The Rheological Behavior of Immiscible Polymer Blends

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Received 1 September 2001; accepted 3 January 2002

ABSTRACT: The complex shear modulus of immiscible polymer blends was measured by a frequency sweep experiment for polystyrene (PS)/low density polyethylene (LDPE) and poly(methylmethacrylate) (PMMA)/LDPE blends at constant composition (13.5/86.5 vol %) and compared with the prediction model of Palierne. Different morphologies of each blend were also prepared using a rheometer with a constant shear rate and different strain. There was morphological dependency on the complex shear modulus at constant temperature. However, this dependency disappeared at specific temperatures in the frequency sweep experiment. There seemed to be a specific temperature like critical flow temperature (T_{cf}) of amorphous polymer. The difference in morphology affected the complex shear modulus of blends below the specific temperature, T_{cf} , but did play a major role in determining the complex shear modulus of blends at over specific temperature. A new method may be needed to determine the critical flow temperature of an amorphous polymer via the measurement of a complex shear modulus for immiscible polymer blends. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 917–924, 2002

INTRODUCTION

The thermorheological properties of polymer, like extrusion, injection molding, calendering, and so on, is important for polymer processing because the rheological properties of polymer determine the processing condition. The rheological behavior of multiphase polymer melts has become a subject of great interest because the use of polymer blends has been increasing recently. The rheology of immiscible polymer blends is related to individual phases. The rheology of heterophase polymer blends has been studied from the theoretical point of view for several decades.[1–10] Several mathematical models have been proposed and investigated, and an agreement of experimental results and the model has been shown. It is generally known that the morphological structure of immiscible polymer blends obtained by melt mixing depends on the rheological properties of individual ingredients. As a result, each component should be investigated for its rheological behavior to predict the rheological behavior of blends. Palierne[11] studied the linear viscoelastic behavior of a dispersion of incompressible viscoelastic materials. A linear viscoelastic modulus at any concentration and polydispersity of spherical inclusions was derived. The development of Palierne's model, starting from the concepts of emulsion rheology, can be used as a theoretical framework to study rheological behavior, like the complex shear modulus of immiscible polymer blends.[12–14] In addition, the morphological dependency on a complex shear modulus of blends seems to be related to the difference in the rheological property of an amorphous polymer as dispersed phase in blends. Han et al. proposed critical flow temperature (T_{cf}) of amorphous polymers.[15] He proposed that the T_{cf} of an amorphous polymer is T_g (glass transition temperature) + ~55 °C. In this study, the complex shear modulus of immiscible polymer blends was investigated and compared with the prediction model of Palierne. The temperature, which has no morphological dependency on the complex shear modulus, seems to be T_{cf} for an amorphous polymer, polystyrene (PS) and poly(methylmethacrylate) (PMMA).

MATERIALS AND METHODS

Materials

The general properties of materials used in this experiment are explained in Table I. The PS and PMMA were commercial grade from LG Chemical Company, Korea. LDPE was also commercial grade from Hanhwa Petrochemical Company, Korea. The PMMA was a copolymer; that is, 5% ethyl acrylate with methyl methacrylate. The constant composition of blends was dispersed phase/matrix = 13.5/86.5 vol % (dispersed phase:PS and PMMA, matrix:LDPE). All of the material was dried for 24 h at 80 °C in a vacuum oven before the experiments.

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Journal of Applied Polymer Science, Vol. 86, 917–924 (2002)

TABLE I
General Properties of the PS and PMMA Materials Used in This Study

Material	T_g[a], T_m (°C)	M_n[b]	M_w[b]	Melt index (g/10 min)
LDPE	113(T_m)	—	—	1.5
PS	121(T_g)	141,975	314,213	10.3
PMMA	125(T_g)	38,114	103,589	0.6

[a] Measured by rheometer (UDS-200, Parr Physica Company) with radius of 8 mm and parallel plates in temperature sweep experiment. The fixed amplitude and frequency were 0.1% and 1 Hz, respectively. The temperature was almost same at the value of tan δ, which was maximum.

[b] Measured by GPC (Waters Inc. Alliance 2000).

Experimental method

Sample preparation

The blends were prepared under a high shear condition using an internal mixer (Brabender Plasticoder) at 100 rpm for 4 min at 200 °C to make fine dispersed droplets and matrix morphology. To prevent thermal degradation of materials during mixing and experiment, a proper amount of Irganox 1010 and Irgafos168 as antioxidants were added to all the blends. The blends were rapidly cooled in an isopropyl alcohol–solid CO_2 mixture after mixing. The morphological change of the samples so prepared was investigated with a rheometer, UDS-200 (Paar Physica Company) that could control shear rates at 200 °C. The steady shear rate was 10 s^{-1}. The retention time of samples on rheometer before starting of rotation was 2 min to make a sample free of normal force. The steady shear rate was applied to samples with various strains (0, 588, 1789, and 17987) to make a samples that have different morphology. The samples were rapid cooled with liquid nitrogen. The quenching time from 200 °C to room temperature was 30 s.

