Characterization of Cellulose Microbeads Prepared by a Viscose-Phase-Separation Method and Their Chemical Modification with Acid Anhydride

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ABSTRACT: Chemically modified cellulose microbeads are useful as cosmetic materials. Cellulose microbeads as supports, prepared by a viscose-phase-separation method, are monodisperse and spherical. However, cellulose shows only slight hydrophilicity, even though it has three hydroxyl groups per pyranose ring, because cellulose possesses high crystallinity on account of the cellulose II structure derived from hydrogen bonds among the hydroxyl groups. To increase the hygroscopicity of cellulose microbeads, we have carboxylated them with succinic and glutaric anhydrides. Their hygroscopicity increases with the addition of succinoyl and glutaroyl groups. Moreover, we have confirmed the increased hygroscopicity of microbeads with sodium salinization. We have investigated the decomposition of these hydrophilic cellulose microbeads in aqueous buffer solutions and have confirmed that succinoylated cellulose is more readily decomposed than glutaroylated cellulose microbeads in aqueous solutions. On the other hand, to increase the lipophilicity of cellulose microbeads, we have acylated them with acetic and hexanoic anhydrides. Hydrophobizing microbeads with hexanoyl groups provides an affinity to benzene but not to H_2O. In contrast, hydrophobizing with acetyl groups provides affinity not only to benzene but also to H_2O. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 149–157, 2005

Key words: esterification; hydrophilic polymers; particle size distribution

INTRODUCTION

Cellulose, which is used in various matrix-forming materials, has long been explored for its potential as a building material. Although cellulose is a sustainable material, it is rigid because of intermolecular and intramolecular hydrogen bonding. Therefore, cellulose has poor workability because of thermal stability, poor controllability of chemical reactions, and low solubility in H_2O and common organic solvents.[1,2] Cellulose derivatives, such as acylate[3–5] and xanthate,[6] or cellulose complexes with copper, such as cupra,[7] are required to mold cellulose. On the other hand, spherical microbeads of cellulose have been used as chromatographic packing materials,[8–10] immobilization supports of microbes,[11] and cosmetic materials.[12,13] The methods for sphering cellulose include the production of porous and spherical particles from cellulose derivative solutions, such as the suspension evaporation method with triacetyl cellulose,[8,9] the viscose-phase-separation method,[14,15] and the precipitation of cellulose particles with alcohol from aqueous cellulose–rhodan calcium solutions.[16] Spherical cellulose microbeads prepared by the viscose-phase-separation method are monodisperse and spherical. Although they possess several advantages, they show not only poor hydrophobicity caused by three hydroxyl groups per pyranose ring but also poor hydrophilicity because of their high crystallinity due to the cellulose II structure.[17–19] Therefore, we have developed a surface chemical modification technique for monodisperse cellulose microbeads with several kinds of acid anhydrides for applications as cosmetic materials, such as humectants and emulsifying agents, as shown in Figure 1. Hydrophilic cellulose microbeads have been prepared with succinic and glutaric anhydrides by an alkali/acetone method to provide hygroscopic properties to the cellulose microbeads. In addition, to provide lipophilic properties, we have prepared hydrophobic cellulose microbeads with acetic or hexanoic anhydride as a hydrophobic modifier reagent by a trifluoroacetic acid method.[20] In this article, we compare the characteristics of cellulose microbeads obtained by the viscose-phase-separation method and

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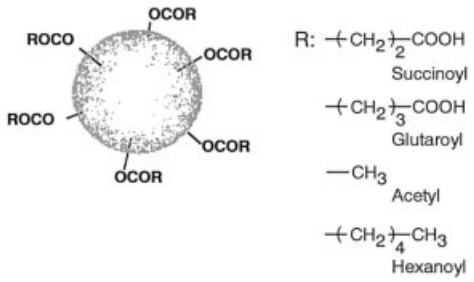


Figure 1 Cellulose microbeads chemically modified with acid anhydrides.

the suspension evaporation method and also report on the preparation and characterization of spherical chemically modified cellulose microbeads.

EXPERIMENTAL

Cellulose microbeads

Spherical cellulose microbeads (Cell-V) were prepared with the viscose-phase-separation method, a unique congealing technology based on the phase-separation phenomenon between cellulose xanthate and H_2O-soluble polymers in H_2O.[14] We also obtained spherical cellulose microbeads (Cell-A) through the saponification of microbeads prepared by the suspension evaporation method with triacetyl cellulose, which was developed by Motozato et al.[8] In this suspension evaporation method, a hydrophobic polymer, dissolved in an H_2O-insoluble organic solvent, is dispersed in a viscous aqueous H_2O-soluble polymer solution and is precipitated as solidified spherical particles by the gradual heating removal of the solvent.

Preparation of the chemically modified cellulose microbeads with acid anhydrides

The chemically modified cellulose microbeads, shown in Table I, were prepared with several kinds of acid anhydrides.

