

SUPERIOR TENSILE EXTENSIBILITY OF PETG/PC AMORPHOUS BLENDS INDUCED *VIA* UNIAXIAL STRETCHING*

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Abstract A simultaneous increase of both stiffness and extensibility of poly(ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate) (PETG)/polycarbonate (PC) blends prepared through the slit die extrusion-uniaxial cold stretching process was observed. The stretched sheets have a unique mechanical character that an increased tensile modulus is accompanied by an increased extensibility with increasing the draw ratio. Especially, a sharp increasing of the extensibility is observed for PETG/PC (70/30 wt%) blends at draw ratios between 8.2 and 20.0, where a nine times increase of extensibility is achieved. The mechanism of stretching-induced superior extensibility is investigated *via* micrograph observation, rheometry and calorimetric analysis. The observed superior extensibility could be tentatively explained by the bridging effect of the PC microfibrils on the crack development during tensile failure.

Keywords: *In situ* fibrillation; Amorphous blends; Extensibility; Uniaxial stretching.

INTRODUCTION

For achieving excellent comprehensive performance, fabrication of polymer blends (polymer alloy) *via* melt compounding process is a convenient means widely used in industrial manufacture. However, it is not simple as merely compounding various polymer components together. The structural/morphological manipulations in blends, including dispersed phase morphology, crystalline structure, interaction between different components, *etc.*, are the important factors determining the final performance. There are many strategies to realize the structural design in polymer blends, such as adjusting blend composition, adding interfacial compatibilizer, varying viscosity ratio of matrix/dispersed species and applying thermal annealing treatment^[1]. Herein, the shear flow and extension effect frequently involved in dynamic melt processing are particularly emphasized to induce anisotropic, oriented structure, resulting in high strength, modulus^[2–6], thermal stability^[7], conductivity^[8, 9] and low gas permeability^[10, 11]. For some appropriate blend systems, the *in situ* fibrillation phenomenon may appear during extrusion, injection molding, blowing film and extension stretching^[12–15].

There exists an experimentalism criterion that the viscosity ratio of dispersed phase to matrix phase should be less than unity, in order to generate *in situ* fibrillar morphology. This criterion, however, is not absolutely proper. In the study by Xu *et al.*^[16, 17], the melt viscosity of fibrillation phase, polycarbonate (PC), was prominently higher than that of matrix, high density polyethylene (HDPE). Therefore, the necessary condition for fibrillation in blend is argued by far. It may be a synergistic effect resulted from various factors. In most

* This work was financially supported by the National Natural Science Foundation of China (Nos. 50533050, 20874064 and 50873063).

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Received January 27, 2010; Revised March 5, 2010; Accepted March 19, 2010

doi: 10.1007/s10118-010-1006-6

researches concerning the *in situ* fibrillation of blend, the investigated subjects are semicrystalline/semicrystalline^[18–22] or semicrystalline/amorphous systems^[15], especially, the basis phase should be a crystallizable polymer. It is imaginable that the crystallizable polymers are favorable for preserving anisotropically oriented structure induced by shear flow or extension field through the formation of crystalline phase with low mobility and relaxation possibility. In a common manner, the highly anisotropic crystalline structure or the formation of stiff fibrillous rods can dramatically improve tensile strength, modulus and rigidity, simultaneously, result in a poor extensibility (low elongation at break)^[20, 23, 24]. On the other hand, the totally amorphous blend in which an easily fibrillated noncrystallizable polymer is dispersed in another noncrystallizable polymer has been rarely investigated in the past studies. It is attractive to probe the differences of mechanical behavior, morphological characteristics and fibrillation mechanism between crystallizable blends and noncrystallizable blends.

