

Crystallization of Poly(ethylene adipate) within γ -Phase Poly(vinylidene fluoride) Matrix^{*}

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Abstract The effects of PEA on the γ -phase PVDF crystal structure and the crystallization of PEA within the pre-existing γ -phase PVDF spherulites have been investigated by optical microscopy (OM), infrared spectroscopy (IR) and scanning electron microscopy (SEM). The results demonstrate that the γ -phase PVDF spherulites consist of the lamellae exhibiting a highly curved scroll-like morphology and develop preferentially in PEA-rich blend. With increasing PEA concentration, the scroll diameter increases and the scrolls are better separated from each other. PEA crystallizes first in the interspherulitic region and transcrystalline layer develops. Subsequently, the transcrystalline layer of PEA continues to grow within the γ -phase PVDF spherulites, e.g., in the region between the scrolls, until impinging on other PEA transcrystalline layers or spherulites. The crystallization kinetics results indicate that the growth rate of PEA crystals in the intraspherulitic region of γ -phase PVDF shows a positive correlation with content of PEA, but a negative one with the crystallization temperature of γ -phase PVDF.

Keywords: Crystallization; Blends; Poly(vinylidene fluoride); Poly(ethylene adipate).

INTRODUCTION

Compared with other ferroelectric materials, the characteristics of high electric breakdown field but lightweight and high flexibility enable poly(vinylidene fluoride) (PVDF) and its blend to be regarded as the cost-effective functional materials for organic electronic devices^[1,2]. So far, lots of polymer blends comprising of PVDF have been extensively studied, such as PVDF/poly(methyl methacrylate) (PMMA)^[3], PVDF/Nylon-6^[4], PVDF/poly(butylene adipate) (PBA)^[5] and PVDF/ poly(butylene succinate-co-24 mol% hexamethylene succinate) (PBHS)^[6]. Among them, more attentions have been paid to the crystallization and morphology of the other low- T_m component, which is strongly affected by the pre-existing crystal framework of PVDF. Through optical microscopy observation, Qiu and Wang *et al.* have found that poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) and poly(butylene succinate) (PBS) can grow into spherulites in the pre-existing PVDF spherulites^[7–9]. Moreover, crystal modification of PBA in its blend with PVDF can be manipulated by the crystallization temperature of PVDF^[10].

Although the crystallization behaviors of the low- T_m component in the pre-existing crystal framework of PVDF have been widely studied, most of the pre-existing PVDF spherulites were developed at low temperatures.

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Usually, crystallization of PVDF from the melt yields two different types of crystalline phases, *e.g.*, α - and γ -form. The non-polar α -form with TGTG conformation is formed at high supercooling, but the polar γ -phase with TTTGTTG conformation is induced by low supercooling^[1]. The polar γ -phase has attracted technological interests because of providing the high pyro- and piezoelectric properties. However, most of the pre-existing PVDF crystals mentioned above belong to the α -form. Less attention has been paid to the crystallization of the low- T_m component in the pre-existing γ -form spherulites of PVDF. Besides, the effect of the low- T_m component on the morphology of γ -form PVDF spherulites is also far away from being really understood till now.

In a previous study, from the melting point data of PVDF, a negative but quite small value of the interaction parameter $\chi_{\text{PVDF-PEA}}$ was derived using the Flory-Huggins equation, implying that PVDF shows some miscibility with PEA. In addition, it was also found that the crystallization kinetics and morphologies of PVDF and poly(ethylene adipate) (PEA) are influenced by each other, where only α -form PVDF obtained at 150 °C was studied^[11].

In this work, the effect of PEA on the morphology and content of γ -form crystals of PVDF is observed by optical microscopy (OM), scanning electron microscopy (SEM) and infrared spectroscopy (IR). Besides, the crystallization kinetics and morphology of PEA in the pre-existing γ -form PVDF spherulites are also investigated.

