Kinetics of adhesion development at PMMA–SAN interfaces

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(*Received 26 November 1986; accepted 3 June 1987*)

The kinetics of adhesion development at interfaces between poly(methyl methacrylate) (PMMA) and styrene/acrylonitrile (SAN) copolymers of varying AN levels have been studied at 130°C by measuring the tensile fracture strength of a butt joint configuration. For miscible pairs, SANs containing about 9.5 to 33% AN, the principal mechanism of adhesion development involves interdiffusion of PMMA and SAN chains with the joint strength growing in proportion to $t^{1/4}$ (where t = time the joint is at 130°C) as predicted by theory. The interdiffusion rate is greatest near 14.7% AN, where the interaction with PMMA is maximum as demonstrated by recent studies of phase behaviour for PMMA–SAN blends. This optimum rate of adhesion development is consistent with a stronger thermodynamic driving force for diffusion. SANs with less AN than necessary for miscibility with PMMA, including polystyrene, rapidly developed a lower but finite extent of adhesion to PMMA, resulting from physical wetting and perhaps limited segmental interpenetration. Such joints do not seem to involve a long-term kinetic process since minimal transport is needed to attain the final equilibrium state, which contrasts with the situation for miscible pairs. In general, more rapid interdiffusion or adhesion development can be expected for miscible pairs of unlike polymers relative to pairs of identical polymers having comparable mobility because of the additional driving force provided by a favourable heat of mixing beyond that of the small combinatorial entropy which is the only driving force available for self-diffusion.

(Keywords: interfaces; adhesion; diffusion; poly(methyl methacrylate); styrene acrylonitrile; miscibility)

INTRODUCTION

Adhesion at polymer–polymer interfaces has become a topic of scientific interest because of its relevance in a variety of technologically important areas, including lamination operations, coextrusion of film and fibres, rubber toughening of plastics and multiphase blends, to mention some of the most obvious. Physical adhesion[1] can develop from adequate wetting at a sharply defined interface or by diffusional interpenetration of segments across the interface when this is thermodynamically possible. The kinetics of adhesion development is an important issue, particularly for the case when diffusional mechanisms are involved. Related to this is a growing body of experimental observations on and theoretical interpretation of the rate at which weld lines or cracks created in a polymer heal by diffusion[2–9]. In most cases, this work has involved the same polymer on both sides of the interface which amounts to a case of polymer–polymer self-diffusion[2–7]. However, with the growing number of known miscible polymer pairs[10–17], there is now a strong interest in the mutual diffusion of unlike polymers as evidenced by recent experimental studies[18,21] and theoretical developments[21–25] in this area. The purpose of this paper is to give a preliminary report on the development of adhesion at the interface between two different but miscible polymers by a simple experimental approach analogous to those used in previous crack healing studies. The premise is that the interactions responsible for miscibility can speed the development of adhesion relative to that expected from self-diffusion of identical polymer chains, as in the case of typical crack healing situations. Experimental evidence for this is provided using poly(methyl methacrylate) (PMMA) and a series of styrene/acrylonitrile (SAN) copolymers whose compositions span the miscibility window for this homopolymer–copolymer system[10,26,27]. The acrylonitrile content of the copolymers provides a useful way of systematically varying the interaction of the polymer–polymer pair.

BACKGROUND

The driving force for mixing of two types of molecules is related to their free energy of mixing. It is this force which drives the process of their mutual diffusion[21,24,25], and it is clear that its magnitude must be a factor in the kinetics of the transport process. The free energy for mixing two identical molecular species, one of which may be tagged in some manner, stems entirely from the combinatorial entropy of mixing, which is quite small for two high molecular weight polymers. On the other hand, two different molecular species may involve a finite heat of mixing contribution to the free energy of mixing in addition to the combinatorial entropy change; and for two high molecular weight polymers to be miscible it is generally necessary for this mixing process to be exothermic. Therefore, the free energy for mixing two miscible polymers will generally be more favourable than that for mixing two identical (e.g. tagged and untagged) polymers when compared at equal molecular weights, owing to the additional energetic attraction present in the former but absent in the latter. This intuitive reasoning

