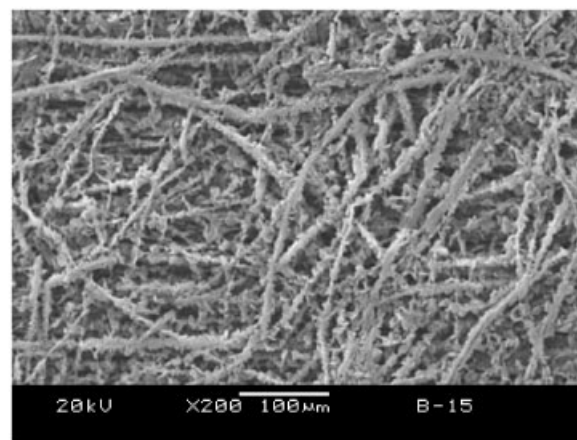


**Summary:** In this present study, the in situ fabrication of a microfibrillar composite based on poly(ethylene terephthalate) (PET), polyethylene (PE), and carbon black (CB) is attempted. PET and CB were first melt mixed. The CB/PET compound and PE were subsequently melt extruded through a slit die and then hot stretched. The morphological observation of the as-stretched extrudate indicated that well-defined microfibers of CB/PET compound could be generated at appropriate CB contents and a fixed hot stretch ratio. In addition, CB was always selectively located in PET. The microfibrillar CB/PET/PE composite has the potential to be a new electrically conductive polymer composite.

Morphology of the carbon black/poly(ethylene terephthalate)/polyethylene (PE) composite after additional mixing in the mixer at the processing temperature of PE.



# Formation of in situ CB/PET Microfibers in CB/PET/PE Composites by Slit Die Extrusion and Hot Stretching

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## Introduction

Blending and alloying have long been demonstrated as an effective way to improve properties of an existing polymer.<sup>[1]</sup> However, most polymer blends are thermodynamically immiscible and also technologically incompatible, hence they form multi-phase systems during processing.<sup>[2]</sup> The immiscibility and/or incompatibility can deteriorate the properties of these types of polymer materials. Fortunately, owing to the deformable nature of the dispersed phase in the immiscible blends, various morphologies can be generated in situ during processing, some of which give rise to the properties of the blends.<sup>[3–6]</sup> It is well known that fibers are capable of greatly enhancing the mechanical properties of the fiber/polymer composite when the mechanical properties of the fibers are superior to

the polymer matrix and the interfacial interaction between fibers and matrix is strong enough. Therefore, some measures have been taken to make the dispersed phase deform in situ into fibers, even microfibers. One typical example is the in situ formation of thermotropic liquid crystalline polymer (TLCP)/thermoplastics (TP) as a composite.<sup>[7–9]</sup> Another example is the in situ microfiber reinforced blend based on two TPs having distinctly different processing temperatures. In the latter case, the specific process of the microfibrillar blend proposed by Evstatiev and his co-workers is:<sup>[10]</sup> (1) extrusion at the processing temperature of the higher melting component of the blend; (2) cold stretching to orient both components of the blend; and (3) annealing at a processing temperature that is between the melting temperature of the low and the high melting components to cause isotropization of the lower melting

component. In the last step, a similar objective can also be reached through extrusion, injection molding, and/or compressive molding at a processing temperature of a lower processing-temperature component. Evstatiev et al.<sup>[10–13]</sup> prepared an in situ composite of poly(ethylene terephthalate) (PET) and polyamide (PA) and found that the composite had large deformability as well as mechanical properties comparable to those of glass-fiber reinforced materials. Recently, a two-step process has also been employed to prepare this type of material.<sup>[14]</sup> They include: 1) in a first extrusion and hot-stretching step at a processing temperature of the higher-melting component, the fibrillar morphology of the higher-melting component is elaborated; and then 2) in a second step, the material containing microfibers is processed through extrusion or/and injection molding at a processing temperature of the lower-melting component so that the fibrous structure of the dispersed phase can be maintained during this processing step. TP/TP in situ composites provide a promising route to enhance properties of general-purpose polymers, and to also deal with the recycling of waste plastics.<sup>[12,14–16]</sup>

In previous work,<sup>[17–20]</sup> we prepared a series of PET/polyolefins (mainly polyethylene (PE) and polypropylene (PP)) microfibrillar blends by a slit die extrusion-hot stretching-quenching process, and reported significant reinforcement to the blend as well as high nucleation for polyolefins of the in situ PET microfibers.