EXPERIMENTAL

Materials

PVDF ($M_w = 275000$ g/mol, $M_n = 107000$ g/mol) and PEA ($M_w = 10000$ g/mol) were purchased from Sigma-Aldrich Company. The melting points were measured to be 174 °C for PVDF and 47 °C for PEA. Both of them were used without further purification. PVDF/PEA blends with different compositions ranging from 100/0, 70/30, 50/50, 30/70 to 0/100 in weight ratio were prepared by solution casting using DMF as a common solvent. The thickness of the result films was estimated to be 5–10 μm . The samples were heat-treated at 190 °C for 5 min to erase the thermal history and then cooled to 155 °C or 160 °C for 96 h to ensure complete crystallization. For SEM observation, the films were immersed in chloroform for 48 h at room temperature to etch away the PEA component.

Characterization

An Olympus BH-2 microscope equipped with a Linkam LK-600 PM temperature controller was used to observe the spherulitic morphology. The lamellar morphology of PVDF/PEA blends was observed using a Field Emission Scanning Electron Microscope (Hitachi S-4800) operated at accelerating voltage of 2.0 kV. ATR FTIR was used to determine the crystalline phases of the PVDF specimen. The spectra were collected with 16 scans and a resolution of 4 cm^{-1} on a Perkin-Elmer model VERTE 70 FTIR single beam spectrometer.

RESULTS AND DISCUSSION

Morphological Study of γ -Form PVDF in PVDF/PEA Blend

It has reported that α -form PVDF is kinetically favorable and γ -phase is more thermodynamically stable than α -form. Crystallization of PVDF from the isotropic melt leads either only to α -phase ($T_c \leq 150$ °C), or to α - and γ -phase (150 °C $< T_c < 170$ °C), or only to γ -phase ($T_c \geq 170$ °C)^[3, 12, 13]. In the previous study, for the purpose of studying the effect of PEA on α -form PVDF, the PVDF component was crystallized at 150 °C. The concern here is γ -form PVDF, so the crystallization temperature of PVDF is increased to 155 °C and 160 °C.

Figure 1 shows the spherulitic morphology of the PVDF component, at various blend compositions, after complete crystallization from the melt at 155 °C. As seen in Fig. 1(a), neat PVDF is mainly crystallized into α -form spherulites characterized by high birefringence and concentric banding. For the PVDF in the blends, the spherulite size and concentric extinction band spacing become progressively larger with increasing PEA concentration. In addition, the spherulites with lower birefringence are frequently observed in PEA-rich blends, as indicated by the white arrows in Fig. 1. Similar to α -form spherulites, their diameters also become larger with

the increment of PEA. These spherulites with lower birefringence are generally believed to correspond to the γ -form^[12–14]. The addition of PEA appears to increase the ratio of γ to α spherulites nucleated. The tendency to generate more γ -form crystals has been also observed in blends of PVDF with PBA and PMMA^[3, 5]. This effect may be related to the interfacial interactions of PVDF with the PEA solvent. It is well known that PVDF favors the γ -form crystallization from certain solvents^[5]. In addition, interactions between PVDF and surface functionalized carbon nanotubes can also induce the formation of β -form PVDF^[15].

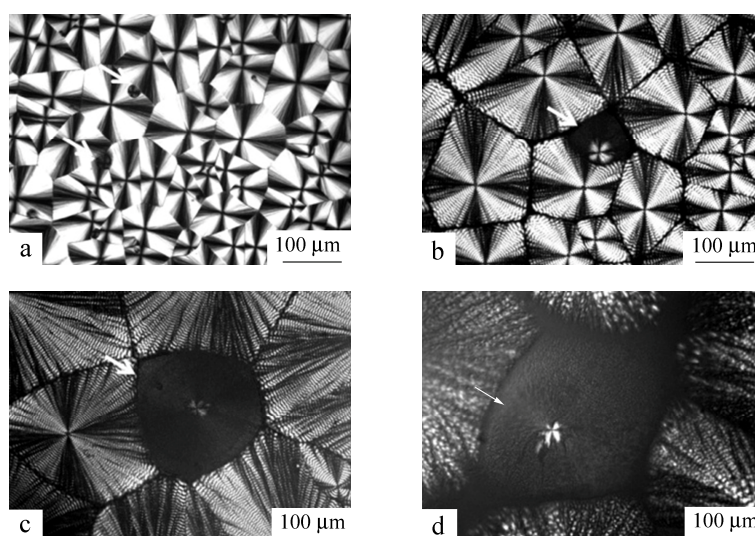


Fig. 1 Optical micrographs of the spherulitic morphologies of PVDF/PEA blends with different PVDF/PEA ratios crystallized at 155 °C: (a) 100/0, (b) 70/30, (c) 50/50 and (d) 30/70