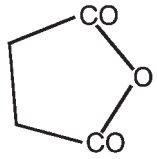
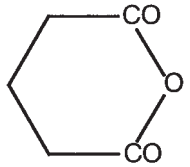
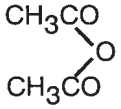
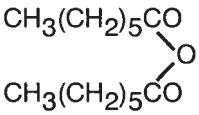
Hydrophilic cellulose microbeads

To provide hygroscopic properties to the cellulose microbeads, we carried out the succinoylation or glutaroylation of the cellulose microbeads as follows. H_2O-containing Cell-V (64.9 g, moisture content = 85%, dry weight = 10.0 g, 61.7 unit mmol) was suspended in acetone (300 mL). With stirring, potassium hydroxide (8.14 g, 123.4 mmol) was added to this suspension for 2 h at 50°C. Succinic anhydride (12.34 g, 123.4 mmol) in acetone (100 mL) was added dropwise to the solution, which was stirred at 50°C for 24 h. The white precipitate was gathered by filtration and then was washed successively with acetone and H_2O. In addition, to convert to COOH from COO^-K^+ in the microbeads, we washed them successively with an aqueous 0.01*M* HCL solution and H_2O and freeze-dried them. Glutaroylated cellulose microbeads (GltCell) were prepared with glutaric anhydride and potassium hydroxide by the same procedure used in the preparation of the succinoylated cellulose microbeads (SucCell). In addition, to convert to COO^-Na^+ from COOH in SucCell and GltCell, we washed the microbeads successively with an aqueous 0.01*M* NaOH solution and H_2O and freeze-dried them. Similarly, to convert to COO^-K^+ from COOH in SucCell and GltCell, we washed the microbeads successively with an aqueous 0.01*M* KOH solution and H_2O and freeze-dried them. The potassium-salinized microbeads are named SucKCell and GltKCell, respectively.

Hydrophobic cellulose microbeads

To give the microbeads oily properties, we carried out acetylation or hexanoylation as follows. Acetic acid (100 mL) was substituted for H_2O in Cell-V (29.4 g, moisture content = 83%, dry weight = 5.0 g, 30.8 unit mmol). Acetic acid containing Cell-V was then suspended in acetic acid (28.1 mL, 500 mmol) and acetic acid anhydride (18.3 mL, 194.0 mmol) at 50°C. With stirring, trifluoroacetic acid (5.4 mL, 70.2 mmol) was added to this suspension at 50°C. The mixture was stirred for 24 h at 50°C. The white precipitates were

TABLE I
Abbreviations and Structures of Modifier Groups and Acid Anhydrides

Microbeads	Modifier Group	Acid Anhydride
Cell	Nonmodfied	—
SucCell	—CO—CH_2—$_2$COOH Succinoyl	
SucNaCell	—CO—CH_2—$_2$COONa Sodium Succinoyl	
GltCell	—CO—CH_2—$_3$COOH Glutaroyl	
GltNaCell	—CO—CH_2—$_3$COONa Sodium Glutaroyl	
AcCell	—CO—CH_3 Acetyl	
HexCell	—CO—CH_2—$_5CH_3$ Hexanoyl	

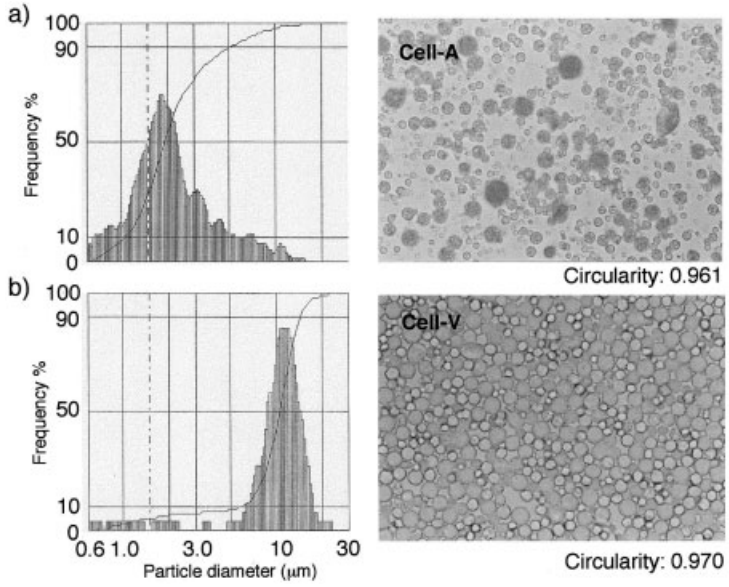


Figure 2 Microscopic observations and particle size distributions measured by the FPIA-2100 with the flat-sheath flow method: (a) Cell-A and (b) Cell-V.

gathered by filtration and washed successively with acetone. H_2O was substituted into the acetone-containing product, and the resulting product was freeze-dried. Hexanoylated cellulose microbeads (HexCell) were prepared with hexanoic acid, hexanoic anhydride, and trifluoroacetic acid by the same procedure used in the preparation of acetylated cellulose microbeads (AcCell).

