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Mechanical effects according to the type of poly(styrene-*co*-methyl methacrylate) copolymers at polystyrene/poly(methyl methacrylate) interfaces

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The effects of incorporating a thin layer of various types of polystyrene–poly(methyl methacrylate) copolymers, i.e. block, random, and graft copolymer on the interfacial adhesion between PS and PMMA have been investigated. The fracture toughness of the interface was measured using an asymmetric double cantilever beam fracture test and the enhanced toughness effect of copolymers was compared. The fracture toughness of the interface increased with increasing layer thickness of the copolymer and each copolymer had the layer thickness of saturated fracture toughness. The fracture toughness increased in the order of block > graft > random copolymer. Copyright © 1996 Elsevier Science Ltd.

(Keywords: adhesion; polystyrene–PMMA copolymer; interface)

Introduction

Polymer–polymer interfaces play a dominant role in various mechanical features such as coextrusion, adhesive properties, and toughness of polymer blends. However, the mechanical strength of the interfaces between immiscible homopolymers is very weak because there is little chain entanglement between homopolymers due to little mixing entropy available.

There are many studies on the use of diblock copolymers as compatibilizers to improve the interfacial properties of immiscible polymers[1–5]. The diblock copolymers, a block of copolymer miscible with one homopolymer joined covalently to a block of copolymer miscible with the other homopolymer, reduce the interfacial tension and improve adhesion between the homopolymers. Both the reduced interfacial tension, which tends to reduce phase size, and the improved interfacial adhesion may be expected to improve the mechanical properties of the blend.

Recently, Kramer and co-workers have reported an elegant set of experiments on the reinforcement of polymer interfaces with random copolymers[6,7]. It was shown that long random copolymers with a symmetric monomer fraction were more effective than those with an asymmetric monomer fraction in strengthening the interfaces between immiscible homopolymers, and also more effective than diblock copolymers. The exceptional effectiveness of the symmetric random copolymer was attributed to the random copolymer crossing the homopolymer interface multiple times, thereby maximizing the number of entanglement with each of the immiscible homopolymers. Also, Brown and coworkers have formerly reported that a long random copolymer was effective in reinforcing polymer interfaces. However, the effectiveness of random copolymer was inferior compared to the results for long diblock copolymer[4,5].

In this paper, we would like to report the effects of the type of copolymers, i.e. block, graft, and random copolymer on the interfacial adhesion between immiscible polymers. The PS–PMMA was selected as an experimental system. The experimental system in this study has some advantages. The adhesion between PS and PMMA is very weak in the absence of copolymer since PS and PMMA are not miscible in a thermodynamic sense. The PS and PMMA have a similar glass transition temperature, which is acceptable for the measurement of adhesion developed by welding and the comparison of other data. Also, the synthesis of PS–PMMA copolymer is easy. We synthesized diblock copolymers anionically, graft copolymers in radical copolymerization with PMMA macromonomer, and random copolymers in radical copolymerization. Then, the effects of incorporating a thin layer of various type of copolymers on PS–PMMA interfacial adhesion have been studied.

Experimental

The PS and PMMA homopolymers used in this study had broad molecular weight distribution. The PS was a commercial moulding grade (Styron 685, Dow Chemical Company, $\overline{M}_w = 355 \times 10^3$). The PMMA was also a commercial grade in the form of fine pellet (Elvacite 2021, DuPont, $\overline{M}_w = 118 \times 10^3$). The PS and PMMA pellets were dried under vacuum at room temperature for 24 h before use.

PS-*b*-PMMA symmetric diblock copolymers were synthesized by a sequential anionic polymerization.

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Table 1 Characteristics of the copolymers

Copolymer	$10^{-3}\overline{M}_w$[a]	Mol% styrene[b]	$\overline{M}_w/\overline{M}_n$[a]
PS-*b*-PMMA	82	50	1.1
	347	44	1.1
PS-*g*-PMMA	87	49	1.7
	116	50	1.6
PS-*r*-PMMA	137	51	2.7
	195	50	1.7
	477	52	2.5

[a] Determined from g.p.c. by the use of polystyrene calibration
[b] Determined from *FT*-n.m.r.

