Enhanced viscoelastic effect of mesoscopic fillers in phase separation

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Received 8th December 2010, Accepted 18th January 2011
DOI: 10.1039/c0sm01445a

Here we report the significant enhancement effect of mesoscopic fillers in viscoelastic phase separation of dynamic asymmetric polymer blends. Mesoscopic fillers with their size much larger than the dimensions of the polymer chains, from nanometres to microns, are preferentially immersed into the slow dynamic phase and phase interface due to the entanglement with polymer chains. For sufficiently high volume fraction and fine dispersion, mesoscopic fillers conduce to the pronounced slowing down of the phase separation process, and result in refined structures with sharply decreased characteristic length scales. The pinning of the phase separation is attributed to the dramatic increase of dynamic asymmetry from the entanglement of polymer chains with mesoscopic fillers. The principal difference between mesoscopic fillers in classic and viscoelastic phase separation is whether there exists a filler enforced elastic-force balance condition. This suggests a general physical scenario of entanglement selection of the polymer chains under stress.

Introduction

Phase separation is one of the most fundamental physical phenomena that control the morphology of heterogeneous structures, which is related to various functions associated with mechanical, electrical, and transport properties.1–3 Recently, Tanaka et al.4–6 and Onuki et al.7–9 have found a novel type of phase separation behavior, named “viscoelastic phase separation”, beyond the classic solid and fluid models. Contrary to the common sense of classical phase separation, there exists a dynamic asymmetry between the two components induced by a large difference either in size or glass-transition temperature, and even the minority phase transiently forms a continuous structure.

The process of viscoelastic phase separation is characterized by a crossover between the characteristic deformation rate and rheological relaxation rate, which can be viewed as viscoelastic relaxation for structure evolution6,10–13

\[ \delta [\Pi_{ij} - \sigma_{ij} + p\delta_{ij}] = 0 \]  

where \( \Pi_{ij} \) is the osmotic stress, \( p \) is the pressure, \( \sigma_{ij} \) is the mechanical stress, and \( \delta_{ij} \) is the Kronecker delta with \( i \) and \( j \) representing one of the Cartesian coordinates \( x, y, z \). It is this force-balance condition that controls the phase structure, rather than interface tension, viscoelastic relaxation of the slow part dominates the phase structure evolution.

In addition to the above binary systems, ternary systems of blends containing fillers have also drawn much attention. Recent studies have shown that the dispersion of nanoscale fillers in polymer systems can change their mechanical, thermal, and electrical properties dramatically.2,4–6 Experimental work7,8 and theoretical simulations9–11 on binary blends containing spherical nano-fillers that interact more attractively with one of the two polymers indicate that the fillers can only slightly affect the phase separation behavior. However, nano-fillers may also act as compatibilizing agents12–14 in immiscible polymer blends by controlling the processing conditions,15–17 where nano-fillers absorb at the interfaces between the immiscible fluids and generate long-lived metastable phase structures.

Although block copolymers15–17 and binary polymer blends containing nano-fillers16,18–20 have been investigated recently, to our knowledge, mesoscopic fillers (meso-fillers) in polymer blends, especially with dynamic asymmetry, have not yet been studied.31,32 Then a question therefore arises: how do meso-fillers, which are much larger than polymer chains, affect the stress coupling and the morphology of an immiscible polymer blend with dynamic asymmetry?

Previous work shows that the viscoelastic effect plays a crucial role during the polymerization induced viscoelastic phase separation process of thermoplastic modified thermoset blends.33–40 Different phase structures can be obtained by varying the dynamic asymmetry between thermoplastics and thermosts, like the composition, molecular weight, and curing temperature etc.41–43 As the stiffness of thermoplastics backbone
increases it sharply enlarges the dynamic asymmetry in these systems, we would expect that the addition of meso-fillers would also have this effect due to their coupling with the slow component.

In this article, we demonstrate an enhanced viscoelastic effect of meso-fillers, which are much larger in size than the polymer chains, in the polymerization induced viscoelastic phase separation. Dynamic asymmetry and chain entanglement lead to the preferential distribution of meso-fillers in slow dynamic phases which enhance the elastic and viscous moduli of the slow thermoplastic-rich component. As a result, viscoelastic relaxation of the slow component which dominates the phase structure evolution is significantly hindered, and thus a refined phase structure with much smaller characteristic length scales can be obtained. We call this “enhanced viscoelastic effect” because the dynamic asymmetry property of the ternary system is enhanced by the fillers compared with binary systems. We have also demonstrated that this kind of “enhanced viscoelastic effect of meso-fillers” would disappear when the dynamic asymmetry of the mixture is diminished.

