

Evaluation of interfacial tension for poly(methyl methacrylate) and polystyrene by rheological measurements and interaction parameter of the two polymers

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Abstract

Morphological and rheological properties of the poly(methyl methacrylate) (PMMA) and polystyrene (PS) blends were studied by scanning electron microscopy (SEM) and advanced rheometric expansion system (ARES). From the SEM results, the PMMA-PS blends showed dispersed morphology and the particle size of the dispersed phase was quite small (0.1 ~ 0.6 μm) compared with other immiscible polymer blends. Values of the interfacial tension of the PMMA-PS blend were obtained from the Choi-Schowalter and the Palierne emulsion models using the storage modulus of the PMMA and PS, and found to be 1.0 and 2.0 mN/m, respectively. The interfacial tension between the PMMA and PS was also calculated from the Flory-Huggins polymer-polymer interaction parameter (χ) and found to be from 0.98 to 1.86 mN/m depending on the molecular weight and composition. Comparing the values of the interfacial tension from the Flory-Huggins polymer-polymer interaction parameter and the values measured by oscillatory rheometer, it is suggested that the interfacial tension of the PMMA-PS blend obtained from the polymer-polymer interaction parameter are in good agreement with the values obtained by rheological measurements.

Keywords : interfacial tension, emulsion models, polymer-polymer interaction parameter

1. Introduction

Polymer blends provide an economic alternative to synthesizing new polymers (Chun *et al.*, 2000; Friedrich *et al.*, 1995; Graebling *et al.*, 1993; Gramespacher and Meissner, 1992; Han *et al.*, 2000; Han *et al.*, 2001a; Han *et al.*, 2001b, Lee and Denn, 1999; Sung *et al.*, 2003). When two immiscible polymers are blended in a mixing equipment, the properties of the final polymer blends depend on the characteristics of the interface which appears at the separation between the components. To characterize these interfacial properties between the blend components under the flow condition, the rheological behavior of immiscible polymer blends has been widely studied (Friedrich *et al.*, 1995; Graebling *et al.*, 1993; Gramespacher and Meissner, 1992; Lee and Denn, 1999; Sung *et al.*, 2003). Especially, comparison of emulsion models with rheological properties proved that it is very useful for predicting the unknown interfacial tension (Graebling *et al.*, 1993; Gramespacher and Meissner, 1992; Lee and Denn, 1999; Sung *et al.*, 2003) and determination of particle size distribution (Friedrich *et al.*, 1995) under shear flow. In addition, inter-

facial properties of immiscible polymer blends have been studied extensively using the polymer-polymer interaction parameter (Broseta *et al.*, 1990; Helfand and Tagami, 1972; Helfand and Sapse, 1975; Helfand *et al.*, 1989; Helfand, 1992; Tang and Freed, 1991a; Tang and Freed, 1991b). With the help of various theoretical models (Broseta *et al.*, 1990; Helfand and Tagami, 1972; Tang and Freed, 1991b), the interfacial tension of polymer blends, such as PMMA-PS blend, can be estimated.

In calculation of the interfacial tension of the PMMA-PS blends in this study, the effect of molecular weight and composition dependence of the polymer-polymer interaction parameter are considered in the theoretical models. Interfacial tension of the PMMA-PS blends obtained by the Flory-Huggins polymer-polymer interaction parameter (χ) were compared to that from the rheological data obtained by the measurement using rotational rheometer.

2. Experimental

2.1. Polymers

The polymers used in this study were obtained from commercial sources. The poly(methyl methacrylate) (PMMA), used IH 830, was provided by LG Chemical Co. The polystyrene (PS), used GP-150, was provided by Han-

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Table 1. Characteristics of polymer samples used in the PMMA-PS blends

	M_w^a	M_n^a	MWD	Zero shear viscosity (Pa·s) ^b	T_g (°C) ^c
PMMA ^d	7.8×10^4	3.8×10^4	2.1	1.1×10^5	105
PS ^e	2.1×10^5	6.9×10^4	3.1	3.2×10^4	100

^aMeasured by GPC.^bMeasured in our laboratory by ARES.^cMeasured in our laboratory by DSC.^dSupplied by LG Chem.Co.^eSupplied by Hannam Chem. Co.

nam Chemical Co. The characteristics and sources of the PMMA and PS are shown in Table 1.