The IR spectra of α - and γ -form PVDF have been studied in detail by several research groups^[16–18]. It is found that IR is a powerful analytical tool suited for identifying the correct phase of PVDF. Figure 2(a) depicts room temperature IR spectra of PVDF/PEA blends as the blend ratios are varied. In these blends PVDF is crystallized at 155 °C while PEA at 35 °C. The distinctive mark of the PEA component is the band at 1734 cm^{-1} attributed to the C=O stretch vibration^[19]. As shown in Fig. 2(a), the intensity of the band at 1734 cm^{-1} gradually increases with the addition of PEA. In the desired wavenumber region, α -form PVDF has characteristic absorption bands at 765, 795, 976 and 1210 cm^{-1} . The intensity of these characteristic bands of α -form PVDF gradually weakens with the increment of PEA, indicating that the crystallization of α -form PVDF crystals is hindered. However, the intensity of the vibrational bands at 835 and 1234 cm^{-1} attributed to the γ -form PVDF crystals gradually increases with PEA content^[16–18]. Next, the IR results are used to quantify the γ -phase content of PVDF. The calculation of the relative fraction of the γ -phase in the samples containing α -phase and γ -phase is based on the following equation^[1]:

$$F_{\gamma} = \frac{A_{\gamma}}{(K_{\gamma}/K_{\alpha})A_{\alpha} + A_{\gamma}} \quad (1)$$

where F_{γ} represents the γ -phase content; A_{α} and A_{γ} are the absorbances at 765 and 835 cm^{-1} ; K_{α} and K_{γ} are the absorption coefficients at the respective wavenumbers, their values are 0.365 and 0.150 μm^{-1} , respectively^[1]. According to the Eq. (1) the γ -phase content F_{γ} was calculated and plotted in Fig. 2(b) as a function of the PEA content. As shown in Fig. 2(b), the γ -phase content of PVDF increases with the PEA content. It turns out that the addition of PEA favors the formation of γ -form PVDF crystals. So, the IR results are well coincident with the morphological observation by POM.

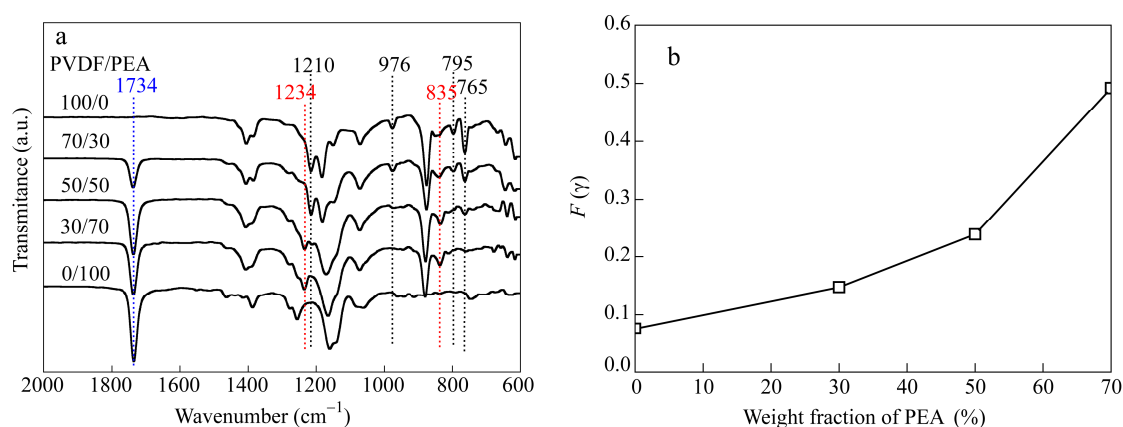


Fig. 2 (a) Infrared spectra of PVDF/PEA blends as a function of blend composition and (b) F_γ deduced from absorbance ratio of the 835 and 765 cm^{-1} bands. The blend samples were first kept at 155 °C for 96 h to completely crystallize PVDF and then quenched to 35 °C to crystallize PEA.

