

The Linear Viscoelastic Behaviors of Nylon1212 Blends Toughened with Elastomer

Wanjie Wang,^{1,2} Yonggang Shangguan,¹ Li Zhao,¹ Jie Yu,³ Li He,³ Hong Tan,³ Qiang Zheng^{1,3}

¹Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

²College of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450052, People's Republic of China

³National Engineering Research Center for Compounding and Modification of Polymeric Materials, Guiyang 550025, People's Republic of China

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ABSTRACT: The linear viscoelastic behaviors of nylon1212 blends toughened with (styrene-[ethylene-(ethylene-propylene)]-styrene block copolymer) (SEEPS) elastomer were carried out. The results show that dynamic storage modulus (G') curves of the blends are located between those of virgin nylon and SEEPS within the frequency (ω) tested, and the G' of blends increases with increasing of the SEEPS content. Moreover, the predictive results of Palierne emulsion model show that it is unsuitable for describing the viscoelastic behaviors of the double phase systems toughened with elastomer, especially for the system with high content of elastomer. The positive deviation

in the plots of G' vs. blend composition demonstrates that the blends are immiscible. From the point of phase transition, the phase inversion region for these blends was predicted to be in the range of 30–50 wt % of SEEPS, which agrees with the morphology analysis of nylon1212/SEEPS blends. In addition, "Cole–Cole" plots of modulus at different temperatures show that the microstructures of blends are unstable in the phase transition region. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1744–1754, 2008

Key words: blends; rheological behavior; nylon1212; SEEPS; toughness; elastomers

INTRODUCTION

For the scientific and industrial objects, multicomponent polymeric blends have attracted increasing attention in recent decades,^{1–5} and blending has been believed to be an efficient way to improve the properties and enlarge the applicative ranges of origin materials. A lot of complex polymeric materials have been developed to satisfy different requirements. In general, polymeric materials of high toughness are always acquired through blending engineering plastics with suitable elastomeric materials, which has become one of the most effective methods to improve the toughness of a brittle polymer. The degree of toughness is determined by the blending ratio, the size of phase domain, the interaction between matrix and elastomer, the blending approaches, processing parameters, etc.^{6–11}

Long-chain nylons (such as nylon 11, nylon 12, nylon1212) have been widely used in machinery, electronic equipments, automobiles, information and aviation industries. It is well accepted that these polymers give superior properties since they provide a combination of high strength and toughness, abrasion resistance, dimensional stability. In comparison with nylon 11 and nylon 12, the mechanical properties of nylon1212 have been improved while other properties kept almost unchanged.¹² Moreover, the abundant and cheap raw materials and low production costs make nylon1212 competitive. It seems that nylon1212 could replace nylon 11 and nylon 12 in many applied fields. However, in some special cases, toughness of nylon1212 could hardly satisfy the requirements. Hence, it is necessary for us to toughen nylon1212. Here, (styrene-[ethylene-(ethylene-propylene)]-styrene block copolymer) (SEEPS) is used as a kind of toughener to blend with nylon1212 and acquire the high toughness nylon material.

In recent two decades, a lot of research concerning nylon/elastomer blends have mostly involved in the aspects of mechanical and thermal properties.^{13–19} To our knowledge, a few reports have been dealt with rheological behaviors of their melts.^{20–24} Because of its highly polar amide end-groups, nylon is incompatible with SEEPS elastomer, resulting in heterogeneous blends. It is noted that the rheological

Correspondence to: Q. Zheng (zhengqiang@zju.edu.cn).

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measurements not only give useful information on material molding and processing, but also provide an effective approach to characterize the structure and properties of polymer materials.^{25,26} The processability of polymers is directly related to the rheological behaviors, and for homopolymers, the rheological behaviors depend mainly on chain and agglomeration structure. In the case of polymer blends, the rheological behaviors are involved in not only the original properties but also in phase morphology, interaction in the interface, and so on. Obviously, it is considerably complex to probe the essence of rheological behaviors of the polymeric blends. The linear viscoelastic behaviors of polymers and their blends have attracted ever-increasing interest of researches, and the correlations of their microstructure and linear viscoelastic behavior have been reported.^{27–31} The aim of this article is to study the linear viscoelastic behaviors of the nylon1212/SEEPS blends, and probe the phase inversion region and the relationship between the rheological behaviors of blends and their morphologies.

EXPERIMENTAL

Materials

Nylon1212 (melt-flow index = 22.43 g/min) used here is a product from Shandong Dongchen Engineering Plastic, China. SEEPS block copolymer (SEEPS 4033, polystyrene end-blocks = 30 wt %, the density = 0.91 g/cm³. The melting index ≤ 0.1 under 2.16 kg pressure at 230°C, the viscosity = 50 mPa·s in the 10 wt % toluene solution, $\overline{M}_n = 67,240$, $\overline{M}_w = 91,365$, $\overline{M}_z = 122,487$, $\overline{M}_w/\overline{M}_n = 1.3588$) is a product of Kuraray, Japan. The antioxidant (B215, the relative molecular weight = 647, $T_m = 453\text{--}458$ K) is a product of Ciba-Geigy, Switzerland.

Preparation of samples

Nylon1212 and SEEPS and 1 wt % antioxidant were blended in a Haake torque rheometer (Rheoflizer Polylab, Germany) at 190°C for 10 min. The samples were compressedly molded at 190°C into disks of 25 mm in diameter and 1.2 mm in thickness.

Rheological measurements

Melt rheological tests were conducted on an ARES Rheometer (Rheometrics, USA) in parallel plates oscillatory mode. The dynamic frequency (ω) sweep was performed from 0.01585 to 100 rad/s, the strain amplitude was maintained as 1% to ensure that rheological behavior is located in the linear viscoelastic region. To record the relaxation modulus varying with time, the stress relaxation tests were

performed under condition of the amplitude being 0.1–100% and the test time being 100 s.

