Viscoelastic Properties of Polyarylene Ether Nitriles/Thermotropic Liquid Crystalline Polymer Blend

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ABSTRACT: Polyarylene ether nitriles (PEN)/thermotropic liquid crystalline polymer (TLCP) blend was prepared via melt mixing. The immiscible phase morphologies, linear and nonlinear, as well as transient viscoelastic properties of the blend were studied using SEM, rheometer, and DMA. The linear dynamic viscoelastic behavior of the blend shows temperature dependence due to further evolution of the immiscible morphology and, as a result, the principle of time-temperature superposition (TTS) is invalid. In the steady shear flow, the discrete TLCP phase is difficult to be broken up because of the high viscosity ratio of the blend systems, while is easy to be coarsened and followed by elongation, and finally, to form fibrous morphology at high TLCP content and high shear level. During this morphological evolution process, the transient stress response presents step increase and nonzero residual relaxation behavior, leading to increase of the dynamic viscoelastic responses after steady preshear. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1934–1941, 2008

Key words: polyarylene ether nitriles; thermotropic liquid crystalline polymer; blend; viscoelastic properties

INTRODUCTION

Recently, as a new type of engineering thermoplastic resin, polyarylene ether nitrile (PEN) has been identified as an excellent matrix resin for high performance composites together with polyether ether ketone (PEEK). Owing to their rigid molecular structure, they exhibit high tensile strength, good radiation resistance, and high thermal and thermooxidative stability, which make them very attractive for the composites to use at elevated temperatures and aggressive chemical environments encountered in the aerospace structural application.[1] In addition, the pendant nitrile group on aromatic ring in PEN appears to promote adhesion of the polymer to many substrates, possibly through polar interaction with other functional groups.[2] It also serves as a potential site for polymer crosslinking.[3] All these merits make PEN present high potential applications in many industrial and automotive areas. So far, many researchers have made various attempts to further enhance the performance of PEN. One approach is the incorporation of alkyl pendant groups or sulfone groups or sulfide groups in the backbone of polymeric chain by copolymerization to improve the solubility of PEN.[4–6] Another approach is to use reinforced PEN with glass fiber or metal oxide to obtain PEN composites.[7–9]

It is well accepted that blending polymer pairs is also an effective and convenient way to obtain new polymeric materials with high performance.[10] Among those polymer blend systems, liquid crystalline polymer (LCP) blends have been studied extensively.[11–15] The motivation is first to use the high-tensile modules of the LCPs in the solid state to reinforce the matrix polymers. Second, the low viscosity of the LCPs can reduce the overall viscosity of the blend and thus act as a good processing aid. In addition, the thermotropic liquid crystalline polymer (TLCP), which is dispersed as spheres or droplets initially, can be elongated by adequate flow deformation to give an *in situ* reinforcement. Thus to blend TLCP with polyarylene ether can obtain materials meeting various applications due to their complementary properties. Recently, these kinds of blend systems, such as poly(phenylene sulfide) (PPS)/TLCP[11–13] and PEEK/TLCP,[14,15] have been prepared, and the phase morphology and physical properties of those blends have been studied extensively. On those results, it can be expected that blending TLCP with PEN is also interesting. The immiscible

morphology and improved processability of PEN can be expected on the PEN/TLCP blend because the presence of the TLCP component may reduce the overall viscosity of the systems, although to our best knowledge, there is no literature report on the PEN/TLCP blend systems.

Generally, the performance of the immiscible polymer blends not only depend on the properties of the polymer pairs, but also highly on the morphology, which change significantly during processing and as a result, is assumed to be a unique function of the flow history and of the properties of the polymer.[16–19] Moreover, good insight into the relation between the morphology development and rheological response is essential to optimize final properties of the blend material. Therefore, in this work, at first we prepared PEN/TLCP blend with various blending ratio by melt mixing. Then, we conducted the linear and nonlinear as well as transient rheological measurements on this immiscible blend system, aiming at relating the viscoelastic properties to the morphology and its evolution. The results can provide some useful information on the processing technique for the immiscible PEN/TLCP blend.

