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Rheological Properties of Polystyrene and Poly(methyl methacrylate) Blends

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Abstract−Rheological properties of the polystyrene (PS) and poly(methyl methacrylate) (PMMA) blends were studied by Advanced Rheometric Expansion System (ARES). Storage modulus and loss modulus of the PS and PMMA blends were measured, and the interfacial tension of the PS and PMMA blends were obtained with various emulsion models by using the storage modulus and loss modulus of the blends. The value of interfacial tension estimated from the Palierne emulsion model was found to be 2.0 mN/m. Also, the interfacial tension between PS and PMMA was calculated by a theoretical model. The values of interfacial tension of the PS and PMMA blends obtained by the experiment and theoretical model were found to be in good agreement.

Key words: Interfacial Tension, Rheological Properties, Emulsion Model, Polymer-Polymer Interaction Parameter

INTRODUCTION

Polymer blends provide an economic alternative to synthesizing new polymers. The mechanical properties of immiscible blends can be optimized by controlling the blend morphology which is created in processing [Larson, 1999; Vinckier et al. 1996; Kim et al., 1994; Hara and Sauer, 1998; Kim and Chun, 1999]. Not only are the properties of the final polymer blends a function of the components, but they also depend on the characteristics of the interface that appears at the separation between the components [Vignaux-Nassiet et al., 1998].

To characterize the interface properties between the blend components under the flow condition, the rheological behavior of immiscible polymer blends has been widely studied [Lee and Denn, 1999, 2000; Kim and Denn 1992; Everaert et al., 2000; Grizzuti et al., 1997, 2000; Liang et al.,1999]. Measurement in the linear viscoelastic domain, such as small amplitude oscillatory shear flow, can yield very useful information on the blends characteristics. Emulsion models take into account the deformation and relaxation of the shape of dispersed droplets in a polymer blend system. Especially, comparison of these models with many experimental results proved that it is very useful for predicting the unknown interfacial tension, determining particle size distribution, and analyzing the deformation of droplets under shear and elongational flow [Friedrich et al., 1995; Grabling et al., 1990, 1991, 1993, 1994].

Interface properties of immiscible polymer blends have been studied extensively by theoretical models [Helfand et al., 1971, 1972, 1975, 1989, 1992; Leiber, 1980; Broseta et al., 1990; Tang and Freed, 1991a, b] based on thermo- and molecular-dynamics. With the help of various theoretical models [Helfand et al., 1972; Broseta et al., 1990; Tang and Freed, 1991b], the interfacial tension of polymer blends, such as PS/PMMA, can be estimated. There are various theories, such as self-consistent field theory, mean field theory, Landau expansion method, which described the interfacial properties of two immiscible polymers.

In this study, the emulsion model is used to determine the interfacial tension of the PS/PMMA blend. Also, we compared the interfacial tension obtained by the theoretical model and from the experimental data obtained by the measurement using a rotation rheometer. In calculating the interfacial tension from the theoretical model, we studied the effect of molecular weight and composition dependence of the polymer-polymer interaction parameter in theoretical model, which might lead to significant theoretical errors.

EXPERIMENTAL

1. Polymers

The polymers used in this study were obtained from commercial sources. The PS (GP 150), which was used, was provided by Hannam Chemical Co. The PMMA used was IH 830, provided by LG Chemical Co. The characteristics and sources of the polystyrene (PS) and poly(methyl methacrylate) (PMMA) are shown in Table 1. In Table 1, the weight average molecular weights and number average molecular weights were measured by Gel permeation chromatography (GPC).

2. Blend Preparations

Table 1. Characteristics of polymer samples used in the PS/PMMA Blend

	M_w[a]	M_n[a]	MWD	T_g (°C)[b]	Zero shear viscosity (Pa·s)[c]	Melt density (g/cm^3)[d]
PS[e]	2.1×10^5	6.9×10^4	3.05	100	3.2×10^4	0.95
PMMA[f]	7.8×10^4	3.8×10^4	2.05	105	1.1×10^4	1.07

[a] Measured in our laboratory by GPC.
[b] Measured in our laboratory by DSC.
[c] Measured in our laboratory by ARES.
[d] Calculated from Van Krevelen [1990].
[e] Supplied by Hannm Chem. Co.
[f] Supplied by LG Chem.Co.

