Effect of Dicarboxy Terminated Polystyrene on Strengthening Immiscible Polystyrene/ Poly(methyl methacrylate) Interface

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SUMMARY: The fracture toughness between polystyrene (PS)/ poly(methyl methacrylate) (PMMA) reinforced with reactive polymers, poly(glycidyl methacrylate) (PGMA) and *dicarboxy or monocarboxy* terminated PS (dcPS and mcPS), was measured by the asymmetric fracture test. Molecular weight effect of mcPS, although the molecular weight distribution is rather polydisperse, on the maximum achievable fracture toughness, G_{max} qualitatively agreed with the results of the monodisperse case[4,5]. In the case of dcPS with $M_w \cong 142$ K, G_{max} reached ca. 170 J/m^2 which is nearly 8 times higher than that of mcPS of molecular weight of about 150K. From the mechanical point of view, dcPS with a degree of polymerization (N) greater than the ratio of chain breaking force to monomeric friction force (f_b/f_{mono}) is more effective in enhancing the interfacial adhesion than mcPS since it provides two *stitches* to the interface. It was also shown by Monte Carlo simulation on reactive polymer system that the di-endfunctional polymers are more effective than mono-endfunctional polymers in reinforcing the week interface between immiscible polymers.

Introduction

One of major goals of using compatibilizers in polymer blends or alloys is to enhance the otherwise weak interfacial adhesion between immiscible polymers. Block copolymers, random copolymers and reactive polymers have been reported as strong candidates to achieve this goal since they provide stress transferring *bridges* or *stitches* to the weak interface by being preferentially located at the interface[1-5].

Recently Kramer and coworkers[4,5] demonstrated that in the study of the fracture behavior of polystyrene (PS)/epoxy interface reinforced with carboxy terminated deuterated PS (d-

PSCOOH) having narrow molecular weight distribution which was used as a model reactive polymer there exists an optimum molecular weight of d-PSCOOH in enhancing the interfacial adhesion which is balanced by the two competing effects: the molecular weight dependency of the nature of craze against the molecular weight effect of the saturation chain areal density (Σ_{sat}) of d-PSCOOH. The fracture toughness showed the maximum value at a molecular weight about N ~ f_b/f_{mono} which corresponds to N ~ 1000 in the case of d-PSCOOH, where f_b is the force to break a chain and f_{mono} is the monomeric friction force. However, the maximum achievable areal density (Σ_{max}) decreased almost linearly with respect to molecular weight (~ 1/N) in the experiment, which is in contrast to $1/N^{0.5}$ in the case of a Gaussian graft chain. To explain this linear decrease they took into account the entropic barrier that resists the addition of new monocarboxy terminated chains to the end grafted chains already formed by the reaction at interface as well as the decrease of Σ_{sat} with increasing the molecular weight of d-PSCOOH[5].

In this study, based on the fracture map mentioned above, we focus on the effect of *dicarboxy* terminated PS (dcPS) containing two carboxyl groups at both ends of a PS chain on the fracture behavior of immiscible polymer interface in comparison with the case with monocarboxy terminated PS (mcPS). PS / poly(methyl methacrylate) (PMMA) were chosen as an immiscible weak polymer interface. poly(glycidyl methacrylate) (PGMA), which is compatible with PMMA, was employed as a reactive polymer. PGMA has inherently epoxy functional groups reacting readily with carboxyl group of carboxy terminated PS (cPS) which was employed as the counterpart reactive polymer. We also performed the Monte Carlo simulations on the mono- and di-endfunctional polymer reaction system and qualitatively compared with the experimental results obtained from the fracture test.

Experimental Part

Materials and measurement methods

Commercial grade PS (from Miwon Petrochemical Co.) and PMMA (from LG Chemical) were dried in a vacuum oven and used to prepare bulk homopolymer sheets by compression molding. PGMA and cPS were synthesized using free radical polymerization. To place a

carboxyl group at the end of a PS chain a small amount of mercapto acetic acid was added as a chain transfer agent[6]. dcPS used in this study was purchased from Aldrich. Details of the reactive polymers used in present study are summarized in Table 1.

Table 1. Reactive polymers used in this study.

Code	M_n	M_w	Source
mcPS29	12 K	29 K	Synthesized
mcPS45	15 K	45 K	Synthesized
mcPS60	34 K	60 K	Synthesized
mcPS150	46 K	147 K	Synthesized
mcPS170	50 K	165 K	Synthesized
mcPS235	120 K	235 K	Aldrich
dcPS142	93 K	142 K	Aldrich
PGMA	230 K	500 K	Synthesized

To prepare specimens for the interfacial adhesion test, PGMA dissolved in methylethylketone (MEK) was spun onto the PMMA plate. The film thickness of PGMA was fixed at 1,500 nm for present study. The counterpart reactive polymer, cPS, was dissolved in toluene. The cPS films with thicknesses ranging from 15 nm to 1500 nm was first spun on glass slides, floated on distilled deionized water and then transferred to PS homopolymer sheet. The PS and PMMA sheets containing reactive polymers on each sheet were then joined together at 190 °C for 1 hour in a hot press. The fracture toughness of interface was measured by the asymmetric fracture test[7].

