

Feature Article

**STUDIES ON STRUCTURE AND PHASE BEHAVIOR OF MULTICOMPONENT
POLYMERS THROUGH RHEOLOGICAL TESTS***

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Abstract Rheological measurement has been a preferred approach to the characterization of the structure and phase behaviors for multi-component multi-phase polymer systems, due to its sensitive response to the changes of structure for these heterogeneous polymers. In the present article, recent progresses in the studies on rheology for heterogeneous polymer systems including phase-separated polymeric blends and block copolymers are reviewed, mainly depending on the results by the authors' research group. By means of rheological measurements, not only some new fingerprints responsible for the evolution of morphology and structure concerning these polymer systems are obtained, also the corresponding results are significant for design and preparation of novel polymeric structural materials and functional materials.

Keywords: Heterogeneous polymers; Dynamic rheological properties; Phase behaviors; Morphology and structure.

INTRODUCTION

Over the past decades, the relationships between miscibility, phase-separation and rheological behavior have attracted more and more researchers' attention to the multi-component polymer material field because the thorough understanding of the phase behavior for multi-phase multi-component polymer mixtures is in favor of peoples' optimizing their phase structure, domain size, and the ultimate mechanical properties^[1, 2].

It has been found that for immiscible or miscible polymer blends, their dynamic rheological response appears quite sensitive to changes of the phase behavior and morphology/structure. Hence, rheological measurements have been recommended to be a preferable approach to characterize phase behaviors of multi-phase/multi-component polymers^[3]. In the linear regime of rheological tests, there are some fingerprints available to infer (qualitatively or quantitatively) the critical point of phase or structure transition in polymers, one of which is the so-called "second plateau"^[3, 5], dealing with the deviation of dynamic viscoelastic functions, like the storage modulus G' and loss modulus G'' , from linear viscoelasticity theory^[2] in low frequencies ω s, especially for phase-separated blends. Similarly, the relationship between the dynamic viscosity η' and the loss viscosity η'' , namely the Cole-Cole diagram, can also be applied to characterize the phase-separation for polymer blends^[6]. It is also a criterion that an additional relaxation appears in the relaxation spectrum $H(\tau)$ of polymer blends^[7]. The other way applied is the isochronal plotting of any rheological function such as viscosity and dynamic modulus of materials with temperatures, which generally presents a clear change in slope in the vicinity of critical point (depending on the system under consideration)^[8].

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Besides these linear rheological responses, the understanding of the correlation between transient structure and nonlinear viscoelastic behavior is also thought to be important to control the structure morphology of polymer systems during processing, although there exist some complexities and difficulties to determine evolution of structure or morphologies in preparation processes and to describe quantitatively the relationship between parameters of phase behavior and rheological properties.

Recently, some studies on the applications of dynamic rheological measurements to multi-component polymer systems have been carried out systematically in the rheology research group of Zhejiang University^[6, 7]. Here, we mainly summarize aspects involving the relationships between the rheological behavior and phase-separation of LCST-type polymer blends and correlations between the microstructure and linear nonlinear viscoelastic behaviors of block copolymers.

RELATIONSHIPS BETWEEN RHEOLOGICAL BEHAVIOR AND PHASE SEPARATION OF POLYMER BLENDS

In order to probe the relationship between dynamic rheological properties and phase behavior of polymer blends

