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The effect of molecular weight and polydispersity of polystyrene on the interfacial tension between polystyrene and polybutadiene

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The effect of molecular weight and polydispersity on the interfacial tensions between polystyrene and polybutadiene homopolymer is examined by using a pendant drop apparatus. The data show that the interfacial tension of the monodisperse homopolymer decreases linearly with temperature and increases with molecular weight. The interfacial tension becomes lower as the polydispersity of polystyrenes having the same number-average molecular weight increases. It is also found that the interfacial tensions of unimodal polystyrene mixtures are quite different from those of bimodal polystyrene mixtures. In the case of bimodal polymer systems, the lower-molecular-weight species is considered to migrate preferentially to the interface in order to reduce the free energy of the interface, which results in lowering the interfacial tension. From the slope of the plot of interfacial tension *versus* temperature, the interfacial entropy increases with the polydispersity, indicating that the higher polydispersity gives rise to more aggregation of the lower-molecular-weight species at the interface.

(Keywords: interfacial tension; molecular weight; polydispersity)

INTRODUCTION

Many polymer materials, such as polymer blends, composites, laminates, coatings and adhesive joints, have multiple-phase structures containing one or more interfaces. The structure and thermodynamic state of polymer interfaces are important features, due to their influences on the morphology and mechanical properties of polymer mixtures[1-8]. However, it is not easy to accurately examine the interface between the two phases since this interface is a very narrow region (usually less than 10 nm). Therefore, many phenomena related to the interface remain left unknown, although the recent remarkable developments of instrumental methods such as forward recoil spectroscopy and neutron reflectivity make it possible to investigate the structure of the interface to a certain extent. The single accessible thermodynamic parameter which characterizes polymer interfaces is interfacial tension, which is directly related to the morphology and interfacial adhesion of the polymer blends.

Recently, the effect of molecular weight and temperature on the interfacial tension has been the subject of a considerable number of investigations[9-15]. It is generally known that the interfacial tension between two immiscible polymers increases with the molecular weight of each of the component polymers, and decreases linearly with increasing temperature. This means that the molecular weight of the polymers and the temperature are important factors with which to control the interfacial tension. In these experiments almost monodispersed polymers were used in order to exclude the polydispersity effect, although such materials are not generally used for any practical purposes. There has not yet been any experimental attempt to examine the effect of the polydispersity on the interfacial tension, despite its practical importance.

It was reported that lower-molecular-weight polystyrene has a much lower interfacial tension than higher-molecular-weight material in polystyrene/poly(hydrogenated butadiene) pairs[13]. Thus, it can be expected that the lower-molecular-weight species are located preferentially at the interface, in order to lower the interfacial energy between polystyrene and polybutadiene, when polydisperse polystyrenes are used. In a recent paper[15], it is predicted theoretically that short chains accumulate more easily at the interface, thus lowering the interfacial tension for a polydispersed system.

In this present study, the effect of molecular weight and polydispersity of polystyrene on the interfacial tension between polystyrene and polybutadiene will be investigated systematically by directly measuring the interfacial tension with a pendant drop interfacial tension apparatus.

EXPERIMENTAL

Materials

The poly(1,2-butadiene)($\bar{M}_n \approx 4100\,\mathrm{g\,mol^{-1}}$) was anionically synthesized in benzene at room temperature

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Table 1 Polymer characteristics[a]

Polymer	Abbreviation	M_n	M_w/M_n
Polystyrene	PS1800	1810	1.04
	PS3600	3574	1.07
	PS5500	5500	1.10
	PS9300	9331	1.08
Polybutadiene	PBD	4100	1.40

[a] Molecular weights determined by gel permeation chromatography

Table 2 Polydispersity data for the polymer mixtures

Mixing ratio PS1800/PS5500/PS9300	Abbreviation	M_n[a]	M_w/M_n[a]
0/1/0	PSM010	5500	1.10
1/2/1	PSM121	5535	1.23
2/1/2	PSM212	5566	1.37
1/0/1	PSM101	5571	1.47