Poly(ethylene glycol-*co*-cyclohexane-1,4-dimethanol terephthalate) (PETG) is a derivative from poly(ethylene terephthalate) (PET), obtained *via* adding certain amount of cyclohexane-1,4-dimethanol (CHDM) to substitute a fraction of ethylene glycol during the synthesis process of ester condensation polymerization. Comparing to PET, the crystalline ability of PETG becomes very weak. Kattan *et al.*^[25] found even upon hot stretching condition the crystallinity of PETG could only reach about 3%. Therefore, PETG is usually used as an amorphous copolyester with good processability to produce high-clarity amorphous parts. Polycarbonate (PC) is an amorphous thermoplastics widely used in industrial manufacture, especially as electrical apparatus, because of its excellent impact resistance, ductility and thermal stability. Moreover, as proved by the previous research^[16], PC is an ideal candidate for *in situ* formation of microfibrillar structure during extrusion stretching process. In this study, our attempt is to achieve self-reinforcement of amorphous PETG/PC blends by *in situ* microfibrillation during a processing of slit die extrusion-uniaxial cold stretching, and establish the draw ratio-microfibrillar structure-macroscopic properties relationship. As a preliminary stage for a series of systematic in-depth investigations, the current results demonstrate manifestly that the *in situ* microfibrillation in the amorphous PETG/PC blend can be conveniently attained through simple cold stretching, and interestingly the microfibrillar amorphous blends exhibit a unique mechanical performance that is high rigidity/modulus accompanied with excellent extensibility. Especially, up to 900% increase of the extensibility is obtained at the highest draw ratio used. Our work provides a new way for the preparation of polymer blends with much enhanced tensile toughness.

EXPERIMENTAL

PETG 0725 with MFI = 41.8 g/10min (220°C, 10 kg) was kindly supplied by Shengxin Co., Sichuan, China, and used as the basis polymer. Such PETG product was recycled from waste films and liquid bottles, has an intrinsic viscosity of 0.58 dL/g. A commercially available polycarbonate (trade marked as PC 201, Dow Chemical Co., USA) with $M_n = 2.63 \times 10^4$ and $M_w/M_n = 1.98$, acted as the microfibrillation component dispersed in the PETG matrix. The amorphous PETG/PC blends were melt compounded in a Haake single screw extruder (HAAKE POLYLAB OS), and uniaxially cold stretched into sheets through a slit die of 2.0 mm thickness $\times$ 25 mm width. In the extruder, the temperatures were maintained at 200°C, 220°C, 240°C and 240°C from the hopper to the die and the screw speed was about 50 r/min. After extrusion, the extrudate was continuously drawn by the stretching rolls at room temperature. The rolls have a diameter of 77 mm, and were operated at room temperature (*ca.* 20°C). By altering the relative draw speed, the sheets obtained with different draw ratios (defined as the sectional area ratio of the sheet to the slit die) were achieved. Before being used, the PETG and PC were dried at 65°C and 110°C, respectively, for 4 h to minimize the hydrolysis effect during processing.

The measurements of tensile behaviors were carried out on the cold stretched PETG/PC sheets directly using an Instron Universal Testing Machine under a crosshead speed of 50 mm/min according to the GB/T1040-92 standard, and the measure temperature was around 23°C. The microscopically morphological observations of the as-prepared PETG/PC sheets were conducted on a FEI Inspect F SEM instrument with an acceleration

voltage of 20 kV. The samples were cryo-fractured in liquid nitrogen along the stretching direction. To learn the mechanism of stretching-induced superior extensibility, the surface of stretched sheets and the tensile fractured surface of the stretched sheets were inspected in the direction parallel to the tensile direction. The rheological behavior of melt was assessed by a Rheograph 2002 high-pressure capillary rheometer (Groettfert co., Germany) at 240°C and within a shear rate range from 100 s⁻¹ to 3000 s⁻¹. The diameter of the capillary die was 1 mm, and its L/D ratio was 10:1. All rheological measurements were conducted under a nitrogen atmosphere to minimize the oxidative degradation of samples. The glass transition temperatures (T_g) of the as-prepared samples were ascertained using a Perkin-Elmer Pyris-I DSC calibrated by indium. The slices, about 5 mg, were cut from the extruded pellets. The slices were heated to a preset temperature (250°C) at a rate of 100 K/min and held for 5 min to eliminate the initial thermal history, then rapidly cooled down to room temperature, after holding for 5 min to achieve thermal equilibrium, the samples were heated again at a rate of 40 K/min.

