

Comparative Study on Water Structures in PolyHEMA and PolyMEA by XRD-DSC Simultaneous Measurement

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ABSTRACT: We have found that poly(2-methoxyethylacrylate) (polyMEA) has excellent blood compatibility and proposed that the property is due to freezing bound water in the polymer. This water is defined as that which cold-crystallizes at around -45°C in the heating process of differential scanning calorimetry (DSC). In addition, we have already reported that the water in polyMEA is classified into three types, nonfreezing, freezing bound, and free waters, whereas the water in other polymers is just classified into two types: free and nonfreezing waters. (J Biomed Mater Res 68A, 2004, 684) However, the phenomenon observed by DSC is the enthalpy change and is not a direct evidence for crystallization. To confirm cold-crystallization, a comparative investigation of the thermal and crystallographical properties of water in hydrated poly-

MEA and poly(2-hydroxyethylmethacrylate) (polyHEMA) as a control was carried out using simultaneous measurements by X-ray diffractometer (XRD) and DSC. In addition, the effect of the water content in the polymers on the properties was studied. As for polyMEA, the finding that XRD crystalline peaks appearing in the heating process were assigned to hexagonal ice indicated cold-crystallization. On the other hand, in the case of polyHEMA, the crystal due to ice was formed only in the cooling process, and during the heating process, the growth of crystal ice was not observed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 476–481, 2009

Key words: poly(2-methoxyethyl acrylate); water structure; crystallization; DSC; WAXS

INTRODUCTION

A number of blood-compatible surfaces for medical devices have been proposed and some of them are in clinical usage.¹ We found that poly(2-methoxyethyl acrylate) (polyMEA) shows excellent blood compatibility in *in vitro* tests,² and that the amount and denaturation degree of proteins adsorbed onto the polyMEA surface are much lower than those on the surfaces of other conventional polymers.³ However, the reason for the superiority of polyMEA has not yet been clarified. There have been many attempts to clarify the mechanism for blood compatibility of an artificial material, but it has not yet been understood fully.^{4,5} Some researchers suggest that the water structure on a material surface is one of the most important factors determining blood compatibility.^{6–10} According to this implication, we focused our attention on the water structure in polyMEA and found, by using DSC, that hydrated poly-

MEA has unique thermal behavior.^{11–13} That is, the DSC heating curve for hydrated polyMEA shows an exothermic peak at around -45°C and an endothermic peak at around 0°C . We attributed this exothermic peak to cold-crystallization of water and defined it as freezing bound water. Thus, we propose that freezing bound water plays a role in determining the blood compatibility of the polymers. However, we did not yet have direct evidence for cold-crystallization because the information obtained from DSC is the thermal change due to the phase transition. Recently, an instrument combining wide-angle X-ray diffraction with DSC (XRD-DSC) was developed. This instrument is valuable in determining the origin of phase transitions in a material. Especially, for a material composed of plural components, it is useful because in the characterization of such materials we sometimes face difficulty in confirming which component contributes to the transition. Thus, this method has been applied to the thermal and structural investigation of many hydrated systems,^{14,15} and it was expected that XRD-DSC simultaneous measurement could determine what causes the exothermic peak in the DSC curve of hydrated polyMEA. Aiming at proving cold-crystallization, we