Morphological observation

The morphologies of the blends were observed using a JSM-5510LV scanning electron microscope (SEM). All samples were fractured in liquid N₂ and etched in boiling xylene for 12 h for removing elastomeric phase of the blends. The etched surface after properly drying was coated with a conductive gold layer before SEM analysis.

RESULT AND DISCUSSION

Rheological behavior of virgin polymers

Figure 1 presents the relationship between complex viscosity [$\eta^*(\omega)$] and frequency (ω) for the virgin nylon1212 and SEEPS at 190, 200, and 210°C, respectively. It can be seen that the curves of SEEPS located above those of nylon1212 in the whole ω , i.e. $\eta^*(\omega)$ of SEEPS is higher than that of nylon1212. For nylon1212, $\eta^*(\omega)$ increases as the ω decrease and approaches constant at low ω region, exhibiting a characteristic of Newtonian fluid. Moreover, ω reaching the Newtonian region shifts to low ω region with increase of temperature. However, for SEEPS elastomer, no Newtonian region in the ω tested appears. Furthermore, it also can be seen that $\eta^*(\omega)$ of nylon1212 and SEEPS decrease as the temperature increase in the whole ω measured and the difference of $\eta^*(\omega)$ at different temperatures decreases as the ω increase, especially for SEEPS. The reason for these is that the motion ability of macromolecular chains

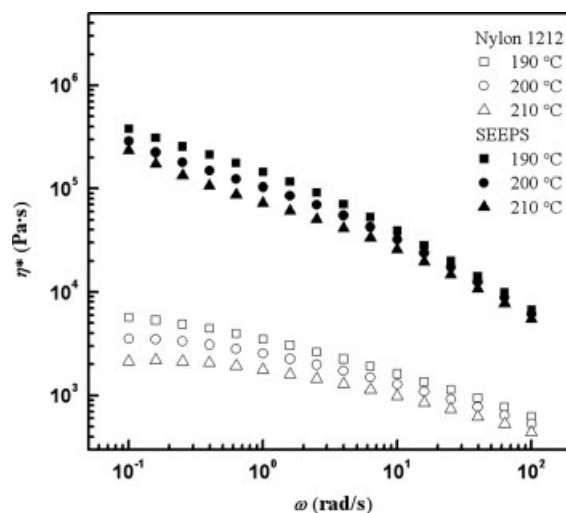


Figure 1 The relationship between complex viscosity [$\eta^*(\omega)$] and frequency (ω) for the pure nylon1212 and SEEPS at three different temperatures, 190, 200 and 210°C.

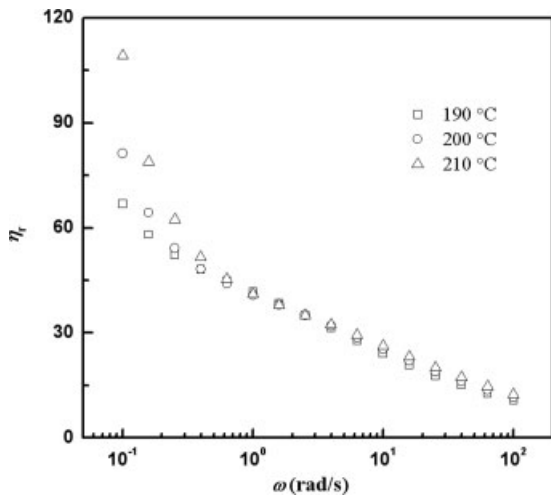


Figure 2 The relationship between the relative viscosity (η_r) and frequency of the pure nylon1212 and SEEPS at three different temperatures, 190, 200 and 210°C.

strengthens with increase of the temperature and the response to stimulation of ω becomes strong, especially for high ω . Moreover, it is well known that the structure of SEEPS elastomer is a micro-phase separation structure, having a long relaxation process.³² In addition, SEEPS behaves as non-Newtonian fluid showing a yield stress at 210°C because of its multi-phase structure.

To explore the difference of viscoelastic behaviors between nylon1212 and SEEPS elastomer, it is meaningful to calculate the relative viscosity (η_r). Here, η_r is equal to $\eta^*(\omega)$ ratio of SEEPS elastomer to nylon1212. Figure 2 gives the relationship between the η_r and ω . It can be seen that η_r decreases with the ω

increasing and a sharp upturn appears in the low ω region, indicating SEEPS has the long relaxation time and its structure is sensitive to the change of ω in the low ω region. Moreover, in the low ω region, the curves measured at three different temperatures show some deviation, and η_r increases with the temperature increasing. The reason for this is attributed that the $\eta^*(\omega)$ change of SEEPS is more sensitive than that of nylon1212, especially in the low ω region. It is well known that, all the changes of rheological parameters of materials are related to their structure. Different rheological curves can be associated with different kinds of microstructures, and appear with different sensitivity in the low ω depending on whether the polymer is of low or high molecular weight, amorphous or crystalline, homogeneous or heterogeneous, and undiluted or mixed with solvent. Here, the structure of SEEPS is a micro-phase separation structure, having a long relaxation time, so SEEPS appears as special rheological behavior in the low ω region. SEEPS could hardly arrive at the “viscosity plateau” in the ω region measured. Meanwhile, the zero shear viscosity (η_0) could be obtained in our previous study.³³ In the relatively higher ω region, because the viscosity curves reflect mainly the characteristic relaxation of PS block for SEEPS and the short relaxation process for nylon1212, the curves of η_r almost overlap each other.