On the other hand, existing polymers are constantly compounded with organic or inorganic fillers for the purpose of decreasing the cost and/or adding some new functions like electrical and thermal conductivity. A problem remains whether a polymer/organic or inorganic filler compound can deform in situ into microfibers in a polymer-based composite during processing. This is crucial in practice, because the microfibers can be functionalized so long as the fillers have functional characteristics. For example, when electrically conductive fillers such as carbon black (CB), carbon fibers, carbon nanotubes, graphite, etc. are distributed into a polymer (carrier polymer), the microfibers of the conductive fillers/carrier polymer compound have electrical conductivity, and the microfibrillar composite is also electrically conductive. In the available literature, this case has not been reported, though deformation and fibrillation of the dispersed phase in a polymer blend have been widely investigated.<sup>[2,21–30]</sup> In this study, our interest lies in the possibility that in situ microfibrillation of a CB/PET compound may occur in a PE matrix through slit die extrusion and hot stretching.

## Experimental Part

### Materials

The main materials used in this study include conductive CB, PET, and high density PE. The CB from National Chemical

Co. Ningxia, China, with a dibutyl phthalate (DBP) absorption of  $120 \text{ cm}^2 \cdot (100 \text{ g})^{-1}$  and an original particle diameter of ca. 34 nm, was dried at  $120^\circ\text{C}$  for 10 h before use. The PET is a commercial grade of textile polyester and is supplied by LuoYang Petroleum Chemical Co., China. Its number-average molecular weight is approximately  $2.3 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$ . PE is 5000S, a commercial product of DaQing Petroleum Chemical Co., China, and its melt flow rate is  $0.9 \text{ g} \cdot (10 \text{ min})^{-1}$  at  $190^\circ\text{C}$ .

### Sample Preparation

PET was dried in a vacuum oven at  $100^\circ\text{C}$  for at least 12 h prior to processing. The CB/PET/PE composite was obtained using the following three steps. First, the binary conductive CB/PET compound was prepared by mixing CB and PET at the processing temperature ( $270^\circ\text{C}$ ) of PET in an internal mixer. The PET was added into the preheated rotating internal mixer and allowed to mix for 5 min. After the addition of the CB, the compound was then allowed to mix for an additional 5 min. Second, the stretched ternary CB/PET/PE composite was obtained by a slit die extrusion-hot stretching-quenching process at the processing temperature of the PET. The extrusion of the mixture of the binary CB/PET blend and the PE was performed in a single-screw extruder. The temperature profile used for the extruder was 190, 250, 280, and  $270^\circ\text{C}$  from hopper to die. The die for the extruder is a slit die, 15 mm wide and 2.0 mm high. The extrudate was hot stretched by a take-up device with two pinching rolls to form the microfibers. The line speed of the rolls was  $16.0 \text{ mm} \cdot \text{s}^{-1}$ . The roll temperature was kept at about  $40^\circ\text{C}$  through adjusting the volume flow rate of tap water in them. Subsequently, the extrudate was immediately quenched in cold water ( $20^\circ\text{C}$ ) after stretching, and finally a thin ribbon with a thickness of about 0.2 mm was obtained. Third, the CB/PET/PE composite ribbon was mixed in the mixer for 2 min at the processing temperature ( $170^\circ\text{C}$ ) of PE (much less than the processing temperature of PET) to produce an isotropic PE matrix and construct a three-dimensional microfiber network. For comparison purposes, the mixture of CB, PET, and PE was directly mixed in the mixer at  $270^\circ\text{C}$  for 10 min. The hot stretched composite is hereafter referred to as *s*-CB/PET/PE composite, and the directly mixed composite as *d*-CB/PET/PE. The composite obtained was compression molded at a pressure of ca. 10 MPa for 20 min at  $170^\circ\text{C}$  into 4.0 mm thick plaques, and was then quenched by cold compression molding (about  $20^\circ\text{C}$ ).

