PREPARATION OF REGENERATED CELLULOSE BEAD AND ITS COATING WITH CYCLODEXTRINS

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A study on grafting functional host molecules of cyclodextrins (CDs) onto cellulose beads is reported in this paper. Cellulose beads were prepared by our self-made circumrotation centrifugal machine. Host molecules of *β*-cyclodextrin (*β*-CD), (2,6-dimethyl)-*β*-cyclodextrin (DM-*β*-CD), and (2-hydroxypropyl)-*β*-cyclodextrin (HP-*β*-CD) were grafted onto the surface of the cellulose beads in the presence of polycarboxylic acids, such as 1,2,3,4-butanetetracarboxylic acid or citric acid. The optimum preparation conditions, including curing temperature, *β*-CD concentration in impregnation solution and catalyst, were evaluated by the grafting rate and the active *β*-CD content, respectively. DM-*β*-CD and HP-*β*-CD, as long as they carried enough remaining OH groups, could be successfully grafted on the cellulose beads. Besides, depending on the results of phenolphthalein probe detection, materials weight gain, FTIR spectroscopy and, SEM microscopic observation, the factors that influence the encapsulation ability of the functional spherical biomaterials were discussed in detail.

Keywords: cellulose bead, cyclodextrin, esterification, encapsulation

INTRODUCTION

Cellulose constitutes the most abundant renewable polymer resource available in the natural world. It is estimated that by photosynthesis, 10^{11} tons of cellulose are synthesized annually. So, its development and utilization have a significant value for scientific research.[1-3] The structure of cellulose as a carbohydrate polymer comprises repeated *β*-1,4 linked D-glycopyranose units, which have a number of hydroxyl groups. Usually, the chemical modification is based on the reactions of these free hydroxyl groups, involving esterification and etherification,[2,4] and cellulose derivatives display excellent functional properties for applications in the industrial field.[4,5]

CDs are torus-shaped cyclic oligosaccharides made up of *α*-1,4 linked D-glycopyranose with 6(*α*-),7(*β*-),8(*γ*-) units. They come from the decomposition of starch with cyclodextrin (CD) glucanotransferase and are nontoxic, which was confirmed by Szejtli.[6] However, only *β*-CD is developed in industry, due to the proper size of its inside cavity and the lower cost of production.[7] Many studies have proved that some molecules, such as organic molecules (ions), inorganic molecules (ions), transition metal complexes, metallorganics, biomolecules, even inert gases, can be easily combined with CDs.[8,9] The binding mechanisms are attributed to chemical bonds or weak intermolecular force, and the later interaction forms large numbers of cyclodextrin supramolecules with distinct structures and properties.[10-12]

The alcoholic hydroxyl groups of CDs can take part at reactions of etherification (methylation), esterification, deoxidation and polymerization, resulting in derivatives with some special properties, such as high water solubility, ideal surface activity and lower water absorption.[8,13-15] To obtain these favored characteristics, scientists have shown great interest in grafting CDs onto nanoparticles,[16] Sol-Gel,[17] and microspheres,[18] due to their great potential in chemistry, biomedicine and biotechnology.

Bead cellulose, as a nontoxic and biocompatible material, plays an important role in various pharmaceutical and biotechnological

applications. The "surface effect", "small size effect" and "good bioaffinity" properties of bead cellulose have attracted much attention.[19-22] If host molecules of CDs are grafted onto cellulose beads and retain the ability of encapsulation, this novel biomaterial product will, no doubt, be a kind of useful functional carrier and will have broad application.

The impregnation or covalent binding of CDs onto cellulose fibers was first reported by Szejtli *et al*.,[23-24] who grafted CDs onto cellulose using epichlorohydrin as a crosslinking agent. Then, Poulakis *et al*.[25] reported the physical or chemical incorporation of CDs into natural or synthetic matter. CD derivatives, such as a monochlorotriazinyl *β*-CD derivative, were fixed permanently onto different polymer materials, including fibers, by Denter *et al*.[26] and Reuscher *et al*.[27] Recently, Le Thuaut *et al*.[28] and Martel *et al*.[29] used polycarboxylic acids as crosslinking agents for grafting CDs onto cotton and wool fabrics. However, in the mentioned researches, the product weight gain was the main way to estimate the amount of CD grafted on the cellulose fibers, while the determination of the product weight gain is heavily affected by the loading of the crosslinking agents and the weight gain of the product could not describe the real encapsulating ability of the grafting CDs, which has practical significance in the field of microscopic studies. So a reliable method is necessary to detect the grafting CDs on the cellulose materials, especially an *in situ* analysis of the surface activity of CDs.

In this study, a rapid preparation method of cellulose beads was carried out and the products were grafted with *β*-cyclodextrin (*β*-CD), (2,6-dimethyl)-*β*-cyclodextrin (DM-*β*-CD), and (2-hydroxypropyl)-*β*-cyclodextrin (HP-*β*-CD), respectively. The encapsulation ability of these prepared functional materials was evaluated by the host-guest interaction between phenolphthalein and CDs. The preparation process parameters of grafting *β*-CD, including crosslinking agent, catalyst, curing temperature and CD concentration in the impregnating bath, were investigated in detail.

