A Novel Method for the Preparation of Spherical Cellulose-Tungsten Carbide Composite Matrix with NMMO as Nonderivatizing Solvent

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ABSTRACT: N-methylmorpholine-N-oxide (NMMO) was used as the nonderivatizing solvent for dissolving cellulose, and the cellulose-tungsten carbide composite particles were prepared with water-in-oil suspension and cooling regeneration. Some key factors, such as dissolution temperature and time, water content, cellulose concentration, dispersion, and cooling were optimized. The solubility of cellulose in the NMMO solution was greatly dependent on the water content, which should be controlled at the range of 11 to 15 wt %. In addition, the influences of water content of the cellulose/NMMO/water solution on the properties of composite beads were studied, including bead size, wet density, and pore properties. It was found that 13 wt % water content was most appropriate. The expansion and liquid mixing properties of composite beads in an expanded bed were also explored. The results indicated that the cellulose composite beads prepared could be used as the matrix for expanded bed adsorption processes. Compared with the traditional technology with cellulose xanthate viscose, new method based on the NMMO dissolution is more environment-friendly, reduces the process time and shows a potential application for large scale preparation. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2985–2992, 2011

Key words: matrix; cellulose; N-methylmorpholine-N-oxide; tungsten carbide; expanded bed adsorption

INTRODUCTION

Cellulose is the most abundant natural polymer in our environment, which represents the most obvious renewable resource for producing biocomposites. Its highly ordered structure is responsible for some desirable mechanical properties but makes it a challenge to find suitable solvents for its dissolution.[1] The production of cellulose-regenerated materials is based largely on the 100-year-old viscose technology, by which fiber, film and other products have been prepared with the soluble cellulose xanthogenate.[2] Some new solvents have been developed to dissolve cellulose, including heavy metal-amine complex solutions,[3,4] concentrated metal salts,[4] NaOH solutions,[5] NaOH/urea solution,[6] thiocyanate/amine,[7] LiCl/dimethylacetamide (DMAc),[8] concentrated H_2SO_4 and H_3PO_4.[9] In general, the traditional cellulose dissolution processes requires relatively harsh conditions and the use of expensive and uncommon solvents, which usually cannot be recovered after the process.[1] Moreover, some environmentally hazardous byproducts (NaOH, H_2SO_4, CS_2, H_2S, or heavy metals) are generated in the traditional processes. To reduce side reactions and the considerable amounts of toxic byproducts, as well as to effectively recover the expensive solvents involved, a method with N-methylmorpholine-N-oxide (NMMO, $C_5H_{11}NO_2$) dissolution was developed in 1979,[2] to prepare cellulose solutions with high concentration of up to 23%. This nonderivatizing dissolution method has been used in the fiber-making industrial Lyocell process.[2,9,10] The direct dissolution process of cellulose has received considerable interest because of its simplicity, environmentally friendly characteristics, and the special properties of the resulting cellulose materials.[11,12] Compared with the fibers with viscose process, Lyocell fibers have higher tenacity and modulus, lower shrinkage in the dry state, and lower reduction of tenacity and modulus in the wet state.[13,14]

Due to the high polarity of the N-O bond in NMMO, NMMO is a compound with strong hydrophilicity, resulting in extremely high solubility in water, complete miscibility with water, a pronounced tendency to form hydrogen bonds and strong hygroscopicity.[11,15,16] NMMO forms a crystalline hydrate at room temperature and melts at 72°C. When heated to around 100°C, NMMO is able to dissolve readily several percent of high molecular

weight cellulose.[17] The dissolution of cellulose in NMMO/water mixtures is a physical process that does not need any chemical derivatization of cellulose. In addition, NMMO can be almost completely recycled, and the recovery reaches more than 99% for commercial large-scale process.[15] The dissolution of cellulose in NMMO involves the breakage of H-bonds networks in the cellulose resource and the formation of new intramolecular and intermolecular H-bond between NMMO and cellulose. However, cellulose dissolution process is extremely complex, and no individual step has been identified so far.[18] In general, the dissolution of cellulose is dependent on the dissolution temperature, water content of the system, and concentration and degree of polymerization of cellulose.[19] After removing NMMO and water, the cellulose chains retain the general morphology in the crystallized solution.[20,21]

As one of the most important polysaccharide resources, cellulose has been used to prepare spherical beads as the matrix for chromatographic separation. In 1970s Peska et al. developed a method for preparing cellulose beads based on the thermal sol-gel transition process of cellulose xanthate viscose.[22] From then on, several series of porous cellulose beads have been developed and widely applied for bioseparation.[23,24] With the addition of some metal densifiers, the novel types of cellulose composite beads were prepared and could be used for expanded bed adsorption (EBA).[24–27] EBA is an integrated technology for capturing target biomolecules directly from unclarified feedstock. The adsorbents should be designed specially to ensure the perfect performance of expanded bed. The essential properties of EBA adsorbents are relatively high densities, appropriate bead size, and size distribution.[28] During past 20 years, several series of EBA adsorbents were developed commercially. In addition, some researcher developed new materials for EBA application, such as agarose-alloy, fluoride modified zirconia supports, β-cyclodextrin polymer/tungsten carbide composite matrix, etc.[29,30] In previous work, some researchers focused on the cellulose composite beads densified by some inorganic densifiers, including cellulose-titanium oxide,[31,32] cellulose-stainless steel,[33] cellulose nickel powder,[34] and cellulose-tungsten carbide.[35] The cellulose composite beads were prepared with the thermal sol-gel transition process of cellulose xanthate viscose and showed a good performance for EBA applications. However, as mentioned above, the disadvantages of xanthate viscose process cause the complexity of operation control and some environmental problem, which limits the scale-up of production.