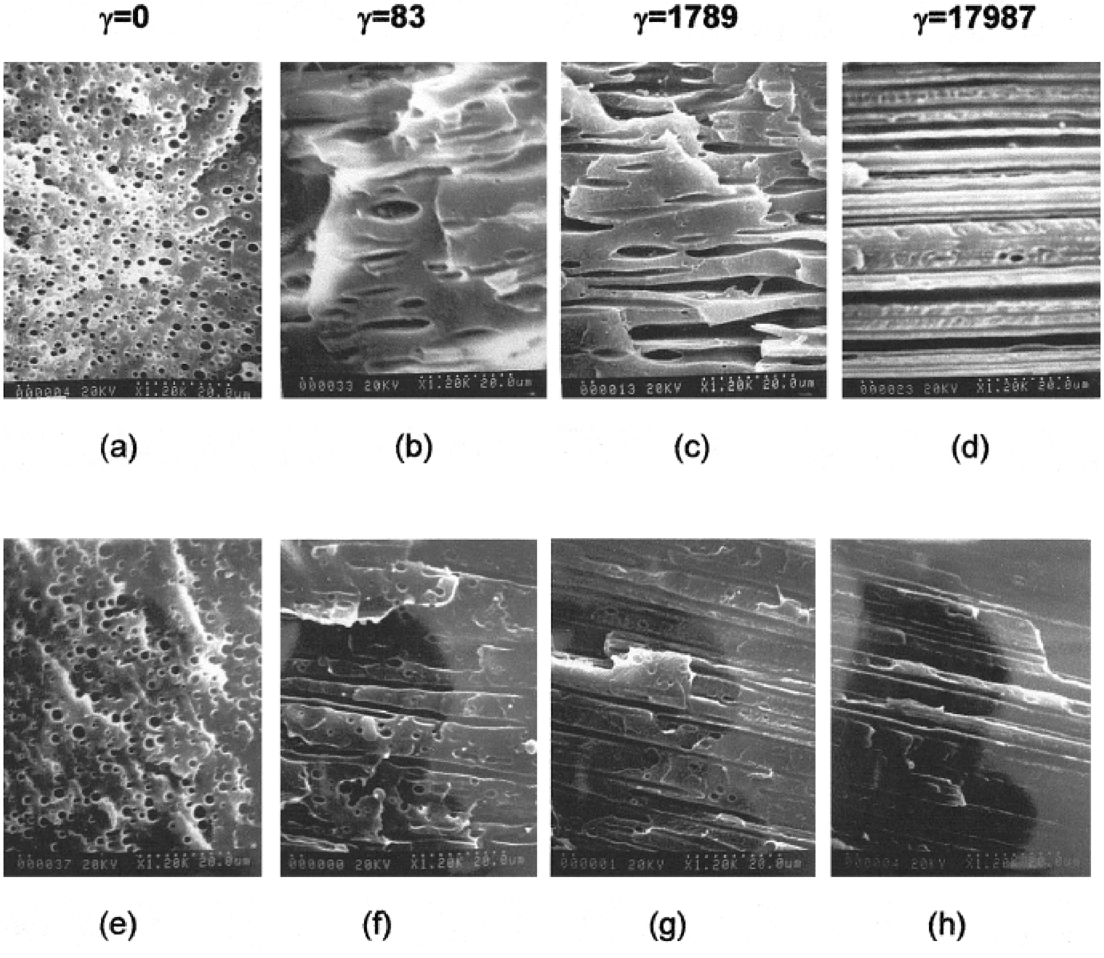

Figure 1 the morphological change for PS/LDPE and PMMA/LDPE (13.5/86.5 vol %) blends at various strain: (a–d) PS/LDPE blends; (e–f) PMMA/LDPE blends.

Observation of morphology

The samples were fractured at liquid nitrogen atmosphere to make a smooth surface by parallel and perpendicular direction of shear force. Additionally, PS was extracted with toluene for 3 days at −40 °C to prevent morphological change during extraction. The morphology of each sample was investigated with a scanning electron microscope (Hitachi Company) after the drying of extracted samples in a vacuum oven for 3 days.

