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Polymer 42 (2001) 5743–5747

polymer

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Relationship between dynamic rheological behavior and phase separation of poly(methyl methacrylate)/poly(styrene-*co*-acrylonitrile) blends

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Received 31 August 2000; received in revised form 6 December 2000; accepted 26 December 2000

Abstract

On the basis of phase separation temperatures (T_s) for poly(methyl methacrylate)/poly(styrene-*co*-acrylonitrile) blends of different compositions, measured by small angle laser light scattering, we have studied dynamic rheological behavior of these blends at different temperatures below, near and above T_s. The results showed that the time–temperature superposition principle could be applied and the linear viscoelastic response emerged in the terminal region at temperatures below T_s. However, it was found that the breakdown of time–temperature superposition principle appeared, and viscoelastic response deviated from the linear behavior in the terminal region at temperatures near and above T_s. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: PMMA/SAN blends; Dynamic rheological behavior; Phase separation

1. Introduction

The study on rheological behavior of multiphase systems has attracted more attention, due to the important academic problems and increasing technological applications [1,2]. In the last two decades, rheological characterization has been a recent surge in the study on the relationship of phase separation and the viscoelastic properties for polymer blends [3–6].

As a good object, poly(styrene-*co*-acrylonitrile) (SAN) mixed with various polymers like poly(methyl methacrylate) (PMMA), has been studied extensively because, the origin of miscibility in such systems has been proposed to be the so-called 'repulsion effect' [7,8] and the acrylonitrile (AN) content of SAN provided a useful means for systematically varying the interaction of polymer–polymer pairs [9,10]. PMMA/SAN blends exhibit a lower critical solution temperature (LCST) behavior, namely for any composition at temperatures below T_s, these blends are miscible and homogenous. With increase of temperature, a dispersed phase forms. But there have been few papers that deal with the phase separation studied by dynamic rheological method for PMMA/SAN blends systems. In this paper, the relationship of the rheological properties with composition and temperature below, near and above T_s of PMMA/SAN blends will be investigated on the basis of discussion about the applicability (or breakdown) of the time–temperature superposition principle to the blends.

2. Experimental

PMMA was obtained from LG chemical Ltd (Korea) with $\overline{M}_n = 3.8 \times 10^4$, and $\overline{M}_w/\overline{M}_n = 2.1$. SAN was obtained from Chimei Corporation (Taiwan) with 28% AN and $\overline{M}_n = 6.4 \times 10^4$.

The samples of PMMA/SAN films for small angle laser light scattering (SALLS) observation were prepared by dissolving the polymers in dichloroethane (CH_2ClCH_2Cl) at a weight fraction of 5%, and then solvent casting on the surface of microscope slides preheated to 30°C. After the solvent evaporated at an ambient environment, the samples were further dried at 100°C in a vacuum oven for at least 24 h to ensure that no residual solvent existed.

The PMMA/SAN blends for rheological measurement were dissolved in methyl ethyl ketone ($CH_3COCH_2CH_3$) at a weight fraction of 15%. After the solvent evaporated at ambient environment over night, the films were heated for 24 h at 60, 80, 100 and 120°C, respectively. For ensuring complete removal of solvent, the films were then dried in a vacuum oven at 140°C for two days. Weight measurements were made until they reached constant weight. The films

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PII: S0032-3861(01)00025-8

with thickness of 80–100 μm were piled up and compression moulded into a specimen disk with a diameter of 30 mm and a thickness of 1.5 mm below 150°C and under 10 MPa for rheological measurements.

Cloud points were measured by SALLS. The blend film was inserted in a hot chamber kept at a constant temperature and was annealed for 12 h. When the scattering ring was observed on the screen, the blend was judged to be in the immiscible region in the cloud point curve. When no appreciable change with annealing was detected, the film was further annealed at the same temperature for 36 h. When the film was still clear and phase separation could not be detected on the screen, even after this long annealing time, we judged that the blend was in the miscible region.

The rheological measurements were carried out on an advance rheometric expansion system with parallel plate geometry of 25 mm in diameter. The frequencies were from 10^{-2} to 10^{2} s^{-1}. Depending on the given temperature, from 150 to 190°C, the strain amplitude was taken between 3.0 and 20% to obtain a high enough value of the torque. It was verified that the behavior of the sample was in the range of linear viscoelasticity.