In the present work, NMMO would be used as the nonderivatizing "green" solvent to dissolve cellulose and prepare the cellulose-tungsten carbide composite beads. The cellulose dissolution, the dispersion of cellulose solution in the oil phase and the regeneration of composite cellulose beads were investigated. Some key factors, such as water concentration in the cellulose/NMMO/water mixture during the preparation, were optimized. The physical properties of composite beads prepared were explored, including wet density, water content, porosity, pore volume, specific surface area, and mean pore diameter. In addition, the expansion characteristic and axial mixing in the expanded bed were investigated for a potential EBA application. Some comparison of the cellulose beads made by NMMO as the nonderivatizing dissolution solvent and the technology of cellulose xanthate viscose were discussed, too.

EXPERIMENTAL

Materials

Refined cotton with the polymerization degree of 1070 was ordered from Haiyan Changchuanba Refined Cotton Co., Ltd. (Zhejiang, China). Ninety-seven wt % N-methylmorpholine-N-oxide (NMMO) powder was purchased from Huai'An Huatai Chemical Co., Ltd. (Jiangsu, China). Tungsten carbide with a density of 15.0 g/cm^3 and a mean particle diameter of 2 to 5 μm was ordered from Ganzhou Tejing Tungsten and Molybdenum Co., Ltd. (Ganzhou, China). Vacuum pump oil was purchased from Sifang Special Oil Factory (Beijing, China). All other reagents were of analytical reagent grade and purchased commercially.

Cellulose composite bead preparation

The cellulose-tungsten carbide composite beads were prepared by the method of water-in-oil suspension and cooling regeneration. Typically, 2 g cellulose was added into 48 g NMMO/water system at 105°C and kept stirring for about 30 min to form 4 wt % cellulose/NMMO/water solution. The cellulose dissolution process was conducted under a dry nitrogen atmosphere. 0.5 g of pyrogallic acid was added as antioxidant, and the water content was controlled at the range of 11 to 15 wt %. Then, 16 g tungsten carbide powder was added into the cellulose/NMMO/water solution and continuously agitated for 20 min. After that, the mixture was dispersed in the vacuum pump oil with 4 wt % Tween 80 under the agitation of 950 rpm for 20 min at 83°C. Then the suspension was cooled down at the rate of 5°C/20 min to about 10°C. The resulting beads were filtered out and washed with 500 mL of 70% v/v isopropyl alcohol and distilled water. By screening with standard sieves (I.S.S Mesh 8 and 30), the cellulose-tungsten carbide composite beads with a

particle size range of 75 to 300 μm and larger than 300 μm were obtained and named Cell-TuC-*N*-S and Cell-TuC-*N*-L, respectively.

Measurement of physical properties

The size distribution and average size (D_p) of composite beads was determined with a laser particle size analyzer, Mastersizer 2000 (Malven Instrument, Worcestershire, UK). The shape and structure of composite beads was observed by the microscope Nikon E200 (Nikon Jiangnan Optical Instruments, Nanjing, China) and a scanning electron microscope (SEM) (Hitachi Instruments, Tokyo, Japan). To keep the real morphology of porous structure and avoid the false impressions of SEM pictures for hydrogels, the composite beads were treated gradually with the solvent displacement from water to 100% ethanol before SEM.

The physical properties were determined as reported in our previous work.[31,33,35] Wet density (ρ_p; g/mL of wet particles) of sucked beads were determined by water replacement in a 5 mL gravity bottle. The water content ω was obtained by dehydration at 120°C to a constant mass. Presuming that all the pores in particles were full of water, porosity (P; %) expressing the pore volume per volume of wet particles can be roughly estimated as follow,

$$P = \left(\frac{\rho_p \omega}{\rho_w}\right) \times 100\% \tag{1}$$

where ρ_w represents the density of water.

The specific surface area (S; m^2/mL of wet particles) was obtained by the adsorption of methylene blue solution and calculated as follow,

$$S = \left(\frac{(C_0 - C)G\rho_p}{m_p}\right) \times 2.45 \tag{2}$$

where C_0 and C are the initial and equilibrium concentrations of methylene blue solution, respectively. G and m_p represent the masses of methylene blue added and sample particles, respectively. The constant of 2.45 (m^2/mg of methylene blue) means that 1 mg of methylene blue could cover an area 2.45 m^2 for the assumption of mono-molecule-layer-adsorption.