Molecular weights of diblock copolymers are 82×10^3 and $347 \times 10^3\,\mathrm{g\,mol^{-1}}$ with narrow polydispersity, $\overline{M}_w/\overline{M}_n$, of about 1.1. PS-*g*-PMMA graft copolymers were radically copolymerized with PMMA macromonomer whose molecular weight is $6000\,\mathrm{g\,mol^{-1}}$. The monomer feed ratio was adjusted so that the styrene weight fraction of the graft copolymer was about 0.5. Residual PS homopolymer and PMMA macromonomer were removed by successive extraction in cyclohexane and acetonitrile, respectively. The absence of PS homopolymer and PMMA macromonomer in the PS-*g*-PMMA graft copolymers was verified by infrared (i.r.) spectroscopy and proton nuclear magnetic resonance (n.m.r.) spectroscopy. The graft copolymer has the structure of a PMMA grafted PS backbone and molecular weights are 87×10^3 and $116 \times 10^3\,\mathrm{g\,mol^{-1}}$. PS-*r*-PMMA random copolymers with styrene weight fraction of about 0.5 were synthesized using free radical copolymerization. The synthetic reaction was terminated at low conversion (10%) to prevent formation of block by one component. The chemical sequence distribution of the random copolymer was more alternating than random because the monomer reactivity ratios of styrene and methyl methacrylate are small (≤ 0.5)[8]. Molecular weights are 137×10^3, 195×10^3 and $477 \times 10^3\,\mathrm{g\,mol^{-1}}$. The copolymers were characterized using i.r., proton n.m.r. and gel permeation chromatography (g.p.c.). The characteristics of the copolymers used in this study are given in *Table 1*.

PS and PMMA homopolymers were compression moulded into a sheet of 2 mm thickness at 160°C using a hot press. To obtain smooth glossy moulding surface, a polished Ferrotype plate was used as a moulding plate. The moulded sheets were stored in a vacuum oven before use in order to prevent contamination. The copolymers, dissolved in toluene, were initially spin coated onto the glass slide, the sides of the slide were scored with a razor, and then copolymer film was floated off the slide onto deionized water. The copolymer film was then picked up onto a PS sheet, and the specimen was dried for 24 h at room temperature. Before the film was floated off the glass slide the thickness of the copolymer film layer was measured using an α-step measurement (Tencor).

The two homopolymer sheets, one now covered by the thin copolymer film, were joined in a hot press at 150°C for 2 h. Light pressure was exerted on the sheets to promote good contact between the surfaces. The joined samples were then cut into strips of 5 mm width. The adhesive joint specimens were fractured at room temperature using an asymmetric double cantilever beam fracture test which drives the crack along the interface. The PS sheet which has lower crazing stress was adhered to a glass slide, then the crack was propagated by inserting a razor blade into the interface. The crack was allowed to propagate slowly for 24 h before measurement. The crack length was measured using a travelling microscope. Details of the asymmetric double cantilever beam fracture test were described elsewhere[9].

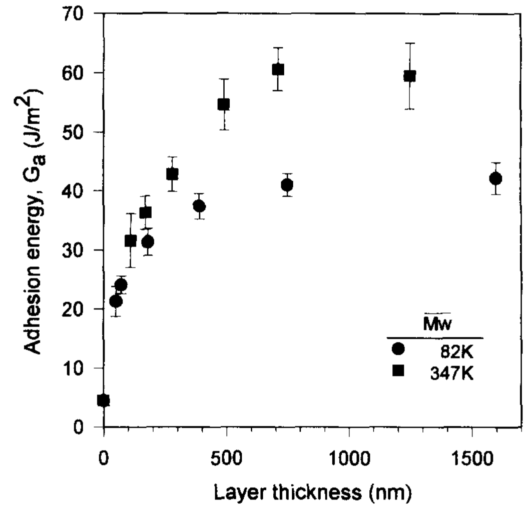

Figure 1 Adhesion energy, G_a, of PS/PS-*b*-PMMA/PMMA adhesive joint as a function of thickness of block copolymer layer

Results and discussion

The adhesion energy, G_a, between PS and PMMA without any copolymer was about $4.5\,\mathrm{J\,m^{-2}}$. It shows that there is little entanglement between PS and PMMA because the system is not miscible. As chain entanglement is a prerequisite for strength in a polymer system, the interface was weak.