[a] Calculated on the basis of mixing ratios

by using n-butyllithium (n-BuLi) as an initiator. Three different molecular weight polystyrenes ($\bar{M}_n \approx 1800$, 5500, and 9300 g mol^{-1}) were also anionically synthesized in benzene by using sec-BuLi as an initiator, and all of the polymers produced are almost completely monodispersed. The above molecular weights of polystyrene are selected because the interfacial tension changes significantly with the molecular weight over the range from 0 to 10 000 g mol^{-1}. The characteristics of these polymers are listed in *Table 1*. Polystyrenes having the same average molecular weight ($\bar{M}_n \approx 5500$), but different polydispersities, were prepared by mixing three polystyrenes with different molecular weights, with each being nearly monodisperse. The polydispersities of the polystyrene mixtures are calculated from the mixing ratios. *Table 2* lists the polydispersity values and the abbreviations used for these polystyrene mixtures.

Measurements

Interfacial tensions were measured by using a pendant drop apparatus constructed in our laboratory. The apparatus consists of a heated sample holder in which a pendant drop is formed, an optical system to capture the image of the drop, and a data acquisition system with a Macintosh computer. The optical system consists of the light source (halogen lamp and optical fibre) and a charge-coupled device (CCD) video camera. A zooming lens is coupled to the CCD camera. The sample holder for the pendant drop consists of an electrically heated cylindrical block with a chamber in which the quartz cell can be placed. The syringe is inserted into a fluid matrix of the polybutadiene (PBD) which is contained in a quartz microcuvette. A fluid drop of the more dense constituent, i.e. the polystyrene (PS), is formed at the tip of a glass capillary tube of a syringe made of Pyrex. Argon gas is purged into the chamber containing the quartz microcuvette to avoid oxidation and degradation of the polybutadiene. The temperature of the chamber is controlled to ± 1°C. An image of the drop is obtained and digitized by a frame grabber in the Macintosh computer. The interfacial tension is calculated by using the equation developed by Andreas *et al.*[16]. This equation requires the densities of polystyrene and polybutadiene, which are taken from the data of Fox and Flory[17], and of Anastasiadis *et al.*[18], respectively. The interfacial tension was determined when the shape did not change with time. All the data are reported by averaging the results of three separate tests. The average standard deviation is 5% (within 0.07 dyn cm^{-1}), whereas the maximum standard deviation is 13%.

RESULTS AND DISCUSSION

The interfacial tension data obtained for the four PS/PBD pairs are plotted as a function of temperature in *Figure 1*. The interfacial tension decreases almost linearly with temperature, as observed in the cases of other immiscible blend systems[10,13]. Applying a least-square regression on the experimental data, the interfacial tension at 0°C and the temperature coefficients of the equation for interfacial tension between PS and PBD are obtained from the intercepts and slopes of *Figure 1*, respectively. The values found are of the same magnitude as those previously reported for other polymer pairs[13]. It is observed that the temperature coefficient of the relatively-lower-molecular-weight PS is larger than that of the higher-molecular-weight PS. This phenomenon has also been observed by Anastasiadis *et al.*[13]. The temperature coefficient of the interfacial tension corresponds to the entropy change of interface formation per unit area at constant volume, as represented by the following equation:

$$\Delta S^{\sigma} = -\frac{d\gamma}{dT} \quad (1)$$

where γ is the interface tension and ΔS^{σ} is the entropy change of interface formation per unit area. Since the coefficient $b(= -d\gamma/dT)$, is the interfacial entropy, the smaller b obtained for the polymer pair having the higher-molecular-weight polymer is attributed to the conformational restrictions of long chain molecules[19]. The plot of interfacial entropy *versus* the molecular weight of PS is shown in *Figure 2*. It is clear that the interfacial entropy increases with decreasing the molecular weight of PS, thus resulting in a lower interfacial tension.