Next, we will focus on the effect of PEA on the lamellar morphology of γ -phase PVDF. Figure 3 reveals the arrangement of lamellae in γ -phase PVDF spherulite. Figure 3(b) is the magnified image of the circled region in Fig. 3(a). In Fig. 3, a γ -form spherulite surrounded by α -form banded spherulite is found in the center of the field of view. The γ -phase spherulite is made of lamellae that are parallel to the spherulite radius. The scroll diameter was measured to be less than 250 nm. Besides, it can be often found that the lamellar bundles are involved in two scrolls or more. This finding is consistent with previous study^[14].

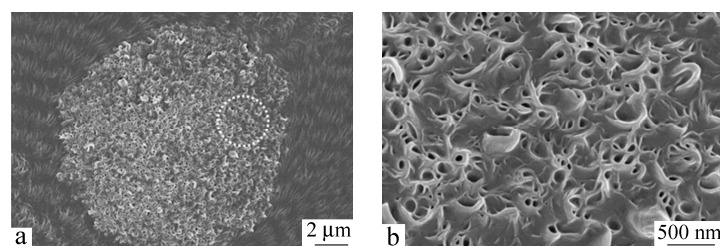


Fig. 3 SEM images of PVDF isothermally crystallized at 155 °C for 96 h

Figure 4 shows the γ -form spherulitic morphologies of the PVDF component in PVDF/PEA blends crystallized at 155 °C. It is noticed that the γ -phase PVDF in the PVDF/PEA blend forms the honeycomb-shaped spherulite composed of the scrolled lamellae. As seen in Fig. 4(a), in the 70/30 PVDF/PEA blend, the lamellar scrolls are often found to stack together closely, indicating that some lamellae are also involved in two scrolls or more. However, as shown in Fig. 4(c), in the 30/70 blend, the scrolls are separated from each other so that the region outside the scrolls is well connected. This confirms that a large portion of PEA resides in the region between the lamellar scrolls in the γ -form PVDF spherulites in PEA-rich blend. In addition, it is also found that the average scroll diameter increases with the PEA content, which suggests the existence of a small portion of PEA inside the scrolls. Generally, α -form lamellae in PVDF spherulites tend to twist, whereas γ -form counterparts prefer scrolling. In essence, both of the lamellar twisting and scrolling originate from unbalanced surface stress^[14, 20]. The scroll diameter increases with the PEA component, indicating that the unbalanced surface stress in favor of lamellar scrolling is probably reduced in the PVDF/PEA blend.

Figure 5 shows the spherulitic morphologies of γ -form PVDF in a 30/70 PVDF/PEA blend crystallized at 160 °C. Compared Fig. 4(c) with Fig. 5(b), it can be found that the scroll diameter increases with the crystallization temperature, even though the increase amplitude is not so high. Although morphological change

from 155 °C and 160 °C is not obvious, the subsequent crystallization of PEA will depend largely on the crystallization temperature of PVDF.

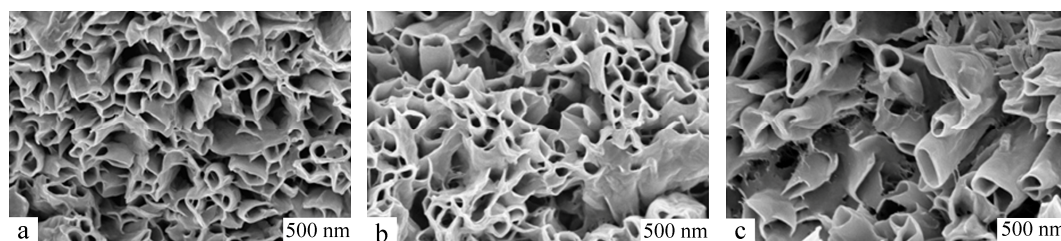


Fig. 4 SEM graphs of γ -phase spherulitic morphologies of PVDF in PVDF/PEA blends with different PVDF/PEA ratios crystallized at 155 °C: (a) 70/30, (b) 50/50 and (c) 30/70