Results of the adhesion energy as a function of the original thickness of diblock copolymer layer are presented in *Figure 1*. Two symmetrical diblock copolymers of molecular weights 82×10^3 and 347×10^3 were used. These diblock copolymers had a very large effect on the toughness of the interface between PS and PMMA homopolymers. We expected that the diblock molecules would organize at the interface with the two halves of the block copolymers dissolved in the relevant homopolymers. The adhesion energy was found to increase with the amount of diblock present and then saturate at a certain diblock layer thickness that depends on the molecular weight of the diblock copolymer, which value is much larger than Brown and co-workers' results[4,5]. They have reported that saturation thickness was approximately equal to one-half the long period of the diblock copolymer. These values were lower than 50 nm. As they did not perform the experiments with a thickness of copolymer layer above 100 nm we cannot compare directly our results with theirs. Also, the layer thickness they used might not be real thickness because they made copolymer film on a slide glass or directly on a polymer sheet by spin coating in which they performed under conditions established by spin coating on a silicon wafer. As the surface conditions between the two materials, i.e. polymer and silicon wafer, were very different the layer thickness reported was not the actual value. However, in

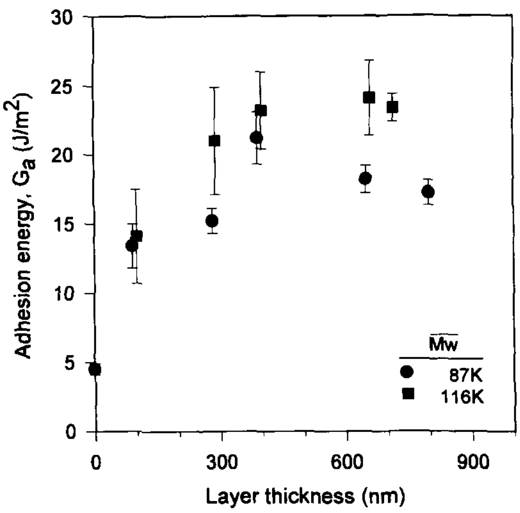

Figure 2 Adhesion energy, G_a, of PS/PS-*g*-PMMA/PMMA adhesive joint as a function of thickness of graft copolymer layer

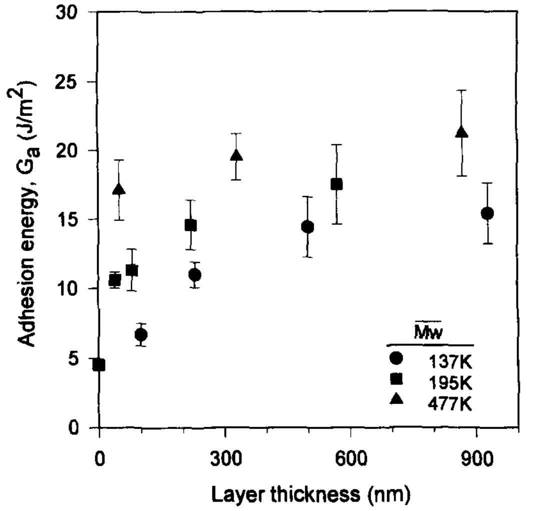

Figure 3 Adhesion energy, G_a, of PS/PS-*r*-PMMA/PMMA adhesive joint as a function of thickness of random copolymer layer

this experiment, we measured the thickness of the copolymer film using an α-step measurement, i.e. mechanical method, before the film was floated off the slide.

The fact that the saturation copolymer layer thickness increased with the increase in copolymer molecular weight is in accordance with other results reported[3–5]. The saturated adhesion energy of 82×10^3 copolymer was found to show a smaller value compared to that of 347×10^3 copolymer as shown in *Figure 1*. This may be due to the fact that the block length of 82×10^3 copolymer is not long enough to make entanglement with homopolymers[3].

The adhesion energy as a function of thickness of graft copolymer layer is shown in *Figure 2*. As in the case of a diblock copolymer the adhesion energies increased with the increase in copolymer layer thickness and levelled off at about 400 nm thickness. However, these adhesion energies with the graft copolymer were much lower than those with the diblock copolymer. It implies that the chains of graft copolymer are not sufficiently diffused to make entanglement with homopolymers due to constraint in the chain conformation and the number of entanglements is relatively low. Therefore, the graft copolymer is not as effective as the diblock copolymer in toughening the interface.

Figure 3 shows the variation of adhesion energies for the adhesive joint with the layer thickness of the random copolymer. As in other types of copolymers the adhesion energies were found to increase with the increase in random copolymer layer thickness and level off. Comparison of the results in *Figure 3* with the adhesion energies obtained with the diblock copolymer (*Figure 1*) shows that the random copolymer is not as effective a coupling agent as the diblock copolymer in this PS/PMMA system. This result coincides with Brown and co-workers' results[4,5]. However, these results are somewhat contradictory to those of Kramer and co-workers[6] in which long random copolymers with a symmetric monomer fraction were a more effective coupling agent than diblock copolymers. They demonstrated that a long random copolymer of polystyrene-*r*-polyvinyl pyridine (PS_f-*r*-PVP_{1-f}), made by free radical copolymerization, reinforced the PS/PVP interface while the maximum fracture toughnesses decreased as the PS fraction (f) is increased from 0.48 to 0.77. They explained that the symmetric random copolymer ($f \cong 0.5$) chain weaves back and forth across the interface multiple times effectively forming entanglement, thereby maximizing the number of entanglements with each of the immiscible homopolymers. The effectiveness decreases markedly as the PS fraction differs significantly from 0.5 because the copolymer becomes less entangled with the homopolymer (corresponding to the minor component in the copolymer) on one side of the interface.

