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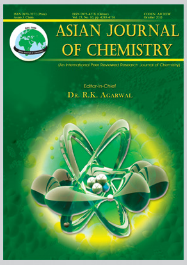

Study on Preparation and Characterization of Cross-linked β-Cyclodextrin Polymers with Hexamethylene Diisocyanate in Ultrasonic

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Through modifying β-cyclodextrin (β-CD) with diisocyanate in ultrasonic conditions, the cross-linked polymer of the modified cyclodextrin was produced. The main influencing factors and optimum synthesis technological conditions of diisocyanate modified cyclodextrin were selected *via* orthogonal experimental method and by taking the yield of cross-linked polymer as an evaluation index: the mole ratio of *n* (isocyanate): *n* (β-CD) was about 1:9; hexamethylene diisocyanate (HDI) was employed as diisocyanate; ultrasonic intensity, 0.1 W cm^{-2}; reaction temperature, 60 ºC; and reaction time was 7 h. After characterizing the cross-linked polymer by means of such test methods as infrared spectrum, scanning electron microscope and thermogravimetric analysis, the result indicated that the modified β-cyclodextrin kept the original cavity structure; the cyclodextrin generated carbamic acid ester base bond through reaction with the diisocyanate and the cross-linked polymer is in a network structure. The synthesis of cyclodextrin polymer in ultrasonic conditions might reduce the reaction temperature and shorten the reaction time and the cross-linked polymer formed a microspheric multi-cavity structure.

Key Words: β-Cyclodextrin, Hexamethylene diisocyanate, Modified, Ultrasonic wave.

INTRODUCTION

Cyclodextrin is a kind of cyclic oligosaccharide linked by D-glucopyranose unit through α-(1 → 4)-glucosidic bond, of which the most common cyclodextrins are α-, β- and γ-cyclodextrin, with their polymerization containing 6, 7 and 8 1,4-glucosidic bond units respectively[1]. Due to the difference of their physicochemical properties, β-cyclodextrin (β-CD) is most frequently studied. The molecular structure of the cyclodextrin is in a pyramidal cylinder, with the hydrophilic hydroxy distributing on the exterior edge of the molecule, C-H bond and C-O-C bond covering inside the molecule[2]. Such a structure enables the cyclodextrin to have externally hydrophilic and internally hydrophobic characteristics. By making use of its external hydroxy's hydrophobic characteristics, in combination with the hydrogen bond and van der Waals, *etc*. formed between hydroxy group of, the cyclodextrin can make clathrate compound with numerous inorganic and organic compounds[3] and this characteristic is widely applicable in the pharmaceuticals industry[4], chemical industry analysis[5] and environmental protection[6], particularly waste water treatment[7], *etc*. The molecular physical properties of cyclodextrin[1] are presented in Table-1.

The solubility of β-cyclodextrin in water is 1.64 %. After generating clathrate compound with other substances, it will have a lower water-solubility and is easily separated from the solution by crystallization. If the action of hydrogen bond or van der Waals' force (VDW) is solely relied on, the clathrate compound can be separated easily. It makes β-cyclodextrin application field greatly limited in t treatment the sewage. To make up the structural deficiency of β-cyclodextrin and enlarge its application range, it's required to carry out modification for β-cyclodextrin. The chemical modification method is to obtain the cross-linked polymer by using the chemical reactions such as etherification, esterification, oxidation and cross linking between the hydroxy in its molecule and other base groups under the condition that the cyclodextrin skeleton is basically kept unchanged. The most frequently used is hydroxypropyl[8], as well as starch[9,10], chitosan[11] and hexamethylene diisocyanate (HDI)[12]. The modified β-cyclodextrin shows a better efficiency in wastewater treatment.

Sonochemistry is an interdisciplinary subject, which speeds up and controls the chemical reaction, improves the reaction yield. It initiates new chemical reactions by taking advantage of the ultrasonic energy. Sonochemistry is mainly derived from the formation, oscillation, growth and contraction and collapse of the cavity in a liquid of acoustic cavitation and the physical and chemical changes caused. The liquid acoustic cavitation process is a process concentrating sound

