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Adhesion between Polystyrene and Polymethylmethacrylate

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Measurements have been made of the energy required to break through unit area of polystyrene (PS), polymethylmethacrylate (PMMA), and joints prepared by molding the two polymers in contact. The results were: $1.23 \pm 0.5 \text{ kJ/m}^2$ (PS), $0.46 \pm 0.10 \text{ kJ/m}^2$ (PMMA), and $0.22 \pm 0.04 \text{ kJ/m}^2$ for the bonded joint. Thus, the interface was significantly weaker than either adherend, but surprisingly strong for two incompatible materials. Microscopy and selective dyeing revealed that fracture took place at the interface itself, with no appreciable transfer of material from one side to the other. It is concluded that Van der Waals interactions are sufficient to create relatively strong bonds.

KEY WORDS Adhesion; failure; fracture; polymethylmethacrylate; polystyrene; polymer interfaces.

1 INTRODUCTION

Various test methods have been used to measure the fracture energy G of relatively stiff materials, and of adhesive joints between them. A simple torsion test, proposed by Outwater and Gerry,¹ has been widely employed because of its many advantages.²⁻⁴ It utilizes simple flat rectangular specimens, and the failure force remains constant, at least in principle, while the crack is driven forward over long distances, so that an average value of the strength is readily obtained. Moreover, the fracture energy is given directly in terms of the specimen stiffness and dimensions and the measured failure force, so that no other measurements are necessary.

A new way of imposing the torsional couple M by means of a pulley arrangement has recently been proposed.⁵ It allows the Outwater torsion test to be carried out with specimens having a wider range of flexibility. Some experimental measurements were reported of the fracture energy of molded polystyrene bars, to demonstrate the utility of the proposed modification.⁵ At the same time, possible ways of measuring the fracture energy of adhesive bonds were proposed. We now wish to describe measurements of the strength of adhesion between two glassy plastics, polymethylmethacrylate and polystyrene, carried out with the new method.

Although these two polymers are unlikely to interdiffuse, the fracture energy required to separate them was found to be relatively high, as described below, comparable to the inherent strength of the two adherends. Studies of the fracture surfaces have therefore been carried out, to establish whether or not a significant degree of interpenetration of the polymers took place.

2 EXPERIMENTAL DETAILS

Sample preparation

Commercial grade polymers were used in the experiments: polystyrene (PS), denoted Styron 685 (Dow Chemical Company) and polymethylmethacrylate (PMMA), denoted Plexiglas V920 (Rohm and Haas Company). Before molding, the PMMA pellets were dried under vacuum for 5 h at 50°C.

Sheets of PS and PMMA were prepared by compression molding at 140°C for about 30 min. They were machined as rectangular plates of various dimensions with a V-shaped groove along the center line of the lower surface. An initial saw cut was made at one end, Figure 1a, and the tip of the cut was sharpened by pressing a razor blade into the material at this point.

For preparing adhesion specimens, molded sheets of each polymer were machined as rectangular plates, 150 mm long and 30 mm wide. They were washed with methanol and rinsed with distilled water. They were then dried under vacuum at 50°C for 5 h and kept in covered dishes to protect them from contamination.

Sheets of PS and PMMA were bonded together along their edges in a mold, as shown in Figure 2, for 1½ h at 150°C. The pressure was

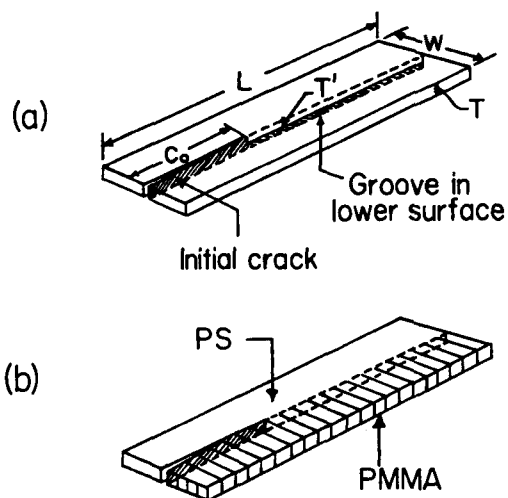
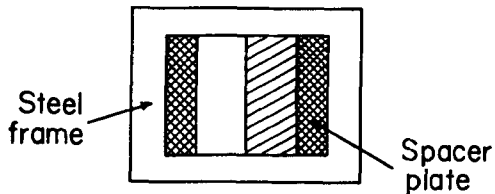