**Experimental**

**Materials**

The epoxy oligomer used, DER331, was provided by Dow Chemical Co. and is a low molecular weight liquid diglycidyl ether of bisphenol A (DGEBA) with an epoxide equivalent of 182–192. o-Cresyl glycidyl ether, provided by Celanese Ltd., is a mono-functional epoxy diluent with an epoxide equivalent of 100–140. The hardener is methyl tetrahydrophthalic anhydride (MTHPA) which is provided by Ciba-Geigy Co. N,N-Dimethylbenzylamine (BDMA) from Aldrich was used as accelerator to modulate curing rate. All above were used as receive without further purification.

Polyethersulfone (PES) were supplied by Jilin University, China, which has a weight-average molecular weight of 4.5 × 10^6 and polydispersity of 2.4. Polystyrene (PS) with a weight-average molecular weight of 1.0 × 10^6 and polydispersity of 1.2 was provided by BASF Co. The molecular weight of PES and PS was measured with a PerkinElmer S-250 gel permeation chromatograph; polystyrene standards (Showa Denko, Ltd.) were employed to make the calibration curve.

Treated fumed silica used (Cab-O-Sil TS-720, Cabot Corp.) has a polydisperse primary particle sizes, ranging from 7 to 40 nm. Clusters with the size from 200 to 300 nm usually form by aggregation when the silica dispersed in various media. Sepiolite, a rod-like mesoscopic inorganic filler approximately 20 nm in diameter and several micrometres in length, was provided by Tolsa (Spain). To ensure good dispersion in polymer blends, sepiolite was surface modified with the silane coupling agent 2,3-epoxy propoxy propyltrimethoxysilicone according to the procedure used in the literature.44 Montmorillonite clay with a cation-exchange capacity of 90 meq/100 g, was obtained from Southern Clay Products Inc. (Gonzales, TX, US). Before use as filler, the clay was organically modified with cetyltrimethyl ammonium bromide (CTAB) by an ion-exchange method.35,46 CuSO₄ whiskers were provided by Shanghai Fuhua Industrial Co. (China) and used without any treatment.

**Specimen preparation**

The compositions of the formulations studied are collected in Table 1. The formulations contain 13 wt% of thermoplastics (PES or PS), which is near the critical composition, and different fillers, filler content and BDMA ratio.

Fillers were added to the epoxy oligomer under a nitrogen atmosphere with vigorous stirring and ultrasonication at 100 °C for 6 h and a homogeneous epoxy suspension was obtained. The thermoplastic was added to MTHPA with stirring in a sealed glass at 90 °C until a homogenous solution was formed. An epoxy suspension or neat epoxy (without filler), thermoplastic/ MTHPA solution and BDMA were blended together with stirring at 90 °C until the mixture was homogeneous. The samples were degassed under vacuum for another few minutes and then cooled to −10 °C to prevent further curing.

**Experimental techniques**

A PerkinElmer Pyris 1 DSC instrument was used for the study of the curing reaction. The isothermal curing conversion was calculated from residual exotherms observed in scans in the temperature range of 50–350 °C, with heating rates of 10 °C min⁻¹ and normalized by the total exotherms for uncured samples.

The phase-separation process during the isothermal curing reaction was observed at real time and in situ on the self-made time-resolved light scattering (TRLS) instrument with controllable hot chamber.45 The change of the light scattering profiles was recorded at appropriate time intervals during isothermal curing. The blend of epoxy monomer with thermoplastics for TRLS observation was prepared by melt-pressing the film.

Optical light microscopy (OM) experiments were performed with an Olympus BX51P microscope equipped with an Instec HCS410 hot stage.

Transmission electronic microscopy (TEM) was performed with a JEM-1200EX TEM; ultrathin films of cured blends for TEM observation were prepared with an ultramicrotome (Leica Ultracut R) equipped with a diamond knife.

The morphologies of the isothermally cured blends were observed under a scanning electron microscope (SEM, Tescan TS 5163MM) for samples fractured in liquid nitrogen. All samples were coated with gold and mounted on copper mounts.