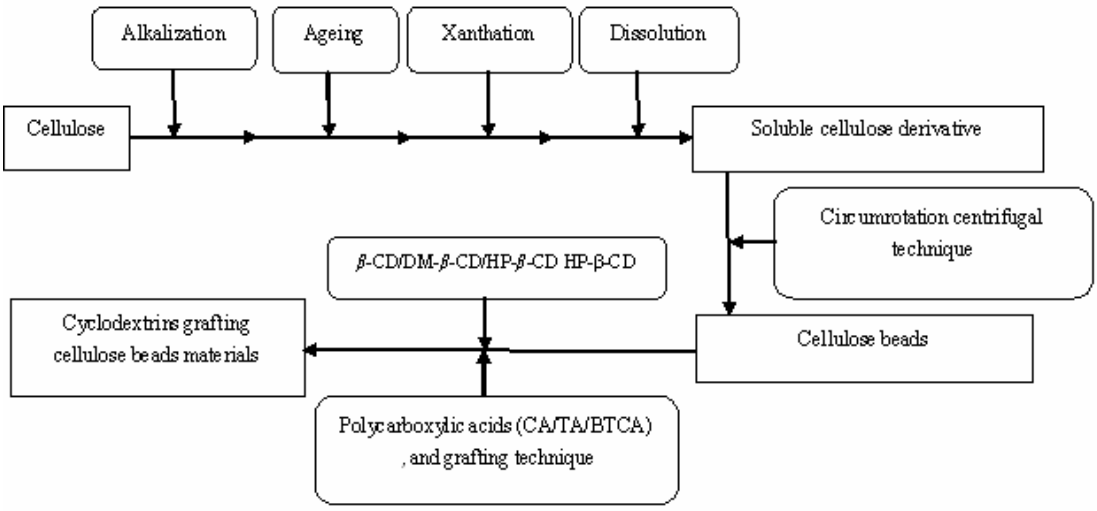
EXPERIMENTAL

Materials

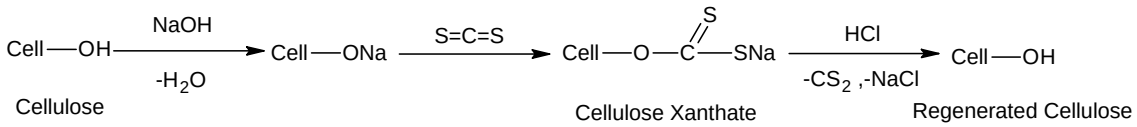
Adsorbent cotton fiber (medical grade) was purchased from Shanghai Medical Instrument Co., Ltd. phenolphthalein, DM-*β*-CD (substitution degree: 14, purity ≥99), HP-*β*-CD (substitution degree: 2 or 3, purity ≥97) was purchased from Aladdin Co., Ltd. (Shanghai, China), and *β*-CD (purity ≥99) was purchased from TCI (Japan). All the chemicals were of guaranteed reagent grade and were dried for 12 h at 105 °C before usage. Ultrapure water was prepared by Milli-Q century system (Millipore, U.S.A.) and was used throughout the entire study.

Preparation of CD grafting onto cellulose beads

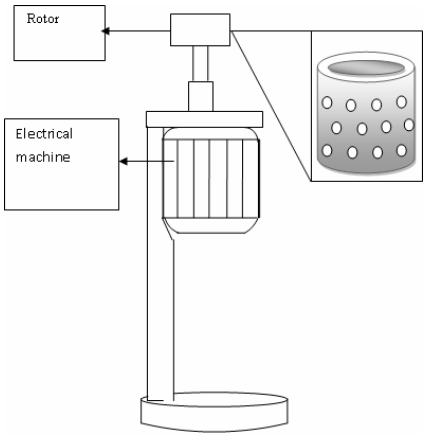
The preparation procedure of CD grafting onto cellulose beads (CGCB) was performed as shown in Scheme 1.



Scheme 1: Preparation procedure of cyclodextrins grafting onto cellulose bead material



Scheme 2: Reactions occurring during preparation of cellulose beads



Scheme 3: Structure of centrifugal circumrotation machine

Preparation of cellulose beads

5 g of absorbent cotton fiber was impregnated in 40 mL 20 wt% NaOH alkali liquor for 3 hours to obtain alkali cellulose fiber (Scheme 2), and then the alkali liquor was squeezed out until the alkali cellulose weight was around 20 g. After aging for 60 hours under room temperature, 2.5 mL CS_2 was added to the alkali cellulose and was sealed for 3 hours to obtain cellulose xanthate (Scheme 2). Then, the cellulose xanthate was dissolved in 40 mL 6 wt% NaOH solution under stirring for 3 hours to obtain transparent cellulose viscose. The viscosity of the cellulose viscose was kept in the range of 2.3-2.5 Pa s.

