ISSN 1749-3889 (print), 1749-3897 (online)
International Journal of Nonlinear Science
Vol.20(2015) No.1,pp.11-14

Fractal Characteristics Under Ultrasonic Condition of Modified β-cyclodextrin

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(Received 12 October 2014, accepted 08 February 2015)

Abstract: Crosslinked β-cyclodextrin (β-CyD) polymer with diisocyanate is prepared under ultrasonic irradiation. The key parameters and optimum synthesis conditions are optimized by orthogonal experiment and evaluated with yield ratio. The optimal reaction conditions are that reaction temperature is 60^0C and reaction time is 6.5 h under ultrasonic intensity 0.1W·cm^{-2}. The reaction temperature is lowered and reaction time shortened under ultrasonic irradiation. The crosslinked polymer has micro-sphere surface topography and multi-hole cavity structure.

Keywords: β- cyclodextrin ; ultrasonic; modified ; fractal

1 Introduction

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

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

The solubility of $\beta-$cyclodextrin is of 1.64×10^{-2} in wate. The inclusion complex with other substances is lower soluble and crystallized easily [6]. So wastewater treatment applications was greatly restricted. To repair the structural defects and expand its range of applications, cyclodextrin was needed to be modified.

Ultrasound chemistry is an interdisciplinary with the use of ultrasound energy accelerating, controlling chemical reactions, improving the reaction yield and leading to new chemical reactions [7].

Cavitation mainly from ultrasonic chemical, cavity formation, oscillation, growth and shrinkage and collapse in liquid. Liquid cavitation process is to focus the sound field and release the energy rapidly. When the cavitation bubbles are collapsed, its temperature was above 5000 K and about 5.05×10^8 Pa and the temperature rate of change up to 10^{10} K/s. It provides the new chemical reaction channels [8, 9]. Using ultrasound unique role, not only can greatly promote the chemical reaction rate, change effectively the chemical reaction process, improve the selectivity of the desired product. This paper studied the optimum reaction conditions under ultrasound.

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IJNS.2015.08.15/871

2 Preparation of β-CD- diisocyanate crosslinked polymer

When the amount of distilled $\beta-$CD, catalyst, DMF solvent is added to 250 mL three-necked flask, the flask is placed in a sonicator, the heater and access N_2. When it is heated to a suitable temperature,a certain percentage of the diisocyanate is added, continuing the heating to the reaction temperature then ultrasounding. Because ultrasound emits some heat during the reaction, ultrasound is stopped after reaction 1h, and continues to open ultrasound after 20 min to end the use of cross-linking reaction. The terminating agent is added after completion of the reaction, then washed with plenty of water, washed and dried in a vacuum oven to constant weight.

3 Results and Discussion

3.1 Influence of ultrasonic intensity on product yield(η)

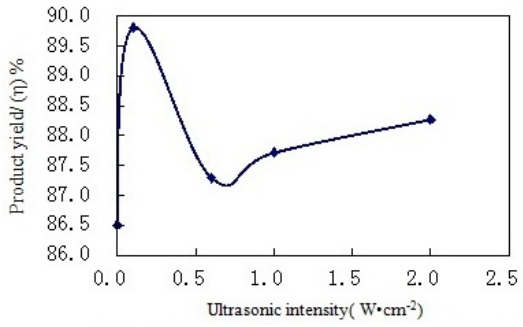

Figure 1: Influence of ultrasonic on product yield.

As can be seen from Figure 1, with the ultrasonic intensity increases, product yield first dropped to the lowest point then gradually increases.When ultrasonic intensity is 0.1W·cm^{-2}, the product yield is up to 89.80%, so choose the ultrasonc intensity of 0.1W·cm^{-2}.

3.2 Influence of reaction time on product yield(η)

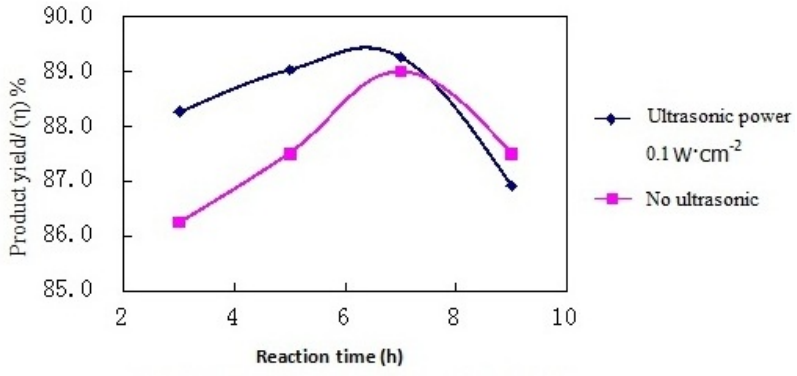

Figure 2: Influence of reaction time on product yield.

