

Clay의 Poly(vinylidene fluoride) 결정화 거동에 미치는 영향

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The Effect of Clay on Crystallization Behavior of Poly(vinylidene fluoride)

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1. Introduction

Polymer/clay nanocomposites have received much attention in recent years, because they often exhibit physical properties that are dramatically different from those observed in their micro- and macrocomposite counterparts. The presence of clay may affect the crystallization behavior of semicrystalline polymer.¹⁻² Poly(vinylidene fluoride) (PVdF) can exist in at least three distinct crystal types, namely, α , β , and γ phases. The α phase is the most common crystal type of PVdF and is normally obtained by crystallization from the melt at moderate or high undercoolings. The β phase is routinely obtained by mechanical deformation of melt-crystallized films. The γ phase is known to be formed through solution crystallization. Although there have been many studies on the effect of various conditions on crystallization behavior of PVdF, any report on the effect of clay on crystallization behavior of PVdF has not been reported yet.

Polymer/clay nanocomposite can be prepared by various methods such as *in-situ* polymerization, solution drying and melt intercalation. In this study, PVdF/clay nanocomposite is prepared by melt blending of PVdF and exfoliated PMMA/clay nanocomposite, where PVdF is miscible with PMMA. In our previous work, it has been observed that SAN/PMMA/clay nanocomposite exhibit an exfoliated structure, where SAN is miscible with PMMA. Therefore, we here investigate the structure of PVdF/PMMA/clay nanocomposite and the crystallization behavior of PVdF in the composite.

2. Experimental Section

PMMA/clay nanocomposite used in this study is synthesized by emulsion polymerization using sodium lauryl sulfate as a emulsifier. PVdF and PMMA are obtained by Solvay Co. and Polysciences Inc., respectively.

PVdF/PMMA/clay nanocomposite is prepared by melt blending of PVdF and PMMA/clay nanocomposite at the various PVdF composition (90 wt%, 70 wt%, and 50 wt%) using a Mini-Max molder at 200 °C. The XRD patterns are observed with a MAC Science M18XHF X-ray diffractometer using Ni-filtered Cu-K α radiation ($\lambda=1.54$ Å; 40 kV; 30 mA) at a scanning rate of 2 °/min. The samples for XRD are prepared in film forms.

Isothermal crystallization experiments are performed as the following procedure. The samples are melted at 200 °C for 10 min using a hot press, and then the samples are isothermally crystallized at 150 °C or at 50 °C on the hot plate for 30 min. Their thermal properties and crystallization behavior are examined with a Perkin-Elmer DSC-7. The samples isothermally crystallized are heated from 50 °C to 220 °C at a heating rate of 10 °C/min and maintained at 220 °C for 10 min, followed by cooling the samples from 220 °C to 50 °C at a cooling rate of 10 °C/min.

For comparison, the properties and crystallization behavior of PVdF homopolymer and PVdF/PMMA melt-blend are also examined under the same conditions.

3. Results & Discussion

The structure of PVdF/PMMA/clay nanocomposite can be identified with XRD pattern, as shown in Figure 1. The absence of d_{001} suggests that PVdF/PMMA/clay nanocomposite has an exfoliated structure. Figure 2 shows that the crystallization temperature of PVdF/PMMA is lower than that of PVdF, indicating that the crystallization rate of PVdF/PMMA is lower than that of PVdF. From Figure 2 (c), it is also showed that the crystallization temperature and rate of PVdF/PMMA/clay nanocomposite are further decreased by the addition of clay.

Figures 3-5 shows the WAXD patterns of samples isothermally crystallized at 150 °C for 30 min. The reflections at $2\theta=17.5$ ° and 18.4 ° are assigned to (100) and (020) reflection of the α phase, respectively.³ It is observed that the intensities of diffraction peaks of PVdF are decreased by the presence of PMMA and clay. In other words, the crystallization of PVdF is hindered by the presence of PMMA and clay. This behavior becomes more significant as the contents of PMMA and clay increase. A closer examination reveals that the intensity of (100) peak of α crystal is relatively increased by the addition of clay, compared to that of (020) peak of α crystal in the PVdF/PMMA/clay nanocomposite. This

indicates that the clay acts as a directional interference of PVdF crystallization: the growth of PVdF crystal is suppressed by the clay in a particular direction.

The WAXD patterns of samples isothermally crystallized at 50 °C for 30 min are shown in Figure 6. Figure 6 shows that PVdF/PMMA (50/50) and PVdF/PMMA/clay (50/45/5) nanocomposite do not form the crystal, indicating that crystallization temperature must be high in order to induce crystallization of PVdF/PMMA and PVdF/PMMA/clay nanocomposite.

