Morphology and non-isothermal crystallization of *in-situ* microfibrillar poly(ethylene terephthalate)/polyethylene blend obtained *via* rod die extrusion and hot stretch

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Recently, much attention was devoted to a new *in-situ* composite, which, unlike the traditional *in-situ* composite based on thermotropic liquid crystalline polymers (TLCP) and thermoplastics (TP), contains generally two thermoplastics having distinctly different processing temperatures [1–4]. This material is usually manufactured by the following three processing steps [1]: (1) melt blending of the starting neat polymers and extrusion, (2) cold drawing of the blend, and (3) subsequent annealing of the drawn blend at constant strain and at $T_1 < T < T_2$, where T_1 is the melting temperature of the lower melting component and T_2 is that of the higher melting one. Besides, a two-step processing is also used to prepare this type of fibrillar material [2–8]: the microfibers of the component with high processing temperature are formed in the extrusion and hot stretching step, and then the blend containing microfibers is processed through extrusion, injection molding, and/or compressive molding at low processing temperature for the second component. The microfibrillar structure of the dispersed phase is preserved during the second processing step. The *in-situ* fibrillar thermoplastic blends have two crucial aspects in polymer materials and engineering field: (1) greatly enhancing the mechanical properties and heat resistance of the general-purpose polymer, mainly polyolefins, at low cost [6–9], and (2) providing a new approach to recycling of plastics [10]. In this study, the microfibrillar reinforced blend of virgin poly(ethylene terephthalate) (PET) and polyethylene (PE) was prepared *via* slit die extrusion and hot stretching, and its non-isothermal crystallization was examined.

PET and high-density PE were used in this study. PET as the microfibrillar polymer is a bottle-grade of polyester and is supplied by Yizheng, China. Its average number molecular weight ($\bar{M}_n$) is approximately 2.6×10^4. PE as the matrix is 5000S, a commercial product of Lanzhou Petroleum Chemical Co., China, and its melt flow rate (MFR) is 0.9 g/10 min at 190 °C. PET was dried in a vacuum oven at 120 °C for at least 10 hrs prior to processing. The dried PET pellets were mixed with PET pellets in a constant weight ratio of 20/80 in this study. The extrusion of PET and PE mixture was done on a common single-screw extruder with a rod-like die. The temperatures from the hopper to the die of the extruder were respectively 170, 210, 225 and 220 °C, and the screw rotation was adjusted at 50 r/m. The extrudate was hot stretched by a take-up device. The roll temperature was kept at about 35 °C. An important parameter, here, hot stretching ratio, is defined as the following: the area of the transverse section of the die to the area of the transverse section of the extrudate. Hot stretch ratio could be obtained by changing the speed of the take-up device. Generally, it was kept at 11.9 in this study. Next, the extrudate was fast quenched in cold water (25 °C).

For morphology observation, the matrix PE in the specimens was selectively dissolved by hot xylene at 110 °C for a desirable time. After the solvent volatilized completely, the surfaces were coated with a layer of gold and the domain morphology was observed in a Jeol JSM-5900LV scanning electron microscope (SEM).

The thermal properties of the three materials were determined on a Netzsch DSC 204 differential scanning calorimeter with the following standard procedure: the samples (about 8–10 mg) were melted at 200 °C for 5 min in order to eliminate any thermal history in the material, then were cooled to 40 °C at predetermined constant rates of 10, 20, 30, 40 °C /min for non-isothermal crystallizing. The experiments were carried out in nitrogen atmosphere.

Fig. 1a and b show the SEM micrographs of PET/PE common and microfibrillar reinforced blends, respectively. It can be seen from Fig. 1a that the common blend has a typical incompatible blend morphology, which comprises discrete domains of the minor component dispersed within a continuous phase of the major component. No phase orientation or difference in shape of the dispersed domains is observed. Besides, no evidence shows that some interfacial interactions or adhesion exists, indicating that these two polymers are extremely immiscible. Fig. 1b displays well-defined microfibrillar morphology and implies that PET microfibers were generated *in situ* during rod extrusion and hot stretching. The diameters of the microfibers are rather uniform, and around 1.0 μm, whereas their length and aspect ratio cannot be known since one cannot see intact fibers [11].