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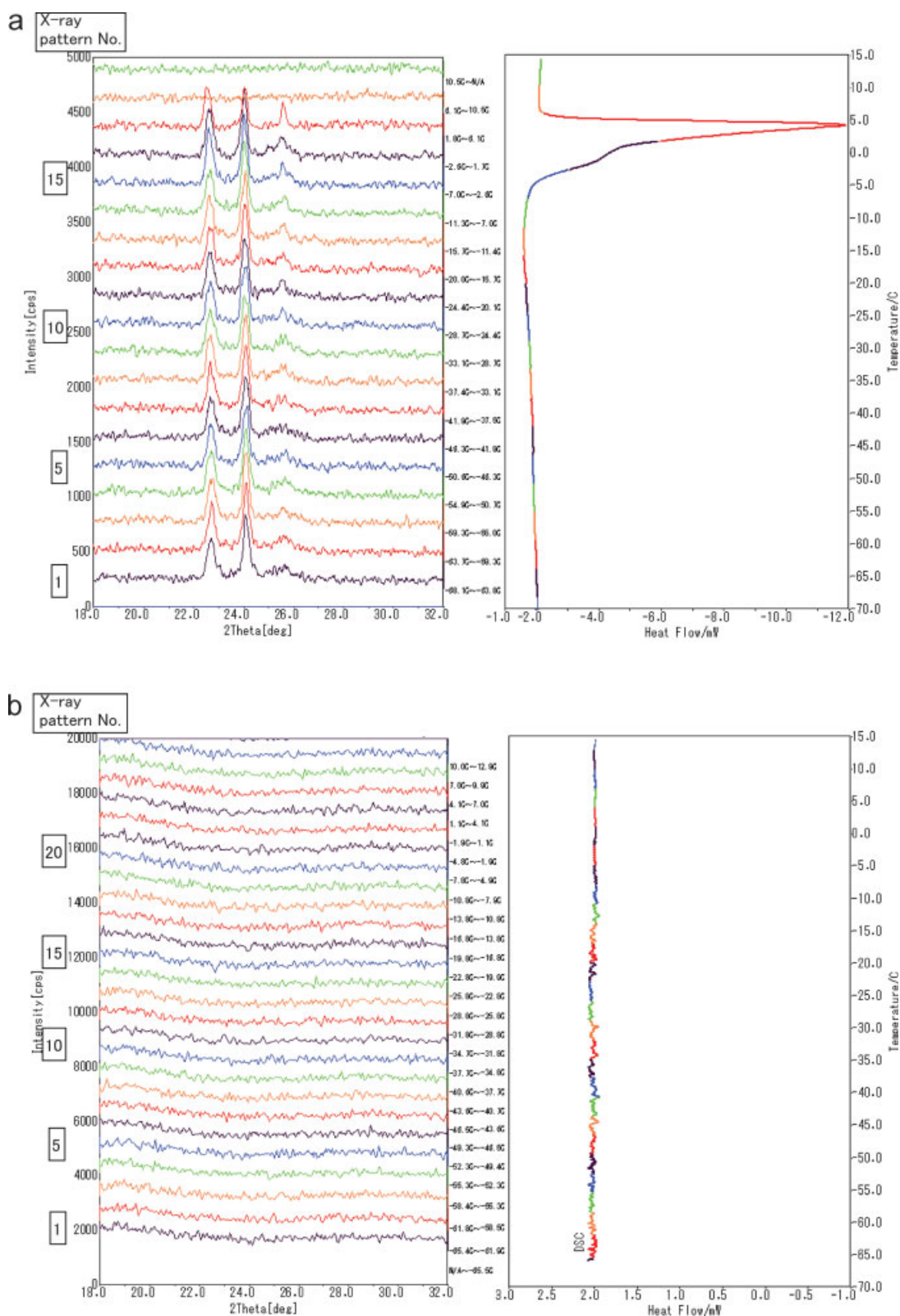


Figure 1 DSC curve and XRD pattern of hydrated polyHEMA. (a) W_c , EWC; (b) W_c , 21.9 wt %. Measurements of DSC and XRD were performed in the heating process from -70°C to $+30^{\circ}\text{C}$. Bottom curve shown in XRD was observed in the lowest temperature range (around -67 to -61°C , and the upper curve was observed in higher temperature range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

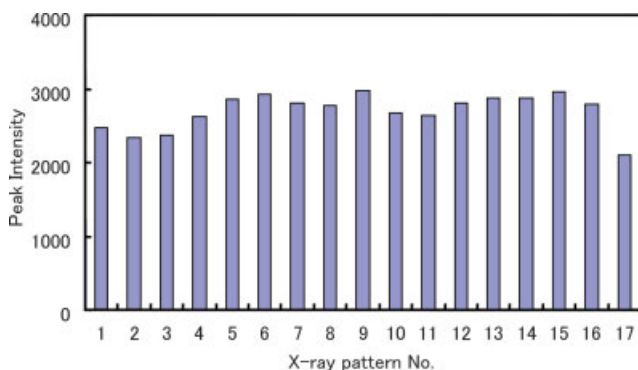


Figure 2 Temperature dependence of peak intensity in X-ray diffractogram of polyHEMA with EWC. Peak intensity: summation of the areas of three peaks ($2\theta = 23.1$, 24.2 , and 26.0°) in each diffractogram. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

compared the phase transition observed for hydrated polyMEA with that for polyHEMA using XRD-DSC. The results are reported here together with the relationship between crystallization of water in hydrated polymers and water content.