0032–3861/87/122145–06$03.00

leads one to expect mutual diffusion of miscible polymer pairs to occur more rapidly than self-diffusion of comparable sized polymer chains. Recently, several theories for polymer–polymer diffusion have been formulated from irreversible thermodynamics, including modern reptation notions of polymer chain motions[21,24,25]. These approaches permit the expression of the above concept in a more formal and quantitative manner. The formulations recently reported[21–25] differ in some details but reduce to the same expression for the ratio of concentration based diffusion coefficients, D, for interacting, $\chi < 0$, or miscible polymer pairs relative to a comparable non-interacting, $\chi = 0$, pair, i.e.:

$$\frac{D(\chi)}{D(0)} = 1 + \frac{2|\chi|}{\dfrac{1}{N_1\phi} + \dfrac{1}{N_2(1-\phi)}} \qquad (1)$$

In this equation, ϕ is the volume fraction of species 1, N_i is the number of segments in each type of chain, while χ is the interaction parameter from Flory–Huggins type theories, which characterizes the heat of mixing. Since this term is generally negative for miscible polymer–polymer pairs, it has become customary in the recent literature on diffusion theory to write it as an absolute quantity to avoid confusion. In the above equation, the last term on the right is the ratio of the enthalpic and combinatorial entropy contributions to the diffusion process. Clearly this ratio can be significant for chains of high molecular weight when $|\chi|$ is finite. In addition, this ratio is also greater the larger is $|\chi|$, which is the intuitive result discussed earlier. Note that equation (1) assumes all segmental friction factors to be identical.

In the situation of interest here the two polymer surfaces are juxtaposed at a temperature where diffusion rates are finite but slow enough to follow, e.g. just above the glass transition temperature. After a specified period of time for diffusion, t, the materials are then cooled to ambient temperature (which stops further diffusion), where the extent of adhesion developed is assessed by measurement of the tensile fracture stress of the joint. Numerous papers have appeared recently[8,9,22], which give mathematical models for relating the mechanical characteristics of the joint to the progress of the diffusional process. The thickness of the interfacial zone affected by significant interdiffusion is expected to grow in proportion to $(Dt)^{1/2}$. The work required to pull out the interpenetrating chains increases in proportion, and the current models[2–5,8,9,22] predict that the fracture energy, G, of the joint follows a relation of the form:

$$G \propto (Dt)^{1/2} \qquad (2)$$

When the interfacial zone becomes large enough, full entanglement of the chains is established and cohesive fracture occurs thereafter. Since the tensile fracture strength, σ, is assumed proportional to $(G)^{1/2}$ via the Griffith criterion[28], then the model prediction for the early stages of diffusion is:

$$\sigma \propto (Dt)^{1/4} \qquad (3)$$

Equations (1) and (3) then provide a link between the rate of development of adhesion by diffusion and the interaction between the two polymers.

The PMMA–SAN system offers a unique opportunity for experimentation to explore the above line of reasoning. First, both PMMA and SAN have essentially the same T_g, such that the two materials being bonded soften at about the same temperature and there is no serious mismatch in mobility factors at temperatures just above this transition. Second, the interaction of PMMA and SAN can be continuously adjusted by changing the acrylonitrile content of the SAN. PMMA is only miscible with SANs having compositions ranging from about 9.5% AN to about 33% AN[10,26,27]. Based on theories for miscibility of copolymers with homopolymers[29–31], one expects the strength of the favourable interaction to be optimal somewhere within this miscibility window and to fall to zero at both edges (see *Figure 1*). This expectation is supported by calorimetric studies of low molecular weight analogues for the PMMA–SAN system[32] and by the effect of AN content on the temperature at which the blends phase separate on heating[27], i.e. lower critical solution temperature (*LCST*) behaviour. The latter reaches maximum values within the range 13 to 15% AN and falls sharply to lower temperatures on either side, as illustrated in *Figure 1*. Thus, the most favourable

