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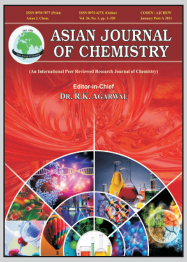

A New Process for Preparation of Polyether Polyols by Catalytic Starch Liquefaction

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This paper reports a new process for the preparation of polyether polyols, with starch as raw material, the mixed polyol as the liquefying agent and methane sulfonic acid as the catalyst. The effect of the ratio of reactants, reaction temperature, reaction time and amount of catalyst on liquefaction process is determined by single factor experiments. The optimal preparation conditions was determined as follows: mass ratio of starch to liquefaction solvent is 1:6, the amount of methane sulfonic acid is 3 % of the mass of liquefying agent, mass ratio of the liquefier PEG200 to glycerol is 7:3, liquefaction time is 0.5 h, liquefaction temperature is 150 °C, under this condition, conversion of starch reached to 98.2 %. NMR analysis of the liquefied product demonstrated that it is the polyether polyol with the hydroxyl value of 200.4 mg KOH/g, the viscosity of 725 mpa s. The polyether polyol product was successfully employed as the raw material for the preparation of the PU and PF foams. The properties of the foam were in line with the national standards (GB/T 6343-2009 and GB/T 8813-2008).

Keywords: Starch liquefaction, Polyether polyols, New process, Foam materials.

INTRODUCTION

Polyether polyol as an important industrial chemical is mainly used for the synthesis of polyurethane resin products, such as polyurethane foam, polyurethane adhesives, polyurethane elastomer, *etc.*[1,2]. In addition, it can also be used for the preparation of non-ionic surfactants, lubricants and so on.

The raw materials for polyether polyol production are the alkylene oxide and the alkylene oxide is a petrochemical products. In recent years, the cost of manufacturing of polyether polyol has been increasing as the rising of petroleum price. Exploring the new process employing renewable biomass to produce polyether polyol by replacing the petroleum routine has been increasingly concerned[3-6]. Starch, as an abundant renewable natural resource, has been used to prepare polyether polyols by the starch liquefaction[7-9]. There are also other biomasses including cellulose and bamboo employed to prepare polyether polyols in China. Huang *et al.*[7] reported a process for producing polyhydric alcohols by the corn starch as the raw material and concentrated sulfuric acid as catalyst. Liu *et al.*[10,11] proposed a process for polyol production using bamboo residues as raw material and concentrated sulfuric acid as catalyst. There are many relevant researches world-widely. For instance, Yamata and Alma[12,13] liquefied fibrous biomass using sodium hydroxide as catalyst and polyol and water as liquefier at high temperature and pressure conditions. In terms of catalyst, the most of the catalyst currently used is sulfuric acid or alkaline-base, which is severely corrosive for reactor and is pollutant for the environment. Some liquefaction processes proceed under severe reaction conditions[14,15]. This paper proposed a new process for making polyether polyol with methylsulfonic acid as environmentally friendly catalyst.

EXPERIMENTAL

PEG200 (AR, Tianjin Guangfu Fine Chemical Research Institute), glycerol (AR, West Long Chemical Co., Ltd.),the starch (Food Grade, Changchun City Hongli Food Co., Ltd.), methylsulfonic acid (AR, Industrial grade, 99.5 %, Tianjin Guangfu Fine Chemical Research Institute)as the catalyst.

Starch conversion rate[10]: Take about 2 g liquefied products for approximately 20 mL mixture of dioxane and water solution (volume ratio of dioxane and water is 8:2) in water bath at 80 °C for 20 min with continuous stirring. The mixture solution was filtered by Buchner funnel with filter paper (medium speed quantitative filter paper) and then rinsed by the mixture of dioxane and water solution several times until achieving the colorless filtrate. The residues with fitter paper were then placed in an oven at 105 °C for 4 h and weighted when the weight discontinued decreasing.

$$P(\%) = w/m \times 100\ \% \quad (1)$$

$$C(\%) = 100\ \% - P(\%) \quad (2)$$

where, P = Residue yield (%); w = Residue quality (g); m = Quality of the liquefied product (g); C = Starch conversion rate (%).