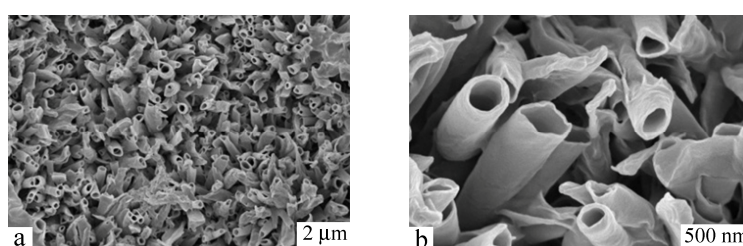


Fig. 5 SEM graphs of γ -phase spherulitic morphologies of PVDF in 30/70 PVDF/PEA blend crystallized at 160 °C

Crystallization of PEA in γ -Form PVDF Matrix

When the PVDF/PEA blend is cooled from 160 °C to 35 °C, the crystallization of PEA will bring the PVDF/PEA blend system into the semicrystalline/semicrystalline state. This process is illustrated with a 30/70 blend in Fig. 6. Figure 6(a) shows the spherulitic morphology of PVDF after the complete crystallization at 160 °C. Three γ -form spherulites of PVDF, as indicated in the right region of Fig. 6(a), exhibit weak birefringence. And it should be also noticed that nonbirefringent regions develop at the spherulitic boundaries. During cooling, no birefringent changes have been recognized at temperatures above the melting point of PEA, indicating the completion of crystallization of PVDF at 160 °C for 96 h. Therefore, the morphological change during further cooling process is mainly caused by the crystallization of PEA.

Figures 6(b)–6(f) represent a time sequence of the crystallization of PEA induced by cooling the sample from 160 °C to 35 °C. The birefringence of the sample changes markedly, reflecting the crystallization of PEA. As illustrated in Fig. 6(b), the commencement of the crystallization of PEA occurs in the interspherulitic regions and continues to proceed in those interspherulitic domains. The crystallization of PEA in the intraspherulitic regions has not been observed until the interspherulitic regions were more or less filled with PEA crystallites, indicating that the crystallization of PEA in the γ -form PVDF spherulites is confined. As shown in Figs. 6(c)–6(f), after the completion of the crystallization in the interspherulitic regions, the PEA crystals keep growing in the peripheral region of the γ -form PVDF spherulites. Due to the high nucleation density, the transcrystalline layer develops. As a whole, the transcrystalline layers grow not along the γ -form spherulite radial direction but perpendicular to the interspherulitic boundary line. In addition, it is seen that several PEA spherulites nucleate at the center of the γ -form spherulite and keep growing, until impinging on the other spherulites or transcrystalline layers.

Next, the spatial distribution of the PEA component is discussed. Firstly, as shown in Fig. 5, the more open structure of the γ -form spherulites in the 30/70 PVDF/PEA blend implies that at least some part of PEA resides in the PVDF spherulites. Secondly, if PEA was expelled onto the top surface of the γ -form spherulites, then PEA would nucleate freely without inhibition. However, as shown in Fig. 6(b), the nucleation and crystal growth of PEA commence in the interspherulitic domains, suggesting that the crystallization of PEA elsewhere is confined.

So, it is safe to say that during the growth of γ -form PVDF spherulite, some part of PEA is expelled into the interspherulitic region and the other is restrained in the intraspherulitic region. The region between the scrolls in γ -form PVDF spherulite is well connected with the interspherulitic region so that the columnar crystals or spherulites can keep growing with residual amorphous PEA in the region between the scrolls.