The crystallization exotherms of neat PE, PET/PE common and microfibrillar blends at a predetermined cooling rate of −20 °C/min are presented in Fig. 2. Based on these curves, some useful parameters, such

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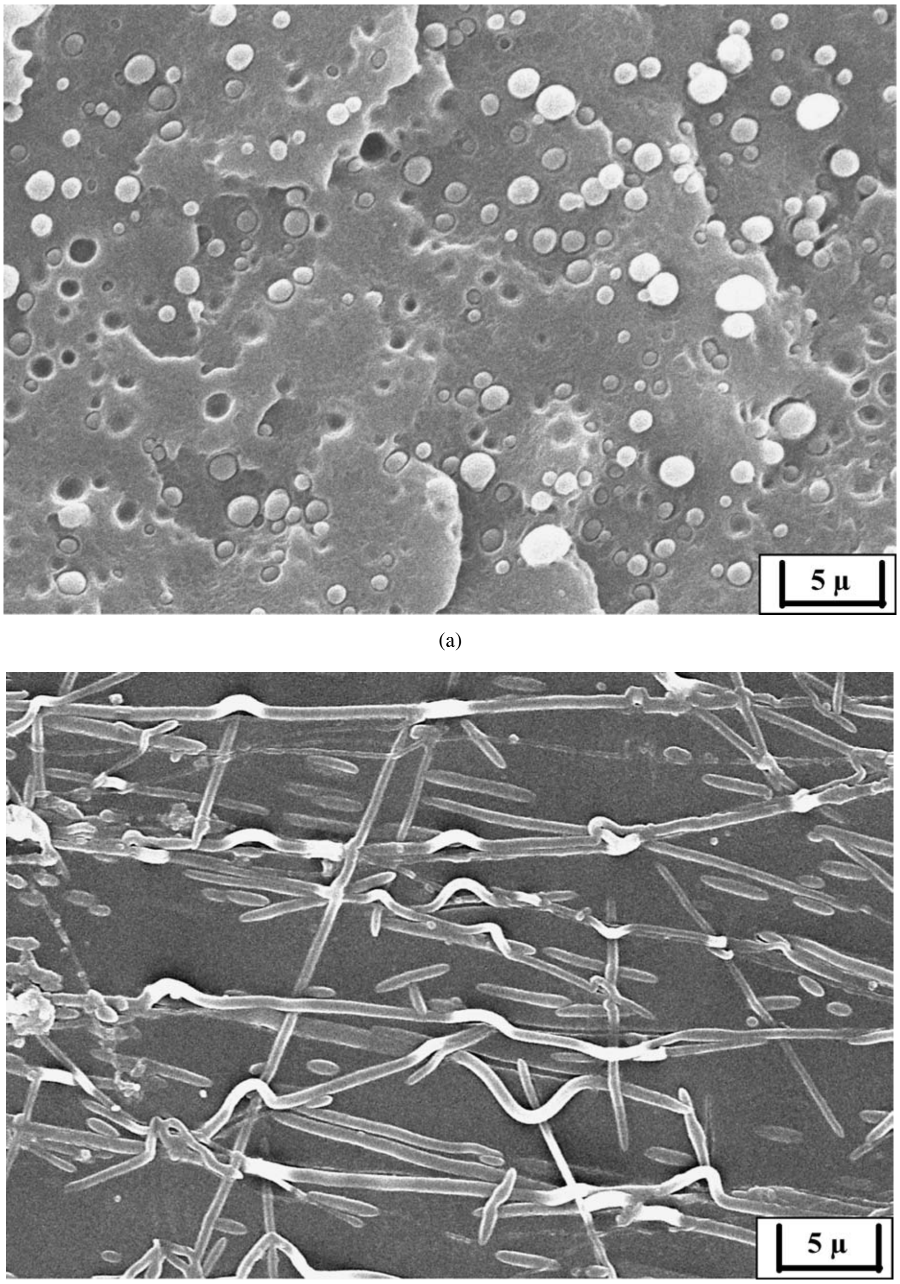

(a)

(b)

Figure 1 SEM micrographs of PET/PE common and microfibrillar reinforced blends, respectively: (a) the frozen fracture surface for common PET/PE blend and (b) the etched surface by hot xylene for PET/PE microfibrillar blend.

