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Load Transfer Through Chain Molecules After Interpenetration at Interfaces

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Abstract

A series of PMMA samples of different molecular weights and degrees of copolymerisation have been tested for their crack-healing behavior. Slightly above T_g, a diffusional interpenetration of chain segments takes place. The fracture toughness in the plane of the interpenetrated interface was measured in short- and longtime experiments. After very short penetration times of only 5 min, full material resistance was regained in short-time experiments, whereas the long-time properties were not restored. A qualitative explanation of these effects, based on structural parameters, is given.

Introduction

The static transmission of mechanical forces at interfaces in polymeric or composite solids is of considerable scientific and technological importance. This is readily illustrated by reference to non-reactive adhesive joints, glass fibers in a polymer matrix, phase boundaries in block copolymers, or butt-welds. In the first case the quality of the adhesive joint depends on the purely physical adhesion between the polymer and the substrate (and on polymer rheology). In the second case effective load transfer is made possible by chemical coupling between the matrix and the fiber.

In semicrystalline homopolymers and in multiphase block copolymers forces at interfaces are as well transmitted by the Van der Waals attraction between contacting segments as by chain molecules which happen to be incorporated simultaneously in the two phases forming the interface. If such an interface is loaded to failure material separation will proceed through the opening up of voids (expenditure of surface free energy), the slippage of chains and plastic deformation of the interface region, and the breakage of highly loaded chains. All of these mechanisms have been directly observed.

In butt-welding one uses the characteristic behavior of thermoplastic materials to become soft and rubbery at elevated tempera-

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tures. If the chains are sufficiently mobile they will not only establish perfect contact between the two surfaces but they will penetrate the initial interface which rapidly disappears. Ideally the melting and pressing together of the two surfaces should give rise to an intimate interdiffusion and entanglement of the molecular chains and to a complete disappearance of any interface. The mechanical behavior of the butt-weld should then correspond to the behavior of the solid material. In particular the material resistance R measured in the plane of the former interface should be equal to the resistance of the bulk material.

Compatible thermoplastic polymers are capable, therefore, of forming joints of different molecular nature at different temperatures T. At temperatures much below the glass transition temperature T_g, mechanical interaction will be limited to Van der Waals attraction between contacting surface spots. At $T \approx T_g$ contact will be established over more or less the whole surface but the mechanical interaction will be confined to a surface layer some tenths of a nm deep. At T_g + 10 K chain ends and segments begin to penetrate the interface and to form physical cross-links and entanglements across the interface. At still higher temperatures entire chains will diffuse and the interface disappears. The strength of the joint between two surfaces is in the absence of any chemical coupling a function of the interpenetration of chain molecules; it is comparable to the surface tension γ ($\approx 0.04 - 0.08$ J m^{-2}) in the case of a purely adhesive contact, and it is equal to the full material resistance (120 - 10 000 J m^{-2}) in the case of a well formed joint in an isotropic glassy thermoplastic (1a).

Measurement of the material resistance of differently formed interfaces offer, therefore, the interesting possibility of learning something about the influence of physical cross-links and chain entanglements on strength. It has been pointed out previously (1b) that the gradual local decrease of physical cross-links, named disentanglement, is responsible for the delayed brittle failure of thermoplastic materials. Despite this general significance only very few investigations of the partial interpenetration of chains have been carried out. Outwater et al. (2) have studied the fracture energy, rehealing velocity, and refracture energy of a thermosetting material (cast epoxy resin). Bister (3) was concerned with the autohesion and the fracture behavior of uncrosslinked elastomers. Recently Wool (4) has discussed the microvoid formation and rehealing in semicrystalline polymers, filled elastomers and block copolymers as measured by the magnitude of the hysteresis in subsequent stress-strain cycles. The first result on the build-up of material resistance with chain interpenetration in glassy thermoplastics have been reported by the authors (5, 6).

