

STUDY ON PHASE-SEPARATION OF PMMA/SAN BLENDS INDUCED BY GLASS BEADS THROUGH DYNAMIC RHEOLOGICAL MEASUREMENTS*

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Abstract Based on the premise that the addition of glass beads (GB) could hardly influence the linear viscoelasticity in low frequency (ω) region for homogeneous polymer systems, the dynamic rheological behaviors of unfilled and filled poly(methyl methacrylate) (PMMA)/poly(styrene-*co*-acrylonitrile) (SAN) blends were studied in order to explore the effect of GB on the phase-separation of binary polymer matrix. Results show that GB has an induced effect on the phase-separation, which embodies that the phase-separation temperature (T_s) of PMMA/SAN blend filled with GB is lower than that of the unfilled system. The higher content of GB, the higher is the “secondary plateau” of ω in the terminal region of storage modulus (G') versus ω plot. The “secondary plateau” appearing in the terminal region is attributed to the phase-separation of PMMA/SAN blends and it becomes more flat for filled polymer blends under the same conditions. However, it is suggested that this kind of “induced effect” is related to the GB content; the higher content of GB particles might enhance the interaction between the particles and polymer matrix. Moreover, it is found that the addition of GB also has an influence more or less on the morphology and domain size of polymer matrix. It is believed that the plot of dynamic viscosity (η') versus the loss viscosity (η'') is sensitive to examine the effect induced by GB on the phase-separation of binary polymer matrix.

Keywords: PMMA/SAN blends; Glass beads; Phase-separation; Rheological behavior.

INTRODUCTION

Polymer blends provide a convenient approach for producing novel material with properties different from, and often superior to, those of the constituent homopolymers. In general, fillers or particles are used to further improve the mechanical, thermal, and barrier properties of these materials^[1–3]. Concerning the case in which the particles with high surface areas are added to a polymer blend rather than a homopolymer, people's interest is to know the effect of their adding on the thermodynamic phase behavior of the blend and on the morphology formed in the two-phase region. It is expected that the higher the surface areas, the more significant the effects are. Recently, a remarkable decrease in domain sizes of strongly incompatible polymer blends due to the addition of organically modified layered silicates has been reported^[4]. The change of phase diagrams and cloud point curves, induced by the addition of the particles, and at the same time the variation of the thermodynamic stability of polymer blends have also been found^[5–8]. In addition, the evolvement of phase morphology in binary mixture containing particles has been simulated^[9–11]. Any changes in the phase-separated structure or the kinetics of their development are thought to be especially important because they endure a significant impact on the processing and properties of materials. But up to now, the phase behavior of a particular system, poly(methyl methacrylate) (PMMA)/poly(styrene-*co*-acrylonitrile) (SAN) blend system which is miscible by the so-called “repulsion effect”

* This project was supported by the National Natural Science Foundation of China (No. 20304014) and the Special Funds for National Science Funds for Distinguished Young Scholars (No. 50125312).

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Received January 17, 2005; Revised April 8, 2005; Accepted April 18, 2005

and exhibits a lower critical solution temperature (LSCT) behavior^[12–15] filled with particles, has not been reported.

Rheological measurement, especially dynamic testing, has been a primary characterization method for polymer blends^[16, 17]. Based on the rheological measurement, many fingerprints can be found out to infer qualitatively or quantitatively the critical point of phase-transition in a polymer blend. The “secondary plateau” on the curves for rheological functions of frequency (ω) at low ω region (terminal region) is especially thought to be a sign for the deviation level of viscoelastic behavior from the linear theory^[18, 19]. In our previous work^[15, 20], we have reported the change of dynamic storage modulus (G') against ω could be used to judge whether the phase-separation takes place in a PMMA/SAN blend system or not, on the basis of whether the relationship between G' or dynamic loss modulus G'' and ω follows $G' \propto \omega^2$ and $G'' \propto \omega$ or not. The determined rheological demixing temperature (T_b) can be considered as phase-separation temperature (T_s). However, there were few systematic investigations concerning the dynamic viscoelastic behavior for PMMA/SAN blends filled with particles near phase-separation.