TABLE-1
DATE OF ORTHOGONAL EXPERIMENT

Parameters	α-Cyclodextrin	β-Cyclodextrin	γ-Cyclodextrin
Glucose units	6	7	8
Relative molecular mass	972	1135	1297
Cavity diameter (nm)	4.7-5.3	6.0-6.5	7.5-8.3
Cavity height (nm)	7.9 ± 0.1	7.9 ± 0.1	7.9 ± 0.1
Crystalline form (in water)	Acicular	Prism	Prism
Outer circle diameter (nm)	14.6 ± 0.4	15.4 ± 0.1	17.5 ± 0.1
Solubility (25 ºC), (g/100 mL)	14.5	1.85	23.2

field energy and releasing rapidly. When the cavitation bubble collapses, a high temperature above 5,000 K and a high pressure of about 5.05×10^8 Pa will be produced in an extremely short time. The minimum space of the cavitation bubble and the speed variation is as high as 10^{10} K/s, accompanied with a strong impact wave and a micro jet with a speed per hour of 400 km, which provides a new and special physical environment and starts a new chemical reaction channel[16,17] for the chemical reactions. These reactions are hard to be or cannot be realized in general conditions. Ultrasonic cavitation lasts for a short time and releases high energy. In high temperature conditions, ultrasonic cavitation has beneficial to the splitting decomposition of reactive species and the production of free radicals, so that more active reactive species are generated. Ultrasonic cavitation has facilitated secondary reaction and improved the rate of chemical reaction. In addition, the high pressure during the collapse of air bubbles is good for high pressure gaseous phase reactions. Which t the impact wave and micro jet phenomenon produce the high pressure, has a good impact effect in the solid and liquid systems, particularly resulting in the strong collision and aggregation between molecules. Ultrasound can not only largely improve the rate of chemical reaction, but also effectively change the chemical reaction mechanism and enhance the selectivity of the target product[18,19]. The paper study the cross-linking reaction of the cyclodextrin by using of ultrasonic and synthetise the cyclodextrin polymers.

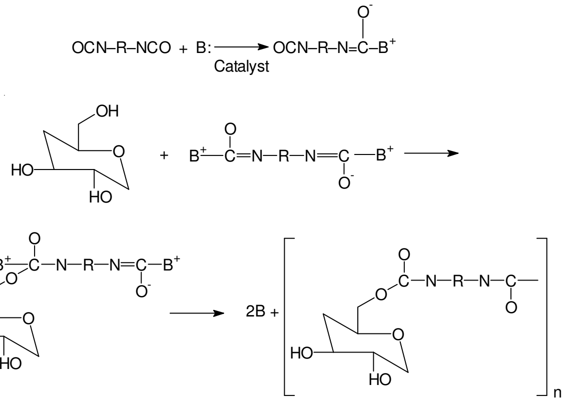
The paper has studied the synthesis conditions and the structural characterization of the cross linked polymers. Cross linked polymers was synthetized by cross linking reaction with β-cyclodextrin and hexamethylene diisocyanate. The polymers structure is characterized by the Fourier transform infrared spectrometer (FTIR) and scanning electron microscope (SEM), thermogravimetry (TG) and elementary analysis methods.

EXPERIMENTAL

N,N-dimethyl formamide (DMF) (AR, Sinopharm Chemical Reagent Co. Ltd.), which is subject to vacuum distillation before being used; 2,4-toluene diisocynate (TDI) (AR, Shanghai Chemical Reagent Co. Ltd.), which is dewatered and dried with a zeolite molecular sieve before being used; mixed toluene diisocynate (mixed TDI); hexamethylene diisocyanate (HDI) (Adamas Reagent Co. Ltd.); Diphenylmethane diisocyanate (MDI) (GR, New Jersey, USA); β-cyclodextrin (AR, Sinopharm Chemical Reagent Co., Ltd.), which is subject to purification through crystallization before being used; chloroform (CR, Shanghai Zhongshi Chemical Corporation); Dibutyltin dilaurate (BTL) (CR, Shanghai No. 4 Reagent Factory); triethylene diamine (AR, Sinopharm Chemical Reagent Co. Ltd.), which is subject to vacuum drying before being used.

Water bath kettle, vacuum pump, ultrasonic generator, QM-3SP ball mill manufactured by Nanjing University Instrument Plant. Infrared spectrometer FTIR NEXUS670, American Nicolet Company. Chemisorption analyzer, CHEMEBET-3000, Quantachrome Corporation, USA. Scanning electron microscope, S-3400N II, Hitachi Corporation, Japan. Differential thermal/thermogravimetric analyzer, STA 449C/6/F. XRD is D8 Advance automatic X-ray diffractometer manufactured by Bruker Corporation, Germany.