EXPERIMENTAL

Hydrated polymer sample for DSC

PolyMEA and polyHEMA were prepared by radical polymerization according to a previous article³ and their number average molecular weights (M_n) by GPC were 34,100 and 189,100, respectively, where the M_n of polyHEMA is the one after benzylation.¹³

The water content of a hydrated sample, W_c , was determined by the gravimetric method and was defined by the following equation:

$$W_c \text{ (wt\%)} = \{(W_1 - W_0)/W_1\} \times 100$$

where W_1 is the weight of the hydrated sample and W_0 is the weight of a dry sample. Samples with equilibrium water content (EWC) were obtained by soaking them in distilled water for over 2 weeks at $25 \pm 0.2^\circ\text{C}$. The EWC for polyMEA and polyHEMA were 9.6 and 39.1 wt %, respectively. Other hydrated samples were prepared by the moisture sorption method as follows: the polymer samples were placed under saturated water vapor pressure at $25.0 \pm 0.2^\circ\text{C}$ until the sorption reached an equilibrium state or a predetermined value. The W_c s thus obtained were 6.7 and 1.7 wt % for polyMEA, and 21.9 wt % for polyHEMA.

Simultaneous XRD-DSC measurement

Simultaneous XRD-DSC measurement was carried out using an instrument, XRD-DSC II (Rigaku Co.,

Tokyo, Japan). This instrument combines a heat-flux type DSC with an X-ray diffractometer based on the Rigaku RINT-ULTIMA+. The hydrated polymer was placed on an aluminum square-shaped container ($8 \text{ mm} \times 8 \text{ mm}$) and was covered with $6\text{-}\mu\text{m}$ -thick aluminum foil to prevent water evaporation. The XRD and DSC measurements were taken during the heating process from -70 to 30°C at a heating rate of $2.0^\circ\text{C}/\text{min}$, where the XRD operating condition was as follows: X-ray source, Cu $K\alpha$; X-ray generation, voltage 40 kV; current 50 mA; 2θ range, $18\text{--}42^\circ$; and scanning rate of $2\theta = 12$ or $18^\circ/\text{min}$.

RESULTS AND DISCUSSION

On the basis of DSC analysis, we have defined the water structure in hydrated polymers as follows: nonfreezing water, freezing bound water, and free water.^{11–13} To confirm the freezing bound water in polyMEA, the water structures of polyMEA and polyHEMA were compared using XRD-DSC analysis.

The results of the simultaneous measurements for the hydrated polyHEMAs are shown in Figure 1, where the X-ray patterns correspond to each point on the DSC curve with the same temperature range. For example, the first X-ray pattern from the bottom in Figure 1(a) was observed at a temperature range from -68 to -64°C . On the basis of the result of Figure 1(a), the change of the peak intensity during the heating process is shown in Figure 2. In the X-ray diffractogram for polyHEMA with EWC [Fig. 1(a)], three crystalline peaks at $2\theta = 23.1$, 24.2 , and 26.0° were observed through a temperature range from -68 to 6°C (peak pattern No. 1–17), and the crystal can be assigned to hexagonal ice.^{16,17} Figure 2 clearly shows that the peak intensity does not change during the heating process until the crystal melts at around 5°C . In addition, Figure 1(a) shows that the temperature where the crystal peak disappears corresponds to the endothermic peak observed in the DSC curve. Therefore, these results lead to the conclusion that the ice in polyHEMA is formed in the cooling process and the growth of the crystal does not occur in the heating process. This finding is in good agreement with earlier studies on the water structure in polyHEMA—that the water in polyHEMA with EWC is composed of free water and nonfreezing water.¹²

In the case of the hydrated polyHEMA with 21.9% W_c , the XRD-DSC measurement [Fig. 1(b)] does not show any crystalline peaks in the diffractogram nor, at the same time, any exo/endothermic peaks in the DSC curve. These results reveal that water in the polyHEMA exists as nonfreezing phase, and suggest that the adsorbed water molecules from water vapor are restricted by the polymer as nonfreezing water.