EXPERIMENTAL

Material preparation

Polyarylene ether nitriles (PEN, trade marked as 1879-52) used in this study is a commercial product of Yangzhou Tianchen Fine Chemical Co., P. R. China. It is a copolymer derived from 2,6-difluorobenzonitrile with hydroquinone and resorcin with the inherent viscosity of 1.32–1.40 dL/g (in N-methyl pyrrolidone, 0.2 g/mL) and the viscosity flow temperature of 255–278°C. The TLCP used in this study is Rodrun LC-5000 supplied by Unitika Co., Japan. It is a random copolyester of 82 mol % PET and 18 mol % poly(hydroxyl benzoicacid) (PHB) with a nematic transition temperature of 280°C.

The PEN/TLCP blend (PEN/TLCPs, where s denotes the weight ratio of TLCP) was prepared by melt mixing using a HAAKE Polylab Rheometer (Thermo Electron Co., USA) at 290°C and 50 rpm for 8 min, then followed by compression molding at 290°C and 10 MPa to obtain the sheet samples. For better comparison, the neat PEN sample was also processed under the same condition. All materials were dried at 100°C under vacuum for 24 h before use.

Morphology characterization

The morphologies of the blend were investigated using a PHILIPS XL-30ESEM scanning electron microscope (SEM) with 20 kV accelerating voltage. The sheet samples were kept in liquid nitrogen and then brittle fractured. An SPI sputter coater was used to coat the fractured surfaces with gold for enhanced conductivity.

Rheological measurements

Rheological measurements were carried out on a rheometer (Haake RS600, Thermo Electron Co., USA) equipped with a parallel plate geometry using 20 mm diameter plates. All measurements were performed with a 200 FRTN1 transducer with a lower resolution limit of 0.02 g cm. The sheet samples in thickness of 1 mm were melted at predetermined temperature for 5 min to eliminate the residual thermal history, and then experiments were carried out immediately. In the dynamic shear measurements, the small amplitude oscillatory shear (SAOS) was applied. The dynamic strain sweep measurements were carried out first to determine a common linear viscoelastic region. Then, the dynamic frequency sweep was carried out on those samples presheared ($\dot{\gamma} = 1$ s^{-1}) or not at the strain level of 10%. In the transient shear measurements, the startup of steady shear was applied. The sample was first annealed quiescently for 300 s, and then experienced steady shear deformation at the predetermined shear rate for identical time. The transient shear stress responses were monitored during this period. The shear rates are 0.1, 0.2, 0.5, and 1 s^{-1}, respectively.

Dynamic mechanic thermal analysis

The dynamic mechanical properties of the neat PEN and its blend were determined using a DMA-242C dynamic mechanical thermal analyzer (NETZSCH Co., USA). The testing was performed in three-point bending mode at a vibration frequency of 1 Hz in the temperature range from 25 to 250°C at a heating rate of 5°C/min in N$_2$ atmosphere.

RESULTS AND DISCUSSION

Morphology of the PEN/TLCP blend

Figure 1 gives the SEM images of fracture surface for the PEN/TLCP blend samples. All samples present typical two-phase structure. It is clear that the TLCP phase is dispersed as the island in PEN matrix and the domain size increases gradually with increase of TLCP contents. However, those randomly dispersed TLCP droplets only present an average size of about 3–4 μm even at the highest content levels of 20 wt %. Such small phase domain indicates that there exists more or less affinity between PEN and TLCP because of their similar rigid macromolecular structure.
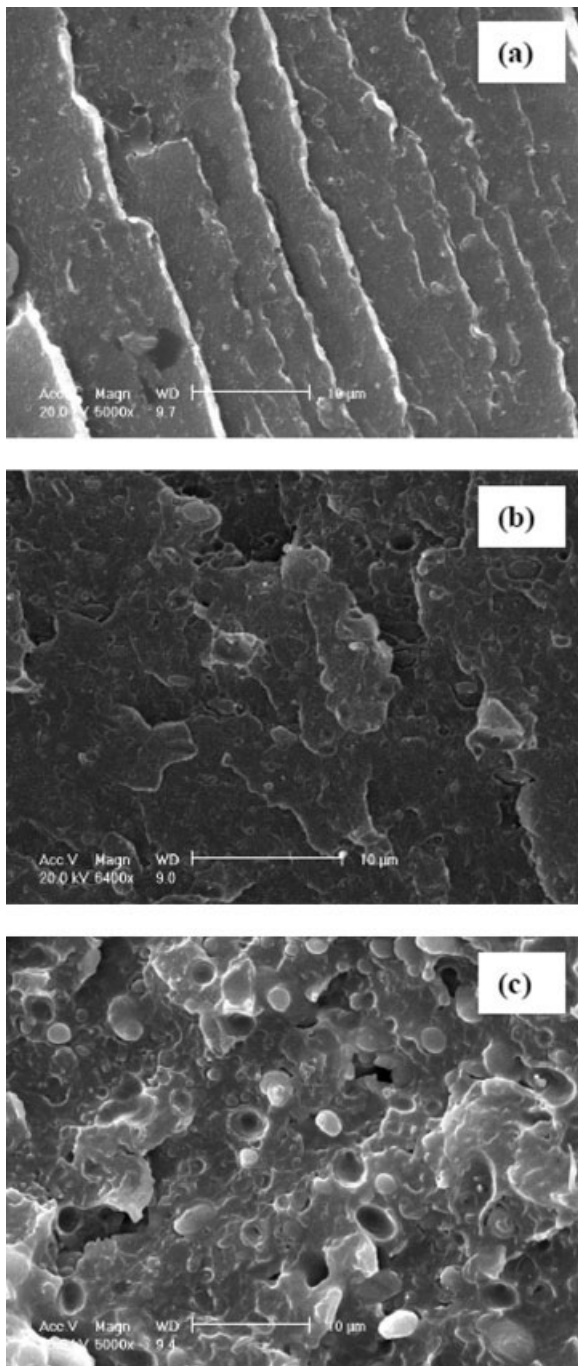
Figure 1 SEM images for the PEN/TLCP samples with various blending ratios (w/w): (a) 95/5, (b) 90/10, and (c) 80/20.