### Morphology Observation

For morphological observations with an electron microscope, the specimens were frozen in liquid nitrogen for one hour, then quickly impact fractured. The surfaces were covered with a layer of gold to make them conductive, and they were then observed with a JEOL JSM-5900LV scanning electron microscope (SEM). In order to clearly examine the morphology of the dispersed phase, some specimens were immersed in hot xylene for 60 min to etch away the PE matrix. To observe the crystalline morphology of the specimens, an optical microscope Olympus BX 51 model was used. In practical examination, it was found that the crystalline morphology for the

undiluted composite was hard to identify. Hence the microfibrillar composite was mixed with some fresh neat PE resin at 200 °C in the attached mixer of a Haake rheometer to be diluted to 1 wt.-% CB/PET concentration. The phase morphology of CB/PET can be maintained under such mixing temperature since the melting temperature of PET is much higher than 200 °C.

### Rheological Property Testing

The rheological behaviors of the CB/PET blend, neat PET, and neat high-density polyethylene (HDPE) were tested by a capillary rheometer GOETTFER RHEOGRAPH 2002 at 270 °C. The diameter of the die was 1.0 mm and its length/diameter ratio was 30.

## Results and Discussion

Figure 1 shows the representative SEM micrographs of the cryofractured surface of a *d*-CB/PET/PE composite. It displays a typical incompatible morphology where the interfaces are very clear and there is no evidence of any adhesion. Taking into account the composition of the ternary composite, it is believed that the continuous phase is PE. The smaller domains with irregular geometry are

exclusively CB agglomerates. The larger domains in the PE matrix are PET, based on the fact that they contain very fine CB particles. Evidently, the CB particles are non-uniformly distributed in the whole system, and preferentially localized in the PET phase. It is interesting that the CB particles in the PET domains seem to be finely dispersed, while those in the PE matrix tend to form agglomerates.

Regarding the mechanism of the heterogeneous distribution of a conductive filler in an incompatible polymer blend, Wu et al.<sup>[31]</sup> recently found that the entropy penalty may play a main role in such systems. Nevertheless, it is still widely accepted to use Young's equation to predict the selective distribution of CB in a polymer blend, which was suggested by Sumita et al.<sup>[32]</sup> for the first time:

$$w_a = \frac{\gamma_{CB-\beta} - \gamma_{CB-\alpha}}{\gamma_{\alpha-\beta}} \quad (1)$$

where  $w_a$  is the wetting coefficient,  $\gamma_{CB-\alpha}$ ,  $\gamma_{CB-\beta}$ , and  $\gamma_{\alpha-\beta}$  are, respectively, the interfacial tension between CB and  $\alpha$ -polymer, between CB and  $\beta$ -polymer, and between  $\alpha$ - and  $\beta$ -polymers. CB particles are expected to be selectively located in one of two polymer phases where the polymer has a higher interaction with the CB surface:  $w_a > 0$ , that is,  $\gamma_{CB-\alpha} > \gamma_{CB-\beta}$ , CB particles in  $\beta$ -polymer or at the interface;  $w_a < 0$ , that is,  $\gamma_{CB-\alpha} < \gamma_{CB-\beta}$ , CB particles in  $\alpha$ -polymer or at the interfaces. These predictions were in agreement with the observation of a transmission electron microscopy (TEM) micrograph in some CB-filled polymer composites.<sup>[32]</sup>

Wu's harmonic mean average equation can estimate the interfacial tension between the two polymers,<sup>[33]</sup> which is

$$\gamma_{\alpha-\beta} = \gamma_{\alpha} + \gamma_{\beta} - 4 \left[ \frac{\gamma_{\alpha}^d \gamma_{\beta}^d}{\gamma_{\alpha}^d + \gamma_{\beta}^d} + \frac{\gamma_{\alpha}^p \gamma_{\beta}^p}{\gamma_{\alpha}^p + \gamma_{\beta}^p} \right] \quad (2)$$

where  $d$  and  $p$  are, respectively, the dispersion component of surface tension and the polar component of surface tension.

According to the available literature,<sup>[33]</sup> in the ternary CB/PET/PE composite, the interfacial tensions between CB and PET is  $5.89 \text{ mN} \cdot \text{m}^{-1}$ , and that between CB and PE is  $13.1 \text{ mN} \cdot \text{m}^{-1}$ . A very high probability exists that CB is better adhered to PET than to PE because of its lower interfacial tension, or the larger affinity characterizing the CB/PET system.