2.2. Blend preparations

Blends with weight fraction of PMMA from 0.1 to 0.9 in increment of 0.1 were prepared 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 before extrusion. The temperature of the extruder was set at 160°C and 200°C in feeding zone and barrel zones, respectively. Samples were compression molded using a hot press at 190°C and 40 psi for 5 min.

2.3. Scanning electron microscopy

The morphology of the cross-section of the extrudate prepared by cryogenic fracturing as 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) was determined by ING Co. image analyzer (Model Image-Pro Plus).

2.4. Rheology

Dynamic measurements were carried out on 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°C and 210°C. The isotherms were shifted to mastercurve with a reference temperature 190°C. For all measurement, it has been verified that the behavior of the sample was linear viscoelastic.

3. Results and discussion

3.1. Complex viscosity of PMMA-PS blends

Complex viscosity of the PMMA-PS blends is shown in Fig. 1. The frequency used in this study was 0.5, 5 and 25 rad/s. From Fig. 1, it is observed that the complex viscosity of the blends show linear additive rule of the viscosities of the PMMA and PS. In the PMMA rich composition, the excess viscosity begins at about 0.6 weight fraction

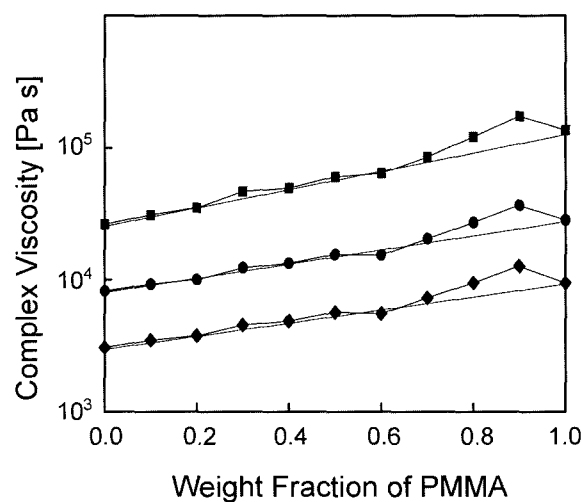


Fig. 1. Complex viscosity of the PMMA-PS blends at various frequency (rad/s) (■) 0.5, (●) 5, (◆) 25.

PMMA. The excess viscosity is shown in the compositions between 0.6 and 1.0 weight fraction for the PMMA in the PMMA-PS blend. From Fig. 1, the onset point of excess viscosity, which represents an abrupt change in viscosity level suggests that morphological changes may occur at about 0.6 weight fraction PMMA in the PMMA-PS blend. Similar results have been reported in the PMMA and polyethylene blend (Martinez and Williams, 1980).

3.2. Morphology of PMMA-PS blends

The morphology of the PMMA-PS blends was studied using scanning electron microscopy. Fig. 2(a)-(f) show micrographs of the cryogenically fractured cross-section surfaces for the 90/10, 70/30, 60/40, 50/50, 20/80 and 10/90 PMMA-PS blends, respectively. In Fig. 2(a)-(f), the PMMA and PS blends show dispersed morphology.