Preparation of cross-linked β-cyclodextrin-diisocyanate polymer: Add a proper amount of distilled β-cyclodextrin, catalyst and *N,N*-dimethyl formamide solvent into a 250 mL three-opening flask. The flask and heater are put in the ultrasonic generator and open N_2 at the same time. After solution reaches an appropriate temperature and add certain proportional hexamethylene diisocyanate into the flask and continue using the ultrasound after it is heated to the reaction temperature. Since the ultrasound releases certain quantity of heat during the reaction, stop the ultrasound after 1 h and then start the ultrasound again 20 min later until the cross-linking reaction is finished. Put in terminator upon complete of the reaction then clean it with lots of water, then put it in the vacuum drying oven until all solvents have been removed. Mill it with a ball mill for future use. Taking the reaction between a-NCO and cyclodextrin as an example, the chemical reaction is as shown in **Scheme-I**.



Scheme-I: Chemical reaction of hexamethylene diisocyanate with β-cyclodextrin

RESULTS AND DISCUSSION

Orthogonal experimental design and data processing: Five factors of influencing the synthetic rate is selected in experiment. They are the molar ratio (A) of reactant *n* (cyclodextrin)

TABLE-2
DATE OF ORTHOGONAL EXPERIMENT

Serial number	Factor A	Factor B	Factor C	Factor D	Factor E	Yield ratio (%)
	Ratio (mol/mol)	Material kind	Ultrasonic intensity (W cm^{-2})	Reaction temperature (ºC)	Reaction time (h)	
1	1(1:5)	1(MDI)	1(0.1)	1(50)	1(9)	86.73
2	1	2(HDI)	2(0.6)	2(60)	2(7)	89.52
3	1	3(2,4-TDI)	3(1.0)	3(70)	3(5)	87.24
4	1	4(blend TDI)	4(2.0)	4(80)	4(3)	83.41
5	2(1:7)	1	3	3	4	87.69
6	2	2	2	4	3	89.52
7	2	3	1	1	2	87.45
8	2	4	4	2	1	86.13
9	3(1:9)	1	3	4	2	87.72
10	3	2	4	3	1	88.27
11	3	3	1	2	4	89.81
12	3	4	2	1	3	87.29
13	4(1:11)	1	4	2	3	89.03
14	4	2	3	1	4	88.27
15	4	3	2	4	1	86.91
16	4	4	1	3	2	89.26
K1	339.52	350.79	353.09	353.47		
K2	344.64	355.58	351.41	346.09		
K3	353.25	353.24	350.92	346.84		
K4	349.74	354.49	352.46	347.56		
K5	348.04	353.95	353.08	349.18		
k1	84.88	87.70	88.27	88.37		
k2	86.16	88.90	87.85	86.52		
k3	88.31	88.31	87.73	86.71		
k4	87.44	88.62	88.12	86.89		
k5	87.01	88.49	88.27	87.30		
Range	3.4875	2.735	1.6025	1.7325	1.26	
Optimum	A_3	B_2	C_1	D_2	E_2	

to *n* (isocyanate), the type of diisocyanate (B), ultrasonic intensity (C), reaction temperature (D) and reaction time (E). The experiment adopts the $L_{16}(4^5)$ orthogonal experiment table and takes the synthetic yield ratio (Y) as an evaluation indicator. The experimental results are shown in Table-2.

The dates of range suggest that the effects of the five factors on synthetic yield ratio are different. They influence order are molar ratio of raw materials > type of diisocyanate > ultrasonic intensity > reaction temperature > reaction time. On the basis of dates of the difference factors and different levels, the optimal technological combination of synthetic reaction is $A_3B_2C_1D_2E_2$. Carrying out experiments based on such combination, the yield ratio is 92.7 %. The optimal technological conditions are equal to 1:9 of the molar ratio of n (cyclodextrin) to n (isocyanate), hexamethylene diisocyanate as material isocyanate, ultrasonic intensity 0.1 W cm^{-2}, reaction temperature 60 ºC and reaction time 7 h.

Infrared spectrum analysis of synthetic polymer: FTIR spectra (IR) of β-CD (1), β-CD-HDI polymer (2) and HDI (3) is shown as Fig. 1. In this spectra, β-cyclodextrin and β-cyclodextrin-HDI have stretching vibration absorption peaks of an OH bond at 3500-3400 cm^{-1}, which shows that the polyhydroxyl functional group exists in β-cyclodextrin and β-cyclodextrin-HDI polymers. The strength of hydroxyl peak of β-cyclodextrin-HDI polymer is apparently weakened compared with that of β-cyclodextrin. In the IR spectra of β-cyclodextrin-HDI, the characteristic absorption peak of N-H bond appears at 1500-1600 cm^{-1}. β-Cyclodextrin-HDI characteristic absorption peak of carboxylate -C=O appears at about 1700 cm^{-1}. The original -NCO peak of HDI at 2300-2200 cm^{-1} disappears in β-cyclodextrin-HDI. It shows that -NCO functional group and hydroxyl react completely and generate urethane group. It mean that cross-linked polymer is generated by synthetic reaction of β-cyclodextrin and hexamethylene diisocyanate.