FIGURE 1 Test specimens: (a) PS and PMMA, (b) PS/PMMA joint.

Top View



Side View

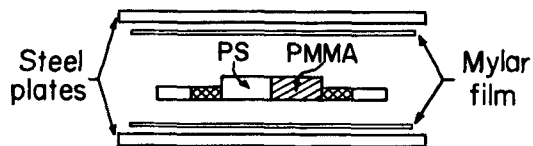


FIGURE 2 Molding arrangement for PS/PMMA joint.

then removed and the samples allowed to cool to room temperature. Testpieces were again prepared as rectangular plates, 130 mm long and 40 mm wide by machining these molded sheets. Also, as before, a initial saw cut was made at one end and the tip of the cut was sharpened by pressing a razor blade into the material. An adhesion specimen is shown schematically in Figure 1b.

Measurement of fracture energy

The modified Outwater torsion test⁵ was used to measure the fracture energy G_c for testpieces of PS and PMMA and to measure the separation energy G_a for PS-PMMA adhesive joints. All tests were carried out at room temperature, using an Instron test machine to apply the torsional couple M with a pulley arrangement as described previously.

Examination of fracture surfaces

Fracture surfaces were examined by two techniques. Direct observation was carried out using either an optical microscope or a scanning electron microscope. In the latter case, parts of the surfaces were removed from the specimen by careful sawing, and thin protective coatings of gold were deposited onto them to prevent surface charging.

A dye treatment was also employed to study the fracture surfaces of PS-PMMA adhesive joints, in order to check the failure mode; *i.e.*, whether interfacial failure or cohesive failure had occurred. A dye solution was prepared by dissolving 0.05 per cent of a commercial dye (Oil Red 4B, Pfaltz and Bauer Company) in cyclohexane and filtering it to yield a clear red solution. Using a microsyringe, a droplet of dye solution was applied to the fractured surfaces in covered dishes, and allowed to penetrate and dry. After dyeing, the samples were stirred in isooctane for 5 min at room temperature and the dyed surfaces were then wiped with a cotton applicator to remove unabsorbed dye. The samples were then washed with water and air-dried and the dyed surfaces were examined with an optical microscope.

3 EXPERIMENTAL RESULTS AND DISCUSSION

Fracture energies for PS and PMMA

Experiments were carried out on molded plates of the two polymers to obtain the fracture energies G_c . In each case, when the initial saw cut tip was sharpened by pressing a razor blade into it, the crack was found to grow in a stable and continuous manner at a well-defined critical value of the applied torque, denoted M_c . On the other hand, when the initial crack tip was not sharpened in this way it developed catastrophically at a relatively high applied torque. It was also found advantageous to make the initial crack length c_0 comparable to or greater than the width $w/2$ of the testpiece arms.

Values of G_c were calculated from the critical values of applied torque at which the crack propagated using the relation⁵

$$G_c = M_c^2/2kT' \quad (1)$$

where k denotes the torsional stiffness of the specimen for a crack length c of unity and T' is the thickness actually broken through (Figure 1). Results for G_c are given in Table I. As can be seen they were largely independent of the specimen dimensions. For PS they yielded an average value of 1.23 ± 0.5 kJ/m², in good agreement with published results, ranging from 0.5 to 3.0 kJ/m².⁶⁻⁸ For PMMA the average value was 0.46 ± 0.10 kJ/m², also in good agreement with previously-reported values, which range from 0.14 to 1.0 kJ/m².⁷⁻⁹

Fracture energy for the PS-PMMA adhesive joint

Smooth and straight interfaces were obtained by molding plates of PS against plates of PMMA as described. Values of the work of separation G_a were determined in the same way as for homogeneous plates; the results are given in Table II.