Figure 2 shows the SEM micrographs of the cryofractured surfaces of the CB/PET/PE composite just at the exit of the slit die without hot stretching. It displays more or less orientation of a dispersed phase but no in situ microfibers. Unlike the *d*-CB/PET/PE composite shown in Figure 1, all CB particles are located in the PET phase in the CB/PET/PE composite. It is reasonable because; (1) the interfacial adhesion between CB and PET is stronger than that between CB and PE, and (2) the previous mixing of CB and PET allows them to have sufficient time to mix harmoniously before addition of PE. As a result of this thermodynamic

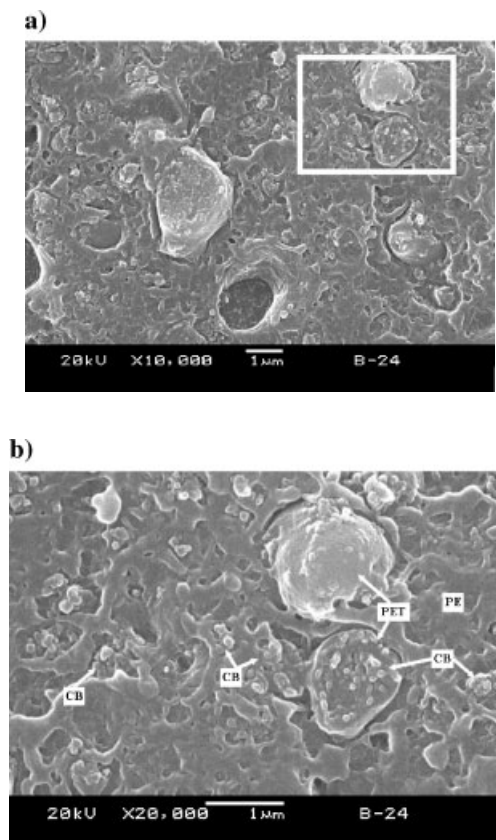


Figure 1. Morphology of the cryofractured surface of directly mixed *d*-CB/PET/PE (10/30/70) composite. (b) The magnified micrograph of the rectangular region in (a).



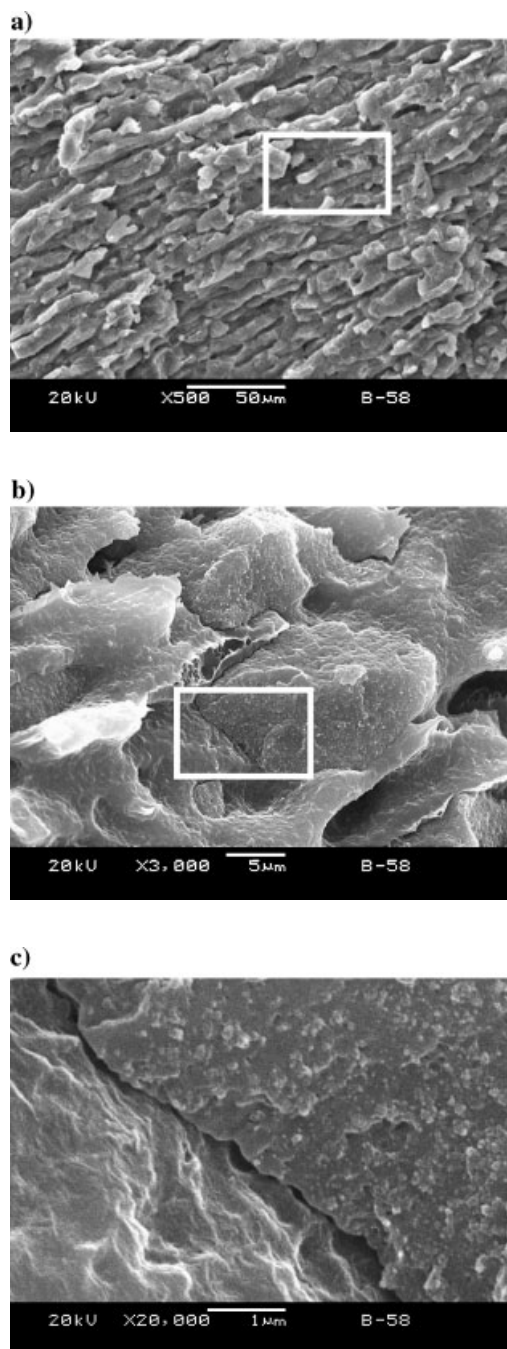


Figure 2. Morphology of the CB/PET/PE composite just at the exit of the slit die (no hot stretching). (b) The magnified micrograph of the rectangular region in (a), and (c) is that in (b).

