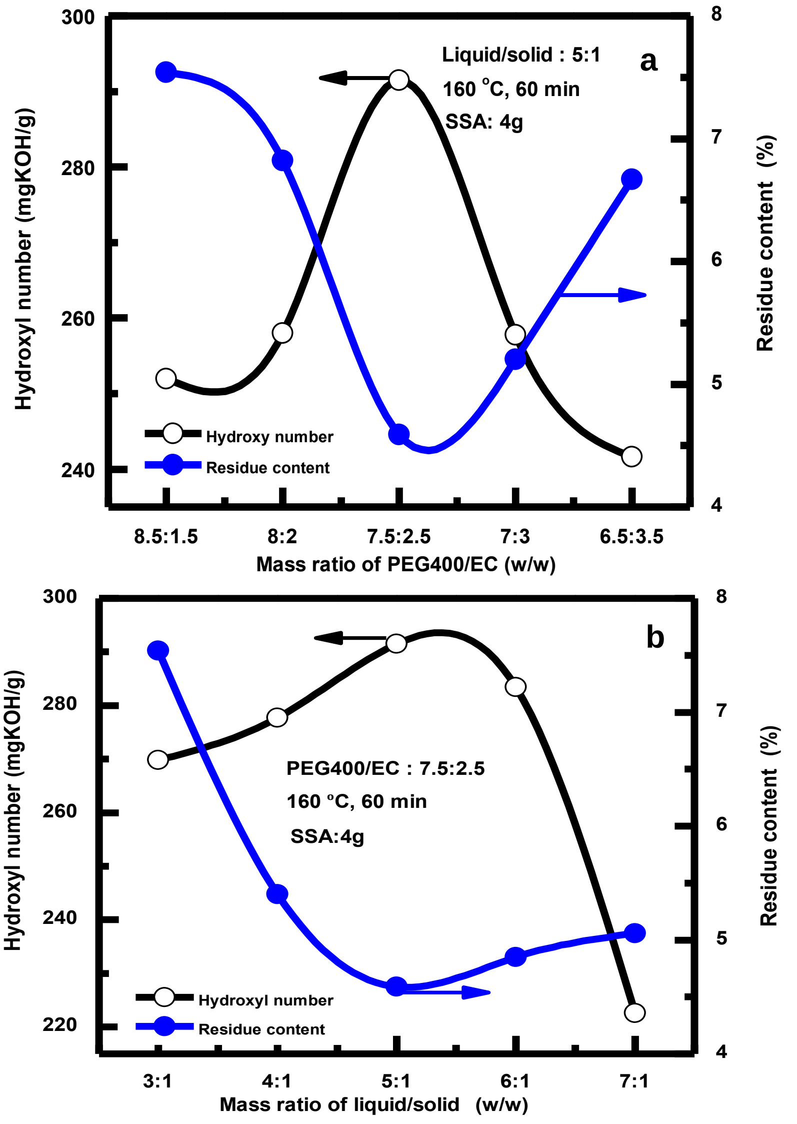
The thermal gravity/differential thermal gravity (TG/DTG) curves of the PUFs were obtained using a thermogravimetric analyzer (Pyris 1; PerkinElmer, Waltham, MA, USA) over temperatures ranging from 25 °C to 600 °C at the heating rate of 10 °C/min under a dry N_2 atmosphere. Morphologies of PUFs were observed using a field emission scanning electron microscope (SUPRA, 55-VP; Carl Zeiss AG, Oberkochen, Germany). The compressive strength of the PUFs was tested using a microcomputer controlled electronic tensile testing machine (CMT6104; SANS Institute, Bethesda, MD, USA) at the compressive rate of 6 mm/min based on the Chinese national standard GB/T 8813 (2008) (Xu *et al.* 2015). The apparent densities of the PUFs were measured according to the Chinese national standard GB/T 6343 (2008) (Dong *et al.* 2015).

RESULTS AND DISCUSSION

Optimization and Effect Factors in the Liquefaction of CRL

According to the research of the authors' group, the liquefaction process consists of two stages: degradation and recondensation (Lu *et al.* 2016). The two stages compete with each other and there is a turning point when the residue content is the lowest. Temperature, time, catalyst dosage, the ratio of PEG400 to EC, and the ratio of liquid to solid (*i.e.*, mixed solvents to cornstalk residue) have an important influence on liquefaction. The effects of these parameters on the liquefaction are shown in Fig. 1.