The mean value was 0.22 ± 0.04 kJ/m², considerably smaller than that obtained for the fracture energy of either PS or PMMA. It is about one-half of the value of G_c for PMMA and about one-fifth of that for PS. Thus, failure is probably not cohesive within either of the contacting layers but probably takes place at the weaker

TABLE I
Measured fracture energies G_c for PS and PMMA plates

Testpiece dimensions				Stiffness	Critical torque	Fracture energy
W	T	T'	c_0	$k \times 10^3$	M_c	G_c
(mm)	(mm)	(mm)	(mm)	(Nm ² /rad)	(Nm)	(kJ/m ²)
PS						
20	1.13	0.52	40	2.0	0.043	0.9
20	2.39	0.94	40	8.5	0.13	1.1
20	3.79	1.90	40	42.1	0.39	1.0
40	1.89	0.67	31	12.1	0.119	0.9
40	2.39	1.15	26	13.4	0.234	1.8
40	3.79	1.62	26	70.0	0.563	1.4
60	1.13	0.37	28	4.1	0.045	0.7
60	1.89	0.54	31	10.9	0.124	1.3
60	3.79	1.76	30	103.0	0.660	1.2
PMMA						
20	2.16	0.84	35	8.4	0.069	0.34
20	3.04	1.48	35	19.0	0.152	0.41
20	3.04	2.02	37	20.8	0.186	0.41
40	2.16	1.02	37	16.4	0.117	0.41
40	3.04	1.56	35	29.4	0.223	0.54
40	4.06	2.13	36	76.4	0.433	0.58

interfacial plane. Attempts to verify this conclusion were made by examining the fracture surfaces microscopically, as described below.

Microscopy of the fracture surfaces

Broken surfaces of PS appeared to be quite rough in comparison to those of PMMA. Typical low-magnification photographs are shown in Figure 3. Characteristic craze bands are clearly evident in the

TABLE II
Measured fracture energies G_a for a PS/PMMA joint

Testpiece dimensions			Stiffness	Critical torque	Fracture energy
W	T'	c_0	$k \times 10^3$	M_c	G_a
(mm)	(mm)	(mm)	(Nm ² /rad)	(Nm)	(kJ/m ²)
30	2.24	33	16.4	0.132	0.24
30	2.80	32	23.9	0.186	0.26
30	2.83	32	23.7	0.168	0.21
40	2.35	33	22.0	0.147	0.21
40	2.79	32	26.4	0.190	0.25
40	2.79	30	26.3	0.142	0.16