**Results and discussion**

**Morphology evolution of blends**

Fig. 1 shows a typical evolution process of the polymerization induced viscoelastic phase separation in the PES–epoxy system (sample PES13) observed by OM. The dark regions correspond to the PES-rich phase, while the bright regions to the epoxy-rich. The blend remains homogeneous after about 700 s heating at 120 °C. Then, a micro-bicontinuous phase structure is observed at the beginning of phase separation. As the polymerization proceeds, the epoxy-anhydride precursors diffuse out from the PES-rich phase and coarsen rapidly. Then the morphology shifts into a phase inverted structure quickly with small epoxy-rich dispersed particles. With the elastic elongation and braking of
the PES-rich regions, irregular PES-rich macro-phase domains dispersed in the epoxy-rich matrix are formed.

In the present dynamic asymmetry system of PES and thermoset precursor with large differences in molecular mobility, molecular weight, and glass transition temperature, during phase separation, the viscoelasticity of the slower dynamic phase (PES-rich phase) increases with the escape of the thermoset precursor from the PES-rich phase and eventually behaves as an elastic body. Meanwhile, the less viscoelastic phase (thermoset-rich phase) starts to coarsen with time, and the elastic force balance dominates the morphology instead of the interface tension, which leads to the anisotropic shape of the domain. As the rate of polymerization is not high enough, the coarsening process proceeds without being vitrificated. The key deformation mode is \( \nabla \cdot \bar{v}_s \), where \( \bar{v}_s \) is the averaged local velocity of the slow component. The PES-rich phase as the slow component tends to shrink because of attractive interactions between its components. This causes mechanical stress if the homogeneous shrinking of the system is prohibited by boundary conditions, or if it is so slow that the stress cannot be relaxed during structure evolution. The stress is then supported selectively by the slow-component-rich phase due to asymmetric stress division. Therefore, the coarsening of thermoset-rich particles is in fact accomplished by the disentanglement of PES

<table>
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<tr>
<th>Sample</th>
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<th>PES</th>
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**Fig. 1** Morphology evolution of PES13 at 120 °C.
chains, and thus the viscoelastic deformation of the PES-rich phase makes the thermoset-rich phase evolve to a continuous structure.

When 2 wt% of surface-modified sepiolite is added to PES modified epoxy system (sample PES13Sep2), the evolution process and phase structure change dramatically (Fig. 2). At the early stage of the phase separation, a micro-bicontinuous phase structure is observed, which is the same as that seen in PES13. However, rather than coarsen rapidly the PES13 and epoxy-rich phases in PES13Sep2 grow slowly till the chemical gelation of the epoxy. Bicontinuous networks with much smaller characteristic length scales are obtained at the end of phase separation. Quite different from the sample without sepiolite, there is no clear inverted phase structure, while the bicontinuous structure formed at the early stage coarsens slowly, and the network formed by the PES-rich phase relaxes tardily.

Enhanced viscoelastic effect of meso-fillers

TRLS is applied to trace the effect of meso-fillers on the phase separation process. Fig. 3 shows typical example of scattering profiles with time for the two systems. PES13Sep2 with meso-fillers has a much larger scattering vector \( q_m \) than that of the sample without fillers. This indicates that the sepiolite added has a refinement effect resulting in a much smaller characteristic length scale, which accords well with the results from OM.

Our previous and recent works\(^{33,40}\) show that the evolution of \( q_m \) corresponds to thermosetting precursor droplets and follows a Maxwell-type relaxation equation (eqn (2)).

\[
q_m(t) = q_0 + A_0 \exp(-t/\tau) \quad (2)
\]

where \( q_m(t) \) is the scattering vector at time \( t \), \( q_0 \) is the initial value at the beginning of phase separation, and \( \tau \) is the characteristic relaxation time. The time-dependent \( q_m \) of both samples (PES13 and PES13Sep2) fits the Maxwell-type relaxation equation very well, i.e., the introduction of fillers does not change the viscoelastic relaxation feature of the phase separation process.

However, the relaxation time of PES13Sep2 is about two times of that of PES13. Table 2 shows the same trend at all temperatures, i.e., the relaxation response of the thermoplastic slows down significantly when sepiolite is introduced. Similar light scattering profiles are exhibited at all temperatures for the samples.