After the afore-mentioned procedure, the cellulose viscose was poured into a self-made round rotor (the machine is illustrated in Scheme 3). The rotating speed of the rotor was fixed at 750 r min^{-1}, both the diameter and the thickness of the holes of the rotor were of 1.0 mm. Then liquid beads were generated, released out of the holes and fell into 1.5 mol L^{-1} HCl solution. It was necessary to make sure that the HCl solution was deep enough to avoid the liquid beads touching the bottom of the container. Following the reactions in Scheme 2, the liquid cellulose viscose beads were solidified and recovered back to cellulose beads.

Grafting with CD

1 g cellulose beads within the diameter range of 320-480 μm were dried at 80 °C until constant weight. Then the beads were dipped into 50 mL impregnating solutions, consisting of 5 g CD, 5 g polycarboxylic acids (PCAs) and 1.5 g catalyst, sonic oscillated for 10 min and stored for 0.5 h. The beads were filtered out and dried at 80 °C for 1 hour. The bead weight was controlled at 1.1 g. The beads were put into another drying oven at 180 °C for reacting for 5 min, and then washed carefully with 100 mL 60 °C water and 100 mL alcohol. The final products were dried at 105 °C until constant weight and placed in desiccators for cooling down to room temperature.

The grafting rate (wt%) was evaluated by the weight gain of the cellulose beads. The control samples were prepared without adding CD (CD blank samples). The grafting rate was calculated by eq. 1.

$$wt\,\% = \frac{m_f - m_i}{m_i} \times 100\% \quad (1)$$

where m_i and m_f are the weight of the cellulose beads before and after treatment with β-CD, HP-β-CD, DM-β-CD, respectively.

Determination of active β-CD

For evaluating the encapsulation ability of β-CD on the cellulose beads, our previous work of phenolphthalein probe technology was applied here.[30] The content of active β-CD (c_{CD}) was determined by UV spectroscopy, and the calibration curve was listed in eq. 2.

$$\Delta A = 1.565 c_{CD} + 0.011 \quad (2)$$

In eq. 2, ΔA denotes the absorbance difference at 553 nm between the filtrates of the samples and the initial phenolphthalein solution without addition of CD.

The content of active *β*-CD on the modified wood flour material was evaluated by eq. 3.

$$\text{Active cyclodextrins content } (\%) = \frac{(c - c_0) \times 0.1 \times M}{m} \times 100\%$$

where c_0 and c denote the CD concentration (mol L^{-1}) of the modified cellulose beads and their corresponding CD blank (impregnated solution without addition of CD). M denotes the molecular weight of the CD (*β*-CD – 1134.98 g mol^{-1}, DM-*β*-CD – 1331.39 g mol^{-1}, HP-*β*-CD – 1380 g mol^{-1}) and m denotes the weight of CGCB (g).

SEM

The morphology of the cellulose and CGCB was characterized by SEM (Quanta200 type) with an accelerating voltage of 20 kv.

FTIR

FTIR samples were prepared in the form of potassium bromide pellets, containing 8~10 mg samples and 400 mg potassium bromide, which were mixed and grounded in an agate mortar. The FTIR spectra were recorded by Avatar 360 spectrometer (Nicolet, USA). 32 scans were taken for each sample at room temperature with a resolution of 4 cm^{-1}, and the scan scope was in the range of 400 cm^{-1}~4000 cm^{-1}.

RESULTS AND DISCUSSION

Viscosity of cellulose viscose and size distribution of cellulose beads

As the rotating speed of the rotating rotor was fixed at 750 r min^{-1}, the viscosity of the cellulose viscose was the main factor influencing the formation of the cellulose beads. Figure 1 shows the curve of the cellulose viscose viscosity vs. the size distribution of cellulose beads. As noted in Figure 1, the particle size of the cellulose beads demonstrated a decreasing tendency with the decrease of the solution viscosity, except the viscosity of 3.1 Pa s. If the viscosity was lower than 1.4 Pa s, the density and mechanical strength of the product were reduced, besides, it was hard to keep the shape of the product beads spherical. If the viscosity was higher than 3.1 Pa s, the cellulose viscose was often too sticky, clogging the holes of the rotating rotor (Scheme 3). Such phenomena could be explained by the surface tension of the cellulose viscose.

Enough surface tension of the viscose is very important for maintaining the spherical shape of the liquid beads, because the intermolecular attractive forces can act to minimize the surface area of a liquid. Generally speaking, high viscosity of the viscose means large surface tension,[31] and it can produce high density spherical cellulose beads. However, too high cellulose viscose viscosity (up to 3.1 Pa s) can clog the rotating rotor and often hinder the preparation. So in our study, the cellulose viscose viscosity was kept between 2.3-2.5 Pa s.

IR Analysis

The FTIR spectra of cellulose beads, *β*-CD, CA washing control, *β*-CD/CA-modified cellulose beads, BTCA washing control, *β*-CD/BTCA-modified cellulose beads are shown in Fig. 2.