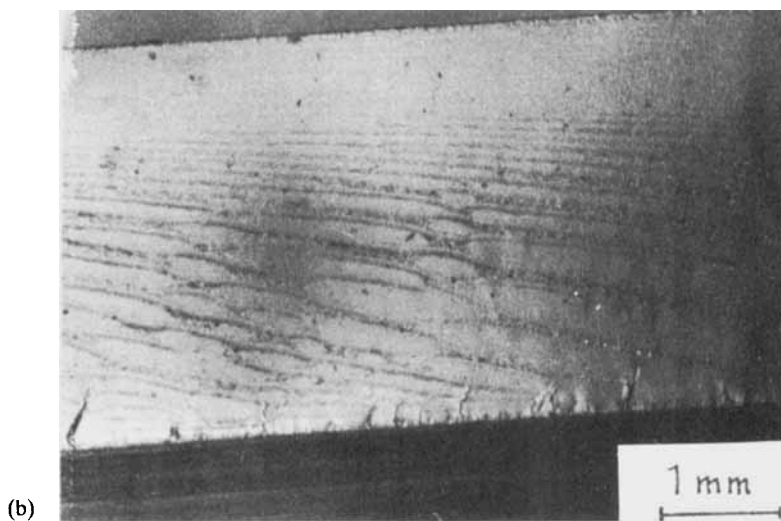
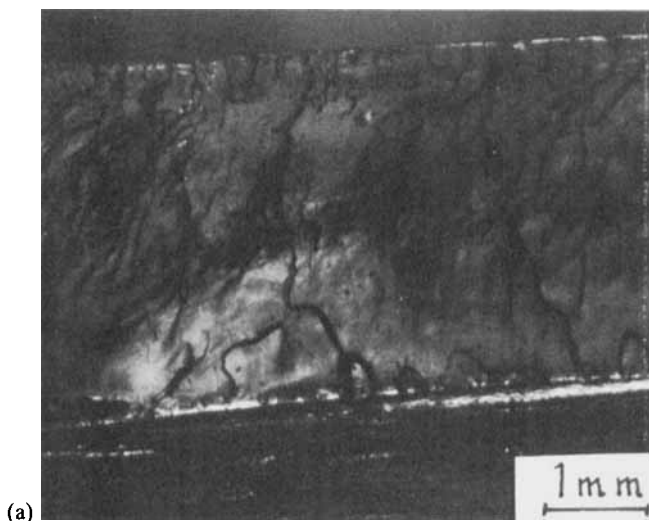


FIGURE 3 Fracture surfaces: (a) PS, (b) PMMA.

PMMA surface, which resembles that reported by Berry,¹⁰ but the PS surface shows only a rough irregular fracture plane. However, photographs at higher magnification, shown in Figure 4, revealed that the PS surface consisted of relatively smooth areas, several hundred μm in size, separated by pronounced steps or surface cracks.

High-magnification views of the surfaces obtained by breaking the interface between the two polymers are shown in Figure 5. The PS and the PMMA side of the interface look identical, and they both show small-scale roughness that is not at all characteristic of a fracture surface of PS (Figure 4a) but more resembles the crazed portions of a PMMA surface (Figure 4b). In fact, R. E. Robertson has shown that failure of a PS/PMMA bond is accompanied by severe crazing on the PMMA side of the joint.¹¹ It is thought that failure takes place at the true interface between the two polymers in the present experiments, even though the fracture surface is different in character from that obtained by cohesive rupture of either polymer and more resembles that of PMMA. Evidence in support of this conclusion was obtained from dye studies, reported below.

Dye studies of separated surfaces

In order to determine whether fracture occurred within either polymer or at the interface between them, a sensitive method was required to detect small amounts of one polymer on the surface of the other. For this purpose a dye treatment was used. A suitable red dye was employed, Oil Red 4B, dissolved in cyclohexane, a good solvent for PS but not for PMMA. Thus, the dye was found to stain only PS and not PMMA. After a brief dye treatment the surfaces were washed with a non-solvent for both polymers, isooctane, to remove unabsorbed dye. A PS surface could then be easily distinguished from a PMMA surface by the red color it acquired.

A dye-treated surface of the PMMA side of a fractured interface is shown in Figure 6. Small red regions, appearing dark in the photograph, show that some PS has been torn away from the bulk and transferred to the PMMA side. However, the surface area occupied by PS is extremely small, only one or two percent of the