The temperature dependent relaxation times listed in Table 2 were fitted by the Williams–Landel–Ferry (WLF) equation:\(^{47,48}\)

\[
\log \frac{\tau}{\tau_s} = \frac{-C_1 \times (T - T_s)}{C_2 + T - T_s} \quad (3)
\]

Assuming that \( C_1 = 8.86 \text{ K} \) and \( C_2 = 101.6 \text{ K} \), the WLF equation can be written as

Fig. 2  Morphology evolution of PES13Sep2 with mesoscopic sepiolite at 120 °C.
As shown in Fig. 4, the relaxation times of both samples obey the time–temperature superposition principle and can be described by the WLF equation well, which means that the addition of fillers does not change the viscoelastic features of the phase separation.

The results of OM and TRLS can also be verified by SEM micrograph (Fig. 5). Both OM and SEM show the same characteristic length scale. It is quite clear that the final phase structure of sample with sepiolite is much more refined and sophisticated compared to that of the sample without fillers.

Dispersion of meso-fillers

TEM was used to observe the location and dispersion conditions of sepiolite in sample PES13Sep2 after final curing at 120 °C. In Fig. 6, the bright regions correspond to the epoxy-rich phase, the gray regions to the PES-rich, and the dark regions to inorganic sepiolite. The TEM micrographs show that most of the sepiolite fillers are in the PES-rich phase, some also cross through the interface of the PES-rich and epoxy-rich, but few distribute in the epoxy-rich phases (bright area). It is noteworthy that most of the rod-like sepiolite particles with high aspect ratio are not randomly dispersed but oriented along the direction of the stress of the PES-rich phase.

This kind of selective distribution of sepiolite in the PES-rich phase rather than in the more polar epoxy-rich phase of stronger affinity is definitely different from that of former nano-fillers in normal binary polymer mixtures, where the nano-fillers are preferentially included in the more wettable component or at the interface during phase separation.\(^\text{17–27}\)

It indicates that dynamic factors rather than thermodynamics factors should be used to explain the distribution of fillers in dynamic asymmetry systems. During the phase separation process, sepiolite has the lowest mobility and is unable to be transported long distances due to its mesoscale size, and the movement of sepiolite is also restricted by the entanglement of sepiolite with long molecular chains; although epoxy precursors may have the chance to gather around the sepiolite particles due to thermodynamic affinity, the large stress of the PES-rich phase pushes the epoxy diffusing away. The main reason of selective distribution of sepiolite comes from the large dynamic difference between the immiscible components and asymmetric stress division during phase separation.

Fig. 3 TRLS profiles of PES13 and PES13Sep2 cured at 110 °C. (a) Intensity versus $q$ at different times; (b) $q_m$ versus time.

$$\tau = \tau_\infty \times \exp \left( \frac{-\ln 10 \times 8.86 \times (T - T_s)}{10.61 + T - T_s} \right) \quad (4)$$

$T_s$ and $T_s'$ correspond to experimental data and the line corresponds to results simulated by WLF Equation.

Table 2 Relaxation time of PES13 and PES13Sep2 curing at different Temperature

<table>
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<tr>
<th>$T/K$</th>
<th>343</th>
<th>353</th>
<th>363</th>
<th>373</th>
<th>383</th>
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<td>PES13 (s)</td>
<td>173</td>
<td>72</td>
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<td>18</td>
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<td>PES13Sep2 (s)</td>
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<td>65</td>
<td>34</td>
<td>21</td>
<td>11</td>
<td>4</td>
<td>3</td>
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</table>

Fig. 4 Plots of the relaxation time versus temperature. The points correspond to experimental data and the line corresponds to results simulated by WLF Equation.