According to the cylindrical pore structural model, the mean pore radius (R; nm)[36] can be estimated by:

$$R = 2 \times 1000 \times \frac{V_p\left(1 - \omega\right)\rho_p}{S} \tag{3}$$

Expansion characteristics and liquid mixing

A homemade column for EBA (0.02 m diameter, 1.0 m long) was used as published previously by Lin

et al.[37] About 5 g of glass bead (0.3 mm diameter) was added to improve flow distribution at the column inlet. A movable adapter was employed to adjust the position of the liquid outlet to the top of the expanded bed. The column vertical alignment was assured in all experiments. Distilled water was used as the liquid phases. The fluid was transported by a peristaltic pump (Longer Precision Pump, Baoding, China). The bed height was measured in three times for each flow rate after the expansion equilibrium. The bed expansion factor E was calculated by comparing the expanded bed height (H) and the sedimented bed height (H_0). In the present work, H_0 was 15 cm.

$$E = \frac{H}{H_0} \tag{4}$$

The test of residence time distribution (RTD) was used to describe liquid mixing behavior in the expanded bed. In each test, 0.5 mL acetone solution (10 wt %) was injected at the bottom inlet of the column as a tracer agent. The output signal was determined by the UV detector (WellChrom fast scanning spectrophotometer K-2600, Knauer, Berlin, Germany). The liquid mixing in expanded bed was analyzed by the following methods.

The number of theoretical plates (N) of the column can be determined according to the response curve from RTD test as following,

$$N = 5.54 \times \left(\frac{t_R}{W_{1/2}}\right)^2 \tag{5}$$

where t_R represents the residence time and $W_{1/2}$ represents the half peak width.

The Bo number and the axial mixing coefficient, D_{ax} relating convective transport of liquid to dispersion is defined as

$$Bo = \frac{UH}{D_{ax}\varepsilon} \tag{6}$$

where U is the flow velocity of fluid phase and ε is the voidage of expanded bed. Bo number can be calculated from the following equation,

$$\frac{1}{N} = \frac{2}{B_0} + \frac{8}{B_0^2} \tag{7}$$

Hence, the D_{ax} in eq. (6) can be determined.

RESULTS AND DISCUSSION

In the present work, spherical cellulose-tungsten carbide composite beads were prepared by the NMMO

dissolution method. The cellulose/NMMO/water solutions were prepared first with refined cotton and NMMO solution, then the water-in-oil suspension and sequential cooling technique were used to prepare the composite beads. Some important preparation parameters were investigated, such as the dissolution temperature and time, cellulose concentration, dispersion system, and cooling control. After that, the key factor of water content in the cellulose/NMMO/water solution was explored on the properties of composite beads. In addition, the expansion and liquid mixing in expanded bed was also studied for a potential application of EBA.

Preparation of composite beads

The preparation of cellulose composite beads with the method of water-in-oil suspension mainly includes three procedures, the cellulose dissolution, the dispersion of cellulose solution in oil phase, and the regeneration of cellulose beads.

First, cellulose was dissolved in the NMMO solution to obtain the viscous cellulose/NMMO/water solution, which should be related to the dissolution temperature and time, as well as cellulose concentration and water content in the cellulose/NMMO/water solution. It was found that the dissolution rate could be improved by increasing the dissolution temperature and time. To prepare 4 wt % cellulose solution, 30 min was enough at the dissolution temperature of 105 to 110°C. Higher temperatures (>120°C) would lead to some degradation of NMMO molecules despite the addition of an antioxidant.[15,38] Therefore, 105°C and 30 min were chosen as the suitable dissolution conditions in the present work. Compared with the traditional method of cellulose xanthate viscose, the dissolution of cellulose with NMMO as nonderivatizing solvent could reduce the preparation time from about 3 days to 30 min and avoid the use of hazardous chemicals.[18]

It was also found that the appropriate water content in the cellulose/NMMO/water solution was very important for preparing a homogeneous viscous cellulose solution. When the water content was lower than 11 wt % or higher than 15 wt %, the cellulose solution obtained was inappropriate and could hardly form the spherical particle with the method of water-in-oil suspension. Therefore, water content in the cellulose/NMMO/water solution was controlled at the range of 11 to 15 wt %. The oxygen of the N-O bond in NMMO is able to form one or two hydrogen bonds with two partners containing hydroxyl group such as with water as in the NMMO monohydrate ($\cong$13.3 wt %).[19] The similar hydrogen bonding could occur between NMMO and cellulose, and cause the cellulose dissolution. Water and cellulose have competitive behavior with NMMO, with water being evidently preferred. This could explain why the NMMO solution at high water contents is not able to dissolve cellulose but to precipitate.[15]

The Cellulose/NMMO/water solutions are known to show a high tendency to exchange water with ambient air.[20] To overcome this disadvantage, the cellulose dissolution process was conducted under a dry nitrogen atmosphere. In addition, the addition of antioxidant (pyrogallic acid) could reduce the radical degradation of NMMO and the scission of cellulose chain at high temperature.[2] The increase of cellulose concentration caused longer dissolution time, and the composite beads were hard to form when the cellulose solution was too viscous. On the contrary, too low viscosity of cellulose solution would lead to the conglutination of beads. After some optimization, the appropriate cellulose content was chosen as 4 wt %.

