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PHASE TRANSITION TEMPERATURE OF WATER RESTRAINED IN POLYSULFONE HOLLOW FIBRES

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The melting and crystallization behaviour of water restrained in polysulfone (PSF) hollow fibre has been investigated by DSC. The PSF hollow fibre was prepared by wet spinning. The morphology of the fibre was observed by scanning electron microscopy. The amount of water was varied by successive evaporation and it was observed that melting and crystallization shifted to temperatures lower than those observed for free water. DSC and NMR studies showed that water in hollow fibres is in a restricted state.

Keywords: crystallization behaviour, DSC, NMR, phase transition, polysulfone hollow fibre, scanning electron microscopy

Introduction

Hollow fibres are used in various fields, such as the separation of blood components, purification of water, etc. [1, 2]. It is important to study not only the structure of the fibre matrix but also the structure and properties of water molecules in various pore sizes [3–6], since the hollow fibre is mostly used in aqueous media. It is well known that water molecules trapped in a small-pore material such as silica gel [7, 8] adopt a structure different from normal water. Structural change of water has also been found in hydrogels [9–10] and water associated with hydrophilic polymers [11–15]. The structure and properties of water restrained in polymers have been investigated by various experimental techniques, such as nuclear magnetic resonance (NMR) [9, 10, 15], thermal analysis [10–16], dielectric measurement [17], etc.

We reported the phase transition behaviour of water restrained in cellulosic hollow fibres and found that the hollow fibres contained a large amount of bound water [14]. NMR studies suggested that the water molecules directly attached to

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the hydroxyl group in the cellulose fibres exhibited behaviour similar to that of a non-rigid [15]. This means that the mobility of the bound water is lower than that of ordinary water, and the inter-molecular hydrogen bonding between water molecules and the hydroxyl group of cellulose must influence the phase transition behaviour of the water. In order to eliminate the above situation, in this study we chose polysulfone and investigated the phase transition behaviour of water in hollow fibres using DSC and NMR.

Experimental

Sample preparation

Polysulfone pellets were obtained from Union Carbide Co. (Grade No., P–1700, density = 1.24 g/cm^3, melt flow index = 6.5). The sample was dissolved in 1-methyl-2-pyrrolidinone and kept for 12 hours at room temperature. The concentration was fixed at 10 weight%. A fibre spinning system constructed in our laboratory was used [14].

The diameter of the sample was measured using Nikon profile projector. Between seven and eleven specimens were measured for each sample. Average values for diameter of the outer tube (D) and the inner tube (d) were calculated. The length of fibre was shown as a unit of meter/gram. The apparent volume (V_s, in m^3/g) of hollow fibre was calculated from the above values.

Water content (W_c) of the sample was measured by weighing, i.e. the water on the fibre surface and in the inner tube was removed using paper and weighed quickly. Following this, the fibres were kept in an oven at 110°C under a reduced pressure of 10^{-2} mmHg for 12 hours. Details of this technique are given in [14]. Water content (W_c) was defined as follows:

$$W_c = W_w/W_s \ (\mathrm{g/g}) \tag{1}$$

where W_w is the weight of water and W_s the weight of dry fibre.

Measurement

An Akashi scanning electron microscope DS–130–WET was used for observing cross-sections of fibres.

A Perkin Elmer differential scanning calorimeter DSC II was used for thermal analysis. The undried sample was sealed in an aluminium capsule immediately after water on the fibre surface was removed. Experimental procedures have been reported previously [18].

A Nicolet FT–NMR, model NT–200 WB, was used for measurement of longitudinal and transverse relaxation times (T_1 and T_2). T_1 was measured by the 180–τ–90 degree pulse method. T_2 was measured by the Meiboom–Gill variant of the Carr–Purcel method. The sample temperature was 20°C.

