Fracture mechanics studies of crack healing and welding of polymers

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Compact tension tests have been performed on re-healed and welded glassy polymers (PMMA–PMMA, SAN–SAN and PMMA–SAN). At temperatures above the glass transition temperature, T_g, it was observed that the facture toughness, K_{Ii}, in the interface increased with contact time, t, as $K_{\mathrm{Ii}} \propto t^{1/4}$ as predicted by a diffusion model. The self-diffusion constant $D(T_g + 15\,\mathrm{K})$ of chains of molecular weight 1.2×10^5 can be estimated as $1 \times 10^{-21}\,\mathrm{sec}^{-1}$ with an activation energy of $274\,\mathrm{kJ\,mol}^{-1}$. For full material resistance, the depth of interdiffusion, $\langle \Delta x^2 \rangle^{1/2}$, was calculated to be between 2 and 3 nm. Vacuum drying of the specimens, as well as polishing the interfaces, decreases the speed of interdiffusion.

1. Introduction

Fracture and welding of polymer solids are two complementary processes which are of great importance in polymer technology. On a microscopic scale, these processes can be described, respectively, as the formation and destruction of surfaces. The forces and energies involved in these processes have been determined by a variety of techniques, including those of fracture mechanics [1,2] and surface physics [3,4], for a large number of polymers, surface geometries and stress histories.

It has become a standard technique to measure the energy release rate, G_{I}, or the fracture toughness K_{I}, associated with the propagation of a planar crack in a rigid elastic specimen [1,2]. It was only recently, however, that the same technique has also been applied [5] to measure quantitatively the strength of a newly-formed bond between two surfaces of thermoplastic materials. Jud and Kausch [5] have used compact tension (CT) specimens for two series of experiments. In one series, CT specimens not completely broken in tension were subjected to a crack healing treatment at an elevated temperature. In a second series

of experiments, the fracture surfaces of the broken CT specimens were first carefully polished[†] and then subjected to a welding treatment at elevated temperature. In both experiments, the fracture toughness, K_{Ii}, of the reformed CT specimens was determined in the conventional manner [5]. The measured K_{Ii} values thus refer to the material in the plane of the former interface between the fracture surfaces. Depending on the time, t_p, allowed for crack healing and on the healing temperature T_p, K_{Ii} was found to vary from very low values (material resistance, R, of the order of the surface free energy, γ) to K_{Io}, the fracture toughness of the original material.

For a quantitative evaluation of the time-dependent build-up of joint-strength between two surfaces, three different concepts have been proposed: (a) polymer–polymer interdiffusion [5, 6]; (b) adhesion between rough surfaces [3, 4, 7]; (c) jointing by flow of molten material [8, 9]. In the diffusion model, it is assumed that at T_p the molecular chains have a mobility which apparently allows chain segments to cross the interface by interdiffusion; it is expected that with increasing

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contact time the chains form new physical cross-links and that the strength of the interface increases [5]. In the adhesion model, the gradual reduction of surface irregularities by local flow of polymer material under the action of adhesive forces is considered. In the case of external stresses sufficient to produce a significant displacement, it is recognized [8, 9] that the flow of matter, the formation of weld beads, and the orientation and interpenetration of the flowing material influence the strength of the joint. In the following section, the first two models are briefly discussed, and a subsequent comparison is made of both models with the experimental findings.

2. Models of cohesive and adhesive joint-strength

A number of experiments [5, 6, 10–14] have given evidence for the existence of diffusion processes which take place across an interface between identical or compatible polymers. The diffusion derives from the random molecular motion at temperatures T greater than the glass transition temperature, T_g. The molecular motion in entangled polymer melts is mostly described by three components. There is a longitudinal displacement by a reptation mode, a segmental transverse re-organisation of the chain and a rotational movement in the chain. Together these three components form the overall chain motion and are characterized by the three-dimensional self-diffusion coefficient, D_s. The diffusion of chain segments across an interface gives rise to an interpenetration of chains and to the formation of physical links between molecules from different sides of the interface. If the interpenetration is sufficiently strong, the interface disappears optically and mechanically, so that static and dynamic forces can be transmitted across the interface. The mechanical strength of the interfacial bond can be quantitatively measured in terms of its energy-to-fracture per unit area, G_c.