Linear viscoelastic properties of the PEN/TLCP blend

The immiscible phase morphology of the PEN/TLCP blend is related closely to its linear viscoelastic properties. Figure 2 shows the dynamic modulus (G' and G'') and complex viscosity (η^*) curves for the neat PEN and the blends obtained from SAOS measurements. The amplitude of 10% is determined from
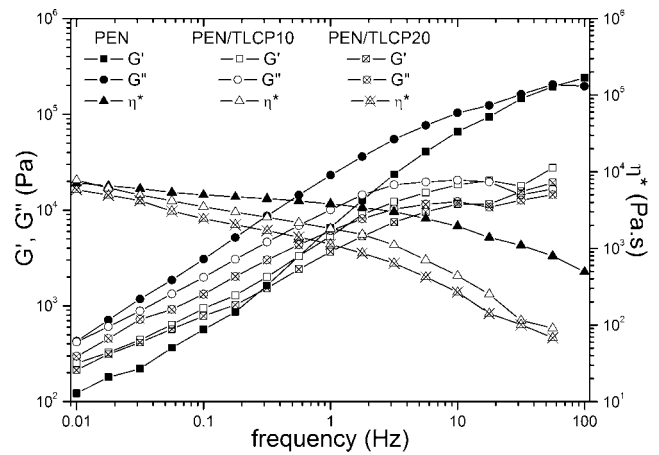

Figure 2 The dynamic storage modulus (G') and dynamic loss modulus (G'') as well as complex viscosity (η^*) for the neat PEN and blend systems obtained from dynamic frequency sweep.

the dynamic strain sweep. Clearly, the presence of less viscous component of TLCP reduces the overall viscosity and loss modulus of the blend system. However, the low-frequency G' of the blend samples increases and presents lower frequency dependency in contrast to those of neat PEN. This is attributed to the shape change of the discrete phase in the matrix during the oscillatory shear deformation, namely shape relaxation.[18–20] The total area of the phase interface is changing during this relaxation process and so are the interfacial energy, and finally, its contribution to the stored elastic energy, which also leads to a remarkable shear thinning behavior of the blend systems compared with that of neat PEN.

Cole-Cole plots[21] are usually used for the description of viscoelastic properties of those materials with a relaxation time distribution such as heterogeneous polymeric systems. Figure 3 shows Cole-Cole plots
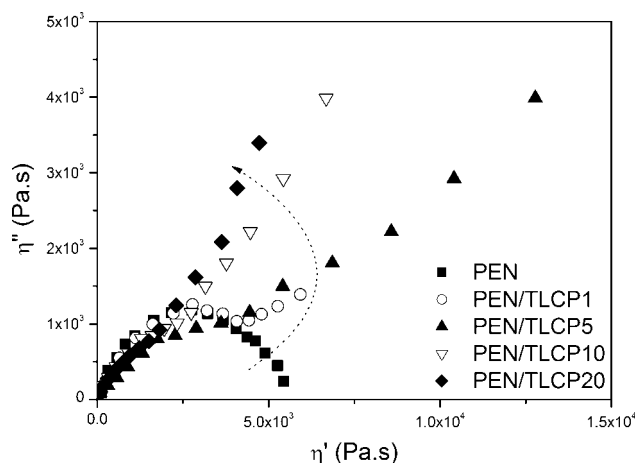