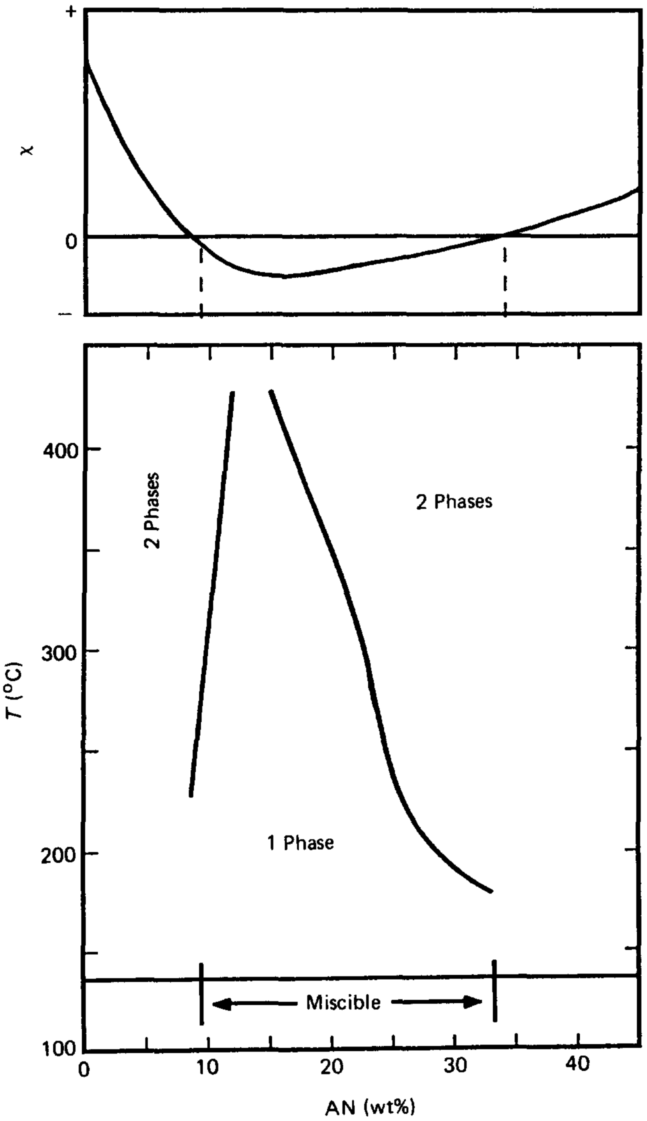

Figure 1 Effect of SAN copolymer composition on phase behaviour and thermodynamic interactions for blends with PMMA

interaction parameter is expected to occur for SANs having about 13 to 15% AN. While no truly quantitative interaction parameters are available, considerable evidence[27,33,34] suggests that the absolute values are rather weak even at the optimum composition.

MATERIALS AND EXPERIMENTAL PROCEDURES

Table 1 lists the various polymers used in this study along with pertinent chemical or physical characteristics and the sources from which they were acquired. The series of SAN copolymers were selected to obtain an appropriate spectrum of AN contents while holding as constant as possible the molecular weight or rheological characteristics, since this can be a factor in the transport process. We believe that these materials are sufficiently similar in the latter regard, such that the main effect is the thermodynamic one influenced by the AN content. The relationship of the AN contents used to the phase behaviour for SAN blends with PMMA can be seen in *Figure 1*. In this figure, the curve indicates the temperature at which a homogeneous SAN blend containing 50% PMMA will phase separate on heating[27]. Polystyrene (0% AN) and the SAN containing 6.3% AN are not fully miscible with PMMA, whereas, all of the other SANs are miscible with PMMA. This figure also illustrates qualitatively how one expects χ to vary with AN content.

The various polymers in *Table 1* were fabricated into standard tensile test bars (ASTM D638-68) using an Arburg injection moulding machine, as described previously for related materials[35]. The machine was operated such that a weld line was formed at the mid-point of the test bar. These bars were annealed at 130°C for a minimum of two days to remove residual stresses from the injection moulding process. Each bar was broken in two at the weld line. The fracture surface was machined and polished by a Tensil-Kut router so that this surface was smooth and normal to the axis of the bar.

The two halves of the same or of different bars are brought together and held in this position using a holder designed for this purpose[36]. Much care was taken to ensure that the specimens were properly aligned and that the two surfaces were in contact across the entire width. Mylar film was placed on both faces of the bar to prevent sticking to the holder.

