

Relationship between Localization of PBSU in Interlamellar/Interfibrillar Regimes and Double Peaks in DSC/SAXS in its Blend with PVDF

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Electronic Supplementary Information

Abstract In this work, phase segregation and localization of PBSU have been investigated with the combination of SAXS and DSC in its blend with PVDF. After stepwise crystallization of PVDF and PBSU, there are double melting peaks of PBSU in DSC and double scattering peaks in SAXS. It has been demonstrated that double peaks can be attributed to the localization of PBSU in interlamellar/interfibrillar region in pre-formed PVDF crystal framework. In the case of low content of PBSU in blend, PBSU is trapped into the interlamellar region of PVDF crystals, resulting in the alternating lamellae crystal of them and the first peak (with low- q) in SAXS. The enhanced confinement effect produces thinner PBSU lamellae, corresponding to the lower melting temperature in DSC. Upon increasing its content in blend, some PBSU segregates in interfibrillar regions in addition to the enrichment in interlamellar regions of PVDF crystal framework. The larger space and higher concentration of PBSU in interfibrillar-regions contribute to periodic lamellae structure of PBSU with higher thickness, which is the reason for the second peak (with high- q) in SAXS and DSC. Our results not only clarify the relationship between localization of PBSU in interlamellar/interfibrillar regions and double peaks in DSC/SAXS, but also provide a novel strategy to detect the interlamellar and interfibrillar segregation of low- T_m component in miscible crystalline/crystalline blend.

Keywords Phase segregation; Localization; Double peaks; DSC/SAXS

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INTRODUCTION

Polymer blending is an effective and simple way to develop polymer materials with desirable properties.^[1–3] According to miscibility between two components, the binary blend system can be classified into miscible and immiscible blends.^[4–6] Especially, the phase structures in the former become interesting when one of components is crystalline polymer. The crystallization behaviors and morphology of crystalline polymer in blends produce significant influence on the properties of materials. Hence, much attention has been paid to crystalline/amorphous miscible blends in the past decades, such as poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA),^[7–9] polycar-

prolactone (PCL)/poly(vinyl chloride) (PVC),^[10,11] poly(L-lactide) (PLLA)/poly(4-vinylphenol) (PVPh), etc.^[12] During the crystallization of crystalline component in blend, the competition between the diffusivity of the amorphous component (D) and growth rate of the crystals (G) will dominate the interlamellar, interfibrillar or interspherulitic segregations of the other component.^[13] It has been demonstrated that crystallization temperature, interaction between two components and compositions, etc. can influence the segregation of amorphous component. There are more complicated crystallization behaviors in crystalline/crystalline blends system such as poly(oxymethylene) (POM)/poly(butylene succinate) (PBSU),^[14–16] poly(ethylene terephthalate) (PET)/poly(trimethylene terephthalate) (PTT),^[17] poly(butylene succinate) (PBSU)/poly(butylene adipate) (PBA),^[18–21] poly(ethylene oxide) (PEO)/poly(butylene succinate) (PBSU)^[22,23] and so on. Here, the crystallization behaviors of binary miscible crystalline/crystalline polymer blends can be divided into simultaneous crystallization and stepwise crystallization which is determined by the difference between melting temperatures (ΔT_m)

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of two components. When ΔT_m is small, both crystalline components can crystallize simultaneously. The spherulites of two components grow to impinge with each other and continue to grow inside the spherulites of the other component, producing interpenetrating spherulites.^[24–27] On the contrary, in the condition of larger ΔT_m , the crystalline component with high- T_m crystallizes firstly at higher temperature. Then, the phase behaviors are similar to that in miscible crystalline/amorphous blend. After completely crystallization of high- T_m component, the localization (interlamellar, interfibrillar and/or interspherulitic regions) of low- T_m component in the pre-formed crystal frameworks has great influence on its crystallization due to confinement effect.^[28–33] No matter in crystalline/amorphous or crystalline/crystalline blend, the localization of amorphous or low- T_m component resulting from the exclusion behaviors plays an important role in determining its final performance.^[34]

Much effort has been made to evaluate the spatial localization of amorphous or low- T_m component in pre-formed crystal frameworks of high- T_m component. In the literature, small angle X-ray scattering (SAXS)^[35,36] and microscopy techniques^[37,38] have been widely employed. For instance, Saito and Stuhn investigated the intra-spherulitic structure of PVDF/PMMA blends *via* the combination of SAXS and DSC.^[9] The ratio of the linear crystallinity (from SAXS) and overall crystallinity (from DSC) can act as a parameter to assess the exclusion of PMMA in blends. Yan *et al.* clarified the dependence of phase segregation of PBA on the blend ratio and crystallization temperature in PBSU/PBA crystalline/crystalline blend using the optical and atomic force microscopies (AFM).^[20] Furthermore, some novel techniques were also adopted to detect the segregation of amorphous or low- T_m component in pre-formed crystal frameworks. Tri *et al.* used AFM-IR (infrared spectroscopy) to investigate the localization of poly(3-hydroxybutyrate) (PHB) in its blends with poly(ethylene glycol) (PEG).^[39] However, there are still some open problems in the developed strategies. On one hand, the sample preparation in some characteristic methods is quite rigorous and complicated. For instance, the thickness of samples during AFM observations is always in the range of hundreds of nanometers. As a result, phase segregation may be different from that in bulk due to the confinement effect in film thickness direction.^[40,41] On the other hand, advanced technology and equipment, such as AFM measurement at high temperature, its combination with IR as well as the synchrotron radiation with high energy and flux, are required. Hence, facile methods for the investigation of localization of amorphous component in the pre-formed crystal frameworks have been highly desired but still challenging.

PVDF/PBSU is a typical miscible crystalline/crystalline blend.^[42–45] PVDF can crystallize firstly at a relatively higher temperature. In the resultant crystal framework of PVDF, PBSU can segregate in interlamellar or interfibrillar regimes. The crystallization of PBSU in two cases can produce crystal lamellae with different morphology and thickness, corresponding to different melting behavior in DSC and scattering peak in SAXS.^[46] In this work, therefore, it is proposed to clarify the relationship between the phase segregation in interlamellar/interfibrillar regions and multiple peaks in DSC and SAXS.