During the dispersion of cellulose/NMMO/water solution in oil phase, three of the most important factors are the ratio of oil phase to cellulose solution, the dispersant and stirring speed. When the stirring speed was below 500 rpm, it was difficult to disperse the cellulose solution in the oil phase. When the stirring speed was too fast or the ratio of oil phase to cellulose solution was low, the opportunities of droplet collision were increased. The results indicated that the suitable stirring speed should be at the range of 700 to 1000 rpm and the ratio of oil phase to cellulose solution at the range of 3 to 6. In addition, the surfactant Tween 80 was used as dispersant, and the addition of Tween 80 was optimized at 4 wt %.

For the regeneration of cellulose beads from the cellulose/NMMO/water solution, the cooling procedure was studied. The fact is that, during the cooling process, the predominant role in the crystallization process belongs to the NMMO that is lying around the cellulose chains, not to the cellulose, and the crystallization kinetics of NMMO is very sensitive to the temperature change.[20] In the present work, the cooling procedure was optimized by decreasing 5°C every 20 min from 105 to 10°C. After that, the resulting beads were filtered out and washed with 70% v/v isopropyl alcohol. NMMO emerged in the composite beads was dissolved into the alcohol/water solution, and the porous cellulose composite beads were regenerated.

Figure 1 shows the morphology of the cellulose composite beads that were prepared. It can be found that the beads have good spherical shape, and the crack and adhesion of particles were hardly found during the preparation. Figure 2 shows the SEM of composite beads. The results indicated that the spherical cellulose composite beads could be prepared with the NMMO solution as the nonderivatizing solvent.

Among varying preparation conditions, water content in the cellulose/NMMO/water solution was

Figure 1 Photographs of the composite bead appearance.

most sensitive for forming the spherical beads. The water content of 13 wt % in the cellulose/NMMO/water solution seemed to be the most suitable condition, which could form the monohydrate of NMMO. Kim et al.[39,40] reported the melting and crystallization behavior of cellulose/NMMO/water solution. The solubility of cellulose in the NMMO hydrates and the physical properties of resultant cellulose/NMMO/water solutions are greatly dependent on the water content of NMMO hydrate. As the value of hydration number (n) of NMMO hydrate decreases, the melting temperature (T_m) of NMMO hydrates increases generally and the solvating power of cellulose enhanced. If $n > 1.65$ the NMMO hydrates never dissolved cellulose but swelled it. The NMMO hydrate with $n < 1.5$ can completely dissolve cellulose at the temperatures higher than its melting point ($T_m = 78°C$ in case of NMMO monohydrate with $n = 1$). However, if $n < 1$ the NMMO hydrate dissolve the cellulose to produce a meso-
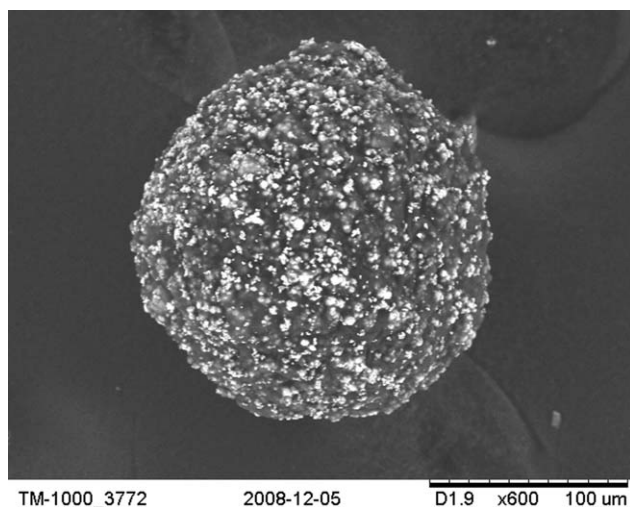
phase.[39,40] Therefore, in this work, water content in the cellulose/NMMO/water solution would be studied systematically to optimize the properties of composite beads for EBA applications.

Bead size and size distribution

The size and size distribution of composite beads are most important characteristic for EBA adsorbents for formation of perfectly classified fluidization in the column. Generally, the beads should have a symmetrical size distribution.[28] The size distribution of composite beads prepared with different water content of the NMMO solution is shown in Figure 3. For one batch, typically about 30% of composite particle were small size fraction (Cell-TuC-N-S), while the proportion of large fraction (Cell-TuC-N-L) was about 50%. The particle size showed a logarithmic symmetrical distribution with the mean particle sizes of 230 to 280 μm and 520 to 560 μm for Cell-TuC-N-S and Cell-TuC-N-L, respectively. The result indicated that varying water content of the cellulose/NMMO/water solution from 11 to 15% has slight effect on the bead size and size distribution. The mean size of spherical cellulose-tungsten carbide composite beads prepared with cellulose xanthate viscose in our previous work were about 124 μm.[35] Some increase in the bead size in the present work might be due to high viscosity of cellulose solution with the nonderivatizing NMMO dissolution.