Once set up and secured, weights were placed on the holder so that a compressive load was imposed axially on each bar. The entire assembly was then placed in an air oven set at 130°C for various times. The holder design helped maintain the initial shape of the bar while heated to this temperature where flow can occur. The Mylar film mentioned above helped ensure that the axial load imposed was transmitted to the interface. This load is needed to maintain good contact at the interface and to speed wetting, but too high a load causes problems of excessive deformation. Preliminary experiments indicated that a load of 10 psi at the interface was about optimum. Since some axial misalignment and some deformation of the bar invariably occurred in the vicinity of the joint, the bars were carefully sanded at the edge of the interface until a uniform, rectangular cross-section was achieved. After thermal treatment for the specified time, the welded bars were uniaxially strained in an Instron at a crosshead speed of 0.2 in min^{-1}. The peak load was divided by the cross-sectional area at the joint to obtain the tensile fracture stress, σ.

Due to the nature of the experiment, some samples failed prematurely because of defects, dust or bubbles at the interface. Such low values of the fracture stress were eliminated from the data set. Each stress reported represents the average for 5 to 10 specimens, where the average deviation about the mean value was typically 10%.

Due to the heat-up time after the sample holder was placed in the oven, the beginning of the welding time at 130°C cannot be defined precisely. In general, it was found that it took about 30 min for the bars to approach thermal equilibrium with the oven. For a series of specimens removed after only 30 min, over 50% were not adhered at all while the remaining fraction had only a very low fracture stress. Therefore, zero time was defined as 30 min after the samples entered the oven. As a result of this uncertainty, it was not possible to explore accurately the kinetics of this process for short times. Therefore, the shortest time used here was about 10 h.

RESULTS AND DISCUSSION

Figure 2 shows the tensile fracture stress *versus* welding time at 130°C for PMMA to PMMA and SAN 25 to SAN 25. In each of these self-diffusion cases, the stress at fracture increases with time; however, the rate of adhesion development is slower for PMMA than SAN 25, apparently owing to the more sluggish nature of diffusion

Table 1 Polymers used in this study

Polymer	Abbreviation	Source	Molecular weight	Tensile strength (psi)
Polystyrene	PS	Cosden Oil and Chemical Co. 550P	$M_n = 100000$ $M_w = 350000$	5290
Poly(styrene-*co*-acrylonitrile) 6.3% AN	SAN 6.3	Dow Chemical USA PA 990-118	Not available	5350
Poly(styrene-*co*-acrylonitrile) 14.7% AN	SAN 14.7	Asahi Chemical Ind. Co. Ltd	$M_n = 82700$ $M_w = 181000$	5280
Poly(styrene-*co*-acrylonitrile) 25%AN)	SAN 25	Dow Chemical USA Tyril 1000	$M_n = 75800$ $M_w = 160000$	7380
Poly(styrene-*co*-acrylonitrile) 30% AN	SAN 30	Dow Chemical USA Tyril 880	$M_n = 82000$ $M_w = 160000$	9410
Poly(styrene-*co*-acrylonitrile) 33% AN	SAN 33	Monsanto Co. 35-1000-357	$M_w = 113000$	9390
Poly(methyl methacrylate)	PMMA	Rohm and Haas V(811)100	$M_n = 52900$ $M_w = 100000$	11420

