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Morphologies and Properties of Polycarbonate/Polyethylene *In Situ* Microfibrillar Composites Prepared Through Multistage Stretching Extrusion

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ABSTRACT: The sheets of polycarbonate (PC)/polyethylene (PE) *in situ* microfibrillar composites are successfully prepared directly through multistage stretching extrusion with an assembly of laminating-multiplying elements (LMEs) instead of the secondary processing. The morphological development of the PC dispersed phase in PE matrix with increasing the number of LMEs during multistage stretching extrusion investigated by scanning electron microscope shows that core-skin structure of the microfibrillar PC/PE composites during multistage stretching extrusion with 4 LMEs is weakened, and the diameter of the PC microfibrils is relatively more uniform, indicating that the shear field in LMEs greatly affects the morphology of PC dispersed phase in PE matrix. The tensile, crystalline, melting, orientation and rheological behavior of the PC/PE microfibrillar composites are also investigated. The results show that the PC microfibrils are helpful to increase complex viscosity and yield stress of the PE/PC composites. In addition, it is found that the glass transition temperature of PC in PE matrix reduced with increasing the number of LMEs during dynamic rheological testing. It is coincided with the results of DSC analysis of the PC/PE composites. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40108.

KEYWORDS: extrusion; morphology; polycarbonates; polyolefins; properties and characterization

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INTRODUCTION

In recent years, high-performance polymer composites have been paid much more attentions because it can be widely used as automobile parts, aircraft parts, and motorcycle components.[1,2] It has been realized that the properties of polymer composites are, to a great degree, determined by the morphology of the dispersed phase. If the dispersed phase of polymer composites forms *in situ* microfibrils, the mechanical properties of the polymer composites are improved remarkably.[3–9] Therefore, *in situ* microfibrillar reinforced composites (MFCs) have attracted more and more attentions. Evstatiev et al. have studied MFCs comprising low-density polyethylene (LDPE) (matrix) and poly(ethylene-terephthalate) (PET) (reinforcing material), their results showed that the MFCs had outstanding mechanical properties in comparison with glass-fiber reinforced LDPE.[10]

Generally, there are two methods to prepare MFCs, one is "cold drawing method," in which the microfibrils of high-melting-temperature component are formed through solid state cold stretching after melt blending process[11–13]; the other is "hot drawing method," in which the extrudate is stretched in melt state so that the microfibrils of high-melting-temperature component can be acquired, and then quenched quickly to preserve the microfibrillar morphology.[14,15]

The microfibrillar composites based on PET and polyolefins (mainly polyethylene (PE) and polypropylene (PP)) have been successfully manufactured by hot drawing.[16] It is found that the PET microfibrils do enhance the mechanical properties of the PET/high density polyethylene (HDPE) blend, especially the tensile strength and modulus as well as the fracture toughness. Moreover, the polycarbonate (PC)/HDPE microfibrillar composites are also successfully prepared by hot drawing, and it is found that the finer microfibrils are obtained at larger hot stretching ratios.[17–19] It is also found that the amount and diameter of microfibrils are nonuniform through the thickness of the extrudate, and the fibrils become coarser and denser towards the core of the extrudate, indicating that the extrudate has "core-skin" structure, which will seriously affect the application of the MFCs. It is ascribed to the following two reasons: on one hand, the gradient distribution of the fibrils is mainly attributed to the nonuniform distribution of PC particles before hot stretching; on the other hand, the nonuniform elongational

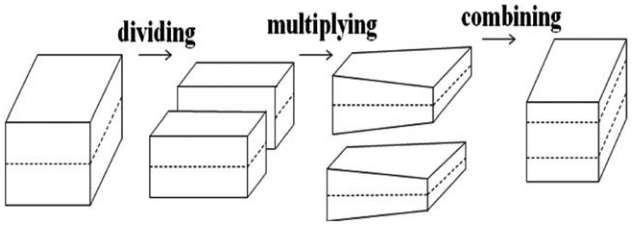

Figure 1. The schematic of a LME.

flow causes the gradient morphology of the PC/HDPE composites. Moreover, in order to obtain final products, the microfibrillar composites usually require secondary processing. However, when the PC/HDPE microfibrillar composites are manufactured into final products through the secondary processing, the microfibrillar morphology may be damaged because the glass transition temperature of PC (about 150°C) is lower than the temperature of the secondary processing.

Therefore, it is very important to find one novel method to manufacture the PC/HDPE microfibrillar composites, which not only have uniform morphology of microfibrils in PC/HDPE composites toward the thickness of the extrudate but also obtain final products directly instead of the secondary processing. These problems can be solved by inducing reasonable shear field during process, which is realized through the invention of a novel extrusion die that has an assembly of laminating-multiplying elements (LMEs, which divided and recombined polymer melts), which has been designed in our lab, as schematically shown in Figure 1. The flowing behavior of a melt in a LME can be divided into three processes: dividing, stretching, and multiplying. When the melt enters into a LME, it is first sliced by a divider evenly into left and right parts, which then enters into two fish-tail ducts, respectively. It has been reported that the flowing behavior in fish-tail duct can be regarded as the combination of extending and convergent flow, indicating that strong shearing or elongational forces existed in LME.[20–23] Increasing the number of LMEs would lead the laminating-multiplying process to happen repeatedly, providing gradually stronger biaxial-stretching forces. Therefore, this processing method is referred to as the multistage stretching extrusion method. In our previous work, polyamide (PA6)/PP *in situ* microfibrillar composites have been successfully prepared by extrusion die with an assembly of LMEs, and the experimental results showed that the mechanical properties of PA6/PP composites were improved remarkably as well as relatively uniform morphology of microfibrils in PA6/PP composites.[24]

