Preparation and Properties of Acrylic Fibers from the Polyacrylonitrile Melt Formed by Hydration(I)
-Isothermal Crystallization Behavior of the Hydrated Melt of Polyacrylonitrile-
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Abstract: Melting and isothermal crystallization behaviors of plasticized polyacrylonitrile (PAN) on adding water in a sealed state were studied. As water was added, the melting point of PAN was depressed sharply to reach a plateau region in which all the nitrile groups of the polymer were hydrated. The crystallization exotherms of PAN/water mixture showed complex profiles. On DSC analysis, it was found that the exotherm from the crystallization (dehydration) heat of the hydrated PAN was overlapped with the latent heats by the neat PAN and water which was not evolved during quenching. Thus, in order to investigate the dehydration kinetics of PAN/water mixture, it was required to separate the exothermic peak by the isothermal crystallization peak from the peaks by the evolution of latent heats of the each component, i.e., PAN and water. By subtraction of the latent heat contributed by neat PAN and water from the all isothermal exothermic heat of PAN/water mixture, the isothermal crystallization peak of PAN/water mixture was successfully obtained according to various crystallization temperature ($T_c$).

Keywords: polyacrylonitrile, hydration, melting point depression, isothermal crystallization

1. Introduction

It is well known that polyacrylonitrile (PAN)-based polymers containing acrylonitrile content higher than 85% do not produce stable melt state because of exothermic reactions such as cyclization, crosslinking and degradation before they reach the unusually high melting point ($T_m$) of around 320°C due to the interactions between polar nitrile groups [1].

Since Coxe [2] first observed that high pressure mixtures of PAN-based polymers and water could be melted extruded, intensive researches have been carried out to lower $T_m$ by plasticizing PAN-based polymers with water to prepare acrylic fibers through melt spinning [3,4]. However, there has been no report on successful mass productions of the acrylic fibers using the plasticization method by industry. This seems to be ascribed to the difficulty in control of foaming caused by high-pressure vapor after extrusion.

It was reported that a fibrillar structure with a high molecular orientation without post-drawing could be obtained by extruding a supercooled melt of wet PAN through a circular or slit die [5,6]. Moreover, they reported successful preparation of synthetic pulps of PAN by beating the bundle-like extrudate of the fibril structure. This novel result was assumed to be originated from the unique properties of the plasticized PAN melt in a supercooled state, that is, the properties similar to that of liquid crystalline melt [7-9].

There were reports about the effects of the comonomers and additives on the melting behavior of PAN and the thermal stability of the plasticized PAN melt using DSC [10-12]. The rheological properties of the hydrated PAN were also investigated [13]. Even though the melting point of PAN can be depressed sufficiently to permit melt processing by addition of water as mentioned above, the lowered $T_m$ of PAN by hydration is still above the natural evaporation temperature of water. Thus, the controlling of water evaporation after extrusion is considered as the key problem in the melt processing of PAN. Moreover, it is important to understand what happens in the supercooled state, particularly for the process to obtain acrylic fibers by extruding the supercooled melt below $T_m$ for the purpose of suppressing forming problem with the effects of lower extruding temperature and higher viscosity.

In this report, we investigated the melting and isothermal
crystallization behaviors of plasticized PAN on adding water in a sealed state. It was because the isothermal crystallization behavior occurred with dehydration would be important for the selection of optimum extrusion temperature of the hydrated melt of PAN.

2. Experimental

The PAN in the form of fine powder having 7.8 mol% of vinyl acetate as a comonomer was used for the experiment. Intrinsic viscosity \( [\eta] \) was measured at 25 °C from dilute dimethylformamide solution. Average molecular weight \( (M_\alpha) \) was then estimated to be 82,000 g/mole according to the Mark-Houwink-Sakurada equation [14].

\[
[\eta] = 2.43 \times 10^{-4} M_\alpha^{0.75}
\]

Since above parameters are strictly for PAN at 25°C, the parameters for the sample in this study are expected to differ slightly. The polymer was dried in vacuum oven at 50°C for 24 hours prior to use.

Thermal analysis was carried out using Perkin Elmer DSC 7 calorimeter and the large volume stainless steel capsules (Perkin Elmer part 319-0218), as depicted in Figure 1. The capsule could withstand the steam pressure up to 220°C because a rubber o-ring was fitted into the top of the capsule. The fine powder of PAN and water were uniformly mixed in a high-speed mixer to give moisturized, free-flowing powder. Approximately, 50 mg of the mixture was packed into the capsule. For observing melting and crystallization behaviors, both heating and cooling rates were set to 10°C/min. On the other hand, for the isothermal tests, the PAN containing 30 wt% of water was heated up to 170°C (\( T_m \) of the wet PAN, 155°C), followed by quenching to a predetermined temperature, \( T_c \), in the range from 150°C to 135°C, after 5 minutes in the melt state.

3. Results and Discussion

The DSC curves in Figure 2 show the melting behavior of the PAN when water was mixed with PAN in the sealed state. The dry PAN without water showed only a glass transition temperature at around 90°C until heating below 200°C, whereas the wet PAN containing 23 wt% of water shows a discrete melting peak around 155°C and a crystallizing peak at 130°C on the heating and cooling scans, respectively.