Measurements

Microscopic observations were made and particle size distributions and circularities were measured by the flat-sheath flow method (FPIA-2100, Sysmex Corp., Kobe, Japan). The circularity was expressed as the perimeter of the circle of an equivalent area divided by the perimeter of the projected image particle image. The circularity was computed with a flow-type particle image analysis apparatus known as the FPIA-2100. The definition was given as a value that was divided by the boundary length, which was computed from the perimeter of the circle of an equivalent area (the diameter with the same projected area as the actually pictured boundary length of a perfect circle) divided by the boundary length of a particle of the actually picture by means of the FPIA-2100. Infrared (IR) spectra were measured as KBr disks with Fourier transform infrared (FTIR) spectroscopy (FT/IR-700, Jasco, Tokyo, Japan). Differential scanning calorimetry (DSC, Tokyo, Japan) of H_2O in the microbeads was carried out at a heating rate of 1°C/min with a DSC-6200 (Seiko Instruments, Inc., Chiba, Japan) with a Haake EK 90/SII as a cooling system. X-ray diffraction (XRD) was carried out with a Rigaku RINT-2000 X-ray diffractometer (Osaka, Japan). The pH determination of the microbead H_2O dispersion was carried out with an IM-40S ion meter with a GS-5015C electrode (DKK TOA Corp., Tokyo, Japan).

RESULTS AND DISCUSSION

Comparison of Cell-A and Cell-V

Figure 2 presents microscopic observations and particle size distributions measured by the FPIA-2100 with the flat-sheath flow method. In addition, the FPIA-2100 could be used to estimate the circularity by measuring the shape parameters of the particles. A perfect circle had a circularity value of 1, and the more complicated a configuration became, the smaller its value was.[21] The mean particle diameter (number base) of Cell-A was 2.62 μm, and that of Cell-V was 10.48 μm. Although the circularity of Cell-A was 0.961 and the sphericity of the particles was high, the particle size distribution was wide; the coefficient of variation (CV; standard deviation/mean particle size) of the particle diameter was 78.7%. On the other hand, the circularity of Cell-V was estimated to be 0.970, and the sphericity of Cell-V was higher. The particle size distribution of Cell-V was narrower than that of Cell-A, as shown in the CV value for Cell-V, which was 37.5%. As shown in typical optical microscopy photographs of Cell-A and Cell-V, it was also evident that the particle size distribution of Cell-V was narrower than that of Cell-A. Figure 3 shows XRD patterns of Cell-A and Cell-V. These figures confirm that the XRD peaks of the cellulose II crystal structure in Cell-A were broader than those of Cell-V. The evaluation of the degree of crys-

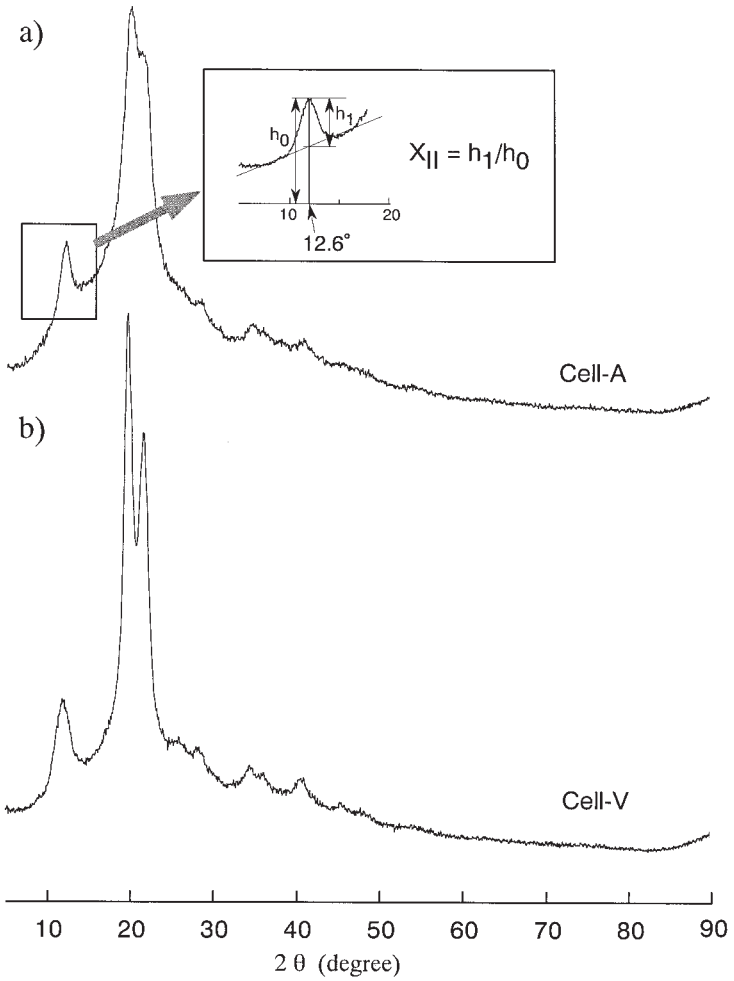


Figure 3 XRD patterns of (a) Cell-A and (b) Cell-V.