In this study, in order to manufacture the PC/HDPE microfibrillar composites with uniform morphology of the microfibrils into final products directly instead of secondary processing, the sheets of the PC/PE microfibrillar composites are prepared through multistage stretching extrusion with an assembly of LMEs. Scanning electron microscope (SEM) is used to observe the morphological development of PC dispersed phase with increasing the number of LMEs during extrusion. The tensile, crystalline, melting, and rheological properties of the PC/PE microfibrillar composites are also investigated.

EXPERIMENTAL

Materials

PC (201-22) with density = 1.2 g/cm^3 was purchased from Dow Chemical Company. A commercial HDPE (DGDA6098) with both MI = 0.08 g/10 min (2.16 kg, 190°C) and density = 0.948 g/cm^3 was supplied by Qilu Petrochemical Co. (China).

Specimens Preparation

PC was dried in a vacuum oven for 4 h at 100°C, then the PC/PE (20/80 wt %) composites was prepared by a co-rotating twin-screw extruder (SHJ-25, Nanjing Giant Machinery Co., Nanjing, China, diameter of screw = 20 mm, length/diameter ratio = 40/1). The temperature profile from feed zone to die zone was set at 200, 235, 240, and 235°C, while the rotation speed of the screw was fixed at 150 rpm. The PE/PC composites was extruded by the experimental equipment designed by our lab, and the multistage stretching extrusion, which contains a single-screw extruder (diameter was 25 mm and a length to diameter ratio was 30), a feed block and some LMEs, and finally formed a 1.5-mm-thick and 40-mm-wide sheet after cooling. More details on LME were stated in Ref. 25. The rotation speed of the screw was 100 rpm during the multistage stretching extrusion, and the temperatures from the hopper to the exit of the extruder were 200, 230, 240, and 240°C, respectively, and the temperature of LMEs was 240°C.

Morphological Observation

SEM was used to examine the morphology of PE/PC composites. Samples were quenched in liquid nitrogen and cryofractured along transverse (TD) directions and flow direction (FD), and the measurements used a Hitachi S3400 + EDY SEM (Japan) at an accelerating voltage of 20 kV.

Rheological Measurement

Capillary Rheological Analysis. The apparent viscosity-shear rate relationship was carried out using a RH7 advanced capillary rheometer (Malvern Instruments, UK). The diameter of the capillary die was 1 mm and its length to diameter (L/D) ratio is 16 : 1. The materials were extruded after a resident time of 4 min in the barrel to ensure the temperature of the material to be uniform 240°C. The shear rate range used was from 20 to 2000 s^{-1}.

Dynamic Rheological Analysis. The samples for rheological measurements obtained directly from the sheets prepared through the multistage stretching extrusion. The thickness of each plate was 1.5 mm, and the diameter was 25 mm. The rheological experiments were carried out using a TA advanced rheometer (AR-1500ex, TA Instruments-Waters LLC, USA) with a 25 mm parallel plates fixture under a nitrogen environment. The strain amplitude was 1% during the frequency sweep at 143°C. Strain amplitude, frequency, and heating rate during the temperature sweep were 1%, 0.628 rad/s and 2°C/min, respectively. The sweep rang of the temperature was 143–170°C.

Differential Scanning Calorimeter (DSC) Analysis

Melting and crystalline behaviors of the microfillar PE/PC composites were measured by a TA-Q20 (USA) thermal system purged with nitrogen. The program for DSC measurement was run from 25 to 143°C, which was the first heating scan. After the sample was equilibrated at 143°C for 3 min to erase previous thermal

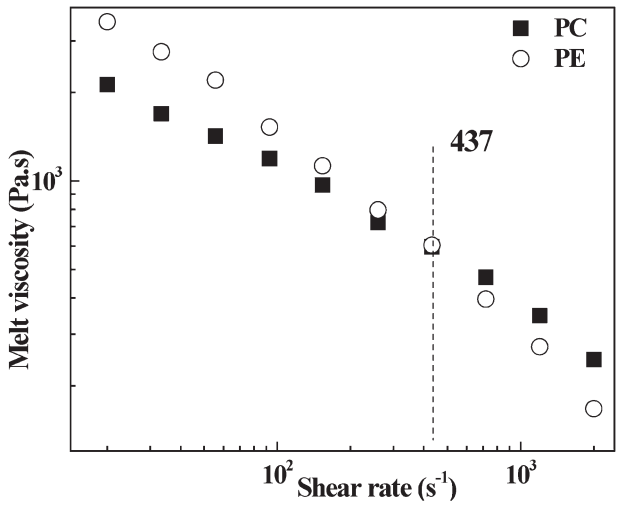

Figure 2. Apparent viscosity of the neat PE and PC as a function of shear rate at 240°C.

and stress history of PE matrix, it was cooled to 25°C, and then heated again to 170°C for the second heating scan. The cooling and heating rates were 10°C/min during the DSC measurement.