Figure 3 Cole-Cole plots of imaginary viscosity (η'') versus real viscosity (η') for the neat PEN and blend systems.
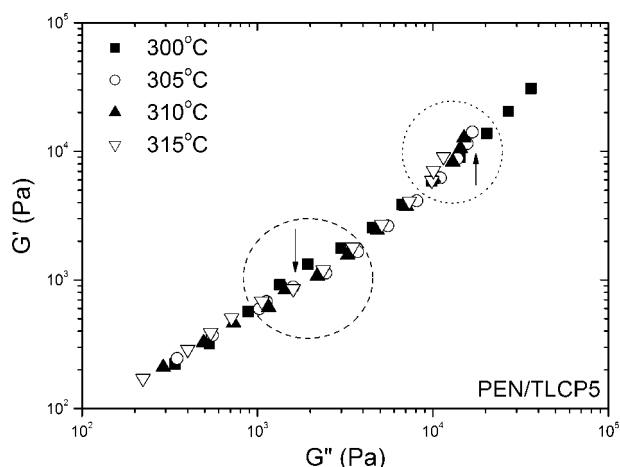
Figure 4 Han plots of dynamic storage modulus (G') versus dynamic loss modulus (G'') at various temperatures for the PEN/TLCP5 sample.

of imaginary viscosity (η'') versus real viscosity (η') for the neat PEN and blend samples. The plots with semicircular shape is obtained for the neat PEN, while with addition of TLCP, a rigid tail appears on the right-hand side of the circular arc, which indicates a second relaxation mechanism appears on the sample of off-symmetric composition,[22,23] further confirming the immiscible morphology of PEN/TLCP blend.

Han and Kim[24] believed that the temperature independence of $G' - G''$ for homogeneous polymer systems could be also applied to the multicomponent/multiphase polymer systems. Figure 4 shows Han plots of $G' - G''$ for the PEN/TLCP blend at various temperatures. Clearly, those plots cannot well coincide, which indicates that the viscoelastic responses of the PEN/TLCP blend depend on the temperature strongly. Similar temperature dependence has also been reported on many other polymer blends.[18,25] As can be seen in Figure 4, the medium-frequency modulus decreases with increasing temperatures. In general, the effective interfacial tension, Γ/R, where R is the average radius of the droplets and Γ is the interfacial tension, affects the $G'_{interface}$ in the medium-frequency region ($\omega > 1$) on the following way[26]:

$$G'_{interface}(\omega) \propto \Gamma/R \qquad (1)$$

It is clear that the medium-frequency modulus presents an inverse ratio relation to the average radius of the droplets in the immiscible polymer blends. With increase of temperature, the dynamic equilibrium between break-up and coalescence of the dispersed phase is broken down. In this case, the less viscous discrete PLCP droplets in the PEN/

TLCP blend are more easily to be coarsened, reducing the corresponding medium-frequency G' as a result. However, it is more or less interesting that the plots of $G' - G''$ at high-frequency region also cannot coincide. One possible mechanism is that the local relaxation of the fabric structure of the TLCP changes within the experimental temperature range, which is worthy of further study. The results of Han plots suggest that the principle of time-temperature superposition (TTS) is invalid for the PEN/TLCP blend systems.