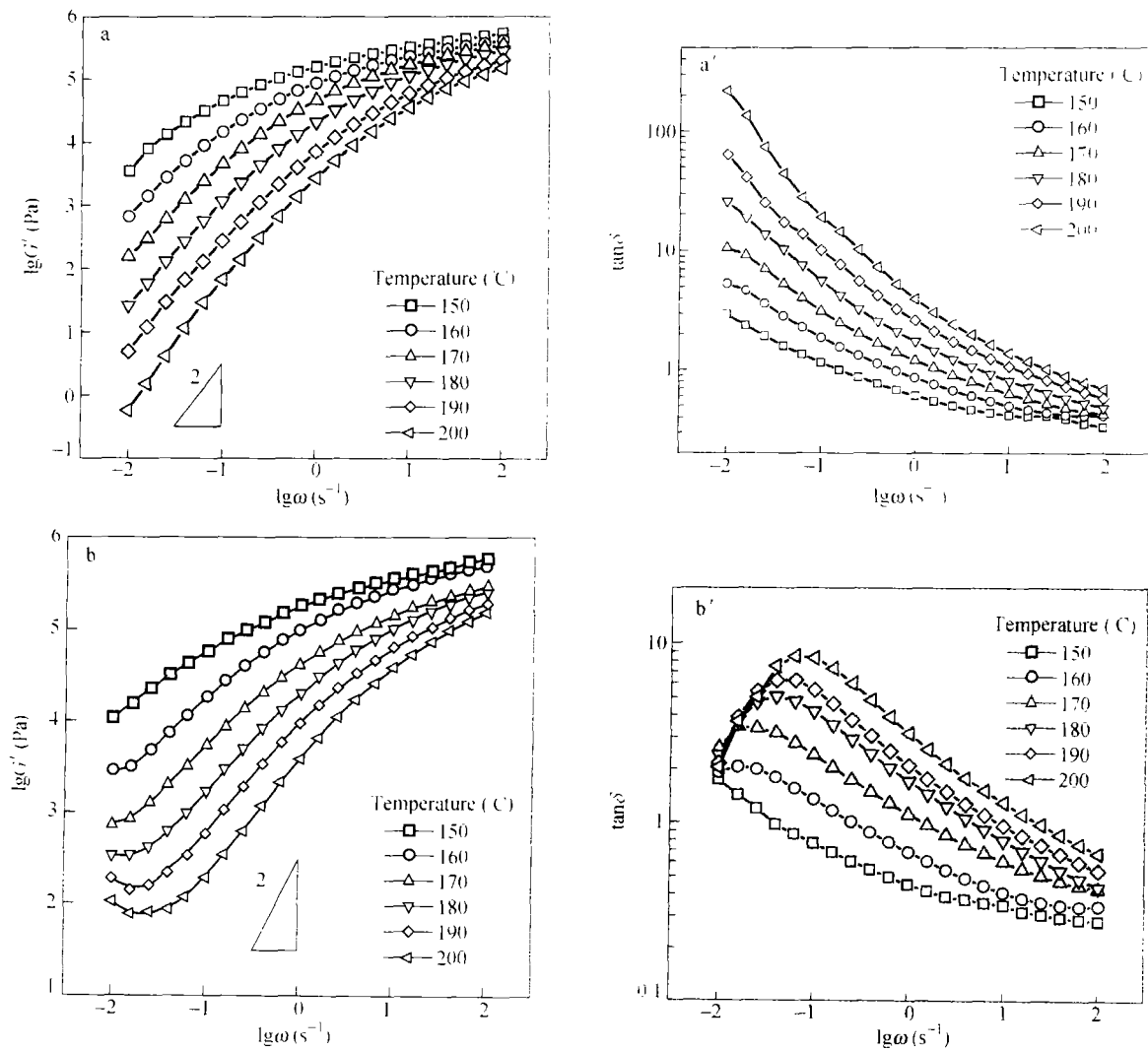


Fig. 1 Dynamic storage modulus (G') and loss tangent ($\tan\delta$) as a function of frequency (ω) for (a, a') PMMA, (b, b') 60/40 PMMA/ α -MSAN at different temperatures

in which miscibility is induced by the so-called “repulsion effect”^[12], the polymer blend consisting of poly(methyl methacrylate)/poly(α -methyl styrene-*co*-acrylonitrile) (PMMA/ α -MSAN) was selected as a model system to investigate the influence of temperature and heating rate on their phase behavior^[13]. It is found that the appearance of peak value in the plot of $\tan\delta$ versus ω can be used to characterize the phase-separation of polymer blends (Fig. 1). The spinodal temperature T_s could be obtained through an examination of the anomalous critical viscoelastic properties in the vicinity of phase-separation induced by the enhanced concentration fluctuation on the basis of the mean field theory. Combined with the results from time-resolved small angle light scattering (SALS), it can be seen in Fig. 2 that the dependence of the critical temperatures determined by dynamic rheological measurements (DRM) and SALS on heating rates both deviate obviously from the linearity, even at the very low heating rates. These suggested that the equilibrium phase-separation temperature could be hardly established by the linear extrapolating to zero in the plotting of cloud points versus heating rates. Furthermore, the cloud-point curves decrease gradually with the decrease in heating rates and present the trend of approaching glass transition temperatures T_g s of the blends, as shown in Fig. 3.