Fourier Transform Infrared Test

The specimens prepared by the multistage stretching extrusion were cut into 10 μm sheets along the melt FD by a turning microtome (YD-2508, Yi Di Medical Device Co., China). The Specimens were conducted ordinary FTIR spectroscopy measurement with Nicolet-IS10 (Thermo Electron Co., USA) spectrometer, the beam was polarized by means of a Spectra-Tech zinc selenide wire grid polarizer from Thermo Electron Corp. if the specimens were oriented, the absorption of plane—polarized radiation by a vibration in two orthogonal directions. The ratio of these two absorption values was defined as the dichroic ratio, D,[26]

$$R = \frac{A_{\parallel}}{A_{\perp}} \quad (1)$$

$A_{\parallel}$ was the absorption parallel, and $A_{\perp}$ was the absorption perpendicular to specific reference axis. The Herman orientation function of this vibration was obtained according to the literature[27]

$$F = \frac{R-1}{R+2} \quad (2)$$

Through aforementioned method, the orientation of the PE and PC molecular in LMEs along the FD was decided.

Tensile Testing

Specimens for tensile testing obtained directly from the sheet through the multistage stretching extrusion. According to ASTMD 638, the testing used an Instron 5567 tension machine (Canton, MA) at 23°C and a rate of 20 mm/min. At least of five specimens for each sample were tested and the average value was calculated.

RESULTS AND DISCUSSION

Capillary Rheological Analysis

It was well known that a low viscosity ratio of the dispersed phase and matrix (usually, less than 1) were a key factor to form the fibrillation of the dispersed phase particles in an immiscible polymer composites.[20–22] Figure 2 showed the apparent viscosity of neat PC and PE as a function of share rate at 240°C. When the shear rate was less than 437 s^{-1}, the viscosity ratio of the PC and PE was less than 1. However, when shear rate was more than 437 s^{-1}, the viscosity ratio of the PC and PE was more than 1. Therefore, in order to fabricate well PC/PE microfibrillar composites, the low shear rate was controlled through choosing low rotation speed of the screw during multistage stretching extrusion.

Morphological Development

Figure 3 showed the scanning electron micrographs (SEM) of the PC/PE composites prepared through multistage stretching

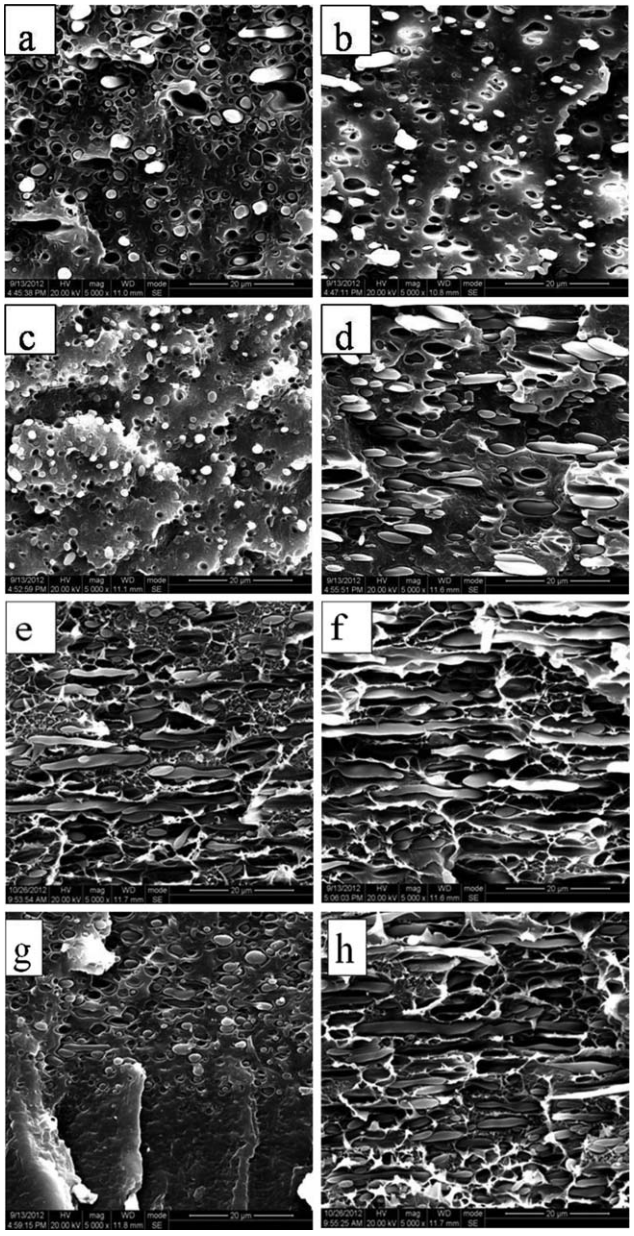

Figure 3. Scanning electron micrographs of the PC/PE composites prepared with different laminating-multiplying elements (LME) number. (a) ND (normal direction), 0 LME; (b) ND, 2 LME; (c) ND, 4 LME; (d) FD (flow direction), 0 LME; (e) FD, 2 LME; (f) FD, 4 LME; (g) near surface in the sheet, 0 LME; (h) near surface in the sheet, 4 LME.

