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Fractal Characteristics of Modified β- cyclodextrin

Dongfeng Zhao[1], Sulan Yu[1], Lixin Tang[2], Genwu Zheng[2], Meifeng Dai[3] *
[1]Department of Chemistry and Chemical Engineering, Weifang Vocational College, Weifang, Shandong, 261041, China
[2]Chemical Engineering Department, Nanjing college of chemical technology, Nanjing, 210048, China
[3]Nonlinear Scientific Research Center, Faculty of Science, Jiangsu University Zhenjiang, Jiangsu, 212013, China
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Abstract: Crosslinked β-cyclodextrin (β-CyD) polymers with diisocyanate was prepared. The main factors and optimum conditions: n (isocyanate): n (β-CD) molar ratio of about 1:9, diisocyanate and hexamethylene selection isocyanate (HDI). Cross-linked products were Fractal characterized by scanning electron microscopy (SEM). The results show that, the modified β-CD cavity retained its original structure, polymer cross-linked network structure with a cavity formed morphology and porous.

Keywords: β- cyclodextrin; hexamethylene diisocyanate; modified; fractal

1 Introduction

Cyclodextrin is D- glucopyranose units through $\alpha-(1\rightarrow 4)$ - glycosidic bond formed by a ring-like oligosaccharides, the most common is the degree of polymerization of 6, 7 and 8, respectively, containing a 1,4 - bond unit glycosidic α-, β-, γ- cyclodextrin (CD), Because of differences in their physicochemical properties, currently the most studied is β-cyclodextrin. Cyclodextrin molecule tapered cylindrical structure, the distribution of hydroxyl groups in the hydrophilic outer edge molecule, C-H bond and C-O-C bond in the molecule inside the cover [1], the structure of the ring dextrin has the characteristics of an external hydrophilic, hydrophobic interior.

Using its external hydrophobic properties, the hydroxyl between hydrogen bonds formed and van der Waals, cyclodextrin with many inorganic and organic compounds form inclusion complexes [2], this feature is widely used in medicine [3], chemical analysis [4], environmental protection, especially wastewater treatment [5] and other fields.

β- cyclodextrin in water solubility of 1.64%, the inclusion complex with other substances which produce lower soluble, easily crystallized from solution[6], or simply rely on hydrogen bonding or van der Waals force effect, inclusion complexes easily separated, so that in the field of wastewater treatment applications is greatly restricted. To repair the structural defects cyclodextrin, to expand its range of applications, modifications need to be modified. Chemical modification is to maintain substantially constant the cyclodextrin skeleton case, the hydroxyl group in its molecule with another chemical reaction group etherification, esterification, oxidation and crosslinking to obtain the crosslinked polymer. Most used is hydroxypropyl, starch [7, 8], chitosan [9], and hexamethylene diisocyanate (HDI) [10], etc., after the modification in terms of its wastewater treatment better than the direct effect of the use.

Ultrasound chemistry is an interdisciplinary, the use of ultrasound energy ultrasound acceleration and control of chemical reactions, improve the reaction yield and lead to new chemical reactions [11].

Cavitation mainly from ultrasonic chemical - a liquid cavity formation, oscillation, growth and shrinkage and collapse of the physical and chemical changes triggered. Liquid cavitation process is to focus the sound field and the rapid release of energy in the process, when the collapse of cavitation bubbles in a very small space within a very short time and cavitation bubbles, resulting in temperatures above 5000 K and about 5.05 $\times$ 10^8Pa of pressure, the temperature rate of change up to 10^{10}K / s, and the associated strong shock wave and speeds up to 400 km of the micro-jet, which is difficult to achieve or chemical reaction can not be achieved under normal conditions provides a new and very special physical environment , opening up new chemical reaction channels [12, 13]. Ultrasound using its unique role, not only can greatly promote the chemical reaction rate, and can effectively change the chemical reaction process, improve the selectivity of the desired product. This paper studies the optimum conditions for the use of isocyanate modified β- cyclodextrin synthesis,

*Corresponding author. *E-mail address*: daimf@mail.ujs.edu.cn

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using Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetry, element analysis method for the preparation of polymeric was characterized.