In this work, fracture mechanics specimens are used to create fracture surfaces under well defined conditions which permit quantitative measurements of the fracture toughness K_I and the material resistance R of the bulk material. The fracture surfaces are then rehealed and K_I and R of the newly formed interfacial region are determined. The experimental method and the effect of the molecular composition and of the interpenetration parameters on K_I are subsequently reported.

Experimental

a) Material

Six different PMMA qualities from the Röhm GmbH., Darmstadt, have been investigated. Their characteristics are given in TABLE I. These data are completed by our own dynamic mechanical measurements.

b) Sample Preparation

Conventional single-edge notch (SEN) specimens were prepared from sheets (length L, width W, depth D) and compact tension specimens (CT) were compression moulded from granulates. The following geometries were employed:

SEN (L x W x D = 150 x 50 x 3 or x 6 mm^3)
CT (L x W x D = 26 x 26 x 3 or x 10 mm^3)

Cracks were introduced by sawing, they were subsequently sharpened by a razor blade. The specimens were fractured as described below. The fracture events led to smooth fracture surfaces. After a time t_r these surfaces were brought in contact again, very lightly pressed together by an elastic band, and the whole specimen was then held between two polished steel plates (Fig. 1).

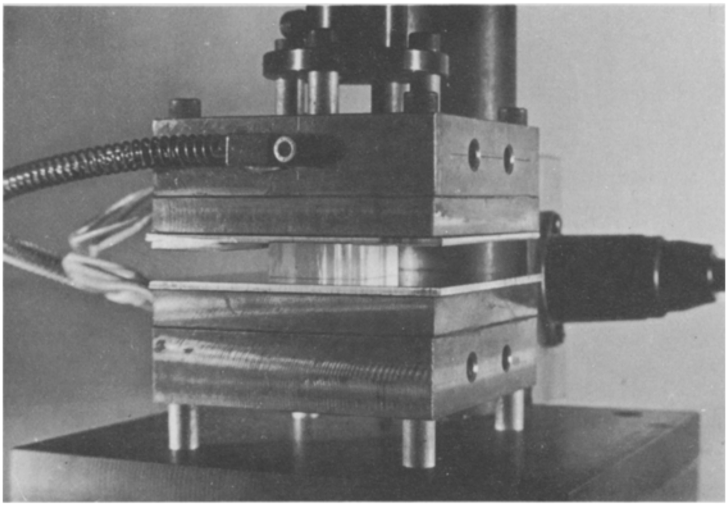

Fig. 1: Hot press for crack healing experiments.

This sandwichlike preparation was placed in a preheated 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 be 5 to 15 K above the glass-transition temperature. At this temperature Poisson's ratio is 0.5 and, therefore, the applied pressure also acts normal to the fracture surface. The pressure was needed to establish elastically a full contact between the fracture surfaces, a contact which, at this temperature, cannot be achieved solely through flow. On the other hand the applied pressure is so small that the specimen geometries were not changed. At T_g, the chains have a certain mobility which apparently allows chain segments to cross the interface by interdiffusion. We expect that with increasing contact time the chains form new physical cross-links and that the strength of the interface increases. The proposed mechanism is shown schematically in Fig. 2.

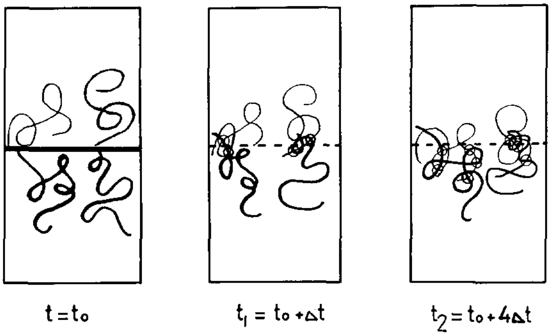

Fig. 2: Scheme of chain interpenetration.

To freeze in certain degrees of chain penetration, the specimens together with the steel plates were removed from the heated press and quenched in cold water.

c) Testing Procedure

For fracture tests at increasing loads a universal tensile testing machine* was at our disposal. In order to have good control of crack initiation and propagation SEN and CT specimens were loaded at the lowest possible cross-head speed of 0.5 mm min^{-1}. In these constant strain-rate experiments the load increased linearly until it reached its maximum P at the moment when the initial crack (of length a_0) began to grow. The testing machine was stopped after the crack had grown to a

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desired size, generally before complete fracture of the SEN or CT specimen had occurred.