nature and thermal history, CB cannot move from PET to PE when the binary CB/PET compound is further melt mixed with PE. It can also be seen in Figure 2 that CB particles distribute in PET very well and there are nearly no obvious CB agglomerates. On the other hand, an evident gap between the CB/PET phase and the PE matrix exists as observed in the SEM micrograph (Figure 2c) with higher

magnification, indicating that the two phases have weak interfacial adhesion. This may be valuable for the formation of in situ microfibers during hot stretching, but goes against the mechanical properties.

Figure 3 shows the SEM micrographs of *s*-CB/PET/PE with various CB loadings. The PE matrix was etched away by hot xylene. Evidently, fine in situ microfibers of the CB/PET compound were generated as the CB content in the composites was 5, 7.5, and 10 phr. The microfibers are so long that they cannot be fully observed in these micrographs, while their diameters for these three CB loadings are all about 5–10 μm, indicating that the CB/PET microfibers have a rather high aspect ratio. When the CB loading reaches 15 phr, the CB/PET dispersed phases can also deform into microfibers, but their lengths are much shorter. As the CB loading increases further up to 20 phr, no in situ microfibers can be found, and the CB/PET compound only exhibits a weak tendency to orientate.

Deformation of a dispersed phase in an incompatible polymer blend has long been studied to understand the nature of deformation of a blend during processing from rheological and morphological points of view.<sup>[34–36]</sup> It is well known that the morphology resulting from blending and processing depends mainly upon the rheological and interfacial properties, the viscosity ratio, the blend composition, the mixing parameters, and the mixing mode. For Newtonian systems,<sup>[26,37]</sup> the dispersed phase deformation process is controlled by the viscosity ratio  $p = \eta_d/\eta_m$  and the capillarity number  $Ca = \eta_m \dot{\gamma}/(\sigma/R)$ , where  $\eta_d$  is the viscosity of the dispersed phase,  $\eta_m$  is the matrix viscosity,  $\dot{\gamma}$  is the shear rate,  $\sigma$  is the interfacial tension, and  $R$  is the dispersed particle radius. The capillarity number  $Ca$  can be understood as the ratio between the hydrodynamic stress  $\eta_m \dot{\gamma}$  acting to deform the particle, and the interfacial stress  $\sigma/R$  leading to minimize the surface energy and to keep the particle in its equilibrium spherical shape. Beyond a critical value  $Ca_{crit}$  of the capillarity number, the particle will be elongated and may break up into smaller droplets. The value of  $Ca_{crit}$  has been revealed to depend strongly on the viscosity ratio  $p$  as well as on the type of flow, simple shear or elongational flow. Many studies have shown that an elongational flow field and a small viscosity ratio (usually less than or close to unity) facilitate the deformation (especially fibrillation) of the dispersed phase in the polymer blend.<sup>[24,25,38,39]</sup> As discussed above, though deformation and fibrillation of the dispersed phase in a polymer blend have been widely studied, the fibrillation of a dispersed phase containing rigid particles is not mentioned in the available literature. Even so, it can also be analyzed by the mechanism of deformation of disperse phase. That is, the viscosity ratio (the ratio of the viscosity of the dispersed phase to the viscosity of the matrix) and the type of flow (shearing flow or stretching flow) are the most important factors influencing the deformation of the dispersed phase or the fibrillation of the dispersed phase. Generally, a low