Wet density

The wet densities of composite beads are shown in Figure 4 as the function of water content in the

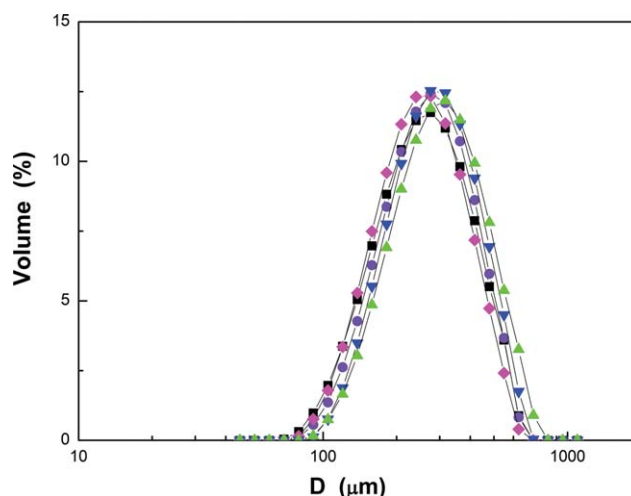**Figure 2** Morphology of the composite beads as determined by scanning electron microscopy.

Figure 3 Size distribution of composite beads Cell-TuC-N-S with different water content in the cellulose/NMMO/water solution: 11 wt %(■), 12 wt % (▲), 13 wt % (▼), 14 wt % (◆), and 15 wt % (●). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
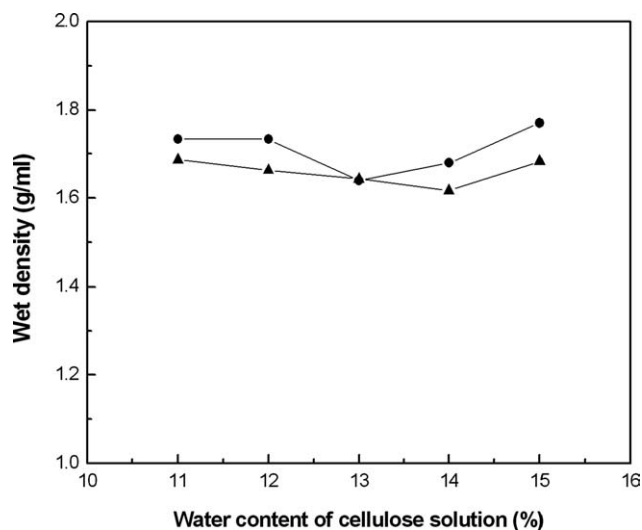
Figure 4 Effect of water content in the cellulose/NMMO/water solution on the wet density of two size fractions composite beads. ● Cell-TuC-*N*-S; ▲ Cell-TuC-*N*-L.

cellulose/NMMO/water solution during the preparation. The wet density of composite beads determines the operation velocity of fluid phase in expanded bed. Normally, the adsorbents require high density to increase the productivity of EBA process.[41,42] In the present work, the tungsten carbide powder with the density of 15.0 g/mL was used as the densifier. The results confirmed that the tungsten carbide powder was successfully entrapped within the cellulose matrix as the inert densifier, which increased the density of composite beads to 1.6 to 1.7 g/mL. The wet density of small fraction Cell-TuC-*N*-S (1.64–1.77 g/mL) was a little higher than that of large fraction Cell-TuC-*N*-L (1.61–1.68 g/mL), which meant that small beads could entrap the tungsten carbide powder with a relative high proportion.

Pore properties and specific surface area

The effects of water content in the cellulose/NMMO/water solution during the preparation on the pore structure of two size fractions are show in Figure 5. For all preparation conditions tested, the composite beads showed high porosity of 80 to 90%. The pore properties of composite beads are essential for the beads used in chromatographic separation, which influence the effective passage in the matrix for target adsorbate, especially for EBA process.[35,43] The results indicate that the cellulose beads prepared by the present method have appropriate porous structure, which has similar values of composite beads prepared with cellulose xanthate viscose in our previous work.[35] The porosity of large fraction (Cell-TuC-*N*-L) was slightly higher than that of small

fraction (Cell-TuC-*N*-S). In addition, it can be found that the change of water content of the NMMO solution from 11 to 15% during the preparation hardly influenced the porosity, which indicated that the regeneration of cellulose beads from the NMMO dissolution with the controlled cooling method was successful in the present work.