Nonlinear viscoelastic properties of the PEN/TLCP blend

In general, the studies on the linear viscoelastic properties of the immiscible polymer blend are limited in a quite narrow strain level because the linear region is very sensitive to the phase morphology. The nonlinear viscoelastic properties investigation, however, may facilitate further insight into the phase behavior of PEN/TLCP blend. Figure 5(a,b) gives
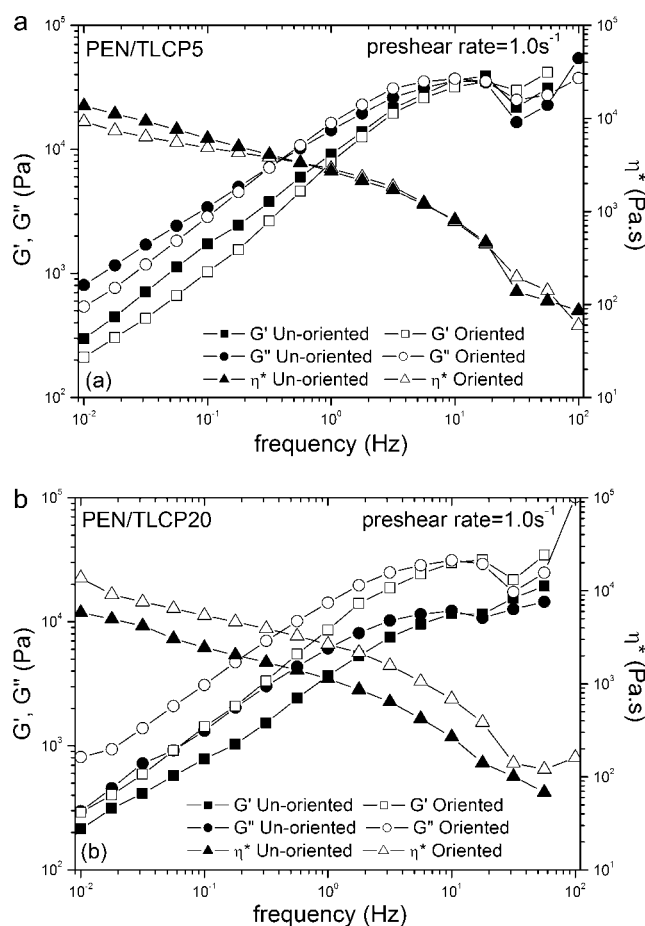

Figure 5 The dynamic storage modulus (G') and dynamic loss modulus (G'') as well as complex viscosity (η^*) before and after steady preshear (shear rate = 1 s^{-1}) for (a) the PEN/TLCP5 and (b) PEN/TLCP20 samples obtained from dynamic frequency sweep.

the effect of steady preshear on the SAOS responses of the PEN/TLCP5 and PEN/TLCP20 blend samples, respectively. Clearly, all viscoelastic responses of the PEN/TLCP5 such as modulus and viscosity decrease after preshear. This is attributed both to the decreased dynamics of oriented local chain and to the orientation and breakup of phase interface. However, the viscoelastic change of the PEN/TLCP20 is contrary to that of the PEN/TLCP5. Both the modulus and viscosity increase after preshear. This suggests that morphology change in the PEN/TLCP20 induced by the steady shear is highly different from that in the PEN/TLCP5. It can be expected that the difference in the droplet size and concentration between these two samples may be the dominant factors contributed to the different changes in their viscoelastic properties.

On the Cole-Cole plots shown in Figure 4, only linear shape can be observed on the PEN/TLCP20, while the semicircular one almost disappears. This suggests that the composition of this blend may be close to the percolation. It is well accepted that phase behavior of the immiscible polymer blend is basically governed by the relative melt viscosities of the two components. Paul and Bucknall[16] proposed the following model:

$$\frac{\varphi_1}{\varphi_2} = \frac{\eta_1}{\eta_2} \tag{2}$$

where φ_i and η_i are the volume fraction and melt viscosity of component i, respectively. On the basis of Tomotika's theory,[27] Metelkin and Blekht[28] developed a capillary model:

$$\varphi_1 = [1 + F(\eta_1/\eta_2)]^{-1} \tag{3}$$

In this equation, F has to be extracted from experiments. Furthermore, Utracki discussed the above two models and developed a new model on the basis of an emulsion one[17,29]:

$$\frac{\eta_2}{\eta_1} = \left(\frac{\phi_m - \phi_{2i}}{\phi_m - \phi_{1i}}\right)^{[\eta]\phi_m} \tag{4}$$