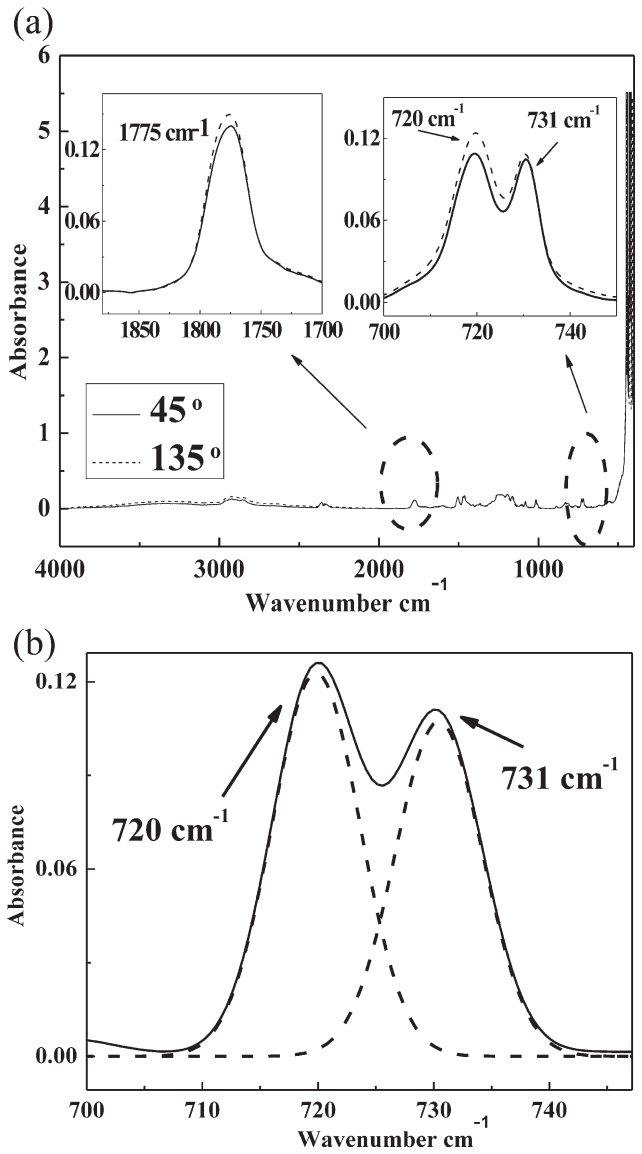

Figure 4. (a) Vertical and parallel polarized infrared spectra of the PC/PE composites; (b) the band at 720 cm^{-1} was assigned to bending vibration C—H of PE, and 731 cm^{-1} corresponded to the bending vibration C—H of PE in crystalline region.

extrusion with different number of the LMEs. (a) TD, 0 LME; (b) TD, 2 LMEs; (c) TD, 4 LMEs; (d) FD, 0 LME; (e) FD, 2 LMEs; (f) FD, 4 LMEs. From the Figure 3(d–f), the morphological development of the PC/PE composites along the FD can be clearly observed. It was apparent that the PC/PE composites showed well-defined microfibrils after it was prepared through the multistage stretching extrusion with 2 and 4 LMEs. From Figure 3(a–c), the morphological development of the PC/PE composites along the TD can also be clearly observed, it is illustrated that the fibrillar diameter reduced with increasing the number of LMEs. Moreover, compared with samples prepared by extrusion without LME, the distribution of the fibrillar diameter of samples prepared through multistage stretching extrusion with 4 LMEs was relatively more uniform and smaller along TD as shown evidently in Figure 3(a,c). According to Figure 3(h), the core-skin structure had been observed obviously, and the PC dispersed phase did not almost exist near the skin layer. However, core-skin structure of the samples was weakened when the samples were prepared through multistage stretching extrusion with 4 LMEs as shown in Figure 3(g). It suggested that the flowing behavior of a polymeric melt in a LME was greatly different from that in conventional slit die, and the flowing behavior of a melt in a LME can be divided into three processes: dividing, stretching, and multiplying, which caused that the interior of polymeric melt have more chances to contact the surfaces of the mould during multistage stretching extrusion in comparison with conventional slit die. Therefore, core-skin structure of microfibrillar PC/PE composites was weakened, and fibrillar diameter was relatively more uniform.

Orientation Behaviors

To understand changes of the molecular structure caused by the shear field in LME during multistage stretching extrusion, the orientation behaviors of the microfibrillar PC/PE composites along the FD was studied by Fourier transform infrared test.

Figure 4(a) showed vertical and parallel polarized infrared spectra of the PC/PE composite; Figure 4(b) showed that the band at 720 cm^{-1} was assigned to bending vibration C—H of PE in both crystalline and amorphous region, and the band at 731 cm^{-1} corresponded to the bending vibration C—H of PE in crystalline region. In addition, the band at 1775 cm^{-1} assigned to the C═O stretching vibration of PC. The changes of the Herman orientation function of the microfibrillar PC/PE composites prepared through multistage stretching extrusion with different number of LMEs were shown in Table I. It was observed that F (0 LME) $< F$ (4 LMEs) $< F$ (8 LMEs) at the same absorption band, suggesting that the strong shear field in LME was conducive to the orientation of the PC and PE molecular chain along the melt FD.