EXPERIMENTAL

Materials and Sample Preparation

Poly(vinylidene fluoride) (PVDF, KF850) and poly(1,4-butylene succinate) (PBSU, TH803S) were purchased from Scientific Polymer Products Inc and Blueridge Tunhe Chemical Industry Co., Ltd., respectively. The blends of PVDF/PBSU with various compositions were prepared by melt-mixing method and the weight fraction of PBSU in blends was ranged from 10% to 90%. Prior to preparing binary blends, PVDF and PBSU were dried in a vacuum oven to remove moisture (80 °C for 12 h). Then, the melt-mixing process was performed at 190 °C in a batch mixer (Haake PolyLab QC) with a twin-screw. The rotation speed of the screw was first set to 20 r/min for 2 min and then raised to 50 r/min for 5 min. The obtained blends were melting at 200 °C for 10 min and then hot-pressed under 10 MPa for 3 min. After cooled to the room temperature, films with a thickness of 300 μm were obtained for further characterization. The thermal treatment of blends was carried out according to the temperature profile shown in Fig. 1. The specimens for polarized optical microscope (POM) observations were prepared by casting the solution of binary blend on clean glass sheets.

Characterization and Instrumentation

The non-isothermal and isothermal crystallization behaviors of binary blends were investigated by a differential scanning calorimeter (DSC Q200) under a dry nitrogen flow. As for non-isothermal crystallization process, the blends were first heated to 200 °C and held for 5 min to eliminate thermal history completely and then cooled to 30 °C at a rate of 10 °C/min. The blends were reheated to 200 °C at the same heating rate. As for the isothermal crystallization process, after eliminated thermal history at 200 °C, the blends were first cooled to 140 °C at a rapid cooling rate (100 °C/min) and held for enough time for the crystallization of PVDF, and then rapidly cooled and kept at 80 °C. In the end, the blend was reheated to 200 °C at a heating rates of 50, 30, 15, 10 °C/min. During this process, the DSC curves were recorded.

The real-time crystallization of PBSU in blends and melting behaviors of binary blends were investigated with the help of *in situ* small angle X-ray scattering (*in situ* SAXS) on beamline BL16B1 in Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of X-ray is 1.24 Å. The sample-to-detector distance was 2008 mm and a SAXS detector (Pilatus3 2M, Dectris) was used to collect the scattered signals. Meantime, the information from *in situ* wide-angle X-ray scattering (*in situ* WAXS) was collected with a WAXS detector (Pilatus3 900K, Dectris). In SAXS and WAXS experiments, the temperature control of specimens was performed on a heating stage (Linkam THMS600). The two-dimensional SAXS patterns were azimuthally integrated to obtain the one-dimensional scattering profiles as a function:

$$q = 4\pi\sin\theta/\lambda \quad (1)$$

where q is the module of the scattering vector, λ is the wavelength of X-ray and 2θ is the scattering angle. The average long period (L) was determined by the maximum of the diffuse intensity (q_{max}) in the Lorentz corrected curves [$Iq^2 - q$] according to Bragg's law:

$$L = 2\pi/q_{\text{max}} \quad (2)$$

The polarized optical microscope (POM Leica DM2700P)

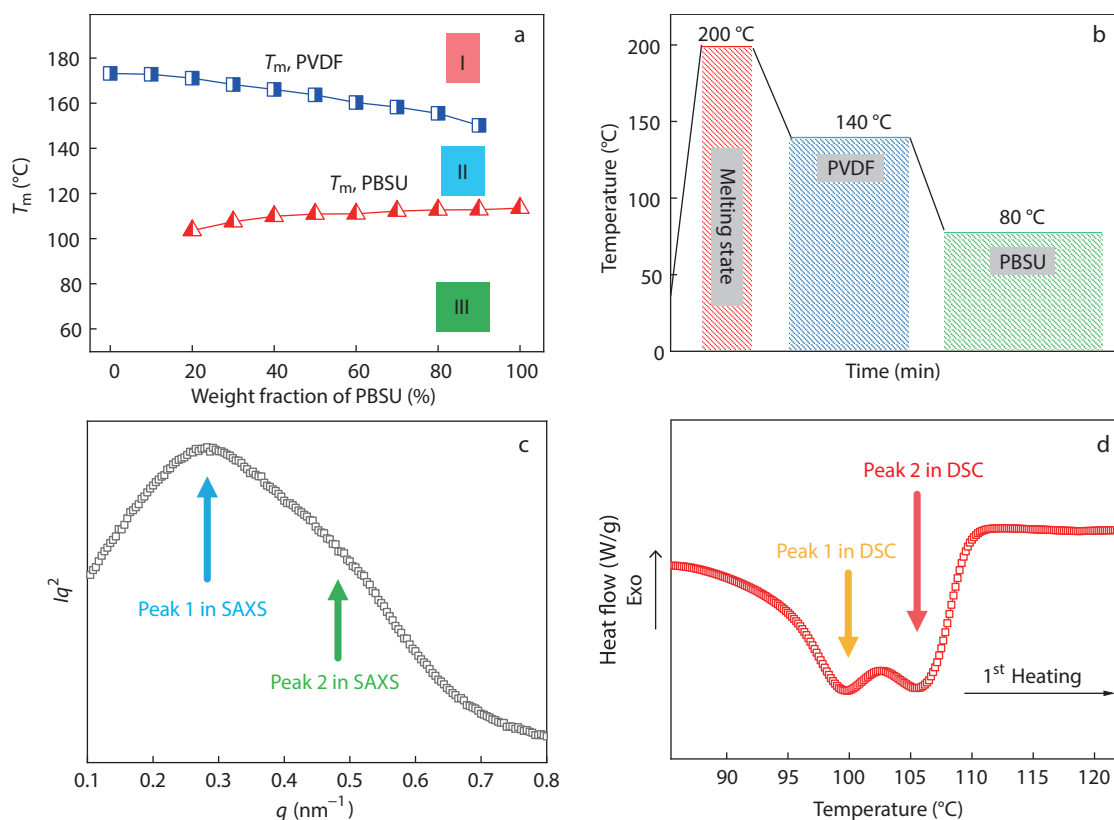


Fig. 1 The statistics of T_m in PVDF/PBSU blend with various compositions (a), procedure of the applied heating treatment on blends (b), Lorentz-corrected SAXS curves (c) and melting behavior of PBSU (d) in PVDF/PBSU blend (70/30, W/W).

equipped with a Linkam THMS600 heating stage was used to investigate the crystallization morphology of PVDF/PBSU blends. The temperature control program was similar to the isothermal crystallization process in DSC testing.

To observe the enrichment of PBSU in binary blends, PBSU was etched by means of selective extraction. The morphologies of blends after etched with chloroform were observed using a field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) with an accelerating voltage of 5 kV. Before observation, the specimens were all freeze fractured in liquid nitrogen.