tallinity in a cellulose II structure was generally computed as a molar fraction (X_{II}) of the cellulose II crystallinity with the wide-angle XRD method. The following equation was obtained from the absolute peak intensity (h_0) at $2\theta = 12.6°$, which belonged to the field (110) peak of a cellulose II crystal structure, and the peak intensity (h_1) from the baseline:[12]

$$X_{II} = h_1/h_0 \quad (1)$$

X_{II} of Cell-V was estimated to be 0.34. In contrast, that of Cell-A was 0.14. This indicated that the crystallinity of Cell-V was higher than that of Cell-A. The spherical shape of Cell-A was formed with the phase separation between oil (a triacetyl cellulose organic solution) and H_2O (an aqueous H_2O-soluble polymer solution). The spherical microbeads molded from the triacetyl cellulose organic solution lacked hydrogen bonds. Because Cell-A was obtained through the solid–liquid saponification of amorphous triacetyl cellulose microbeads, we thought that the cellulose main chain remained a disordered structure, even though hydroxyl groups were produced by the saponification and hydrogen bonding occurred partially, as shown in the following speculation (Fig. 4). On the contrary, the molding of the spherical shape of Cell-V was based on droplet generation by means of the electric repulsion between the CSS^- group of cellulose xanthate and the COO^- group of sodium polyacrylate, and the solidification was carried out by hydrogen bonding produced by the elimination of xanthate groups with hydrochloric acid. Consequently, the cellulose II structures of Cell-V became tight.

Preparation of the chemically modified cellulose microbeads

A high powder fluidity is required for cosmetic materials if they are to feel smooth on human skin. Therefore, Cell-V was adopted as a support material for chemical modification with anhydrides because of the advantages of Cell-V's high sphericity and narrow particle size distribution. Figure 5(b) shows FTIR spectra of cellulose microbeads succinoylated with suc-

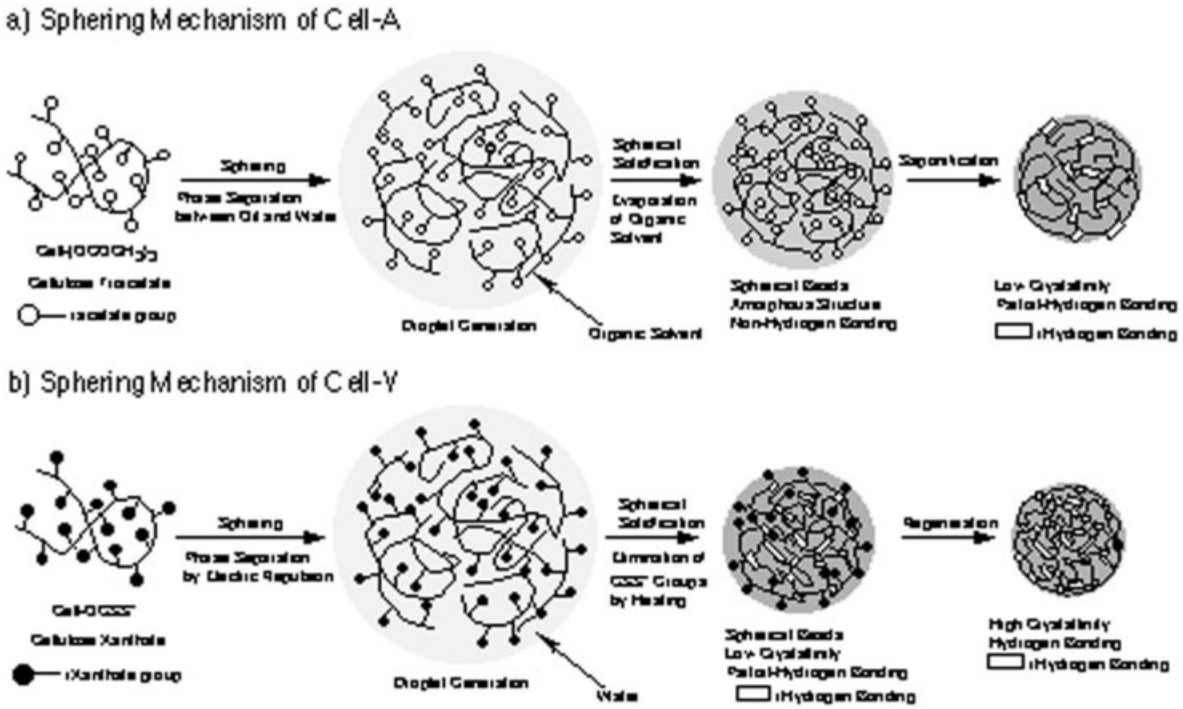


Figure 4 Schematic illustration of the sphering mechanism of cellulose: (a) Cell-A and (b) Cell-V.