Glass bead (GB) is a kind of conventional particles, and can be used to improve the insulating property and heat resistant property, *etc.*^[21–23]. The hollow glass beads (HGB) can even depress the density of the polymer. To our knowledge, few researches concerning the dynamic rheological behavior for HGB filled polymers have been reported. In this paper, we try to investigate the dynamic viscoelasticity evolution in the vicinity of phase-separation region for PMMA/SAN blends filled with HGB by measuring dynamic rheological behavior.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA: $\overline{M}_n = 3.8 \times 10^4$, $\overline{M}_w / \overline{M}_n = 2.1$) and poly(styrene-*co*-acrylonitrile) (SAN: $\overline{M}_n = 6.4 \times 10^4$, $\overline{M}_w / \overline{M}_n = 1.9$, AN = 28%) were obtained from LG Chemical Ltd. and Chimei Corporation, respectively, and used without further purification. Two kinds of HGB (HGB800N and HGB5000N) were supplied by Shanghai Zhengmeiya Nanomaterials Ltd. Co., with an average particle diameter of 8.06 μm and 1.44 μm , respectively.

Sample Preparation

The samples for dynamic rheological measurements were prepared by dissolving the polymers in methyl ethyl ketone ($\text{CH}_3\text{COCH}_2\text{CH}_3$) at a weight fraction of 15%. The polymer solution was cast on the surface of glass plates. After the solvent evaporated overnight at ambient environment, the films were dried in a vacuum at 60, 80, 100, 130°C, respectively for 72 h to remove the solvent completely. The films were then dried in a vacuum oven at 140°C for 48 h until constant weight. The films with the thickness of 80–100 μm were folded up and compression molded into disc form having a diameter of 25 mm and thickness of 1.2 mm at 10 MPa below 150°C. The components of samples were listed in Table 1.

Table 1 The compositions of samples

HGB content	PMMA/SAN (20/80)	PMMA/SAN (40/60)	PMMA/SAN (60/40)	PMMA/SAN (80/20)	SAN
none	✓	✓	✓	✓	✓
800N, 5 wt%	✓	✓	✓	✓	✓
800N, 10 wt%	✓	✓	✓	✓	✓
5000N, 5 wt%	✓	✓	✓	✓	—

Dynamic Rheological Measurements

The rheological tests were conducted on an Advance Rheometric Expansion System (2ARES-9A) with parallel plate geometry of 25 mm in diameter. The frequencies in the dynamic frequency sweep tests were from $10^{-2} \text{ rad} \cdot \text{s}^{-1}$ to $10^2 \text{ rad} \cdot \text{s}^{-1}$. Depending on the measured temperatures from 150°C to 190°C by a temperature

increment of 10 K per step, the strain amplitude was controlled between 1.0% and 20% to gain a high torque. All applied strains were in the linear viscoelastic region.

Transmission electron microscopy (TEM) was used to observe the morphology of the blends. The samples were stained using osmium tetroxide (OsO_4) for 24 h. TEM micrographs of specimen sections with thickness of 200 nm were taken with a JEM-1200EX transmission electron microscope.

RESULTS AND DISCUSSION

Dynamic Viscoelastic Response of SAN Filled with HGB

Figure 1 shows the frequency (ω) dependence of the storage modulus (G') for HGB filled SAN or unfilled SAN at 170°C. Similar to most polymer composites filled with particles, SAN filled with HGB800N tends to store more elastic energy (G'), which slightly increases with increasing HGB content. According to the linear viscoelasticity theory, the important result involving in viscoelastic properties in the terminal region can be reduced to $\lg G' \propto 2\lg \omega$ when ω approaches zero for homogenous polymer melt, such as SAN and PMMA. However, for a heterogeneous system, *i.e.* a polymer composite filled with particles, there appears a “secondary plateau” or a trend of pseudo solid-like in the plots of G' versus ω at the low ω , if the content of particles is higher than a critical content, suggesting that a network structure of the fillers formed in the composite system. However, there is no “secondary plateau” for SAN filled with HGB even in a high content of fillers (20 wt%), which reveals that no particles’ network structure is formed, *i.e.* HGB have hardly influence on the linear viscoelasticity in terminal region for SAN at measurable range in the present paper. Hence, this makes it reasonably convenient to study the dynamic rheological behavior near phase separation region for the unfilled/filled polymer blends.