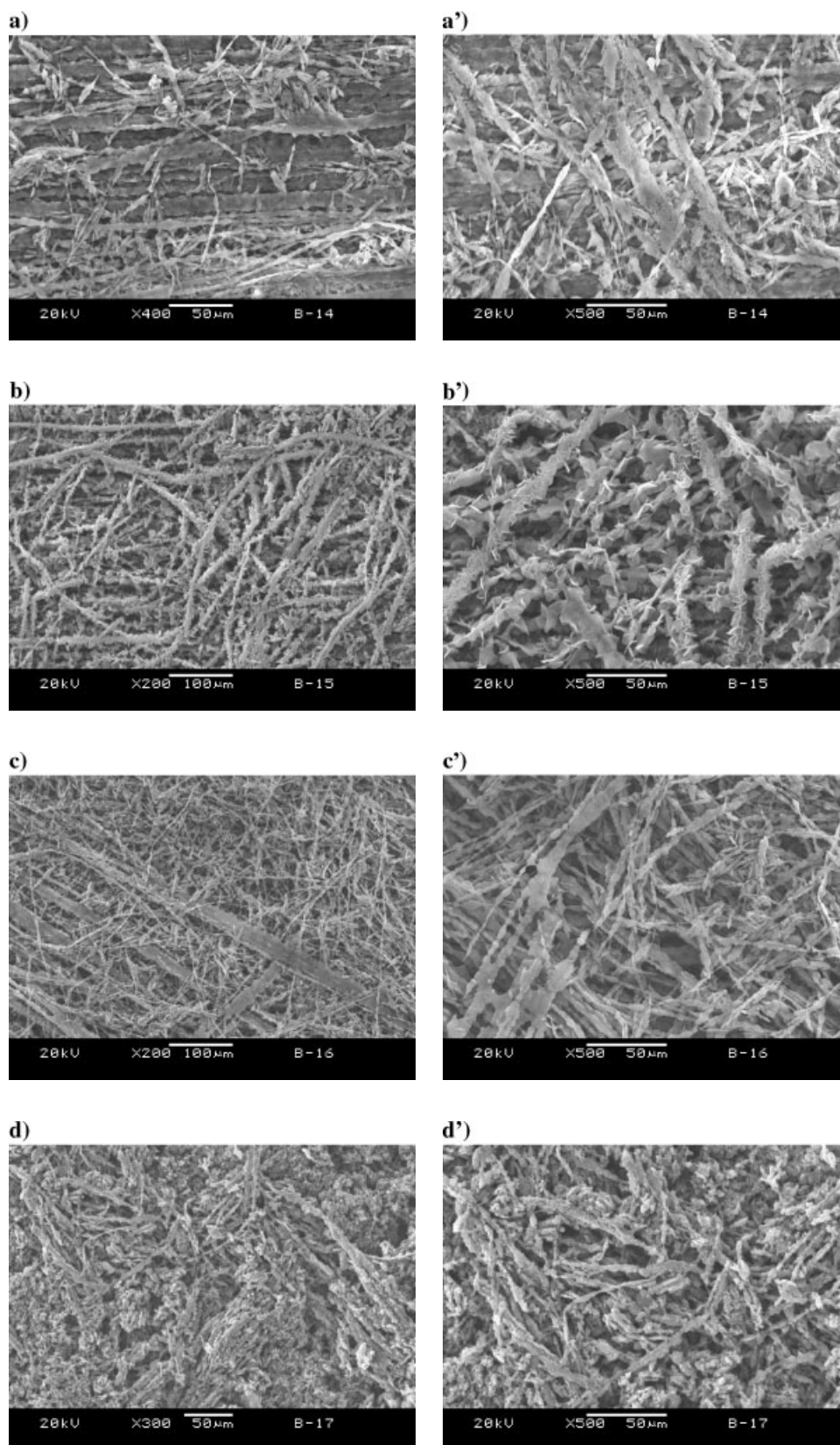


Figure 3. SEM micrographs of the *s*-CB/PET/PE composites with different CB loading. The CB loading: (a) and (a') 5 phr; (b) and (b') 7.5 phr; (c) and (c') 10 phr; (d) and (d') 15 phr; (e) and (e') 20 phr. The composition for PET and PE is 30:70 by weight.