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Blends with weight fraction of PMMA from 0.1 to 0.9 in increments of 0.1 were prepared by using a 20 mm diameter laboratory scale screw extruder, with a 24 : 1 length to diameter screw. The polymer samples were dried under vacuum (<1 mmHg) at 100 °C for 24 hours and extruded at an apparent shear rate ($4Q/\pi R^3$) of 189 s^{-1}. The temperature of the extruder was set at 160 °C and 200 °C in feeding zone and barrel zones, respectively. Samples were compression molded by using a hot press at 190 °C and 40 psi for 5 min.

3. Scanning Electron Microscopy

The morphology of the cross-section of the extrudate prepared by cryogenic fracturing was examined by Hitachi Field emission scanning electron microscopy (Model S-4300) at 20 kV accelerating voltage after platinum sputter coating (500 Å). The volume-average radius of droplets (R_v) and number-average radius of droplets (R_n) were determined by ING Co. image analyzer (Model Image-Pro Plus).

4. Rheological Properties

Dynamic measurements were carried out on an Advanced Rheometric Expansion System (ARES) in oscillatory shear at 8% strain in the parallel-plate arrangement with 25 mm plate. The sample used in this study was fabricated in a disk with 2 mm in thickness. The frequency sweeps from 0.01 to 100 rad/sec were carried out at 190-220 °C. Since the morphology of the blends was stable during the time of measurements for these experimental conditions, the complex modulus G' and G" measured at 190, 200, and 220 °C were superimposed into a master curve at 190 °C according to the time-temperature superposition principle [Ferry, 1980]. For all measurements, it has been verified that the behavior of the sample was linear viscoelastic.

RESULTS AND DISCUSSION

1. Interfacial Tension from Emulsion Model

Fig. 1 shows the storage (G') and loss modulus (G") as a function of frequency for the pure PS and PMMA at 190 °C. In Fig. 1, the PS and PMMA melts show the characteristic behavior of the low frequency terminal zone. However, a very weak secondary plateau zone is observed, which can be seen in many polymer melts at low frequency region. Therefore, the components of the blends can be considered as weak viscoelastic liquids at low frequency region.

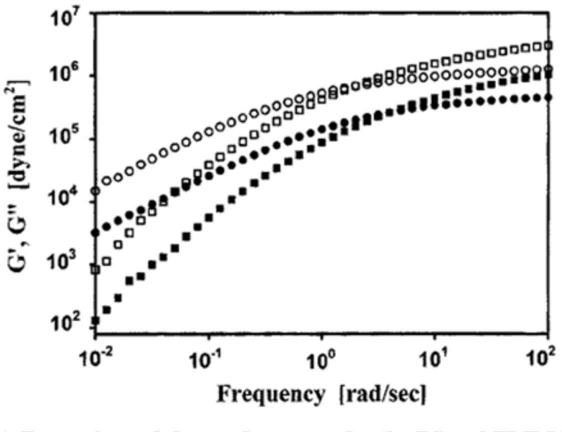

Fig. 1. Dynamic modulus vs. frequency for the PS and PMMA at 190 °C. PS: G' (■), G" (●); PMMA: G' (□), G" (○).

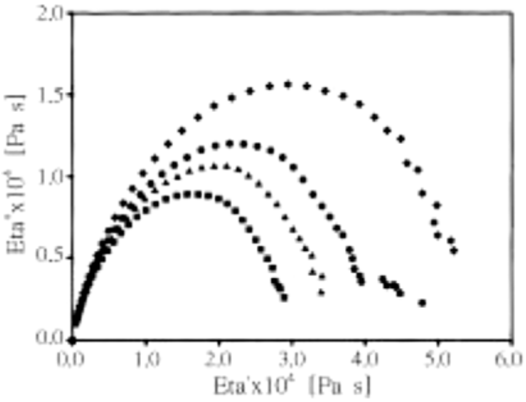

Fig. 2. Cole-Cole plot of dynamic viscosities at 190 °C. PS (■), 9/1 PS/PMMA (▲), 8/2 PS/PMMA (●), 7/3 PS/PMMA (◆).