Rheological properties

The frequency sweep and temperature sweep experiments were carried out using UDS-200 parallel plates with a rheometer with a radius of 8 mm to measure the rheological properties of materials. A constant amplitude and frequency, 0.1% and 1 Hz, respectively, were imposed to measure the viscoelastic property for PS and PMMA at a wide range of temperatures. To investigate the frequency dependency of the complex modulus $G^*(\omega)$ of PS/LDPE and PMMA/LDPE blends at various temperatures, the constant amplitude and range of angular frequency were used at 0.1% of amplitude and from 100 to 0.1 rad/s.

RESULTS AND DISCUSSION

There are two basic mechanisms to determine the morphology of a polymer blend after the deformation and coalescence of droplets.[1–10,16–33] During mixing, the dispersed phase is deformed and reaches small droplets until the critical state. The size of the droplets can be calculated from Taylor's theory;[2] that is, the ratio of the viscous stress to the interfacial stress. When the viscous stress is stronger than the interfacial stress, the droplet should become deformed and break up until the critical size of the droplet is reached, which is the general rule for the morphological change of a droplet:

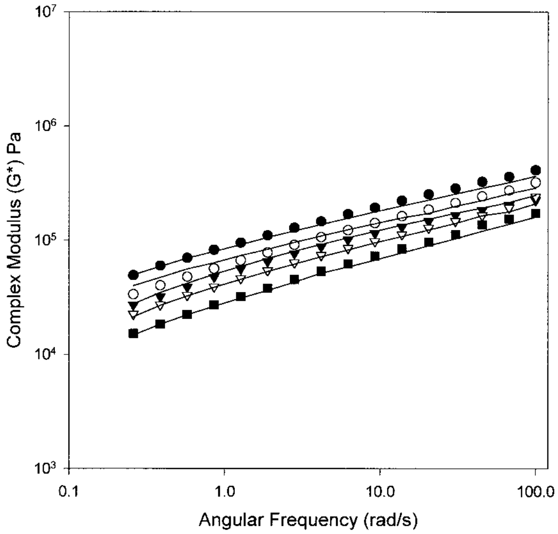

Figure 2 The comparison between experimental results and emulsion model for PS/LDPE (13.5/86.5 vol %) blends at various temperatures. Key: (●) 150 °C; (○) 160 °C; (▲) 170 °C; (△) 180 °C; (■) 190 °C; (—) Palierne's model prediction.

$$\mathrm{Ca} = (\text{viscous stress})/(\text{interfacial stress}) = (\eta_{\mathrm{m}}\gamma)/(\nu_{12}/R) \quad (1)$$

where η_{m} is the viscosity of the matrix, γ is the shear rate, R is radius of droplet, and ν_{12} is interfacial tension. The relationship just described is for Newtonian fluids and small volume fractions of the dispersed phase of a blend system. In a simple flow system, a critical capillary number can be calculated. De Bruijn[4] found the dependency of critical capillary number with a viscosity ratio between the matrix and domain ($\lambda = \eta_{\mathrm{d}}/\eta_{\mathrm{m}}$) in simple shear flow. The author reported that the viscosity ratio is important in determining the morphological change of polymer blend and also suggested empirical equation,[2] in which the critical capillary number for droplet break-up is a function of the viscosity ratio:

$$\log(\mathrm{Ca}_{\mathrm{cri}}/2) = C_1 + C_2 \log\lambda + C_3(\log\lambda)^2 + C_4 0.1150/(\log\lambda + C_5) \quad (2)$$

where $C_1 = -0.5060$, $C_2 = -0.0994$, $C_3 = 0.1240$, $C_4 = -0.1150$, and $C_5 = -0.6110$.

The stability of the droplet may be determined by a comparison between the local capillary number and critical capillary number. Some choices have been suggested as follows: when $\mathrm{Ca} < \mathrm{Ca}_{\mathrm{cri}}$, droplets may deform, but not break up; when $\mathrm{Ca}_{\mathrm{cri}} < \mathrm{Ca} < 2\mathrm{Ca}_{\mathrm{cri}}$, droplets are unstable and may break up; when $\mathrm{Ca} > 2\mathrm{Ca}_{\mathrm{cri}}$, droplets are deformed into fiber smaller droplets that are given under two conditions, when the diameter of fiber falls under the critical value and after cessation of flow.