Results and discussion

Fourteen specimens having fibre diameters from 0.400 to 1.122 mm were prepared under varying spinning condition as shown in Table 1. Electron micrographs of cross-sections showed numerous pores in the curved structure. The diameter of inner tube (*d*) increased and unit length of fibre decreased with increasing outer diameter (*D*). The value of V_S varied from 3.1×10^{-6} to 4.8×10^{-6} (m^3/g) depending on preparative conditions. Water content of fibre calculated as weight ranged from 3.4 to 3.7 (water/dry PSF, g/g). Water content calculated as volume was in the range 0.8 to 1.3.

Table 1 Spinning conditions of hollow fibres

Concentration of dope / %	10	10	10
Dope supply / g·min^{-1}	13.4	13.4	13.4
Coagulating water supply / g·min^{-1}	20	12	8
Winding speed / m·min^{-1}	0*	0*	0*
	8	8	8
	16(IV)**	16(III)	16
	24	24	24(III)
	32(I)	32	***

* spun by self weight without winding ** Roman numerals correspond to those in Figs 1 and 2
*** could not be spun

Figure 1 shows representative DSC curves of water trapped in hollow fibres prepared under different spinning conditions as shown in Table 1. Increase in sample number shown in Roman numerals corresponds with increase in *D* value. The W_c value was almost the same for all samples (W_c = ca. 3.5 g/g). It is clearly seen that the main crystallization peak attributed to crystallization of free water shifts to higher temperature with increasing *D*. At the same time, two or three exothermic crystallization peaks of water appear on the low-temperature side of the main peak.

The peaks observed at lower temperatures were found in all three samples shown in Fig. 1. Previous studies of crystallization of water in hydrophilic polymers indicated that the small peak observed at 230 to 240 K is due to the freezing of bound water having an irregular structure [13]. It is noteworthy that the S = 0 group in the main chain of PSF seems to form inter-molecular hydrogen bonds with water. The temperature of the above peak maintained a constant value throughout the whole range of D independent of spinning conditions. This strongly suggests that the third peak can be attributed to crystallization of bound water associated with the sulfonyl group of PSF.

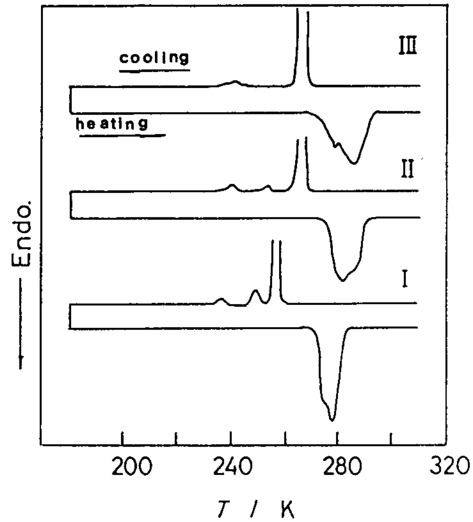

Fig. 1 Representative DSC curves of water restrained in PSF hollow fibre. I: D = 4.0 x 10–4 m, d = 1.6 x 10–4 m; II: D = 5.5, d = 2.0; III: D = 7.3, d = 1.0, W_c = ca. 3.6 g/g

The intermediate peak appearing between the main and small peak can be observed for samples with small D values. The temperature difference between the main peak and the second peak decreased with increasing apparent volume, V_s. Ishikiriyama *et al.* [19] and Homshow [20, 21] reported a similar type of peak on the lower-temperature side of the main crystallization peak for poly(methyl methacrylate) hollow fibre. They attributed this peak to crystallization of free water trapped in the pores of hollow fibres.

Although shapes of melting peaks are not as well resolved as those of crystallization peaks, the melting peak temperature shifts to higher temperatures with increasing D. At the same time, the temperature range of melting increases with increasing D. The DSC data shown in Fig. 1 suggest that the pore size in the fibre increases with increasing D.