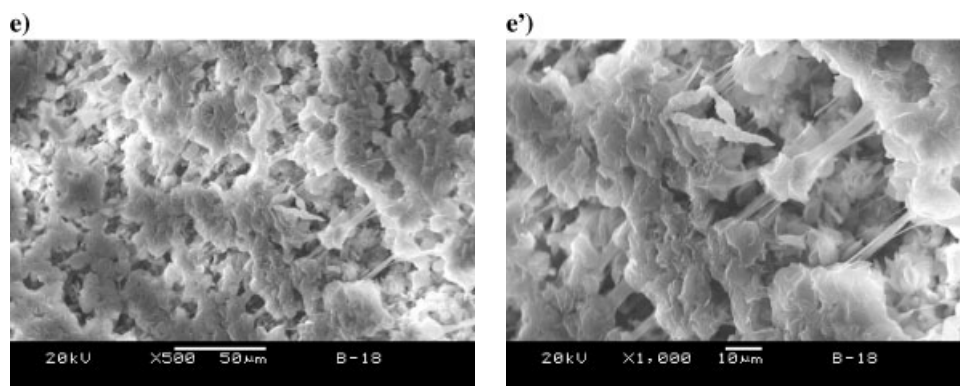


Figure 3. (Continued)

viscosity ratio ( $\leq 1$ ) and stretching flow can facilitate the deformation and fibrillation of the dispersed phase in a blend.<sup>[34–39]</sup> However, in a previous study, it was proved that some systems with a viscosity ratio higher than unity, such as a PC/PE blend can also form in situ microfibers under the influence of hot stretching.<sup>[40]</sup> In this study, CB can greatly increase the melt viscosity and, at the same time, decrease the melt strength of CB/PET because of its solid state at the processing temperature of PET. The higher the CB content is, the larger the melt viscosity of CB/PET, and thus the larger the viscosity ratio of the CB/PET and PE matrix. Figure 4 shows the relationship between the apparent viscosity and the shear rate for neat PE, neat PET, and CB/PET compounds with different CB loadings at 270 °C. Over the range of shear rates tested, the viscosity of neat PET is the lowest, and then the CB/PET blends. The melt viscosity of neat PE is larger than the CB/PET compounds with 5/30, 7.5/30, and 10/30 (by weight), corresponding to

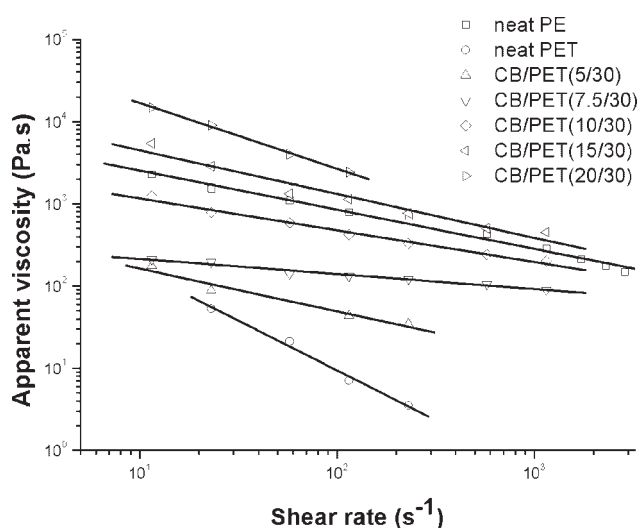


Figure 4. Correlation between apparent viscosity and shear rate of neat PET, neat PE, and CB/PET compounds with different CB loading.

*s*-CB/PET/PE with 5, 7.5, and 10 phr CB loadings, respectively, and lower than the compounds with 15/30 and 20/30, corresponding to *s*-CB/PET/PE with 15 and 20 phr CB loadings, respectively. Hence, the viscosity ratios of CB/PET compounds to the matrix PE at CB contents of 5, 7.5, and 10 phr are less than 1, and those at 15 and 20 phr are larger than 1. As a result, fibrillation is easy for the former, and hard for the latter. This is in agreement with the experimental results shown in Figure 3. It must be pointed out that the hot-stretching effect should not be ignored, which can be confirmed by two points: (1) the CB/PET dispersed phases cannot deform into microfibers without stretching effect, even though the viscosity ratio is less than 1 (see Figure 2), and (2) in situ microfibers can also come into being even if the viscosity ratio is larger than 1 if the system has experienced stretching flow (see Figure 3d).