4. Reference

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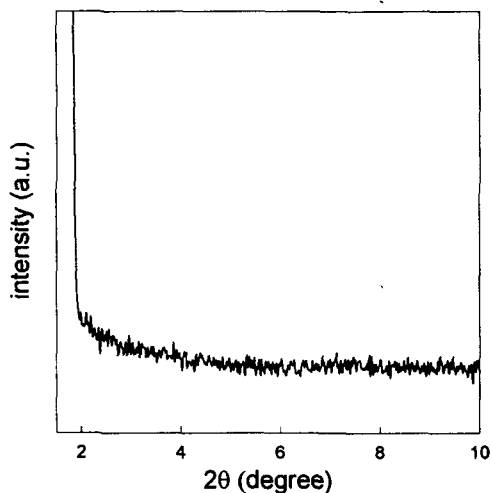


Figure 2. XRD pattern for the PVdF/PMMA/clay (70/27/3)

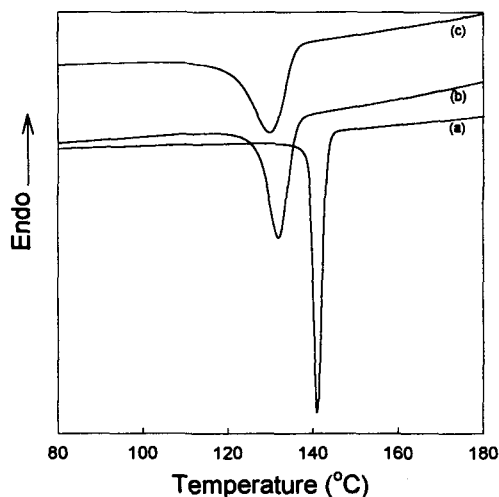


Figure 2. DSC cooling thermograms: (a) PVdF; (b) PVdF/PMMA(70/30); (c) PVdF/PMMA/clay (70/27/3)

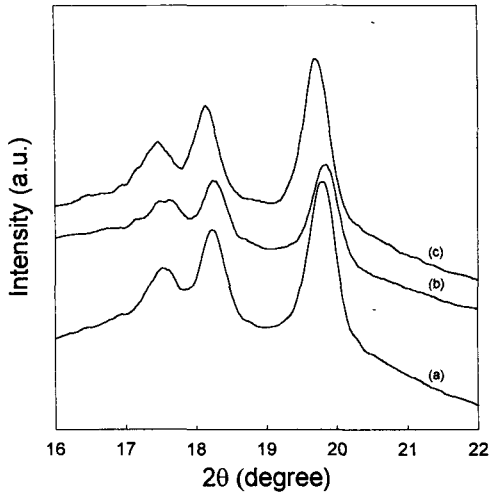


Figure 3. WAXD patterns for the isothermally crystallized samples at 150 °C for 30 min: (a) PVdF; (b) PVdF/PMMA (90/10); (c) PVdF/PMMA/clay (90/9/1)

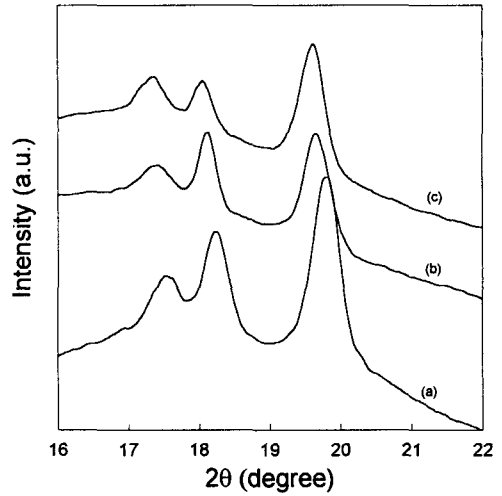


Figure 4. WAXD patterns for the isothermally crystallized samples at 150 °C for 30 min: (a) PVdF; (b) PVdF/PMMA (70/30); (c) PVdF/PMMA/clay (70/27/3)

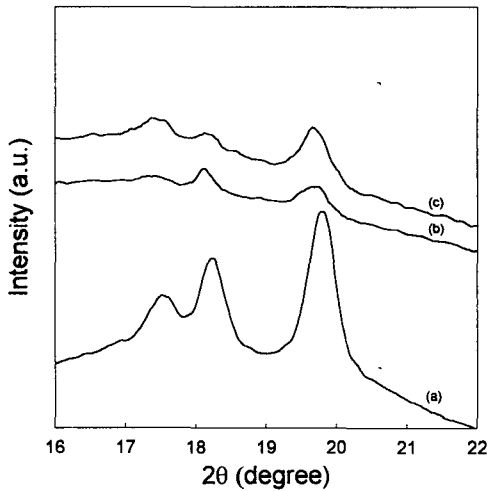


Figure 6. WAXD patterns for the isothermally crystallized samples at 150 °C for 30 min: (a) PVdF; (b) PVdF/PMMA (50/50); (c) PVdF/PMMA/clay (50/45/5)

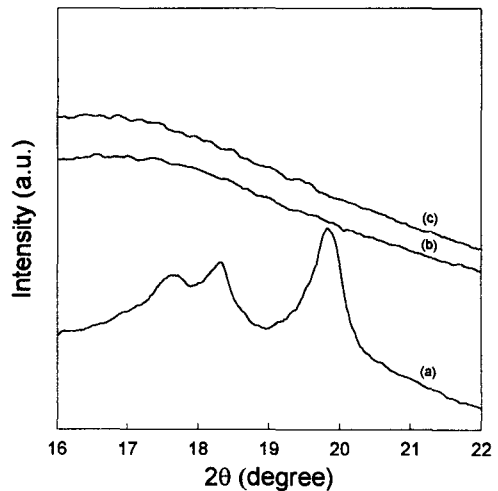


Figure 5. WAXD patterns for the isothermally crystallized samples at 50 °C for 30 min: (a) PVdF; (b) PVdF/PMMA (50/50); (c) PVdF/PMMA/clay (50/45/5)