RESULTS AND DISCUSSION

The crystallization behaviors of PVDF and PBSU in blends have been investigated by DSC and melting temperatures (T_m) of them have been concluded in Fig. 1(a). PVDF/PBSU is a miscible crystalline/crystalline blend system and the miscibility of them has been confirmed in detail.^[37,42,43,45] As shown in Fig. 1(a), with the increase of PBSU weight fraction in binary blends, the melting temperature of PVDF decreases from 173 °C to 150 °C gradually. The results show good agreement with the “ T_m -depression” effect, in which the dynamics of crystallization are reduced by dilution. Likewise, the melting temperature of PBSU decreases because of the dilution effects of amorphous PVDF. Obviously, PVDF/PBSU blend exhibits typical stepwise crystallization. According to the melting temperatures of them, there are three regions in Fig. 1(a). In Region I, PVDF and PBSU are miscible in melting state. Upon cooling to the crystallization temperature of PVDF, PVDF in blends crystallizes

at a higher temperature, whereas PBSU is still in melting state (Region II in Fig. 1a). Until cooling to its crystallization temperature, PBSU starts to nucleate and crystallize within the crystal frameworks of PVDF (Region III in Fig. 1a). So, it is possible to investigate the influence of PVDF crystal frameworks on the crystallization of PBSU. Furthermore, PVDF crystal frameworks can be tailored by the means of blend ratio. Based on the stepwise crystallization behavior in PVDF/PBSU blends, the heating treatment was performed according to the temperature profile shown in Fig. 1(b). At beginning, the blends were heated to 200 °C and held for 5 min to eliminate thermal history completely. Then, the blends were cooled from 200 °C to 140 °C rapidly (100 °C/min) and kept at this temperature for the fully crystallization of PVDF. Until the formation of PVDF crystal frameworks finished, the blends were cooled to 80 °C at a rate of 100 °C/min, a temperature at which PBSU can crystallize. After completely crystallization of PVDF and PBSU step by step, the Lorentz-corrected SAXS curves and melting behavior of PBSU in PVDF/PBSU blend with the weight ratio of 70/30 are shown in Figs. 1(c) and 1(d). It is interesting that the double peaks are obvious both in curves of SAXS and DSC. So, the origin of multiple peaks in SAXS and DSC has been investigated respectively in the following sections to clarify the relationship between them.

The crystallization behavior of PBSU within the crystal frameworks of PVDF was first investigated with the help of the *in situ* synchrotron SAXS. Fig. 2(a) shows the Lorentz-corrected SAXS profiles for PVDF/PBSU blend with the weight ra-

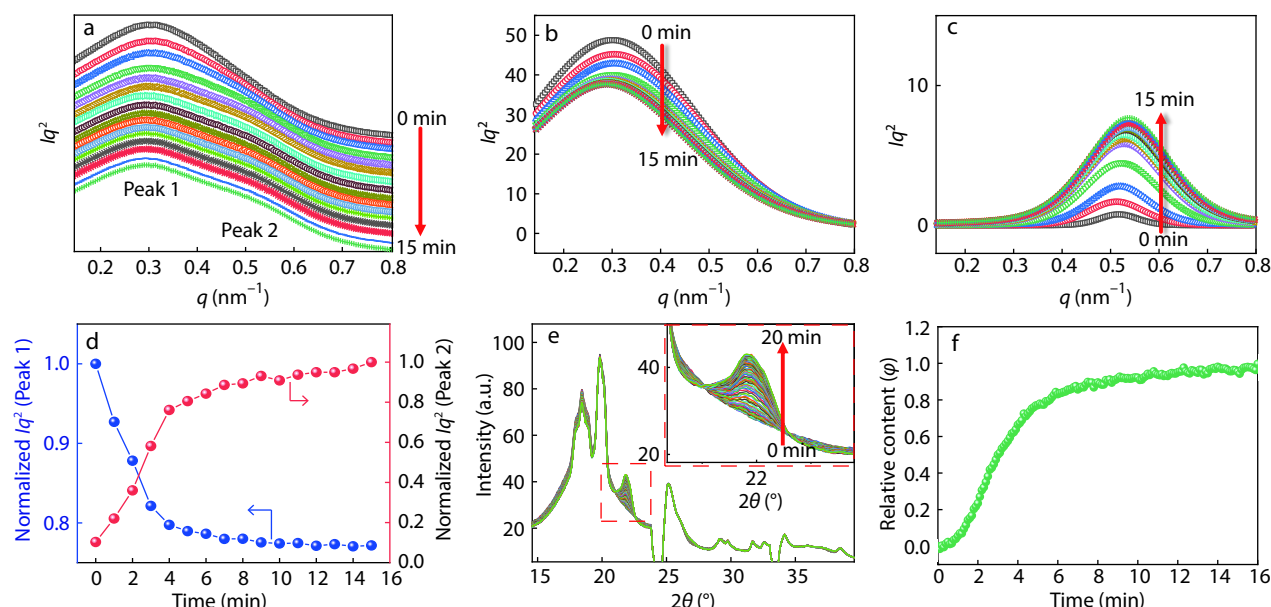


Fig. 2 (a–c): *In situ* synchrotron SAXS profiles of PVDF/PBSU (70/30) crystallized at 80 °C (PVDF was fully crystallized at 140 °C); (b, c) The evolution of two peaks during the crystallization of PBSU (after peak separation in a); (d) Normalized Iq^2 of Peak 1 and Peak 2; (e) *In situ* WAXS profiles of PVDF/PBSU (70/30) crystallized at 80 °C (PVDF was fully crystallized at 140 °C); (f) Relative content of (110) plane reflection of PBSU.

tio of 70/30 during isothermal crystallization of PBSU (PVDF has been fully crystallized at 140 °C). The curves of different crystallization time were separated because of the overlap. From up to down, the crystallization time is 0 min to 15 min. At the beginning of the crystallization of PBSU, there is only one scattering peak locating at $q_1=0.305 \text{ nm}^{-1}$ (named Peak 1), corresponding to the long period of 20.6 nm. Due to the good miscibility between PVDF and PBSU, PBSU mixed with amorphous PVDF locates between the lamellae of PVDF, resulting in the much higher long period in binary blend than that of pure PVDF shown in Fig. S2 ($q=0.465 \text{ nm}^{-1}$, $L=13.5 \text{ nm}$, in the electronic supplementary information, ESI). In addition, it is obvious that another peak (named Peak 2) appears during the isothermal crystallization of PBSU. For differentiation and quantitative analysis, the Peakfit software was used to separate the Peak 1 and Peak 2 in Fig. 2(a). As shown in Figs. 2(b) and 2(c), the intensity of Peak 1 decreases significantly during the crystallization of PBSU. Meanwhile, the intensity of Peak 2 increases gradually and the peak finally locates at $q_2=0.535 \text{ nm}^{-1}$, corresponding to the long period of 11.7 nm. The occurrence of Peak 2 and intensity decrease of Peak 1 can be analyzed preliminarily as follows. Firstly, it should be clarified that PBSU is still amorphous when PVDF crystallizes at 140 °C. Furthermore, only PBSU can crystallize during the isothermal crystallization process (at 80 °C). It means that the variation of intensity and occurrence of new peak should be attributed to the crystallization of PBSU. Secondly, as mentioned before, PBSU is miscible with amorphous PVDF between the lamellae of PVDF. Therefore, the decreasing intensity of Peak 1 comes from the decrease of electron density difference between PVDF lamellae and mixed amorphous layers (amorphous PVDF and PBSU) caused by the crystallization of PBSU. The second peak (Peak 2) represents the correlation among lamellar structure of PBSU crystals. PVDF in the lamellar structure of PBSU results in the higher long period of PBSU crystals