Figure 3 represents the dependence of melting temperature \( (T_m) \) and \( T_c \) of the hydrated PAN on water content. We already reported that the critical water content above which there was no further decreasing of \( T_m \) was equivalent to the theoretically predicted value on an assumption that one nitrile group of PAN would be combined with one water molecule [10] The critical content of water for the PAN used in this test was determined as c.a. 23 wt%. Blickenstaff [15]

\[ \text{Figure 1. Schematic diagram of the large volume stainless steel DSC capsule.} \]

\[ \text{Figure 2. DSC thermograms of dry PAN (A) and wet PAN containing 23 wt% of water (B) when water is mixed with PAN in a sealed state.} \]

\[ \text{Figure 3. Dependence of melting point of PAN on water content.} \]
showed that hydration occurred between water and nitrile groups of PAN by detecting shift of nitrile peak after melting using Laser Raman Spectroscopy. Therefore, it was suggested that the melting depression of PAN by water would be obliged to the reduced interactions of nitrile groups mainly due to the decoupling of the coupled nitriles and replacement with hydration.

The nitrile groups in PAN are classified as associated and non-associated ones. Krigbaum and Tokita [1] proposed that the non-associated nitrile groups be not arranged freely but distorted due to the repulsions between them. This would make the molecule chains form a semi-rigid helical structure. In addition, they have attributed the unusually high $T_m$ of PAN to the chain rigidity resulted from the repulsions rather than from the attractions. It is worth noting in this conjuncture that variation of $T_m$ with the water content in Figure 3 suggests that the hydration reaction takes place more readily in non-associated nitrile groups than in the associated ones. In other words, the hydration of non-associated nitrile groups has more prevalent effect on the $T_m$ depression than that of associated ones.

When a polymer melt is conditioned, phase transformations including crystallization involve two kinetic processes: nucleation and growth of the nuclei. Since PAN, however, does not form 3-dimensional crystalline structure, crystallization behavior of PAN melt is basically different from a crystallization of general crystalline polymers such as polyethylene (PE) or nylon 6.

Figure 4 shows isothermal exotherms of different crystallization temperature for the polymer containing 23 wt% of water. As noted in the figure, crystallization exotherms had complex profiles. A distinct peak that was independent on $T_c$ was appeared. Accordingly, it was reasonable to think that the secondary peak was related to the crystallization.

In order to separate secondary peak, the exotherms for the dry polymer and pure water were also obtained, as shown in Figure 5(a) and (b), respectively. Comparing the figures, it was noted that the exotherms from the PAN/water mixture included the heat evolved by dry polymer and water, that is, the exotherms from the mixture consisted of dehydration heat as well as the heat by the components that could not evolved during quenching from the melt. If crystallization rate is slow as poly(ethylene terephthalate), the latent heat due to quenching and heat of crystallization would be separated clearly because the evolution of the latent heat is relatively fast. However, dehydration rate for the hydrated melt of PAN was too fast to be separated from the evolution of latent heat, which resulted in superposition of the three exotherms.

Therefore, in order to investigate the dehydration kinetics of PAN/water mixture, it was essential to separate the exothermic peak by dehydration with the peaks by the evolution of latent heat of the each component, i.e., PAN and water.

This separation was performed successfully by the data

![Figure 4](image)

*Figure 4.* Change of isothermal exotherms according to crystallization temperature ($T_c$) for PAN containing 23 wt% of water when the PAN-water mixture was quenched from the melt state at 170°C.

![Figure 5](image)

*Figure 5.* Isothermal exotherms of neat PAN without water (a) and pure water and (b) quenched from 170°C.
Figure 6. A typical isothermal crystallization curve of wet PAN obtained by subtracting the exotherms of neat PAN and pure water from the exotherm of PAN/water mixture.

Figure 8. Dependence of heat of crystallization on isothermal crystallization temperature.

Figure 7. Change of isothermal crystallization curves obtained by the subtraction method according to crystallization temperature ($T_c$) for PAN containing 23 wt% of water when the PAN/water mixture was quenched from the melt state at 170°C.

Figure 9. Isothermal crystallization curves at $T_c=138°C$ for the mixtures of PAN/water and PAN/water/PAA.

obtained from DSC 7 using SigmaPlot® program for Windows®. Figure 6 is a typical graph that illustrates the process to separate dehydration curve by subtracting the contributions of dry polymer and pure water from the source curve of the wet PAN.

This operation was done for the isothermal experiments at various crystallization temperatures from 136°C to 150°C. Figure 7 shows the change of isothermal crystallization curves obtained by subtraction method at various $T_c$. It was well noted in the figure that isothermal crystallization rate decreased and the shape of peak became broad with increasing $T_c$. Above 150°C of $T_c$, no dehydration peak was obtained.

In the case of PE, the overall heat evolved ($\Delta H_c$) at isothermal crystallization is almost same irrespective of the crystallization temperature, though the rate of heat evolution changes. However, $\Delta H_c$ of the hydrated PAN was dependent on the crystallization temperature, as shown in Figure 8. It was considered that hydration of nitrile groups was com-
petitive with dipole-dipole interaction between nitrile groups. In addition, it is obvious that each nitrile group has different interaction energy, i.e., different circumstance, because the PAN molecules have somewhat irregular conformation. Thus, it could be supposed that hydration as well as dehydration was a function of temperature. At high $T_0$, the water molecules associated to the nitrile groups having high dipole-dipole interaction energy would be dissociated. Addition of hydrophilic polymer, poly(acrylic acid) (PAA), made the dehydration rate slow, as shown in Figure 9. Thus, PAA was expected to contribute to spinnability of hydrated PAN melt.

4. Conclusion

For the isothermal crystallization, exotherm from the hydration melt of PAN was found to include the crystallization (dehydration) heat of the hydrated PAN as well as the latent heat by the neat PAN and water which could not be evolved during quenching. Thus a subtraction method was applied to obtain a real isothermal exotherm of crystallization of the PAN melt. Isothermal crystallization of PAN/water mixture was concluded to occur with dehydration by showing the enthalpy of crystallization was proportional to the supercooling from the hydration melt.

References