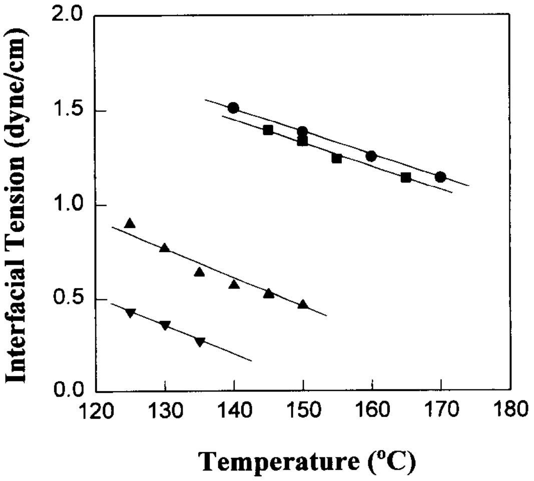

Figure 1 Temperature dependence of the interfacial tension for the various PS/PBD pairs: (●) PS9300/PBD; (■) PS5500/PBD; (▲) PS3600/PBD; (▼) PS1800/PBD

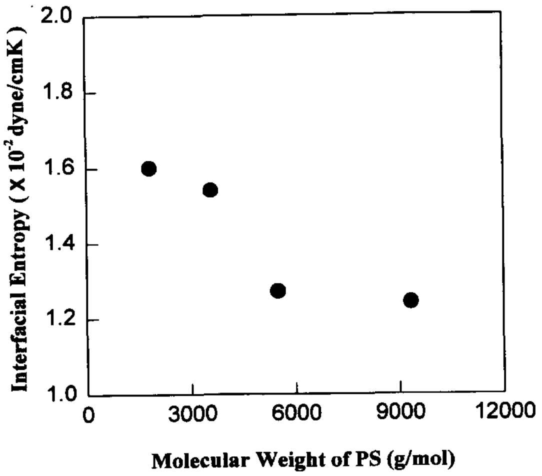

Figure 2 Relationship between the interfacial entropy and the molecular weight of PS for the various PS/PBD pairs

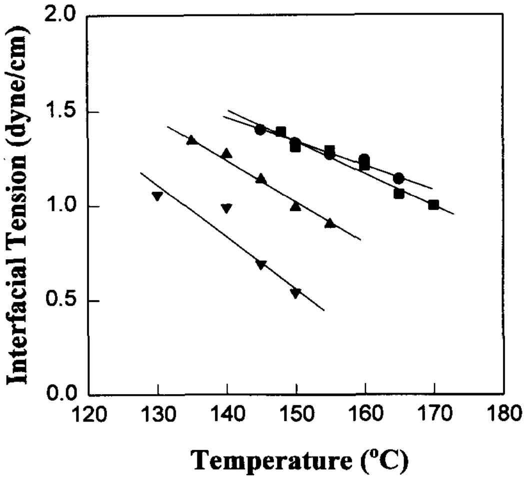

Figure 4 Temperature dependence of the interfacial tension of PS/PBD pairs having different polydispersity indices: (●) PSM010; (■) PSM121; (▲) PSM212; (▼) PSM101

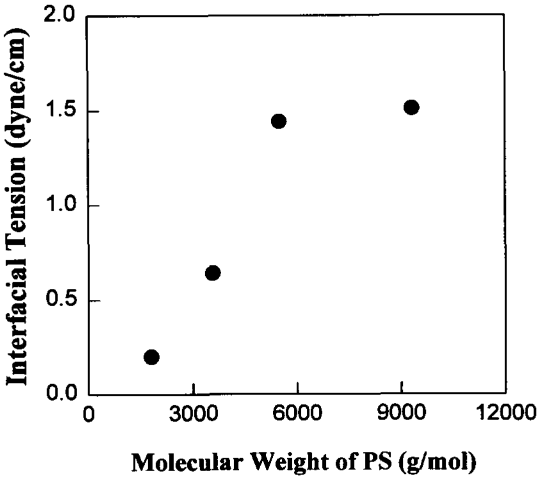

Figure 3 The dependence of the interfacial tension between PS and PBD at 140°C on the molecular weight of PS; the data points are obtained from extrapolation of the lines shown in *Figure 1*

The molecular weight dependence of the interfacial tension is shown in *Figure 3*. It is seen that the interfacial tension first increases with the molecular weight and then levels off. Gains and coworkers[9,12] suggested that the molecular weight dependence of the interfacial tension can be represented by the following equation[20]:

$$\gamma = \gamma_\infty - k_{\gamma A}(\bar{M}_n)_A^{-x} - k_{\gamma B}(\bar{M}_n)_B^{-x} \qquad (2)$$

where γ_∞, $(\bar{M}_n)_i$, x and $k_{\gamma i}$ are the interfacial tension at infinite molecular weight, the number-average molecular weight, the scaling exponent and the proportionality constant, respectively. Equation (2) predicts that the interfacial tension decreases with increasing the number-average molecular weight of the polymers.

