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CRACK HEALING IN POLYMERS(U) ILLINOIS UNIV AT URBANA  
DEPT OF METALLURGY AND MINING ENGINEERING R P WOOL  
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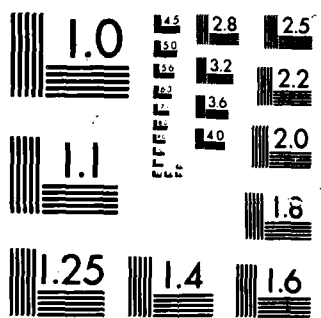
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER <b>ARO 19990-6-MS</b>	2. GOVT ACCESSION NO. <b>N/A</b>	3. RECIPIENT'S CATALOG NUMBER <b>N/A</b>
4. TITLE (and Subtitle) <b>Crack Healing in Polymers</b>		5. TYPE OF REPORT & PERIOD COVERED <b>Final; 4-18-83 to 9-30-85</b>
7. AUTHOR(s) <b>R.P. Wool</b>		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS <b>Metallurgy Department University of Illinois 1304 W. Green St., Urbana, IL 61801</b>		8. CONTRACT OR GRANT NUMBER(s) <b>DAAG29-83-K-0073</b>
11. CONTROLLING OFFICE NAME AND ADDRESS <b>U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709</b>		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS <b>Research</b>
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE <b>12-20-85</b>
		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report) <b>Unclassified</b>
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) <b>Approved for public release; distribution unlimited.</b>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) <b>NA</b>		
18. SUPPLEMENTARY NOTES <b>The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.</b>		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <b>Healing, Welding, Strength Development, Polymer Interfaces, Fatigue, Fracture, Diffusion, Reptation, Entanglements</b>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <b>see attached Final Report</b>		

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CRACK HEALING IN POLYMERS

FINAL REPORT

R.P. WOOL

DEC. 20, 1985

U.S. ARMY RESEARCH OFFICE

DAAG 29-83-K-0073

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## Crack Healing in Polymers

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### ABSTRACT

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When two similar polymers contact in the melt to form a polymer-polymer interface, interdiffusion of random-coil chains occurs. For this case, we determine a set of properties,  $H$ , as a function of time,  $t$ , and molecular weight,  $M$ . They include the number of chains,  $n$ , number of bridges,  $p$ , average monomer interpenetration depth,  $X$ , the total monomer depth,  $X_0$ , the center of mass diffusion,  $X_{cm}$ , the average contour interpenetration length,  $l$ , the total contour length,  $L_0$ , and the average bridge length,  $l_p$ . The time dependent,  $H(t)$ , and equilibrium solutions,  $H_\infty$ , can be summarized as

$$H(t) \sim t^{r/4} M^{-s/4}; H_\infty \sim M^{(3r-s)/4}, \text{ where } r, s = 1, 2, 3, 4, \dots$$

or

$$H(t) = H_\infty (t/t_\infty)^{r/4}, \text{ where } t_\infty \sim M^3$$

The set of properties in terms of integers  $H(r,s)$  are as follows:  $n(1,5)$ ,  $p(2,6)$ ,  $X(1,1)$ ,  $X_0(2,6)$ ,  $X_{cm}(2,2)$ ,  $L_0(3,7)$  and  $l_p(1,1)$ . The fracture stress,  $\sigma$ , fracture energy  $G$ , and fatigue crack propagation rate,  $\frac{da}{dN}$ , depended on the interdiffusion properties  $H(t)$ , and a set of deformation mechanisms involving chain pullout via disentanglement and bond rupture. When disentanglement dominates the deformation process  $r = s$ , and we find that  $\sigma \sim t^{1/4} M^{-1/4}$ ,  $\sigma \sim M^{1/2}$ ,  $G \sim t^{1/2} M^{-1/2}$ ,  $G_\infty \sim M$ ,  $da/dN \sim t^{-5/4} M^{5/4}$ , and  $(da/dN)_\infty \sim M^{-5/4}$ . When chain fracture dominates,  $s = 3r$ . For glassy polymer fracture, disentanglement dominates the fracture process but is influenced by bond rupture. The number of broken bonds per unit surface area was determined exactly for polystyrene as  $N_f = 7 \times 10^{17}/m^2$  and was independent of molecular weight for  $M > 10^5$ . The critical entanglement molecular weight,  $M_c$ , was described in terms of a bridge model for vinyl polymers as,  $M_c = 30.89 (bz/c)^2 C_\infty M_0 j$ , where  $b$ ,  $c$ ,  $z$ ,  $C_\infty M_0$  and  $j$  are the bond length,  $c$ -axis length, number of monomers per  $c$ -axis, characteristic ratio, monomer molecular weight, and number of bonds per monomer, respectively.