In Fig. 2, the absorption bands at 1732 cm^{-1} and 1051 cm^{-1} are ascribed to ester carbonyl group and C-O-C bond stretching vibration of cellulose, respectively. Compared to the spectrum of cellulose beads, the spectra of CA washing control and BTCA washing control show no significant difference. These results demonstrate that the absorbed polycarboxylic acid and *β*-CD can be removed by the washing process. While the band intensity from 1732 cm^{-1} to 1051 cm^{-1} in the spectra of *β*-CD/CA-modified cellulose beads and *β*-CD/BTCA-modified cellulose beads is higher than that of their corresponding washing control. Thus, it is confirmed that the increase of the ester carbonyl band in the *β*-CD-modified cellulose spectrum is due to the formation of the ester band between the polycarboxlic acid, cellulose and *β*-CD. In addition, the bands of *β*-CD can not be distinguished in the spectra of modified cellulose beads, because of overlapping by the spectra of cellulose.

Surface active CD content analysis

A purple phenolphthalein solution becomes colorless in the presence of CD, due to the encapsulation of phenolphthalein with the inner cavity of CD.

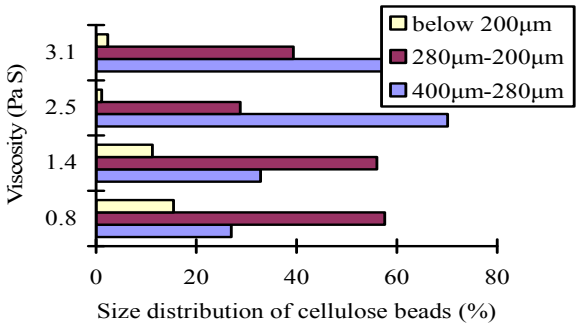


Figure 1: Viscosity of cellulose viscose vs. size distribution of cellulose beads

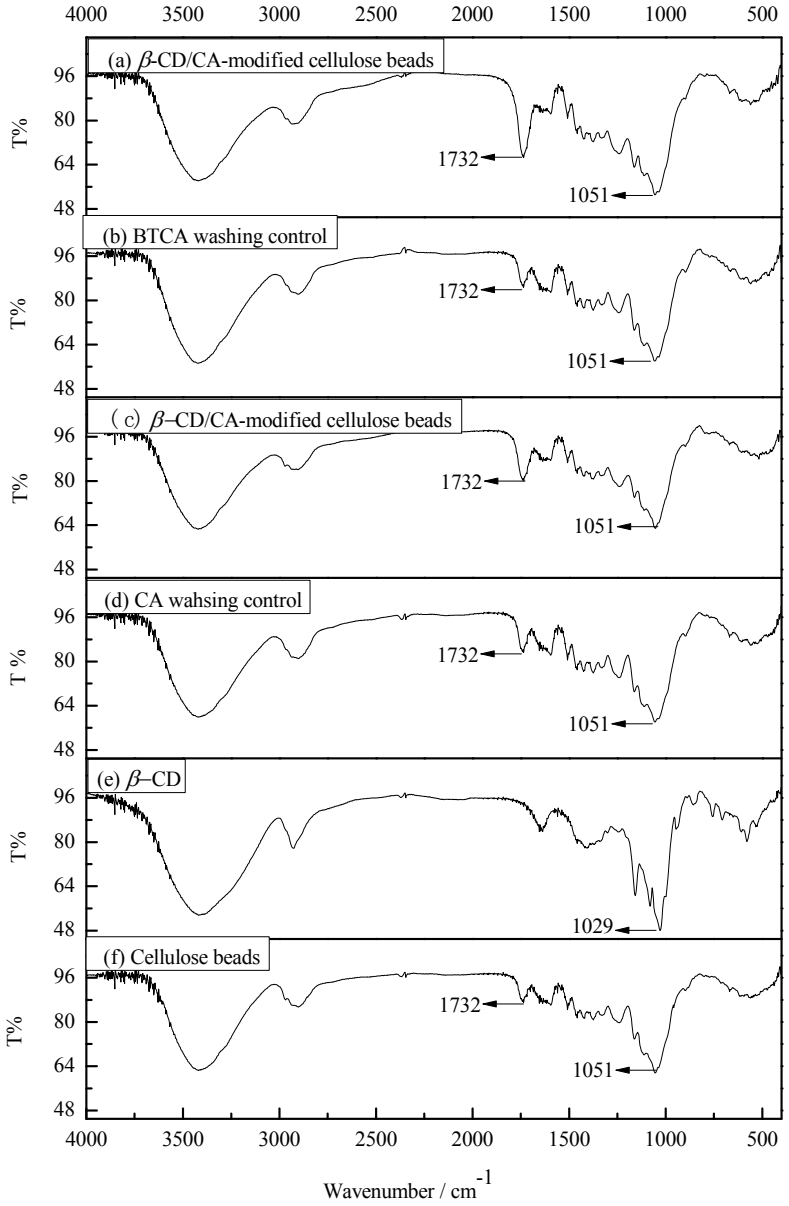


Figure 2: IR spectra

As demonstrated in our previous works,[30] this encapsulation by CD inner cavities converts the conjugated structure of phenolphthalein to a lactone and gives relatively high binding affinities for determining the surface active CD content. In this work, all the CD modified cellulose beads turned the purple phenolphthalein solution faded to some extent. The phenomena confirm a successful grafting of CD. The quantitative results of phenolphthalein probe detection are used to study the preparation conditions of CD grafting, including curing temperature, *β*-CD concentration in impregnation solution and catalyst.