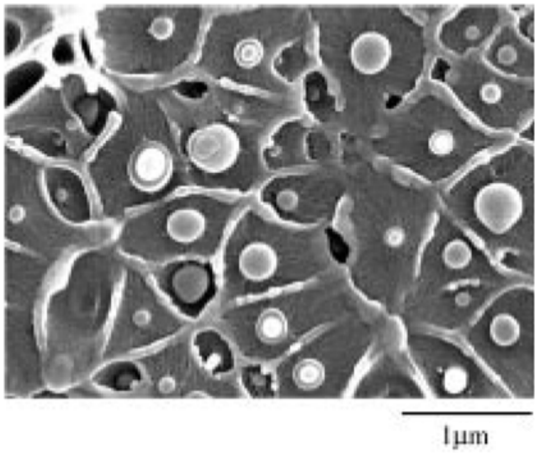

Fig. 3. SEM micrographs for 8/2 PS/PMMA blend prepared at 190 °C.

For the immiscible blend system, zero shear viscosity of the blends can be obtained from the Cole-Cole plot of the PS/PMMA blend with various compositions (Fig. 2). In Fig. 2, the two relaxation mechanisms in emulsions were clearly observed in the 8/2 PS/PMMA blend. In Fig. 2, high-frequency relaxation of the matrix represents PS and low-frequency relaxation of droplets represents PMMA. Zero shear viscosity of 8/2 PS/PMMA blend was obtained by extrapolation at zero frequency of Fig. 2 and founded to be 5.6×10^4 Pa·s [Graebling et al., 1990]. The morphology of the 8/2 PS/PMMA blend by scanning electron microscopy is shown in Fig. 3. In Fig. 3, it is observed that the PS and PMMA are the matrix and droplets, respectively, in the 8/2 PS/PMMA blend.

As mentioned in the introduction, dynamic interfacial tension of polymer blends can be obtained by fitting of emulsion model to the experimental results. From Fig. 4 and Eq. (1), the interfacial tension of the PS and PMMA blend has been calculated and found to be 1.0 mN/m. The work by Choi and Schowalter [1975] on the rheological behavior of semidilute emulsion of two Newtonian liquids leads to the establishment of a constitutive equation.

$$G'(w) = \frac{\eta_0 w^2 (h_1 - h_2)}{1 + w^2 h_1^2} \tag{1}$$

with

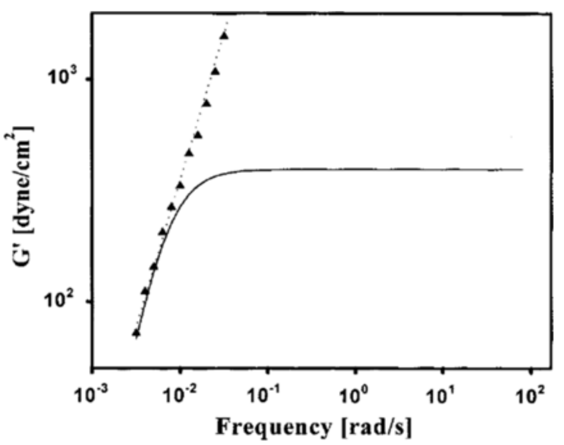

Fig. 4. Comparison of the experimental data (▲) for G' to the Choi-Schowalter model (—) predictions for the 8/2 PS/PMMA blend.

$$\eta_a = \eta_0\left[1+\frac{(5k+2)}{2(k+1)}\phi+\frac{5(5k+2)^2}{8(k+1)^2}\phi^2\right]$$

$$h_1 = \frac{\eta_0 R}{\alpha}\frac{(19k+16)(2k+3)}{40(k+1)}\left[1+\frac{5(19k+16)}{4(k+1)(2k+3)}\phi\right]$$

$$h_2 = \frac{\eta_0 R}{\alpha}\frac{(19k+16)(2k+3)}{40(k+1)}\left[1+\frac{3(19k+16)}{4(k+1)(2k+3)}\phi\right]$$

where η_0 is the viscosity of the suspending medium, k is the ratio of the droplet phase viscosity to the suspending medium viscosity, α is interfacial tension, R is the radius of the droplet phase and ϕ is the volume fraction of the droplet phase.

