Adhesion and welding in the system SAN/PMMA

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Welding experiments using a double cantilever beam test geometry for a miscible poly(styrene-*co*-acrylonitrile)/poly(methyl methacrylate) (SAN/PMMA) system showed the expected linear increase of the fracture toughness, G_a, with the root of annealing time. For immiscible pairs of PMMA and SAN it was found that G_a increases linearly with the equilibrium interfacial thickness or, equivalently, to $\chi^{-1/2}$, χ being the Flory interaction parameter.

(Keywords: poly(methyl methacrylate); poly(styrene-*co*-acrylonitrile); fracture toughness)

Introduction

It is known that the miscibility behaviour of blends of poly(styrene-*co*-acrylonitrile) (SAN) and poly(methyl methacrylate) (PMMA) depends strongly on the copolymer composition[1]. Blends containing SANs with acrylonitrile contents from about 9 to 34 wt% were found to be miscible[2], while blends outside this miscibility window are immiscible. The miscibility in random copolymer blends is caused by unfavourable intramolecular interactions in the random copolymer itself[3] and can be described in terms of a mean-field theory[4]. The difference in the free energy of mixing in SAN/PMMA blends with different copolymer compositions should also influence the adhesion behaviour of immiscible pairs and the welding behaviour of miscible pairs. Thus, it was found in welding experiments that the copolymer composition for miscible SAN/PMMA pairs has a large influence on the adhesion strength and tensile fracture strength of butt joint test specimens[5]. Furthermore, healing experiments showed that the full material resistance was regained in short-time experiments after less than 5 min[6]. The main aim of this study is to correlate such quantities as the equilibrium interfacial thickness and the interaction parameter with the fracture toughness for immiscible SAN/PMMA pairs. Therefore, a number of double cantilever beam test specimens containing different SANs, with compositions located outside the miscibility window, were prepared in order to measure the fracture toughness. For one miscible SAN/PMMA pair the increase of the material strength in welding experiments was measured.

Experimental

All materials used are listed in *Table 1*. The PMMA and polystyrene (PS) are commercial grade and the SANs with different copolymer compositions were prepared by free-radical copolymerization. The PMMA was compression moulded between high-gloss metal plates into sheets of 5 cm × 5 cm × 0.2 cm at 190°C for 10 min. PS and SAN-5.7 were dissolved in toluene and all other SANs were dissolved in cyclohexanone. All solutions were filtered by 0.22 μm Millipore membrane to remove dust particles. The polymer concentration in the solutions was varied in order to give a film about 200 nm thick during spin-casting on a glass plate at 3000 rev min^{-1}. The film thickness was confirmed by ellipsometry. The film was then floated off onto the water surface and picked up with the prepared PMMA plate. The coated PMMA plate was dried at 60°C for 12 h under vacuum. The SAN-coated PMMA plate was placed on top of a moulded PMMA plate and the sandwich specimen (PMMA plate/SAN film/PMMA plate) was annealed for 2 h at 160°C under light pressure using a hot press. To ensure good contact between the two PMMA plates, a thin rubber sheet was placed between the hot press and the sandwich specimen. The sandwich specimen was then cut into thin strips (5 cm × 0.5 cm × 0.2 cm). Sandwich specimens of PMMA and SAN-25.0 without an interlayer were prepared at 130°C for the desired period of time by the same method. Finally, all samples were mounted onto a glass plate, so that only the upper PMMA plate was

Table 1 Molecular weight data and number of segments, N, of all polymers used. The interaction parameter, χ, calculated using equation (3) and the equilibrium interfacial thickness, λ, calculated by equation (5) are listed

Polymer	$M_w \times 10^{-3}$ (g mol^{-1})	M_w/M_n	N	χ	λ (nm)
PS	180	2.0	541	0.0262	4.7
SAN-5.7[a]	259	2.2	815	0.00214	29.4
SAN-25.0	160	2.4	500	−0.01586	∞
SAN-38.2	75	2.3	305	0.00375	21.3
SAN-45.8	72	1.8	312	0.01934	5.6
SAN-55.6	21	1.8	99	0.289	3.7
PMMA	151	2.1	472	–	–