cinic anhydride (SucCell). The main characteristic peak was attributable to the adsorption due to $\nu_{C=O}$ (ester and carboxyl) at 1740 cm^{-1}, which was not detected in the IR spectrum of nonmodified cellulose (Cell) in Figure 5(a). As a result, the presence of succinoyl groups was confirmed, and their content was estimated to be 2.15 mequiv/g by the titration method. Figure 5(c) shows the FTIR spectra of sodium-salinized succinoylated cellulose microbeads (SucNaCell). The intensity of the adsorption at 1740 cm^{-1} decreased, whereas an adsorption at 1570 cm^{-1} appeared. The adsorptions at 1740 and 1570 cm^{-1} corresponded to $\nu_{C=O}$ (ester) and $\nu_{C=O}$ (carbanion), respectively. Therefore, the presence of monosodium succinate was confirmed. In IR spectra of glutaroylate cellulose microbeads (GltCell), the main characteristic peak attributed to $\nu_{C=O}$ (ester and carboxyl) also appeared at 1740 cm^{-1}, just as for SucCell, and this indicated the presence of glutaroyl groups; the content was estimated to be 1.84 mequiv/g by the aforementioned method. In addition, we carried out the sodium salinization of glutaroylate cellulose microbeads (GltNaCell) with the same procedure used for SucCell, and the presence of monosodium glutarate was confirmed with IR spectra. Figure 5(d) shows the FTIR spectra of cellulose microbeads acetylated with acetic anhydride (AcCell). The main characteristic peak was attributable to the adsorption due to $\nu_{C=O}$ (ester) at 1740 cm^{-1}, which disappeared in the IR spectrum of Cell in Figure 5(a). This indicated the presence of acetyl groups. The content of the acetyl groups was estimated to be 7.51 mequiv/g according to the JIS K 6726 1994 method.[22] In the IR spectra of hexanoylated cellulose microbeads (HexCell), the main characteristic peak attributed to $\nu_{C=O}$ (ester) also appeared at 1740 cm^{-1}, as was the case for AcCell, as shown in Figure 5(e). This indicated the presence of a hexanoyl group; the content was estimated to be 2.13 mequiv/g by the previous method.

Characterization of the hygroscopic and lipophilic properties of the microbeads

To investigate the hygroscopic and lipophilic properties of the microbeads, we added 5 μL of H_2O and benzene for the hygroscopic property evaluation and lipophilic property evaluation, respectively, to 10 mg of the obtained microbeads and then measured their melting point peaks with DSC. We then investigated the hygroscopic properties of the microbeads modified by hydrophilic functional groups, that is, succinoyl and glutaroyl groups. Figure 6 shows the DSC thermograms of H_2O added to the microbeads. For H_2O, the endothermic peak corresponding to the freezing of H_2O was observed around 0°C. The DSC curve of H_2O added to Cell had its main peak around −1.0°C (free H_2O region), as shown in Figure 6(a). In contrast, the main peak was observed around −1.9°C for SucCell, as shown in Figure 6(b). This indicated that the H_2O molecule was bound by the SucCell matrix. In addition, the main peak due to H_2O in SucNaCell showed a broadening and tailing phenom-

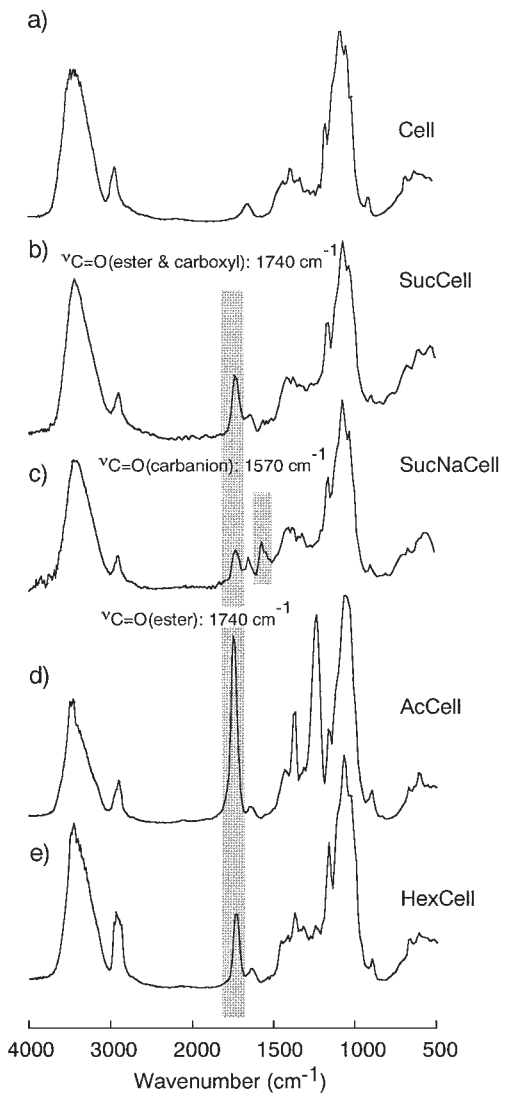


Figure 5 FTIR spectra of chemically modified cellulose microbeads: (a) Cell, (b) SucCell, (c) SucNaCell, (d) AcCell, and (e) HexCell