($L=11.7 \text{ nm}$) relative to pure PBSU ($q=8.75 \text{ nm}$). Additionally, the normalized Iq^2 has been used to quantitate the decreasing or increasing rate of two peaks. As shown in Fig. 2(d), the intensities of Peak 1 and Peak 2 reach a plateau after 10 min, which has good agreement with the result of isothermal crystallization behavior shown in Fig. S3 (in ESI). The confined crystallization of PBSU is also evaluated with the help of *in situ* synchrotron WAXS. Fig. 2(e) shows the one-dimensional WAXS profiles of PBSU for different crystallization time at 80 °C. After completely crystallization of PVDF, the peaks of PVDF crystals are almost not changed during the crystallization of PBSU, implying that there is no recrystallization or cold crystallization of PVDF at this temperature (80 °C). Simultaneously, there are two obvious peaks at 21.5° and 21.9° , corresponding to the (021) and (110) planes of PBSU α crystal, respectively. The intensities of them increase remarkably during the isothermal crystallization of PBSU (inset in Fig. 2e). The relative content of the (110) plane of PBSU shown in Fig. 2(f) suggests that the crystallization of PBSU in the PVDF crystal frameworks has finished after 10 min. It also agrees well with the results in Fig. 2(d) and Fig. S3 (in ESI).

The investigation on reheating process of binary blend ($W/W=70/30$) which has fully crystallized at 140 and 80 °C can further confirm the analysis discussed above. The evolution of peaks in Lorentz-corrected SAXS curves with temperature is shown in Fig. 3. In the temperature range of 80 °C to 100 °C (Fig. 3a), the intensities of Peak 1 and Peak 2 remain almost constant. Upon further elevating temperature to 120 °C, both Peak 1 and Peak 2 exhibit remarkable evolution. Until the temperature reaches 160 °C, the intensity of Peak 1 declines drastically. To discuss the evolution of two peaks in detail, the temperature range was separated into two parts as shown in Figs. 3(b) and 3(c), which are from 80 °C to 120 °C and from 150 °C to 200 °C, respectively. The evolution of peaks from 120 °C to 150 °C is not shown since there are no obvious

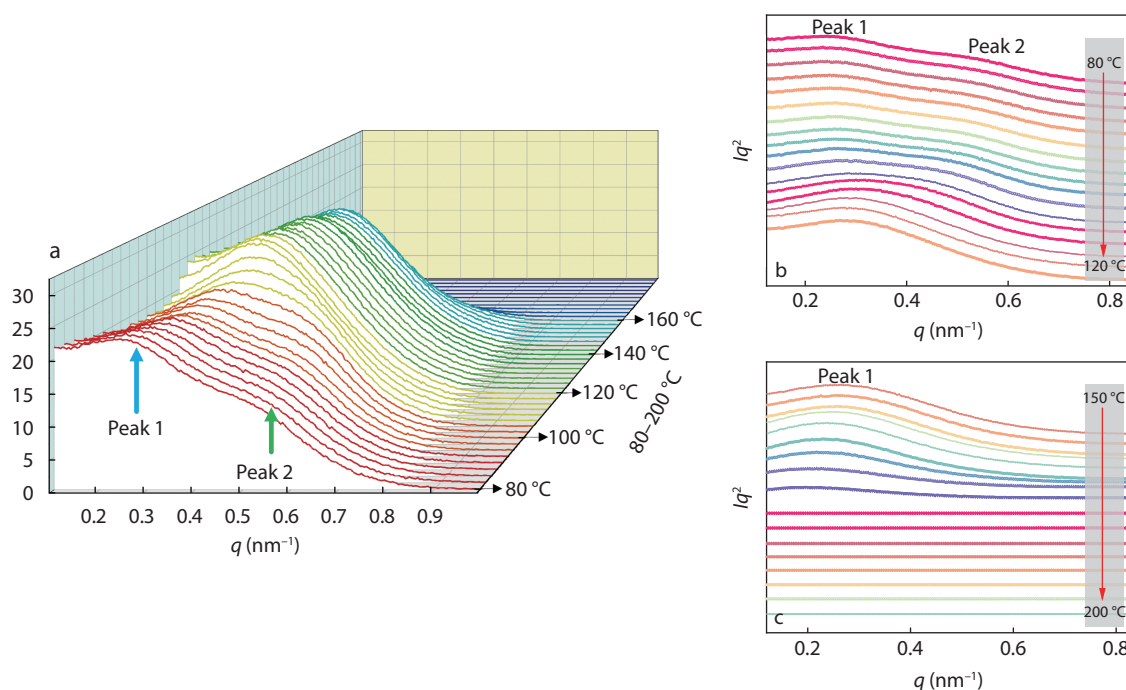


Fig. 3 *In situ* synchrotron SAXS profiles of the reheating process of PVDF/PBSU (70/30, fully crystallized at 140 and 80 °C).

changes. According to Fig. 1, only the crystals of PBSU can be melted before 120 °C, whereas PVDF crystals will not be affected by heating. Hence, for one thing, the peak with high- q (Peak 2) disappears during the reheating process from 100 °C to 120 °C, indicating the direct relationship between Peak 2 and periodic lamellae structure of PBSU. For another thing, the intensity of Peak 1 increases significantly and reaches a stable value at the same time, indicating the enlargement of electron density difference between PVDF lamellae and mixed amorphous layers.^[47] In periodic lamellae structure of PVDF, the electron densities of PVDF lamellae and amorphous PVDF are almost not influenced by rising temperature. The only reason for the enlargement of electron density is the transition of PBSU from crystals to amorphous state in this range of temperature. So, it can be inferred that some crystals of PBSU have been trapped and inserted into the interlamellar regions of PVDF. The melting of PBSU in the interlamellar region enlarges the electron density difference between PVDF lamellae and mixed amorphous layers. When the specimen is heated from 150 °C to 200 °C, the scattering peak with low- q (Peak 1) declines and finally vanishes. There is no doubt that it corresponds to the melting behavior of PVDF lamellae. Variation of Peak 1 is well coincident with the melting behaviors of PVDF in Fig. 1. Consequently, the segregation and localization of PBSU during stepwise isothermal crystallization can be described as follow in the specimen containing 70% PVDF. Firstly, during the isothermal crystallization of PVDF, PBSU is still in amorphous state. The exclusion behavior caused by crystallization produces the “interlamellar” and “interfibrillar” segregation in binary blend (the interspherulitic segregation has been neglected since PVDF/PBSU is miscible^[37,42,43,45,48]). In other words, a part of PBSU component in melting state has been included into the interlamellar region of PVDF. After isothermally crystallized at 80

°C, alternating structure of PVDF and PBSU lamellae forms, which is the reason for Peak 1 with higher long periods. Another part of PBSU component is excluded into the lamellae stacks of PVDF (interfibrillar region). Enough space and higher content of PBSU between the lamellae stacks of PVDF make it possible for PBSU to form its own periodic lamellae structure, corresponding to Peak 2 in SAXS.