When two polymer surfaces are brought into contact, there is an immediate adhesion arising from the effects of surface work changes, but the adhesive strength achieved by this process is low and is of the order of the "true surface energy", γ. To achieve the practical strength, there must be an interchange of material across the interface by some sort of diffusion process. For this to occur, there must be intimate contact between the surfaces. It is reasonable to assume, therefore, that

the strength of two surfaces brought into contact will be proportional to the contact surface area ratio A/A_0 where A is the contact area and A_0 is the total cross-sectional area of the bond, and the proportion of the links formed across that area, N/N_0 where N is the number of links formed across the bond and N_0 is the concentration of links at "full strength", G_{co}. Thus,

$$\frac{G_c}{G_{co}} = \frac{A}{A_0} \frac{N}{N_0}. \tag{1}$$

The achievement of complete contact (i.e. when $A/A_0 = 1$) for a surface with some initial roughness requires the distortion of that roughness under the action of interfacial pressure, both external and from surface work. In polymers, the time-dependence of this process will arise from viscoelasticity and the duration will be governed by the current material stiffness. Clearly, for high temperatures $(T > T_g)$, the modulus is low and, even under small external pressures (pressure, $p \simeq 0.8$ bar), complete contact will be achieved rapidly.

Some estimate of the time-dependence of contact area changes can be made by assuming that the modulus of the material has the form

$$E = E_0(t/t_0)^{-m}, \tag{2}$$

where E is the Young's modulus at time t, E_0 is a reference modulus at time t_0, and m is a constant. Then, Hertzian contact theory [15] gives

$$A \propto \left(\frac{\sigma}{E}\right)^{2/3}, \tag{3}$$

where σ is the applied compressive stress. Surface energy may contribute to the effective σ. By now assuming an extreme condition, namely that the development of strength is exclusively due to the increase in contact area, i.e. that $N(t) = N_0$, Equation 1 gives $G_c \propto A$. Thus, it would be expected that the dependence of K_I on time would be of the form

$$K_I \propto \left(\frac{\sigma}{E_0}\right)^{1/3} t^{m/3}. \tag{4}$$

For low temperatures, i.e. for elastic behaviour, m goes to zero and $E_0 \gg \sigma$, the degree of contact is small and remains almost constant. For $T > T_g$, σ/E_0 can be significant even for modest contact pressures and m approaches 1 for viscous type behaviour, leading to a rapid establishment of complete contact. The constant of proportionality

will, of course, be governed by the roughness of the two surfaces.

There will be a separate time-dependence of K_I associated with the self-diffusion of the polymer. The time-dependence observed in G_c will depend on which of the two mechanisms is the slower, and thus the controlling process. It is, of course, possible to visualize a rather complex interactive process when the two time scales are similar with each section of the area having a different diffusion time depending on its time in contact. Such a mechanism could be modelled but as a first approach the two time scales will be considered to be distinctly different. For smooth surfaces at temperatures $T > T_g$, it is likely that intimate contact is achieved very quickly and that diffusion is the governing process. The actual diffusion rate may be dependent on the state of the surface.

According to the diffusion model it is then assumed that the number of physical links per unit surface area, $n(t) = AN(t)$ is proportional to the average depth of penetration, Δx, of molecules. If Δx is derived from the Einstein diffusion equation then

$$\langle \Delta x^2(t) \rangle = 2Dt \tag{5}$$

and this gives

$$\frac{n(t)}{n_0} = \frac{(\langle \Delta x^2(t) \rangle)^{1/2}}{(\langle \Delta x^2(\tau_0) \rangle)^{1/2}}. \tag{6}$$

This means that $n = 0$ at $t = 0$ and $n = n_0$ at a characteristic time $\tau_0(T_p)$ which is the time necessary for the diffusing molecules to establish N_0 links per unit contact area. It follows from Equation 5 that τ_0 is inversely proportional to D and proportional to the square of the critical depth of penetration, $\langle \Delta x^2(\tau_0) \rangle$.

The time-dependence of the joint strength in terms of G_c is now derived from Equations 1, 5 and 6:

$$\frac{G_c(t)}{G_{co}} = \frac{n(t)A_0}{n_0 A_0} = \left(\frac{t}{\tau_0}\right)^{1/2}. \tag{7}$$

In terms of the stress intensity factor, K_I, this is

$$\frac{K_I}{K_{Io}} = \left(\frac{G_c}{G_{co}}\right)^{1/2} = \left(\frac{t}{\tau_0}\right)^{1/4}. \tag{8}$$