In the liquefaction, the mixture of PEG400 and EC was used as the liquefaction reagent. PEG400, containing two hydroxyl groups in one structure unit, can introduce many hydroxyl groups into the chain of CRL by reacting with the fragments of lignin and cellulose. Meanwhile, the EC can hinder the recondensation between the fragments and produce ethylene glycol, which provides more hydroxyl groups and accelerates the liquefaction (Lu *et al*. 2016). As shown in Fig. 1a, the hydroxyl number first increased and then decreased, and the residue content first decreased and then increased when the mass ratio of PEG400/EC was changed from 8.5:1.5 to 6.5:3.5 (w/w). When the mass ratio of PEG400/EC was 7.5:2.5, the hydroxyl number was the highest at 292 mgKOH/g and the residue content was the lowest at 4.59%. If the mass ratio of PEG400/EC was higher than 7.5:2.5, EC might participate in the recondensation and resulted in lower hydroxyl number and higher residue content.



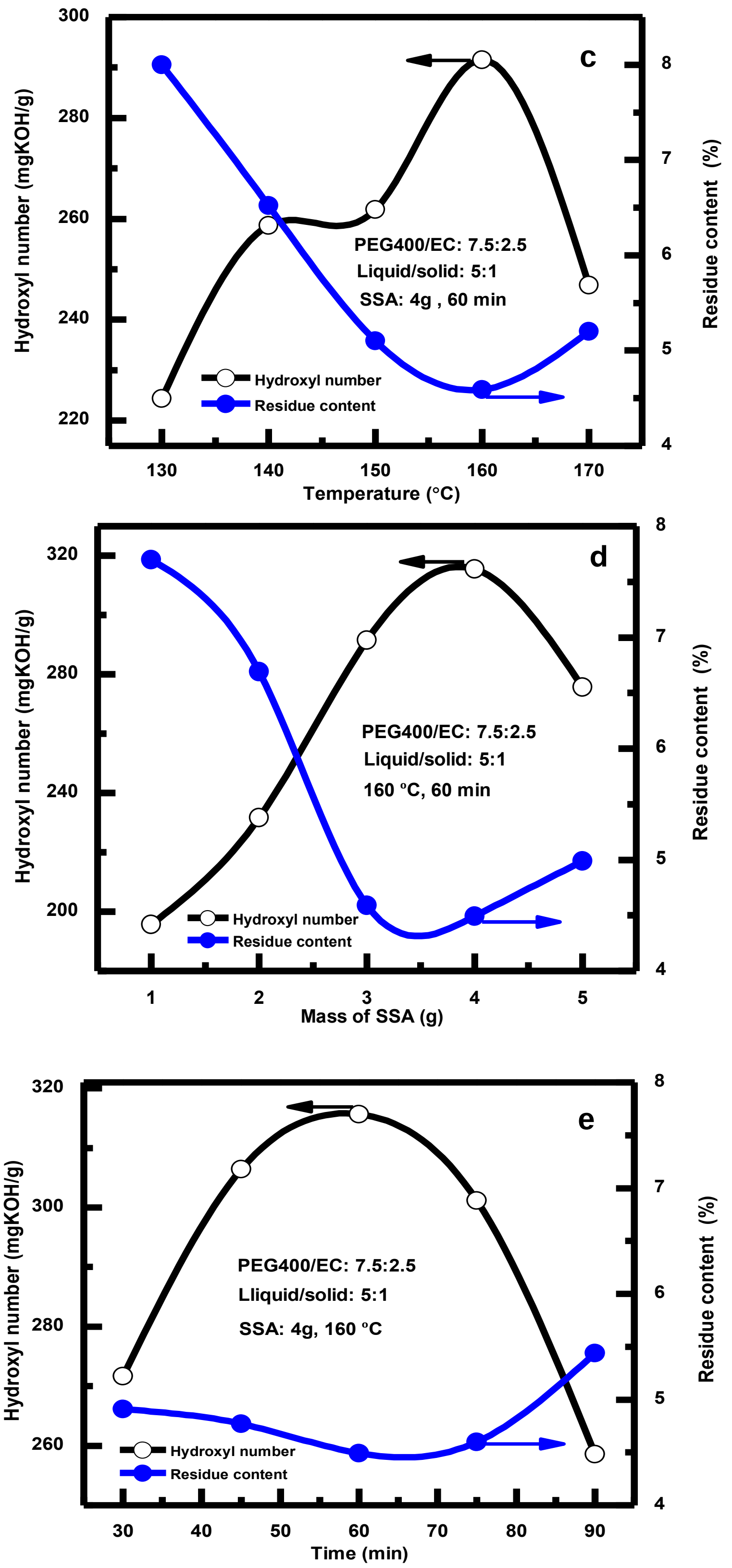


Fig. 1. The effects of different parameters on the liquefaction

Figure 1b shows the effect of the mass ratio of liquid/solid on the liquefaction. Liquid represents the liquefaction reagent (*i.e.*, the mixture of PEG400 and EC) and solid represents the cornstalk residue. When the mass ratio of liquid/solid was 5:1, the cornstalk residue was sufficiently degraded and completely dissolved into the liquefaction reagent (Kim *et al*. 2016). The hydroxyl number of CRL was the highest 292 mg KOH/g and the residue content was the lowest 4.59%. Once the mass ratio of liquid/solid was lower or higher than 5:1, the hydroxyl number decreased and the residue content increased.

Temperature had a remarkable effect on the liquefaction. As shown in Fig. 1c, the hydroxyl number first increased and then decreased, while the residue content rapidly decreased before increasing when the temperature increased from 130 °C to 160 °C. These changes indicated that the cornstalk residue was not adequately liquefied when the temperature was below 160 °C. The hydroxyl number was 292 mg KOH/g and the residue content was 4.59% at 160 °C. A higher temperature was beneficial to the degradation of cornstalk residue, but it promoted recondensation and thus resulted in a higher residue content (Jo *et al.* 2015). It can be seen that the hydroxyl number was fell to 247 mg KOH/g and the residue content was raised to 5.20% when the temperature was 170 °C. Hence 160 °C was the suitable liquefaction temperature.