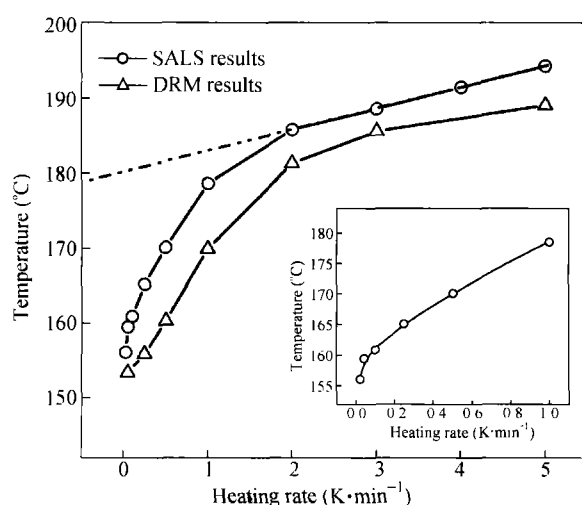


Fig. 2 Dependence of phase-separated temperature on heating rates for 60/40 PMMA/ α -MSAN blends detected by DRM and SALS
The inlay presents the local enlarged plot of SALS results.

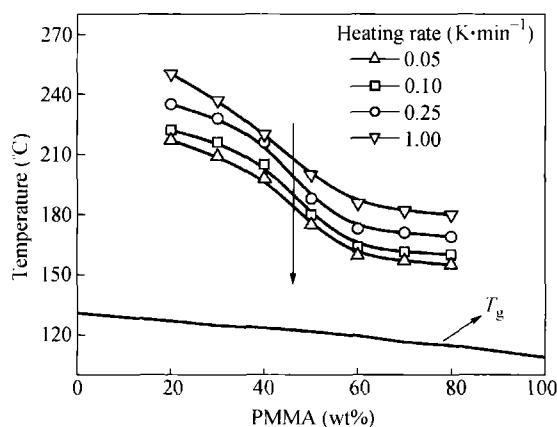


Fig. 3 Dependence of cloud points on PMMA content for PMMA/ α -MSAN blends at different heating rates detected by SALS method
The solid line is the glass transition temperatures T_g for blends of different compositions.

Some rheological functions, *e.g.* WLF-like equation, can also be introduced to deal with data of small angle light scattering in order to examine the “true” spinodal decomposition (SD) temperatures of the blends^[12]. It is found that the time-temperature superposition (TTS) principle is applied for describing the phase-separation of binary polymer mixtures over a relatively wide temperature region and the temperature-dependent apparent diffusion coefficient $D_{app}(T)$ could be described by a WLF-like function (Fig. 4) given as:

$$\lg \alpha_T = \lg \frac{D_{app}(T_r)}{D_{app}(T)} = \frac{-C_1(T - T_r)}{C_2 + T - T_r} \quad (1)$$

where α_T is the shifting factor, T_r is the reference temperature. C_1 and C_2 are constants. It is interesting that for the investigated PMMA/ α -MSAN blends with two compositions, the values of the constants C_1 and C_2 in Eq. (1) are considerably close to the empirical constants of 8.86 and 101.6 in the universal WLF function for polymer melt viscosity, where the reference temperature is usually selected about 50 K higher than T_g . This indicates that the phase-separation behavior of PMMA/SAN blend also follows the TTS principle, which is consistent with the phase-separation behavior of PMMA/SAN reported in our previous paper. Obviously, it presents another valuable evidence for the applicability of the TTS principle and WLF-like function for describing the phase-separation behavior of binary polymer mixtures over a relatively large temperature range.