DSC Analysis

Through above morphological analysis, it was found that the shear field in LME can induce the deformation and orientation of PC dispersed phase, which will change the structure of PC/PE composites. In order to understand well the changed structure of the PC/PE composites, DSC was used to analyze the melt and crystalline behaviors of PC/PE composites.

First of all, pure PE and PC were analyzed by DSC. Figure 5 showed melting point of the PE and glass transition temperature of the PC were 131.6°C and 148°C, respectively. Moreover, 143°C was a special temperature because PE has completely melted, but glass transition of PC did not occur in this

Table I. The Herman Orientation Function of Microfibrillar PC/PE Composites Prepared Through Multistage Stretching Extrusion with Different Number of the LMEs

LME	F (720 cm^{-1})	F (731 cm^{-1})	F (1775 cm^{-1})
0	0.53	0.39	0.26
2	0.57	0.54	0.63
4	0.74	0.67	0.78

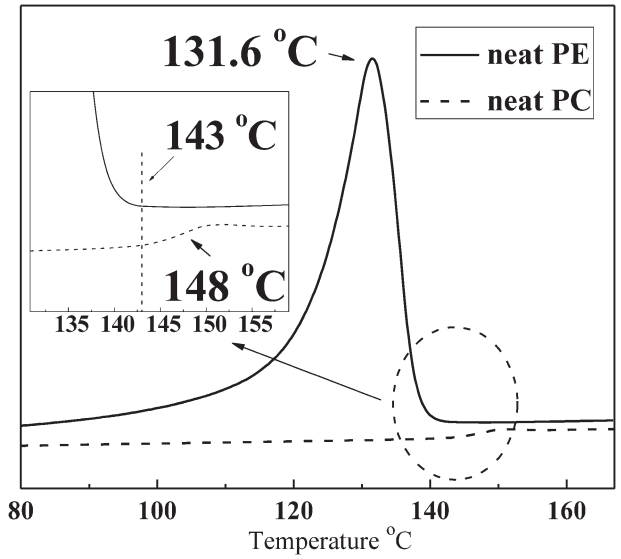

Figure 5. DSC curves of neat PC and PE from 80 to 170°C. The heating rate was 10°C/min.

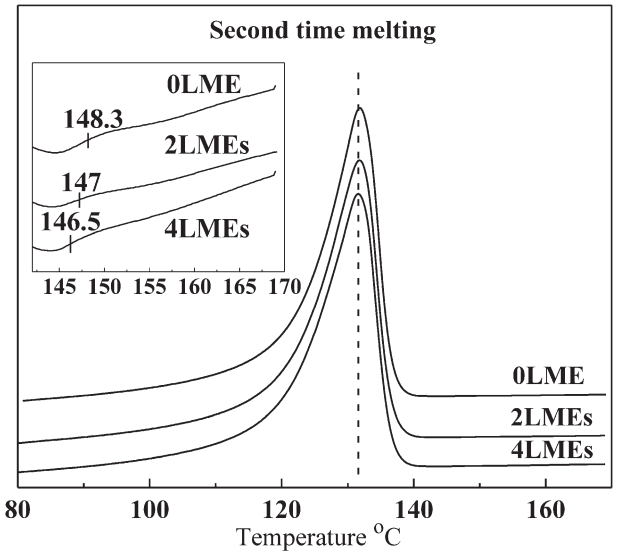

Figure 7. The second time melting DSC curves of the PC/PE composite 80 to 170°C. The heating rate was 10°C/min.

temperature. This result indicated that the fibrillar morphology of PC can be maintained at 143°C. Figure 6 showed the first melting DSC curves of the PC/PE composite from 80 to 140°C. Figure 7 showed the second melting DSC curves of the PC/PE composite from 80 to 170°C. It was illustrated that the melting point of PE was increased with increasing the number of LMEs. However, the melting point of PE was change slightly in the second melting, implying that the shear field in LME induced the orientation of PE molecular chains along the FD, which was beneficial to increasing the melt point of PE. Besides, through partial enlarged graph at 143–170°C, it is also found that T_g (0 LME) = 148.3 > T_g (2 LME) = 147 > T_g (4 LME) = 146.5. Figure 8 showed the crystalline behavior of the PC/PE composites. It was observed that the crystalline temperature changed slightly, implying that the morphology of PC dispersed phase has a little effect on the crystalline behavior of PE in microfibrillar PC/PE composites.

Dynamic Rheological Analysis

Dynamic rheological properties were sensitive to the morphology of dispersed phase in polymer matrix. In order to reveal the effects of the LME on morphology of PC dispersed phase in microfibrillar PE/PC composites, the PC/PE composites prepared through multistage stretching extrusion with different number of LMEs were analyzed by dynamic rheology. The frequency sweep experiments for rheological measurements were carried out at a temperature of 143°C. According to the results of DSC analysis of microfibrillar PC/PE composites, at this temperature, the PC phase is in a solid state, whereas the PE matrix is molten state. Hence, the PC can be considered to be rigid in