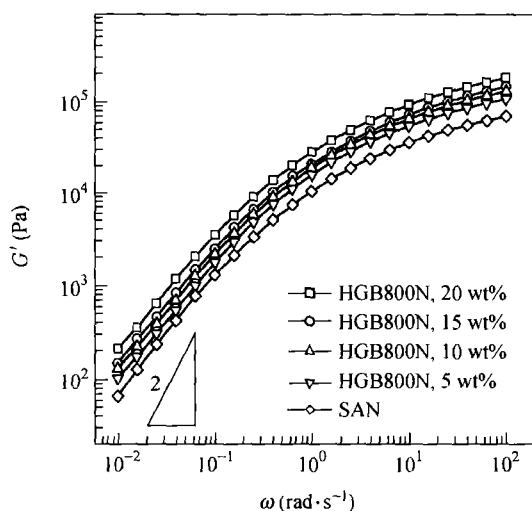


Fig. 1 The frequency ω dependence of the dynamic storage modulus G' for SAN and SAN containing HGB with different weight fractions (wt%) at 170°C

Dynamic Viscoelastic Response of PMMA/SAN Blend Filled with HGB

PMMA/SAN blends exhibited a LCST-type behavior, which obeys spinodal decomposition (SD) mechanism due to the concentration fluctuation in the adjacent region near phase separation temperature (T_s). Accordingly, it can be accepted that the adding of HGB hardly influences the linear viscoelastic properties at low frequencies for a single-phase SAN system in measured range (< 20 wt%). However, in the case of PMMA/SAN blends containing HGB, the effect of particles on phase-separation during the transition from a single phase into dual phases needs attention. Thus, the values of G' for the 20/80, 40/60, 60/40 and 80/20 PMMA/SAN blends filled with HGB are measured as a function of ω in the temperature range from 150°C to 200°C with a temperature increment of 10 K

per step. In order to clarify matters, the discussion in the present paper is mainly focused on the 60/40 and 20/80 PMMA/SAN blends.

Figure 2 presents the typical isotherms of G' versus ω for HGB unfilled and filled 60/40 PMMA/SAN blends. On the basis of our previous work^[15], it is known that when temperature was above T_s , the plot of G' versus ω exhibited a slight flattening in the terminal region, which developed further with the increase in temperature. These phenomena have been proven to be the result of microstructure transition from homogenous to heterogeneous. As shown in Fig. 2, unfilled PMMA/SAN (60/40) blend (a) and the blend filled with 5 wt% HGB800N (b) and 10 wt% HGB800N (c) exhibit the same uptrends when the temperature is above a certain value, which illuminates that phase-separation has taken place in the three systems. These temperatures corresponding to phase separation for each system can be termed as T_s . When a dynamic rheological measurement was performed with a temperature increment of 1 K per step, it can be seen that the T_s of PMMA/SAN blends filled with HGB800N were lower than that of unfilled PMMA/SAN blend. There existed