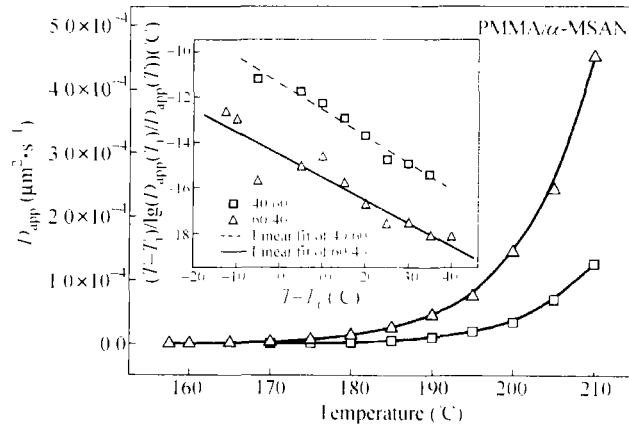


Fig. 4 Temperature dependence of $D_{app}(T)$ for PMMA α -MSAN blends: 60/40 blends (Δ), 40/60 blends (\square). The inlays present the $(T - T_r)^{-1} \lg(D_{app}(T_r)/D_{app}(T)) - (T - T_r)$ relationship, respectively, at the corresponding reference temperatures.

On the other hand, as can be noticed from Fig. 4, during isothermal annealing the temperature dependence of D_{app} is not strictly linear, and the T_r could be hardly obtained precisely through the simple linear extrapolation. This result verifies the above-mentioned nonlinear phase-separation behavior obtained from DRM, which suggests the nonlinear and non-equilibrium phase-separation characteristics.

CORRELATIONS BETWEEN THE MICROSTRUCTURE AND LINEAR/NONLINEAR VISCOELASTIC BEHAVIORS OF BLOCK COPOLYMERS

For block copolymers, different chain segments in block copolymers may form their individual micro-phases due to the thermodynamic immiscibility, and these structures are endowed with special mechanical properties different from those of homopolymers polymerized through corresponding blocks. Hence, the correlations of their microstructure and linear/nonlinear viscoelastic behavior are important factors to determine processing and ultimate properties for these materials. Owing to the predominant properties of styrene-[ethylene-(ethylene-propylene)]-styrene block copolymer (SEEPS), the studies on the linear and nonlinear viscoelastic behavior of SEEPS were also carried out in our group^[15-17].

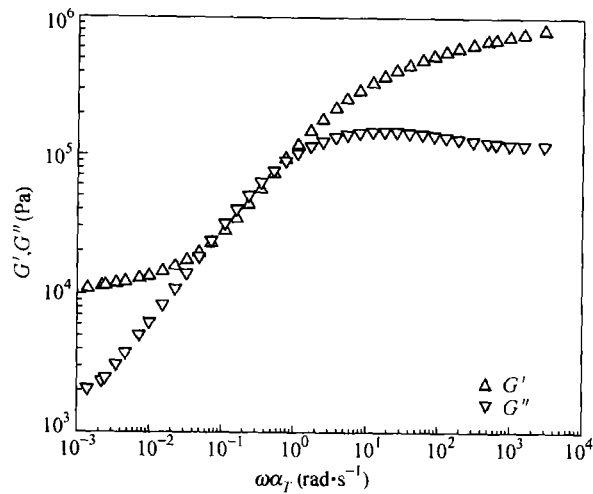


Fig. 5 The master curves of dynamic storage modulus (G') and loss modulus (G'') for SEEPS at the reference temperature $T = 190^\circ\text{C}$

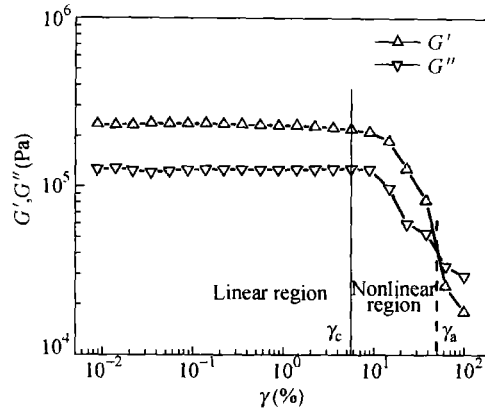


Fig. 6 Effect of shear strain on the dynamic storage and loss modulus, G' and G'' , at 1 rad/s and 190°C for SEEP