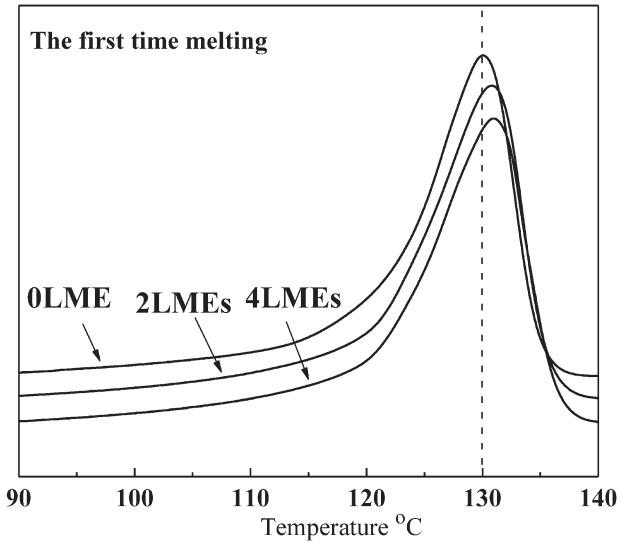

Figure 6. The first time melting DSC curves of the PC/PE composite from 90 to 140°C. The heating rate was 10°C/min.

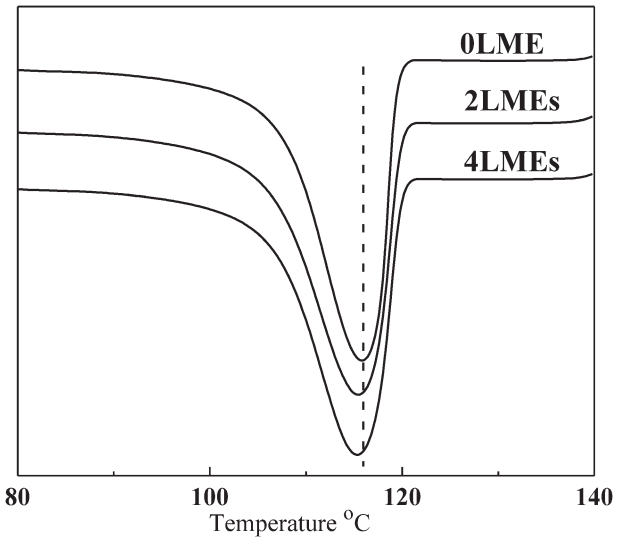

Figure 8. DSC curves of the PE/PC composites. The cooling rate was 10°C/min.

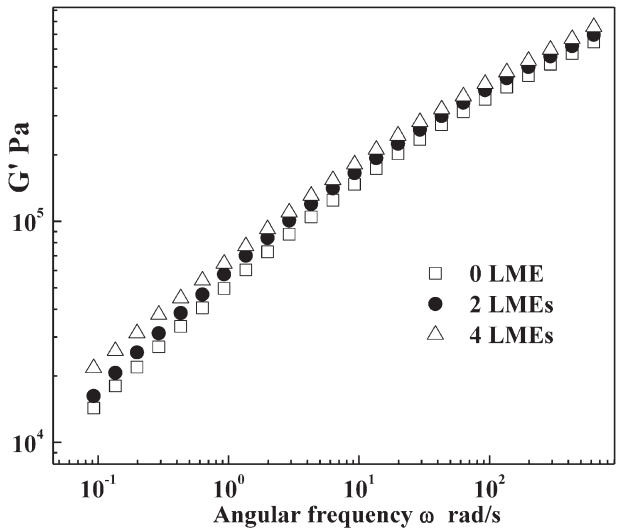

Figure 9. The frequency ω dependence of storage modules G' for the PE/PC composites at 143°C.

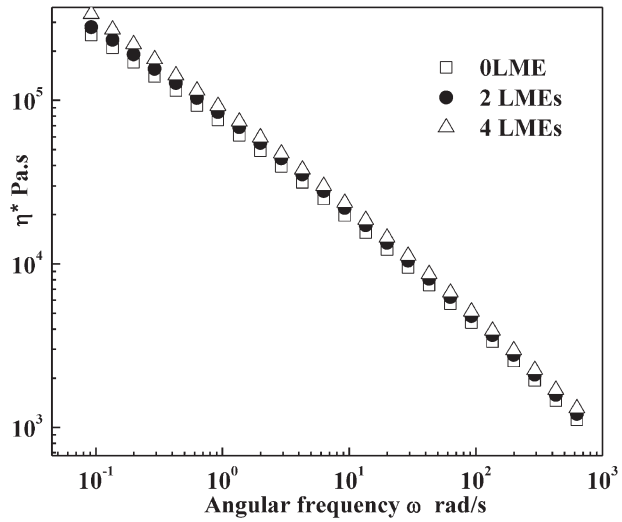

Figure 11. The frequency ω dependence of complex viscosity for the PE/PC composites at 143°C.