[a] The number represents wt% acrylonitrile in SAN

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bent by insertion of a razor blade. The fracture toughness of the interface, G_a, was measured by the wedge method[7]. A razor blade was inserted at the interface and the length of the crack ahead of the razor blade was measured using a measuring microscope after 24 h of inserting the razor blade. The fracture toughness G_a was then calculated from[8]:

$$G_a = \frac{3Ed^3b^2}{8a^4[1+(0.64d/a)]^4} \qquad (1)$$

where E is Young's modulus, b is the thickness of the razor blade, a is the crack length and d is the thickness of the upper plate. PMMA has a Young's modulus[9] of 2940 MPa. At least six test specimens were used for one experimental point. For each test specimen three values of fracture energy were obtained by repeated insertion of the razor blade. Stable crack growth was observed for each test specimen.

Results and discussion

The criterion for miscibility in blends is given by the free energy of mixing, ΔF^m, which in terms of the Flory–Huggins theory is given for binary polymer blends by[10,11]:

$$\frac{\Delta F^m}{kT} = \frac{\phi_1}{N_1}\ln\phi_1 + \frac{(1-\phi_1)}{N_2}\ln(1-\phi_1) + \phi_1(1-\phi_1)\chi \qquad (2)$$

where k is the Boltzmann constant, T is the temperature, N_i is the number of segments and ϕ_1 is the volume fraction of component 1. The interaction parameter χ takes into account all contributions that are not given by the combinatorial entropy (the first two terms at the right-hand side of equation (2)). In the framework of a mean-field theory the interaction parameter for blends of PMMA and SAN is given by[4]:

$$\chi = \beta\chi_{S/MMA} + (1-\beta)\chi_{AN/MMA} - \beta(1-\beta)\chi_{S/AN} \qquad (3)$$

where β is the mole fraction of styrene in SAN and $\chi_{i/j}$ are the segmental interaction parameters. Furthermore, it is generally accepted that the interfacial thickness, λ, between two immiscible polymers is related to the interaction parameter by $\lambda \propto c\chi^{-1/2}$, where c is the segment length[12]. For infinite molecular weight the interfacial thickness can be derived by applying a simple lattice model and is given by[13]:

$$\lambda = \frac{2c}{(6\chi)^{1/2}} \qquad (4)$$

Figure 1 shows the calculated values of the χ parameter and the interfacial thickness using equations (3) and (4), respectively, as a function of copolymer composition, assuming an infinite molecular weight. The segmental χ parameters[14] at 160°C are: $\chi_{S/MMA} = 0.0262$, $\chi_{AN/MMA} = 0.172$ and $\chi_{S/AN} = 0.417$. The miscibility window for infinite molecular weight occurs in the range where the χ parameter is negative. In this area the equilibrium interfacial thickness would be infinite. The interfacial thickness decreases for immiscible blends with the distance of the copolymer composition from the miscibility window.

A welding experiment for a miscible SAN/PMMA pair was carried out in order to check the suitability of the double cantilever beam geometry. This geometry was used to study the effect of block copolymers in the interface[7] but only up to fracture toughness values of about 100 J m^{-2}. For welding experiments it is generally expected that the fracture toughness, G_a, increases linearly with the root of the annealing time, $t^{1/2}$. This is equivalent to the common $t^{1/4}$ dependence of the fracture stress, σ, or the stress intensity factor, K_{IC}. This prediction is derived by four models, which differ only in the molecular weight dependence of their fracture toughness after healing experiments[15–18]. The dependence arises from simple diffusion kinetics and assumes that the fracture toughness is proportional to the number of bonds crossing the interface. This number of bonds is again proportional to the interfacial thickness. The inset in *Figure 2* shows the expected result. The fracture toughness, G_a, increases linearly with $t^{1/2}$ for a specimen of PMMA and a SAN containing 25 wt% acrylonitrile at a welding temperature of 130°C. For a small fracture toughness the error of the method is very small and in the range of the marker. At a higher fracture toughness the error becomes larger because the crack length, a, becomes very small (a few millimetres) and enters into equation (1) with the power of 4. Thus it seems that this test geometry performs best for fracture toughnesses smaller than 100 J m^{-2}. It should also be mentioned that there is a small induction period, i.e. no significant fracture toughness can be observed for the initial welding time. This may be caused by contact problems, which might vanish if a slightly higher pressure is applied during sample preparation. Also the heat transfer from the hot press to the sample should not be neglected. Thus without any induction period, the full line of the inset in *Figure 2* should start at the origin.