where ϕ_{1i} and ϕ_{2i} are the volume fractions of the continuous and dispersed phase, respectively, at the phase inversion (i), and ϕ_m is the volume fractions of the matrix. All those models predict that the less viscous phase will have the greatest tendency to be the continuous phase. For the PEN/TLCP blend, the η_0 of the TLCP component is far lower than that of PEN (about 7000 Pa s) and is only about 140 Pa s. Thus it is a blend system with very high viscosity ratio. According to the models earlier, the calculated phase inversion point is even smaller than 5/95 (TLCP/PEN), which is not in accordance with the
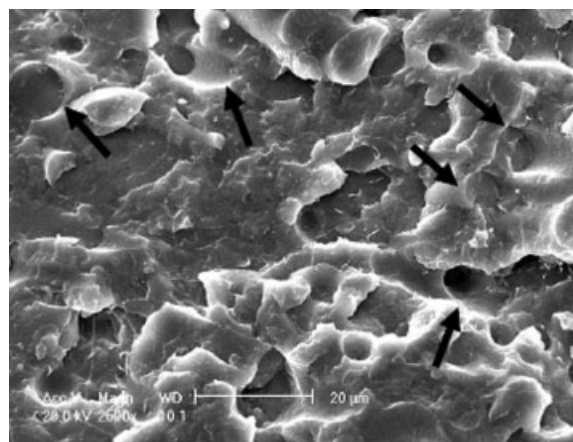

Figure 6 SEM image for the PEN/TLCP20 sample after steady preshear.

SEM observations. Paul and Bucknall[16] proposed that for the immiscible polymer blend, the minor component is always the dispersed phase in spite of the viscosity ratio when its weight ratio is lower than 25 wt %. In this case, therefore, the composition of PEN/TLCP20 is close to the percolation. Additionally, on the SEM image shown in Figure 1(c), it can be seen that the distance among droplets is almost equal to or even smaller than the droplet size, also indicating that the TLCP content is close to the percolation threshold. It is accepted that in the case of polymer blends with a high viscosity ratio ($\lambda > 4$), the deformed droplet is hard to be broken up by steady shear.[30,31] Thus for the PEN/TLCP20, those deformed droplets are easy to be coarsened instead of breakup in the steady shear flow and, the dynamic viscoelastic responses increases after preshear as a result.

Such a shear induced phase coarsening is further confirmed by the SEM observation. Figure 6 gives SEM image for the PEN/TLCP20 sample after steady preshear. Much elongated or fibrous structure of the TLCP phase is dispersed in the PEN matrix along shear direction (see the arrows). On the one hand, this indicates that the simple steady shear flow can also result in the formation of *in situ* microfibril in the parallel plate geometry, more or less like that of elongation flow. On the other hand, it can be seen that the average diameter (about 7–9 µm) of those fibrous structure is larger than that of the droplets without preshear history, which further confirms the coalescence of TLCP droplets before elongation during the steady preshear process.

Transient viscoelastic properties of the PEN/TLCP blend

The submicroscopic morphology of the PEN/TLCP blend hence can further evolve during quiescent
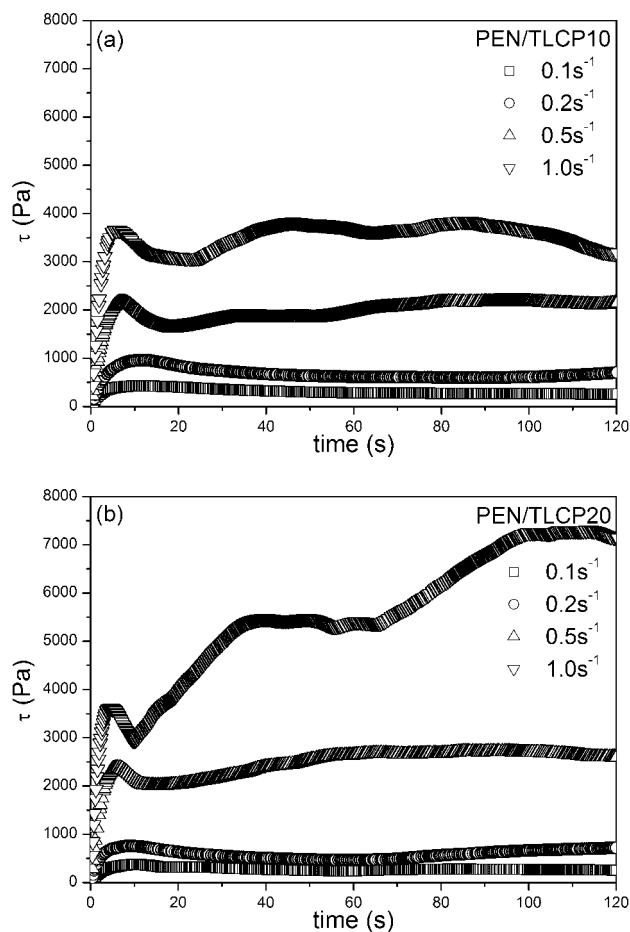
Figure 7 Transient shear stress responses as a function of time for (a) PEN/TLCP10 and (b) PEN/TLCP20 samples to the startup of steady shear flows.

shear annealing process, and finally to a new dynamic equilibrium between break-up and coalescence. In other words, the final phase structure highly depends on the thermal and shear history. Both the linear and nonlinear dynamic rheological studies earlier, however, only give the viscoelastic responses in steady state, which cannot reflect evolution process of the phase morphology. Thus, it is necessary to conduct transient rheological studies to further explore morphological evolution during special annealing process.