Hydroxyl value of the liquefied products (GB/T 12008.3-89)[10]: About 1 g liquefied products were put into a 150 mL beaker. Additional 10 mL phthalic anhydride solution was also added (15 g of phthalic anhydride solution dissolved in 90 mL dioxane and 10 mL pyridine). The breaker was covered by aluminum foil and then boiled in water bath for 20 min. Cooling the solution to ambient condition, 20 mL of dioxane and water (volume ratio: 8:2) and 5 mL distilled water was added into the beaker. Titrate the solution to pH 8.3 by 1 mol/L NaOH standard solutions (use a pH meter recording the terminal point).

$$OHV\ (mgKOH/g) = (B - A)N \times 5.61/M \quad (3)$$

where, A = Volume of the NaOH consumed by the titration liquefied product (mL); B = Volume of NaOH consumed in the blank test (mL); N = Concentration of NaOH (mol/L); M = Quality of the liquefied product (g).

Viscosity of liquefied products: The viscosity of the liquefied product was measured by NDJ-1 viscometer (Shanghai Qunchang Scientific Instrument Co., Ltd.).

Molecular structure identification of liquefied products: The FT-IR analysis of sample was performed on FT04-035 FTIR spectrometer. Due to the colorless product liquid, the sample was treated with coating method: grind the dry KBr to powder. The powder was pressed to transparent slice in a mould. Then coat a small portion of sample on KBr slice to form a very thin liquid layer of membrane to be measured in the sample chamber.

The NMR analysis of the product was analyzed by the Nuclear Magnetic Resonance Spectrometer (Bruker AVANCE 400) and measured by the 1H NMR and DMSO as the solvent.

RESULTS AND DISCUSSION

The experimental investigations were conducted on the effect of the ratio and dosage of liquefier, the liquefaction time and temperature and catalyst dosage on the starch conversion and the hydroxyl value of liquefaction product, in order to achieve the optimal conditions for the process.

Ratio of liquefaction agents: At the condition of liquefaction temperature 150 °C, time 0.5 h, 20 g liquefier, the mass ratio of starch to liquefier is 1:6 and the amount of methylsulfonic acid catalyst as 3 % amount of liquefier. The effect of mass ratio of PEG200 to glycerol in liquefier on liquefaction process is shown in Table-1.

TABLE -1
EFFECT OF THE MASS RATIO OF PEG200 TO GLYCEROL ON THE LIQUEFACTION PROCESS

No.	PEG200: Glycerin	Starch conversion rate (%)	OHV/mgKOH/g
1	9:1	96.2	124.5
2	7:3	97.4	360.0
3	5:5	97.6	223.4
4	3:7	97.9	126.2
5	1:9	98.1	128.5

Table-1 indicates that starch conversion rate decreased at the beginning and then increased as the increase of proportion of glycerol in the liquefier. The conversion rate of starch and hydroxyl value reached the peak at the mass ratio of 7:3. The color of the product is yellow brown and slightly transparent. Therefore, the mass ratio of PEG200 and glycerol in the liquefier was chosen as 7:3.

Amount of liquefaction agent: At the condition of liquefaction temperature 150 °C, time 0.5 h, 20 g liquefier, the mass ratio of PEG200 to glycerol is 7:3 and the amount of methanesulfonic acid catalyst as 3 amount of liquefier. The effect of mass ratio of starch and liquefier on liquefaction process is shown in Table-2.

TABLE-2
EFFECT OF THE MASS RATIO OF STARCH AND LIQUEFIER ON THE LIQUEFACTION PROCESS

No.	Starch: Liquefier	Starch conversion rate /%	OHV/mgKOH/g
1	1:4	96.7	200.3
2	1:5	96.9	260.8
3	1:6	97.4	360.0
4	1:7	97.6	240.5
5	1:8	97.9	137.5

Table-2 indicates that the starch conversion rate reached the peak at 1:6 by changing liquefier dosage. The principle functions of the liquefier include dissolving and dispersing liquefaction products, limiting product blending and reducing residue rate. The liquefier can rapidly drop down and reach the balance, limiting re-blending of intermediate products from the decomposition of starch components[16]. Therefore, the mass ratio of starch and liquefier was chosen as 1:6.