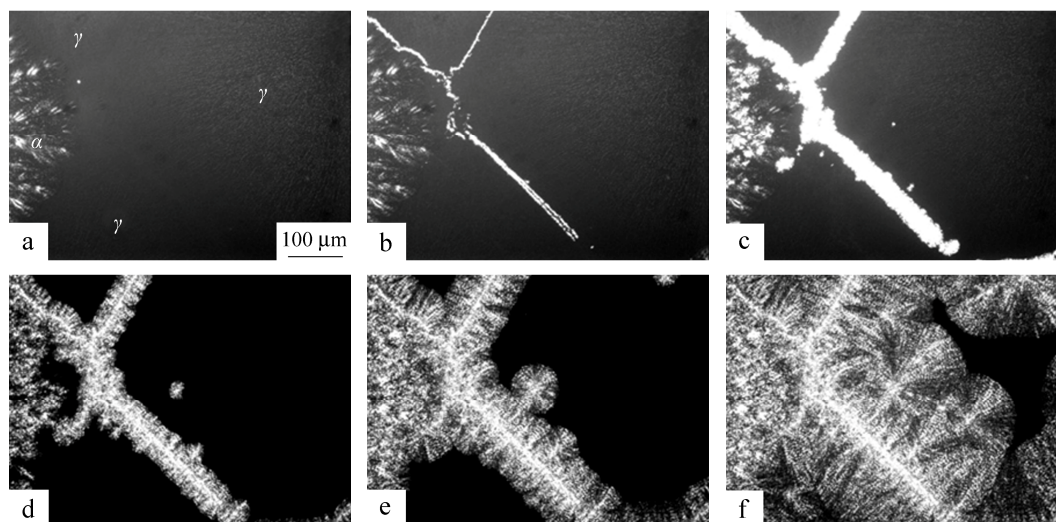


Fig. 6 POM images of a 30/70 PVDF/PEA blend crystallized at 160 °C and subsequently quenched to 35 °C for (a) 0 min, (b) 20 min, (c) 25 min, (d) 30 min, (e) 35 min and (f) 80 min

As shown in Fig. 7, the growth rate of PEA transcrystalline layers within γ -form spherulites in the 30/70 and 20/80 PVDF/PBA blends was determined by monitoring the crystal length as a function of time during isothermal crystallization. From the data shown in Fig. 7, it can be seen that the growth rate of PEA crystals shows a positive correlation with content of PEA, but a negative one with the crystallization temperature of γ -phase PVDF. A similar monotonic growth rate dependence of PBS in the PVDF/PBS (30/70) blend on the crystallization temperature of α -form PVDF has been reported by Wang *et al.*^[8, 9]. And the variation of growth rate of PEA crystals with the crystallization temperature of PVDF is probably related to the diffusion coefficient of PEA melt. The diffusivity of PEA melt in front of growing PVDF crystals should increase with increasing temperature^[21]. This leads to more PEA being excluded from the growing γ -form PVDF spherulites at higher temperature. Meanwhile, the scrolls in the γ -form PVDF spherulites are put together more tightly and the region between the scrolls becomes less well-connected, which will greatly confine the crystallization of PEA.

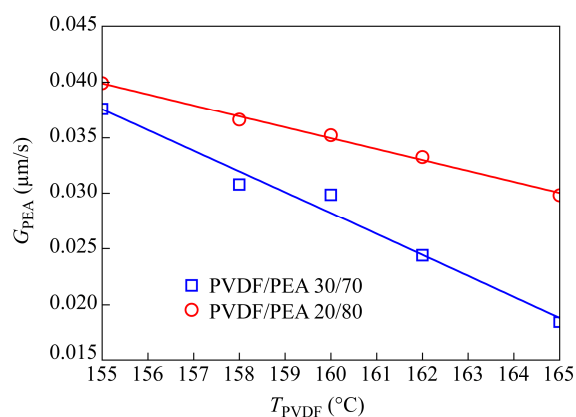


Fig. 7 Variation of PEA growth rate at 35 °C as a function of the crystallization temperature of the γ -phase PVDF matrix

CONCLUSIONS

The effects of the blend ratio and temperature on the crystallization of poly(vinylidene fluoride) (PVDF) and poly(ethylene adipate) (PEA) in their blends have been investigated by optical microscopy (OM), infrared spectroscopy (IR) and scanning electron microscopy (SEM). It was found that the content of γ -phase PVDF increases with increasing PEA concentration when PVDF is crystallized at high temperatures. The γ -phase PVDF lamellae exhibit a highly curved profile and the scroll diameter increases with PEA content. In PEA-rich blend, the scrolls are well separated from each other. When the temperature is decreased below the melting point of PEA, the crystallization of PEA occurs first in the interspherulitic region. The high nucleation density in the interspherulitic region induces transcrystalline structures of PEA. The transcrystalline layer of PEA continues to grow in the region between the scrolls in γ -phase PVDF spherulites until impinging on other PEA transcrystalline layers or spherulites. The spherulitic growth rate of PEA dispersed in the intraspherulitic region of γ -phase PVDF increases with PEA content but decreases with the crystallization temperature of PVDF.

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