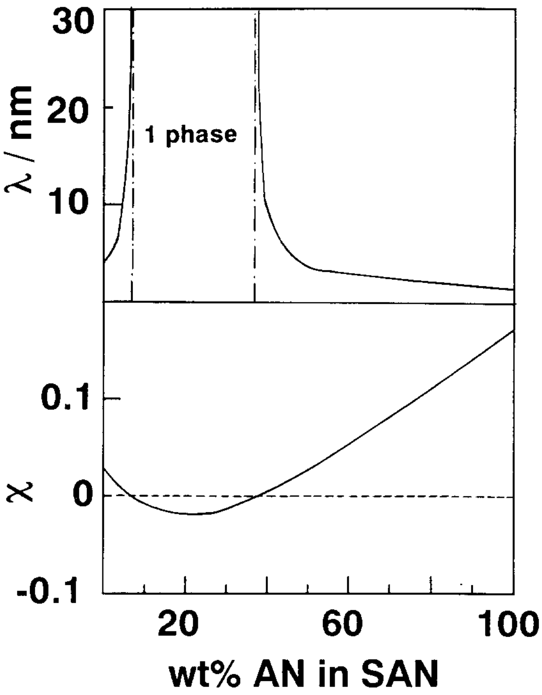

Figure 1 Interaction parameter, χ, and the equilibrium interfacial thickness, λ, for infinite molecular weight in the system SAN/PMMA as a function of copolymer composition at 160°C

It is most interesting to study the fracture toughness of immiscible systems containing different copolymers outside the miscibility window. Thus it is possible to vary the magnitude of the interaction parameter χ and the interfacial thickness λ (see *Table 1*). The interfacial

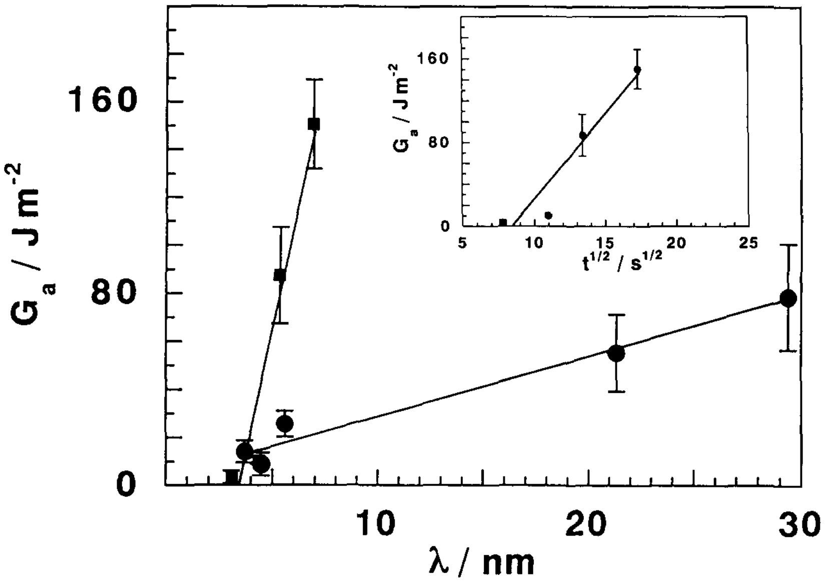

Figure 2 Fracture toughness, G_a, as a function of the interfacial thickness for immiscible SAN(PS)/PMMA samples (●) and for the system SAN-25.0/PMMA (■). The inset shows the fracture toughness, G_a, as a function of the annealing time for a bilayer specimen of SAN-25 and PMMA at 130°C. The full lines represent the linear best fit