To validate the conclusion above, further investigation has been carried out in binary blends with different compositions. *In situ* synchrotron SAXS profiles of PVDF/PBSU crystallized at 80 °C are shown in Fig. S4 (in ESI). The appearance and intensity of peak with high- q are strongly dependent on the content of PBSU in binary blends. In the process of PBSU crystallization, the shoulder at high- q appears and becomes more and more significant. Similar to the results in blend with weight ratio of 70/30, in blends with weight ratio of 50/50 and 80/20, the intensity of peak with low- q decreases, implying the decrease of electron density difference between PVDF lamellae and mixed amorphous layers caused by the crystallization of PBSU in the interlamellar region of PVDF crystals. Final Lorentz-corrected SAXS curves of each blend which related to the organization of PBSU and PVDF crystals are shown in Fig. 4. Similar to the analysis method applied in Fig. 2, Peak 1 and Peak 2 in Figs. 4(a)–4(c) were also separated with the help of the Peakfit software. The location and area of each peak have a strong relationship with the weight ratio of PBSU in blends. On one hand, the peaks with low- q in PVDF/PBSU blends with weight ratio of 50/50, 70/30 and 80/20 locate at 0.245, 0.283 and 0.334 nm^{−1} corresponding to the long periods of 25.5, 22.8 and 18.8 nm, respectively. With increasing weight ratio of PBSU in blends, more PBSU is trapped into the interlamellar region of PVDF, which is the reason for the larger long period of PVDF lamellar structure. On the other hand, Peak 2 (high- q) becomes more and more significant in

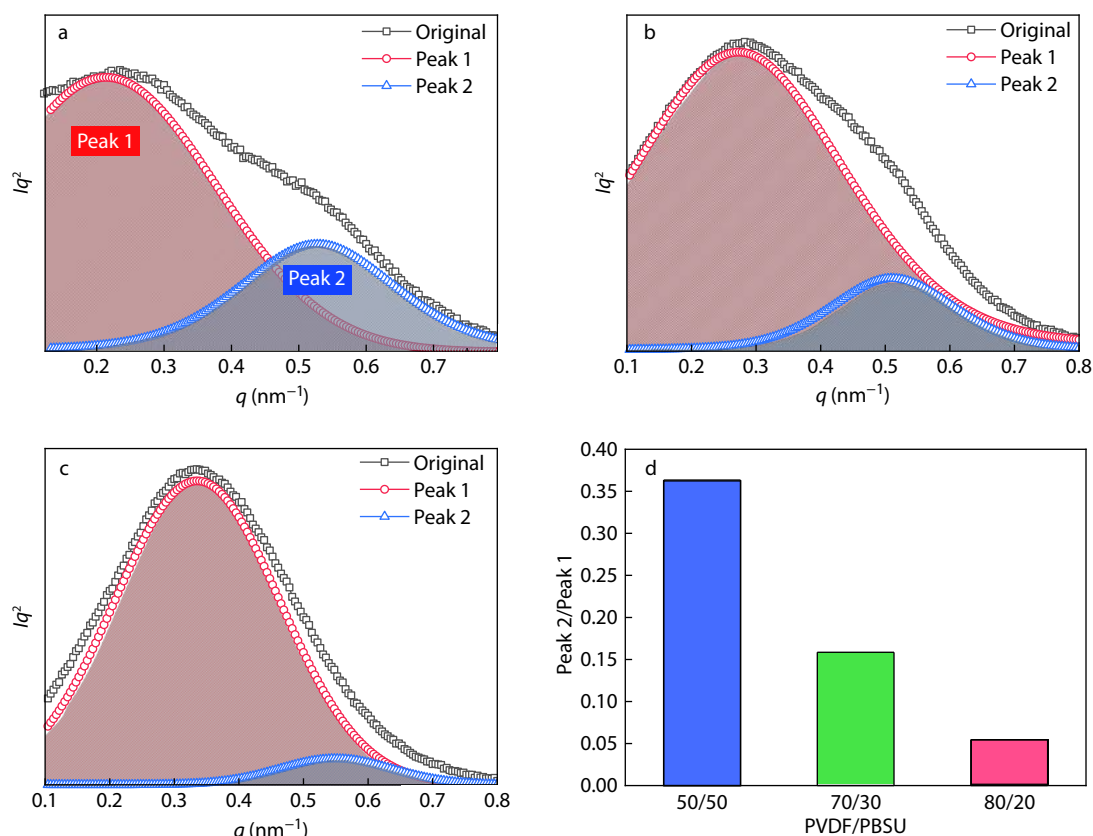


Fig. 4 Lorentz-corrected SAXS curves of PBSU fully crystallized at 80 °C (PVDF was fully crystallized at 140 °C) (a: 50/50; b: 70/30; c: 80/20) and the area ratios of Peak 2 and Peak 1 (d).

the case of higher PBSU weight fraction. In the specimen of 50% PBSU, the shoulder at high- q is much stronger than those in blends of 80/20 and 70/30. In Fig. 4(d), the area ratio of Peak 2 and Peak 1 increases from 0.05 to 0.36 with the increase of PBSU in blends. To clarify the markable changes of two peaks in different blends, our attention should be paid to the following issues. For one thing, the emergence of the second peak (Peak 2) relates to the formation of periodic structure. It has been proved that the Peak 2 can be indexed to the periodic lamellar structure of PBSU. Due to the dramatic exclusion behavior caused by slower crystallization of PVDF and higher content of PBSU in blend, the phase segregation of PBSU changes from interlamellar regime to interfibrillar regime, resulting in the formation of PBSU periodic lamellae structure and enhancement of Peak 2. Furthermore, PBSU in interfibrillar region becomes freer and the spatial confinement level of PBSU decreases due to the larger segregation space. For another thing, the intensity of peaks in SAXS depends mainly on the content of periodic structure in system and electron density difference between lamellae and amorphous layer. The decrease of weight ratio of PVDF in blends results in the decline in intensity of Peak 1, which comes from the periodic lamellae structure of PVDF crystals. Hence, it has been demonstrated that double peaks in SAXS can be related to the exclusion behavior and phase segregation structure in miscible crystalline/crystalline blend. The emergence and enhancement of the second peak (Peak 2) during the crystallization of low- T_m component indicate that the segregation of

PBSU changes from “interlamellar” regime to the co-existence of “interlamellar” and “interfibrillar” regimes.