comparison with the viscoelastic nature of PE. Moreover, the fibrillar morphology of the PC phase was preserved in the PE matrix to create an environment similar to that of fiber-reinforced thermoplastic composites. It was found that the storage modulus (G') values of all the samples increased with increasing angular frequency as evident from Figure 9. The storage modulus values of the sample prepared by multistage stretching extrusion with 4 LMEs were the highest in the whole test frequency range. However, the storage modulus values of sample prepared by extrusion without LME were the lowest in the whole test frequency range. These results were attributed to the different morphologies of the PC dispersed phase in PE matrix as showed in Figure 2. Similarly, according to Figure 10, loss modulus values of the PC/PE composites at 143°C in the test frequency range were also found that: G'' (4 LMEs) > G'' (2 LMEs) > G'' (0 LME). Storage modulus values of the PC/PE composites had more obviously changes in comparison with loss modulus values at low frequency ($\omega < 1$ rad/s), indicating that the microfibrillar morphology of the PC dispersed phase have a more significant effect on the elastic behavior in comparison with the viscous behavior. Figure 11 showed the frequency dependence of complex viscosity for the PC/PE composite at 143°C. It was illustrated that η^* (4 LMEs) > η^* (2 LMEs) > η^* (0 LME) at low frequency, implying that the motion of PE chain segments was hindered due to the presence of the fibrillar morphology of the PC dispersed phase in PE matrix. Figure12 showed the frequency dependence of tan δ for the PC/PE composites at 143°C. It was found that the tan δ values of sample prepared through multistage stretching extrusion with 4 LMEs was lowest at low frequency, indicating that the presence of the microfibrillar morphology of the PC dispersed phase with a high respect ratio can hinder the relaxation of the PE phase. Moreover, storage modulus, loss modulus, complex viscosity, and tan δ had a little difference at high frequency (such as

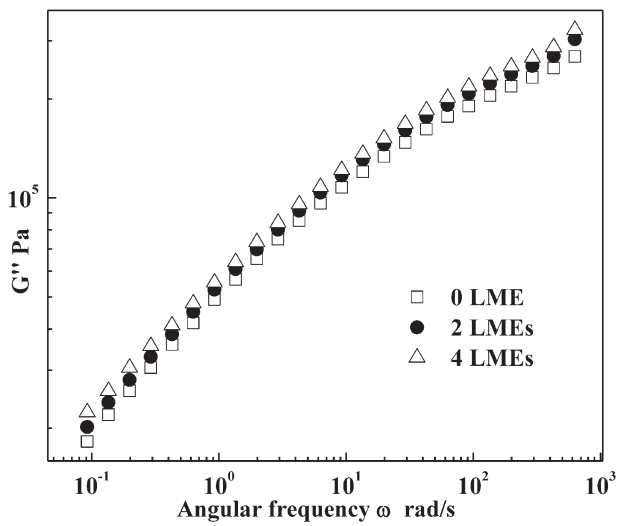

Figure 10. The frequency ω dependence of loss modules G'' for the PE/PC composites at 143°C.

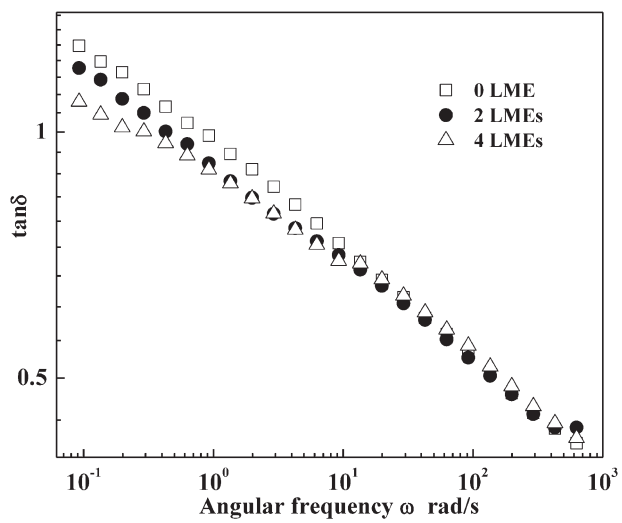

Figure 12. The frequency ω dependence of tan δ for the PE/PC composites at 143°C.

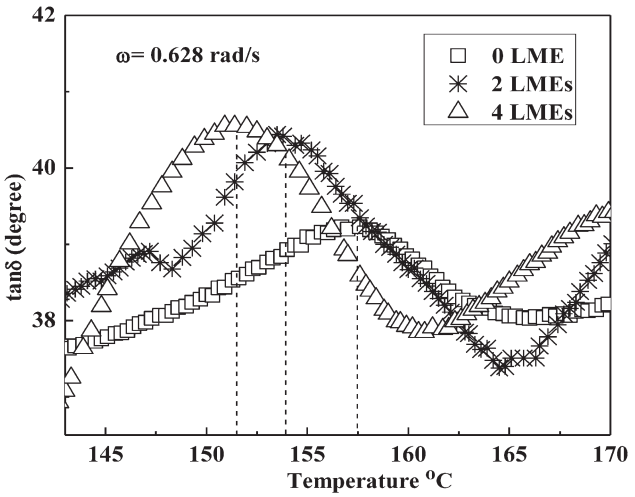

Figure 13. The temperature dependence of tan δ for the PE/PC composites prepared through multistage extrusion with different number of the LMEs.

$\omega > 100$ rad/s), this result indicates morphologies of PC dispersed phase in PE/PC composites had a little effect on the viscous behavior at high frequencies.

Figure 13 showed the temperature dependence of tan δ for PC/PE composites prepared through multistage stretching extrusion with different number of LMEs. Three peaks were clearly observed at 151.4, 154.1, and 157.2°C in Figure 13 due to the glass transition of differently morphological PC in PE matrix. The samples prepared through multistage stretching extrusion with 4 LMEs had the lowest glass transition temperature, and this result was coincided with the results of DSC analysis of the PC/PE composites. According to analysis of the orientation behaviors the PC/PE composites, this result may be relevant to the orientation of PC phase in PE matrix.