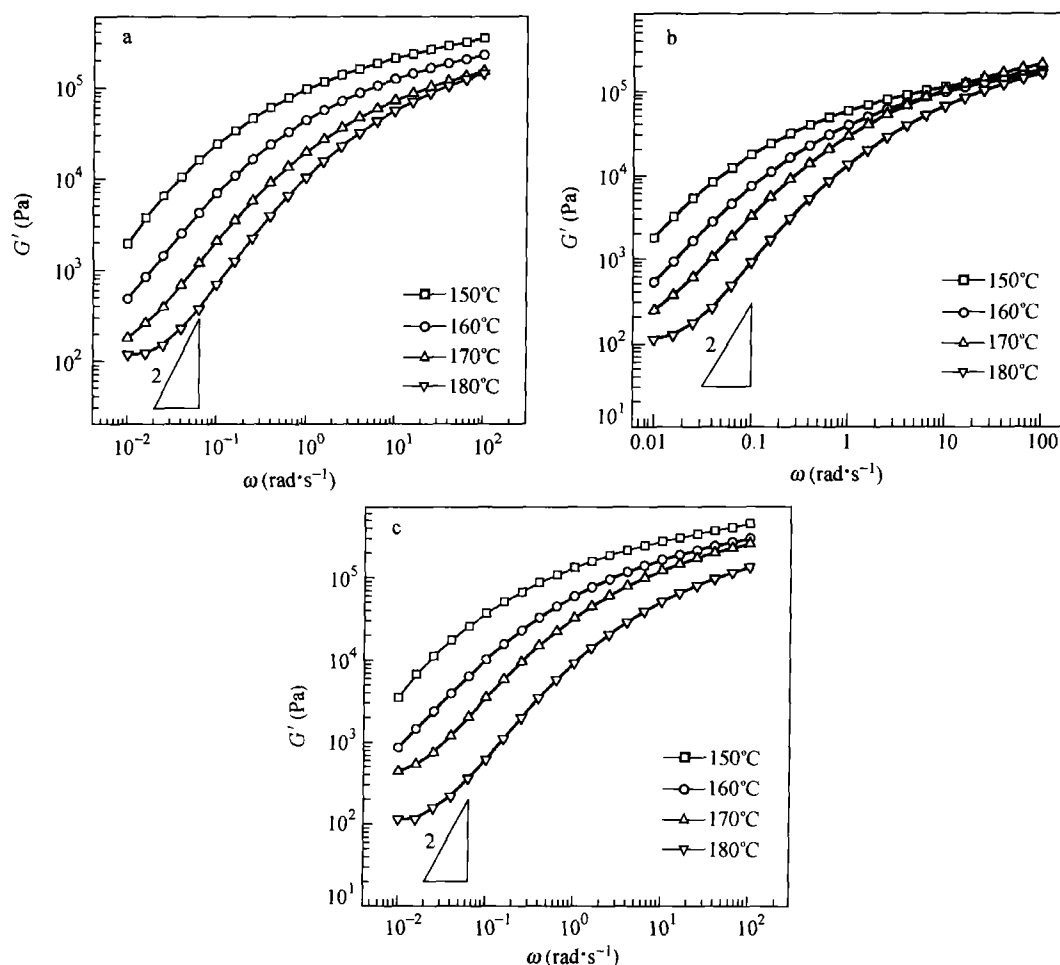


Fig. 2 Plots of dynamic storage modulus G' as a function of frequency for unfilled/filled PMMA/SAN (60/40) blends at different temperatures

a) Unfilled; b) Filled with 5 wt% HGB800N; c) Filled with 10 wt% HGB800N

more obvious differences between unfilled and filled polymer blends, according to the curves of G' as a function of ω for PMMA/SAN (60/40) blend and its composites filled with 5 wt% and 10 wt% HGB800N at 170°C (above T_s) as shown in Fig. 3. Similar to that of filled SAN, the G' for filled PMMA/SAN (60/40) blend increases with the increase in HGB800N content in the whole ω region. However, it is interested that the more the content of HGB800N in the PMMA/SAN blend, the higher the frequency at which the “secondary plateau” of

the curve in terminal region appears. Based on the forementioned results, we believed that this “secondary plateau” was not caused by the network structure of HGB800N in these composites within measured scope. Hence, it is reasonable to believe that this phenomenon is the result of phase-separation and becomes more obvious flattening for PMMA/SAN blend filled with HGB content. Furthermore, these results show that the introduction of fillers has an “induced effect” on the structure rearrangement during phase-separation and then lowers the T_g of the PMMA/SAN matrix. On the other hand, we believe that this effect is resulted from the interaction between fillers and polymer matrix. Usually, the strength of the interaction between fillers and polymer matrix is proportional to their interfacial areas controlling the formation of interphase, and therefore corresponding to dynamic rheological behavior during the phase-separating of polymer matrix. The presence of fillers leads to an internal friction between the fillers and the polymer matrix, which makes G' increase at the whole ω region. At the same time, the internal friction induces the occurrence of phase separation for polymer matrix and influences the rheological response of the system, which embodies that the slight flattening of G' versus ω plotting moves to higher ω for the filled systems. Apparently, the higher content of fillers, the larger interfacial areas that intensifies the interaction between the fillers and polymer matrix, and therefore also the more obvious “secondary plateau” image.