As mentioned above, this in situ microfibrillar CB/PET compound has the potential to make the composite electrically conductive because CB is a typical conductive filler, and in particular, CB/PET microfibers may form a three-dimensional (3-D) conductive network. In the present work, we did a preliminary study of the construction of the 3-D conductive network. In order for isotropization of the orientation alignment of the microfibers in the extrudate, *s*-CB/PET/PE was additionally mixed at the processing temperature of PE matrix (170 °C), which is much lower than the processing temperature of PET (about 260 °C), and the in situ CB/PET microfibers can survive in the system. Figure 5 shows a micrograph of the cryofractured surface of a *s*-CB/PET/PE composite after additional mixing. Apparently, the microfibers are successfully maintained. Figure 5b shows the enlarged view of Figure 5a. It can be seen that all the CB particles are selectively located in the microfiber, which is the same as in the composite before stretching (see Figure 2). This can further confirm that CB cannot migrate from the PET to the PE matrix during the processing. Note that Figure 5 only shows a limited region of the microfibers network. To observe the network of microfibers better, CB/PET microfibers was diluted to 1 wt.-% and observed by an optical microscope. Figure 6 shows



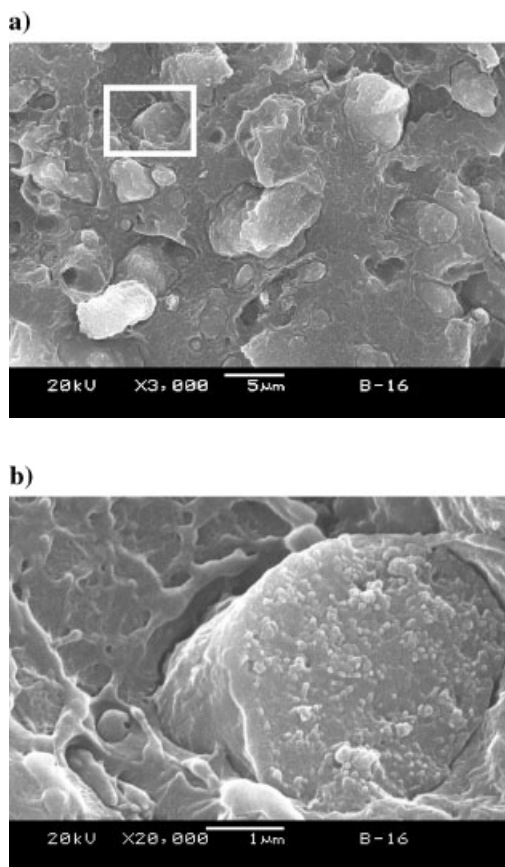


Figure 5. Morphology of the *s*-CB/PET/PE composite after additional mixing in the mixer at the processing temperature of PE (170 °C). (b) The magnified micrograph of the rectangular region in (a).

the OM micrograph of the diluted composite. It displays a CB/PET microfibrillar network. However, the integrated network cannot yet be observed because the content of microfibers in the diluted system is too low. Unfortunately, as observed from Figure 6, some microfibers have broken during the additional mixing.

## Conclusions

1. Through slit die extrusion and hot stretching, a new in situ microfibrillar composite based on CB, PET, and PE was prepared, in which an in situ CB/PET compound is deformed into microfibers. CB particles are always selectively located in PET phase as a result of thermodynamics.

2. CB content is one of the important factors to control the formation of in situ microfibers. The well-defined CB/PET microfibers can be formed at lower CB contents. Hot stretching is another important factor. Microfibers can also come into being when the viscosity ratio is higher than 1 under the influence of hot stretching.

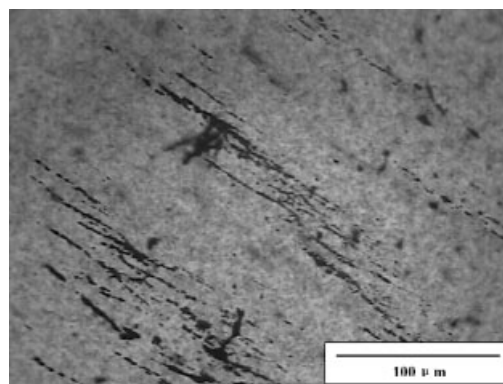


Figure 6. OM micrograph of the *s*-CB/PET/PE composite with 1 wt.-% CB/PET microfibers.

3. In situ CB/PET microfibers can survive after further processing at the processing temperature of the PE matrix, which makes it possible to generate a composite with an electrical in situ microfibrillar network.

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