The fracture toughness K_I is determined in the conventional manner (7) and refers here to the point of initiation of crack propagation. It will be designated, therefore, as K_{Ii}:

$$K_{Ii} = Y \frac{P\sqrt{a_0}}{WD} . \qquad (1)$$

The K-calibration factor Y is a function of specimen width and crack length, it is tabulated (e.g. 8, 9); in our experiments with the SEN specimen Y was between 2 and 3, with the CT specimen between 11 and 16. The K_{Ii} values measured for a particular material with original CT or SEN specimens correspond to each other and are slightly smaller than literature values of K_{Ic} (1a, 1c). The constant load experiments were done on a testing rig constructed in our laboratory. In these tests K_I values smaller than K_{Ii} were applied and the time to fracture was measured.

Results

Penetration experiments have been carried out to study the effect on fracture toughness of the duration t_p and the temperature T_p of the rehealing procedure (Fig. 3), of molecular composition (Fig. 4), and of normal pressure (Fig. 5).

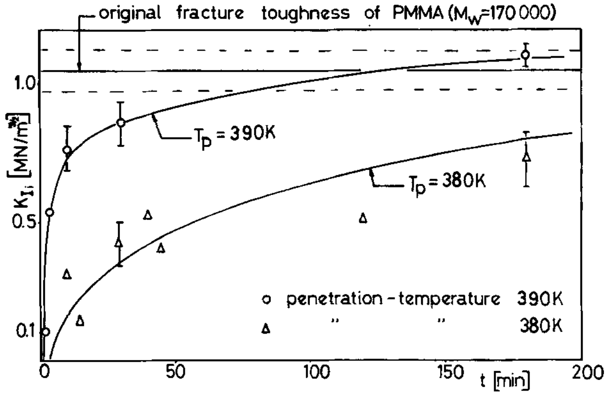

Fig. 3: Fracture toughness of specimens rehealed after several days as a function of penetration time and temperature (PMMA 7 H).

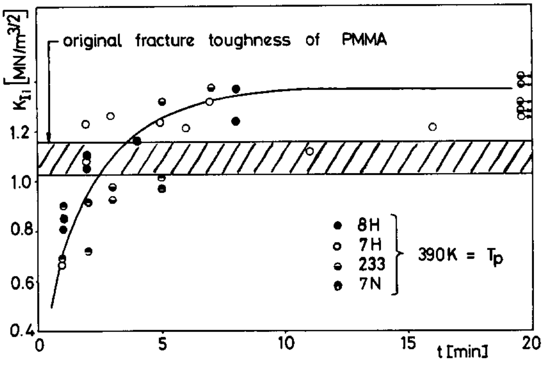

Fig. 4: Fracture toughness of specimens rehealed several minutes after fracture as a function of T_p.

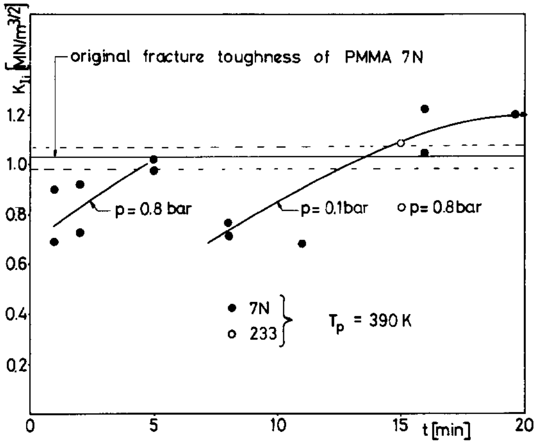

Fig. 5: Effect of normal pressure during rehealing on the reestablishment of fracture toughness.