Liquefaction time: At the condition of liquefaction temperature 150 °C, 20 g liquefier, the mass ratio of PEG200 and glycerol is 7:3, the mass ratio of starch and liquefier is 1:6 and the amount of methanesulfonic acid catalyst as 3 % amount of liquefier. The effect of liquefaction time on the liquefaction process is shown in Table-3.

TABLE-3
EFFECT OF LIQUEFACTION TIME ON THE LIQUEFACTION PROCESS

No.	Time/min	Starch conversion rate (%)	OHV/mgKOH/g
1	20	97.5	180.1
2	30	98.2	360.0
3	40	98.4	137.5

Table-3 indicates that the hydroxyl value reached the maximum at 0.5 h, due to the completely liquefied products, pure products and relatively less residues[17] at 0.5 h. Therefore, the liquefaction time was chosen as 0.5 h.

Liquefaction temperature: At the condition of liquefaction time 0.5 min, 20 g liquefier, the mass ratio of PEG200 and glycerol is 7:3, the mass ratio of starch and liquefier is 1:6 and the amount of methanesulfonic acid catalyst as 3 % amount of liquefier. The effect of liquefaction temperature on the liquefaction process is shown in Table-4.

TABLE-4
EFFECT OF LIQUEFACTION TEMPERATURE ON THE LIQUEFACTION PROCESS

No.	Temperature/°C	Starch conversion rate (%)	OHV/mgKOH/g
1	140	97.0	180.8
2	150	98.2	360.0
3	160	98.5	200.4
4	170	98.7	180.6
5	180	98.9	137.5

Table-4 indicates that the starch conversion rate was higher at higher temperature. During the experiment, when the liquefaction temperature stayed between 90 and 110 °C, the residue rate of liquefaction was high. The liquefaction products were milk white thick liquid with clear stratification and light brown particles, which indicates that the starch was not liquefied completely. There is almost no residue when the temperature was elevated to 150 °C. The residue rate did not change significantly when the reaction temperature was further increased to 180 °C but this high temperature caused the blending among the liquefaction products and high-temperature cracking reactions so that the hydroxyl value of liquefaction decreased[18,19]. Therefore, the liquefaction temperature was chosen as 150 °C.

Amount of catalyst input: At the condition of liquefaction temperature 150 °C, time 0.5 h, 20 g liquefier, the mass ratio of PEG200 and glycerol is 7:3 and the mass ratio of starch and liquefier is 1:6. The effect of the amount of catalyst on the liquefaction process is shown in Table-5.

TABLE-5
EFFECT OF THE AMOUNT OF CATALYST ON THE LIQUEFACTION PROCESS

No.	Dosage (%)	Starch conversion rate (%)	OHV/mgKOH/g
1	1.0	97.4	175
2	2.0	97.8	220.2
3	3.0	98.2	360
4	4.0	98.6	270.4
5	5.0	98.8	245.2

Table-5 indicates that the hydroxyl value of liquefaction products increases gradually when the amount of catalyst was used more. The hydroxyl value and starch conversion rate were the highest when the amount of methylsulfonic acid catalyst was 3 % of the amount of liquefier. The liquefaction was most remarkable when the amount of methylsulfonic acid catalyst was more than 3 % of the amount of liquefier, which mainly resulted from the condensation reactions occurred among the liquefaction products under the action of methylsulfonic acid. In addition, oxidation and condensation side reactions happened when methylsulfonic acid was over used, which leads to the decrease of liquefaction rate[20]. Therefore, the amount of methylsulfonic acid catalyst as 3 % amount of liquefier was optimal.

Overall, through the comparison of the effects of various factors on liquefaction and the hydroxyl value of liquefaction products, the optimal starch liquefaction conditions were determined as follows: the mass ratio of potato starch and liquefier is 1:6; the amount of methylsulfonic acid catalyst is 3 % of the amount of liquefier; the mass ration of PEG200 and glycerol in liquefier is 7:3; the liquefaction time is 30 min; the liquefaction temperature is 150 °C.

FT-IR analysis: The infrared spectrogram of liquefaction products and raw starch are shown in Fig. 1.