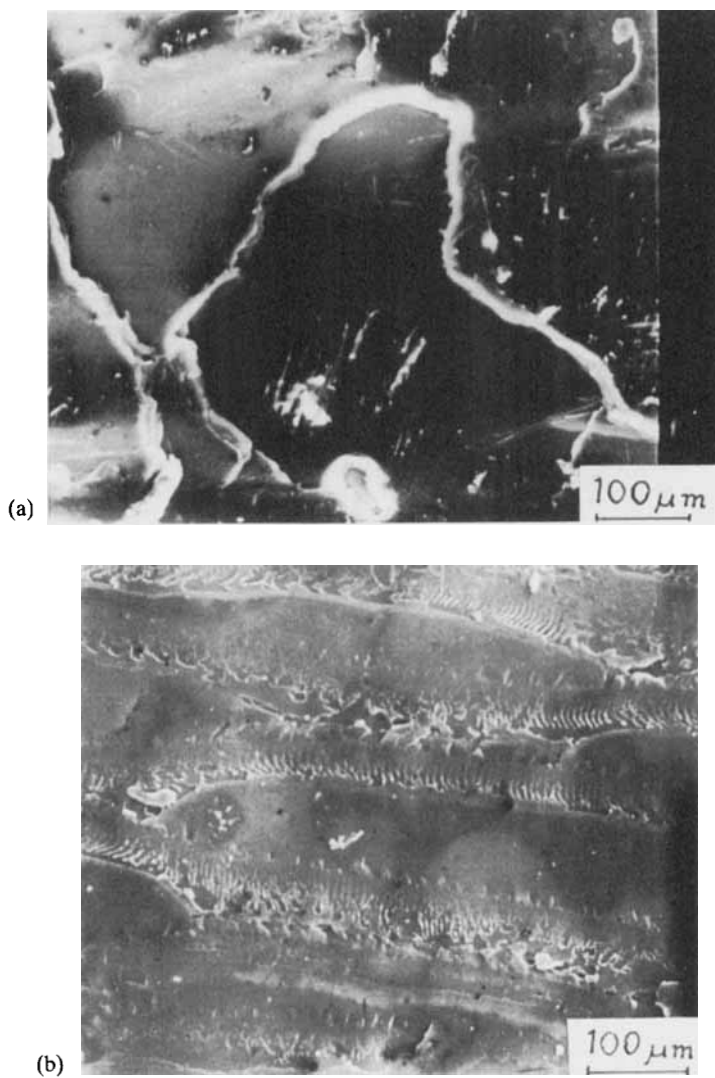


FIGURE 4 Fracture surfaces at higher magnification: (a) PS, (b) PMMA.