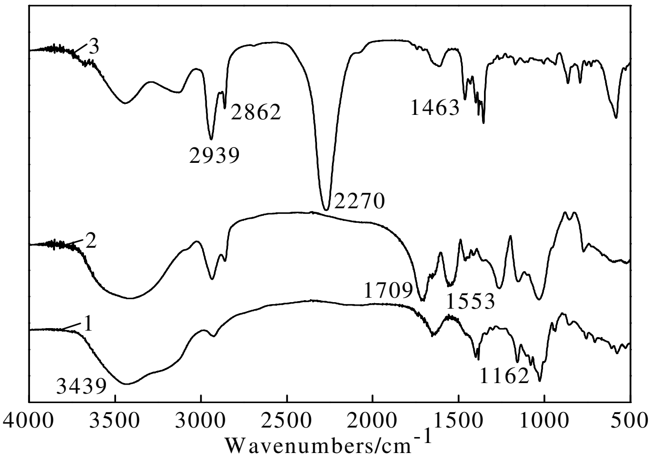


Fig. 1. FTIR spectra of β-cyclodextrin (1), β-cyclodextrin-HDI polymer (2) and HDI (3)

Thermogravimetric analysis of cross-linked β-cyclodextrin-hexamethylene diisocyanate polymer: Thermogravimetric analysis curves of β-cyclodextrin (a) and β-cyclodextrin-HDI (b) is showed in Fig. 2.

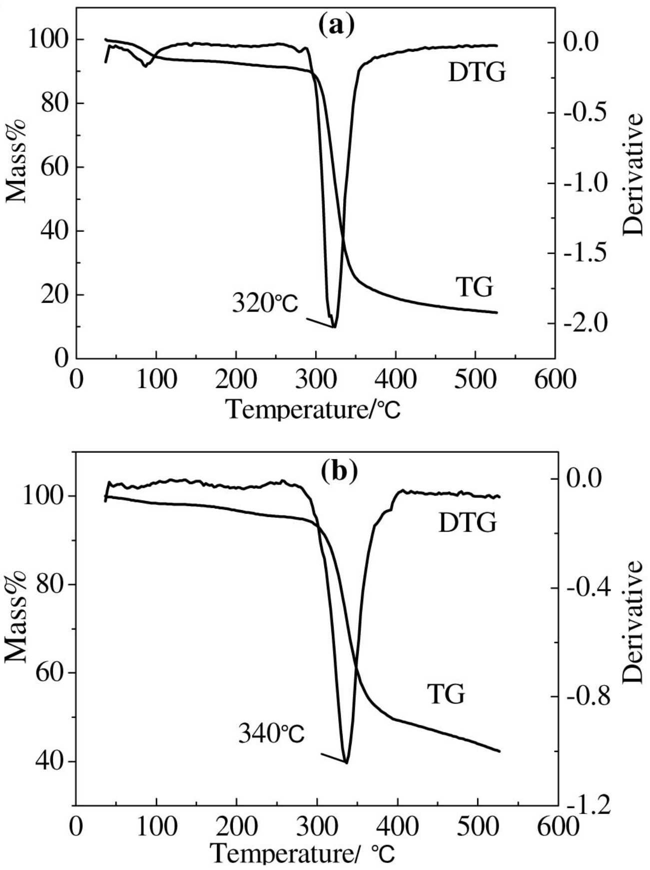
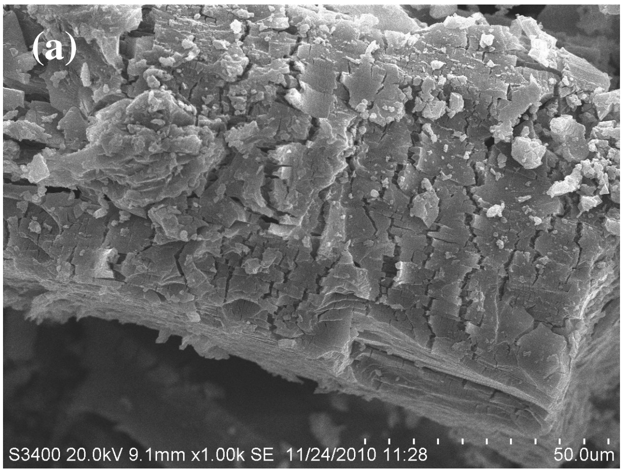