3. Results and discussion

The cloud point curve of the PMMA/SAN blends measured by SALLS is shown in Fig. 1. The cloud points varying with composition indicated that these blends exhibited LCST-type behavior in low SAN content range. At temperatures below this curve, the samples were transparent and homogenous. In other words, at temperatures above this curve, phase separation occurred. As a result, the films became cloudy and the scattering ring appeared. It should be noted that the cloud points temperature of the 20/80 PMMA/SAN blend (In this paper, the composition of the blends is weight fraction.) could not be measured precisely because its phase separation could not be observed until the temperature reached 200°C. Thus, the section of cloud point curve is shown in a broken line.

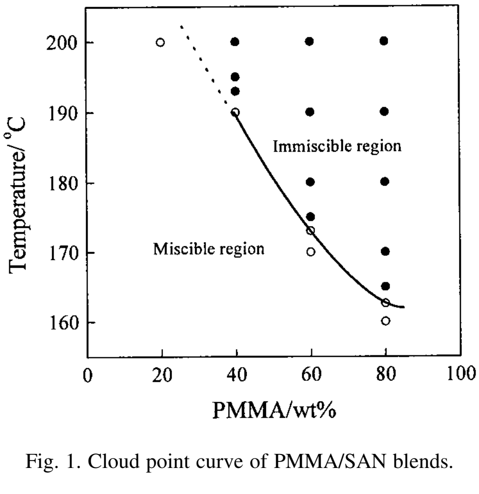

Fig. 1. Cloud point curve of PMMA/SAN blends.

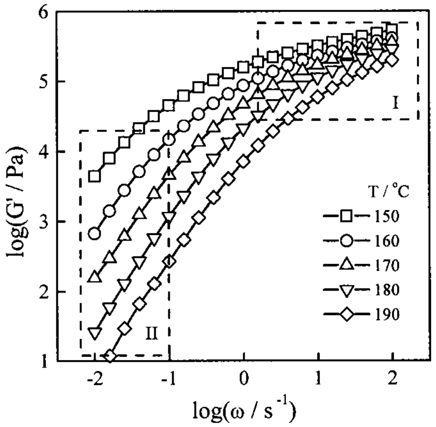

Fig. 2. Frequency dependence of storage modulus G' for PMMA at different temperatures.

Figs. 2 and 3 present frequency dependence of the storage modulus (G') for PMMA and 80/20 PMMA/SAN blend at different temperatures. It is obvious that at higher frequencies, from 1 to 10^{2} s^{-1}, the G' values of the 80/20 PMMA/SAN blend are similar to those of the PMMA component over the temperature region selected, as noted in zone (I) and zone (I′). On the contrary, at lower frequencies, less than 10^{-1} s^{-1}, the G' values of this blend are elevated as compared with those of PMMA when temperatures are higher than T_s, i.e. 160°C, as noted in zone (II) and zone (II′). It is very interesting that at lower frequencies, the curves of the plot log G' against log ω exhibit a slight flattening which becomes more pronounced as the temperature increases. These appearances have been believed to be the result of change from homogenous to heterogenous structure according to Onogi's analysis [11]. This behavior is also involved in concentration fluctuations near T_s as is suggested for block copolymers [12].

Fig. 4 shows the master curve of G' for PMMA at a reference temperature 160°C. It is clear that the master curve is smooth within the whole frequencies measured,

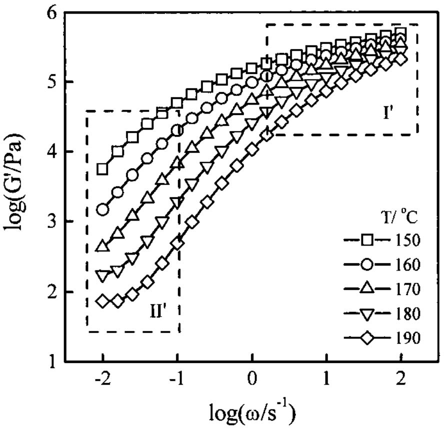

Fig. 3. Frequency dependence of storage modulus G' for the 80/20 PMMA/SAN blend at different temperatures.

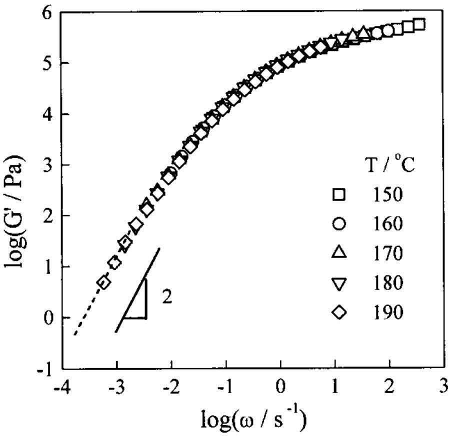

Fig. 4. Master curve of G' for PMMA at reference temperature 160°C.

namely the time–temperature superposition principle can be applied to PMMA.