In all of these experiments "optical" rehealing was achieved first; the initially clearly visible interface disappeared after a few minutes. The mechanical healing, as measured by K_{Ii} in a constant-strain experiment at 20 °C, required somewhat longer times (from 3 to 1000 min). Some comments are appropriate.

At T_g + 5 K rehealing occurs, but much slower than at T_g + 15 K (Fig. 3). The fracture toughness calculated for the rehealed specimens was found to be about 5 to 20 % larger than the K_{Ii} of the original material (Figs. 4-6). We have ascertained that this increase is not a material aging effect. It must be attributed to a certain crack blunting during the rehealing procedure. If we sharpen the crack of "completely" rehealed specimens ($t_p > 5$ min) by a razor notch, we measure the fracture toughness of the original material. Despite the systematic increase, we have used this method because it permitted measurement of the very delicate first stages of rehealing and because the systematic "error" does not interfere with any comparative conclusions.

Different normal pressures were used during rehealing but a common T_p was employed to obtain the data in Fig. 4. Although the PMMA samples have quite different molecular weights and compositions, they apparently establish bonds of comparable strength across the interface.

The slight normal pressure applied during rehealing does not seem to influence the interpenetration but the initial contact between the surfaces. With a low molecular weight material (7 N) rehealing curves are shifted towards shorter times t_p, even if the higher pressure is only applied for about one minute. Comparable rehealing effects can be obtained for the two widely different molecular weight materials 7 N and 233 (Fig. 5) but the stiffer material needs a higher pressure to establish a good contact which is necessary for rehealing.

The effect which has a delay t_r between the time of the first rupture and the beginning of the rehealing experiment is shown in Fig. 6. Immediate penetration (t_r = 2 - 10 min) has led to a notably faster rehealing than a penetration delayed by several days. Since the fresh fracture surfaces were not protected from atmosphere, surface reactions cannot be excluded.

Some preliminary measurements were made of the time to fracture, t_b, under constant load. Original samples of PMMA 233, subjected to 0.8 K_{Ii} at room temperature failed after 70 min whereas the apparently completely rehealed CT specimens broke under the same conditions after some 2 to 5 minutes. Constant load experiments at 47 °C and 0.7 K_{Ii} led to times to fracture of 15 to 100 s if t_p had been 10 min and to t_b = 21.5 to 22.2 min if t_p had been 30 min.

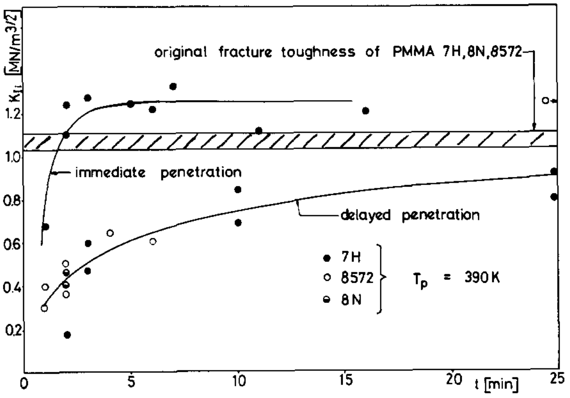

Fig. 6: Effect of delay of the rehealing on K_{Ii}.

Discussion

The experiments were undertaken to elucidate the mechanisms of stress transfer across differently prepared polymer-polymer interfaces. The results show that PMMA surfaces brought into contact at $T_p > T_g + 5$ K for $t_p > 1$ min establish a bond which is considerably stronger than that of pure adhesion. Even the weakest of our incompletely healed samples had K_{Ii} values of 0.3 MN m$^{-3/2}$ which correspond to G_{Ii} values of 30 J m^{-2}, i.e. they are 400 times larger than the contribution 2γ to be expected from the surface tension.

On the other hand the preliminary longtime experiments clearly show that the apparently "completely healed" specimens fail ten times faster than the original material. This means that under the employed penetration conditions no fully entangled network has been established. The latter conclusion is supported by a consideration of the diffusion of the chain molecules.