Fig. 2. TG curves of β-cyclodextrin (a) and β-cyclodextrin-HDI polymer(b)

Fig. 2 (a) shows that the thermo decomposing temperature of β-cyclodextrin is about 320 ºC and that of the polymer after cross-linking modification is about 340 ºC. It means that the thermo decomposing temperature of β-cyclodextrin has been increased by about 20 ºC due to modification. The modified β-cyclodextrin polymers exists urethane bond due to cross-linking the β-cyclodextrin with hexamethylene diisocyanate. The structure increases polymers molecular weight, strengthens of bonds and the heat stability.

SEM and XRD analysis of cross-linked β-cyclodextrin polymer: The SEM photo of β-cyclodextrin (a) and β-cyclodextrin-HDI (b-f) display in Fig. 3. Surface features of cross-linked polymer can be seen through SEM in the following pictures.



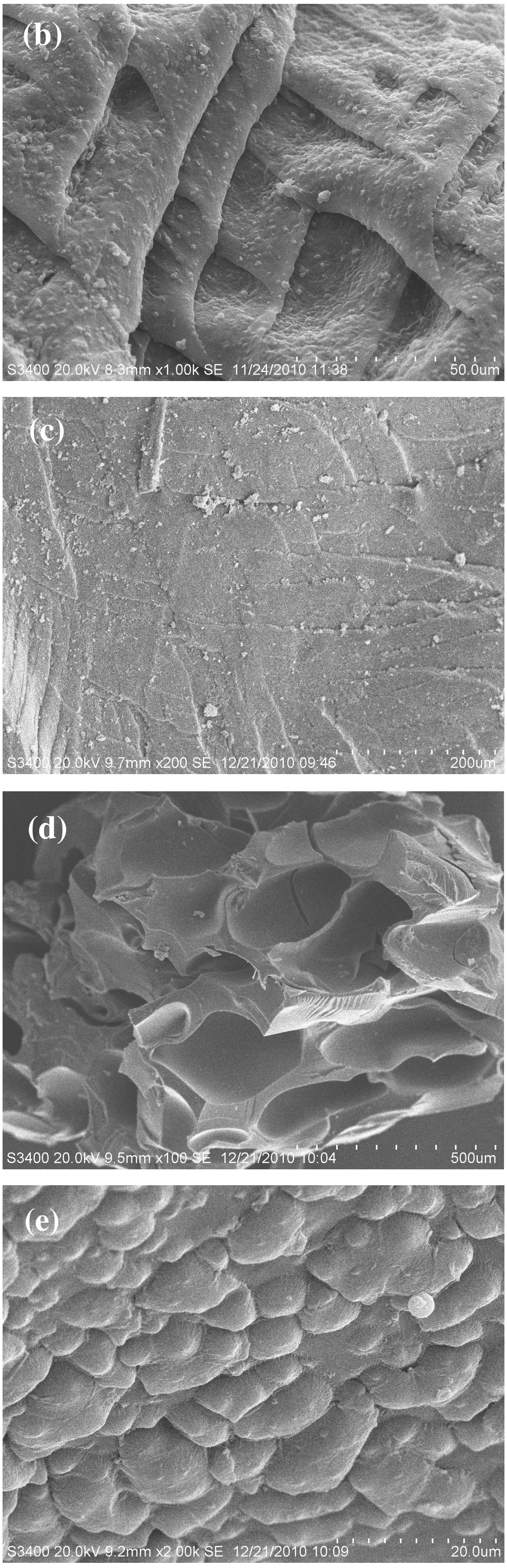


Fig. 3. SEM of β-cyclodextrin (a), β-cyclodextrin-HDI (b) and ultrasound synthesizing β-cyclodextrin-HDI (c-f) polymer