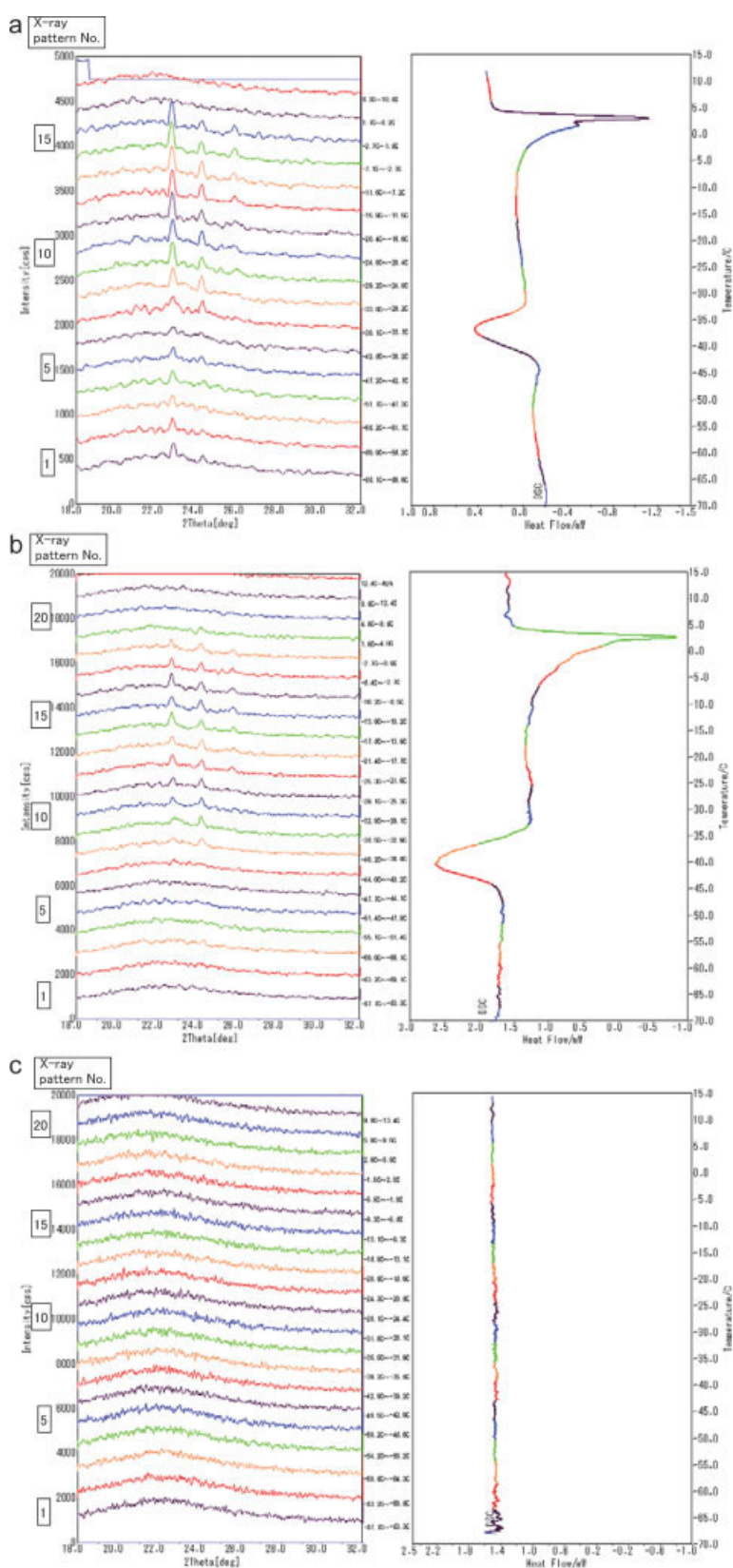


Figure 3 DSC curve and XRD pattern of hydrated polyMEA. (a) W_c , EWC; (b) W_c , 6.7 wt %; (c) W_c , 1.7 wt %. Measurements of DSC and XRD were performed in the heating process from -70°C to $+30^\circ\text{C}$. Bottom curve shown in XRD was observed in the lowest temperature range (around -67 to -61°C), and the upper curve was observed in higher temperature range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