Rheological behaviors of blends

Figure 3 shows the dynamic storage modulus (G') and the dynamic loss modulus (G'') varying with ω

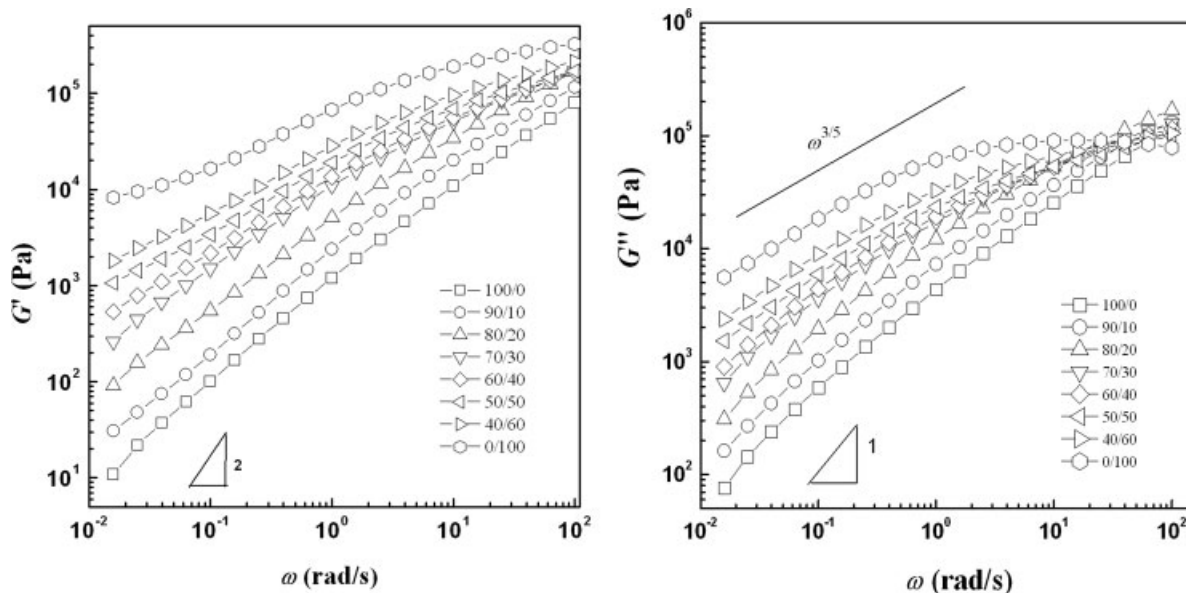


Figure 3 The relationship between the dynamic storage modulus (G') and the dynamic loss modulus (G'') and the frequency for nylon1212/SEEPS blends.

for nylon1212/SEEPS blends containing different amounts of SEEPS at 190°C. It can be seen that within the ω region tested, curves of $G' - \omega$ for blends are located between that of virgin nylon and SEEPS, and the G' of blends increase with increase of the content of SEEPS. The virgin nylon seems to obey the linear viscoelasticity models,³⁴ i.e. $G' \propto \omega^2$, $G'' \propto \omega$ at low ω , to $\log G' \propto 2\log \omega$ and $\log G'' \propto \log \omega$; while the blends do not. These are in agreement with the results for other blend systems.³⁵ It is worth noting that whether the slope of plotting $\log G' \propto \log \omega$ at low ω is close to 2 or not is in general used as a criterion for examining whether heterogeneous (or homogenous) structure in multicomponent polymer systems exists or not.³⁶ On the other hand, compared with the virgin nylon, the slopes of blends at low ω region appear as slightly increased. The reason for this is owed to that the dynamic rheological behavior of blends is mainly dependent on matrix and in possession of self-similarity behavior. Thus, when the content of SEEPS is low, the curve shape of blends is similar to that of virgin nylon1212; while in the case of high content of SEEPS, the blends show mainly the rheological behavior of SEEPS and emerge as the "second plateau" phenomenon at the bottom of G' curves. According to the self-similar behavior, from the slopes of curves in the low ω region, it can also be found that the phase transition region of blends is located in the range of 30–50% SEEPS.

It can be found that the curve of G'' for SEEPS shows a peak at $\omega = 15.85$ rad/s, which is more

readily identified as the glass transition frequency, represented as a peak of the so-called "α-relaxation". At ω just below the glass transition, G'' drops with a scaling, which can be identified as $G'' \propto \omega^{3/5}$. Moreover, as for the virgin nylon1212, the glass transition frequency could hardly be obtained in the ω region observed. It is well known that G' is related to the elastic behavior of the material and is considered as the amount of stored energy, while G'' represents the amount of dissipated energy. The dependence of G' and G'' on ω reflects the relative motion of all molecules in the bulk and can give important information on the rheological behavior of melts. From Figure 3, it can be concluded that SEEPS is much more elastic than nylon1212 and the difference between them increases with ω decrease. Also, the increase in the G' demonstrates that the blends are more elastic than virgin nylon1212, whereas the increase in the G'' shows that the SEEPS elastomer can toughen the nylon1212 effectively.

For two phase system composed of a dispersion of viscoelastic incompressible inclusions in a viscoelastic incompressible matrix, Palierne emulsion model can usually be used to describe the viscoelastic behavior of these blends.^{37–39} This model can be expressed generally as

$$G_b^*(\omega) = G_M^*(\omega) \frac{1 + 3 \sum_i \phi_i H_i(\omega)}{1 - 2 \sum_i \phi_i H_i(\omega)} \quad (1)$$

here

$$H_i(\omega) = \frac{4(\alpha/R_i)[2G_M^*(\omega) + 5G_I^*(\omega)] + [G_I^*(\omega) - G_M^*(\omega)][16G_M^*(\omega) + 19G_I^*(\omega)]}{40(\alpha/R_i)[G_I^*(\omega) + G_M^*(\omega)] + [2G_I^*(\omega) + 3G_M^*(\omega)][16G_M^*(\omega) + 19G_I^*(\omega)]} \quad (2)$$

in which, α is the interfacial tension, ϕ_i is the volume fraction of droplets with radius R_i ; G_I^* , and G_M^* are the complex shear modulus of inclusions and matrix, respectively; G_b^* is the complex shear modulus of blends.