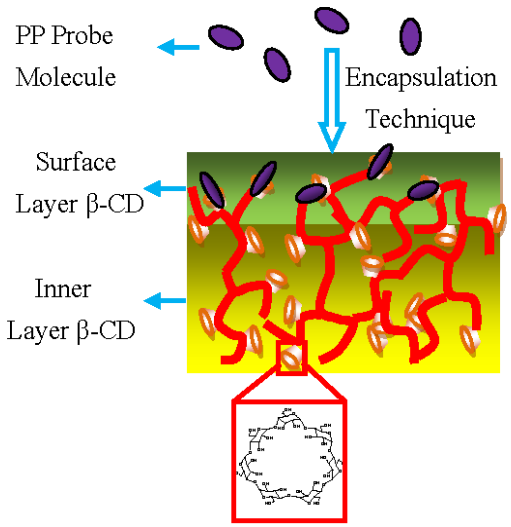
Influence of curing temperature on *β*-CD grafting

Higher temperature accelerates the formation of cyclic anhydride intermediate.[32] Consequently, as presented in Figure 3(a), when the curing temperature increases from 140-200 °C, the grafting yield increases significantly. However, according to Figure 3(b), the increase of the active *β*-CD content was moderate, especially beyond the temperature of 180 °C. Besides, the determining values are much lower than the results of grafting rate.

Although higher *β*-CD grafting rate can be obtained when the temperature is above 180 °C, the modified bead material will turn yellowish-brown due to the effect of charring. Thereafter, 180 °C was eventually chosen as the curing temperature during the following experiment. As for the moderate increase of the active *β*-CD content, we presume that it is attributed to the effect of steric hindrance.

Esterification of cellulose beads with *β*-CD by PCAs requires spare surface space on the cellulose beads. If the surface is "saturated" with grafting PCAs and *β*-CDs, which we named the inner *β*-CDs, the excessive PCA and *β*-CD will only react outside and form surface *β*-CDs, as illustrated in Scheme 4. The microscopic observation of SEM is shown in Figure 4.

As observed in Figure 4, the diameter and the shape of the cellulose beads were not significantly changed (Figure 4(a) and Figure 4(c)), but the microscopic surface of the cellulose beads was covered with some stratified sediment (Figure 4(b) and Figure 4(d)). On the one hand, it demonstrates a successful grafting of *β*-CD. On the other hand, the steric hindrance of the surface *β*-CD restricts the mobility of phenolphthalein molecules to access the inner β-CD (Scheme 4), which means some of the inner *β*-CDs lose their encapsulation ability. So, even though the results show an obvious increase in grafting rate with different PCAs, the amount of active *β*-CD content does not present a similar trend.



Scheme 4: Illustration of CGCB structure

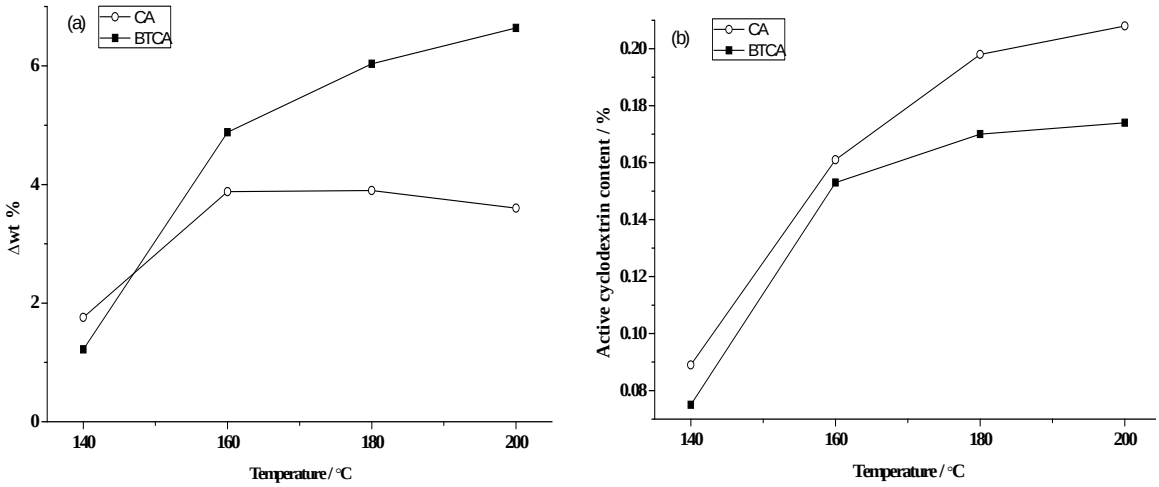


Figure 3: Influence of curing temperature (curing time = 5 min) on grafting, in presence of PCAs (100 g L^{-1}), with NaH_2PO_4 (30 g L^{-1})as catalyst and β-CD concentration of 100 g L^{-1}; (a) grafting rate; (b) active cyclodextrin content