In this work, SSA was used as the catalyst because it contained hydroxyl, carboxyl, and sulfonic groups. Figure 1d displays the effect of the SSA mass on the liquefaction. When the SSA mass increased from 1 g to 4 g, the hydroxyl number of the CRL increased from 196 mg KOH/g to 316 mg KOH/g and the residue content decreased from 7.70% to 4.49%. This showed that the SSA actually accelerated the liquefaction. However, more SSA was unfavorable to the liquefaction. When the SSA mass was 5 g, the hydroxyl number of the CRL decreased, but the residue content increased. That might be due to the reaction of the hydroxyl groups of the CRL and the carboxyl groups of the excessive SSA.

The liquefaction time was kept within an appropriate range. Insufficient time causes incomplete liquefaction, but too much time can promote the recondensation of fragments and results in a higher residue content (Ye *et al.* 2014). The effect of liquefaction time on the liquefaction was investigated (Fig. 1e). The highest hydroxyl number (316 mg KOH/g) and the lowest residue content (4.49%) occurred when the liquefaction was ended at 60 min. When the time was prolonged to 90 min, the hydroxyl number of the CRL decreased to 258 mg KOH/g and the residue content increased to 5.44%.

The results show that the optimum liquefaction conditions were as follows: the PEG400/EC mixture ratio was 7.5:2.5 (w/w), the ratio of liquid/solid was 5:1 (w/w), the liquefaction temperature was 160 °C, the mass of SSA was 4 g, and the liquefaction time was 60 min.

Effect of CRL Percentage on PUFs

The effects of the CRL percentage on the compressive strength and apparent density of PUFs are illustrated in Fig. 2. The apparent density of PUFs changed slightly as the CRL percentage increased, and it was kept within a smaller range (62 kg/m^3 to 112 kg/m^3). However, the CRL percentage greatly affected the compressive strength of the PUFs. With increased CRL percentage, the compressive strength first slightly increased and then remarkably increased when the CRL percentage was lower than 90 wt%. The highest compressive strength (205.5 kPa) occurred when the CRL percentage was 90 wt%. This could have been a result of the different reaction activities of CRL and GE-220. The hydroxyl number of the CRL used in the preparation of PUFs was 316 mg KOH/g, which was much higher than that of GE-220 (56 mg KOH/g). When GE-220 was mostly replaced by CRL, the reaction between isocyanate and hydroxyl groups was promoted, thus improving the crosslinking degree of PUFs. In addition, the benzene rings in lignin were introduced into the structure of the PUFs because CRL contains the fragments and polycondensate of lignin produced during the liquefaction (Mahmood *et al.* 2016; Yue *et al*. 2017). These rigid groups were beneficial to enhance the compressive strength. However, when the CRL percentage was higher than 100 wt%, the compressive strength dropped to 184.7 kPa and the apparent density was 62.5 kg/m^3. Perhaps it was because the viscosity of the CRL (870 mPa × s) was higher than that of GE-220 (350 mPa × s) and caused the bubble expansion to be hindered during the foaming process, thus shrinking the foam.