Figure 4 gives the predictions of G' and G'' curves of blends by Palierne emulsion model. Here, the predicted values of G' and G'' of blends are determined from G' and G'' values of virgin nylon1212 and SEEPS according to Palierne emulsion model based on the matlab software. It can be seen that this model can describe the viscoelastic of blends (90/10). Although the values of prediction are slightly higher than the experiment data, the model not only gives satisfactory results in the low ω but also describes the multiphase relaxation processes. As for the blend (80/20), the model can hardly give the satisfactory prediction and the values of prediction are

less than the experiment, which demonstrates that the Palierne model is unsuitable to describe the viscoelastic behavior of blends containing a large amount of SEEPS. The reasons for these are attributed to that the viscosity of SEEPS is higher than that of nylon1212. When the blends are under stimulation of external factor, SEEPS cannot give the same response with nylon1212 because SEEPS has long characteristic relaxation time.

For two-phase blends, the composition dependence of viscoelastic functions gives much information on the level of miscibility of the blended material. It is believed that the shape of plotting rheological functions versus composition and their maxima/minima are related to the morphology of the materials at composition ratios, phase interactions, and interfacial tension, and hydrodynamic effects. The method of blend preparation and the type of form-

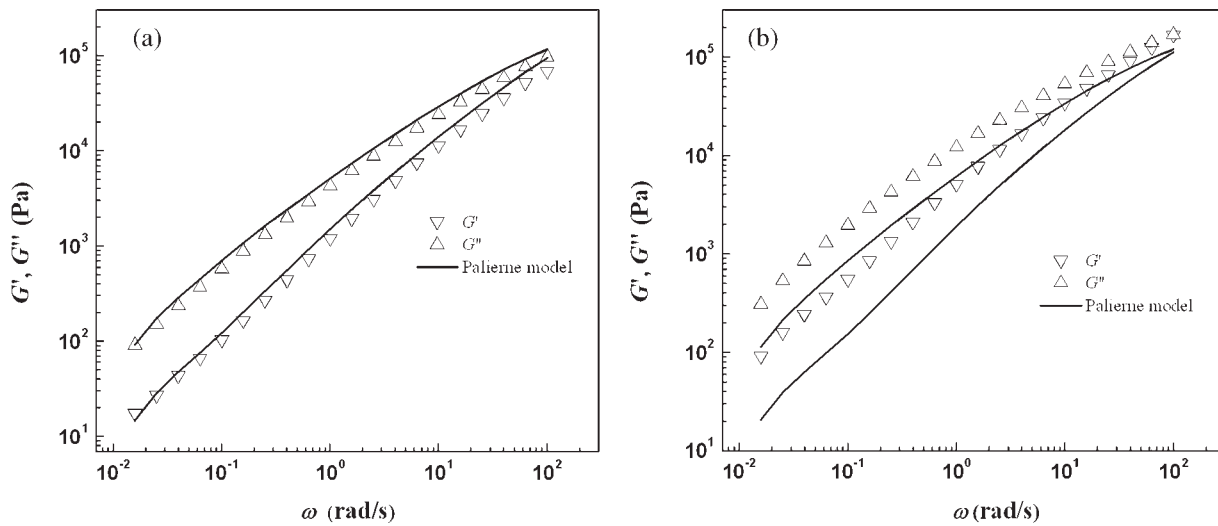


Figure 4 Comparison between the experiment data and the predictions of Palierne model at 190°C for (a) 90/10 (nylon1212/SEEPS) and (b) 80/20 (nylon1212/SEEPS).

ing operation are among other parameters controlling the observed interactions between melt- or solid-state morphology and rheology. Phase inversion, droplet size and shape, co-continuity, and conversion of droplets into fibrils with different degrees of alignment depending on stress level are all parameters that have been suggested to be responsible for the shape of rheological curves.⁴⁰

The viscoelastic functions of the miscible blends usually follow the log-additivity rule^{41,42}

$$\log F_b = w_m \log F_m + w_d \log F_d \quad (3)$$

where F is a viscoelastic function, w is the weight fraction; and subscripts b , m , and d indicate the values for the blend, the matrix, and the dispersed phase, respectively. However, there exists some deviation from the log-additivity rule for the immiscible blends, in which immiscible polymer blends can be divided into three categories, i.e. positive deviation, negative deviation, and positive–negative deviation, depending on the blend-composition dependence of the viscoelastic function.

Figure 5 presents the composition dependence of the G' at different ω for nylon1212/SEEPS blends. It can be seen that G' of blends shows positive deviations and the deviation increases with the ω decrease. The reason for this is that the viscosity ratio of inclusions to matrix is very high and SEEPS with long characteristic relaxation time can hardly keep the same motion as the matrix. At high ω ($\omega = 10$ and 100 rad/s), when the weight fraction of SEEPS is less than 30%, the curves of G' versus the composition of blends appear almost straight line, which demonstrates that there is little interaction among droplets and matrix; whereas when the weight fraction of SEEPS is higher

than 30%, a plateau region can be observed at intermediate composition, involving in their co-continuous morphology. Accordingly, it is suggested that phase inversion region is from 30 to 50% SEEPS. At low ω region, no “plateau region” in the curves emerges but has a transition point about 30% SEEPS. Compared with the experiment data, the phase inversion point seems to shift to a lower amount of SEEPS in the blend, although no change takes place in phase-morphology for the sample within ω region tested. The reason for this is that the inclusions have relatively adequate time to relax because the measured time in the low ω is long and the deviation induced by the difference of characteristic relaxation time between inclusions and matrix can be lessened to minimization.

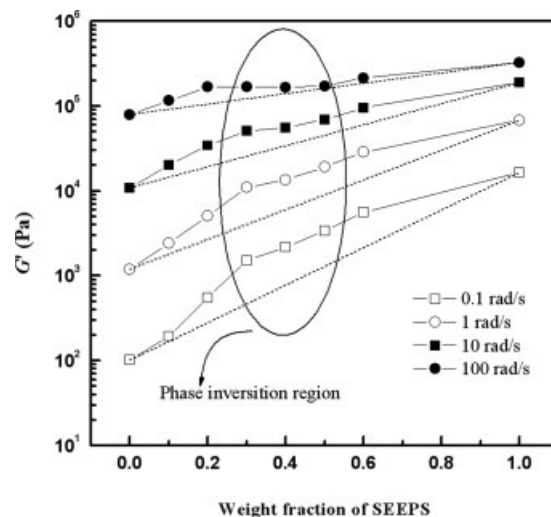


Figure 5 The dependence for the storage modulus on the compositions of nylon1212/SEEPS blends at different frequencies.