RESULTS AND DISCUSSION

For the pure PETG sample, the tensile strength is about 47.8 MPa, while the elongation at break is only 4.8%. After adding 30 wt% PC, a slightly improved tensile strength and extensibility are observed, that is: the tensile strength becomes 51.4 MPa, and extensibility is 10%. To the blend containing isotropic morphology, the mechanically reinforcing effect of PC is very limited. Following, taking the blend of PETG/PC with fixed composition of 70/30 wt% as example, the influence of stretching ratio on the tensile behavior is evaluated in detail. Typical stress-strain curves for the PETG/PC 70/30 wt% sheets prepared with different draw ratios are shown in Fig. 1(a). In order to quantitatively estimate the tensile behavior, some values for tensile strength, modulus and elongation at break are picked up from the stress-strain curves, which are plotted versus draw ratio, as shown in Figs. 1(b)–1(d). The reported values of tensile properties were calculated as averages over five specimens for each sample. The tensile strength is independent on variation of draw ratio, within a narrow range

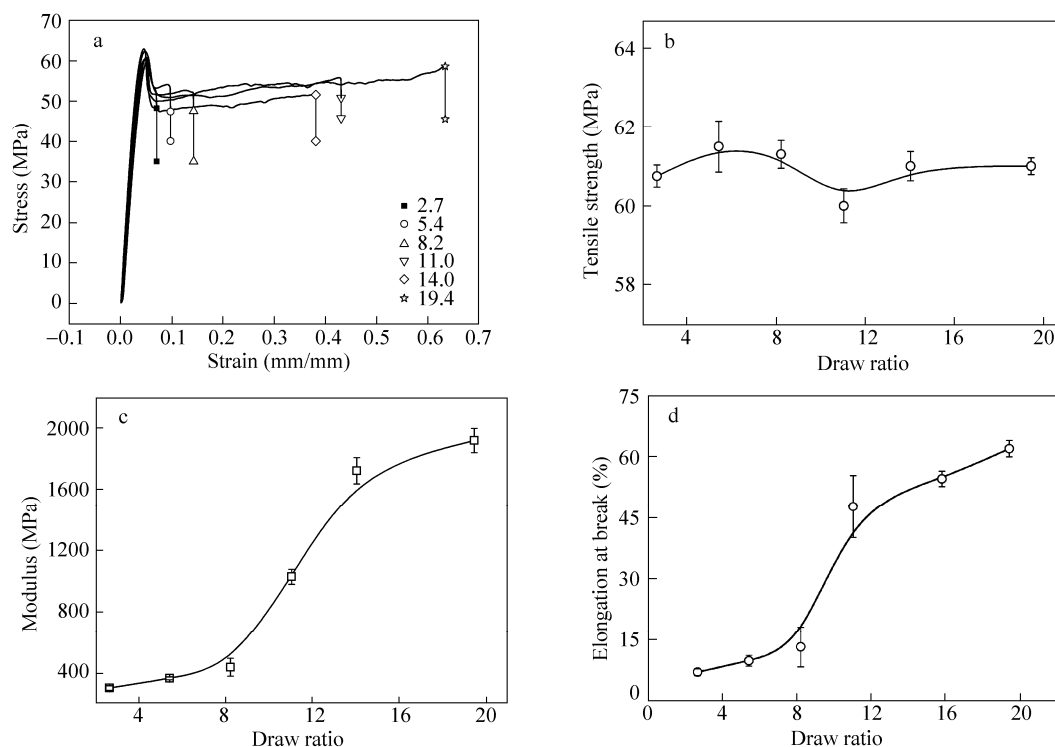


Fig. 1 (a) Typical stress-strain curves for the PETG/PC 70/30 sheets prepared with different draw ratios, (b) tensile strength, (c) modulus and (d) elongation at break versus draw ratio curves

from 60.0 MPa to 61.5 MPa. However, continuous improving the tensile modulus with increasing the draw ratio is observed. Higher draw ratio implies stronger stretching deformation intensity, thus induces higher level of anisotropy and orientation. The increase of the tensile modulus with increasing the draw ratio indicates that the uniaxially stretched sheets possess high rigidity and structural anisotropy. Especially, an abrupt increase for the tensile modulus is found at a threshold draw ratio of 8.2. Some direct evidences for accessing the orientation degree of amorphous blend structure will be collected by using IR and this is under going in our group. The developed trend of elongation at break versus draw ratio is consistent well with the case of modulus as that: the elongation at break is continuously improved as increasing of the draw ratio, meanwhile, the abrupt increasing point is also located at the draw ratio of 8.2. The impact of draw ratio on the extensibility of amorphous PETG/PC blends is very distinct that a nine times increment for the elongation (from 7% to 62%) and a five times increment for modulus (from 350 MPa to 1900 MPa) are achieved when the draw ratio increases from 2.7 to 19.4. This is an interesting phenomenon for the mechanical behavior of polymer blends that higher rigidity is companied with more excellent extensibility. To the best of our knowledge, such result is reported for the first time, and it may be a unique character of tensile behavior for the amorphous stretched blends, which is very much different from that of the crystallizable stretched ones. It should be noted that Fig. 1 shows an almost constant tensile strength whereas a significant increase of the modulus. This cannot normally happen and worth to be further investigated.