thickness can be calculated from χ for finite molecular weights by[19]:

$$\lambda = \frac{2c}{6\chi^{1/2}}\left[1 + \frac{\ln 2}{\chi}\left(\frac{1}{N_1} + \frac{1}{N_2}\right)\right] \qquad (5)$$

where the segment length c was assumed to be 0.8 nm. The calculated interfacial thickness data were confirmed independently by ellipsometry and transmission electron microscopy for selected samples[20]. *Figure 2* shows that a linear relationship between G_a and λ seems to be reasonable for immiscible systems as well. It should also be mentioned that all systems belong to the strong segregation limit, i.e. even when the interface reaches nearly 30 nm, the value of $N\chi$ is much larger than 2, which is considered to be the borderline to the weak segregation limit[21]. It is surprising that the fracture toughness increases linearly up to a value of about 30 nm, which is much more than the radius of gyration, $R_0 = N^{1/2}c$. The linear relationship should fail owing to the fact that a further increase of the interfacial thickness does not lead to an increase in the number of bonds crossing the interface. In that region the fracture toughness should reach a constant value reflecting G_a of the mixed bulk phase.

Figure 2 also shows G_a as a function of the interfacial thickness for the data obtained in the welding experiment. From the welding time the interfacial thickness can be estimated by [22]:

$$\lambda = 2(Dt)^{1/2} \qquad (6)$$

where D is the mutual diffusion coefficient. The mutual diffusion coefficient[23] for these polymers at 130°C is $3.98 \times 10^{-16}\,\mathrm{cm^2\,s^{-1}}$. A comparison between the fracture toughness of miscible and immiscible blends having the same interfacial thickness leads to the result that the G_a value for the miscible system is higher. This means that miscible systems have a higher fracture toughness than immiscible systems when referred to equal interfacial thickness. This result is not yet fully understood. A possible explanation would be a different chain conformation for miscible and immiscible polymers at the interface. This could result in different concentration profiles leading to a different number of bonds crossing the interface or a different number of entanglements between the dissimilar polymers in the interface. It should be mentioned that a slightly different sample geometry was used for the welding experiment. But it was confirmed that the geometry, where a thin film of SAN-25.0 is placed between two PMMA plates, leads to the same results in the welding experiments.

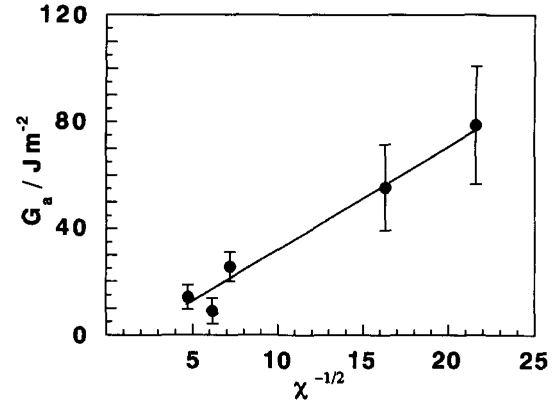

Figure 3 Fracture toughness, G_a, as a function of $\chi^{-1/2}$ for different immiscible SAN(PS)/PMMA samples. The full line is the linear best fit

Figure 3 shows the fracture toughness, G_a, as a function of χ. Because of the relation $\lambda \propto \chi^{-1/2}$ for immiscible systems, it can be assumed that $G_a \propto \chi^{-1/2}$. Again, this relation should hold only for systems reasonably far away from the critical χ parameter, i.e. in the strong segregation limit.

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