enon, which shifted to a lower temperature than that of SucCell, around −5.3°C, as shown in Figure 6(c). This indicated that the H_2O molecule was further bound by the matrix, which was spread by repulsion among COO^- groups. Similarly, the main peak due to H_2O was observed near −1.4°C in GltCell and shifted to −4.9°C through sodium salinization. We investigated the hygroscopic and lipophilic properties of the microbeads with modified hydrophobic functional groups, that is, the acetyl (AcCell) and hexanoyl (HexCell) groups, respectively. In AcCell, the main peak due to H_2O was observed near −2.1°C, as shown in Figure 7(a). The main peak due to H_2O added to AcCell shifted to a lower temperature than that in Cell. This phenomenon was attributable to the fact that loose binding of the H_2O molecule from the matrix of AcCell occurred easily because acetyl groups added partially to hydroxyl groups of cellulose prevented intermolecular and intramolecular hydrogen bonding among the hydroxyl groups and H_2O molecules were then able to permeate the matrix and combine with residual hydroxyl groups. In contrast, for HexCell, the main peak was observed around −0.2°C, as shown in Figure 7(b). This suggested that HexCell possessed high hydrophobicity and that the affinity to H_2O was poor. Figure 8 shows DSC thermograms of benzene added to microbeads. For benzene, an endothermic peak around 5.0°C, corresponding to the freezing of benzene, was observed. The DSC curve of benzene added to Cell had a sharp peak around 4.7°C, as shown in Figure 8(a). This suggested that the affinity of benzene to cellulose was poor. In contrast, the endothermic peak of benzene added to HexCell did not appear, as shown in Figure 8(b). It is evident that the affinity of benzene to HexCell was high. However, contrary to our expectation, the DSC curve of benzene added to AcCell also had no peak, as shown in Figure 8(c). These results indicated that AcCell had an affinity not only to H_2O but also to benzene. This indicated that AcCell possessed amphiphilic properties. Figure 9 shows the distribution of Cell, AcCell, and HexCell in two layers of a mixture of hexane and H_2O. Cell was

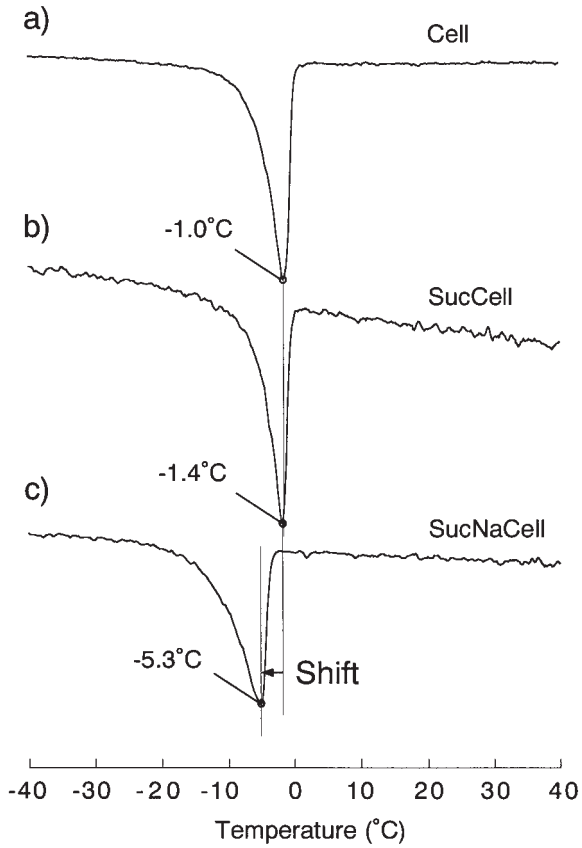


Figure 6 DSC thermograms of H_2O added to microbeads: (a) Cell, (b) SucCell, and (c) SucNaCell (5 μL of H_2O and 10 mg of microbeads).

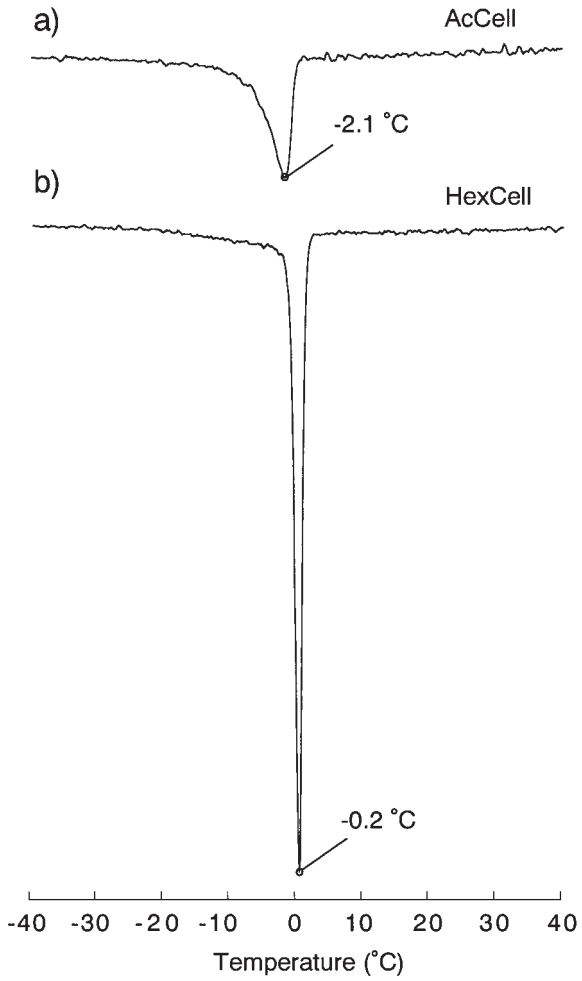


Figure 7 DSC thermograms of H_2O added to microbeads: (a) AcCell and (b) HexCell (5 μL of H_2O and 10 mg of microbeads).

distributed in the H_2O layer. In contrast, HexCell was distributed in the hexane layer because it possessed high hydrophobicity. On the other hand, AcCell was distributed in a boundary between the two layers. This indicated that AcCell possessed amphiphilicity, which is favorable for emulsifying agents.