To uncover the intrinsic structural origins for the macroscopic properties, the microscopic morphologies of the uniaxially stretched sheets have been inspected. The SEM micrographs for the cryo-fractured surfaces of the PETG/PC 70/30 wt% sheets prepared with different draw ratios are presented in Fig. 2, the observed planes are parallel to the stretching direction. Obviously, for the amorphous PETG/PC blend, the *in situ* microfibrillation of PC is easily achieved during the uniaxially cold stretching process. The distinct fibrillous objects are found even the draw ratio is as low as 2.7. Moreover, a good preferential orientation of PC microfibrils along the stretching direction is found for all the draw ratios. It should be noted that the orientation of fibrils at draw ratio of 8.2 seems poorer than that at draw ratio of 11.0 (compare Fig. 2b with Fig. 2c). This is probably due to the fact that the fracture direction of sample C is not perfectly parallel to the stretching direction. As increasing the draw ratio, the PC microfibrils become smaller in diameter but larger in length, thus an increased aspect ratio is expected. However, one observes a saturation of microfibrils diameter as the draw ratio reaches to 14.

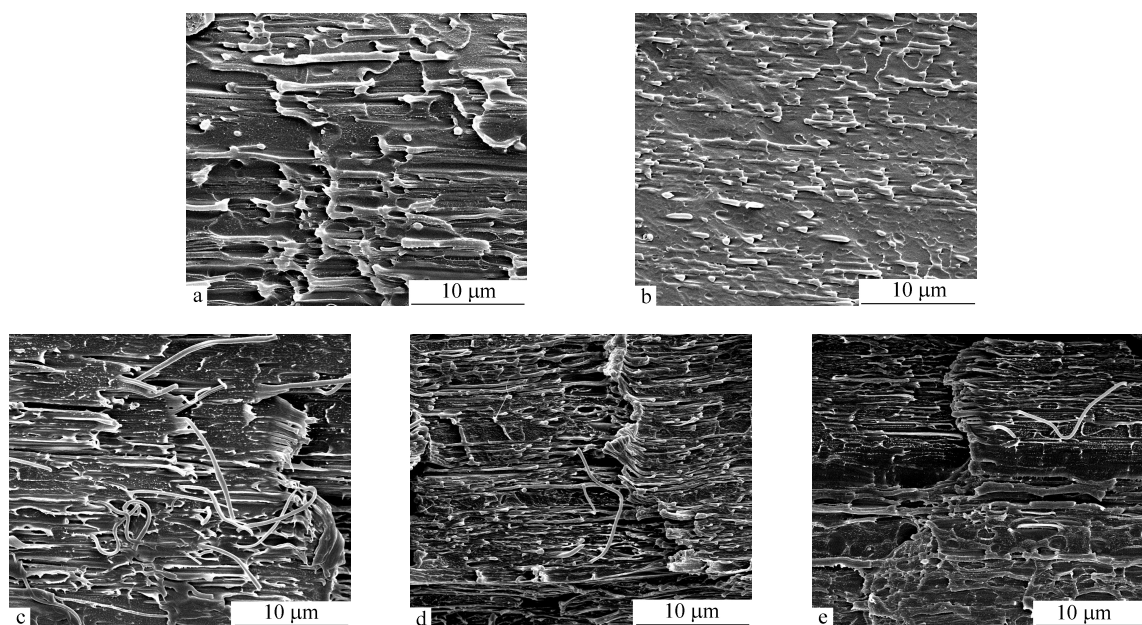


Fig. 2 The SEM micrographs for the cryo-fractured surfaces parallel to the stretching deformation direction of the PETG/PC 70/30 sheets prepared with different draw ratios: (a) 2.7, (b) 8.2, (c) 11.0, (d) 14.0 and (e) 19.4