Fig. 4 shows the storage modulus versus frequency of experimental data and theoretical curve calculated from Choi-Schowalter model. The effect of a size distribution is more difficult to take into account in the case of a Choi-Schowalter model. Hence, R was taken as the radius of the largest particles, because in polydisperse emulsion the contribution of the smaller domains to the storage modulus can be neglected in the terminal zone [Scholz et al., 1989]. Note that loss modulus is almost unaffected with droplet radius and interfacial tension in fitting Choi-Schowalter model to experimental curves; it was not represented in Fig. 4. With a largest radius of about 0.28 μm for the PMMA and dynamic interfacial tension of about 1.0 mN/m, a good agreement between emulsion model and experimental curves is obtained over the whole frequency range for the 8/2 PS/PMMA blend.

The model by Palierne [1990] accounts for the linear viscoelastic behavior of a dispersion of viscoelastic inclusions in a viscoelastic matrix, where the inclusions forming the dispersed phase are spherical in equilibrium.

$$G^*(w) = G_m^*(w)\left[\frac{1+3\sum_i \phi_i H}{1-2\sum_i \phi_i H}\right] \tag{3}$$

with

$$H_i(\omega)=4\alpha/R[2G_M^*(\omega)+5G_i^*(\omega)]+[(G_i^*(\omega)-G_M^*(\omega))(16G_M^*(\omega)$$
$$+19G_i^*(\omega))]/40\alpha/R[G_M^*(\omega)+G_i^*(\omega)]$$
$$+[(2G_i^*(\omega)-3G_M^*(\omega))(16G_M^*(\omega)+19G_i^*(\omega))]$$

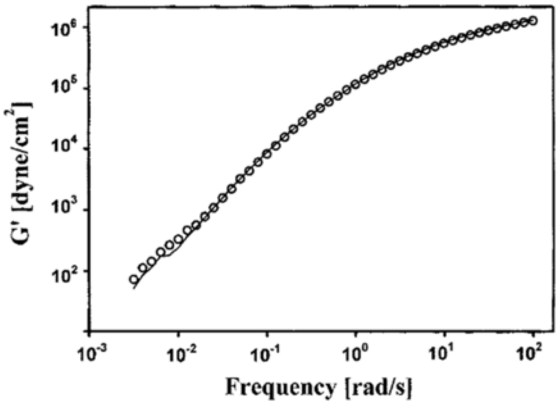

Fig. 5. Comparison of the experimental data (○) for G' to the Palierne model (—) predictions for the 8/2 PS/PMMA blend.

The number average radius (R_n) and volume average radius (R_v) of the 8/2 PS/PMMA blend were determined from SEM micrograph by using an image analyzer. The R_n and R_v of the 8/2 PS/PMMA blend were found to be 0.10 and 0.13 μm, respectively. Fig. 5 shows the storage modulus versus frequency of the experimental data and theoretical curve calculated from Palierne model [Eq. (3)] of the 8/2 PS/PMMA blend. The interfacial tension is directly related to the secondary plateau in G' [Graebling et al., 1993]. Therefore, as in Fig. 4, the loss modulus (G") was not represented in Fig. 5. In Fig. 5, the theoretical curves are in good agreement with experimental values when the value of dynamic interfacial tension is 2.0 mN/m.