The morphologies for PS/LDPE and PMMA/LDPE (13.5/86.5 vol %) blends with $\gamma = 0$, 83, 1789, and 17,987 are shown in Figure 1. The thread and matrix morphology for each of the blends is at high strains. Also, there was thread and droplet for PMMA/LDPE blends at small strain, but all of droplet was deformed as soon as the strain was applied for PS/LDPE blends. In case of PS/LDPE blends, the droplet seemed to be deformed according to strain, gradually. The long thread was seen at high strain and was too long to calculate the length. In all the blends, the values of the local capillary number seemed to be >2 times that of the critical capillary number. As a result, the droplets are deformed into thread and may break up under the critical diameter of thread. However, there was no break up of droplets. The diameters of each blend were as follows: PS/LDPE blend = 0.7 μm and

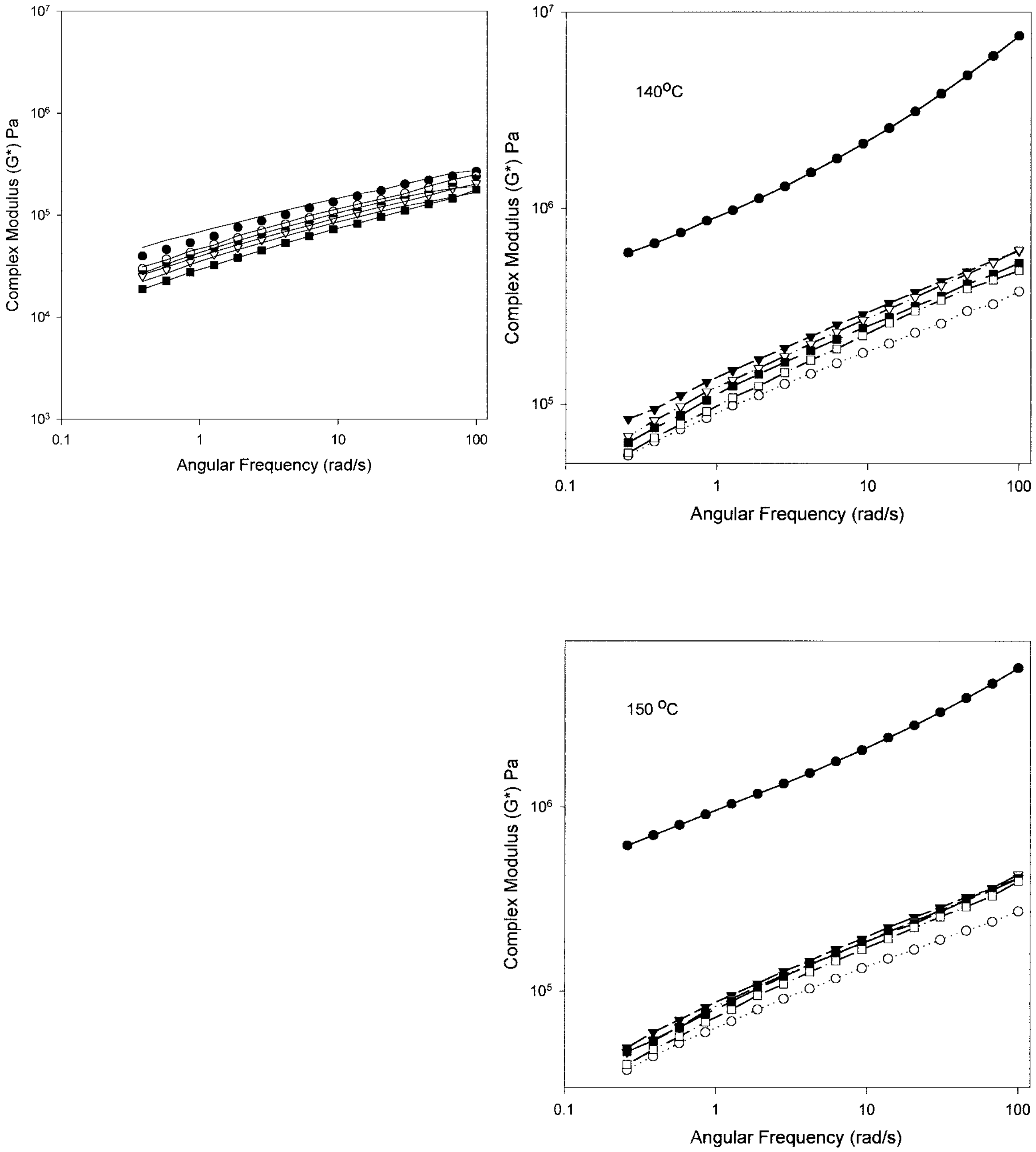

Figure 3 The comparison between experimental results and emulsion model for PMMA/LDPE (13.5/86.5 vol %) blends at various temperatures. Key: (●) 150 °C; (○) 160 °C; (▲) 170 °C; (△) 180 °C; (■) 190 °C; (—) Palierne's model prediction.

PMMA/LDPE blend = 1.7 μm. These were the average number values from manual calculation. The evolution of morphology for each blend is not a major subject in this study because a number of experimental results and theories have been investigated and proposed. So, we don't want to mention the evolution of morphology for blend in this study.