The relationship of different phase segregation and melting behavior of PBSU were investigated with the help of DSC. After PBSU crystallized completely, the blends were quenched to 30 °C and then heated to 200 °C at a heating rate of 10 °C/min. The endothermic curves in this process were recorded. Firstly, our attention should be paid to the melting peaks of PBSU in the blend with weight ratio of 70/30. As shown in Fig. 5, different from the melting behavior of PBSU in non-iso-

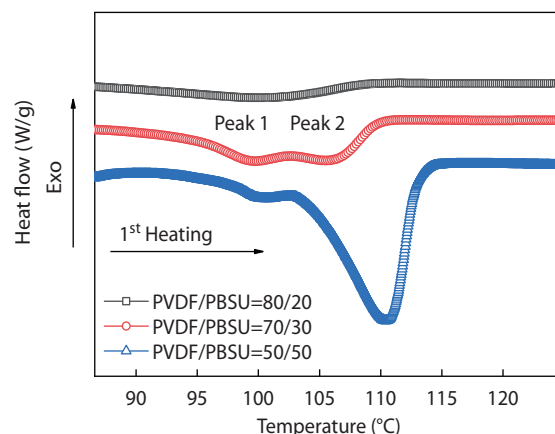


Fig. 5 The melting behavior of PBSU in PVDF/PBSU blends with different ratios (PVDF and PBSU were fully crystallized at 140 °C and 80 °C stepwise).

thermal crystallization process (Fig. S1 in ESI), it is interesting that there are two melting peaks during the heating process, locating at 99.7 and 105.6 °C, respectively. The multiple melting phenomenon takes place in many semicrystalline polymers, which can be mainly ascribed to: (a) different crystal types, (b) melting-recrystallization behavior, (c) variation of morphology (lamellar thickness, perfection of crystals).^[49,50] Normally, PBSU exhibits α crystal form. Only under stretching, it exhibits a transition between α - β crystal form. In this work, as shown in Fig. 6, there are (021), (110), (121) and (111) re-

flections of α crystal, indicating that PBSU in its blend with PVDF exhibits only α crystal form. In addition, the heating rate will produce a remarkable influence on melting-recrystallization behavior. For this purpose, the heating-rate dependence of melting behaviors of PBSU was investigated. As shown in Fig. 7, it is obvious that the double melting peaks can be observed during the heating process with different heating rates. Moreover, upon decreasing heating rate, there is no obvious change of the shapes of melting peaks. Therefore, it can be confirmed that the double melting peaks of PBSU are re-

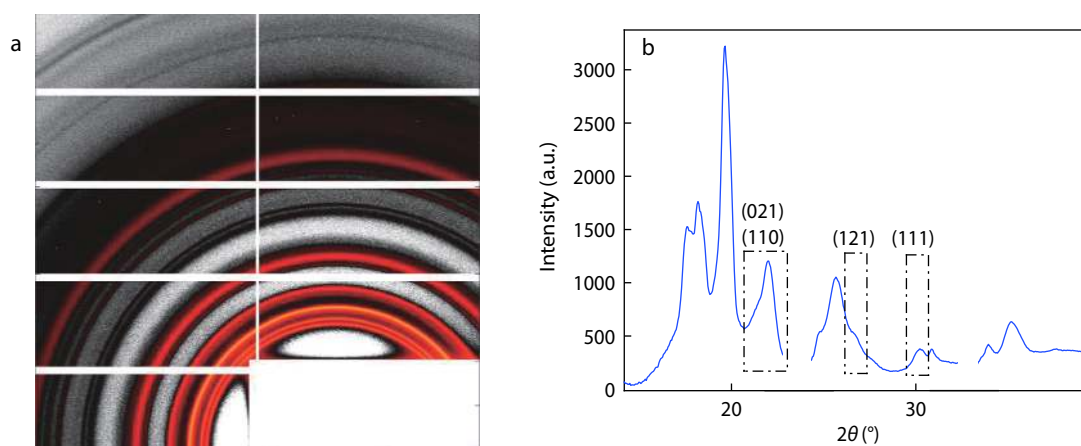


Fig. 6 WAXS image and curve of PVDF/PBSU blend (70/30, W/W) which were fully crystallized at 140 and 80 °C.

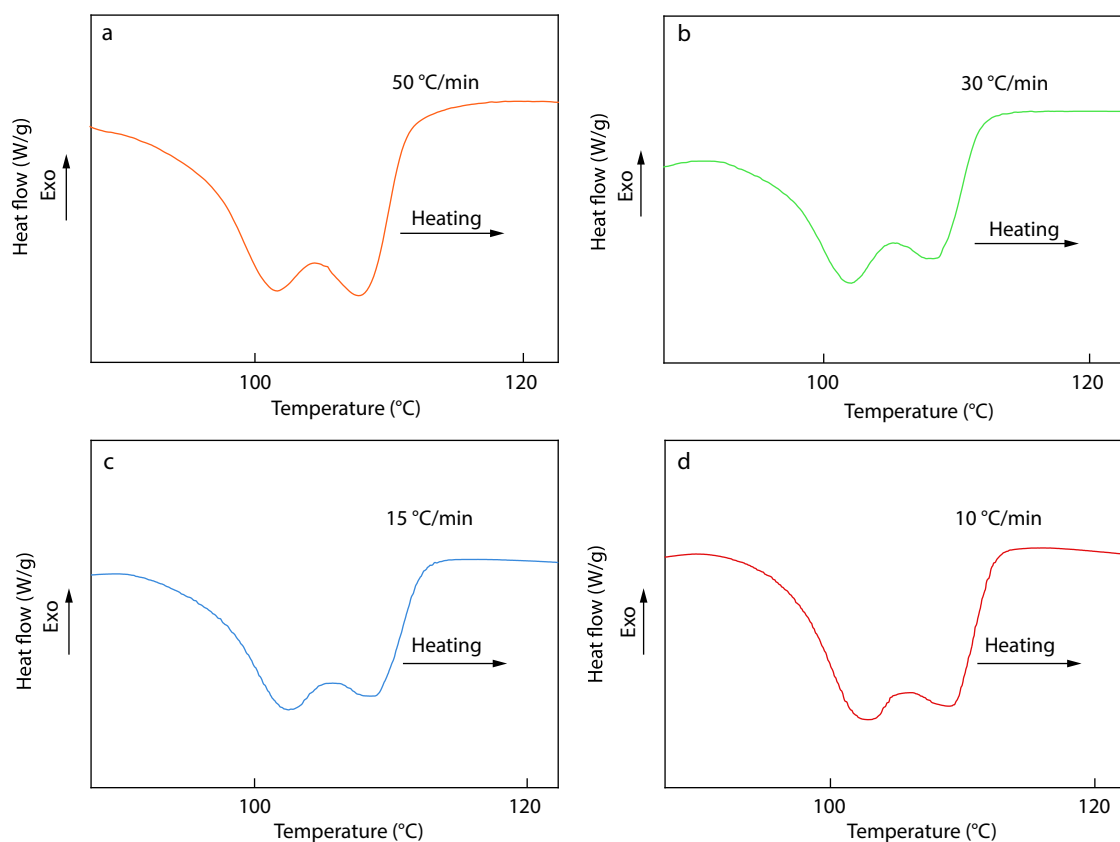


Fig. 7 The melting behavior of PBSU in PVDF/PBSU (70/30, W/W) with the indicated heating rates (PVDF and PBSU were fully crystallized at 140 and 80 °C stepwise).