The change of microfibrils average diameter as function of draw ratio is shown in Fig. 3. The microfibrils diameter was calculated as averages over five photos for each sample. The diameter could be down to about 200–300 nm as the draw ratio reaches to more than 14. Therefore, the unique mechanical character of simultaneous high rigidity and high extensibility can be attributed to the *in situ* microfibrillation structure with decreased microfibrils diameter and increased aspect ratio of PC phase induced by uniaxial stretching. For further manifesting the microfibrillation-tensile property relationship, the content of PC in blend was altered, and the extensibility versus draw ratio and the surfacial micrographs of the blends with different PC contents are shown in Fig. 4. It should be noted that the fracture direction is perpendicular to the stretching direction.

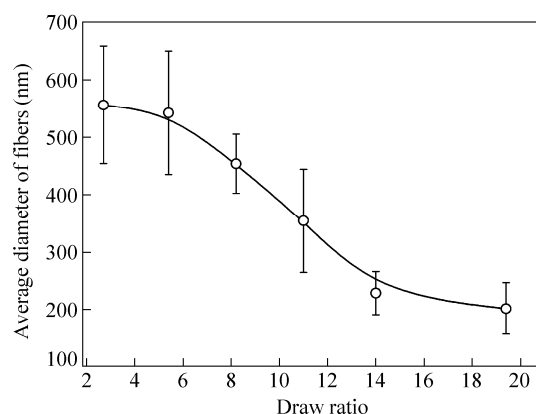


Fig. 3 The diameter of microfibril as function of draw ratio for PETG/PC 70/30 blends

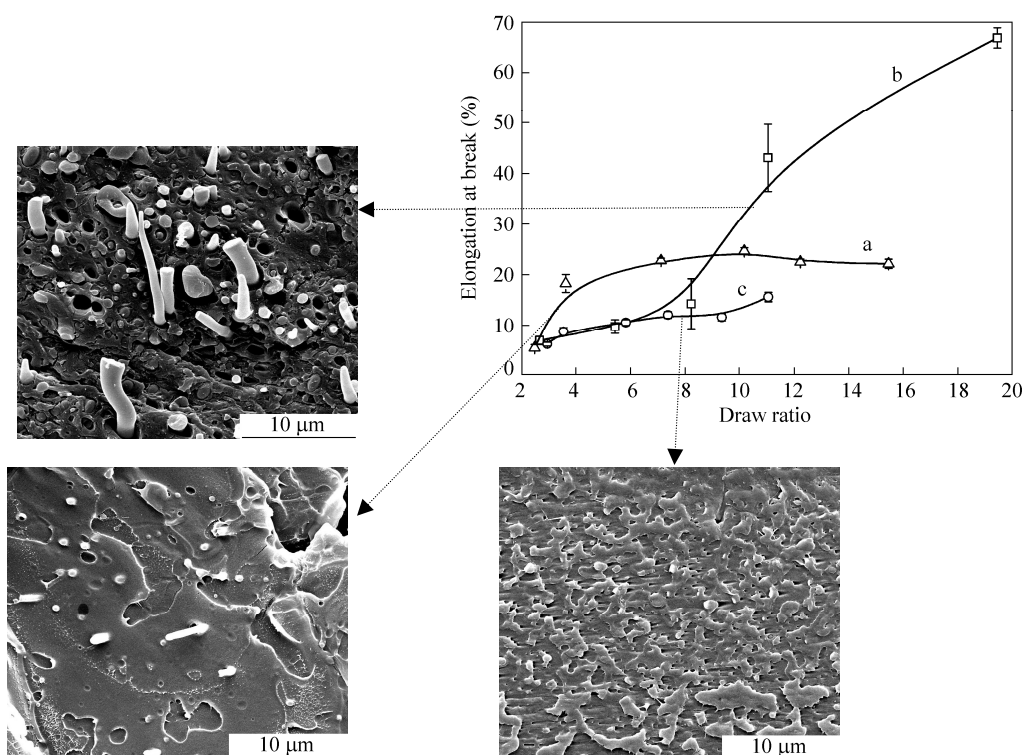


Fig. 4 The extensibility versus draw ratio curves and micrographs for the cryo-fractured surfaces of the PETG/PC blends containing different PC contents: (a) PETG/PC = 90/10, (b) PETG/PC = 70/30 and (c) PETG/PC = 50/50