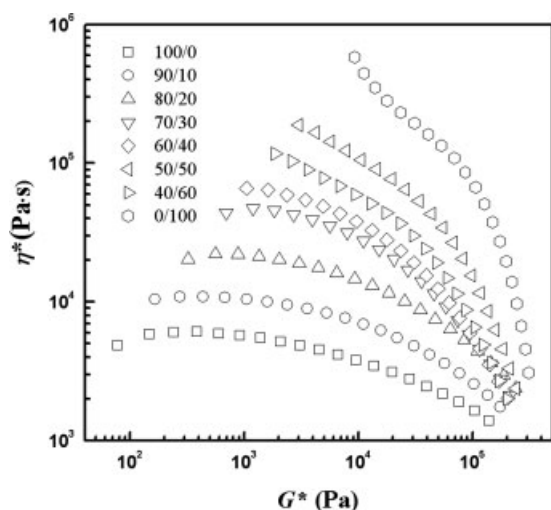


Figure 6 The relationship between the complex viscosity (η^*) and the complex modulus (G^*) of nylon1212/SEEPS blends.

Figure 6 shows the relationship between $\eta^*(\omega)$ and the complex modulus (G^*) for nylon1212/SEEPS blends. Such curves are important for examining yield stress behavior,³⁹ even though they could hardly be observed in some miscible blends. A sharp upturn in $\eta^*(\omega)$ at low $G^*(\omega)$ indicates the existence of yield stress, which generally exists in immiscible and filled polymer systems. It can be seen that from Figure 6 a sharp increase in $\eta^*(\omega)$ as $G^*(\omega)$ decreases seems to be responsible for existence of yield stress in SEEPS elastomer, which is resulted from the micro-phase separation structure. As for the virgin nylon1212, $\eta^*(\omega)$ approaches a constant with increase of $G^*(\omega)$, exhibiting a Newtonian behavior at the low ω . Compared with those of nylon1212 and SEEPS, all of the blends do not show the yield stress behavior, although SEEPS and nylon1212 blends belong to thermodynamic incompatible systems.

To distinguish homogeneous and heterogeneous blends, Han and Chuang⁴³ and Han and Yang⁴⁴ provided a criterion based on the plotting G' vs. G'' . Accordingly, a master curve at different temperatures could be obtained for miscible blends, while for immiscible blends there exist a series of curves, and each one shifts with respect to the other for different compositions at different temperatures. Regardless of homopolymer or blends, such plots yield temperature-independent correlations. In other words, one does not need a shift factor for obtaining temperature-independently reduced plots. Hence, to obtain temperature-independent correlations, such plotting may be more useful than the time-temperature superposition principle, and can be obtained by shifting values of G' and G'' along the ω axis. In such an attempt, one chooses a particular tempera-

ture as a reference temperature (T_r) and shifts the values of G' and G'' obtained at all other temperatures to the corresponding values at T_r . However, as shown in plotting G' vs. G'' , it is no requirement of manipulation for data to achieve a master curve.⁴⁵

Figure 7 presents the relationship between G' and G'' for nylon1212/SEEPS blends at three temperatures. It is noted that these curves were used by Han and Chuang to investigate temperature-induced changes in the microstructure of homopolymers, block polymers, and blends, and it was proposed that if no change in the microstructure with temperature takes place, curves at different temperatures should coincide, as is the case in the single-phase melts. When the microstructure changes with temperature, different curves are expected.⁴³ It can be seen from Figure 7 that curves of virgin nylon1212 almost coincide completely and all of the experiment data seem to be a straight line, indicating that the microstructure of nylon1212 melts is stable and independent of temperatures. When the content of SEEPS is relatively low (10–30%), the microstructures of blends are also not affected by the temperature. However, it is noted that the shapes of curves are not similar to that of virgin nylon1212 and have upturn in the low ω region, which means that the addition of SEEPS changes the melting flow behavior of nylon1212 and the interactions between nylon1212 and SEEPS are weak when SEEPS forms the disperse phase in the form of droplet. When the weight fraction of SEEPS is higher than 30%, curves measured at different temperatures show some deviation, indicating that the microstructures of blends are involved in temperature and are unstable in the phase transition region. As for the SEEPS, the micro-phase separation structure is unrelated with the temperatures, and the shapes of curves are not a straight line but a segment of arc, which is perhaps a sign of particular structure of copolymer.

Figure 8 presents comparison of curves of G' versus G'' for different composition nylon1212/SEEPS blends. Curves of plots of G' vs. G'' , i.e. the so-called "Cole-Cole" plots of modulus had been used by Han and Yang to investigate miscibility of polymer blends; they suggested that plotting G' against G'' gives rise to correlations that may become independent of blend composition for the compatible blend systems, but dependent upon blend composition for the incompatible blend systems.⁴⁴ It is well known that there exists no intermolecular or chemical interaction between nylon1212 and SEEPS. Therefore, each blend with a different blends ratio would have different domain size, and thus its rheological response would be different. It can be seen that curves of each blend with a different blend ratio exhibit a strong dependence on blend compositions, which demonstrates that these blends are incompati-