lated to the existence of two or more lamellar morphologies (e.g., different lamellar thicknesses). According to the well-known Gibbs-Thomson equation, the lamellar thickness distribution determines the specific melting temperature.^[51] Furthermore, the enhanced confinement will result in the fragmented and thin lamellae corresponding to lower melting temperature.^[52–54] In the PVDF/PBSU blend with weight ratio of 70/30, the crystallization of PVDF results in the interlamellar and interfibrillar segregation of PBSU, which leads to the different confinement of PBSU in the PVDF crystal frameworks. Consequently, based on the discussion above, as shown in Fig. 5 (red curve), it can be inferred that the low melting temperature (Peak 1) corresponds to the thin lamellae nucleated and grown in the confined region between the PVDF lamellae while the high melting temperature (Peak 2) corresponds to the thick lamellae resulting from the crystallization of PBSU in the interfibrillar regions. When the content of PBSU in blend decreases, the SAXS results demonstrate that PBSU is trapped into the interlamellar regions. The low content and high confinement level of PBSU in interlamellar region led to thin lamellar structure and consequent lower melting temperature. So, due to the imperfect crystallization in the blend of 80/20, the melting peak of PBSU is wide and locates at 100.0 °C (black curve in Fig. 5). On the contrary, with increasing content of PBSU in blend, more and more PBSU has been expelled into the interfibrillar region, accounting for the co-existence of “interlamellar” and “interfibrillar” segregation. Relative to region between lamellae, the interfibrillar region exhibits large space and less confinement of PBSU, producing more perfect and thick lamellar structure during the isothermal crystallization. Thus, the melting temperature of PBSU crystals in interfibrillar region exhibits higher magnitudes. As shown in Fig. 5, a higher melting temperature is obvious in the blend with higher content of PBSU (blue curve, 50/50). Furthermore, because of reduced “ T_m depression” effect, the melting temperature of two peaks (100.5 and 110.5 °C) in PVDF/PBSU blend with 50 wt% of PBSU is higher than those (99.6 and 105.9 °C) in blend with 30 wt% of PBSU. In

one word, it can be confirmed that double melting peaks of PBSU in DSC have a strong relationship with double peaks in SAXS. Both of them reflect the phase segregation of PBSU during the crystallization of PVDF. Peak 1 and Peak 2 correspond to the localization of PBSU in interlamellar and interfibrillar regions, respectively.

The localization and connectivity of PBSU have a great influence on the nucleation and crystal growth of PBSU within the PVDF crystal frameworks. As shown in Fig. 8, the isothermal crystallization of PBSU was tracked by means of polarized optical microscopy (POM). All the blends were first crystallized at 140 °C, then cooled to the crystallization temperature of PBSU (80 °C). Before the crystallization of PBSU, the spherulites of PVDF with different weight ratios of PBSU are shown in Figs. 8(a), 8(d) and 8(g). The PVDF spherulites are compact in the blend with lower weight fraction of PBSU. On the contrary, the spherulites of PVDF become coarse, implying the occurrence of interfibrillar segregation.^[8] Based on the different phase segregation and confinement, the crystallization of PBSU in the PVDF crystal frameworks are quite different. For the blend with 20 wt% PBSU, PBSU is trapped into the interlamellar region of PVDF, resulting in the less connectivity of them. As a result, the crystallization of PBSU cannot be observed even after 50 min (enough time for the crystallization of PBSU). In the case of 70/30 (PVDF/PBSU), color changes (Figs. 8d–8f) reflect the crystallization of PBSU during isothermal crystallization at 80 °C, whereas there is still no obvious crystal growth. In the case of PVDF/PBSU 50/50, due to the PBSU-rich phase in the interfibrillar region and less confinement, the crystallization of PBSU in PVDF crystal frameworks becomes much more remarkable. The crystal growth of PBSU starts from the center of the PVDF spherulites and gradually fills all over the specimen. The growth rate of PBSU exhibits much higher magnitude relative to the specimen with lower PBSU content.

In order to investigate the phase segregation and localization of PBSU during the crystallization of PVDF, the fracture structure of specimens has been observed after selective re-

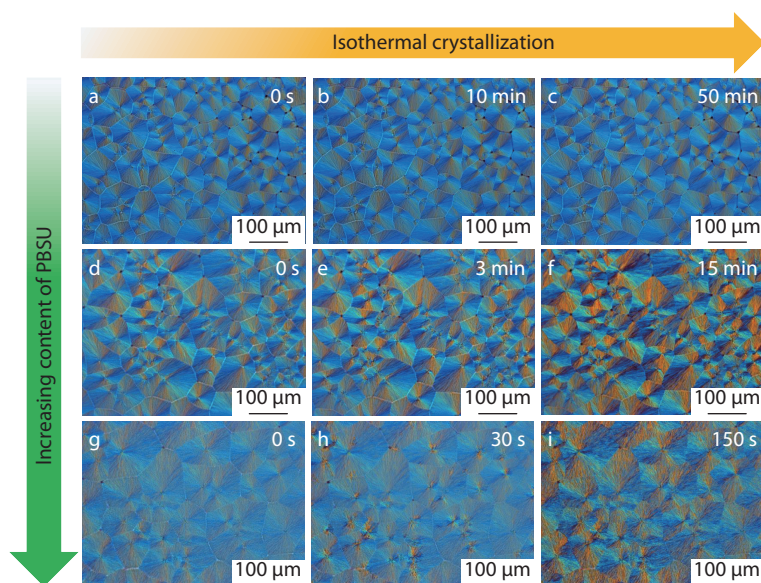


Fig. 8 POM images of PVDF/PBSU crystallized at 80 °C (PVDF was fully crystallized at 140 °C) (a–c: 80/20; d–f: 70/30; g–i: 50/50).