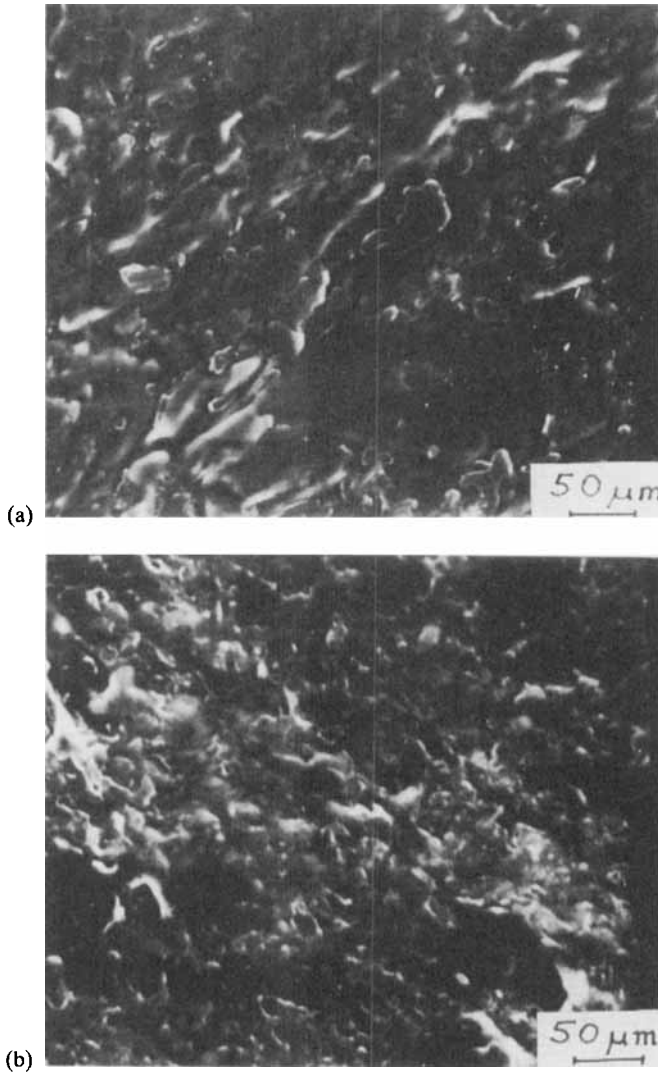


FIGURE 5 Fracture surfaces of a PS/PMMA joint: (a) PS side, (b) PMMA side.

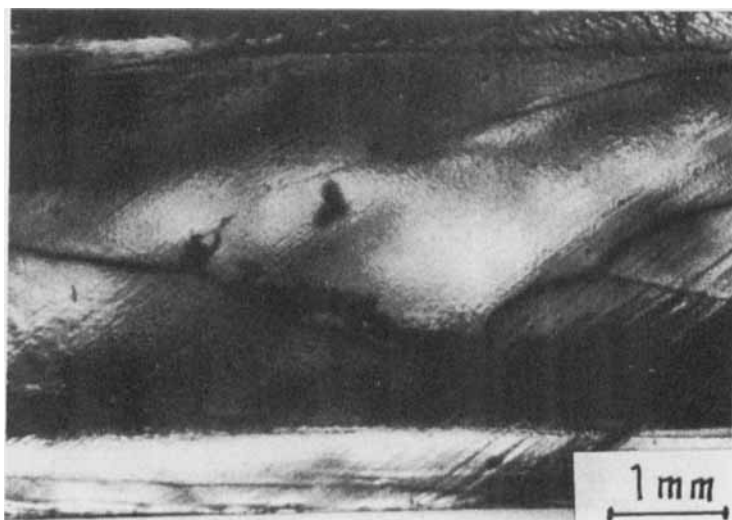


FIGURE 6 Dye-treated fracture surface of a PS/PMMA joint, PMMA side. The dark regions were dyed red in the original view.

total, so that the surface is substantially all PMMA. When the other fracture surface was examined in the same way, it was found to stain uniformly red, indicating that it consisted solely of PS. Thus, fracture appeared to have separated the two polymers rather cleanly.

However, it is possible that a thin layer of PMMA, too thin to be detected by the dye technique, had been transferred to the PS side of the interface. In order to check whether any PMMA was present on the PS surface, test specimens were prepared by coating a pure PS surface with a dilute solution (0.5 %) of PMMA in methylmethacrylate and drying them to give an extremely thin PMMA surface coating. On treating these specimens with dye solution, they were found not to show any red color, indicating that even a thin layer of PMMA will prevent PS from absorbing the dye under the experimental conditions used here. Thus it seems certain that fracture separated the two adhering polymers cleanly, at least on a scale of $0.1 \mu\text{m}$ or so, because only one of the surfaces could be dyed. This observation is consistent with the lower fracture energy found for separation in comparison with the fracture energies for cohesive rupture of the two polymers themselves (Tables I and II).

4 CONCLUSIONS

The following conclusions are obtained.

i) Fracture energies G_c for PS and PMMA plates are 1.23 ± 0.5 kJ/m² and 0.46 ± 0.10 kJ/m², respectively, in good agreement with previously-reported values.

ii) When PS and PMMA are molded in contact they adhere together quite strongly, the fracture energy for the joint being 0.22 ± 0.04 kJ/m².

iii) Nevertheless, failure appears to take place at the interface between the two polymers, and not to any significant degree away from the interface.

iv) It is concluded that van der Waals interactions, without any direct chemical bonding or molecular interdiffusion, are sufficient to provide relatively strong adhesive joints.¹¹

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