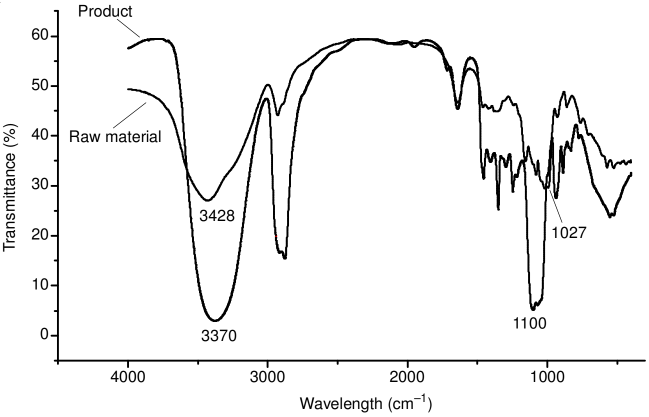

Fig. 1. FT-IR spectrum of the liquefied product and starch

It is seen from Fig.1, the strong absorption peak around 1100 cm^{-1} was the anti-symmetric stretching vibration characteristic absorption peak of ether bond (C-O-C) in the polyether polyol. The peak of product was much stronger than that from raw material. It indicates that new C-O-C bond was created and therefore proves that the product was polyether polyol. In the meantime, the wide and strong absorption peak around 3400 cm^{-1} was the stretching vibration characteristic absorption peak of polyether polyol end hydroxyl group (-OH).

^{1}H NMR analysis: It is seen from Fig. 2, the hydrogen is from -OH at 5.5 ppm; the hydrogen near oxygen atom proves the existence of ether bond. It can draw a preliminary conclusion that the product includes hydroxyl and ether bond component, which is polyether polyol.

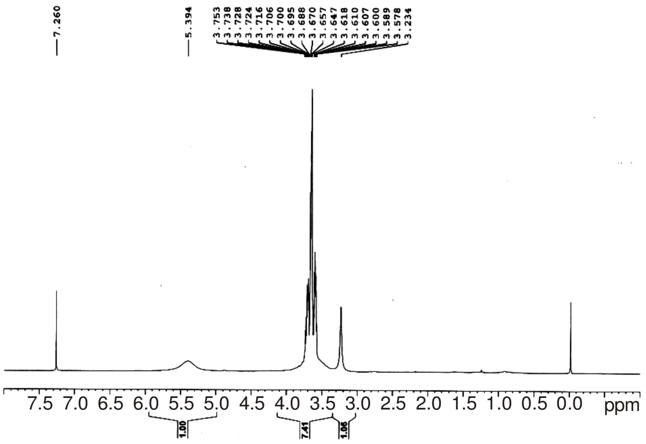

Fig. 2. ^{1}H NMR of the liquefied product

Properties of the liquefied products: Liquefaction properties of the products prepared under optimum conditions are as follows:

Viscosity = 725 mpa · s; OHV = 360 mg KOH/g

Preparation of PF[21,22]: 53 g Phenolic resion was added by 1 g emulsifier, foaming agent (petroleum ether) 3 g, self-made polyol 5 g, curing agent (mixture of hydrochloric acid and methyl benzene sulfonic acid) 6 g, which were well-mixed and poured into a mould and then placed in the oven at 75 °C for foaming solidification. The solidified product was PF foam. The compression strength, bending strength and mean apparent density of PF foam produced are 0.24 MPa, 0.32Mpa and 42 kg/m, respectively.

Preparation of PU[19]: 135 g MDI was first weighted for further use. 50 g polyester polyol, 50 g polyether polyol, 15 g Self-made polyol, 8 g water, 15 g petroleum ether, 0.9 g dilauric acid dibutyl tin catalyst were well mixed and poured into the beaker with MDI and fully stirred. When the system stayed uniform and there was bubble intending to rise, the mixture was immediately poured into the mould for foaming. The rigid PU foam can be obtained after the foam solidification. The performances were measured as follows: the compression strength, bending strength and mean apparent density of PF foam produced are 0.24 MPa, 0.32 Mpa and 42 kg/m, respectively.

The polyether polyol product was successfully employed as the raw material for the preparation of the PU and PF foams. The properties of the foam were in line with the national standards (GB/T 6343-2009 and GB/T 8813-2008).