The glass transition temperature was observed only through partially enlarged graph at 143–170°C in DSC curves. However, the glass transition temperature was easily observed through

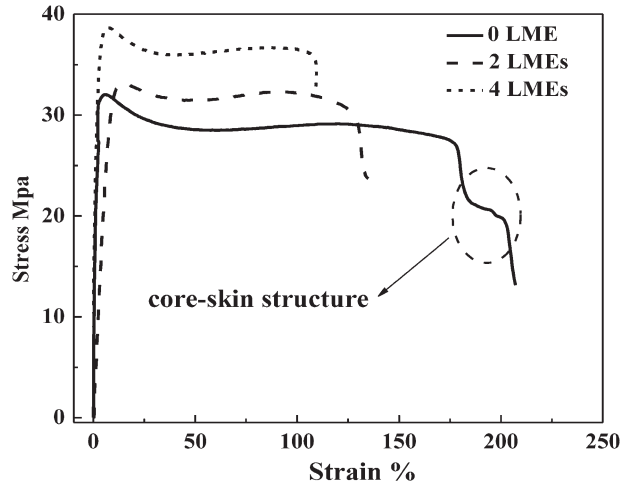

Figure 14. The strain dependence of stress for the PC/PE composites prepared through multistage extrusion with different number of the LMEs.

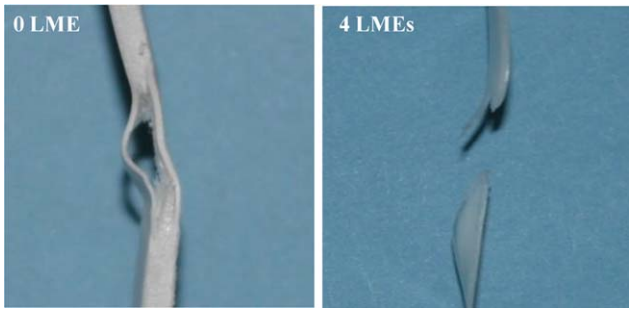

Figure 15. Failure images of the PC/PE composites prepared through multistage extrusion with 0 LME and 4 LMEs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature sweep during dynamic rheological testing. Therefore, compared with DSC analysis of the PC/PE composites, temperature sweep during dynamic rheological testing was a good method to obtain the glass transition temperature of PC phase in the PC/PE composites.

Tensile Testing

If PC/PE microfibrillar composites was manufactured into final product through the second processing, the microfibrillar morphology maybe be damaged, which would lead mechanical properties to become poor. The main reason may be that the movements of PC molecular chains caused the morphology of dispersed phase to change in PE matrix due to the lower glass transition temperature of PC (about 150°C) in comparison with the secondary processing temperature of the PC/PE microfibrillar composites. Therefore, in order to preserve the fibrillar morphology of PC dispersed phase in PE matrix, the sheets prepared by multistage stretching extrusion were fabricated directly into samples for tensile testing. Figure 14 showed the stress–strain curves for microfibrillar composites prepared by multistage stretching extrusion with different LMEs. When the number of LME changed from 0 to 4, the yield stress increased from 31.9 to 38.4 MPa. This result suggested that the fibrillar morphology of PC dispersed phase and orientation of PE and PC molecular chains, which caused by shear field in LME, were contributed to the improvement of the yield stress. Moreover, the samples prepared by multistage stretching extrusion without LME had obvious core-skin structure as shown in Figure 2(g), leading to generate nonuniform failure in comparison with the samples prepared multistage stretching extrusion with 4 LMEs, the difference of failure was observed in Figure 15. It was found that not only the relatively uniform samples can be obtain directly through multistage stretching extrusion but also the yield stress of the composites was improved obviously.

CONCLUSION

The PC/PE *in situ* microfibrillar composites was successfully fabricated by multistage stretching extrusion with an assembly of LMEs. The shear field in LME had greatly affected the morphology of the PC dispersed phase in PE matrix during multistage stretching extrusion. Compared with the PC/PE composites prepared without LME, the core-skin structure of microfibrillar PC/PE composites during multistage stretching extrusion with 4 LMEs was weakened, and fibrillar diameter

was relatively more uniform. Moreover, the morphological development of *in situ* microfibrillar PC/PE composites with increasing the number of LMEs can be also described through dynamic rheological measurement. In addition, it was found that the glass transition temperature of PC in PE matrix reduced with increasing the number of LMEs during dynamic rheological testing. It was coincided with the results of DSC analysis of the PC/PE composites. Compared with DSC analysis of the PC/PE composites, temperature sweep during dynamic rheological testing was a good method to obtain the glass transition temperature of PC phase in the PC/PE composites. It was also found that the shear field in LMEs was helpful to increase the orientation degree of the PE and PC molecular chains, complex viscosity and yield stress of the PE/PC composites as well as melting point of PE. Moreover, the final products of the PC/HDPE *in situ* microfibrils composites can be obtained directly through multistage stretching extrusion instead of the secondary processing. The data obtained in this article was helpful to construct the technical foundation for manufacture of the microfibrillar composites with a novel processing technique.

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