removal of PBSU by chloroform. For the sample containing 80 wt% PVDF, based on the investigation and discussion above, nearly all PBSU has been trapped into the interlamellar region of PVDF lamellae. Moreover, the interlamellar region is too narrow to observe by means of SEM. Consequently, there is no obvious porous structure after the removal of PBSU (shown in Figs. 9a and 9d). When the weight ratio of PBSU reaches 30 wt% in blend, numerous narrow pores appear and locate in the interfibrillar regions of PVDF crystal frameworks. There are also many compact parts shown in Fig. 9(e). In the case of 50% PBSU, more and more porous structure appears, suggesting the enhanced interfibrillar segregation of PBSU during the crystallization of PVDF. Meantime, the compact structure disappears as shown in Figs. 9(c) and 9(f). According to the SEM results, with increasing content of PBSU, more and more PBSU component is expelled into the interfibrillar regions of PVDF spherulites, which has a good agreement with the results shown in SAXS and DSC. The spatial confinement level of PBSU reduces since interfibrillar regime dominates the segregation of the blend. As a result, PBSU has

enough space and time to form thick lamellae, corresponding to higher melting temperature in DSC.

According to the discussion above, we can describe the exclusion behaviors of PBSU during the crystallization of PVDF, the localization of PBSU in the PVDF crystal frameworks, double peaks in SAXS and DSC results as follows (Scheme 1). In melting state, PVDF and PBSU are miscible in various compositions. Upon cooling to the crystallization temperature of PVDF, PVDF crystallizes firstly to form its crystal frameworks, and results in the phase segregation of PBSU. PBSU is confined in the interlamellar or/and interfibrillar regions of the PVDF crystal frameworks, which is dependent on the composition in blends. Low content of PBSU in blend corresponds to interlamellar segregation, accounting for the enhanced confinement effect, thinner lamellae and alternating PVDF/PBSU crystal lamellae. This is the reason for lower melting temperature in DSC (Peak 1) and higher long period in SAXS (Peak 1). On the contrary, some PBSU enriches in interfibrillar regions in addition to interlamellar regions. The larger space and higher concentration of PBSU produce own periodic lamellae

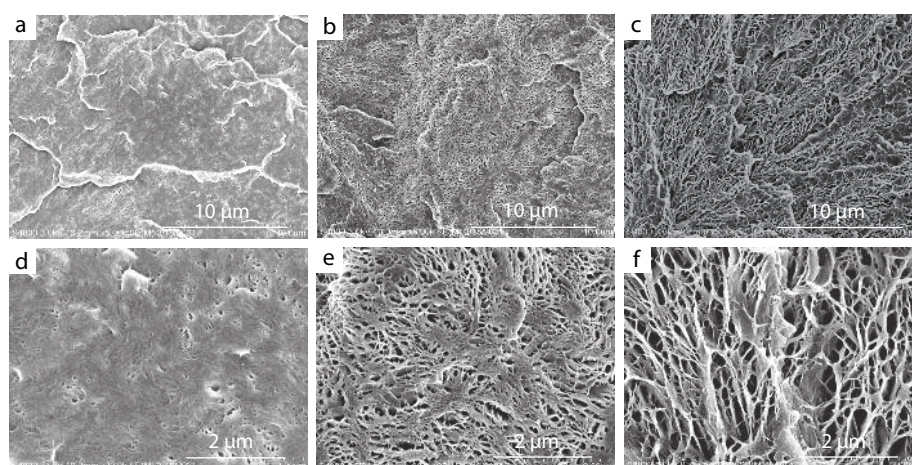
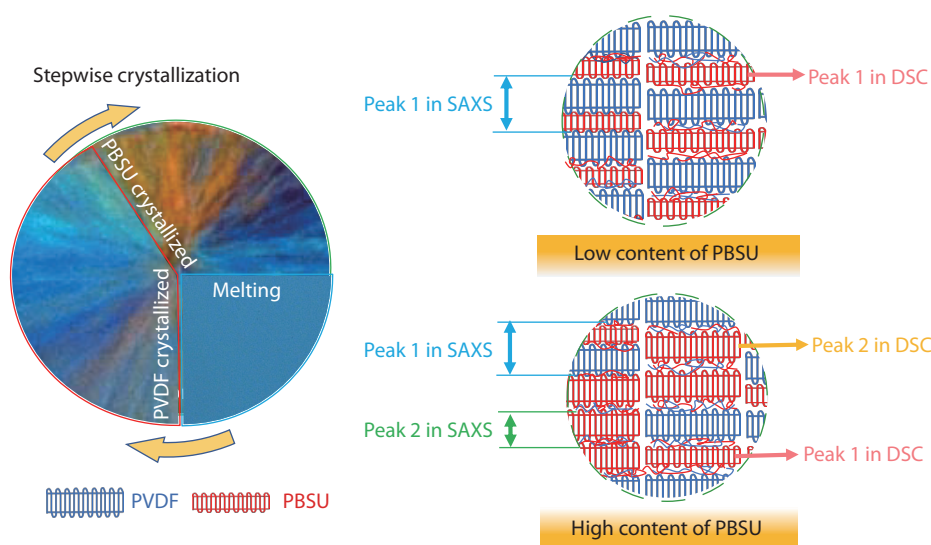


Fig. 9 SEM images of fracture structure fabricated from PVDF 80% (a, d), 70% (b, e) and 50% (c, f) after selective removal of PBSU by chloroform.



Scheme 1 Schematic illustration of Peak 1 and Peak 2 in PVDF/PBSU blend.

structure of PBSU (corresponding to comparable value of q with pure PBSU, i.e., Peak 2 in SAXS) and higher thickness of them (higher melting temperature, Peak 2 in DSC).

CONCLUSIONS

In summary, the phase segregation during the crystallization of PVDF and localization of PBSU in PVDF crystal frameworks have been investigated with the combination of SAXS and DSC. Upon stepwise crystallization at 140 °C and 80 °C, double peaks in SAXS exhibit a strong relationship with the double melting peaks of PBSU in DSC. In the case of low content of PBSU in blend, most of the PBSU has been trapped into the interlamellar region of PVDF crystal frameworks, resulting in the only long period of PVDF lamellae in SAXS and the single melting temperature of PBSU in DSC. With increasing PBSU weight fraction, the crystallization of PVDF produces co-existence of interlamellar and interfibrillar segregation of PBSU. The larger space and higher concentration of PBSU in interfibrillar region contribute to the formation of periodic lamellae structure of PBSU with higher thickness, which is the reason for the second peak in SAXS (with higher- q) and DSC (at higher temperature). Our results not only clarify the relationship between localization of PBSU in interlamellar/interfibrillar regions and double peaks behavior in DSC/SAXS, but also provide a novel strategy for detecting the interlamellar and interfibrillar segregation of low- T_m component in miscible crystalline/crystalline blend.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2718-0>.

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