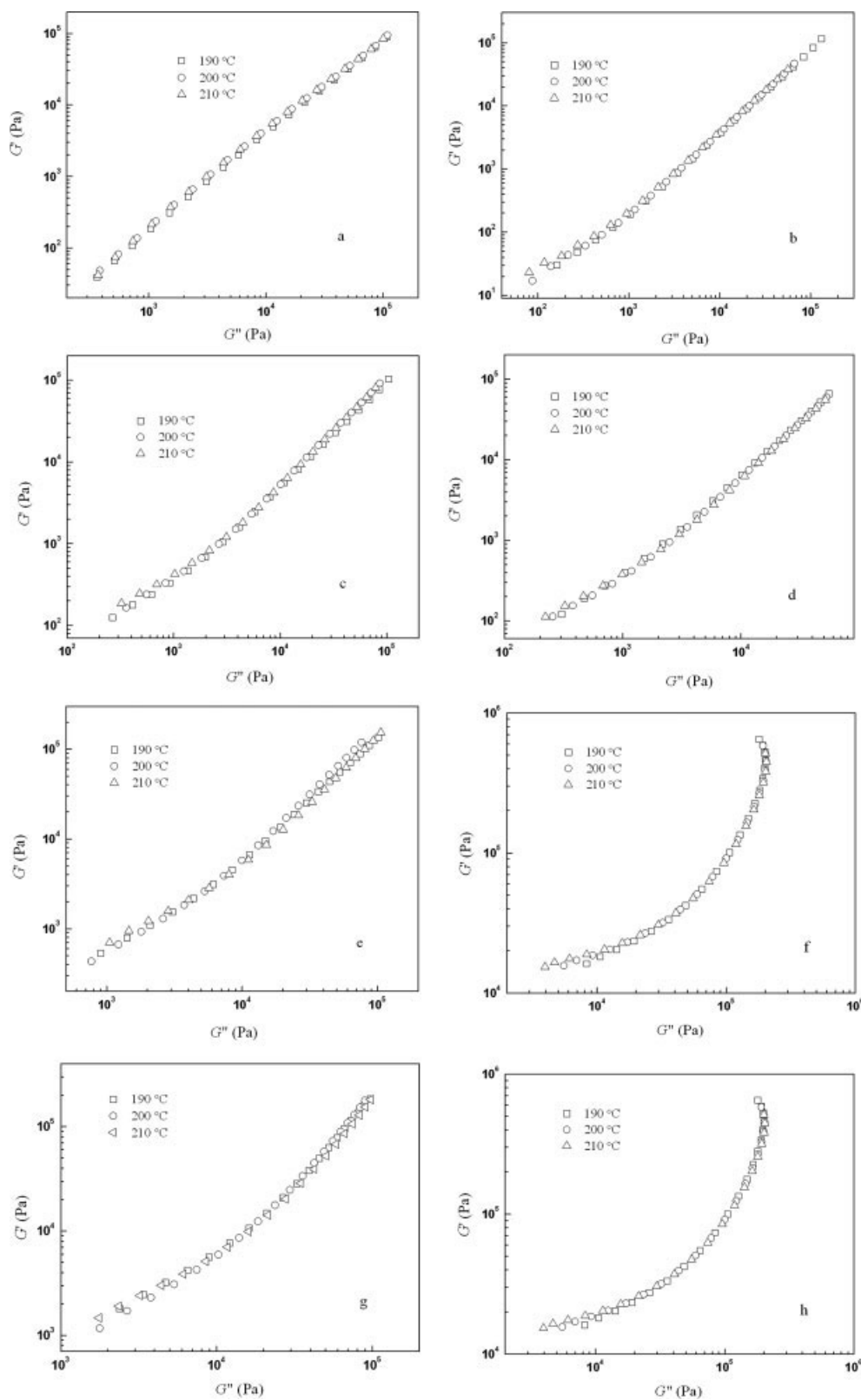


Figure 7 The relationship between G' and G'' for nylon1212/SEEPS blends at different temperatures: (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30, (e) 60/40, (f) 50/50, (g) 40/60, and (h) 0/100.

ble. Obviously, the reason for this can be attributed to morphological change accompanying the change of compositions. Furthermore, curves of blends

locate in the left side of that of nylon1212, indicating that the addition of elastomer enhances the elasticity of blends and changes the processing properties.

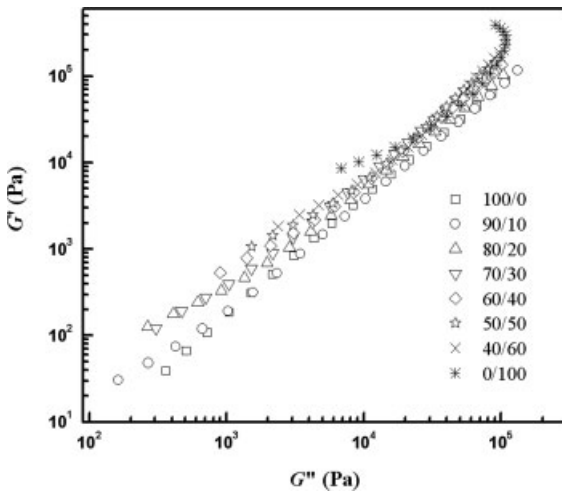


Figure 8 The relationship between G' and G'' for nylon1212/SEEPS blends at 190°C.

Relaxation behaviors of blends

Figure 9 gives the linear relaxation modulus $[G(t)]-t$ curves of nylon1212/SEEPS blends. It can be observed that the $G(t)$ of blends increase with SEEPS loading, similar to that observed in the dynamic viscoelastic measurements. Furthermore, for the blends with low content of elastomer, the relaxation behaviors are qualitatively similar for virgin nylon1212, while the relaxation behaviors of the blends with high content of elastomer exhibit that of SEEPS. The virgin nylon1212 demonstrates a fast relaxation process, while the virgin SEEPS first exhibits fast and then slow relaxation processes. The former corresponds to the relaxation behavior of hard block (PS), while the latter, the relaxation behavior of random copolymer block.