The specific surface area and the mean pore radius of composite beads are shown in Figures 6 and 7 for two fractions, Cell-TuC-*N*-S and Cell-TuC-*N*-L. The composite beads prepared with 13 wt % water content in the cellulose/NMMO/water solution showed the highest value of specific surface area, corresponding to the smallest pore size. For all
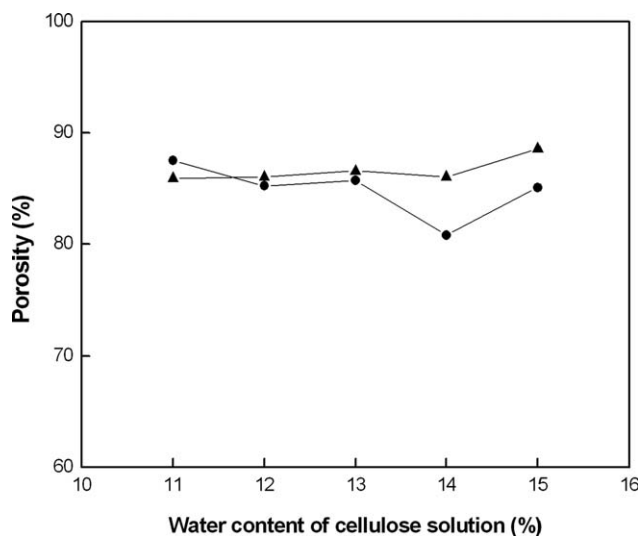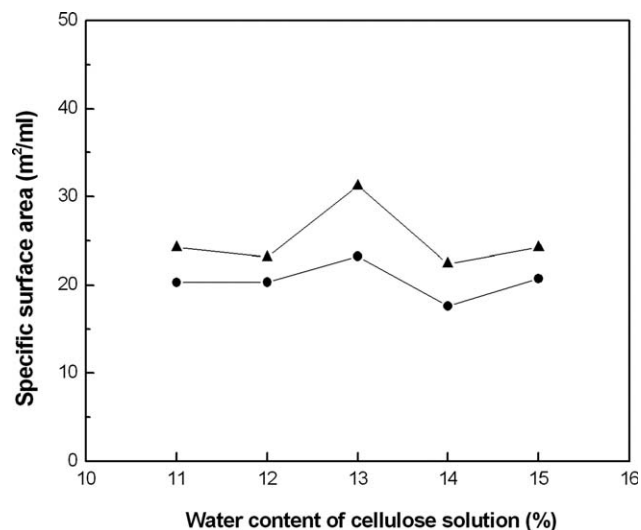

Figure 5 Effect of water content in the cellulose/NMMO/water solution on the porosity of two size fractions composite beads. ● Cell-TuC-*N*-S; ▲ Cell-TuC-*N*-L.

Figure 6 Effect of water content in the cellulose/NMMO/water solution on the specific surface area of two size fractions composite beads. ● Cell-TuC-*N*-S; ▲ Cell-TuC-*N*-L.

preparation conditions tested, the fractions of Cell-TuC-N-S have slightly lower specific surface area and larger pore size than Cell-TuC-N-L. With the cooling regeneration, the pore structures was affected by the complex crystallization kinetics of NMMO solution.[9,44] The average value of special surface area reached 20.5 and 25.1 m²/mL, while the mean pore radius reached the average values of 83 and 70 nm for Cell-TuC-N-S and Cell-TuC-N-L, respectively. Compared with the cellulose composite beads prepared with the xanthate viscose as our previous work,[32,33,35] the composite beads prepared in present work have a little large pore size and low special surface area.

In general, the cellulose-tungsten carbide composite beads prepared in the present work have appropriate porosity and specific surface area, which could provide abundant inner space and surface to bind the biomolecules such as bovine serum albumin (67 kDa). In addition, the relatively large pore radius would benefit the passage of the high molecular weight biomolecules and reduce the transfer limitation,[45] for example, the immunoglobulin G (150 kDa).

Performances in expanded bed

The Cell-TuC-N-S prepared with 13 wt % water content in the cellulose/NMMO/water solution were chosen for further studies on the EBA applications. As shown in Figure 8, the expansion factor of composite beads increased linearly as the flow velocity increased. Normally, the expansion factor of EBA might be controlled in the range of about 2 to 3, corresponding the flow velocities of 1100 to 1800 cm/h,
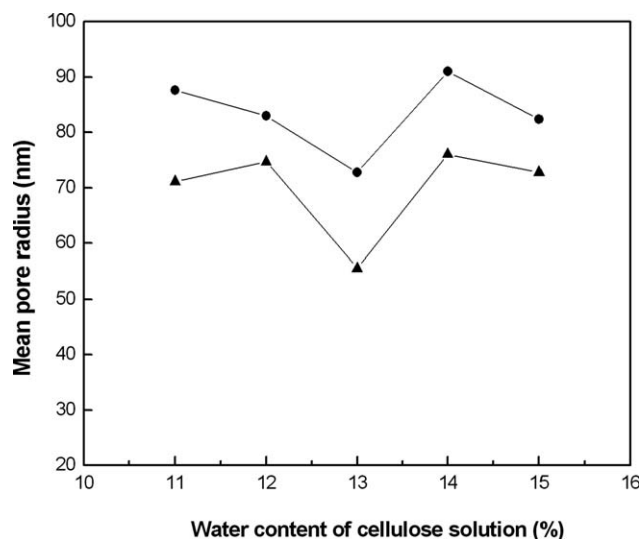