Figure 7 shows the transient stress responses to shear time for the PEN/TLCP blend obtained from the start-up flow experiments. The stress overshoot responses to the shear deformation can be seen clearly on the blend especially at high shear rate levels. Similar phenomenon can also be observed on many other immiscible polymer blends.[32–35] This strong dependence of the stress overshoot on the shear deformation is indicative of the structural evolution in the samples during the quiescent shear period, which is attributed to the deformation of the dispersed phase domain. At the initial stage of shear

flow, the TLCP droplets orientate along with shear direction rapidly and, begin to deform at the overshoot point, then followed breakup and finally to the stable morphology after relaxation. The stress responses hence regress to the steady-state value. As can be seen in Figure 7, at the low shear rate level (0.1 and 0.2 s^{-1}), the stress responses of all blend samples relaxed rapidly, while at high shear rate level (0.5 and 1 s^{-1}), the overshoots for the PEN/ TLCP10 present a blunt peak in shape and long relaxation time with nonzero residual stress [Fig. 7(a)]. This is due to the rotation and slide of those deformed TLCP droplets, which also confirms that those deformed droplets are difficult to be broken up in the blend system with very high viscosity ratio by the steady shear flow. However, it is very interesting that the transient stress responses for the PEN/TLCP20 present a step increase at high shear rate level [Fig. 7(b)]. It is well known that viscoelastic responses depend on many factors such as concentration of dispersed phase, interfacial tension, annealing time, flow fields, and so on. The effect of concentration of dispersed phase is very clear
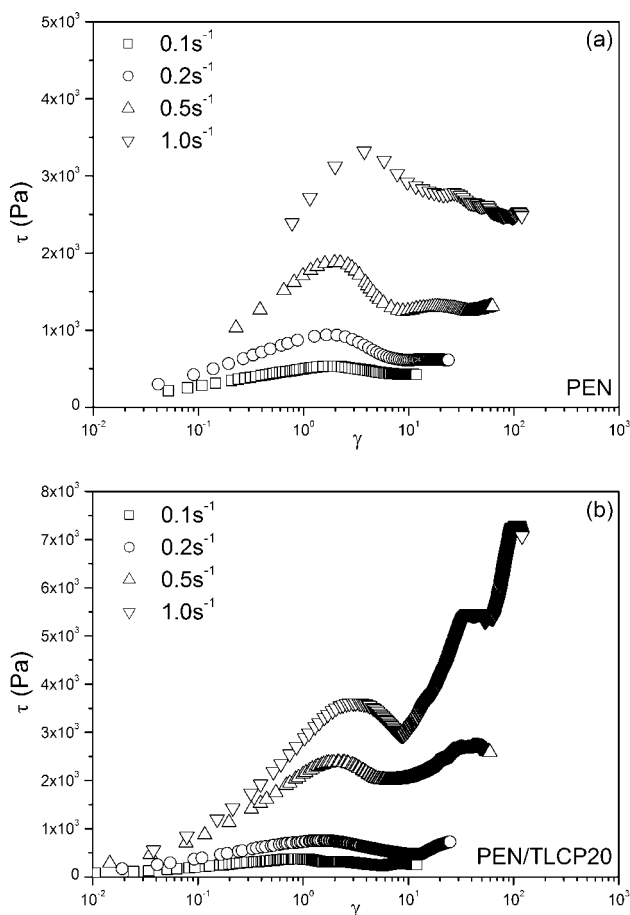