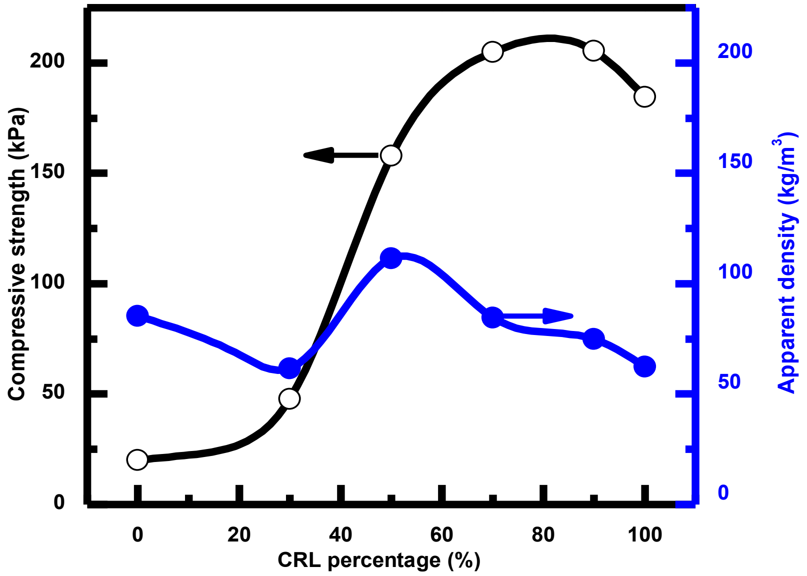


Fig. 2. Effect of CRL percentage on the properties of the PUFs

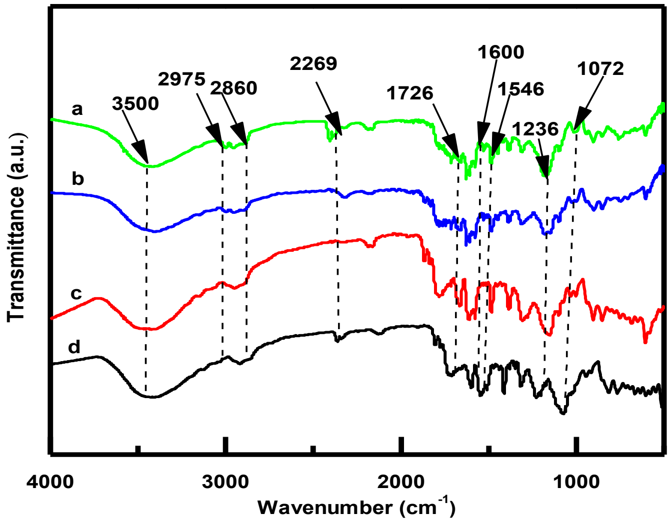


Fig. 3. FT-IR spectra of PUFs with different CRL percentages; (a) 0 wt%, (b) 50 wt%, (c) 90 wt%, (d) 100 wt%

FT-IR Spectral Analysis of PUFs

The FT-IR spectra of the PUFs with different CRL percentages are shown in Fig. 3. The peak at 3430 cm^{-1} was attributed to the vibrational absorption peak of hydroxyl or amino groups, which were not involved in the reaction (Bui *et al*. 2015). The peaks between 2975 cm^{-1} and 2860 cm^{-1} were attributed to the stretching vibration of -CH$_3$ and -CH$_2$. There was a weak peak at 2269 cm^{-1}, which was attributed to the -C=N=O group, on curves a and b. The appearance of the peaks indicated that not all -C=N=O groups in MDI reacted when the CRL percentage was 0 wt% or 50 wt%. However, the peak of the -C=N=O group did not appear at the wavenumber 2269 cm^{-1} on curves c and d when the CRL percentage was 90 wt% or 100 wt%. This indicated that -C=N=O groups in MDI had completely reacted with -OH groups in polyols and formed urea groups (*i.e.*, urethanes).