Figure 7 Effect of water content in the cellulose/NMMO/water solution on the mean pore radius of two size fractions composite beads. ● Cell-TuC-N-S; ▲ Cell-TuC-N-L.
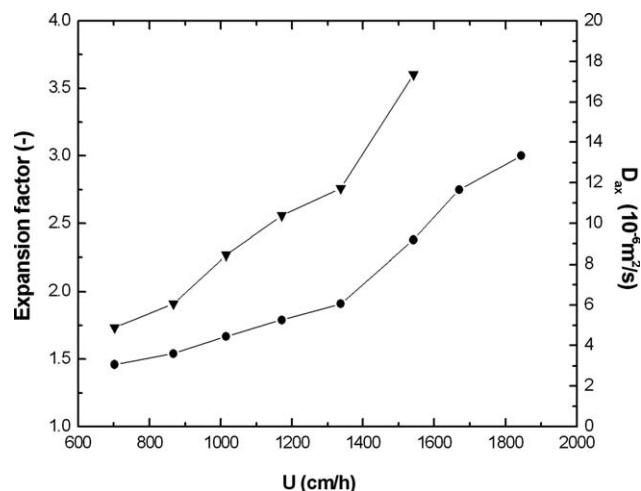

Figure 8 Expansion factor (●) and axial mixing coefficient D_{ax} (▲) as the function of flow velocity for Cell-TuC-N-S prepared with 13% of water content in the cellulose/NMMO/water solution.

which is quite higher than Streamline series of 200 to 400 cm/h and Streamline Direct of 400 to 800 cm/h.[42,46] The results indicated that the cellulose composite beads prepared have a good expansion property and could be used at high operation flow velocity.

The fluidization stability of composite beads in the expanded bed is another important factor that should be considered for the EBA applications. The Bodenstein number (Bo) and the axial mixing coefficient (D_{ax}) can be used to evaluate the properties of liquid mixing in the column. Bo values decreased from 127 to 94 as the flow velocity increased (data not shown). Even for high flow velocity, all Bo values tested were higher than 40, of which the Bo value for plug flow performance is considered as the critical in expanded bed.[45] The values of D_{ax} as the function flow velocity are also shown in Figure 8. For the operation velocity of 1000 cm/h, the values of D_{ax} was about 8.47×10^{-6} m²/s, which is lower than 1×10^{-5} m²/s for ensuring the adsorption efficiency in expanded bed. Compared with the cellulose composite beads prepared with the xanthate viscose as our previous work,[35] the value of D_{ax} in the present work was lower. The result indicated that the cellulose composite beads prepared in the present work could form quite stable expanded bed in the column even at high flow velocity and have a potential application for EBA process.

CONCLUSIONS

With the NMMO as the nonderivatizing dissolution solvent, cellulose can be dissolved directly, then dispersed in an oil phase and regenerated with the control of cooling to prepare the cellulose beads. With

the addition of tungsten carbide powder as the densifier, the cellulose-tungsten carbide composite particles could be formed through the method of water-in-oil suspension. The dissolution temperature and time, water content of the cellulose/NMMO/water solution, cellulose concentration, dispersion system, and cooling control were optimized. Moreover, the influences of water content in the cellulose/NMMO/water solution during the preparation on the properties of composite beads prepared were investigated. In general, the composite particles have the spherical appearance, suitable size distribution, appropriate wet density of 1.6 to 1.7 g/mL, porosity of 80 to 90%, pore radius of 72 to 91 nm, and specific surface area of 17.64 to 23.25 m^2/mL. In addition, the behaviors of expansion and liquid mixing in expanded bed illuminated that the cellulose composite beads prepared in the present work could be used as the matrix for EBA processes. Compared with the traditional technology with cellulose xanthate viscose, new method based on the NMMO dissolution is more environment-friendly, reduces the preparation time and shows a potential application for large scale.