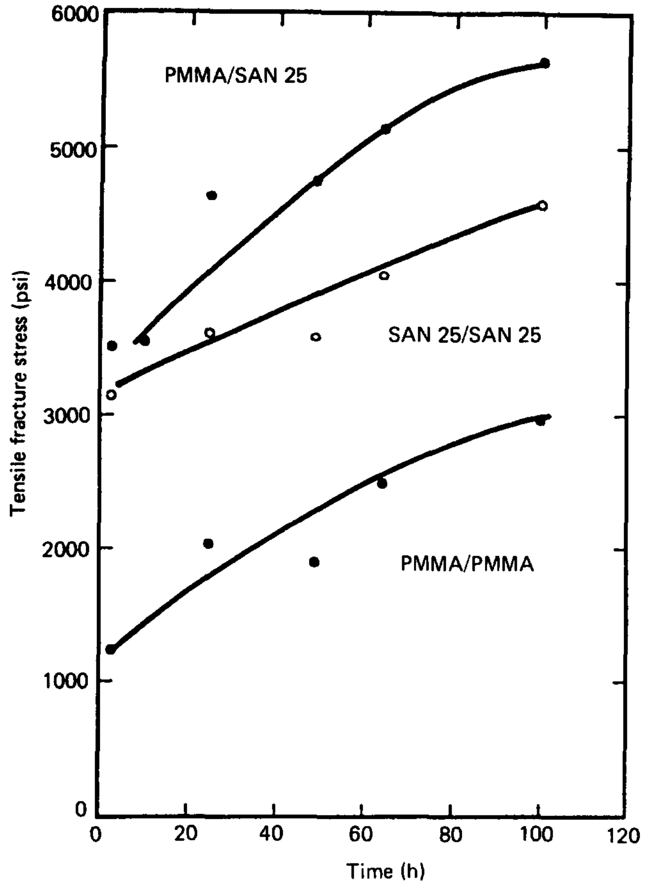

Figure 2 Kinetics of adhesion development at 130°C for: PMMA/PMMA, SAN 25/SAN 25, and PMMA/SAN 25 joints

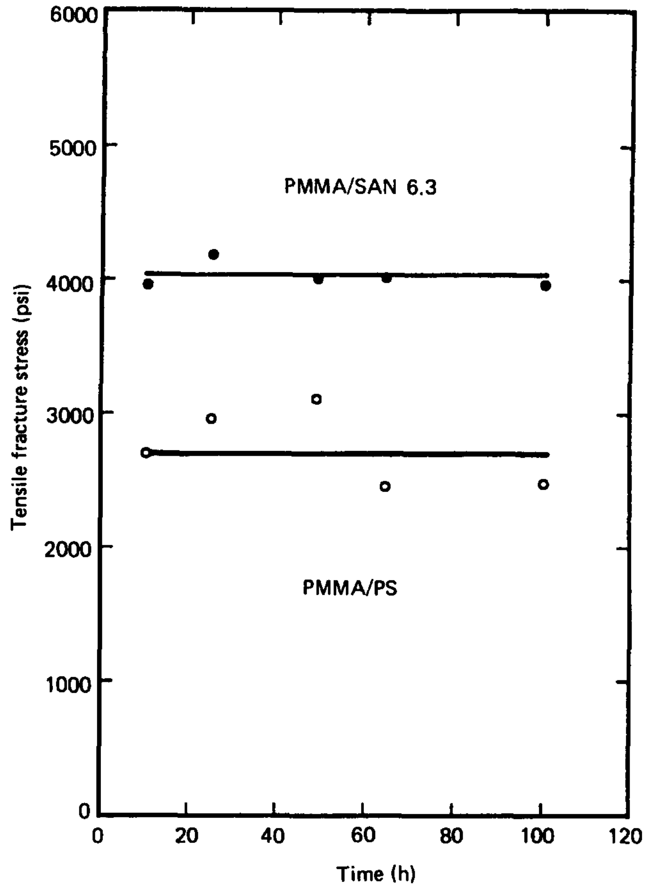

Figure 3 Joint strength for PMMA to polystyrene and to SAN 6.3. All pairs are immiscible

for the former at this temperature. A similar experiment with SAN 14.7 (not shown) revealed a slightly more rapid rate of adhesion development than for SAN 25, which is again probably related to intrinsic mobility considerations. *Figure 2* also shows the rate relation for adhesion of SAN 25 to PMMA, which interestingly is more rapid than for either self-diffusion case, as expected from the previous discussion. For every case, the ultimate joint strength was not achieved even after 100 h.