From Fig. 2, the dispersed droplet size shows smaller in the PMMA-rich composition (Fig. 2(a)-(c)) because of higher viscosity of the PMMA (continuous phase) compared to the PS (dispersed phase). This result is somewhat consistent with the complex viscosity results (Fig. 1), which is the excess viscosity is shown in the compositions between 0.6 and 1.0 weight fraction PMMA. The existence of such excess viscosity suggests the morphological

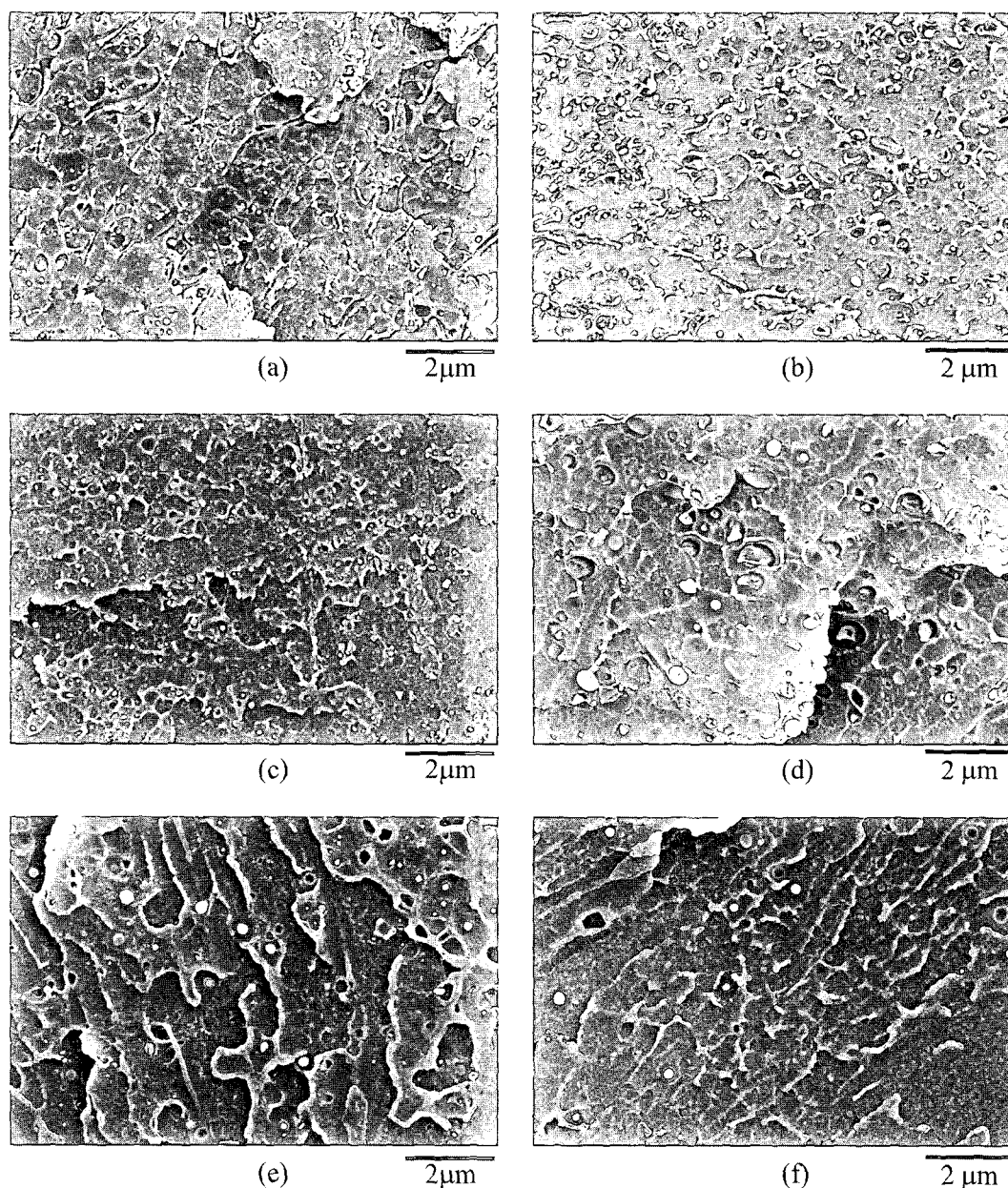


Fig. 2. Scanning electron micrographs obtained from cryogenically fractured cross-section surfaces of the PMMA-PS blends: (a) 90/10; (b) 70/30; (c) 60/40; (d) 50/50; (e) 20/80; (f) 10/90.

change of the PMMA-PS blends (Martinez and Williams, 1980). Also, it is observed that the particle size of the dispersed phase is about 0.1 ~ 0.6 μm for the PMMA-PS blends, which is quite small compared with other immiscible polymer blends.