Figure 2 shows under the ultrasonic intensity being $0.1\text{W}\cdot\text{cm}^{-2}$ and no ultrasonic, reaction time influences on the product yield. With the reaction time increasing, the yield gradually increases, reaches the maximum value and then gradually decreases. When the ultrasonic is $0.1\text{W}\cdot\text{cm}^{-2}$, the yield was maximum at 6.5 h. While no ultrasonic, the yield was maximum at 7h. So when the ultrasonic power is $0.1\text{W}\cdot\text{cm}^{-2}$, the reaction time decreases by 0.5 h.

3.3 Influence of reaction temperature on product yield(η)

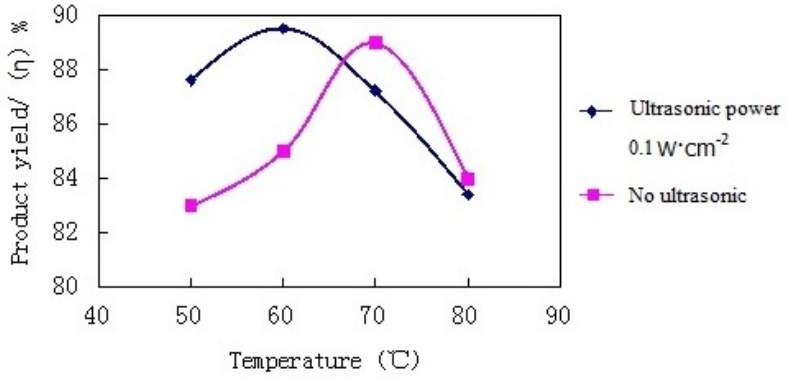

Figure 3: Influence of reaction temperature on product yield.

Figure 3 shows the effect of reaction temperature on the yield. It is investigated at 50^0C, 60^0C, 70^0C, 80^0C. With the increase of temperature, the yield increases, and reaches the maximum then decreases. When the ultrasonic is $0.1\text{W}\cdot\text{cm}^{-2}$, the yield was maximum at 60^0C. While no ultrasonic, the yield was maximum at 70^0C. So when the ultrasonic power is $0.1\text{W}\cdot\text{cm}^{-2}$, the reaction temperature decreases by 10 degrees.

3.4 SEM analysis of ultrasound-modified β-cyclodextrin

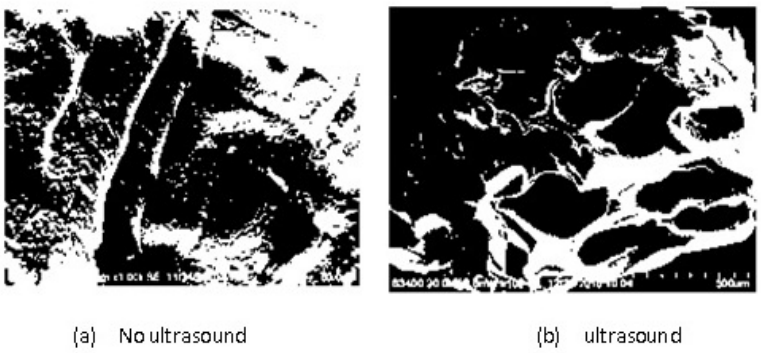

Figure 4: SEM of β-cyclodextrin.

Figure 4(a) 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. Figure 4(b) shows the cross-linked polymer internal ultrasound conditions have cavity structure, retaining the original cyclodextrin cavity structure. This empty cavity increases the inclusion of organic molecules, broadening the polymer scope and effect of the drug and the wastewater

treatment. Meanwhile, using box-counting, fractal dimension is 1.8213 and 1.8580 in Figure 4(a) and (b), indicating that the surface area of ultrasound-modified β-cyclodextrin increases, improves the absorption rate.

4 Conclusions

Optimum conditions for preparing modified cross-linked polymer β-CD under ultrasound: ultrasonic intensity was $0.1\mathrm{W}\cdot\mathrm{cm}^{-2}$, the reaction temperature is 60^0C, reaction time of 6.5h. The temperature conditions reduces 10^0C, reaction time reduces 2.5h without adding ultrasonic irradiation. Modified cross-linked polymer β-CD has a porous structure.

The results of scanning electron microscopy (SEM) to characterize cross-linked products show that: β-CD cavity with modification and ultrasound retains its original structure, and forms a three-dimensional network structure and criss-cross a large specific surface area. This structure has high stability and absorption, may have broad prospects in organic wastewater treatment.

Acknowledgements

Research is supported by the Humanistic and Social Science Foundation from Ministry of Education of China (Grants 14YJAZH012).

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