However, from our results this explanation cannot be applied to our system. So we would like to explain our results with another mechanism. The random copolymer diffused a little to the homopolymer phase and formed some very small loops that were pulled out on failure instead of multiple crossings of the random copolymer across the homopolymer interface effectively forming entangled loops in both phases. This discrepancy may be due to the difference in miscibility between homopolymers such as PS vs PMMA and PS vs PVP and different chemical sequence distribution of random copolymers. The Flory interaction parameter χ between PS and PMMA is known to be smaller than the χ between PS and PVP[10,11]. Especially, the conformation of random copolymer chains at interfaces is much affected by the chemical sequence distribution that depends on the reactivity ratio between monomers[12]. The sequence distribution of PS–PMMA random copolymer is more alternating than the PS–PVP random copolymer as a result of the difference in monomer reactivity ratio in radical copolymerization[8]. It means that in contrast to the PS–PVP random copolymer the PS–PMMA random copolymer may form very small size loops which are not long enough to make entanglement with homopolymer chains. The small loops may be pulled out on failure. Thus the toughening of the interface with random copolymer in our system was not as effective as with the diblock copolymer.

Through comparison of our results with Kramer and co-workers' results, we concluded that the toughening of

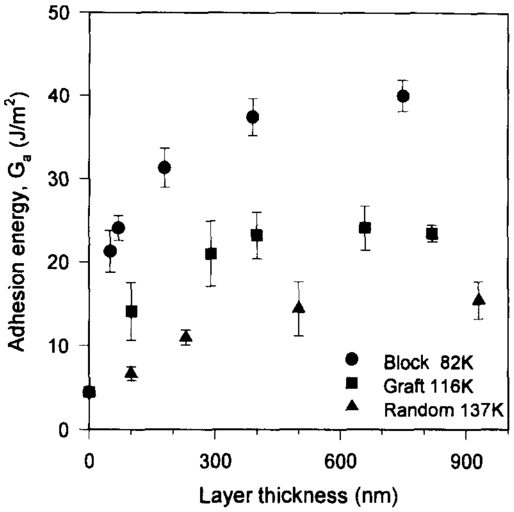

Figure 4 Adhesion energy, G_a, of various types of copolymers with comparable molecular weight as a function of thickness of copolymer layer

interfaces between immiscible polymers by random copolymers is very sensitive to many factors such as miscibility, sequence distribution of the copolymer, and welding temperature. As shown in *Figure 3* the saturation thickness of the random copolymer layer was lower than that of the diblock copolymer. The different regimes of interface toughening between random copolymer and diblock copolymer suggest that the random copolymer was able to mix a little with the homopolymers and so form some loops at very low coverage.

When we consider only the data obtained from the thickness of copolymer layer less than 100 nm the trend is very similar to other data[3–6]. That is to say, the random copolymer showed comparable adhesion energies with the diblock copolymer in this thickness region. Also, the random copolymer was more efficient as a coupling agent than the graft copolymer at large molecular weight (477×10^3) although less than the diblock copolymer. However, in the case of high loading of the copolymer at the interface the diblock copolymer was best choice as coupling agent in the PS/PMMA system.

Figure 4 shows the adhesion energy of various types of copolymers with the comparable molecular weight as a function of copolymer layer thickness. The adhesion energy increased in the order of block > graft > random copolymer in this thickness region. In all cases the failure mechanism is crazing followed by craze failure, confirmed by microscopy of the fracture surface. We cannot compare the adhesion energies according to the type of copolymers with high molecular weights because PS-*g*-PMMA graft copolymers could be synthesized due to low reactivity of macromonomer[13]. This result implies that the effectiveness of random copolymer is also much affected by their molecular weight.

Conclusion

Kramer and co-workers have recently reported that the long symmetric random copolymer could be more effective as a coupling agent than the diblock copolymer[6]. However, from our results it cannot be applied universally to various systems. We found that the random copolymer was as effective as the diblock copolymer just at low coverage, but with increasing incorporation layer of the copolymer the diblock copolymer was the most effective coupling agent in PS/PMMA system.

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