3.3. Interfacial tension from rheological measurements

As mentioned in the introduction section, interfacial tension of the polymer blends can be obtained by fitting the emulsion models to the experimental results. The work by Choi and Schowalter (Choi and Schowalter, 1975) on the

rheological behavior of semidilute emulsion of two Newtonian liquids leads to the establishment of a constitutive equation as follows:

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

with

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

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

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

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 the interfacial tension, R is the radius of the droplet phase and ϕ is the volume fraction of the droplet phase. 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).

The model by Palierne (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 as follows:

$$G^*(\omega) = G_m^*(\omega) \left[\frac{1 + 3 \sum_i \phi_i H_i}{1 - 2 \sum_i \phi_i H_i} \right] \quad (2)$$

with

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

where α is the interfacial tension, R_v is the volume average radius of the dispersed phase, ϕ_i is the volume fraction of the dispersed phase, G_M^* is the complex modulus of the matrix, and G_i^* is complex modulus of the dispersed phase.

Figs. 3 and 4 show the storage modulus versus frequency

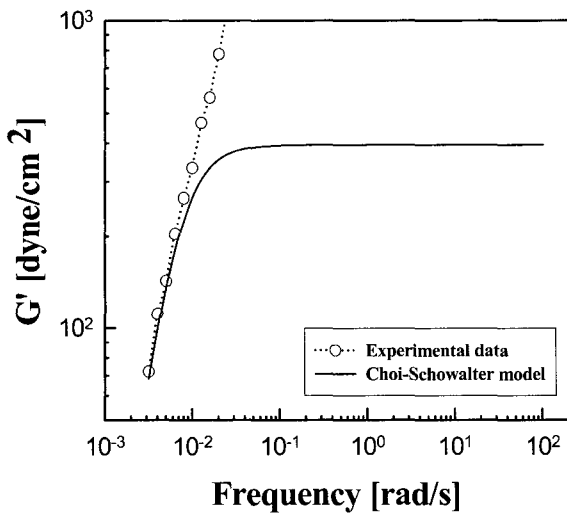


Fig. 3. Comparison of experimental data for G' to the Choi-Schowalter model predictions for the 20/80 PMMA-PS blend.

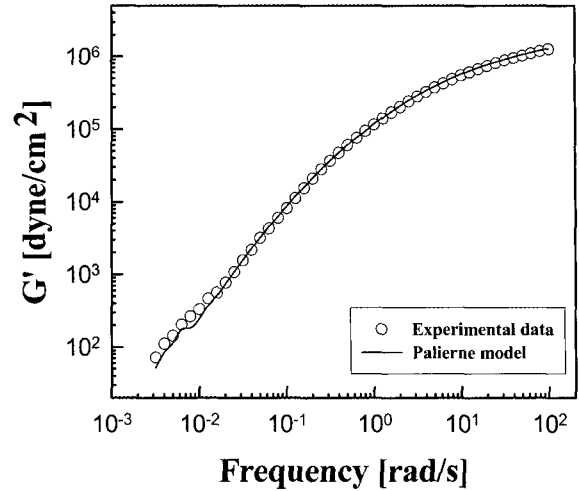


Fig. 4. Comparison of experimental data for G' to the Palierne model predictions for the 20/80 PMMA-PS blend.