A strong C=O absorbance peak appeared at 1726 cm^{-1} on curves b, c, and d, which indicated that aromatic ester compounds were formed when the CRL was used to prepare the PUFs. The peaks observed at 1600 cm^{-1} and 1546 cm^{-1} were due to the C=C skeleton stretching vibration of the benzene ring, and the peaks that appeared at 1236 cm^{-1} and 1072 cm^{-1} were caused by the C-O-C asymmetric stretching vibration in O=C-O-R. In general, the spectra of the samples in Fig. 3 were similar.

It was indicated that the CRL had a similar chemical structure to GE-220 and reacted with the MDI to produce polyurethane materials.

The Microstructure of PUFs

The SEM images of the PUFs with different CRL percentages are displayed in Fig. 4. As shown in Fig. 4a, most of the cells were closed cells when no CRL was used to replace commercial GE-220. The cell diameters were 30 μm to 50 μm; however, the cell diameters' distribution showed inhomogeneity, which resulted in a lower compressive strength (20 kPa) (Fig. 2).

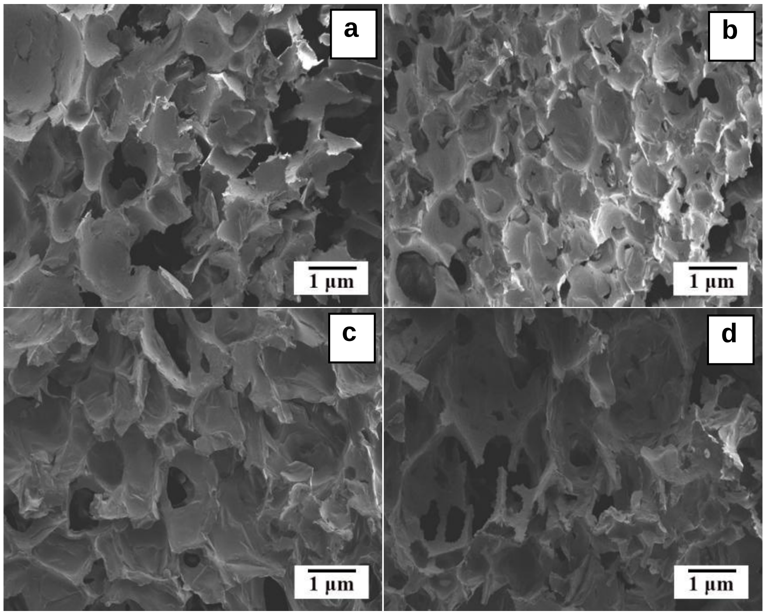


Fig. 4. SEM images of PUFs with different CRL percentages; (a) 0 wt%, (b) 50 wt%, (c) 90 wt%, and (d) 100 wt% (×50)

When the CRL percentage was 50 wt% or 90 wt%, the number of open cells increased and the cell diameters were 30 µm to 40 µm. The cell diameters' distribution was uniform, and the cell walls were relatively smooth (Figs. 4b and 4c). A higher CRL percentage offered more rigid benzene rings (these existed in the lignin structure) and thus the PU chains had harder segments and presented higher compressive strengths (see Fig. 2).

However, when the CRL percentage was increased to 100 wt%, the cell diameters were 30 µm to 65 µm, and the inhomogeneity of the cell diameters' distribution became more obvious. In addition, some microcracks appeared on the cell walls, the channels between cells became denser (Fig. 4d), and as a result, the compressive strength decreased to 184.7 kPa.