It is found that “second plateau” appears in low ω s of the master curves for G' versus ω through TTS (Fig. 5), which is attributed to the entanglement of macromolecular chains. This implies that hard blocks, polystyrene, act as entanglement points, resulting in a topology restraint to the movement of macro-molecular chains^[15, 16]. On the other hand, the nonlinear viscoelastic region can be determined through dynamic strain sweep test, and the critical shear strain γ_c of transition from linear viscoelastic region to nonlinear viscoelastic region can be figured out, as shown in Fig. 6. These indicate that the elastic mechanism of SEEPS is destroyed by the cumulate strain^[17]. When the strain is lower than γ_c , the simulated curve by Maxwell model (Eq. (2)) can describe the linear relaxation process of SEEPS well in the wider range than that by Ninomiya and Ferry equations (Eq. (3)). These two models are given as

$$G(t) = \sum_{i=1}^n G_i e^{-(t-t')/\lambda_i} \quad (2)$$

$$G(t) = [G'(\omega) - 0.4G''(\omega) + 0.014G''(10\omega)]_{\omega=1/t} \quad (3)$$

where G_i and λ_i are the modulus and the relaxation time of the i th relaxation mode, respectively. Meanwhile, it is noted that there exists a plateau in the long time region, which is due to the complex heterogeneous structure of

SEEPS (Fig. 7). As is noted in Fig. 8, the nonlinear relaxation modulus obtained at relatively low shear strains follows the strain-time separation principle (STS), and when $\gamma > 50\%$, a new characteristic relaxation process appears for the change of microstructure in SEEPS, which coincides with the results of dynamic strain sweep.

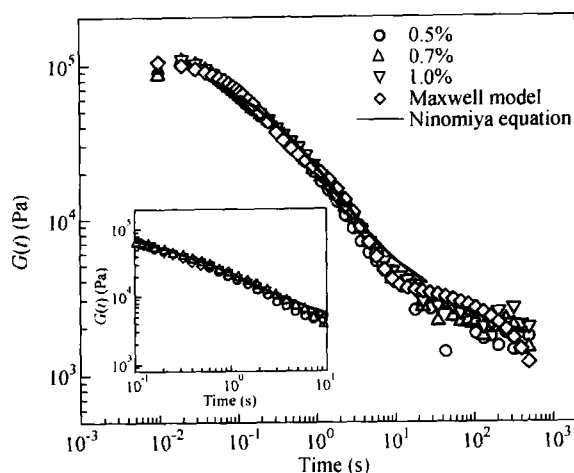


Fig. 7 Linear relaxation modulus $G(t)$ at various shear strains γ of SEEPS at 190°C and fits with Maxwell and Ninomiya equation

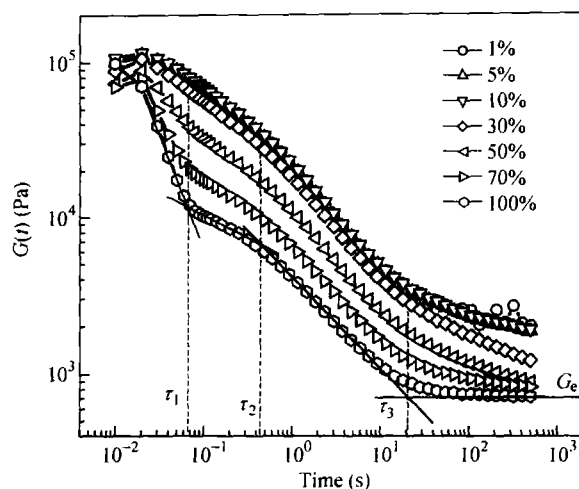


Fig. 8 The nonlinear stress relaxation behaviors for SEEPS at various large strains

SUMMARY AND REMARKS

It has been verified that the rheological tests are an effective approach to characterize the structure-properties relationship of heterogeneous polymers. For the systems like LCST-type phase-separated polymeric blends and block copolymers, their rheological behaviors for structure/morphology evolution are characteristic. It has been believed that in the linear regime of rheological tests, some phenomena, such as the so-called “second plateau” in low ω s, the appearance of peak value in the plot of $\tan\delta$ versus ω and the relaxation modulus plateau in the long time region, are all available to characterize the variation of structure or the phase-separation in polymer blends as well as the entanglement of macromolecular chains in block copolymers. Meanwhile, in the nonlinear regime, the occurrence of new relaxation process has also been attributed to the change of microstructure.

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