2 Preparation of β-CD- diisocyanate crosslinked polymer

When the amount of distilled β-CD, catalyst, DMF solvent was added to 250 mL three-necked flask, the flask was p 1afa laced in a sonicator and the heater and through the protection of N_2, heated to a suitable temperature, a certain percentage of the flask was added di isocyanate, continuing the heating to the reaction temperature after ultrasound. Because ultrasound emit some heat during the reaction, ultrasound stopped after 1h, 20 min after continue to open ultrasound, to end the use of cross-linking reaction. After completion of the reaction terminating agent was added, then washed with plenty of water, washed and dried in a vacuum oven to constant weight, ground using a ball mill after use.

3 Results and Discussion

3.1 Influence of β-CD/HDI(molar ratio) on product yield(η)

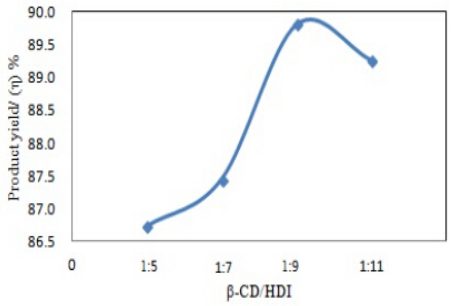

Figure 1: Influence of β-CD/HDI (molar ratio) on product yield.

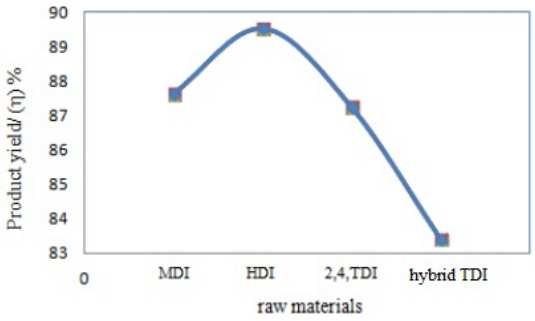

Figure 2: Influence of raw materials on product yield

In ultrasonic intensity of 0.1W·cm^{-2}, the reaction temperature of 60°C, the reaction time under conditions of 7 h, impact on the yield β-CD/HDI been studied. Figure 1 shows that, with increasing the molar ratio of the yield gradually increased, in 1:9, maximum yield, and therefore the optimal molar ratio of 1:9.

3.2 Influence of raw materials on product yield(η)

As can be seen from Figure 2, Under the other same conditions, using HDI modifier, the yield is maximum, using hybrid TDI modifier, the yield is minimum, So use HDI as a modifier.

3.3 β-CD crosslinked polymer SEM analysis

Figure 3 (a) show, β-CD is a layered structure, with fluorescence. Figure 3 (b) is a β-CD-HDI crosslinked polymer with HDI with β-CD formed under no ultrasonic condition, the surface showed a layered, three-dimensional network structure can be seen, no fluorescence, which is the original β-CD molecule fluorescence disappeared, indicating that the β-CD molecule and HDI molecular crosslinking reaction, changes the molecular structure of the original model, modified cyclodextrins were very good. Meanwhile, using box-countingfractal dimension is 1.7990 and 1.8213 in Figure 3(a) and (b), indicating that the modified cyclodextrin through the surface area increases, the absorption enhancement.

3.4 Influence of reaction time on product yield(η)

Figure 4 shows reaction time influences the product yield. With the reaction time increasing, the yield gradually increases, reaching a maximum value and then gradually decreases , and the contents 6.5h, the maximum yield.

(a) (b)

Figure 3: SEM of β-CD and β-CD-HDI.