Fig. 5 SEM micrographs of the fracture cross-section morphologies of samples fully cured at 120 °C. (a) PES13, (b) PES13Sep2.
From another perspective, the fillers hindered by PES entanglement cause growth in the elastic and viscous moduli of the PES-rich phase resulting in the elongation of the relaxation time of the network. Previous studies show that when particles are introduced to high molecular weight polymers, the resulting composites increase their elasticity and viscoelastic moduli, signaling a lengthening of the relaxation time. Fillers distributed in a polymer matrix create confinement of polymer chains and slow down chain dynamics. Entanglements trapped in a confined space become more difficult to relax. Sepiolite concentration in PES-rich phase increases with the escaping of epoxy during phase separation. Epoxy-rich phase growth leads to significant strain hardening of the PES-rich phase because the entanglements of the long molecular chains cannot relax over the time scale of phase separation. As a result, the network formed by the PES-rich phase is preserved. In other word, the decrease in the rate of growth of epoxy-rich is due to the hindrance of meso-fillers which are in the PES-rich phase, and are unable to migrate to the epoxy phase due to dynamic asymmetry in the relaxation and diffusion of molecular chains from the large difference in the \( T_g \) and molecular weight of the blend components. The fillers added enlarge the dynamic asymmetry between the fast and slow components by distributing in and hardening the slow component-rich phase. It is the reason why we call this phenomenon “enhanced viscoelastic effect” of meso-fillers in phase separation.

**Effect of meso-filler shape and size**

Based on the above reasons, we can predict that mesoscopic particles, regardless of the shape, would all have this enhanced effect. Indeed, similar phase structures were observed when fillers with sphere and layer structures, like sample PES13Silica2 and PES13MMT2 were cured under the same conditions (Fig. 7). The relaxations of PES-rich structures are hindered significantly. Phase structures with much smaller scale length are obtained at the late stage of phase separation.

Furthermore, we can also expect that increase of the size of fillers would diminish this effect due to difficulty of chain entanglement. When the filler size is further increased to microns as for the CaSO\(_4\) whisker, OM results clearly indicate the disappearance of the filler effect. However, when the curing rate is increased (shorter phase separation time), CaSO\(_4\) whiskers can also show the enhanced effect.

Therefore, the enhanced viscoelastic effect of meso-fillers in dynamic asymmetry systems is a general rule independent of the filler size and shape. The effect of filler size is closely connected to the dynamic asymmetry in the systems. This suggests a general physical scenario of entanglement selection of the polymer chains with fillers under stress.

**Kinetic effect rather than thermodynamic**

To confirm that this dramatic change of phase separation process comes from kinetic rather than thermodynamic changes, we studied the phase diagram of the PES modifying epoxy systems with and without meso-filler sepiolite. For phase diagram study, the fog times are determined by light scattering. With the fog time, the curing conversion at fog time can be obtained directly by the DSC isothermal study results. Fig. 8 shows the phase diagram (the weight percentage of PES) with polymerization conversion at fog point observed by light scattering. To avoid the
effect of polymerization rate (or quench depth due to quick polymerization), epoxy-anhydride without amine system were chosen. Conversion data at the fog point are calculated from calorimetric curves during isothermal curing at 120 °C.

As the size of the meso-fillers is much larger than that of the PES and epoxy precursors, the addition of sepiolite shows a minor effect on the phase diagram. In fact, previous work has shown that only when the size of the particles is comparable to that of the polymers, does the miscibility show large differences. From the phase diagram, one can clearly exclude the thermodynamic effect of meso-fillers during phase separation.

Moreover, this kind of enhanced viscoelastic effect of fillers is quite different from the emulsifying effect which can also result in smaller phase domains. With the emulsifying effect fillers usually stay at the phase interface and the phase domains preferably form sphere-like particles due to interface tension. However, the enhanced viscoelastic effect leads to sharp anisotropic shapes of phase structures as one can see from the OM, SEM and TEM results.

One may wonder that the distribution of sepiolite in the PES-rich phase may come from some kind of special interaction between the fillers and the PES rather than the enhanced viscoelastic effect, we choose another thermoplastic PS, which has the lowest polarity among thermoplastics that can be dissolved into epoxy to replace the polar PES to demonstrate the universal effect of meso-fillers in viscoelastic phase separation.

Phase separation processes and final structures of PS/epoxy blends curing at 60 °C without or with different meso-fillers (Sample PS13, PS13Silica2, PS13Sep2 and PS13MMT2 in Table 1) were studied by OM (Fig. 9). The results are quite similar to that of the PES modified systems. TRLS results further demonstrate the enhanced viscoelastic effect as the relaxation times of phase separation are elongated significantly with the addition of meso-fillers. For example, the characteristic relaxation time of sample PS13, PS13Silica2, PS13Sep2 and PS13MMT2 at 60 °C are ca. 690, 1310, 1240, and 1180 s respectively.