H_2O-absorbing properties

Figure 10 shows the H_2O-absorbing properties of the obtained microbeads. The degree of H_2O absorbing is given by degree of H_2O-absorbing = Wt/W0 where Wt and W0 are the weight of microbeads after incubation and their original weight. After the Cell microbeads were kept in a chamber at 40°C and 90% humidity for 54 h, their weight increased only 1.12-fold. On the other hand, the weight of SucCell increased 1.17-fold with the same H_2O-absorbing experiment. Furthermore, that of SucNaCell increased 1.19-fold. In contrast, in hydrophobic cellulose microbeads,

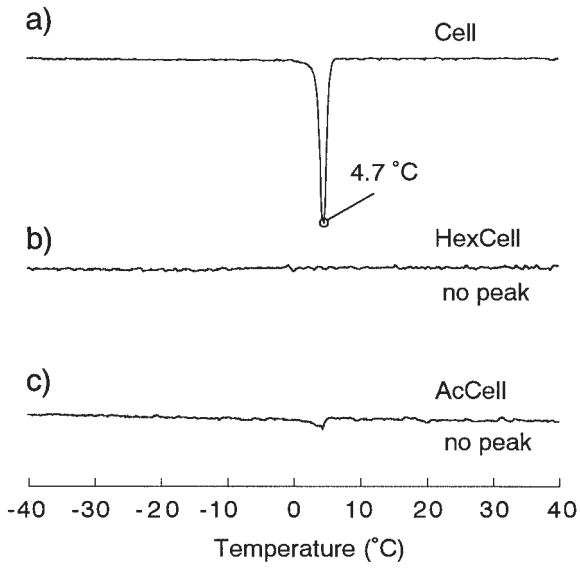


Figure 8 DSC thermograms of benzene added to microbeads: (a) Cell, (b) HexCell, and (c) AcCell (5 μL of benzene and 10 mg of microbeads).

the weight of AcCell increased only 1.09-fold. The H_2O-absorbing capacity of AcCell was smaller than that of Cell. This indicated that there were fewer absorbing sites for H_2O in AcCell than in Cell. Although the matrix of AcCell could more strongly bind 5 μL of H_2O for 10 mg of microbeads than that of Cell, in light of the DSC measurements, the binding site in Cell that restrained H_2O weakly was larger than that in AcCell. Because HexCell had the highest hydrophobicity of all the microbeads that we tested, its weight increase was lowest at only 1.06-fold.

Decomposition of the hydrophilic cellulose microbeads

We investigated the decomposition of the hydrophilic cellulose microbeads in an aqueous succinic acid/potassium succinate buffer solution (pH 5.4, concentration = 0.84%) at 55°C. As shown in Figure 11, the

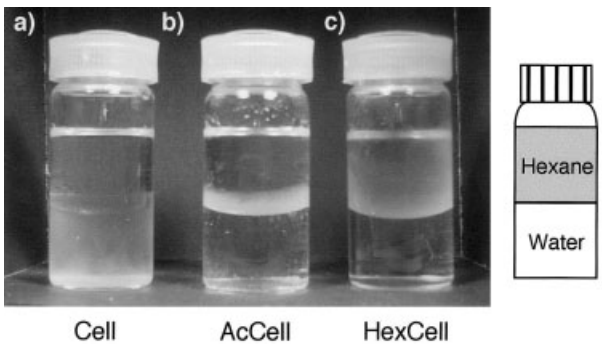


Figure 9 Distributions of (a) Cell, (b) AcCell, and (c) HexCell in two layers of a mixture of hexane and H_2O.

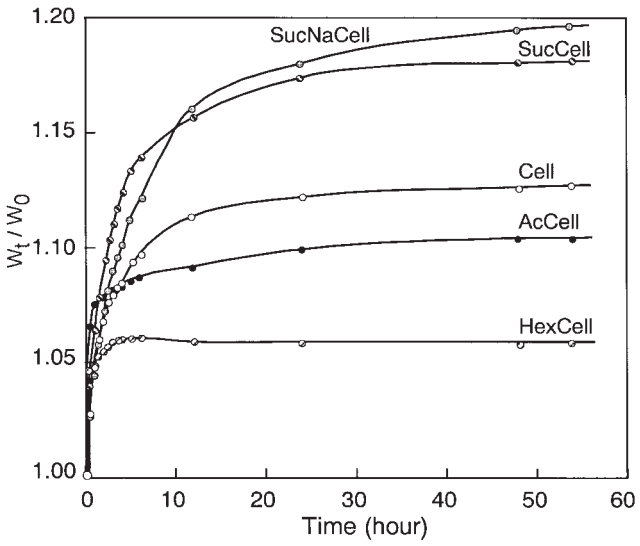


Figure 10 Weight changes in microbeads in a chamber at 40°C and 90% humidity: (○) Cell, (●) AcCell, (▨) the MS for a shape) HexCell, (◔) SucCell, and (◔) SucNaCell.