The rheological responses for both the PS/LDPE and PMMA/LDPE (13.5/86.5 vol %) blends in the frequency sweep experiment at various temperatures are shown in Figures 2 and 3. The complex modulus with a frequency range from 100 to 0.1 rad/s was measured for each blends. For a binary mixture of viscoelastic materials without interparticle interactions, Palierne proposed the complex shear modulus $G^*(\omega)$ as a function of an individual complex shear modulus. When the dispersed phase is made of rigid and elastic spheres, the complex shear modulus of blend is expressed by eq. 3:

$$G^*(\omega) = G^*_{\mathrm{m}}(\omega)(1 + 3\sum \phi_{\mathrm{i}}\mathrm{H}_{\mathrm{i}}(\omega)/1 - 2\sum \phi_{\mathrm{i}}\mathrm{H}_{\mathrm{i}}(\omega)) \tag{3}$$

$$H_{\mathrm{i}} = \{4(\gamma_{12}/R_{\mathrm{i}})[2G^*_{\mathrm{m}}(\omega) + 5G^*_{\mathrm{i}}(\omega)] + [G^*_{\mathrm{i}}(\omega) - \mathrm{G}^*_{\mathrm{m}}(\omega)]16G^*_{\mathrm{m}}(\omega)$$

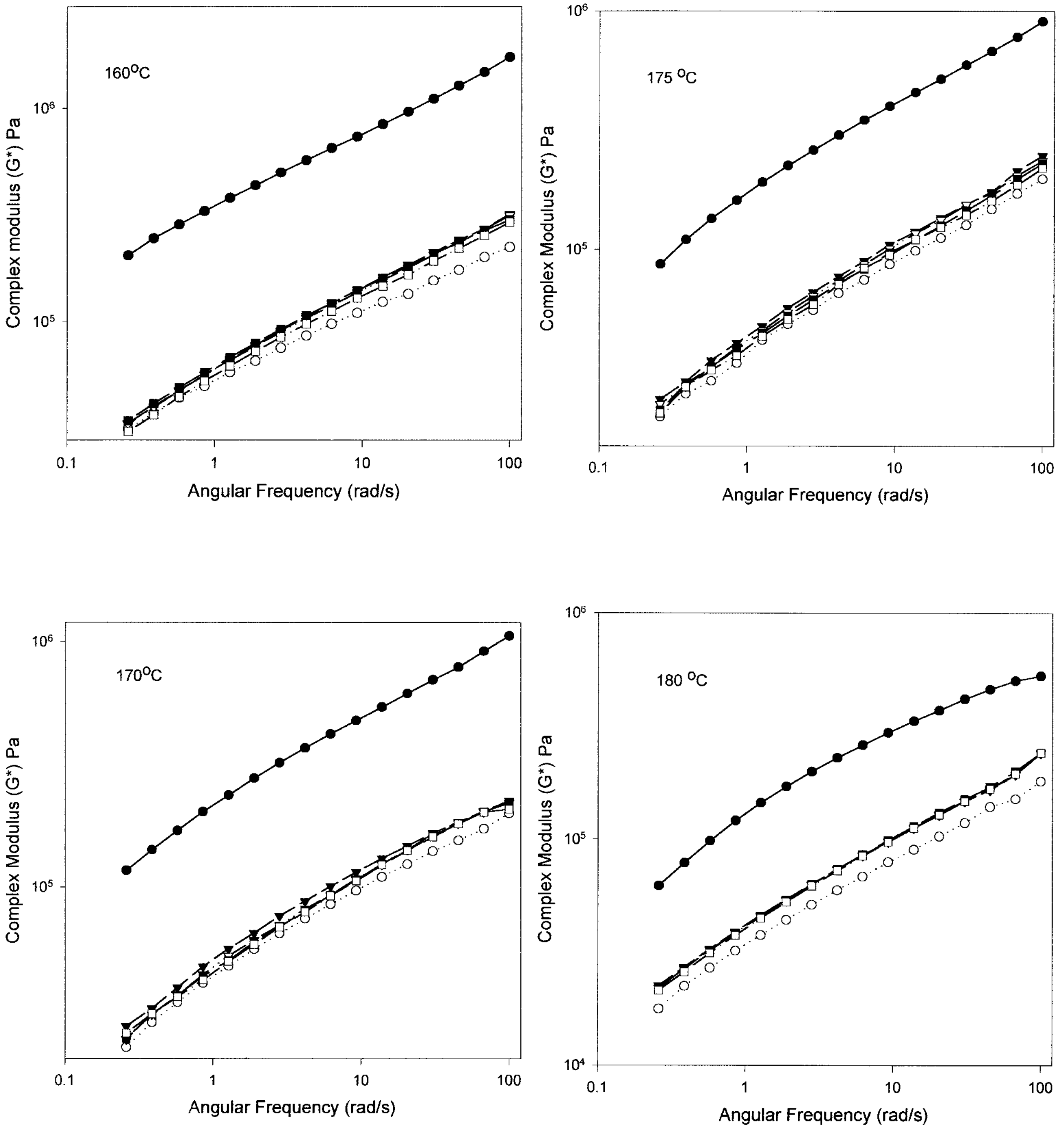

Figure 3 (*Continued from the previous page*)