Figure 8 Transient shear stress responses as a function of strain for (a) the neat PEN and (b) PEN/TLCP20 samples to the startup of steady shear flows.
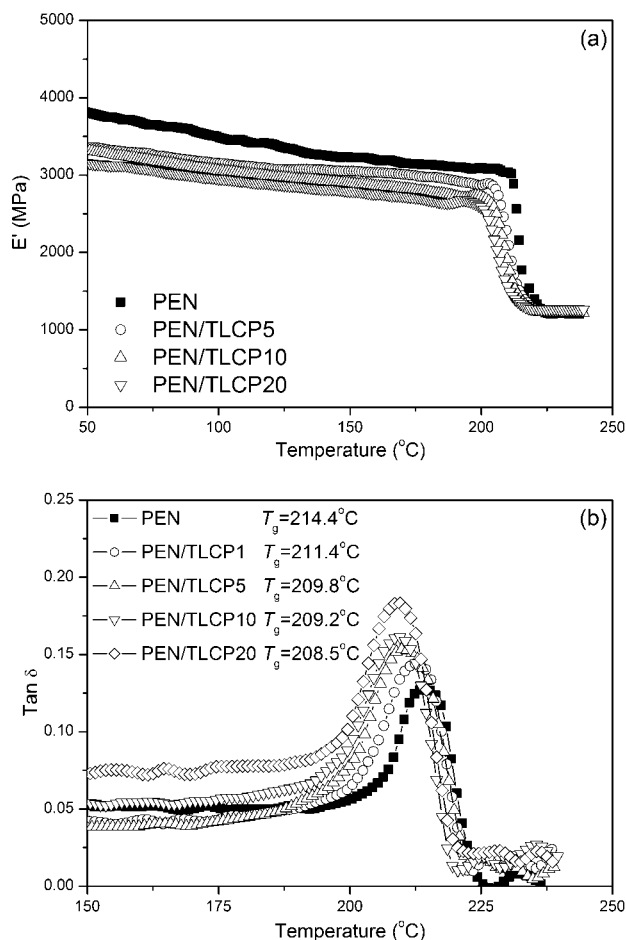
Figure 9 DMTA thermograms of (a) dynamic storage modulus (E') and (b) loss factor (tan δ) for the neat PEN and blend systems.

because the two samples of PEN/TLCP20 and PEN/TLCP5 present different transient stress responses in the experimental time scale. The interfacial tension depends on the flow fields and history strongly, which also influences the rheological responses. But considering the volume fraction of TLCP is close to the percolation point, the phase coarsening may be attributed to this increase of transient stress. Thus, it is reasonable to propose that the oriented TLCP droplets begin to deform at the overshoot point, then followed coalescence to the second stage, and finally to the stable elongated or fibrous morphology at third stage. This is in agreement with those observations from nonlinear dynamic rheological and SEM measurements.

Furthermore, the transient stress responses depend highly on the strain level both for the neat PEN and for blend systems. Figure 8 gives the plots of transient stress against strain. Clearly, the stress overshoots increase with increase of strain levels for all samples. However, only the blend shows nonzero residual stress behavior [Fig. 8(b)], corresponding to

the long-time relaxation process of those evolving or evolved phase morphologies.

Solid-state viscoelastic properties of the PEN/TLCP blend

Figure 9 shows the dynamic mechanical thermal properties for the neat PEN and the blend systems. All blend samples present lower storage modulus (E') than that of neat PEN, and E' decreases with increasing TLCP contents [Fig. 9(a)]. This is due to the relative low modulus of TLCP and the weak interface adhesion between two phases. In addition, the glass transition temperature (T_g) of the blend system also decreases in contrast to that of neat PEN [Fig. 9(b)]. Thus, the reduced melt viscosity and T_g with small addition of TLCP component is very propitious to the processing of PEN. Furthermore, in contrast to that of the PEN/TLCP blend with island phase structure, high modulus can be observed on the blend with *in situ* microfibrillar morphology, which is currently ongoing and will be reported soon together with the melt-state viscoelasticity of the microfibrillar PEN/TLCP blend.

CONCLUSIONS

In this study, the immiscible PEN/PLCP blend, which has a high viscosity ratio between PEN and PLCP components, was prepared by melt mixing for rheological measurements. The results show that the viscoelastic responses of the blend highly depend on the shear history, presenting different sensitivity to the steady preshear. At low TLCP content, the dynamic viscoelastic responses decrease after preshear, while at high TLCP content, the dynamic viscoelastic responses increase after preshear. This is due to phase coarsening and formation of the microfibrillar morphology especially at high shear rate levels, which results in appearance of the step increase and nonzero residual relaxation behavior on the transient stress response. In addition, TTS is invalid for the blend system because the immiscible morphology shows temperature dependence.

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