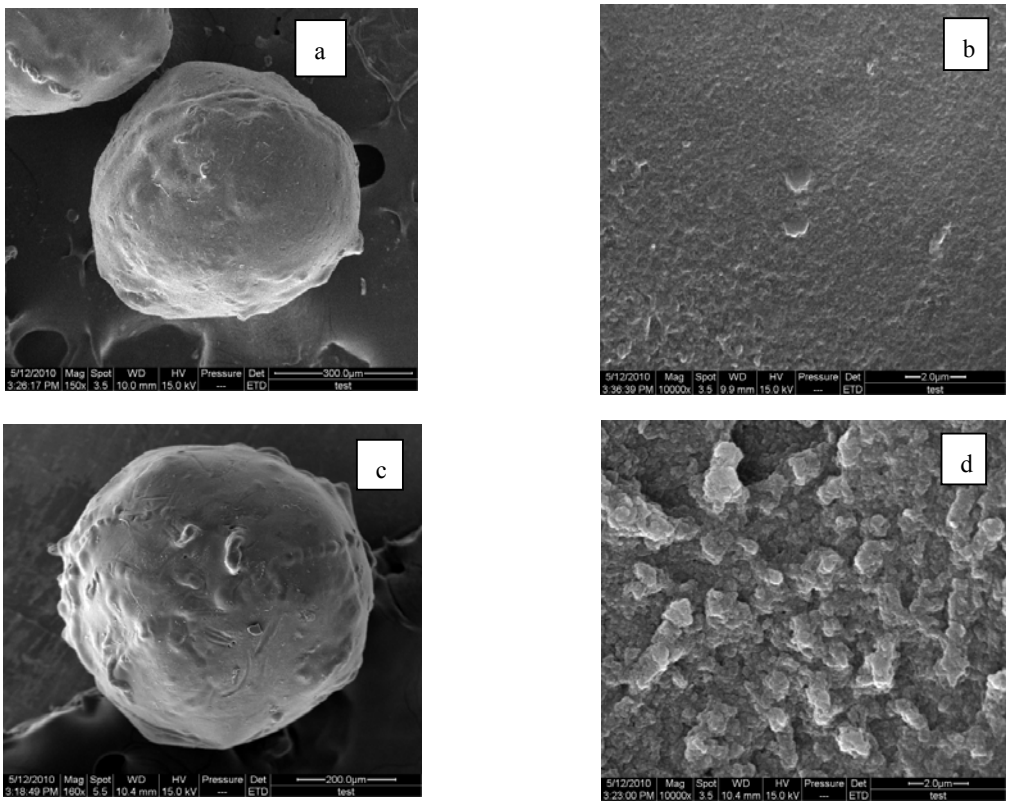


Figure 4: SEM pictures of cellulose beads (a, b) and β-CD grafted onto cellulose beads (c, d)

Besides, the translational and rotational degrees of freedom of the grafting β-CD will be restricted due to the fixing of the β-CDs on the cellulose beads, which increases the difficulty of encapsulating the phenolphthalein probe molecule into the β-CD cavity. This could explain why BTCA has a higher grafting rate, but a lower active β-CD content compared with CA.

It has been proposed that an individual BTCA molecule can fix more than one *β*-CD molecule,[32-34] if two *β*-CDs are simultaneously crosslinked by the same BTCA molecule, their translational and rotational degrees of freedom will be restricted significantly due to the limitation of BTCA molecular chain. The steric hindrance of the phenolphthalein probe molecule can be enlarged and restrict the phenolphthalein probe molecule approaching to both of the two grafting *β*-CD molecules. As a result, phenolphthalein probe technology could only determine partial *β*-CD fixed by BTCA, which leads to a lower active *β*-CD content result.

Influence of catalyst on *β*-CD grafting

The grafting reaction of *β*-CD onto cellulose beads by PCAs proceeds in two steps: the formation of a cyclic anhydride intermediate by dehydration of two carboxylic acid groups, and the formation of ester links between *β*-CD and cellulose molecule by anhydride intermediate.[35] The type of catalyst can facilitate the afore-mentioned two steps and influence the grafting results.[34] Therefore, three phosphatic catalysts – NaH_2PO_2, NaH_2PO_4 and Na_2HPO_4 – were compared in the experiment. The results are presented in Figure 5. The ternary combinations of NaH_2PO_4/CA/*β*-CD and NaH_2PO_2/BTCA /*β*-CD demonstrate the best result of grafting rate and active *β*-CD content. This phenomenon is attributed to the influence of the acidic reaction environment. The impregnation solutions containing Na_2HPO_4 and NaH_2PO_2 give a relatively weaker acidic environment than NaH_2PO_4. The low pH value favours for the existence of the acidic form of the carboxylic groups, which is favorable to the formation of the five-membered cyclic anhydride intermediate.

Influence of *β*-CD concentration on *β*-CD grafting

Some organic acids have a remarkable influence on the enhancement of CD solubility.[36] So, through experiment, it was observed that CA and BTCA impregnation bath could dissolve more *β*-CD than pure water. Figure 6(a) shows that the grafting rate of the cellulose beads varied with *β*-CD concentration in the impregnation bath. In the stage of 0-100 g L^{-1}, with the increase of the *β*-CD addition, grafting rate also presented an increasing trend. This phenomenon may be explained by the increment of reactant *β*-CD concentration, which in fact raises the molecule collision probability. But in the stage of 100-180 g L^{-1}, with the increase of *β*-CD, grafting rate decreased, which was due to the over addition of reactant *β*-CD.