$$+ 19G^*_i(\omega)/40(\gamma_{12}/R_i)[G^*_m(\omega) + G^*_i(\omega)]$$
$$+ [2G^*_i(\omega) + 3G^*_m(\omega)][16G^*_m(\omega) + 19G^*_i(\omega)]\}$$

where G^*_m and G^*_i are the complex shear modulus of matrix and inclusion, respectively, and ϕ_i is the volume fraction, γ_{12} is the interfacial tension (4.5 and 8.6 mN/m^6 for the PS/LDPE and PMMA/LDPE blends, respectively), and R_i is the diameter of inclusion.

There is agreement between the model predictions and experimental results for each blend when the dispersed phase is rigid and an elastic sphere, as in Figures 2 and 3 at various temperatures.

The morphological dependency for the complex shear modulus can be observed at various temperatures in Figures 4 and 5. When the morphology of the blend was a thread/matrix, the complex shear modulus moved to the lower region of the whole experimental frequency range. The lower the value of the complex shear modulus that was measured, the higher the strain that was applied to the blends. In the case of the PMMA/LDPE blend, there was little strain

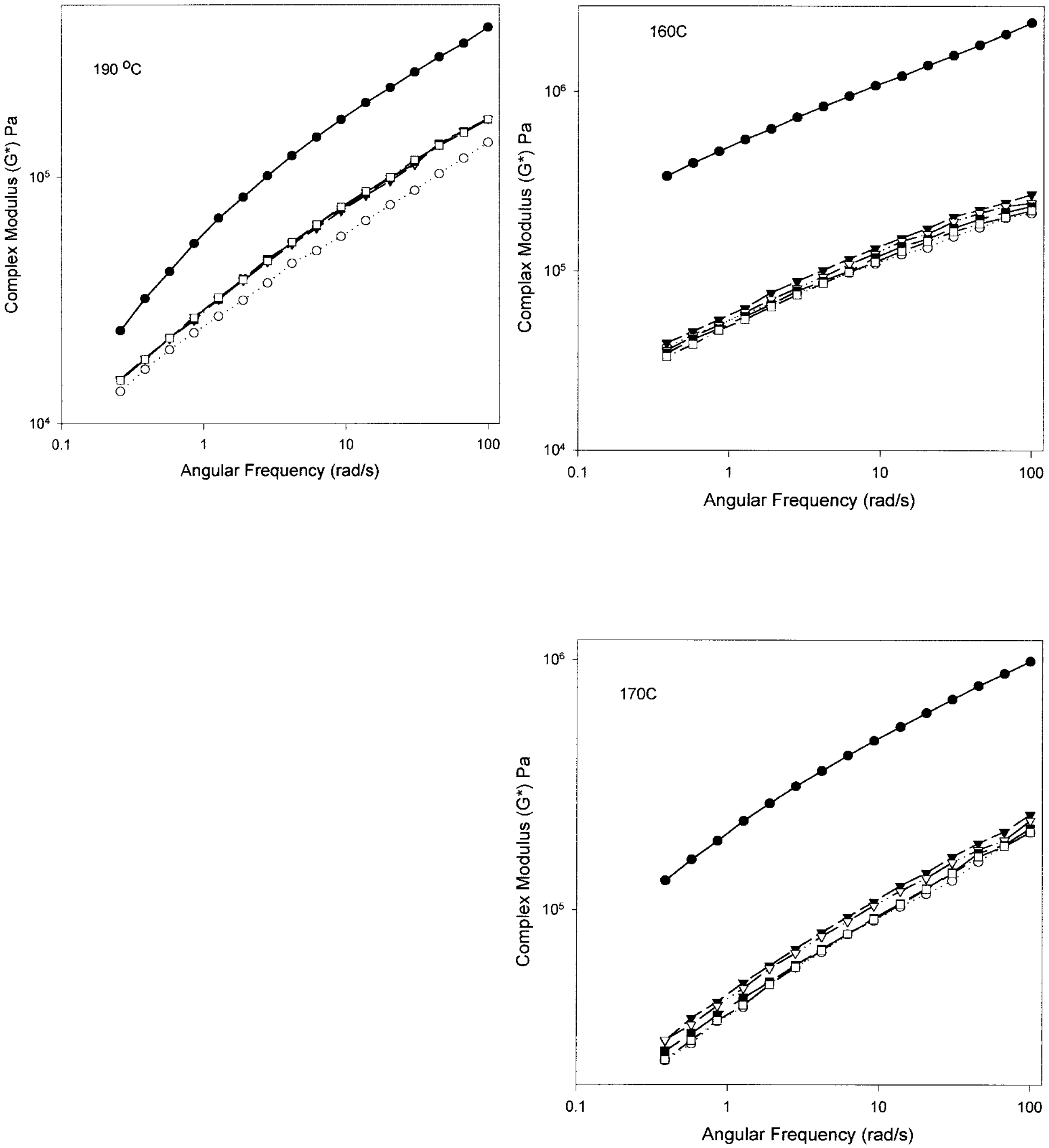

Figure 4 Morphological dependency due to applied strain of PS/LDPE (13.5/86.5 vol %) blends with various temperatures. Key: (●) PS 1; (○) LDPE; (▲) $\gamma = 0$; (△) $\gamma = 83.2$; (■) $\gamma = 1789$; (□) $\gamma = 17{,}987$.