Results and discussion

The results of the fracture toughness between PS and PMMA measured as a function of cPS thickness are given in Fig. 1. The fracture toughness of PS/PMMA initially increases with increasing cPS thickness and then levels off at a constant value. This implies that the amount of copolymer formed *in-situ* at the PS/PMMA interface increases up to a plateau value and further increase in the amount of copolymer at the interface is not possible even though cPS thickness is increased up to 1,500 nm. The effect of the initial amount of the reactive cPS polymers on the interfacial adhesion can be explained by the result of the competition between the reaction at interface and the dilution of cPS concentration at the interface due to
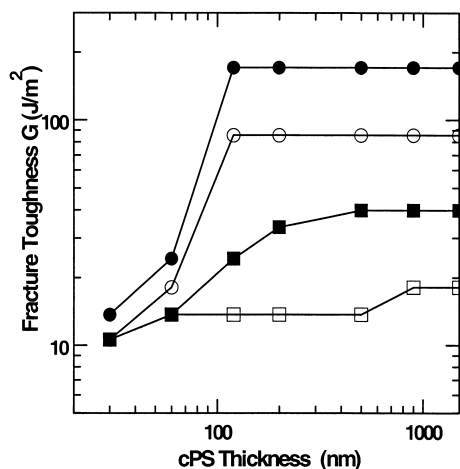
Fig. 1: Fracture toughness between PS/ PMMA plotted against initial thickness cPS: (●) dcPS142, (○) mcPS60, (■) mcps45, (□) mcps235.
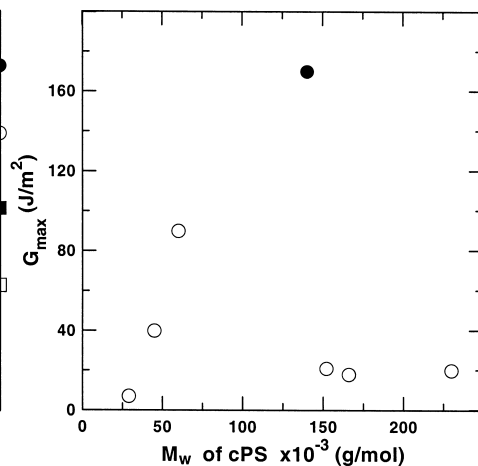
Fig. 2: The maximum achievable fracture toughness as a function of M_w of cPS: (○) mcPS, (●) dcPS.

the diffusive mixing of the reactive polymers with bulk homopolymer. Detailed results of the effect of cPS thickness on the fracture toughness of PS/PMMA will be given elsewhere[8]. In this paper, our main focus is placed on the maximum achievable fracture toughness value for a given molecular weight of cPS.

As shown in Fig. 2, the maximum fracture toughnesses was plotted against the weight average molecular weight (M_w) of cPS. Since cPS used in this study is polydisperse in molecular weight distribution, the number average molecular weight (M_n) instead of M_w may be an alternative to plot the fracture data. But in comparison of the data for mcPS29 with those for mcPS45 the difference in M_w (16 K) describes the difference in fracture toughness better than that in M_n (3 K) and thus M_w is chosen in this study as a molecular weight variable. In case of mcPS, if the polydispersity of cPS is taken into account, the fracture behavior in Fig. 2 qualitatively agrees with the previous results with monodisperse mcPS[4,5]. It is quite interesting to note the different fracture toughness result with dcPS. The fracture toughness of dcPS142 yields the highest value among all cPS's used in this study as shown in Fig. 2. The

fracture toughness reaches ca. 170 J/m^2 which is about 8 times higher than that for mcPS150.

To better understand the fracture behavior, we indirectly estimated the maximum areal densities at the interface (Σ_{max}) by using the measured maximum fracture toughness values and eq 1 given below:

$$G = 2\pi\left(1-\tfrac{1}{\lambda}\right)\sigma_c D\left[-\alpha\ln\left(1-\left[\sigma_c/f_b \Sigma_{eff}\right]^2\right)\right]^{-1} \qquad (1)$$