References

1. Pinkert, A.; Marsh, K. N.; Pang, S. S.; Staiger, M. P. Chem Rev 2009, 109, 6712.
2. Fink, H. F.; Weigel, P.; Purz, H. F.; Ganster, J. Prog Polym Sci 2001, 26, 1473.
3. Saalwaechter, K.; Burchard, W.; Kluefers, P.; Kettenbach, G.; Mayer, P.; Klemm, D.; Dugarmaa, S. Macromolecules 2000, 33, 4094.
4. El Seoud, O. A.; Heinze, T. Adv Polym Sci 2005, 186, 103.
5. Isogai, A. Cellulose 1998, 5, 309.
6. Qi, H. S.; Chang, C. Y.; Zhang, L. N. Cellulose 2008, 15, 779.
7. Xiao, M.; Frey, M. W. Cellulose 2007, 14, 225.
8. Potthast, A.; Rosenau, T.; Buchner, R.; Roder, T.; Ebner, G.; Bruglachner, H.; Sixta, H.; Kosma, P. Cellulose 2002, 9, 41.
9. Zhao, H. B.; Kwak, J. H.; Wang, Y.; Franz, J. A.; White, J. M.; Holladay, J. E. Carbohydr Polym 2007, 67, 97.
10. Ruan, D.; Zhang, L.; Zhou, J. P.; Jin, H. M.; Chen, H. Macromol Biosci 2004, 4, 1105.
11. Bentivoglio, G.; Roder, T.; Fasching, M.; Buchberger, M.; Schottenberger, H.; Sixta, H. Lenzinger Berichte 2006, 86, 154.
12. Hermanutz, F.; Gahr, F.; Uerdingen, E.; Meister, F.; Kosan, B. Macromol Symp 2008, 262, 23.
13. Niekraszewicz, B.; Czarnecki, P. J Appl Polym Sci 2002, 86, 907.
14. Khare, V. P.; Greenberg, A. R.; Kelley, S. S.; Pilath, H.; Roh, I. J.; Tyber, J. J Appl Polym Sci 2007, 105, 1228.
15. Rosenau, T.; Potthast, A.; Sixta, H.; Kosma, P. Prog Polym Sci 2001, 26, 1763.
16. Eckelt, J.; Eich, T.; Roder, T.; Ruf, H.; Sixta, H.; Wolf, B. A. Cellulose 2009, 16, 373.
17. Chanzy, H.; Dube, M. J. Polym Sci Part C: Polym Lett 1979, 17, 219.
18. Rosenau, T.; Hofinger, A.; Potthast, A.; Kosma, P. Polymer 2003, 44, 6153.
19. Maia, E.; Peguy, A.; Perez, S. Acta Crystallogr 1981, 37, 1858.
20. Biganska, O.; Navard, P.; Bedue, O. Polymer 2002, 43, 6139.
21. Dube, M. J Polym Sci Part C: Polym Lett 1984, 22, 163.
22. Peska, J.; Stamberg, J.; Hradil, J.; Ilavsky, M. J Chromatogr A 1976, 125, 455.
23. Roy, I.; Pai, A.; Lali, A.; Gupta, M. N. Bioseparation 1999, 8, 317.
24. Wang, D. M.; Hao, G.; Shi, Q. H.; Sun, Y. J Chromatogr A 2007, 1146, 32.
25. Palsson, E.; Gustavsson, P. E.; Larsson, P. O. J Chromatogr A 2002, 878, 17.
26. Tong, X. D.; Sun, Y. J Chromatogr A 2001, 943, 63.
27. Zhou, X.; Shi, Q. H.; Bai, S.; Sun, Y. Biochem Eng J 2004, 18, 81.
28. Zhao, J.; Yao, S. J.; Lin, D. Q. Chin J Chem Eng 2009, 17, 678.
29. Nayak, D. P.; Ponrathnam, S.; Rajan, C. R. J Chromatogr A 2001, 92, 63.
30. Zhao, J.; Lin, D. Q.; Wang, Y. C.; Yao, S. J. Carbohydr Polym 2010, 80, 1085.
31. Lei, Y. L.; Lin, D. Q.; Yao, S. J.; Zhu, Z. Q. J Appl Polym Sci 2003, 90, 2848.
32. Lei, Y. L.; Lin, D. Q.; Yao, S. J.; Zhu, Z. Q. Chin J Chem Eng 2003, 11, 141.
33. Miao, Z. J.; Lin, D. Q.; Yao, S. J Ind Eng Chem Res 2005, 44, 8218.
34. Xia, H. F.; Lin, D. Q.; Yao, S. J. J Appl Polym Sci 2007, 104, 740.
35. Xia, H. F.; Lin, D. Q.; Yao, S. J. J Chromatogr A 2007, 1175, 55.
36. Turner, M. B.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Biomacromolecules 2004, 5, 1379.
37. Lin, D. Q.; Miao, Z. J.; Yao, S. J. J Chromatogr A 2006, 1107, 265.
38. Blachot, J. F.; Brunet; N.; Navard, P.; Caville, J. Y. Rheol Acta 1998, 37, 107.
39. Kim, D. B.; Lee, Y. M.; Lee, W. S.; Jo, S. M.; Kim, B. C. Eur Polym Mater 2002, 38, 109.
40. Kim, D. B.; Jo, S. M.; Lee, W. S.; Pak, J. J. J Appl Polym Sci 2004, 93, 1687.
41. Hubbuch, J.; Thommes, J.; Kula, M. R. Adv Biochem Eng Biotechnol 2005, 92, 101.
42. Amersham Pharmacia Biotech. Expanded Bed Adsorption-Principle and Methods, Code No. 18-1124-26; Amersham Pharmacia Biotech: Uppsala, Sweden, 1998.
43. Xia, H. F.; Lin, D. Q.; Yao, S. J. J Chromatogr A 2008, 1195, 60.
44. Biganska, O.; Navard, P. Biomacromolecules 1948, 2005, 6.
45. Thommes, J. Adv Biochem Eng Biotechnol 1997, 58, 185.
46. Amersham Biosciences. Expanded Bed Adsorption, Streamline™ Direct CST-1: Adsorbent for Capture Proteins from Crude Feed; Amersham Biosciences: Uppsala, Sweden, 2005.