The Fig. 3 (a) shows that β-cyclodextrin has a layer structure and fluorescence. Fig. 3 (b) is a picture of cross-linked β-cyclodextrin-HDI polymer formed by β-cyclodextrin and hexamethylene diisocyanate without ultrasound. The network structure surface feature can be seen. The fluorescence of β-cyclodextrin is disappeared in β-cyclodextrin-HDI. This phenomenon indicates that the structural mode of original molecule of β-cyclodextrin has been modified by crosslinker HDI. The appearance of crosslinked polymer synthesized in ultrasound is shown in Fig.3 (c-f). The cross-linked polymer synthesized in ultrasound is smooth and dense with crossing network lines in Fig. 3 (c). The Fig. 3 (d) shows that the cross-linked polymer has a cavity structure inside, *i.e.* the original cavity structure of cyclodextrin is retained. These cavities structure enhances the inclusion complex capacity through host-guest interactions and increases porosity of the adsorbent. The compactness and the lack of pore are solved by this method. Because the lack of pore influences molecular diffusivity of guest. The unique structure character of the adsorbent broadens the application range. The polymer may apply drags liberation and waste water treatment. The microballoon surface of polymer is exhibited in Fig. 3 (e) and (f). The microballoon surface structure increases the specific surface area of polymer and improve adsorption capability. The microballoon particle may be prepared by controlling reaction conditions.

XRD of β-cyclodextrin (a) and β-cyclodextrin-HDI (b) are shown in Fig. 4.

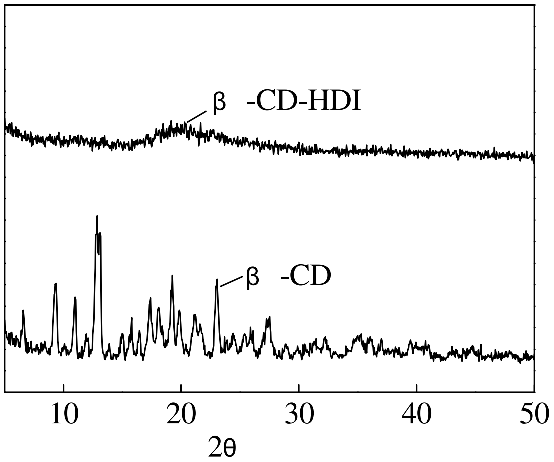


Fig. 4. XRD of β-cyclodextrin (β-CD) and ß-CD-HDI polymer

Fig. 4 shows that β-cyclodextrin has a strong characteristic diffraction peak in the range of 10º-15º and 20º-25º of 2θ. β-Cyclodextrin-HDI polymer has no obvious diffraction peak in the range of 10º-15º and 20º-25º of 2θ in Fig. 4. The phenomenon suggests that the cross-linked polymers are amorphous aggregation and the characteristic diffraction peaks of β-cyclodextrin disappear. The carbonic acid ester bonds are generated by cross linking reaction of the hydroxyl in β-cyclodextrin with carbonyl in HDI. The reaction weakens the strength of the hydrogen bond and van der Waals' force and results in the reduction of the crystallization ability of polymer.

Specific surface area of cross-linked polymer: Table-3 shows specific surface area data of the cross-linked β-cyclodextrin polymer before and after using the ultrasound.

TABLE-3
DATE OF ANALYTICAL SPECIFIC SURFACE AREA

Polymer	BET (m^2g^{-1})
β-Cyclodextrin-HDI (without ultrasonic)	0.74116
β-Cyclodextrin-HDI (in ultrasonic)	1.9648

Table-3 means that the specific surface area of β-cyclodextrin-HDI after cross-linking modification increases. The specific surface area using the ultrasound (1.965 m^2/g) is larger than without using ultrasound (0.74116 m^2/g). This results may be owing to ultrasound's homogeneous role in the synthesis process.

Conclusion

The optimum technology conditions are found by orthogonality experiment. The results mean that the molar ratio of n (isocyanate) to n (β-CD) is equivalent to about 1:9, hexamethylene diisocyanate (HDI) is optimal diisocyanate, ultrasonic intensity selects 0.1 W cm^{-2}, reaction temperature is 60 ºC and reaction time is 7 h. Compared with the synthesis reaction without ultrasonic irradiation, the technology parameters obviously change. The reaction temperature is decreased by 10 ºC. The reaction time is shorted by 2 h. The β-cyclodextrin-HDI polymer shows a micro-spherical multi-cavity network structure. The results of characterizing the crosslinked polymer show that the crosslinked β-cyclodextrin-HDI polymer possesses of β-cyclodextrin original cavity structure. The crosslinked reaction generates urethane bond. The crosslinked polymer forms the crossing network structure and microballoon surface topography. The microballoon surface topography has larger specific surface area. This structure characteristics provides higher stability and absorption efficiency. The property facilitate the use of organic waste water treatment.

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