Conclusion

This study successfully developed a new process for producing polyether polyols by using starch as raw material and methyl sulfonic as catalyst. The optimal liquefaction conditions were determined as follows: the mass ratio of PEG-200 to glycerol in the liquefier is 7:3; the mass ratio of starch to liquefier is 1:6; the amount of methane sulfonic acid is 3 % of the liquefying agent; the liquefaction time is 30 min; the liquefaction temperature is 150 °C. Under this condition, the starch conversion rate can reach to 98.2 %.

The liquefaction product was identified as the polyether polyols with low molecular weight via the analysis of the IR and nuclear magnetic measurements. Its viscosity is 725 mpa s; the hydroxyl value is 360 mgKOH/g.

The performances of PF and PU materials produced with the liquefaction products as raw materials meet the national standard (GB/T 6343-2009 and GB/T 8813-2008) requirements.

REFERENCES

1. M. Desroches, M. Escouvois, R. Auvergne, S. Caillol and B. Boutevin, *Polym. Rev.*, **52**, 38 (2012).
2. M. Ionescu, Chemistry and Technology of Polyols for Polyurethanes, Rapra Technology, Ltd.: Shawbury, Shrewsburty, Shropshire, UK (2005).
3. F. Budija, C. Tavzes, L. Zupancic-Kralj and M. Petric, *Bioresour. Technol.*, **100**, 3316 (2009).
4. National Bureau of Statistics of China, 2004 Statistics Communication, p. 230 (2005).
5. A.L. Maksimov, A.I. Nekhaev, D.N. Ramazanov, Yu. A. Arinicheva, A.A. Dzyubenko and S.N. Khadzhiev, *Petrol. Chem.*, **51**, 61 (2011).
6. T. Yamada and H. Ono, *J. Wood Sci.*, **47**, 458 (2001).
7. Y. Huang, Y. Zheng, Z. Zheng *et al.*, *J. Southwest Forestry University*, **31**, 72 (2011).
8. J. Enrione, F. Osorio, F. Pedreschi and S. Hill, *Food Bioprocess Technol.*, **3**, 791 (2010).
9. J. Yamazaki, E. Minami and S. Saka, *J. Wood Sci.*, **52**, 527 (2006).
10. Y.-H. Liu, L.-L. Gao, H. Peng, H.-D. Zhou and R.-S. Ruan, *Modern Chem. Ind.*, **28(S2)**, 214 (2008).
11. Y. Liu, L. Gao, X. Ai, S. Rong and C. Liu, *Acta Polym. Sinica*, **8**, 544 (2008).
12. M.H. Alma and N. Shiraishi, *Holz Roh Werkst*, **56**, 245 (1998).
13. D. Maldas and N. Shiraishi, *Int. J. Polym. Mater.*, **33**, 61 (1996).
14. G.Y. Li, T.F. Qin and A. Ikeda, *Chinese Forest. Sci. Technol.*, **1**, 63 (2002).
15. M.H. Alma, M. Yoshioka, Y. Yao and N. Shiraishi, *Wood Sci. Technol.*, **30**, 39 (1995).
16. L. Lin, M.H. Alma, M. Yoshioka, Y. Yao and N. Shiraishi, Kyoto Conference on Cellulose, p. 121 (1994).
17. Y. Kurimoto, K. Shirakawa, M. Yoshioka and N. Shiraishi, Liquefaction of Untreated Wood With Polyhydric Alcohols and Its Application to Polyurethane Foams, Chemical Modification of Lignocellulosics, FRI Bulletin No. 176, pp. 163-172 (1992).
18. L. Lin, M. Yoshioka, Y. Yao and N. Shiraishi, *Holzforschung*, **51**, 333 (1997).
19. Y. Yao, M. Yoshioka and N. Shiraishi, *Mokuzai Gakkaishi*, **39**, 930 (1993).
20. Y. Kurimoto, S. Doi and Y. Tamura, *Holzforschung*, **53**, 617 (1999).
21. G.- Li, T.- Qin, S.- Tohmura and A. Ikeda, *J. For. Res.*, **15**, 211 (2004).
22. Z.H. Zhuang, B. He and Z.G. Yang, *Plastic, Rubber and Composites*, **39**, 460 (2010).