It is estimated from DSC curves shown in Fig. 1 that a large number of water molecules restrained in hollow fibres are free water. However, the longitudinal relaxation time T_1 obtained from the inversion recovery measurement of water in hollow fibre (sample IV, Table 1) was 2.1 sec. The transverse relaxation time obtained by the Meiboom–Gill method, T_2, was 0.24 sec. It is well known that the T_1 and T_2 of free water (ordinary water) are ca. 3.5 sec, showing the same value when the extreme narrowing conditions are fulfilled. However, for water in the hollow fibres, the T_2 value was far smaller than the T_1 value. This suggests that the water molecules in hollow fibres are restricted by the PSF matrix.

The DSC and NMR results suggest that water molecules in hollow fibres are affected by the PSF matrix. In order to investigate the effect of W_c on the thermal behaviour of water, the W_c value was varied as described in the experimental section. Figure 2 shows representative DSC curves of water in the hollow fibres (sample IV) having various water contents. The melting peak shifts to the low-temperature side and the peak is resolved into two peaks in the sample with $W_c = 0.4$. In the sample with $W_c = 0.4$, the main crystallization peak is completely resolved into two peaks, although even the higher-temperature component is at a markedly lower temperature.

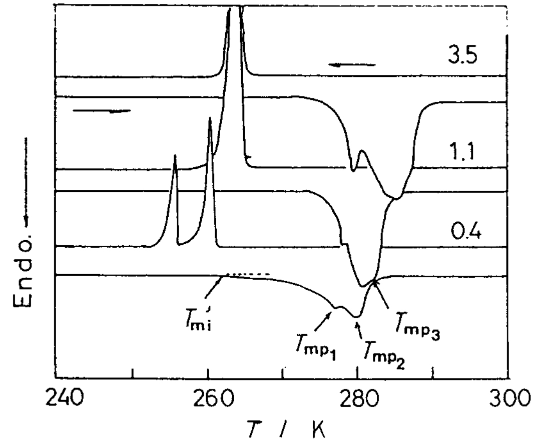

Fig. 2 Representative DSC curves of water in PSF hollow fibre during the drying process. Numerals in figure show W_c(g/g)

Figure 3 shows melting peak temperatures (T_{mp1}, T_{mp2} indicated in Fig. 2), shoulder of melting peak (T_{ms}), and starting temperature of melting (T_{mi}, indicated in Fig. 2) as a function of water content (W_c). Temperatures of melting shifted to lower temperatures with decreasing W_c. At a W_c of 0.4, the melting peak becomes markedly broader. From Fig. 3 it can be seen that the water structure immediately changes when the W_c in the hollow fibre decreases. The low-temperature peaks appearing in both crystallization and melting are evidence that free water molecules evaporate in the first stage from the hollow fibre. Moreover, the fact that a new large peak appears on the low temperature side at low W_c values shows that free water and freezing bound water separate clearly, due to the structure of the PSF matrix. This can be found mainly in undried samples. In ordinary polymeric films, especially once-dried samples, it is difficult to find such good peak resolution.

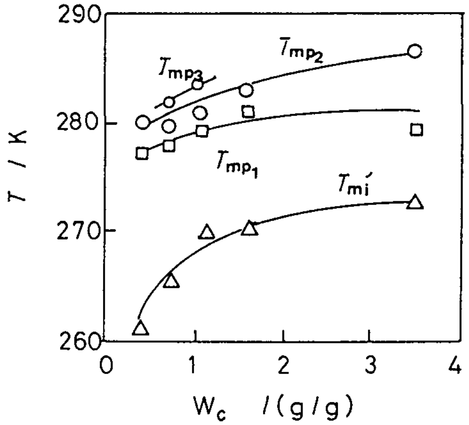

Fig. 3 Relationship between starting temperature of melting (T_{mi}), peak temperatures of melting (T_{mp1}, T_{mp2}) and W_{cr} of water restrained in PSF hollow fibre. Sample No. IV

The results shown in Figs 2 and 3 suggest that water molecules in the hollow fibres evaporate from free water, and that in the latter stage of evaporation, the remaining water molecules behave like freezing bound water. During the drying process, it is also possible that changes occur in size and structure of the pores. These changes would also affect the phase transition behaviour of water. On this account, pore size calculation from super-cooling temperature [19–21] is limited to conditions in which the sample contains an excess amount of water. DSC results obtained in this study indicate that the phase transition behaviour of water molecules in undried hollow fibres is almost the same as ordinary free water, although the temperature range of transition is wider and the transition peak is not smooth. The difference between T_1 and T_2 values of water obtained by NMR measurement indicates that the water molecules are restricted by the matrix PSF. These facts suggest that the pore size has a broad distribution. The molecular mobility of water molecules in small pores decreases due to the surrounding matrix and this is directly reflected by the T_2 value.