Broseta and coworkers[15] developed analytically the equation describing the relationship between the interfacial tension and the immiscibility degree ($\omega_A = \chi_{AB}N_A$, and $\omega_B = \chi_{AB}N_B$) by following a mean-field procedure, as follows:

$$\gamma = \gamma_\infty\left[1 - \frac{\pi^2}{12\chi_{AB}}\left(\frac{1}{N_A} + \frac{1}{N_B}\right) + \cdots\cdots\right] \qquad (3)$$

where N_A, N_B and χ_{AB} are the degree of polymerization of components A and B, and the Flory interaction parameter, respectively. Equation (3) predicts that the interfacial tension increases with the molecular weight and then levels off (compare with equation (2) when $x = 1$). In degree of incompatibility, N is related to the entropic part of the free energy, whereas χ is the enthalpic term. Equation (3) is reduced to equation (2) when $x = 1$. The molecular weight dependence of the interfacial tension shown in *Figure 3* can be well represented by the expression ($C_1 + C_2\bar{M}_n^{-z}$, where C_1 and C_2 are constants). Considering the results of *Figures 2* and *3*, it is concluded that lower-molecular-weight PS gives a lower interfacial free energy between PS and PBD than the higher-molecular-weight material, as a result of its entropic nature.

Figure 4 shows the temperature dependence of the interfacial tension of polymer mixtures having different polydispersities. It should be noted that the polydispersities are different from each other while the average molecular weights of all of the polystyrene mixtures are the same ($\bar{M}_n \approx 5500$) (see *Table 2*). The interfacial tensions of monodisperse PS (PSM010, i.e. PS5500 homopolymer) and unimodal PS (PSM121) show no significant difference in the temperature range from 145 to 155°C. In the higher-temperature range, however, PSM121 has slightly lower interfacial tensions than PSM010. On the other hand, the interfacial tensions of bimodal PS (PSM101) and almost bimodal PS (PSM212) are much lower than those of the unimodal systems over the entire temperature range. *Figure 5* shows the variation of the interfacial tension with the polydispersity at a given temperature. The interfacial tension decreases with increasing polydispersity at the same temperature.

It is also observed in *Figure 4* that the slope of the plot, which corresponds to the interfacial entropy, increases with the polydispersity index. This increase in the interfacial entropy may arise from the less conformational restrictions of the short-chain molecules when compared with the case of the long-chain molecules. The interfacial tensions of unimodal PS are quite different from those of bimodal PS. In other words, the interfacial tension of bimodal molecular weight samples (PSM101 and PSM212) are much lower than those of other PS