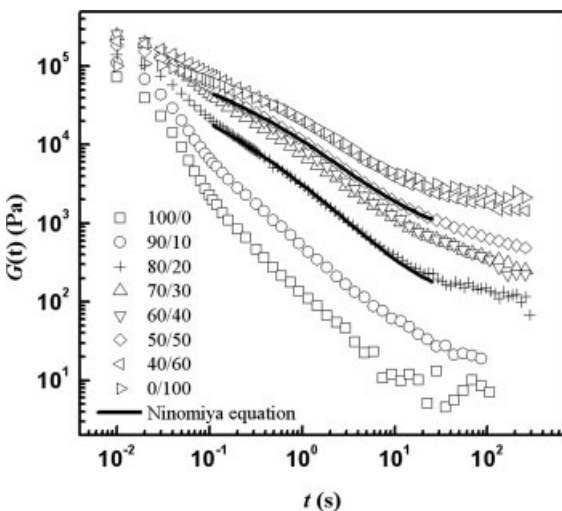


Figure 9 Linear relaxation modulus $G(t)$ of nylon1212/SEEPS blends.

On the other hand, after about 10 s, the trail of $G(t)$ becomes too small, leading to slight scattering on the results. This is because the measured torque is below the lower limitation of the transducer. For further evaluating the linear viscoelastic behavior of blends at small γ , the Ninomiya and Ferry equation can be used to calculate $G(t)$ from dynamic data in the linear viscoelastic region³⁴

$$G(t) = [G'(\omega) - 0.4G''(\omega) + 0.014G''(10\omega)]_{\omega=1/t} \quad (4)$$

It can be seen from the calculated results as shown by the solid line in Figure 9 that the calculated data are close to the experimental data. Moreover, there exists some deviation in the long time region between the calculated and the experimental one. We believe that the long time data of stress relaxation are responsible for the low ω data of dynamic ω sweep. Although both kinds of data reflect the same viscoelastic essence, the response at low ω to external stimulation is highly sensitive as compared with that of long time because of the complex structure of blends.

To more accurately evaluate the relaxation process, the weighted relaxation spectrums $[\tau H(\tau)]$ have been calculated based on the Schwarzl and Staverman differential eq. (5).⁴⁶ Figure 10 gives the curves of $\tau H(\tau)$ as a function of the τ . It can be observed that

$$H(\tau) = -G(t) \left[\frac{d \log G(t)}{d \log t} - \left(\frac{d \log G(t)}{d \log t} \right)^2 - \frac{1}{2.303} \frac{d^2 \log G(t)}{d(\log t)^2} \right]_{t=2\tau} \quad (5)$$

the weighted relaxation spectrum of virgin nylon1212 exhibits two maxima, corresponding to short and long

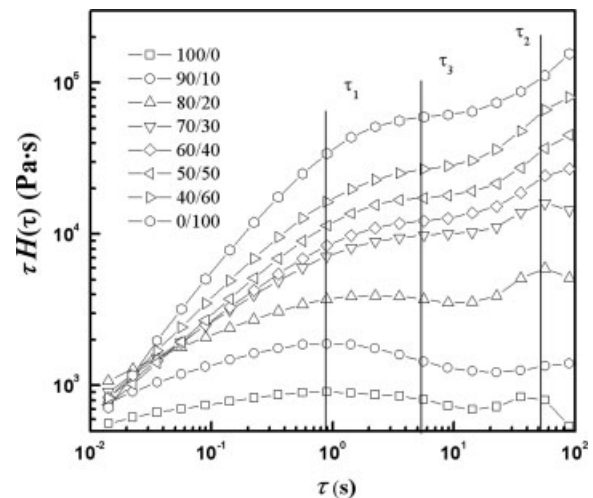


Figure 10 The weighted relaxation time spectrums for nylon1212/SEEPS blends at 190°C.