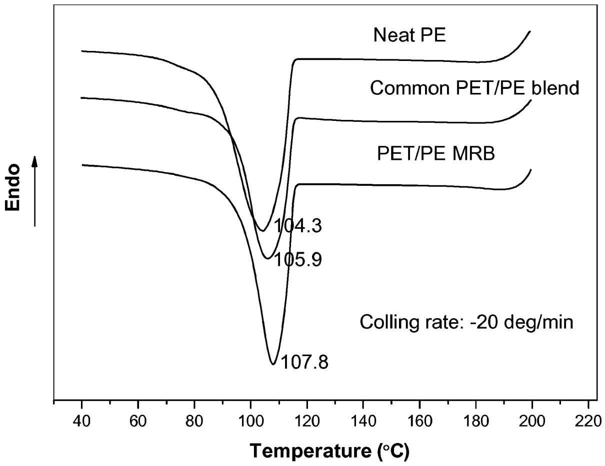

Figure 2 Nonisothermal crystallization thermograms of neat PE, PET/PE common and *in-situ* microfibrillar blends at a predetermined cooling rate of −20 °C/min.

as onset and peak or maximum crystallization rate temperatures (T_0 and T_p, respectively), undercooling temperature (ΔT_c), maximum crystallization time (t_{max}, time required to crystallize from T_0 to T_p) and half crystallization time ($t_{1/2}$) can be obtained for describing the non-isothermal crystallization behavior of these three materials studied [11]. As shown in Table I, at a cooling rate of −20 °C/min, for PET/PE microfibrillar blend, T_0 and T_p are the highest, while t_{max} and $t_{1/2}$ are lowest among three materials, and for PET/PE common blend, T_0 and T_p are higher, t_{max} and $t_{1/2}$ are lower than those for neat PE. On the basis of these results, it implies that the PET/PE *in-situ* microfibrillar blend crystallizes faster than does PET/PE common blend, and PET/PE common blend crystallizes faster than does neat PE. In other words, PET phase in PE acts as heterogeneous nuclei during non-isothermal crystallization process [12], and hence the crystallization rate

TABLE I Crystallization parameters of neat PE, PET/PE common and *in-situ* microfibrillar blends obtained directly from DSC curves.

	PE							PET
Sample	T_0 (°C)	T_p (°C)	ΔT_c (°C)	t_{max}(s)	$t_{1/2}$(s)	T_m (°C)	X_c (%)	T_m (°C)
Neat PE	118.3	104.3	32.9	21.0	25.6	137.2	73.9	
PET/PE common blend	118.3	105.9	29.6	18.6	20.2	135.5	63.4	255.1
PET/PE microfibrillar blend	117.4	107.8	27.0	14.4	17.0	134.8	61.6	253.6

of PE phase is enhanced, especially, when PET phase is deformed into microfibers during processing, and its effect on PE crystallization is considerably enhanced [10].

The relative crystallinity (X(T)) is expressed as

$$X(T) = \int_{T_0}^{T} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t \bigg/ \int_{T_0}^{T_2} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t \qquad (1)$$

where T_0 and T_2 are the onset and end of crystallization temperatures, respectively; $\mathrm{d}H/\mathrm{d}t$ is the heat-evolution rate. Fig. 3 shows the relative crystallinity, $X(T)$, as a function of temperature for PE, PET/PE common and microfibrillar blends at a predetermined cooling rate of $-20\,^{\circ}$C/min. All these curves have the same sigmoidal shape, indicating the lag effect of cooling rate upon crystallization. Using the following expression, $t = (T_0 - T)/R$ (where T is the temperature at crystallization time t, and R is the cooling rate), the abscissa of temperature in Fig. 3 can be transformed into a time scale as shown in Fig. 4. These curves show that at the same crystallization time, PET/PE *in-situ* microfibrillar blend has the highest relative crystallinity among three materials; the relative crystallinity of PET/PE common blend is higher than that of neat PE.

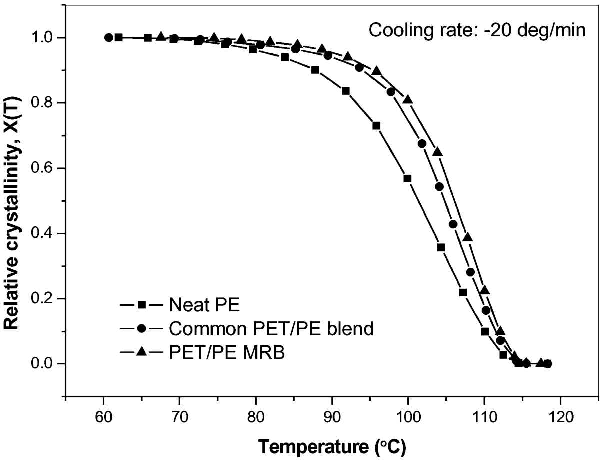

Figure 3 Relation between relative crystallinity and temperature for PE, PET/PE common *in-situ* microfibrillar blends in nonisothermal processes at a predetermined cooling rate of –20 °C/min.