Compared to PS13, samples with meso-fillers (PS13Silica2, PS13Sep2 and PS13MMT2) show significantly slowed down growth rate of phase domains and refined final structures due to the enhanced viscoelastic effect. In other words, in dynamic asymmetry mixtures, due to the large difference in mobility, fillers preferentially distribute in the dynamically slow part and make the slow part even slower.

Diminishing of dynamic asymmetry

On the contrary, we can also expect that this kind of “enhanced viscoelastic effect” would diminish or disappear in systems with low viscoelastic effect or dynamic symmetry. To verify this point, we deliberately manipulate the phase separation by weakening the viscoelastic effect through increasing the polymer chain mobility at high temperature and prolonging the phase separation time at low curing rate.

The morphology evolution of PS13Sep2 cured at 120 °C is shown in Fig. 10. Unlike the phase separation behavior at 60 °C, the network constructed from the PS-rich phase breaks quickly and shrinks to separate PS-rich domains. Obviously, the enhanced viscoelastic effect of meso-fillers has disappeared.

When curing at 120 °C, which is much higher than the \( T_g \) of PS (94 °C), increased energy allotted to the long chains permits them to reorient through the entanglements rapidly and flow as individual molecules. Fillers are more likely to stay in the epoxy which has strong affinity for them. The transient network structure formed during phase separation indicates that the PS-rich phase at 120 °C still acts like a viscoelastic body. However, the relaxation time of the thermoplastic network becomes much shorter due to the high temperature. As a result, the transient network breaks before the gelation of epoxy and an island structure is finally obtained. The influence of meso-fillers at 120 °C is negligible compared to that at 60 °C. In other words, the enhanced viscoelastic effect of mesosopic fillers diminishes in the condition that the different components have no or weak dynamic asymmetry.

According to the time–temperature superposition principle, one can imagine that the characteristics of morphology evolution at a slow curing rate are similar to those at high temperature discussed above. Morphology evolution of sample sPS13Sep2 with a long phase separation time was studied and the results are quite similar to PS13Sep2 cured at 120 °C. Similarly, sPES13-Sep2 also shows this tendency. Due to the slow curing rate, the phase structure develops extraordinary slowly and the final morphology is an island structure in which the thermoplastic-rich phase shrinks into round domains. The added fillers cannot hinder the evolution of the phase structure at the stage of phase inversion, i.e., the long phase separation time provides enough time for molecular motions to disentangle them from each other, as a result, the network formed during phase separation has enough time to relax and break into domains before the gelation.

**Fig. 9** Phase structure of PS13 (a), PS13Sep2 (b), PS13Silica2 (c) and PS13MMT2 (d) cured at 60 °C.
of the epoxy. In other words, entanglements of PS or with fillers have enough time to relax which diminishes the enhanced viscoelastic effect.

Conclusions

In this paper, we systematically studied the polymerization induced viscoelastic phase separation behavior in filler included dynamic asymmetry blends. The enhanced viscoelastic effect of mesoscopic fillers is attributed to the refined material structure by exclusion of other factors, which are the emulsifying effect, filler shape, thermodynamic affinity (polymer polarity) and thermodynamic changes. The effect of fillers in phase separation is closely related to selective polymer chain entanglement under stress. Fillers are preferentially immersed in the slow part due to chain entanglements, and thus prolong the relaxation time of the network formed by the slow part because of the strain hardening effect. The difference between the two components in dynamic asymmetry systems is enlarged by the added fillers. This enhanced viscoelastic effect diminishes with a lower degree of chain entanglement or quicker disentanglement when the dynamic asymmetry is weakened. The effect of filler size and surface affinity originate from the polymer chain entanglement with the filler surface: to keep enough chain entanglement requires smaller fillers size and/or higher affinity, i.e., only nano-fillers with very high affinity show the enhanced viscoelastic effect in low dynamic asymmetric systems, previous work has shown this effect. In other words, one would also anticipate that macroscopic fillers may also have the enhanced effect in quite high dynamic asymmetric systems due to the low chain entanglement at high stress. This reflects the general physical scenario of polymer chain entanglement under stress: more entanglement points (nano-size and/or high affinity) are equivalent to higher stress (dynamic asymmetry) for chain disentanglement.

Acknowledgements

The authors acknowledge support from the National Nature Science Foundation of China (Grant 20704008, 20974027), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, and the Specialized Research Fund for the Doctoral Program of Higher Education of China (SRFDP, No. 20070246001).

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