In a very early study Büche (10) proposed a model based on viscosity data to obtain self diffusion constants of polymer melts. As an experimental method he used the radioactive tracer technique, and consequently it seemed possible to calculate diffusion distances directly from viscosity data.

Some years later De Gennes (11) and Edwards (12) proposed a qualitatively rather different model on diffusion in polymer melts, which considered the entanglement-coupling points to be topological fix points showing a certain fluctuation. This "reptation model" describes the longitudinal chain diffusion. Some experimental studies backed the reptation model and its prediction that the self diffusion coefficient depends on the molecular weight as M^{-2}. In order to apply the reptation model and calculate $D(M_w)$ the diffusion coefficient must be determined experimentally for at least one molecular weight fraction. Klein (13) has recently made such measurements on polyethylene of $M_w = 11000$ at 176 °C, for which he found a D of $3.7 \cdot 10^{-9}$ cm^2 s^{-1}. According to the Büche theory D is given by:

$$D = \frac{\langle R^2 \rangle}{M} \cdot \frac{\rho N A}{36} \cdot \frac{k \cdot T}{\eta_0} \qquad (2)$$

where $\langle R^2 \rangle^{1/2}$ is the radius of gyration. This equation yields a D value of $1.4 \cdot 10^{-10}$ cm^2 s^{-1} for the above PE fraction. In the absence of experimental data on $D(M_w)$ for PMMA we have to use Eq. (2) for an estimate of D, which gives $1.6 \cdot 10^{-18}$ cm^2 s^{-1} for our PMMA 7 H. According to the Einstein relation, diffusion distances Δx can then be calculated:

$$\langle \Delta x^2 \rangle = 2\ \Delta t\ D. \qquad (3)$$

Taking $\Delta t = 5$ min and $T = 390$ K we find $\langle \Delta x^2 \rangle^{1/2}$ in the 0.01 to 0.1 nm bracket.

We have to conclude, therefore, that under our rehealing conditions the diffusion of whole molecular coils ($\phi \simeq 20$ nm) across the interface is very unlikely. This may also account for the apparently small effect of molecular weight on rehealing. The diffusion of chain ends or segments comprising about 1/20 of the length of an average molecule seems to be possible, however. These ends and segments penetrate like (bent) prongs of a fork into the opposite matrix. Through kinks in the main chain and through the sidegroups each prong forms a number of physical cross-links with the matrix. These cross-links are sufficiently stable at room temperature to initiate the plastic deformation of the matrix in a constant strain-rate test. The interpenetration of chain segments seems to be more effective if the fracture surfaces are freshly prepared (Fig. 6). This might be related to the presence of elongated, relaxing craze fibrils in the fracture surface. This observation certainly needs further study.

In long time loading the number of the established physical cross-links obviously decreases with time leading to the premature failure of the rehealed specimens. This observation and some studies on the kinetics of free radical recombination (1d) led us to conclude that chemical cross-linking reactions at the contacting surfaces contribute very little, if at all, to the bond between the two surfaces.

Further work as to the nature, origin and concentration of the physical cross-links, the depth of interpenetration of the chain molecules, and the effect of these cross-links on the fracture behavior of such interfaces is necessary and will be done in our laboratory.

TABLE I

MOLECULAR AND MECHANICAL CHARACTERISTICS OF THE USED POLYMETHYLMETHACRYLATE MATERIALS OF THE ROEHM GMBH

Designation	Chemical Nature	M_w	Polydispersity M_w/M_n-1	T_g (Röhm)	T_g (Torsion)	K_{Ii} (Original)
7 N	PMMA/PMEA 5-10%	123'000	0.62	102	106	1.04±0.05
8 N	PMMA	123'000	0.86	109	108	1.03±0.04
7 H	PMMA/PMEA 5-10%	170'000	1	102	104	1.08±0.06
8 H	PMMA	170'000	1.1	107	109	1.11±0.05
8572	PMMA/PMEA 5-10%	350'000	1.66	106	106	1.08±0.06
233	PMMA	4'000'000	3	112	109	1.15±0.07

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