dependency, though the PS/LDPE blend was shown to have different deformation according to the applied strain. However, a long and thin thread was observed by SEM at a high strain for both blends. When the morphology of the blend was a thread-like dispersed phase, the complex shear modulus was not in good agreement between Palierne's prediction and the results. The morphological dependency for a complex shear modulus on the whole experimental window was measured, which means that the resistance of blends by external force is larger when the shape of the dispersed phase is a sphere. If the shape of the dispersed phase is a thread, the external force may be easy to pass through matrix. Therefore, the complex shear modulus was gradually decreased. But this tendency disappeared at the specific temperature for both of blends. The complex shear modulus for blends which had different morphologies overlapped at the specific temperature of 180 °C for both PS/LDPE and PMMA/LDPE. It is thought these identical temperatures seem to be some rheological response like critical flow temperature (T_{cf}) for an amorphous polymer. A

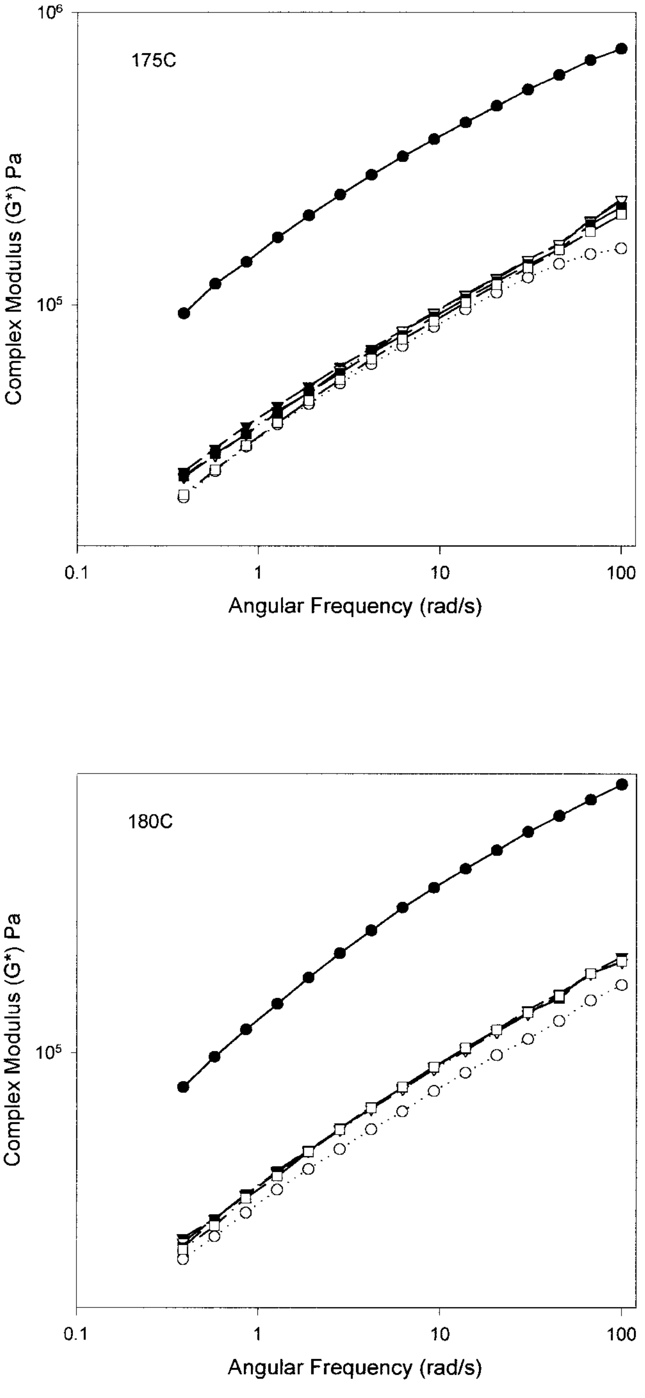

Figure 4 (*Continued from the previous page*)