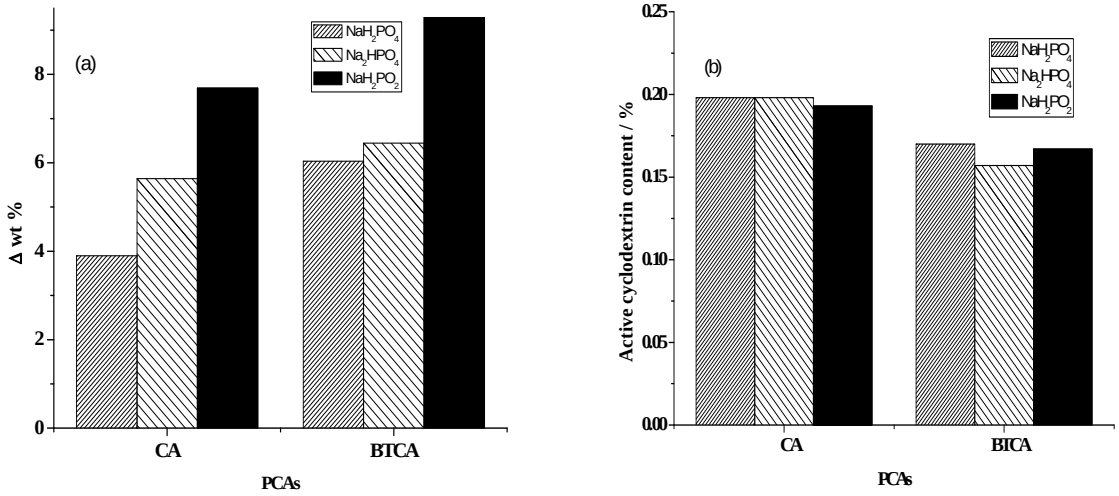


Figure 5: Influence of catalyst (30 g L^{-1}) on grafting yield, in presence of PCAs (100 g L^{-1}), at curing temperature of 180 °C for 5 min and with *β*-CD concentration of 100 g L^{-1};
(a) grafting rate; (b) active cyclodextrin content

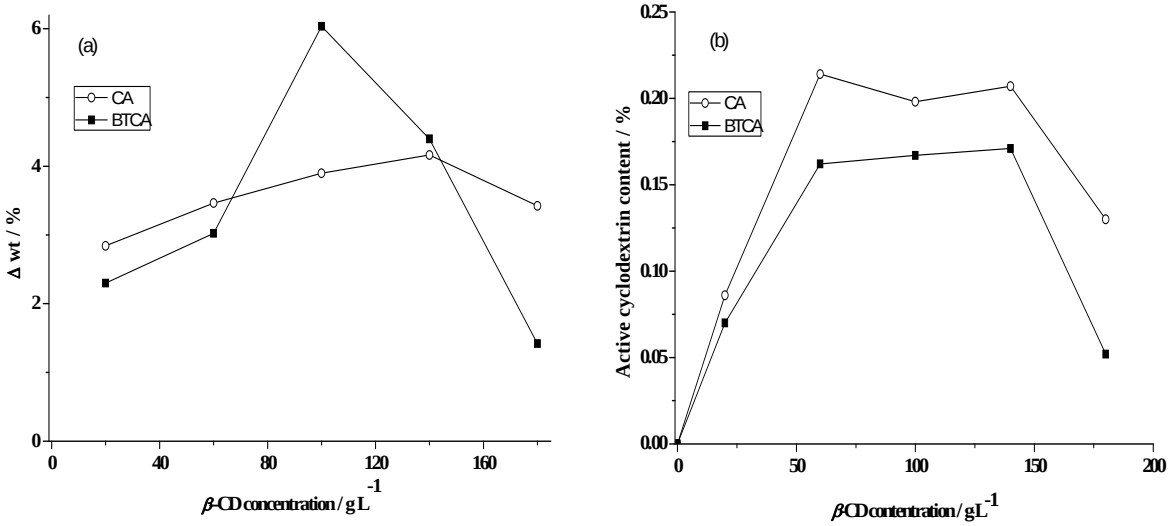


Figure 6: Influence of β-CD concentration in the impregnating bath on grafting yield, in presence of PCAs (100 g L^{-1}), at curing temperature of 180 °C for 5 min and with NaH_2PO_4 (30 g L^{-1}) as catalyst; (a) grafting rate; (b) active cyclodextrin content