According to the linear viscoelastic theory, the important result involved in viscoelastic properties in the terminal region can be reduced to $\log G' \propto 2\log \omega$ when ω approaches zero. Apparently, the slope of $\log G'$ versus $\log \omega a_T$ plots for PMMA is about 2 in the terminal region, as shown in Fig. 4. Therefore, this system is believed to follow the linear viscoelastic theory.

The time–temperature superposition principle can also be applied below and above T_s for the PMMA/SAN blends. The results of the master curve of G' for the 20/80 PMMA/SAN blend at the reference temperature 160°C was essentially the same as Fig. 4. It is found that the time–temperature superposition principle can also be applied and the dynamic rheological behavior obey the linear viscoelastic theory. At the same time, on the basis of the results measured by SALLS, it can be deduced that the phase separation temperatures for the 20/80 PMMA/SAN blend is above 200°C, which means that rheological measurement is made in the miscible region of the blends. Therefore, it can be concluded that the rheological behavior of homogenous blends is similar to that of the homopolymer. For a given composition, the viscoelastic properties of the blend change substantially when temperature approaches the phase-separation temperatures. A typical example illustrating the effects of phase separation on the dynamic rheological behavior is shown in Fig. 5. It reveals that the time–temperature superposition principle can be applied and the dynamic rheological behavior obeys the linear viscoelastic theory at different temperatures below 190°C for the 40/60 PMMA/SAN blend. When the temperature approaches 190°C, the phase boundary and pretransitional region emerge, leading to breakdown of the time–temperature superposition principle, namely the occurrence of nonlinear viscoelastic behavior.

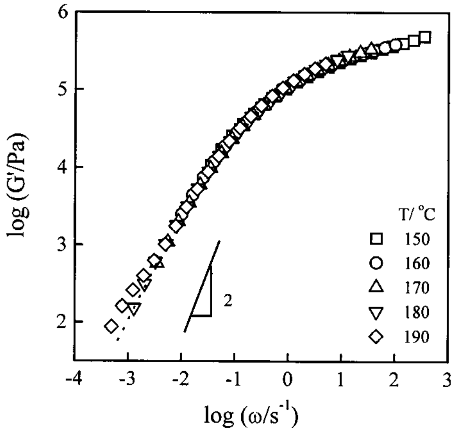

Fig. 5. Master curve of G' for the 40/60 PMMA/SAN blend at reference temperature 160°C.

The 60/40 PMMA/SAN blend also exhibited a similar behavior as shown in Fig. 5. In the lower frequency region, the master curves of G' for the 60/40 PMMA/SAN blend even show a section of plateau, which appeared often for polymer composites and has been called ‘second plateau’ associated with a structure formation in the blend. Recently, Kapnistos [5] obtained a similar experimental result associated with the rheological behavior of PS/PVME blends. Accordingly, the concentration fluctuation leads to the thermorheological complexity of the PS/PVME blends in the homogenous region approaching the phase separation state, which makes viscoelastic response deviate from the linear viscoelastic model. We believe that it is also involved in concentration fluctuation near T_s for the 40/60 and 60/40 PMMA/SAN blends.

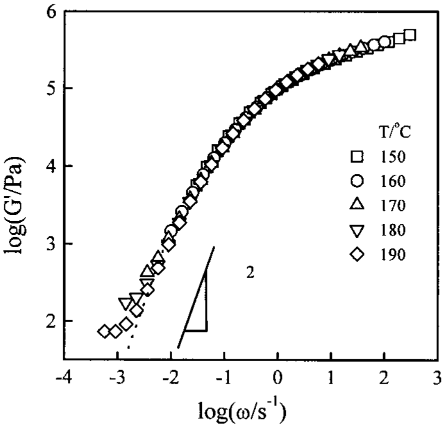

Fig. 6. Master curve of G' for the 80/20 PMMA/SAN blend at reference temperature 160°C.

Fig. 6 shows the master curve of G' for the 80/20 PMMA/SAN blend at a reference temperature 160°C. The relationship between G' and ω for this blend superpose satisfactorily below T_s, i.e. 163°C, meaning that the time–temperature superposition principle can be applied and the dynamic rheological behavior obey the linear viscoelastic theory at different temperatures.