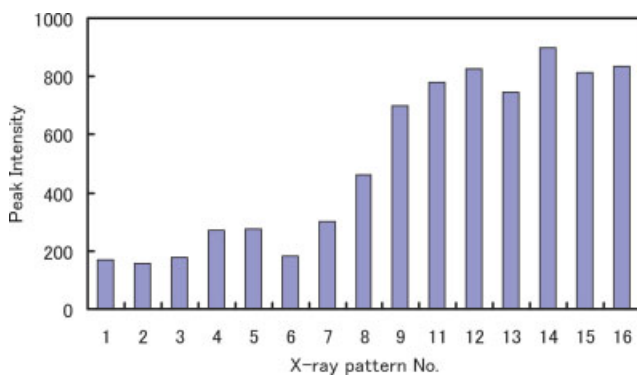


Figure 4 Temperature dependence of peak intensity in X-ray diffractogram of polyMEA with EWC. Peak intensity: summation of the areas of three peaks ($2\theta = 23.1$, 24.2 , and 26.0°) in each diffractogram. The number on abscissa axis corresponds to the X-ray pattern number in Figure 3. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The results for the hydrated polyMEAs are shown in Figure 3. As for polyMEA with EWC [Fig. 3(a)], the change in peak intensity of the ice plotted as a function of temperature is exhibited in Figure 4. In Figure 3(a) (polyMEA with EWC), the three small crystalline peaks were observed in a temperature range from -62 to -38°C (X-ray pattern No. 1–6) and were assigned to hexagonal ice from their 2θ . This ice is due to free water in polyMEA and is formed in the cooling process. The figure shows that the peaks are strengthened gradually when the temperature is over -38°C (X-ray pattern No. 7–12) and disappear at over 1.7°C . That is, the figure clearly reveals the growth of the crystal in the heating process. The DSC curve measured simultaneously shows an exothermic peak and an endothermic peak at -35 and 2°C , respectively, which are in the same temperature ranges for the appearance and disappearance of the XRD peaks. Therefore, it can be concluded that the exothermic peak in the DSC heating curve is attributed to cold-crystallization of water. This conclusion is supported by the following. The ratio, cold-crystallization peak/fusion peak in DSC curve is in agreement with the area ratio of the crystallization peak at -68°C /the ones over -29°C in XRD peak intensity. The former ratio is about 0.61 and the latter is around 0.63.

The DSC curve shows an endothermic peak due to the fusion of ice, which has two peak tops. These peaks at lower and higher temperatures will be derived from the freezing bound water and free water, respectively.

In the case of polyMEA with 6.7 wt % of W_c , which is obtained by the equilibrium moisture sorption method, three crystalline peaks due to hexagonal ice could not be observed under -40°C ; however, they appeared when the temperature

exceeded around -40°C [X-ray pattern No. 8 in Fig. 3(b)]. These peaks finally disappeared at over 5°C . This behavior corresponds to that of the DSC heating curve. These findings indicate that this hydrated sample does not have free water, and that the water adsorbed in the polymer from water vapor is restricted, resulting in nonfreezing and freezing bound water.

In the case of polyMEA with 1.7 wt % of W_c , we cannot observe any peaks on either the X-ray diffractogram or the DSC curve [Fig. 3(c)]. This result shows that the water in polyMEA is nonfreezing water.

We have already reported that the W_c had little effect on the glass transition point (T_g) of polyMEA, and that the endothermic phenomenon occurs when the temperature of the sample is beyond T_g (around -50°C).¹⁸ On the other hand, it is known that in polyHEMA, the W_c strongly affects T_g , resulting in a drastic decrease in T_g with an increase in W_c .¹⁹ These facts imply that the interaction of water molecules with the polyMEA chain is not significantly strong when compared with that of polyHEMA. Thus, the beginning of motion of the polymer chain will induce the reconstruction of *meta*-stable water molecules restricted by polyMEA, resulting in cold-crystallization.

CONCLUSIONS

We have reported that hydrated polyMEA has an exothermic peak at around -45°C in the DSC heating curve and interpreted this peak to be due to cold-crystallization of water. Thus, we classified the water in polyMEA into three types; nonfreezing, freezing bound, and free waters, whereas the water in other polymers was composed of just two types; nonfreezing and free waters. To clarify the cold-crystallization of water, the water structures in hydrated polyMEA and polyHEMA as a control were investigated using an instrument that can make simultaneous XRD and DSC measurements. In the temperature region where the exothermic peak is observed in the DSC heating curve, three crystalline peaks appear for polyMEA with more than 6 wt % of W_c . The peak pattern leads to the conclusion that the exothermic peak in the DSC heating curve of polyMEA is assigned to hexagonal ice. That is, the exothermic peak is because of cold-crystallization of water. In hydrated polyHEMA, though it has hexagonal ice, the crystal was formed in the cooling process, and its growth did not occur in the heating process from -70 to 0°C .

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