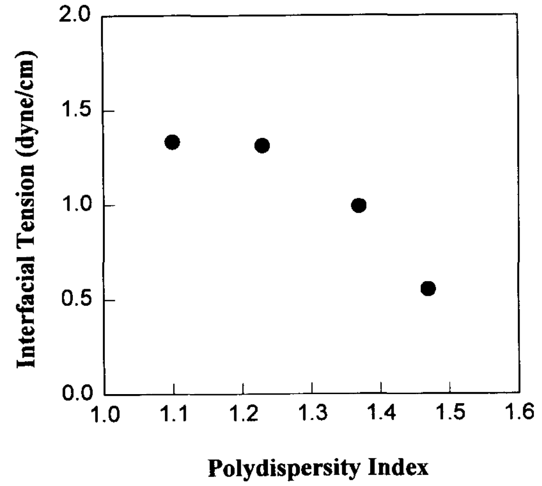

Figure 5 Interfacial tension as a function of polydispersity at 150°C

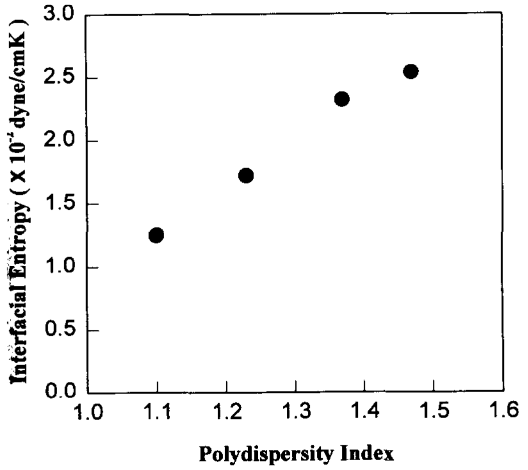

Figure 6 Relationship between the interfacial entropy and the polydispersity of PS for various PS/PBD pairs; the number-average molecular weights of the PS samples are all approximately the same ($M_n \approx 5500$)

mixtures at the same temperature, although the average molecular weight is the same. The difference in interfacial tension between PSM101 and PSM010 becomes larger as the temperature increases. Another point that should be noted is that a relatively small amount of the lower-molecular-weight species does not lead to a significant interfacial tension reduction as in the case of PSM121. However, in those cases where the mixtures have higher contents of lower-molecular-weight species (e.g. PSM101), the latter is considered to preferentially migrate to the interface, thus lowering the interfacial tension. Moreover, the interfacial tension reduction increases with the amount of lower-molecular-weight species, particularly at higher temperatures. On the other hand, the polydispersity of PBD is slightly larger than PSM121. Considering, however, that the polydispersities of PSM121, PSM212 and PSM101 are calculated from the assumption that each homopolymer is monodispersed, the real polydispersities are thought to be much larger than the calculated ones. Moreover, the molecular-weight distribution of PBD is unimodal. Considering the results obtained for PSM121/PBD, the effect of the polydispersity of PBD is not significant enough to change the results.

The effect of the polydispersity of polystyrene on the interfacial entropy ($\Delta S^{\sigma} = b$) is shown in *Figure 6*. The interfacial entropy increases monotonously with increasing polydispersity. This indicates that the higher polydispersity results in more aggregation of the lower-molecular-weight species at the interface. It is thus clearly recognized from the results of *Figures 5* and *6* that interfacial tension reduction can be achieved by a higher interfacial entropy. Broseta *et al.*[15] developed the thermodynamic theory of the polymer interface for the case of a polydisperse system. They concluded that the origin of the effects of molecular weight and polydispersity on the properties of polymer–polymer interfaces is purely entropic. The interface becomes broader for short chains because the interfacial entropy of short chains is higher than that of long chains, and for a polydisperse system it is entropically more advantageous to expel long chains from the interface. Therefore, a higher interfacial entropy leads to the preferential location of the lower-molecular-weight polymer chains at the interface, thus making the interface broader.

It is concluded from the above results and discussion that the interfacial tension between polymer pairs comprising polydispersed species is lower than that of systems comprising monodispersed species. Thus, it is expected that the domain size of the minor phase of a polydisperse system becomes smaller when compared with a monodisperse system. However, the interfacial adhesion of a polydispersed system may become poor because the preferential migration of the small chains at the interface prevents the large chains from forming entanglements between the two phases.

CONCLUSIONS

The interfacial tension between PS and PBD decreases linearly as a function of increasing temperature, but increases with the molecular weight of the PS. Thus, the lower-molecular-weight PS has a lower interfacial energy between PS and PBD than the higher-molecular-weight polymer. It is found that the interfacial tension of a unimodal polystyrene mixture (PSM121) is slightly lower than that of monodisperse polystyrene (PSM010). However, the interfacial tensions of bimodal polystyrene mixtures are considerably lower than that of monodisperse polystyrene. In the case of bimodal polystyrene mixtures (PSM101 and PSM212), the lower-molecular-weight species is considered to preferentially migrate to the interface in order to reduce the free energy of the interface, which results in lowering the interfacial tension. The reduction in interfacial tension for polydispersed systems may mainly result from the higher entropy of the short chain components.

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