3. Experimental procedure

Poly(methyl methacrylate), PMMA 7H (of molecular weight $M_w = 1.20 \times 10^5$; and of molecular weight to molecular number ratio $M_w/M_n = 2$) from Röhm GmbH, and styrene acrylonitrile (SAN), Luran 368R co-polymer (25 mol% AN, of $M_w = 1.20 \times 10^5$) from BASF, have been investigated. Both have the same glass transition temperature, $T_g = 375–377$ K, and are completely compatible [16, 17]. Compact tension (CT) specimens were compression moulded from granules. The specimens were of length 26 mm, width 26 mm and depth 3 mm, and cracks were introduced in the samples by sawing and were subsequently sharpened by a razor blade. The specimens were fractured in tension and gave smooth fracture surfaces. For one series of specimens, these surfaces were brought in contact again and very lightly pressed together by an elastic band. This sandwhich-like preparation was then placed in a pre-heated hot-press, and a slight pressure of about 1 bar was applied normal to the major specimen surface. The specimen temperature, T_p, was set to between 1 and 15 K above the glass transition temperature, T_g. The pressure was needed to establish full contact between the fracture surfaces, but it was so small that the specimen geometry was not affected. The samples for this experiment, which could be called "crack healing", have always been held at ambient atmosphere. They had a humidity of about 1%.

In a second series of experiments, vacuum-dried samples were taken and treated as above. For the third series of experiments, flat surfaces were prepared by polishing the fracture surfaces. Again the specimens were dried at 373 K for 50 to 100 h under vacuum. Arbitrarily-selected surfaces were then welded together as described above. In each case the re-healed or welded specimens were completely uniform and transparent and did not show any trace of the former surfaces.

4. Results and observations

The fracture toughness, K_{Ii} at crack initiation, was measured as described before [5] on re-healed and welded CT samples as a function of contact time, t_p, and temperature, T_p. The fairly large scatter involved in these measurements required a large number of experiments. In Figs 1 and 2, the results of Series 1 (Curves 1 to 4) and Series 3 (Curve 5) are presented. Each point on Curves 1 to 4 is an average value from about 20 to 30 measurements. On Curve 5, all the measured data are indicated. The data are very well represented by straight lines
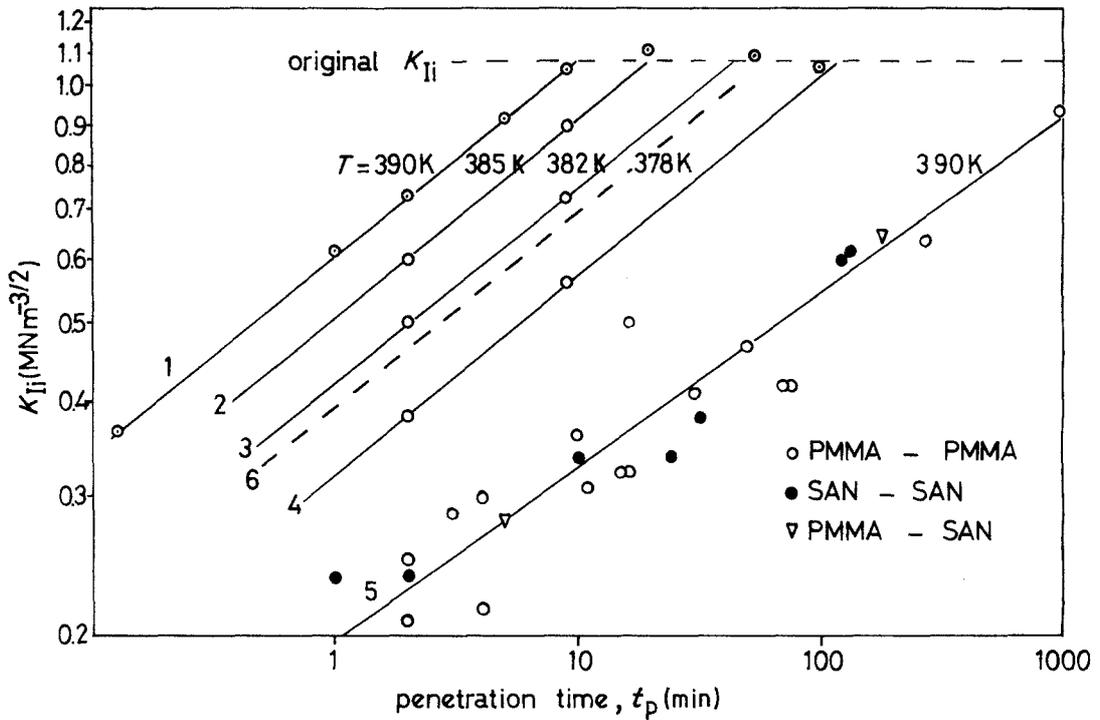
Figure 1 Double logarithmic plot of fracture toughness K_{Ii} against penetration time. Curves 1–4: healing of broken PMMA specimens immediately after fracture (the points are average values taken from 20 to 30 measurements). Curve 5: surfaces welded after vacuum drying and polishing (all data points are indicated individually). Curve 6: healing at 390 K immediately after fracture of dried PMMA samples.