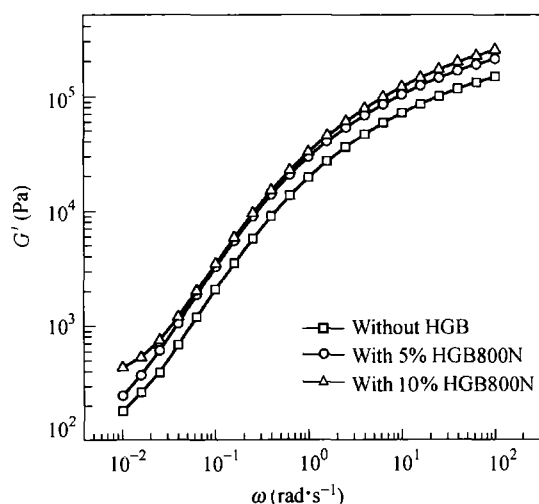


Fig. 3 Effect of HGB content on the plots of dynamic storage modulus G' as a function of frequency ω for PMMA/SAN (60/40) blend at 170°C

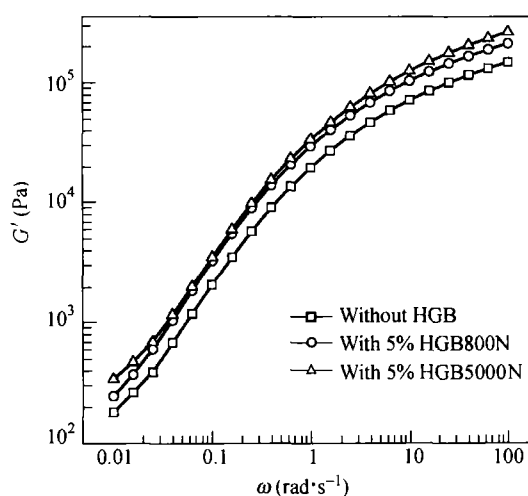


Fig. 4 Effect of HGB type on the plots of storage modulus G' as a function of frequency ω for PMMA/SAN (60/40) blend at 170°C

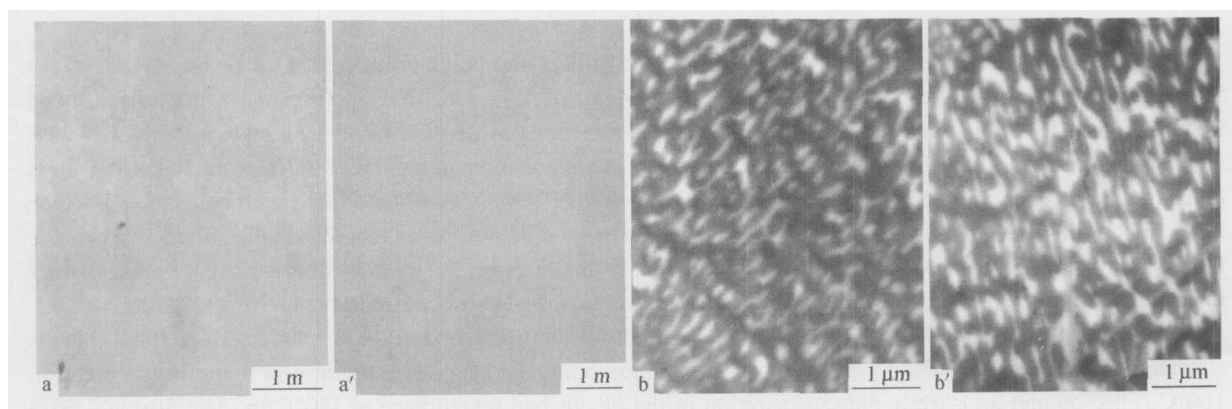


Fig. 5 TEM photomicrograph of unfilled/filled PMMA/SAN (60/40) blend
a) PMMA/SAN (60/40) blend at 160°C annealed 30 min; a') PMMA/SAN (60/40) blend filled with 5 wt% HGB5000N at 160°C annealed 30 min; b) PMMA/SAN (60/40) blend at 180°C annealed 30 min; b') PMMA/SAN (60/40) blend filled with 5 wt% HGB5000N at 180°C annealed 30 min