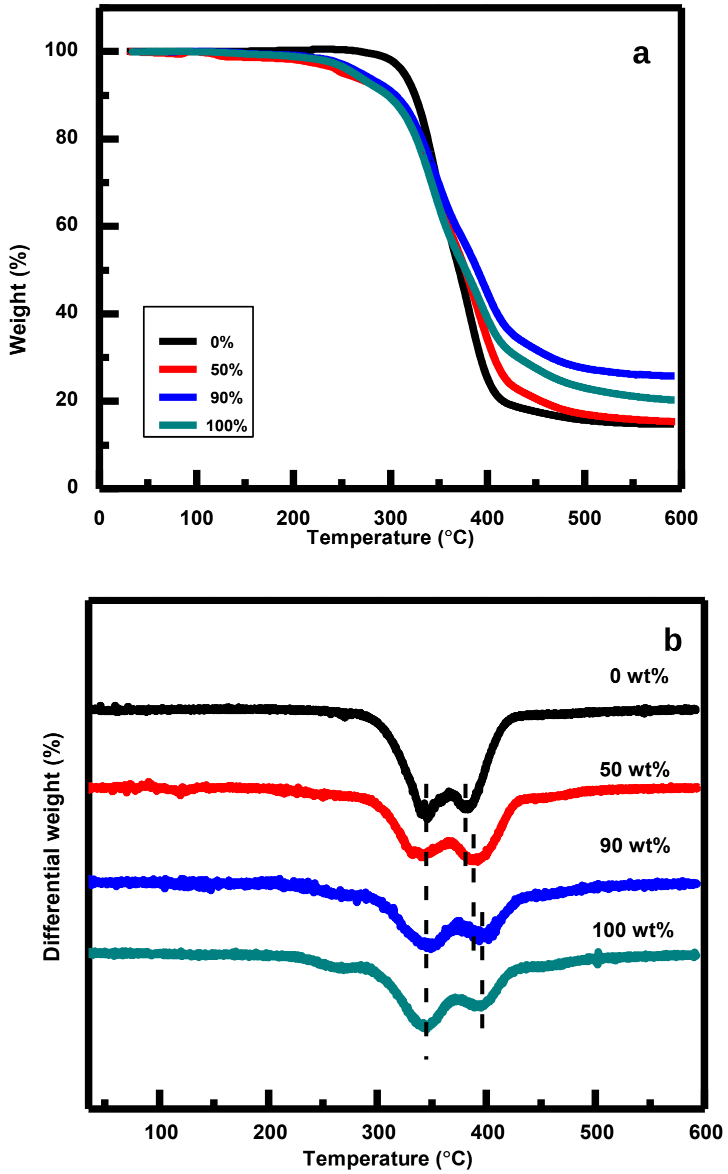


Fig. 5. TG-DTG curves of PUFs with different CRL percentage

Thermal Stability of PUFs

The thermal stability of the PUFs with different CRL percentages was investigated through TG-DTG analysis. The TG-DTG curves of the PUFs are shown in Fig. 5. The initial decompositions that occurred at temperatures lower than 300 °C are mostly due to the volatilization of small molecules (Mahmood *et al*. 2016). The initial decomposition temperature of PUFs without the CRL was 282 °C. However, the initial decomposition temperature of the other three samples all decreased to approximately 214 °C when the CRL percentage was 50 wt%, 90 wt%, or 100 wt%. The reduction of the initial decomposition temperature was mainly because the CRL contained more small molecules that were produced during the liquefaction process.

In addition, Fig. 5b shows that the PUFs had two weight loss stages (Bernardini *et al*. 2015). The first stage was associated with the degradation of the urethane bonds. Additionally, the maximum weight loss rate temperature of the samples in the first stage was 345 °C. The second stage was mainly associated with the degradation of the main chain. When the CRL percentage changed from 0 wt% to 50 wt%, 90 wt%, and 100 wt%, the maximum weight loss rate temperature increased from 381 °C to 389 °C, 396 °C, and 392 °C, respectively. The results showed that the PUFs with different CRL percentages still had good thermal stability at high temperatures. When the CRL percentage was 90 wt%, the residue of the PUFs at 600 °C was as high as 26% (Fig. 5a). The higher residue makes it possible for PUFs to be promising self-flame-retardant foams. The carbon residue rate of PUFs was as high as 26% in an air atmosphere at 600 °C. The high carbon residue rate indicates that PUFs are easier to form a carbon layer to insulate the heat and oxygen transmission during combustion and thus show the potential of being self-flame-retardant foams.

CONCLUSIONS

1. Cornstalk residue was liquefied and converted into biopolyol using a mixture of polyethylene glycol (PEG400) and ethylene carbonate (EC) as the liquefaction reagent and 5-sulfosalicylic acid as the catalyst.
2. The hydroxyl number of CRL was 315.7 mg KOH/g and the residue content was 4.5% at the optimized reaction conditions of the mixed solution of PEG400/EC at a ratio of 7.5:2.5 (w/w). The ratio of liquid to solid was 5:1 (w/w), the liquefaction temperature was 160 °C, the dosage of sulfosalicylic acid was 4 g, and the liquefaction time was 60 min.
3. The CRL replaced most of the commercial petroleum polyol and prepared flexible polyurethane foams (PUFs). When the CRL percentage was 90 wt%, the compressive strength and apparent density of the PUF were 205.6 kPa and 0.075 g/cm^3, respectively.