with a slope of 0.25 (Fig. 1). In a K_{Ii} against $t_p^{1/4}$ plot, all the lines are straight and go through the origin (Figs 2 and 3). In Fig. 3 and, for comparison, Curve 6 in Fig. 1, the results from Series 2 are shown (vacuum dried samples). From Figs 1 to 3, one can determine $t_p(n = n_0)$ and thus $\tau_0(T) = t_p(N_0, T)$. If it is assumed that the critical number of links, n_0, and their volume density do not
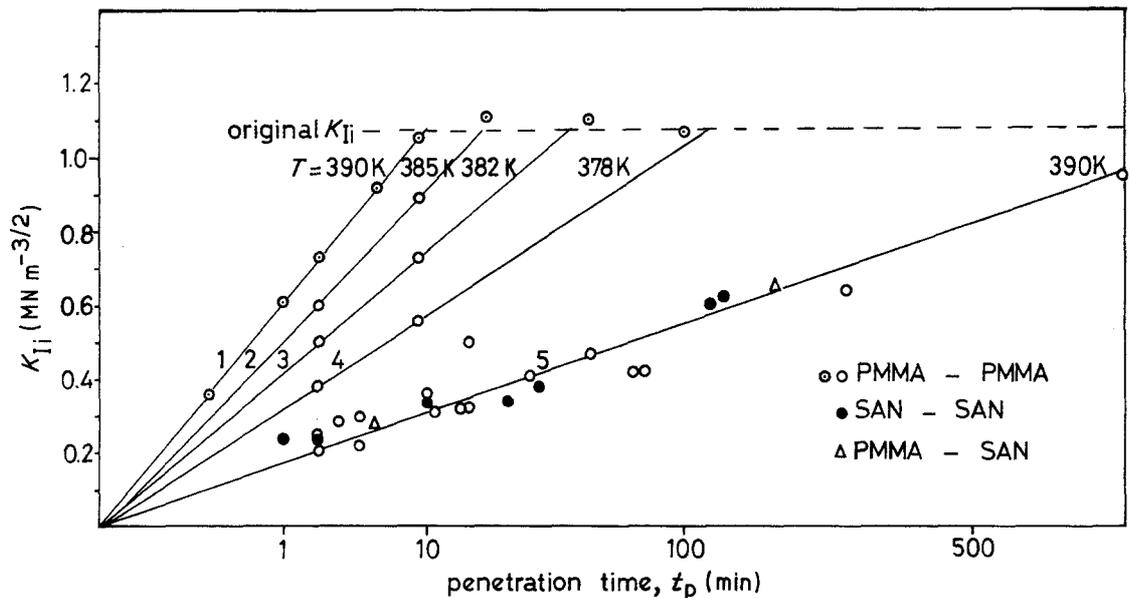

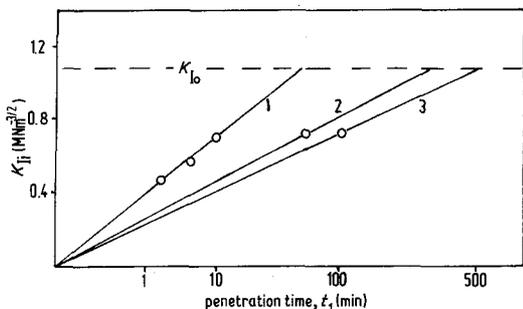*Figure 2* Plot of fracture toughness against $t_p^{1/4}$ (using the same data as used in Fig. 1).

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Figure 3 Plot of fracture toughness against $t_p^{1/4}$ for dried PMMA. Curve 1: $T_p = 390\,\mathrm{K}$. Curve 2: $T_p = 385\,\mathrm{K}$. Curve 3: $T_p = 382\,\mathrm{K}$.

depend on temperature, then it follows from Equations 5 and 6 that

$$\frac{D(T)}{D_0} = \frac{\tau_0(T_0)}{\tau_0(T)}. \tag{9}$$

The experimental values obtained from Figs 1 and 2 are very well represented by an Arrhenius law of D

$$D(T) = D_0 \exp\left(-\frac{E_a}{RT}\right), \tag{10}$$

with the activation energy, E_a, equal to 274 kJ mol^{-1}. This value of E_a is of a magnitude similar to that given for PMMA in [18] for the α-transition ($\simeq 400\,\mathrm{kJ\,mol^{-1}}$) which describes main-chain motion. It is much larger than the activation energies thus far reported for the self-diffusion coefficient which have been collected in Table I; however, the data are all for experiments carried out at temperatures T distinctly higher than T_g.