couple of years ago, Han et al. introduced the concept of critical flow temperature (T_{cf}) for amorphous polymers, in which an amorphous polymer acts as a solid-like rubber below the T_{cf}, but may be regarded as a polymer melt above the T_{cf}. They proposed that the value of the T_{cf} is ~55 °C above the T_g of amorphous polymers. He also discovered that the T_{cf} of PS was 155 °C and that of PC was ~198 °C. In this study, the T_g values of the PS and PMMA were 121 and 125 °C, respectively. These value were determined using a rheometer with a radius of 8 mm, with parallel plates through the temperature sweep experiment. The constant amplitude and frequency were 0.1 % and 1 Hz, respectively. These temperatures could be measured at the value of tan δ was maximum. The T_{cf} of PS and PMMA in this study should be 176 and 180 °C, respectively, according to Han's model. These temperatures were roughly the same as the temperatures at the point that morphological dependency disappeared for blends in the frequency sweep experiment. It was previously elucidated that the resistance for external force of dispersed amorphous polymers does not depend on the morphology above T_{cf}. As a result, the same rheological state was shown at T_{cf} in most amorphous polymers. This result well explains that the morphological dependency of amorphous polymers disappears over the whole frequency range.

CONCLUSION

The four types of morphology for PS/LDPE and PMMA/LDPE, prepared at a constant shear rate and temperature with different strains, were also observed by SEM. The complex shear modulus of the PS/LDPE and PMMA/LDPE blend systems were measured by frequency sweep experiments at constant composition using a rheometer. The results were compared with the Palierne model only for the droplet type of dispersed phase (i.e., at $\gamma = 0$). The morphological dependency of blends on the complex shear modulus was also investigated at various temperatures. There was morphological dependency on the complex shear modulus below the specific temperature in the frequency sweep experiment. This temperature was the

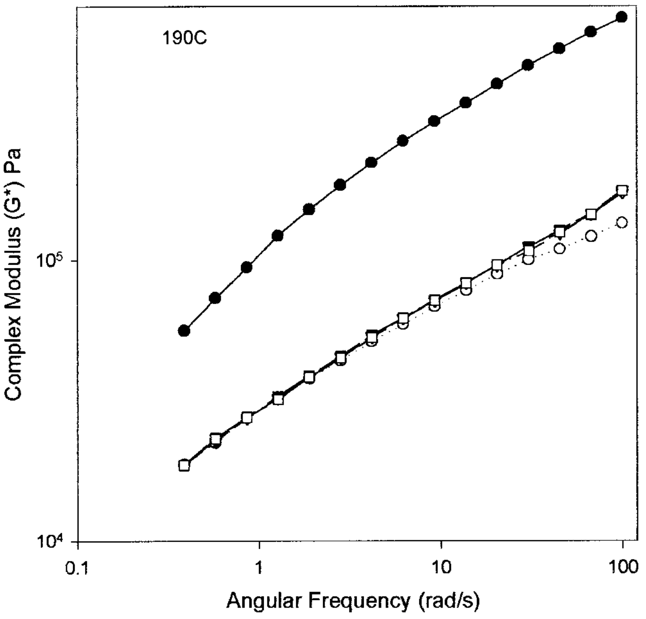

Figure 5 Morphological dependency due to applied strain of PMMA/LDPE (13.5/86.5 vol %) blends with various temperatures. Key: (●) PS 1; (○) LDPE; (▲) $\gamma = 0$; (△) $\gamma = 83.2$; (■) $\gamma = 1789$; (□) $\gamma = 17{,}987$.

same, 180 °C, two different blends. Above this temperature, there was no morphological dependency on the complex shear modulus for either blend. This phenomenon at specific temperature seems to be a rheological response of a dispersed polymer like critical flow temperature, T_{cf}, which was introduced by Han et al.[15] In this study, The T_g values of the dispersed polymers, PS and PMMA, were 121 and 125 °C, respectively. The T_{cf} of PS and PMMA is close to 180 °C. Therefore, there is a relationship between Han's proposal and our results, which means that the dispersed polymer is in an isorheological state above T_{cf}. However, below this temperature, the dispersed polymer acts as an elastic solid and affects rheological properties of the blend, like the difference in the complex shear modulus for each blend, which have different morphologies.

In this study, a new method to determine the critical flow temperature of an amorphous polymer may be needed via the measurement of a complex shear modulus for immiscible polymer blends that have a different morphologies in the frequency sweep experiment.

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