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REFERENCES CITED

Amran, U. A., Chia, C. H., Jaafar, S. N. S., Roslan, R., Salleh, K. M., and Zakaria, S. (2019). “Polyols and rigid polyurethane foams derived from liquefied lignocellulosic and cellulosic biomass,” *Cellulose* 26:3231. DOI: 10.1007/s10570-019-02271-w

Atabani, A. E., Silitonga, A. S., Badruddin, I. A., Mahlia, T. M. I., Masjuki, H. H., and Mekhilef, S. (2012). “A comprehensive review on biodiesel as an alternative energy resource and its characteristics,” *Renew. Sust. Energ. Rev.* 16(4), 2070-2093. DOI: 10.1016/j.rser.2012.01.003

Bernardini, J., Cinelli, P., Anguillesi, I., Coltelli, M.-B., and Lazzeri, A. (2015). “Flexible polyurethane foams green production employing lignin or oxypropylated lignin,” *Eur. Polym. J.* 64, 147-156. DOI: 10.1016/j.eurpolymj.2014.11.039

Briones, R., Serrano, L., Llano-Ponte, R., and Labidi, J. (2011). “Polyols obtained from solvolysis liquefaction of biodiesel production solid residues,” *Chem. Eng. J.* 175, 169-175. DOI: 10.1016/j.cej.2011.09.090

Bui, N. Q., Fongarland, P., Rataboul, F., Dartiguelongue, C., Charon, N., Vallée, C., and Essayem, N. (2015). “FTIR as a simple tool to quantify unconverted lignin from chars in biomass liquefaction process: Application to SC ethanol liquefaction of pine wood,” *Fuel Process. Technol.* 134, 378-386. DOI: 10.1016/j.fuproc.2015.02.020

Chen, F., and Lu, Z. (2008). “Liquefaction of wheat straw and preparation of rigid polyurethane foam from the liquefaction products,” *J. Appl. Polym. Sci.* 111(1), 508-516. DOI: 10.1002/app.29107

Cinelli, P., Anguillesi, I., and Lazzeri, A. (2013). “Green synthesis of flexible polyurethane foams from liquefied lignin,” *Eur. Polym. J.* 49(6), 1174-1184. DOI: 10.1016/j.eurpolymj.2013.04.005

Cui, S. X., Yun, Z., and Gui, X. (2017). “Modification of methyl oleate for silicon-based biological lubricating base oil,” *Chin. J. Chem. Eng.* 25(1), 130-136. DOI: 10.1016/j.cjche.2016.06.001

Dong, J., Zheng, F., Wei, H., Luo, Z. Y., Jiang, X. B., Wang, T. W., and Kai, G. (2015). “Polyurethane rigid foams formed from different soy-based polyols by the ring opening of epoxidised soybean oil with methanol, phenol, and cyclohexanol,” *Ind. Crops Prod.* 74, 76-82. DOI: 10.1016/j.indcrop.2015.04.041

Durak, H., and Aysu, T. (2016). “Thermochemical liquefaction of algae for bio-oil production in supercritical acetone/ethanol/isopropanol,” *J. Supercrit. Fluid.* 111, 179-198. DOI: 10.1016/j.supflu.2015.11.021

Feng, G. Z., Qu, H., Cui, Y. D., Li, H. P., and Lu, K. (2007). “Synthesis and kinetic studies on dimer fatty acid/polyethylene glycol polyester,” *J. Polym. Res.* 14(2), 115-119. DOI: 10.1007/s10965-006-9090-6

Formela, K., Haponiuk, J., Hejna, A., Kosmela, P., and Piszczyk, L. (2018). “The study on application of biopolyols obtained by cellulose biomass liquefaction performed with crude glycerol for the synthesis of rigid polyurethane foams,” *J. Polym. Environ.* 26(6), 2546-2554. DOI: 10.1007/s10924-017-1145-8

Freire, C. S. R., Gama, N. V., Netoa, C. P., Silvab, R., Soares, B., Timmonsa, A. B., and Ferreiraac, A. (2015). “Bio-based polyurethane foams toward applications beyond thermal insulation,” *Mater. Des.* 76, 77-85. DOI: 10.1016/j.matdes.2015.03.032

Gollakota, A. R. K., Kishore, N., and Gu, S. (2018). “A review on hydrothermal liquefaction of biomass,” *Renew. Sust. Energ. Rev.* 81(Part 1), 1378-1392. DOI: 10.1016/j.rser.2017.05.178