As a contrast to this type of behaviour, *Figure 3* shows the joint strength for two immiscible pairs, PMMA to PS and PMMA to SAN 6.3, as a function of time. Here, a finite fracture stress is achieved after a time shorter than accessible by this approach and does not change thereafter. In this case, the adhesion apparently results from simple wetting and perhaps limited interpenetration of chains across the interface[1]. The kinetics for this process is fast compared with that for the diffusion mechanism of miscible or like systems. The absolute level of adhesion for these two cases is surprisingly high. The higher level for SAN 6.3 than for PS is reasonable based on the thermodynamics of this homopolymer–copolymer system (see *Figure 1*), which leads one to expect PMMA to have a greater affinity for SAN 6.3 than for PS.

Equation (3) predicts that the joint strength for a miscible system ought to grow in proportion to $t^{1/4}$, so the remaining results are presented in this format. As seen in *Figure 4*, the data conform to this expectation quite nicely. However, the linear σ vs. $t^{1/4}$ relation does not extrapolate to the origin but, rather, to a finite stress intercept of about 500 to 1800 psi. Similar behaviour has been noted before[2–5,8,9], and the cause may stem from

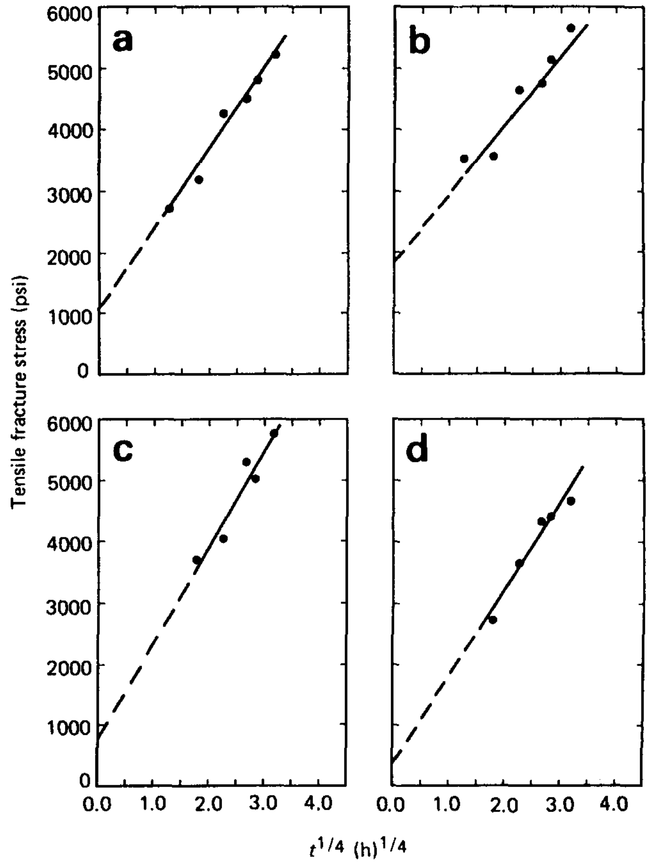

Figure 4 Joint strength development for miscible pairs plotted according to theory. AN: (a) 14.7%; (b) 25.0%; (c) 30.0%; (d) 33.0%

several factors. First, there is the imprecise nature of $t = 0$ mentioned before. One might also speculate that this intercept is the result of an initial rapid wetting at the interface, giving rise to a type of adhesion found for immiscible pairs (see *Figure 3*). However, it is puzzling that the extrapolated stress for these miscible pairs is a relatively small fraction of the fracture stresses measured for the immiscible pairs. No definitive explanation can be offered at this time, but it would be of interest to explore this question using techniques which can give more precise information at shorter times or to use a lower temperature to prolong the kinetic process.

A more revealing presentation of these data for the present objective is given in *Figure 5*. Here, the fracture stress for joints formed with PMMA are plotted *versus* the AN content of the SANs for fixed welding times. To properly normalize the joint strength comparison among these different materials, the fracture strength at time t, σ_t, has been divided by the ultimate strength of the joint, which is the cohesive tensile strength of the weaker polymer for each pair (see values in *Table 1*). As the welding time increases, the bond strength will approach this limiting cohesive value denoted here by σ_∞. For the short time of 10 h, the maximum normalized strength is for the immiscible pair, PMMA/SAN 6.3. This is, however, something of an artefact of the rapid development of adhesion for this non-miscible pair relative to the miscible ones. At longer times, the relative strengths of joints for the latter move up while those for the immiscible ones do not change. At these longer times, maximum strength is seen in every case for the PMMA/SAN 14.7 pair, and at 100 h the theoretical limit has been approached. For longer times, we expect the points to the right of 14.7% AN to move up to the limit $\sigma_t/\sigma_\infty = 1$ while those to the left of this value will remain fixed, reflecting the superiority of the ultimate joint strength of a miscible system with complete interpenetration *versus* physical wetting or partial interpenetration for immiscible polymer–polymer pairs.