References

1 A. Kawai, Sen-i Gakkaishi, J. Soc. Fiber Sci., Japan, 41 (1985) 143.
2 T. Nogi, Sen-i Gakkaishi, J. Soc. Fiber Sci., Japan, 41 (1985) 151.
3 I. Cabasso, E. Klein and J. K. Smith, J. Appl. Polym. Sci., 20 (1976) 2377.
4 J. G. Wijmans, J. P. B. Baaij and C. A. Smolders, J. Membrane Sci., 14 (1983) 263.
5 M. Kurihara Sen-i Gakkishi, J. Soc Fiber Sci. Japan, 40 (1984) 671.
6 P. Aptel, N. Abidine, F. Ivaldi and P. Lafaille, J. Membrane Sci., 22 (1985) 199.
7 J. R. Zimmerman and W. E. Brittin, J. Phys. Chem., 61 (1957) 1328.
8 M. N. Plooster and S. N. Gitlin, J. Phys. Chem., 75 (1971) 3322.
9 D. E. Woessner and B. S. Snowden, Jr., J. Colloid Interface Sci., 34 (1970) 290.
10 F. X. Quinn, E. Kampff, G. Smyth and V. J. McBrierty, Macromolecules, 21 (1988) 3191.
11 H. G. Burghoff and W. Pusch, Polym. Eng. Sci., 20 (1980) 305.
12 W. Pusch and A. Walch, Angew. Chem. Int. Ed. Engl., 21 (1982) 660.
13 T. Hatakeyama, Y. Ikeda and H. Hatakeyama, Makromol. Chem., 199 (1987) 1875.
14 T. Hatakeyama, S. Yamamoto, S. Hirose and H. Hatakeyama, Cellulose and Wood, Chemistry and Technology, Ed. C. Schuerch, John Wiley and Sons, 1989 p. 431.
15 H. Hatakeyama, K. Nakamura and T. Hatakeyama, Cellulose and Wood, Chemistry and Technology, Ed. C. Shuerch, John Wiley & Sons, Inc. 1989 p. 419.
16 T. Hatakeyama, K. Nakamura and H. Hatakeyama, Thermochim. Acta, 123 (1988) 153.
17 D. J. Crofton and R. A. Pethrick, Polym., 22 (1981) 1048.
18 S. Nakamura, M. Todoki, K. Nakamura and H. Kanetsuna, Thermochim. Acta, 136 (1988) 163.
19 K. Ishikiriyama and M. Todoki, Netsu Sokutei, J. Soc. Calorimetry and Thermal Analysis, Japan, 14 (1987) 125.
20 L. G. Homshaw, J. Colloid Interface Sci., 84 (1981) 127.
21 L. G. Homshaw, J. Colloid Interface Sci., 84 (1981) 141.

Zusammenfassung — Mittels DSC wurde das Schmelz- und Kristallisationsverhalten von Wasser in Polysulfon (PSF) Hohlfasern untersucht. Die PSF Hohlfasern wurden durch Naßspinnen hergestellt. Die Morphologie der Fasern wurde mittels Scanning-Elektronenmikroskopie beobachtet. Die Wassermenge wurde durch aufeinanderfolgendes Verdampfen variiert und es wurde beobachtet, daß Schmelzen und Kristallisieren im Vergleich zu freiem Wasser zu tieferen Temperaturen hin verschoben wird. DSC und NMR Untersuchungen zeigen, daß sich das Wasser in den Hohlfasern in einem eingeschlossenen Zustand befindet.