Hassan, Z., Asim, R., and Jaehoon, K. (2017). "Understanding the effect of biomass-to-solvent ratio on macroalgae (*Saccharina japonica*) liquefaction in supercritical ethanol," *J. Supercrit. Fluid.* 120(Part 1), 65-74. DOI: 10.1016/j.supflu.2016.10.013

Hu, S., Wan, C., and Li, Y. (2012). "Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw," *Bioresource Technol.* 103(1), 227-233. DOI: 10.1016/j.biortech.2011.09.125

Jo, Y. J., Ly, H. V., Kim, J., Kim, S.-S., and Lee, E. (2015). "Preparation of biopolyol by liquefaction of palm kernel cake using PEG#400 blended glycerol," *J. Ind. Eng. Chem.* 29, 304-313. DOI: 10.1016/j.jiec.2015.04.010

Kim, K. H., Yu, J.-H., and Lee, E. Y. (2016). "Crude glycerol-mediated liquefaction of saccharification residues of sunflower stalks for production of lignin biopolyols," *J. Ind. Eng. Chem.* 38, 175-180. DOI: 10.1016/j.jiec.2016.05.002

Li, R., Li, B., Yang, T., Kai, X., Wang, W., Jie, Y., Zhang, Y., and Chen, G. (2015). "Sub-supercritical liquefaction of rice stalk for the production of bio-oil: Effect of solvents," *Bioresource Technol.* 198, 94-100. DOI: 10.1016/j.biortech.2015.08.088

Lu, J., Li, X., Yang, R., Zhao, J., Liu, Y., and Qu, Y. (2014). "Liquefaction of fermentation residue of reed- and corn stover-pretreated with liquid hot water in the presence of ethanol with aluminum chloride as the catalyst," *Chem. Eng. J.* 247, 142-151. DOI: 10.1016/j.cej.2014.02.094

Lu, X., Wang, Y., Zhang, Y., Cheng, X., Yu, Y., and Jin, Y. (2016). "Preparation of bio-polyols by liquefaction of hardwood residue and their application in the modification of polyurethane foams," *J. Wuhan Univ. Technol.* 31(4), 918-924. DOI: 10.1007/s11595-016-1468-7

Mahmood, N., Yuan, Z., Schmidt, J., Tymchyshyn, M., and Xu, C. (2016). "Hydrolytic liquefaction of hydrolysis lignin for the preparation of bio-based rigid polyurethane foam," *Green Chem.* 18(8), 2385-2398. DOI: 10.1039/C5GC02876K

Peterson, A. A., Vogel, F., Lachance, R. P., Fröling, M., Antal, Jr., M. J., and Tester, J. W. (2008). "Thermochemical biofuel production in hydrothermal media: A review of sub-and supercritical water technologies," *Energ. Environ. Sci.* 1(1), 32-65. DOI: 10.1039/B810100K

Sawpan, M. A. (2018). "Polyurethanes from vegetable oils and applications: A review," *J. Polym. Res.* 25, Article ID 184. DOI: 10.1007/s10965-018-1578-3

Tilman, D., Socolow, R., Foley, J. A., Hill, J., Larson, E., Lynd, L., Pacala, S., Reilly, J., Searchinger, T., Somerville, C., and Williams, R. (2009). "Beneficial biofuels – The food, energy, and environment trilemma," *Science* 325(5938), 270-271. DOI: 10.1126/science.1177970

Xu, D. M., Xiu, L., Jie, F., and Hao, J. W. (2015). "Preparation of boron-coated expandable graphite and its application in flame retardant rigid polyurethane foam," *Chem. Res. Chin. Univ.* 31(2), 315-320. DOI: 10.1007/s40242-015-4101-y

Ye, L., Zhang, J., Zhao, J., and Tu, S. (2014). "Liquefaction of bamboo shoot shell for the production of polyols," *Bioresource Technol.* 153, 147-153. DOI: 10.1016/j.biortech.2013.11.070

Yin, S., and Tan, Z. (2012). "Hydrothermal liquefaction of cellulose to bio-oil under acidic, neutral and alkaline conditions," *Appl. Energ.* 92, 234-239. DOI: 10.1016/j.apenergy.2011.10.041

Yue, D., Oribayo, O., Rempel, G. L., and Pan, Q. (2017). "Liquefaction of waste pine wood and its application in the synthesis of a flame retardant polyurethane foam," *RSC Adv.* 7(48), 30334-30344. DOI: 10.1039/C7RA03546B

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