The diffusion model predicts very well the time-dependence of the re-healing experiments but it leaves a number of questions open concerning the physical interpretation of the observed diffusion mechanism, such as the absolute value of D, the role of chain-ends and of molecular weight, the influence of relaxing fibrils, formed in the first fracture event, and the nature of the established physical links. Absolute values of a diffusion coef-
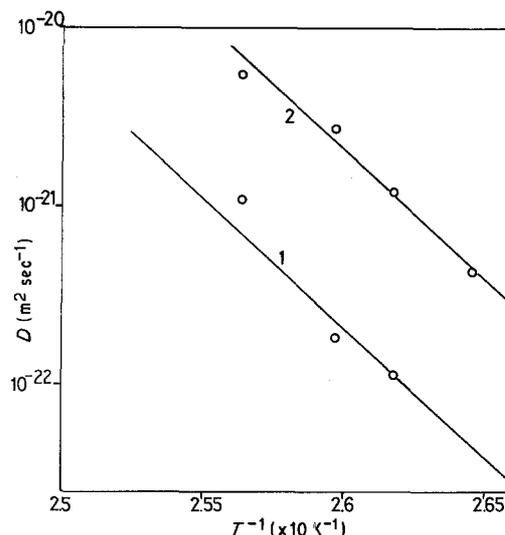

Figure 4 Diffusion coefficient, D, as calculated from Equation 11, using the data from Table II. Experimental points are obtained after fitting $D(T = 382\,\mathrm{K})$ to the curves. Curve 1: dried PMMA. Curve 2: undried PMMA.

ficient, D, can be estimated, however, using the reptation model [21]. According to a recent theory of Graessley [22], based on the work of Doi and Edwards [21], D can be related to measurable viscoelastic and structural parameters such that

$$D = \frac{G_0}{135} \left(\frac{\rho RT}{G_0}\right)^2 \left(\frac{R_g^2}{M}\right) \frac{M_c}{M^2 \eta_0(M_c)}; \tag{11}$$

the definitions and values of the quantities used in this equation are given in Table II. From Equation 11, the value of $D(T)$ is obtained and shown as a solid line in Fig. 4. The calculated values of D also permit the determination of the depth of penetration, $\langle \Delta x^2 \rangle^{1/2}$; for fully re-healed specimens $\langle \Delta x^2 \rangle^{1/2}$ is found to have a value of 2.5 nm. This seems to be a reasonable depth, since the radius of gyration for PMMA of the critical molecular weight is about 5 nm.

The specimens using polished interfaces were much slower to heal (Fig. 1, Curve 5). This can presumably be explained to be as a result of an

TABLE I Activation energies of (self)diffusion coefficient

Material	Temperature range	Activation energy (kJ mol^{-1})	Reference number
Polyethylene	$T_g + \sim 200\,\mathrm{K}$	25	[11, 19, 20]
Polyvinylchloride/ Polyamide 6	343–385 K	50	[12, 13]
Polypropylene	$T_g + 45\,\mathrm{K} < T < T_g + 97\,\mathrm{K}$	117	[7]
Polyisobutylene	$T_g + 50\,\mathrm{K} < T < T_g + 87\,\mathrm{K}$	165	[6]
Polymethylmethacrylate	$T_g + 2\,\mathrm{K} < T < T_g + 15\,\mathrm{K}$	274	this work

TABLE II Significance and values of quantities used for calculation of the diffusion constant of PMMA 7H

Symbol	Quantity	Value	Reference
$G_0(T)$	Plateau modulus	6.36×10^4 Nm^{-2} $(0.52 \rho RT/M_c)$	
$\rho(T_0)$	Density	1.14×10^3 kg m^{-3}	[23]
R	Universal gas constant		
T	Absolute temperature		
M	Molecular weight	1.2×10^5	(own GPC* measurements)
R_e^2/M	Mean square end-to-end distance/M	0.456×10^{-20} m^2 mol g^{-1}	[24]
M_c	Critical M for entanglement	3×10^4 g mol^{-1}	[25] p. 339
$\eta_0(T, M_c)$	Zero shear viscosity for M_c	3.78×10^8 Nsec m^{-2} at $T = 387$ K	[25] p. 342
		2.14×10^7 Nsec m^{-2} at $T = 390$ K	[25] p. 342

*GPC = gel permeation chromatography.

increased resistance to diffusional flow [9]; the diffusion constant is more than one order of magnitude lower $(D = 5 \times 10^{-23}$ m^2 sec$^{-1})$.