of the experimental data and fitting curves obtained from Choi-Schowalter and Palierne models for the PMMA-PS 20/80 blend, respectively. The interfacial tension is directly related to the secondary plateau in the storage modulus (G') (Graebing *et al.*, 1993; Gramespacher and Meissner, 1992; Sung *et al.*, 2003). For the Choi-Schowalter model in Fig. 3, a good agreement between the fitting curve and the experimental data is obtained at the low frequency range when the interfacial tension is 1.0 mN/m and the largest radius of the PMMA is 0.28 μm . For the Palierne model in Fig. 4, the fitting curve is in good agreement with the experimental data when the interfacial tension is 2.0 mN/m and the volume average radius (R_v) of the PMMA is 0.13 μm .

Values of the interfacial tension for the PMMA-PS blends by other research groups are listed in Table 2. Values of the interfacial tension for the PMMA-PS blend were reported by deformation drop retraction method and found to be 1.0 mN/m (Luciani *et al.*, 1997). Also, for the imbedded disk retraction method (Rundqvist *et al.*, 1996) and transient recovery method (Gramespacher and Meissner, 1997), the interfacial tension was found to be 0.9 – 1.3 and 1.5 – 2.2 mN/m, respectively. The values of the interfacial tension by other research groups are ranged from 0.9 to 2.2 mN/m for the PMMA-PS blend, which is reasonably consistent with the results obtained in this study.

3.4. Interfacial tension from theoretical models

The interfacial tension between the PMMA and PS can also be calculated using the polymer-polymer interaction parameter. There are various theoretical models which are related with the interfacial properties of the two immiscible polymers, e.g., A and B, to the microscopic interactions described by the polymer-polymer interaction parameter (Broseta *et al.*, 1990; Helfand and Tagami, 1972; Helfand and Sapse, 1975; Helfand *et al.*, 1989; Helfand, 1992; Tang

Table 2. Comparison of interfacial tension determined by rheological and other measurements for the PMMA-PS blends

Research group	Measurement method	Interfacial tension (mN/m)
Gramespacher and Meissner (1992)	Rheological measurement (Choi-Schowalter)	1.8 – 2.2
Graebbling <i>et al.</i> (1993)	Rheological measurement (Paliarne)	1.12
Luciani <i>et al.</i> (1997)	Deformed drop retraction	1.0
Rundqvist <i>et al.</i> (1996)	Imbedded disk retraction	0.9 – 1.3
Gramespacher and Meissner (1997)	Transient recovery	1.5 – 2.2
In this study	Rheological measurement and polymer-polymer interaction parameter	1.0 – 2.0

and Freed, 1991a; Tang and Freed, 1991b).

Helfand and Tagami constructed a self-consistent field theory of polymer interface (Helfand and Tagami, 1972). In their theory, interfacial tension of the blend, which composed by infinite molecular weight polymer, can be simply expressed to the relation of Flory-Huggins polymer-polymer interaction parameter (χ), interfacial thickness, and monomer density.

$$\alpha = (\chi/6)^{0.5} \rho_0 b k T \quad (3)$$

where ρ_0 is the monomer density, b is the effective length per monomer unit, k is the Boltzman constant, and T is the temperature. In general, effective length b per monomer unit is typically 6.5 Å and density ρ_0 is typically 10^{-2} times Avogadro number monomer unit/cm³ in the PS/PMMA blend (Broseta *et al.*, 1990). Broseta *et al.* proposed that the theory of polymer interfaces should be taken account the effects of molecular weight and polydispersity (Broseta *et al.*, 1990). The theory is as follows:

$$\alpha = (\chi/6)^{0.5} \rho_0 b k T \left[1 - \frac{\pi^2}{12\chi} \left(\frac{1}{N_1} + \frac{1}{N_2} \right) \right] \quad (4)$$

where N_i is the degree of polymerization of i polymer. Tang and Freed proposed general forms for the interfacial width and tension that apply to the entire two-phase region (Tang and Freed, 1991a; Tang and Freed, 1991b). From Tang and Freed, the interfacial tension of the half-width can be written as follows:

$$\alpha = (\chi/6)^{0.5} \rho_0 b k T \left[1 - 1.35 \left(\frac{2}{\chi N} \right) \right] \quad (5)$$

where N is the degree of polymerization of polymers and assumed to be as follows: $N = N_1 = N_2$. Eq. 5 is restricted to

symmetric, incompressible binary blends with correlation functions taken in the random phase approximation.