$$\Sigma_{eff} = q\Sigma\left(1-\left(M_e/qM_n\right)\right)$$

Eq. 1, which was successfully developed by others[9,10], relates the macroscopic fracture toughness, G, to the microscopic chain areal density, Σ. The material properties of PS related to the microstructures of crazes formed at the crack tip are found as follows[10,11]: α (parameter related to the angle between main fibril and cross tie fibril) = 0.055, λ (craze fibril extension ratio) = 4, σ_c (craze stress) = 3.5 x 10^7 N/m^2, f_b (force to break a chain) = 2 x 10^{-9} N, D (craze fibril diameter) = 8.65 nm, q (probability that a chain is in the craze after crazing) = 0.6, and M_e (entanglement molecular weight) = 18,000 g/mol. The estimated maximum areal densities (Σ_{max}) are given in Fig. 3. Fig. 3 also shows, for comparison, the reported best fit of the Kramer group's data[4]. While the estimated Σ_{max} of mcPS in this study is almost the same as that of d-PSCOOH for the PS/epoxy interface, Σ_{max} for dcPS is about twice the Σ_{max} for the same molecular weight of mcPS. Considering the possible structure of the resulting copolymer formed, mcPS similar to block copolymer provides only one stress transferring *stitch or bridge* to the weak interface while dcPS provides two *stitches* to the interface. In the region where cPS molecular weight is greater than 100 K (N ~ f_b/f_{mono}), one reason that causes the decrease in the fracture toughness is the decrease in the saturation areal density with increasing the cPS molecular weight which in turn results in the decrease of the number of stitches per interfacial area. This effect is dominant over the strong craze formed in this molecular weight region[5]. Consequently, the increase in the number of stitches per chain such as the case for dcPS has a significant effect on the increase of interfacial adhesion from the mechanical point of view.
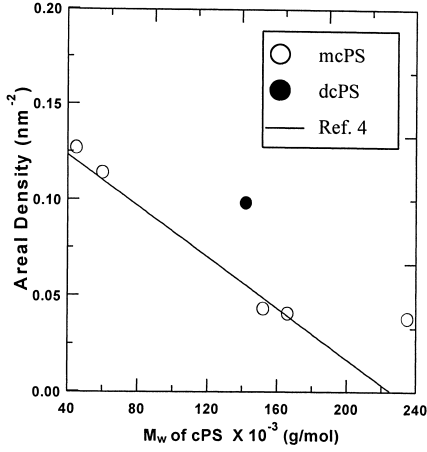
Fig. 3: The estimated Σ_{max} as a function of M_w of cPS: (○) mcPS, (●) dcPS. The line is the reported best fit of Kramer group's data[4].
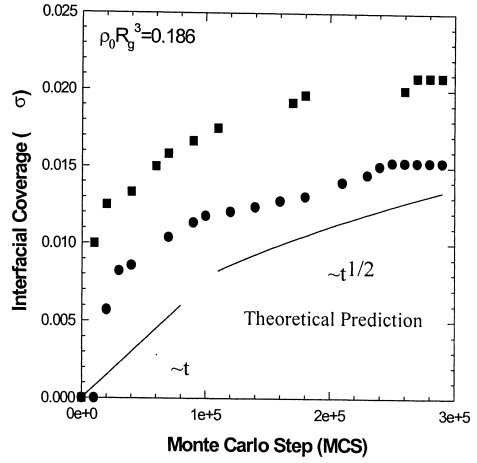
Fig. 4: Time dependence of copolymers formed at the interface due to reaction for $\rho_0 R_g^3 = 0.186$: (●) mono- and (■) di-endfunctional polymer reaction system, respectively.

In order to investigate the effectiveness of multiple reaction sites in detail, the reactions at immiscible polymer interface are examined by using the Monte Carlo (MC) simulation technique[12-14]. MC simulation results provide the information on time-dependence of the copolymer formation at the interface. Fig. 4 shows one example of the MC simlations with $\rho_0 R_g^3 = 0.186$, where ρ_0 is the number density of reactive polymers and R_g is the radius of gyration.

In Fig. 4 the early reaction rate and the plateau value of the interfacial copolymer coverage for di-endfunctional polymer reaction system are much larger than those for mono-endfunctional polymer reaction system. In the case of di-endfunctional polymer reaction system, there are two possibilities for the conformation of the copolymer formed due to reaction at the interface: loops and tails. For the case of the di-endfunctional reactive polymers, we investigated the distribution of loop and tail conformation as shown in Table 2. Loop conformations are dominant over the tail conformation. This implies that various

polymer conformations, such as loops and tails, obtained with the di-endfunctional reactive polymers support the effectiveness of multiple reaction sites in enhancing interfacial properties like interfacial width and fracture toughness as mentioned above.

Table 2. Distribution of loop and tail conformation of copolymers formed at interfaces for di-endfunctional polymer reaction system with $\rho_0 R_g^3 = 0.557$.

Di-endfunctional Polymer Conformation	Loop	Tail
%	89.4	6.7

Conclusion

There exists a molecular weight range of cPS ($N > f_b/f_{mono}$) where dcPS is more efficient than mcPS in increasing the interfacial strength of immiscible polymers since it has potential to provide more than one *stitch* per molecule from a mechanical point of view and the formation of loop structure for dcPS which is necessary to provide two stitches per chain to the interface is possible from a thermodynamic point of view.

Monte Carlo simulation results also demonstrated that the di-endfunctional reactive polymer has advantage over the mono-endfunctional polymer in terms of the increase in the initial reaction rate and the amount of copolymers necessary to reinforce the weak interface.

Acknowledgment

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