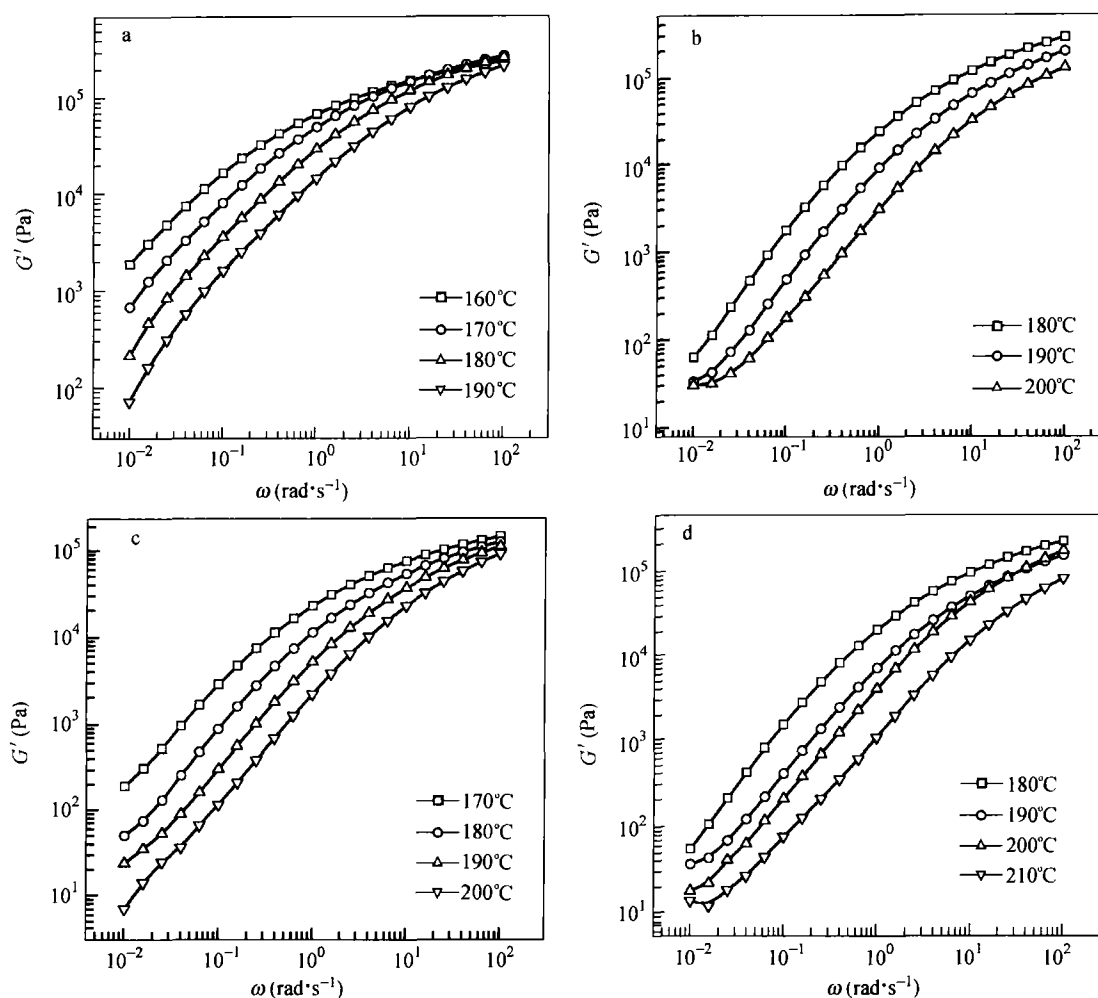


Fig. 6 Plots of storage modulus G' as a function of frequency ω for unfilled/filled PMMA/SAN (20/80) blends at different temperatures
a) Unfilled; b) Filled with 5 wt% HGB800N; c) Filled with 10 wt% HGB800N and d) Filled with 5 wt% HGB5000N

In order to illustrate the effect of interaction between fillers and polymer matrix on the phase-separation for PMMA/SAN blends, another kind of HGB with a diameter of 1.44 μm , HGB5000N, was added to the blend system. Figure 4 exhibits the relation of ω dependence of G' for PMMA/SAN (60/40) blends filled with 5 wt% HGB800N or HGB5000N at 170°C. Compared with the blend containing HGB800N, with the same mass percent, the “secondary plateau” shifts to a higher ω region for PMMA/SAN blend filled with HGB5000N, which has a smaller diameter than that of HGB800N. This phenomenon demonstrates that the smaller fillers can provide larger interfacial areas at the same mass percent, and so the stronger interaction between fillers and polymer matrix, resulting in the phase-separation of polymer matrix taking place at considerable higher ω regions.