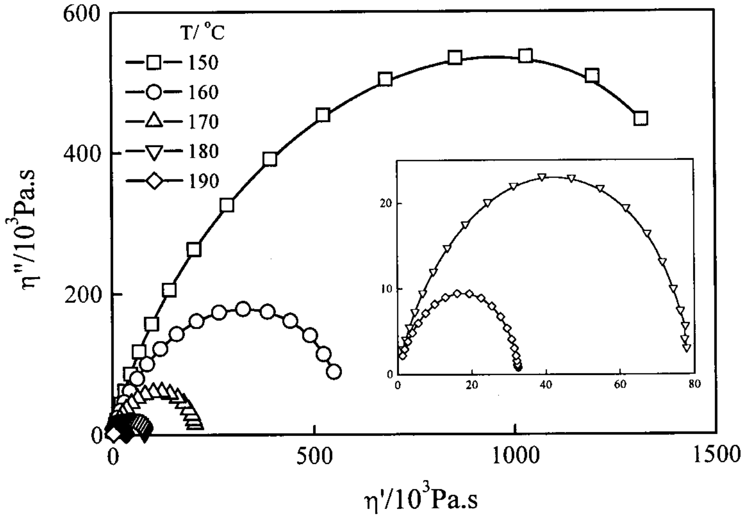

Fig. 7. η'–η'' curve of PMMA at different temperatures.

However, at temperatures above T_s, the superposition holds only in the intermediate frequency region. It is worth noting that the breakdown of time–temperature superposition principle appears differently from the 40/60 and 60/40 PMMA/SAN blends; no appreciable influence can be found for the 80/20 PMMA/SAN blend near T_s. Therefore, it is necessary for us to investigate further, the relationship between the rheological behavior and the concentration fluctuation near T_s.

It has been well known that the relationship between the dynamic viscosity (η') and the loss viscosity (η'') can also be used to characterize the phase separation for polymer blends [4]. Fig. 7 shows that the η'–η'' curve for PMMA is smooth within whole frequencies measured at different temperatures. However, different results were obtained for the 60/40 PMMA/SAN blend as shown in Fig. 8. It can be found that there is only one circular arc as shown as the curves obtained at 150 and 160°C, exhibiting characteristic of a homogenous blend below T_s. As temperatures come closer to T_s, a tail develops on the right-hand side of the arc, as shown in megascopic graphs in Fig. 8. At higher temperatures, a second circular arc should emerge on as shown by other researchers [4]. The results mentioned above are considered to be related to the formation of a second phase. The η'–η'' curve for the 40/60 and 80/20 PMMA/SAN blends are essentially the same as shown in Fig. 8.

4. Conclusions

Rheological studies on PMMA/SAN blends of various compositions were carried out, at below, near and above their phase separation temperature. The results showed

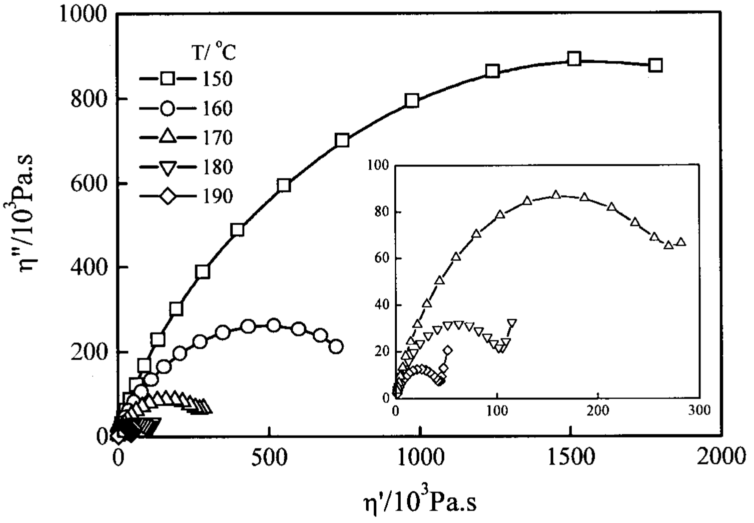

Fig. 8. η'–η'' curve of the 60/40 PMMA/SAN blend at different temperatures.

that the time–temperature superposition principle could be applied and a linear viscoelastic response emerged in the terminal region at temperatures below T_s. In the homogenous region near T_s, concentration fluctuation could induce the thermorheological complexity of the PMMA/SAN blends. The relationship between the dynamic viscosity and the loss viscosity can also be used to characterize the phase separation for PMMA/SAN blends.

Acknowledgements

This project was supported by the Special Funds for Major State Basic Research Projects (Grant No. G1999064800) and National Nature Science Foundation of China (NSFC) (Grants 59973018).

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