If the Flory-Huggins polymer-polymer interaction parameter (χ) is known in Eqs. 3-5, the interfacial tension between the components can be estimated by applying the polymer-polymer interaction parameter to the Eqs. 3-5.

In our previous work (Burns and Kim, 1988), the blends were made of a low molecular weight PS ($\bar{M}_n = 8,900$) with three PMMAs having number-average molecular weights of 18,300 (PMMA-1), 37,000 (PMMA-2), and 211,000 (PMMA-3), and the composition dependent values of the polymer-polymer interaction parameter were determined and shows in Table 3. In Table 3, it is observed that the values of interfacial tension calculated by Eqs. 3-5 is found to be from 0.98 to 1.86 mN/m. The molecular weight and composition dependence of the polymer-polymer interaction parameter is considered in the calculation of the interfacial tension in the composition was 30/70 and 70/30 PMMA-PS blend (Table 3). From the rheological measurements, the composition dependence of the interfacial tension of polymer blends has been also reported (Gramespacher and Meissner, 1992) because of the change of the dispersed phase size and relaxation time.

From the ARES measurement, values of the interfacial tension of the PMMA-PS blend is found to be 1.0 mN/m in Choi and Schowalter model and 2.0 mN/m in Paliarne model. Comparing the values measured by oscillatory rheometry and the values obtained by the polymer-polymer interaction parameter (χ) of the two polymers, the interfacial tension of the PMMA-PS blends obtained from the polymer-polymer interaction parameter of the two polymers are in good agreement with the values obtained by rheological measurements.

Table 3. Values of interfacial tension calculated from the polymer-polymer interaction parameter of the PMMA-PS blends

Blend (composition)	Polymer-polymer interaction parameter ^a	Helfand and Tagami (mN/m)	Broseta <i>et al.</i> (mN/m)	Tang and Freed (mN/m)
PMMA-1/PS (30/70,70/30)	0.020, 0.024	1.54, 1.69	1.35, 1.45	1.22, 1.40
PMMA-2/PS (30/70,70/30)	0.015, 0.021	1.34, 1.58	1.04, 1.32	0.98, 1.28
PMMA-3/PS (30/70,70/30)	0.015, 0.029	1.34, 1.86	1.04, 1.64	0.98, 1.60

^aAll values of polymer-polymer interaction parameter obtained from our previous work (Burns and Kim, 1988).

4. Conclusions

In the study of morphology by SEM for the PMMA-PS blends, the PMMA-PS blends showed dispersed morphology and the particle size of the dispersed phase was quite small (0.1–0.6 μm) compared with other immiscible polymer blends.

From the results of rheological studies, values of the interfacial tension of the PMMA-PS blend were obtained from the Choi-Schowalter and the Palierne emulsion models using the storage modulus of the PMMA and PS, and found to be 1.0 and 2.0 mN/m, respectively.

From the Helfand-Tagami, the Broseta *et al.*, and the Tang-Freed models, interfacial tension of the PMMA-PS blend was calculated using composition dependent polymer-polymer interaction parameter and found to be from 0.98 to 1.86 mN/m. Comparing the values of the interfacial tension from the Flory-Huggins polymer-polymer interaction parameter (χ) of the PMMA-PS blends and the values measured by oscillatory rheometer, it is concluded that the interfacial tension of the PMMA-PS blend obtained from the polymer-polymer interaction parameter of the two polymers are in good agreement with the values obtained by rheological measurements.

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