Figure 5 demonstrates the TEM microphotographs of unfilled and filled PMMA/SAN (60/40) blends annealed at 160°C and 180°C for 30 min. Obviously, the homogenous phase structure is found in the blend at 160°C (Figs. 5a and 5a'), while phase-separation of the blends had taken place at 180°C in Figs. 5(b) and 5(b') (the dark domain is SAN and the white domain belongs to PMMA). It can be seen from Fig. 5 that the introduction of HGB has some influence on the morphology and domain size of polymer matrix. There is a clear phase boundary for the unfilled and filled PMMA/SAN (60/40) blends. However, it is interesting that the extent

of separated phase evolution is further enhanced for the filled system than that for the unfilled one. Under the same conditions, double continuous network structure is very clear in the filled PMMA/SAN (60/40) blend system, and subsequently it may lead to the increase in G' at low ω . Hence, the interaction between fillers and polymer matrix perhaps results in the acceleration of evolution of phase-separation.

An interesting situation happens in the case of PMMA/SAN (20/80) blend. Under the measured temperatures below 200°C, no phase-separation for 20/80 PMMA/SAN blend occurs, and a single phase always appears^[15]. Correspondingly, the plot of G' versus ω at various temperatures is shown in Fig. 6(a). However, for the PMMA/SAN (20/80) blend filled with HGB800N and HGB5000N, the “secondary plateau” appears at low ω even at 190°C (Figs. 6b, 6c and 6d). The phenomena illuminate again that the interaction between the fillers and polymer matrix induces the phase-separation for polymer matrix and the microstructure of this system became diversified because of the introduction of fillers.