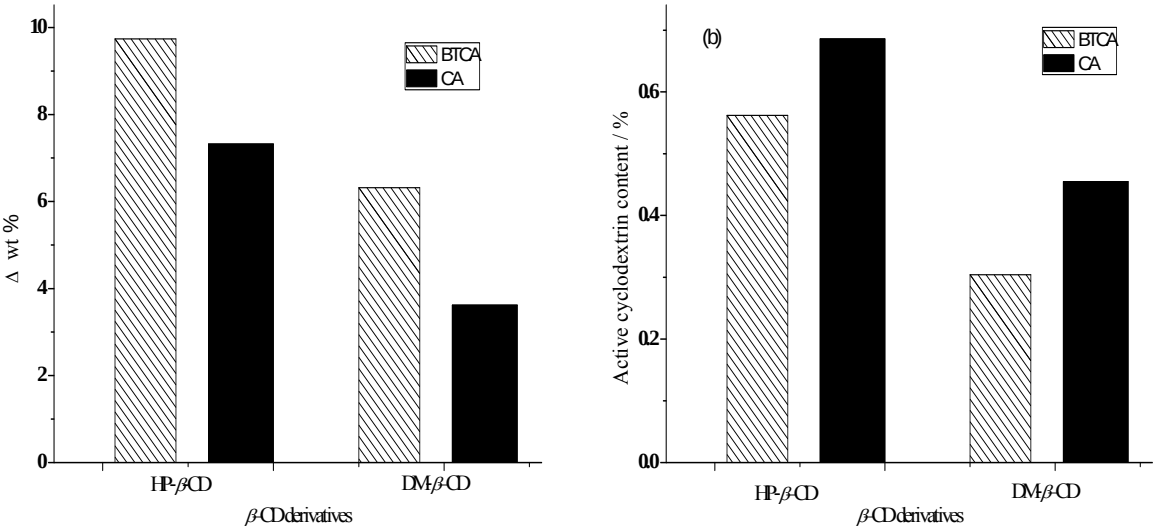


Figure 7: Cellulose beads grafting with HP-β-CD and DM-β-CD by different PCAs, in presence of PCAs (100 g L^{-1}), at curing temperature of 180 °C for 5 min and with NaH_2PO_4/CA (30 g L^{-1}) and NaH_2PO_2/BTCA (30 g L^{-1}) as catalysts; (a) grafting rate; (b) active cyclodextrin content

The excessive β-CD molecules probably consume quickly a specified amount of PCAs and do not graft on the cellulose beads, this part of the by-product being washed out by the hot water, leading to a decrease in the grafting rate. Therefore, the higher the β-CD addition, the more of the PCAs are consumed, and the lower the grafting rate is. As noted in Figure 6(b), with the increase of β-CD addition, the active grafting β-CD content first increased and then reached a plateau, a phenomenon that is attributed to the effect of steric hindrance. When the addition of β-CD was 0 g L^{-1}, there was no active β-CD detected, when β-CD addition reached 60 g L^{-1}, the active β-CD content also increased. Given the limited surface of the cellulose beads, when continuing to increase β-CD addition to 100 g L^{-1}, there was no significant change in the active

β-CD content, which means the addition of 60 g L^{-1} of *β*-CD is just suitable for the grafting reaction. Besides, over addition of *β*-CD could consume more PCAs and lead to a lower grafting rate, therefore 60 g L^{-1} of *β*-CD and 100 g L^{-1} PCAs are considered sufficient for grafting 20 g cellulose beads.

Grafting of other CDs

Beta-CD derivatives are used for grafting on the cellulose beads, the results are shown in Figure 7. Figure 7 demonstrates that HP- and DM-*β*-CD could be grafted on the cellulose beads. Considering the active CD content (Figure 7(b)), the product grafted by CA demonstrated stronger encapsulation ability.

The determined grafting rate of *β*-CD derivatives was found to be a little higher than that of the natural *β*-CD, which is attributed to the influence of molecular weight. With a similar grafting ability and similar surface area of the cellulose beads, *β*-CD derivatives have a larger molecular weight than the natural *β*-CD.

Comparing the grafting of HP-*β*-CD with DM-*β*-CD (Figure 7(a) and Figure 7(b)), HP-*β*-CD appears to have a higher grafting efficiency than DM-*β*-CD. This difference is due to more hydroxyl reacting units existent on every HP-*β*-CD molecule.

CONCLUSION

In this research, cellulose beads, with a diameter range of 320-480 μm, have been prepared using the approach of centrifugal circumrotation. The viscose viscosity of 2.3-2.5 Pa s was found to be suitable for preparing the cellulose beads. 5 g cotton fiber was broken down into 1.5 mm×0.5 mm pieces, basified in 40 mL 20 wt% NaOH solution, aged for 60 hours; to it 2.5 mL CS_2 was added and dissolved in 60 mL 6 wt% NaOH solution, to obtain a final solution viscosity around 2.4 Pa s. *β*-CD, HP-*β*-CD and DM-*β*-CD were successfully grafted onto the cellulose beads by the nonformaldehyde crosslinking agents of PCAs. The curing temperature was of 180 °C, the optimal composition of the impregnating solutions were NaH_2PO_4/CA and NaH_2PO_2/BTCA, the impregnation bath with *β*-CD concentration of 60 g L^{-1} and PCAs concentration of 100 g L^{-1} could graft 20 g of cellulose beads. In future reports, the complex-forming ability of grafted CDs towards some functional molecules and its application will be detailed and investigated.

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