It should be noted that all combinations of the two polymers, SAN–SAN, SAN–PMMA and PMMA–PMMA, behave in exactly the same way.

This is not too surprising in view of the identity of the molecular weights and glass transition temperatures of the used PMMA and SAN materials.

5. Conclusions

The mechanical tests clearly reveal that at temperatures T where T is greater than the glass transition temperature, T_g, physical links between molecular coils have been established across interfaces by interdiffusion. These links are able to transmit forces larger than those of pure adhesion and give rise to a plastic deformation of the penetrated interface. In Fig. 5 some characteristic scanning electron micrographs of specimen surfaces are shown. On the polished surfaces (Fig. 5a and b) the markings produced by the polishing-knife of 0.1 to 0.2 μm in depth are clearly visible. The main
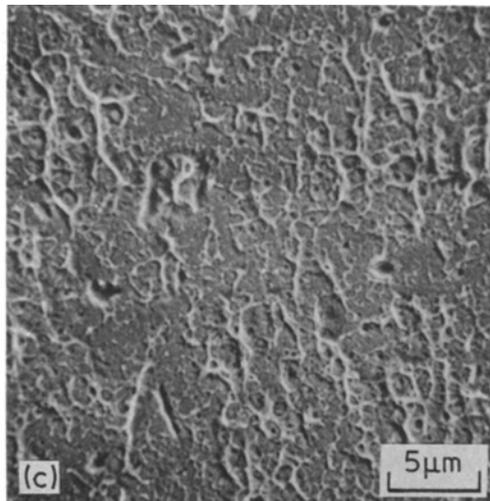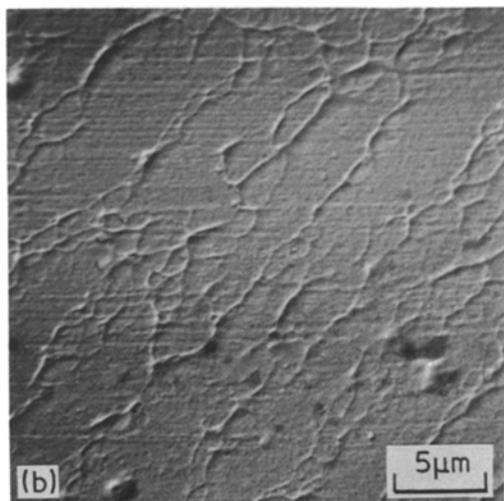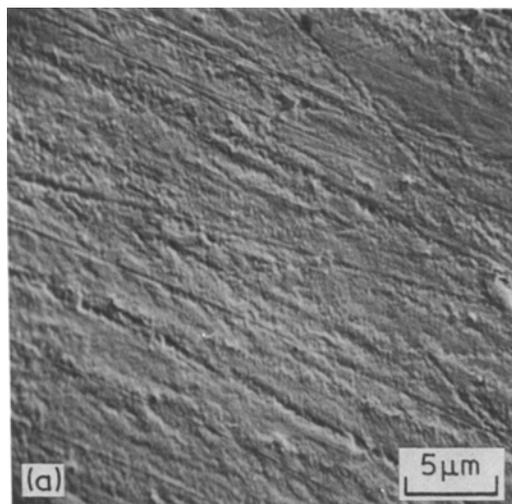
Figure 5 Characteristic scanning electron micrographs of: (a) PMMA 7H polished and etched; (b) PMMA 7H polished and penetrated for 50 min at 390 K; (c) PMMA 7H penetrated on plate surface for 900 min at 390 K.

feature of the welded and broken samples are the plastically deformed ridges of about 0.2 to 0.5 μm depth which are seen to be deeper and more numerous the longer the time of interpenetration. However, traces of plastic deformation are also visible in the regions between the ridges.

The influence of surface morphology and of chain structure, compatibility and molecular weight, especially of low molecular weight components, on the diffusional behaviour, on the "true contact area", and on the fracture surface morphology needs more attention and is being studied at present.

Acknowledgements

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