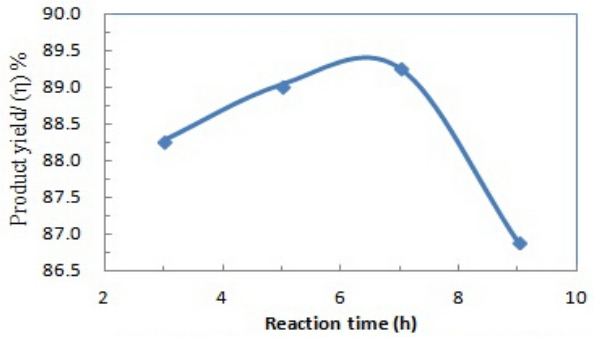

Fig 4 Influence of reaction time on product yield

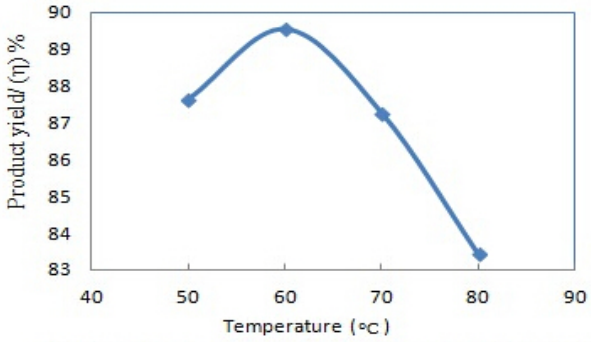

Fig 5 Influence of reaction temperature on product yield

3.5 Influence of reaction temperature on product yield (η)

Figure 5 shows the effect of reaction temperature on the yield , were investigated 50°C, 60°C, 70°C, 80°C four reaction temperature influence on the yield. At 60C , the product yield reaches maximum.

4 Conclusions

(1) Preparation of cross-linked β-CD crosslinked polymer optimum conditions : an isocyanate with β-CD molar ratio of about 1:9; optional diisocyanate, hexamethylene diisocyanate (HDI) reaction time 6.5h; reaction temperature 60°C.

(2) The results of scanning electron microscopy (SEM) to characterize cross-linked products show that: the modified β-CD cavity retained its original structure, and reaction of the diisocyanate-based carbamate bond, cross-linked polymer formed of a three-dimensional network structure and criss-cross larger specific surface area. This structure has high stability and absorption, may have broad prospects in organic wastewater treatment.

Acknowledgements

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References

[1] Crinia G, Morin N, Rouland J C, et al. Adsorption de bta-naphtol sur des gels de cyclodextrine-carboxyméthylcellulose réticulés. *European Polymer Journal*, 38(2002): 1095-1103.

[2] Kozlowski C A, Walkowiak W. Removal of chromiumVIfrom aqueous solutions by polymer inclusion membranes. *Water Res.*, 36(2002): 4870-4875.

[3] J. S. LiH. N. XiaoJ. H. Liet al. Drug carrier systems based on water-soluble cationic β-cyclodextrin polymers. *International Journal of Pharmaceutics*, 278(2004): 329-342.

[4] Schneiderman E, Stalcup A M. CyclodextrinsA versatile tool in separation science. *J. Chromatogr. B*, 745(2000): 83-102.

[5] Hedges A R. Industrial applications of cyclodextrins. *Chem. Rev.*, 98(1998): 2035-2044.

[6] Grégorio Crini. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci.*, 30(2005): 38-70.

[7] Goncharuk V V, Kucheruk D D, Kochkodan V M, et al. Removal of organic substances from aqueous solutions by reagent enhanced reverse osmosis. *Desalination*, 143(2002): 45-51.

[8] Lee J M, Kim M S, Hwang B, et al. Photodegradation of acid red 114 dissolved using a photo-Fenton process with TiO2. *Dyes Pigments*, 56(2003): 59-67.

[9] Hirohito Yamasaki, Yousuke Makihata, Kimitoshi Fukunaga. Preparation of crosslinked β-cyclodextrin polymer beads and their application as a sorbent for removal of phenol from wastewater. *J. Chem. Technol. Biotechnol.*, 83(2008): 991-997.

[10] Majumdar Sukti, Kumar P Senthil, Pandit A B. Effect of liquid-phase properties on ultrasound intensity and cavitational activity. *Ultrasonics Sonochemistry*, 5(1998): 113-118.

[11] Giancarlo Cravotto, Luisa BoffaMarta Turello, et al. Chemical modifications of bile acids under high-intensity ultrasound or microwave irradiation. *Steroids*, 70(2005): 77-83.

[12] Jórg Hofmann, Ute Freier, Mike Wecks. Ultrasound promoted C-alkylation of benzyl cyanide–Effect of reactor and ultrasound parameters. *Ultrasonics Sonochemistry*, 10(2003): 271-275.

[13] R. Feng, Y. Y. ZhaoC. G. Bao. Sonochemistry in China. *Ultrasonics Sonochemistry*, 4(1997): 183-187.