change in the pH of aqueous-solution-soaking GltK-Cell was small after 70 days. In contrast, the pH of aqueous-solution-soaking SucKCell decreased from 5.54 to around 5.25, and this caused the elimination of succinoyl groups from cellulose microbeads. The fact that the IR spectrum of the microbeads soaked in the aqueous buffer solution for 70 days did not show a peak due to succinoyl groups suggested that the self-cyclization of the dicarboxylate monoester depended on the spacer length among the carboxyl groups, as noted previously by Breslow.[23] These results were attributed to the fact that the succinate monoester self-cyclized more easily than the glutarate monoester,

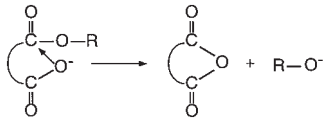


Figure 12 Self-cyclization of the dicarboxylic acid monoester.

as shown in Figure 12. As a result, the succinoyl group was more readily eliminated from the cellulose supports than the glutaroyl group in aqueous solutions.

CONCLUSIONS

We investigated the properties of typical cellulose microbeads, Cell-A and Cell-V, obtained by the suspension evaporation method with triacetyl cellulose and by the viscose-phase-separation method with cellulose xanthate, respectively. The sphericity of Cell-V was higher than that of Cell-A. The particle size distribution of Cell-V was narrower than that of Cell-A. The cellulose II structure of Cell-V was tighter than that of Cell-A according to XRD patterns. As a result of these differences, Cell-V was adopted as a support material for chemical modification with anhydrides. The hydrophilic cellulose microbeads were prepared with succinic and glutaric anhydrides by the alkali/acetone method. The hygroscopicity of the microbeads increased with the addition of succinoyl and glutaroyl groups. In addition, the increased hygroscopicity of the microbeads with sodium salinization was confirmed. In contrast, the hydrophobic cellulose microbeads were prepared with acetic or hexanoic anhydride as a hydrophobic modifier reagent by the trifluoroacetic acid method. The lipophilicity of the microbeads increased with the addition of acetyl and

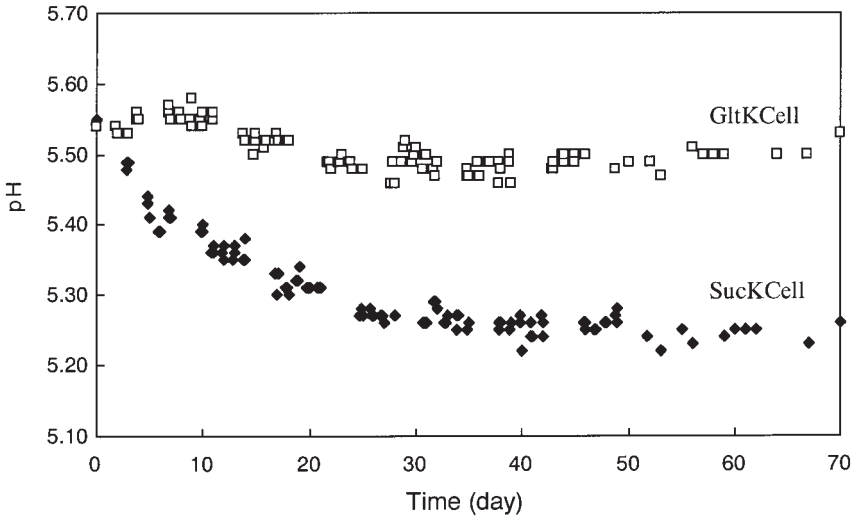


Figure 11 Changes in the pH of succinic acid/potassium succinate buffer aqueous solutions with the soaking of (□) GltKCell and (♦) SucKCell (buffer conditions: pH 5.4, concentration = 0.84%).

hexanoyl groups. Hydrophobizing with hexanoyl groups provided affinity to benzene but not to H_2O. In contrast, hydrophobizing with acetyl groups provided affinity to both benzene and H_2O. We investigated the decomposition of hydrophilic cellulose microbeads in a buffer of an aqueous solution. The shorter the spacer length was among carboxyl groups in a dicarboxylic acid, the more dicarboxylic acid was eliminated by self-cyclization. As a result, we confirmed that SucCell was more decomposed than GltCell in an aqueous solution. For hygroscopicity, cellulose microbeads were carboxylated with succinic and glutaric anhydrides. SucCell and GltCell could be used as humectants because of their high hygroscopicity. In addition, for lipophilicity, cellulose microbeads were acylated with acetic anhydride or hexanoic anhydride. In particular, AcCell could be used as an emulsifying agent because of its amphiphilicity.

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