Surprisingly, for three PC contents (10 wt%, 30 wt% and 50 wt%), the superior extensibility appeared with increasing the draw ratio is observed only for the PC content of 30 wt%. When the PC content is low, 10 wt%, the amount of PC microfibril is less and insufficient for ensuring continuously improved elongation, thus the elongation reaches saturation state quickly with the increase of draw ratio. As to the blend with PC content of 50 wt%, no microfibrillar structure but a co-continuous morphology is generated in this blend. So, for high PC content, the influence of increasing draw ratio on the improvement of extensibility is very limited. The dependence of extensibility on PC content strongly indicates the important role of *in situ* microfibrillation for the observed unique mechanical character of the amorphous stretched blend.

Finally, we would like to discuss the primary causes of *in situ* fibrillation in the amorphous PETG/PC blends. The curves of viscosity versus shear rate for the pure PETG and PC are presented in Fig. 5. Although in a whole shear rate range the viscosity of PC is significantly larger than that of PETG, a strong shear-thinning behavior is observed for the PC melt; while it is very weak for the PETG melt. The strong shear-thinning behavior implies a sensitive response to shear flow field, namely, the PC melt could be easily oriented and deformed upon stretching, thus forms highly anisotropic microfibrillar structure. So, the shear response capability of melt should be an important criterion for determining whether a polymer melt is suitable for *in situ* fibrillation. Another necessary condition for PC phase to form *in situ* fibrils may be the good interaction between PETG and PC. The good compatibility between PETG and PC can be approved by Fig. 6. The glass transition temperatures (T_g) for the pure PETG and the pure PC are 80°C and 156°C, respectively. The T_g difference between the two polymers is 76 K. While, for the PETG/PC 70/30 wt% blend, the T_g s of the two components shift closely to each other. The T_g is 84°C for the PETG phase, and 123°C for the PC phase, the T_g difference is only 39 K. The decrease of T_g difference between PETG and PC indicates the good compatibility between the two components in the blend. As the DSC results have already shown certain compatibility of PETG and PC (indicated by the change of T_g s), the PETG matrix is actually a PETG rich phase and the dispersed PC is a PC rich phase, and between them there should exist the interface. The extension stress could be efficiently transfer from the PETG matrix to the dispersed PC phase due to the good compatibility between the two components, thus resulting in the microfibrillation of PC phase. Now let's discuss the possible mechanism for the observed superior extensibility. A tentatively explanation could be ascribed to the increased mobility of the dispersed PC phase as it becomes fiber and oriented along the direction of tensile deformation. Recently, molecular-dynamics studies have suggested that the mobility of the nanoparticles in polymer might be crucial for introducing new energy-dissipating mechanism that lead to enhanced toughness in the nanocomposite^[26–29]. Furthermore, Kim *et al.*^[26] presented experimental evidence that nanoparticle orientation and alignment under tensile stress was responsible for this energy-dissipation mechanism, and the mobility of polymer matrix was a precondition for this mechanism to be effective. Since stretching treatment will lead to chain extension and orientation and, obviously, reduces their mobility in comparison with the relaxed state of the macromolecules before the stretching procedure. On the other hand, the experimental temperature of tensile testing is about 23°C, is well below the T_g of the PETG matrix, the macromolecular chain of PETG should be difficult to move. Thus here the mobility of both PETG matrix and dispersed PC microfibrils can not be used to explain the observed improvement of extensibility. Since cavitations are a common phenomenon observed during stretching deformation of semicrystalline polymers with high degree of crystallinity and perfection of crystals, such as high-density polyethylene^[30], and are also a stretching rate dependent process^[31], we also checked the possible formation of cavities in these amorphous blends, particularly for the stretched sheets with higher draw ratios. A smooth surface and no cavities or micro-crack was observed for all the stretched sheets, which suggests the formation of cavities does not correspond to the observed increased extensibility. However, by checking the tensile fractured surface of the stretched sheets in the direction parallel to the tensile direction, it is found that the stretched sheets could be easily cracked during tensile deformation, which suggests a toughening mechanism *via* multiple crazing and shear yielding. More importantly, most of PC microfibers are found to be located in the center of the crack and serve as a bridge for connecting the cracks, as shown in Fig. 7. One may visualize a sliding process of the cracks along the oriented PC microfibers until breakup, resulting in a large elongation thus

a great improvement of extensibility. Thus it is understandable that an increased aspect ratio induced by stretching will cause a large extensibility.