It is worthwhile to compare these results to data obtained on the same system with the results of other research groups [Friedrich et al., 1995; Graebling et al., 1990, 1993; Gramespacher and Meissner, 1992] and different transient methods, e.g. deformation drop retraction method, imbedded disk retraction method, transient recovery method etc. The values of interfacial tension for the PS/PMMA blend have been estimated by deformation drop retraction method [Luciani et al., 1997] and found to be 1.0 mN/m. Also, from the imbedded disk retraction method [Rundqvist et al., 1996] and transient recovery method [Gramespacher and Meissner, 1997], the interfacial tensions were found to be 0.9-1.3 and 1.5-2.2 mN/m, respectively. Although the values of interfacial tension between the melts of the PS and PMMA differ from each other according to the emulsion model and experimental methods, values of the interfacial tension can be found from 0.9 to 2.2 mN/m for the PS/PMMA blend, which is reasonably consistent with results obtained in this study.

2. Interfacial Tension from Theoretical Model

The interfacial tension between the PS and PMMA can be calculated by using a theoretical model based on thermo- and molecular-dynamics. There are various theoretical models which relate the interfacial properties of two immiscible polymers, e.g., A and B, to the microscopic interactions described by the polymer-polymer interaction parameter (χ_{AB}) between the corresponding monomers [Broseta et al., 1990].

Helfand and Tagami [1972, 1975] constructed a self-consistent field theory of polymer interfaces. In their theory, interfacial tension of blend, which composed by infinite molecular weight polymer, can be simply expressed to the relation of polymer-polymer interaction parameter, interfacial thickness, and monomer density.

$$\gamma=(\chi/6)^{0.5}\rho_0 bkT \quad (4)$$

where ρ_0 is the monomer density, b is the effective length per monomer unit, k is the Boltzmann constant, and T is a temperature.

If the polymer-polymer interaction parameter is known in the Helfand and Tagami model, the interfacial tension between the blend components can be estimated by applying the polymer-polymer interaction parameter to the Helfand and Tagami model. So far, when the interfacial tension has been calculated by Helfand and Tagami model, composition dependence of the polymer-polymer interaction parameter has not been considered. Ignoring the composition dependence of polymer-polymer interaction parameter might lead to significant theoretical errors [Broseta et al., 1990; Tang and Freed, 1991b] in the interfacial tension of the components.

The interfacial tension was obtained by using the Eq. (4) and polymer-polymer interaction parameter results of previous work [Burns and Kim, 1988] of the PS/PMMA blend and found to be 1.40-1.65 mN/m. The composition dependence of the polymer-polymer interaction parameter was considered in the calculation of the interfacial tension in this study and the composition was 3/7, 4/6, 5/5, 6/4, and 7/3 PS/PMMA blend.

From the ARES measurement, values of the interfacial tension of the PS/PMMA blend were found to be 1.0 mN/m in Choi and Schowalter model and 2.0 mN/m in Palierne model. From the theoretical model, values of the interfacial tension of the PS/PMMA blend were found to be 1.40-1.65 mN/m with the blend composition. Minor differences between the measured and calculated values are suspected to predominantly arise from the inconsistency of sample in the calculations and experimental. Comparing the calculated values and experimental values measured by oscillatory rheometry in this study, it is observed that the interfacial tension of the PS/PMMA blend obtained from the theoretical model agrees qualitatively well with the measured transient experimental data.

CONCLUSIONS

Rheological properties of the polystyrene (PS) and poly(methyl methacrylate) (PMMA) blend were studied by Advanced Rheometric Expansion System (ARES). Storage modulus and loss modulus of the PS and PMMA blend were measured and the interfacial tension of the PS and PMMA blends was obtained by the various emulsion models using the storage modulus and loss modulus of the blend.

From the ARES measurement, values of the interfacial tension of the PS/PMMA blend were found to be 1.0 mN/m in Choi and Schowalter model and 2.0 mN/m in Palierne model. The interfacial tension obtained by using the Helfand and Tagami model and polymer-polymer interaction parameter, which considered composition dependence of the PS/PMMA blend, was found to be 1.40-1.65 mN/m. Comparing the calculated values and experimental values measured by oscillatory rheometry in this study, it is observed that the interfacial tension of the PS/PMMA blend obtained from the theoretical model agrees qualitatively well with the measured transient experimental data.

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