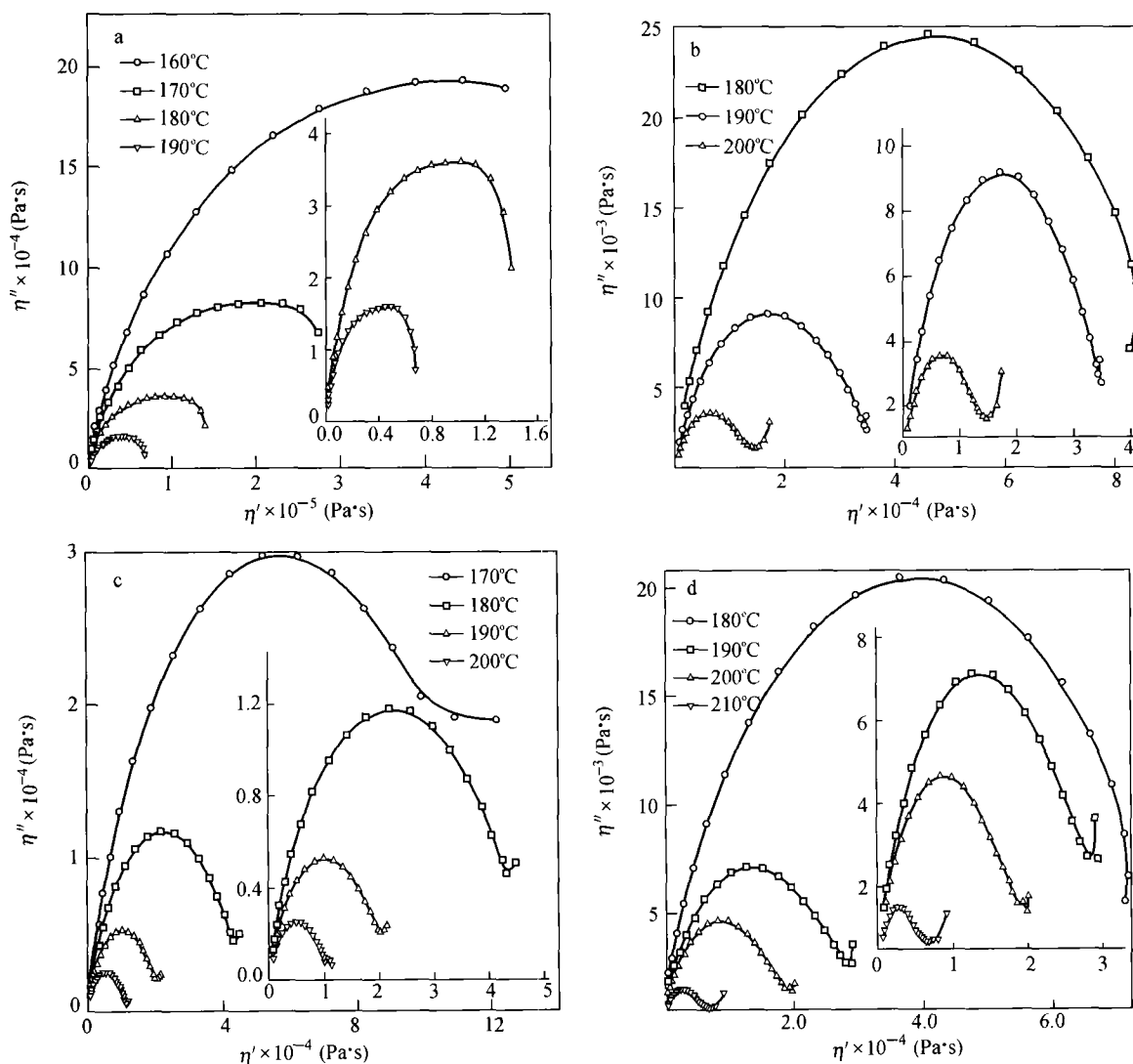


Fig. 7 η' - η'' curve of unfilled / filled PMMA/SAN (20/80) blends at various temperatures
a) Unfilled; b) Filled with 5 wt% HGB800N; c) Filled with 10 wt% HGB800N; d) Filled with 5 wt% HGB5000N

It is well known that the relationship between the dynamic viscosity (η') and the loss viscosity (η'') can also be used to characterize the phase-separation of polymer blends^[4]. Figure 7 shows the η'' - η' curve for unfilled and filled PMMA/SAN (20/80) blends. It can be seen that η'' - η' curves of unfilled PMMA/SAN (20/80) blends appear smooth within the whole frequencies measured at different temperatures (Fig. 7a). However, different results for filled PMMA/SAN blend can be found in Figs. 7(b), 7(c) and 7(d) that there appears only one circular arc, exhibiting the characteristic of a homogeneous blend below T_g . Compared with Fig. 7(a), as temperature becomes close to T_g , on the right hand side of the arc, an inflection develops as shown in megascopic graphs in the insets of Figs. 7(b), 7(c) and 7(d), which are considered to be related to the formation of a second phase during phase-separation induced by interaction between HGB and polymer matrix.

CONCLUSIONS

The results show that the incorporation of HGB has an induced effect on the phase-separation of PMMA/SAN blends, which embodies that the phase-separation temperature (T_g) of PMMA/SAN blends filled with glass beads seems to be lower than that of unfilled systems, and the higher the content of HGB, the higher is the ω of "secondary plateau" in the terminal region of storage modulus (G') versus ω curves. The "secondary plateau" in the terminal region is due to the phase-separation of PMMA/SAN blends and becomes more flat for filled polymer blend at the same conditions. It is suggested that this "induced effect" by the interaction between particles and polymer matrix is related to the content of HGB, the higher content of particles, the larger interfacial areas is, leading to a stronger interaction between the particles and polymer matrix. And as a result, the more obvious "secondary plateau" image of the G' - ω curve can be seen. Moreover, the incorporation of HGB also has an influence on the morphology and domain size of polymer matrix to some extent. On the basis of the plot of dynamic viscosity (η') versus the loss viscosity (η''), we can also find the representation of induced effect by HGB on the phase-separation of binary polymer matrix. However, it is still uncertain that whether incorporation of particle into binary polymer mixture can lead to the change phase separation mechanism or not. A detailed and quantitative study is now in progress and will be reported.

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