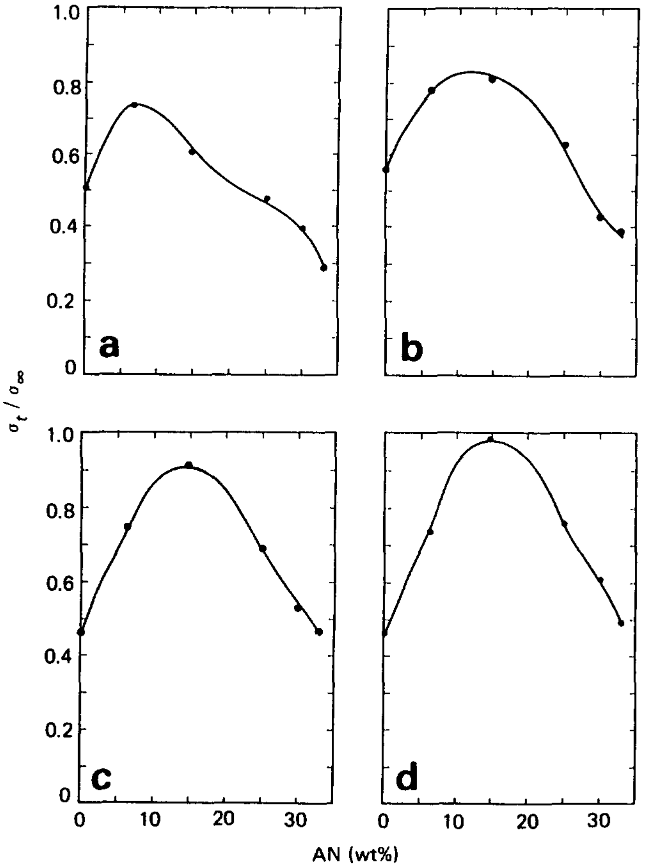

Figure 5 Effect of composition of SAN copolymer on normalized joint strength for PMMA–SAN pairs shown for various bonding times at 130°C. Time, t: (a) 10 h; (b) 25 h; (c) 64 h; (d) 100 h

CONCLUSION

For non-interacting polymer–polymer pairs, the only driving force for diffusion is entropic in origin and very small, owing to their high molar masses. For most miscible polymer pairs, there must be a favourable enthalpic driving force which ought to lead to faster diffusion. This point has been examined here by simple experiments to follow the kinetics of adhesion between PMMA and a series of SAN copolymers. The analysis used has been only qualitative; however, the results seem to be fully consistent with this intuitive expectation. A more quantitative approach would require having complete information about interaction parameters and about the segmental friction factors, which have all been assumed identical in equation (1). To execute a more thorough investigation of the kinetics of diffusion a more precise approach than adhesion is suggested. Several diffusion techniques described in the recent literature[20–22] appear to be good candidates for such a study.

Our interest in this problem has been in the area of polymer–polymer adhesion which has many practical applications, as mentioned earlier. Again, more precise techniques, such as those based on fracture mechanics of better defined geometries[1–8,37–41], will be needed to refine some of the finer details of this issue. Finally, we point out that this study deliberately used a low temperature near the glass transition so that the kinetic features could be followed over a convenient time-scale. In practical cases of more realistic process temperatures, the kinetics would be much more rapid.

ACKNOWLEDGEMENTS

This research was supported by the Army Research Office and in part by a fellowship to M. E. Fowler by the IBM Corporation. The authors express their appreciation to Dr H. Keskkula for many helpful discussions and to the various companies who graciously provided the materials used.

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