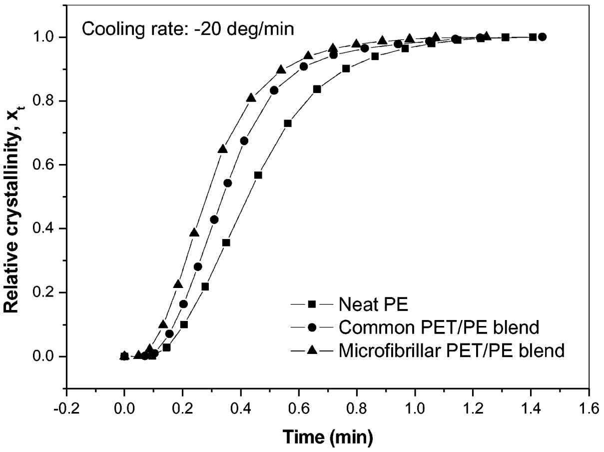

Figure 4 Relation between relative crystallinity and time for PE, PET/PE common *in-situ* microfibrillar blends in nonisothermal processes at a predetermined cooling rate of $-20\,^{\circ}$C/min.

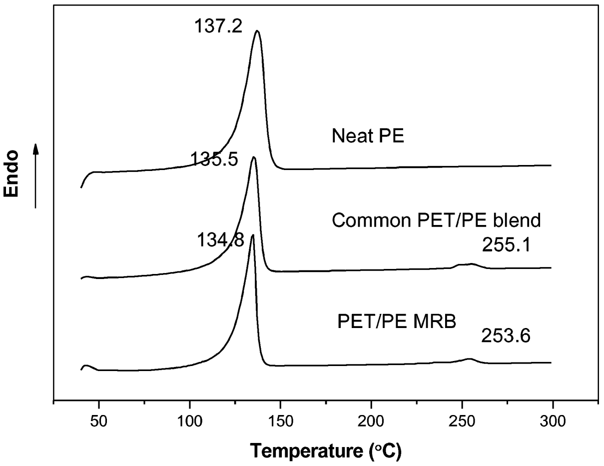

Figure 5 DSC curves (a heating rate of 20 °C/min) of PE phase in neat PE, PET/PE common and *in-situ* microfibrillar blends which were obtained by nonisothermally crystallized at a predetermined cooling rate of $-20\,^{\circ}$C/min (see Fig. 2).

The melting behaviors of the neat PE, PET/PE common and microfibrillar blends are shown in Fig. 5. Furthermore, melting temperatures and crystallinity of neat PE, and PE and PET in the blends, obtained from DSC scans of the non-isothermally crystallized samples, are also presented in Table I. Some investigations show that the incorporation of the existing PET fibers has little or no effect on the melting temperature of polymer matrix under isothermal conditions [13]. In this case, a slight decrease in melting temperature and crystallinity of PE for PET/PE common and microfibrillar blends is observed as compared to the neat PE. This implies that incorporation of PET droplets and *in-situ* microfibers makes PE crystals imperfect. For PET phase, the factors influencing its melting temperature are various: (1) during fabrication of the microfibrillar blend, hot stretching gives rise to some molecular orientation of PET, which facilitates its crystallization; (2) on the other hand, to preserve the *in-situ* microfibers in the blend, quenching of the extrudate was used, which results in imperfect PET crystals; (3) In the process of the non-thermal crystallization of PE, PET phase has secondary crystallization. The combined result of these factors makes the melting temperature of PET microfibrillar phase in the microfibrilar blend slightly lower than that of PET droplets in the PET/PE common blend.

In summary, rod die extrusion and hot stretch can produce well-defined PET *in-situ* microfibers in PET/PE blend. No matter whether the PET phase in the PE matrix are spherical particle or microfibers, they have heterogeneous nucleation for PE crystallization, but the effect of microfibers is more marked.

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