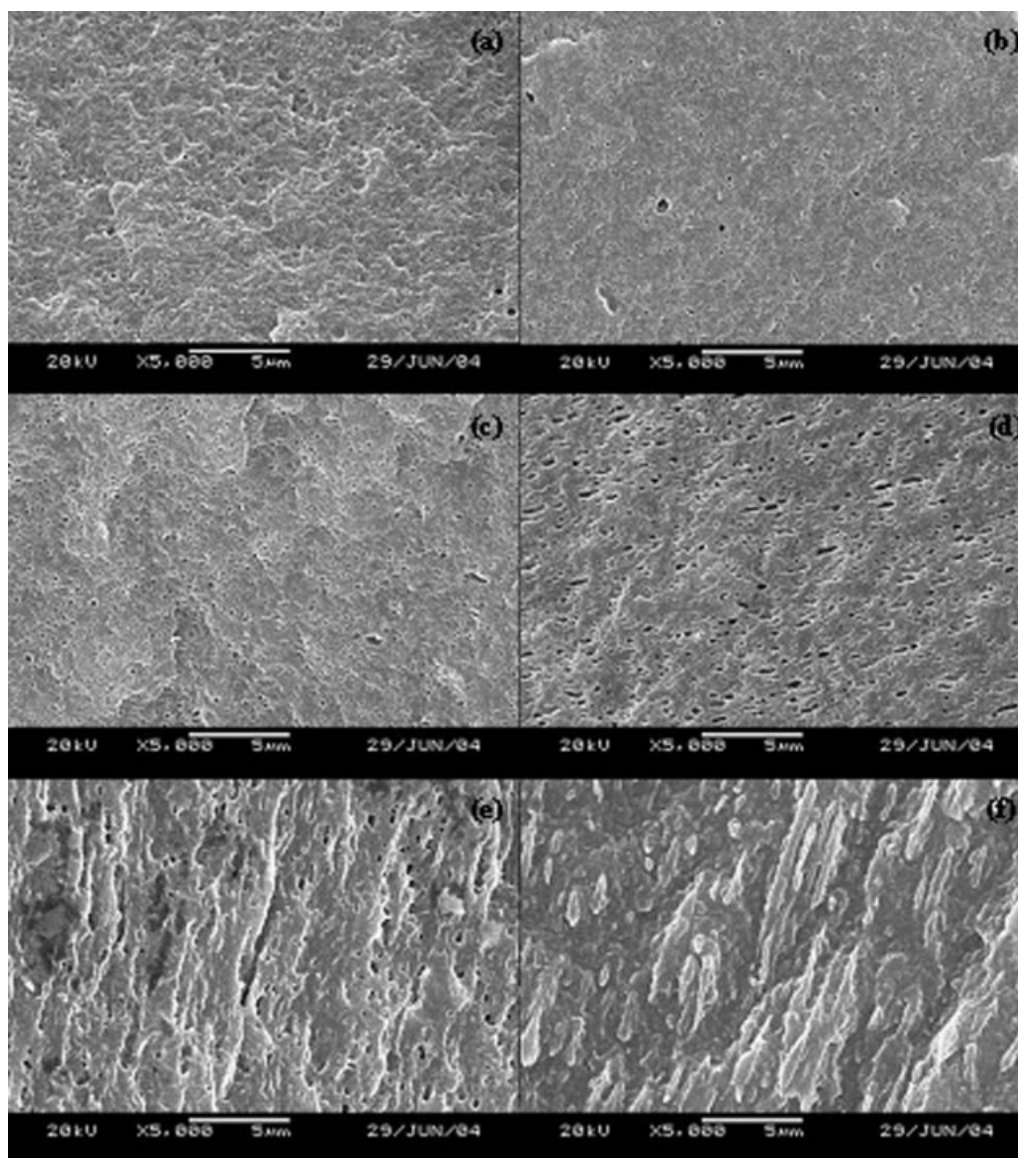


Figure 11 SEM images of surface deal with the boiling xylene of nylon1212/SEEPS blends. (a) 90/10, (b) 80/20, (c) 70/30, (d) 60/40, (e) 50/50, and (f) 40/60.

relaxation times. The corresponding characteristics relaxation times are 0.87 and 58.12 s, respectively. It is worth noting that the short relaxation time of blends having low content of elastomer coincides with that of the matrix, suggesting that the viscoelastic behavior of these blends in the high ω region is dominated by the behavior of the matrix. By contrary, the blends with high content of elastomer show the relaxation behavior of pure SEEPS, which gives a short characteristic time but do not exhibit the peak corresponding to the long characteristic time because its location is beyond the measured time scale.

Morphology analysis of blends

It is well known that the viscoelastic behaviors of polymer systems can sensitively reflect differences of

their morphology. Consequently, it is necessary to analysis the morphology of blends to understand the rheological behaviors of blends more clearly. According to the SEM images of etched surface of blends as given in Figure 11, we believe that the SEEPS phases erase in the broken surfaces after extraction with the boiling xylene for 12 h and the images of SEM reflect the distributions of SEEPS phases.

When the content of SEEPS is relatively low, it can be seen that from Figure 11(a,b) the phases of SEEPS are dispersed and distribute relatively orderly in the matrix of nylon1212, and the shape of SEEPS is spherical. Moreover, the slight agglomeration of SEEPS is found from the relatively large holes, and the edges of holes are relatively smooth and the distance between two elastomeric particles is relatively

far, which indicates that the interaction between the disperse phases and matrix is weak. It is noted that the existing interaction could hardly affect the rheological behaviors of blends greatly. Therefore, the rheological behaviors of blends with low content of SEEPS are similar to that of virgin nylon1212. In the case of blends with 30% SEEPS, the number of disperse particles in the same area increases and the size of particles also increases. Furthermore, some particles are not spherical but ellipsoidal, which means that the blends enter gradually into phase transition region. Accordingly, the rheological behaviors changes to some extent, which can be seen from plots of the dynamic modulus versus the compositions of blends. With the increase of SEEPS content increasing farther, most particles turn into long strands. When the content of SEEPS is 50%, morphology of blends exhibits obvious double phase co-continuity structure although there are still some spherical particles distributing in the surface. It can be seen from Figure 11(f) that nylon1212 becomes dispersed phase and SEEPS acts as continuous phase. As a result, the rheological behaviors of blends are mainly depended on that of SEEPS.

CONCLUSION

Studies on the linear viscoelastic behavior of nylon1212 toughened with SEEPS elastomer have been carried out. It can be found that complex viscosity [$\eta^*(\omega)$] of the virgin polymers, nylon1212, increases as the frequency (ω) decreases and approaches a constant value at the low frequency region, which exhibits a characteristic of behavior of Newtonian fluid; while for SEEPS elastomer, no appearance of Newtonian behavior similar to nylon1212 can be found. On the other hand, curves of the dynamic storage modulus G' - ω for the blends are located between that of virgin nylon and SEEPS in measured ω region, and G' of blends increases with the content of SEEPS. Moreover, there appears a slight increase in the slopes of plotting G' vs. ω for blends at low ω , which is owed to that the dynamic rheological behavior of blends is mainly dependent on matrix and in possession of self-similarity behavior. Furthermore, Palierne emulsion model is used to describe the viscoelastic behaviors of blends, and the results of prediction show that it is unsuitable to describe the viscoelastic behaviors of the double phase system toughened with elastomer, especially for the high content of elastomer.

The positive deviation observed in the plot of G' vs. blend compositions implies that the blends are immiscible. From the point of phase transition, the phase inversion region for these blends is predicted to be in the range of 30–50% weight fractions of

SEEPS, which agrees with the morphology analysis of nylon1212/SEEPS blends. Furthermore, it can be found from the curves of $G^*(\omega)$ versus $\eta^*(\omega)$ that no stress yield behavior exists for the blends but SEEPS elastomer show the character of stress yield behavior. However, the Cole–Cole plots of modulus show that the microstructures of blends with relatively low content SEEPS seems to be independent of the variation of temperatures, but when the weight fraction of SEEPS is higher than 30%, curves measured at different temperatures show some deviation, indicating that the microstructures of blends are dependent of temperature and unstable in the phase transition region. In addition, the weighted relaxation spectrums [$\tau H(\tau)$] have been calculated on the basis of Schwarzl and Staverman differential equation, and the spectrums present the particular relaxation behavior for virgin polymers and their blends.

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