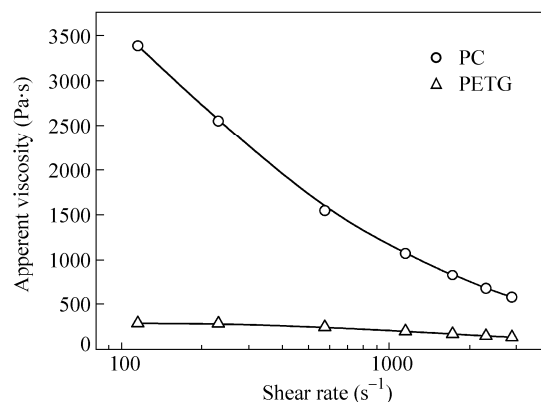


Fig. 5 The melt viscosity versus shear rate curves for the pure PETG and PC

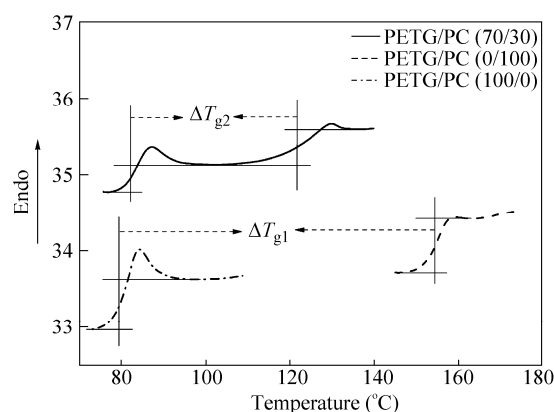


Fig. 6 Calorimetric diagrams indicating T_g for the pure PETG, pure PC and PETG/PC 70/30 blend

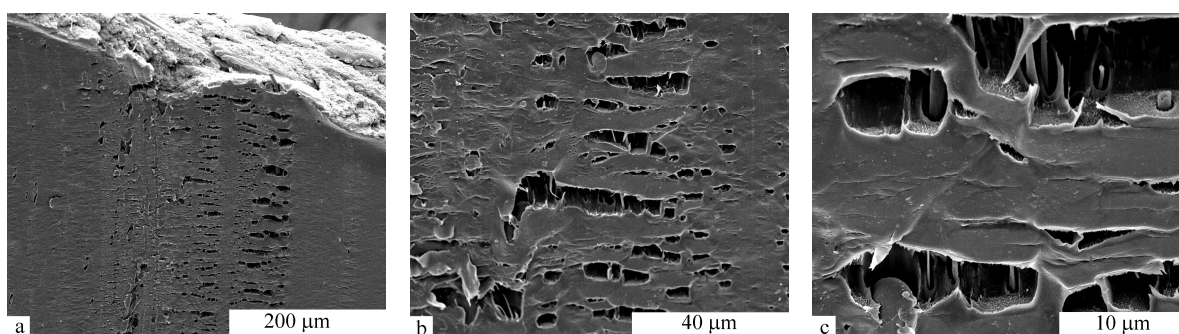


Fig. 7 The SEM micrographs of the tensile fractured surface along the tensile direction of the stretched sheets prepared with draw ratio of 19.4 at different magnifications

CONCLUSIONS

The *in situ* microfibrillation can be conveniently achieved in the amorphous PETG/PC blend through the simple uniaxial cold stretching process. The tensile properties of the amorphous stretched blend are distinctly different from those of the crystallizable stretched one. Simultaneous enhancement of the modulus and improvement of

the extensibility were achieved with increasing the draw ratio. A 900% increase of the elongation at break is attained at the highest draw ratio for the PETG/PC 70/30 wt% blend. This study is the preliminary stage for the systematic investigation about the tensile behavior and mechanism of the amorphous stretched blends. The detailed evaluation of orientation of amorphous polymers, the motion capability of PETG and PC chains in the stretched sheet, the temperature dependence of the tensile behavior for the amorphous stretched blends, *etc.*, will be implemented in our future work.

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