## Crack Healing in Polymers

### The Problem

When two similar amorphous polymers make good contact to form a polymer-polymer interface, we ask how strength develops as a function of contact time,  $t$ , and molecular weight,  $M$ , of the polymers. Fracture stress,  $\sigma$ , shear stress  $\tau$ , critical fracture energy,  $G_{IC}$ , and fatigue crack propagation rates,  $da/dN$ , are determined as functions of  $t$  and  $M$ . Solutions to this problem have application to polymer processing, internal weld-lines, coatings, welding, lamination and the physics of fracture mechanics.

### Solutions

The problem is divided into three parts. The first part consists of determining a set of molecular properties for the interface,  $H(t)$ . The second part relates the properties of the interface to the mechanical properties via a set of deformation mechanisms involving chain disentanglement and bond rupture. The third part of the solution consists of determining the fracture mechanics of a crack propagating through an interface using solutions of the first two parts. This method of solution involves the evaluation of three different but interconnected problems and results in an understanding of fracture mechanics of polymers, in terms of the physics and chemistry of the interface.

The properties of the interface were determined using the molecular dynamics model of deGennes and Doi-Edwards. Our version of the reptation model is shown in Fig. 1, as developed by Wool and Kim for polymer-polymer interdiffusion. Following contact at  $t = 0$ , the chains interdiffuse across the interface as shown in Fig. 2. For this case, we determine a set of properties,  $H$ , as a function of time,  $t$ , and molecular weight,  $M$ . They

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include the number of chains,  $n$ , number of bridges,  $p$ , average monomer interpenetration depth,  $X$ , the total monomer depth,  $X_0$ , the center of mass diffusion,  $X_{cm}$ , the average contour interpenetration length,  $l$ , the total contour length,  $L_0$ , and the average bridge length,  $l_p$ . The time dependent,  $H(t)$ , and equilibrium solutions,  $H_\infty$ , can be summarized as

$$H(t) \sim t^{r/4} M^{-s/4}; H_\infty \sim M^{(3r-s)/4}, \text{ where } r, s = 1, 2, 3, 4, \dots$$

or as a scaling law,

$$H(t) \approx H_\infty (t/t_\infty)^{r/4}$$

where  $t_\infty \sim M^3$ . The set of properties in terms of integers  $H(r,s)$  are as follows:  $n(1,5)$ ,  $p(2,6)$ ,  $X(1,1)$ ,  $X_0(2,4)$ ,  $L(2,2)$ ,  $L_0(3,7)$  and  $l_p(1,1)$ .

Table 1 summarizes the molecular aspects of interdiffusion at a polymer-polymer interface. These relations can be used to test hypotheses of

**Table 1. Molecular aspects of interdiffusion at a polymer-polymer interface.**

Molecular Aspect	Symbol	Dynamic Relation, $H(t)$	Static Relation, $H_\infty$
Number of Chains	$n(t)$	$t^{1/4} M^{-5/4}$	$M^{-1/2}$
Number of Bridges	$p(t)$	$t^{1/2} M^{-3/2}$	$M^0$
Average Depth	$X(t)$	$t^{1/4} M^{-1/4}$	$M^{1/2}$
Total Depth	$X_0(t)$	$t^{1/2} M^{-3/2}$	$M^0$
Center of Mass	$X_{cm}(t)$	$t^{1/2} M^{-1}$	$M^{1/2}$
Total Length	$L_0(t)$	$t^{3/4} M^{-7/4}$	$M^{1/2}$
Average Length	$l(t)$	$t^{1/2} M^{-1/2}$	$M$
Average Bridge Length	$l_p(t)$	$t^{1/4} M^{-1/4}$	$M^{1/2}$
General Property	$H(t)$	$t^{r/4} M^{-s/4}$	$M^{(3r-s)/4}$
		$r, s = 1, 2, 3, 4, \dots$	

strength development by us and others. If a mechanical property is directly related to  $H(t)$  or a product of several  $H(t)$  properties, then the time

dependence, molecular weight dependence of healing and the molecular weight dependence of the virgin (healed) state must be simultaneously predicted. This approach suggests critical experiments to be performed and provides a method of testing virgin state theories of strength.

When chain disentanglement dominates the strength of the interface, a microscopic fracture analysis results in  $\sigma \sim \chi(t)$ . From Table 1, substituting for  $\chi(t)$ , we have the following results:

$$\begin{array}{ll} \sigma(t) \sim t^{1/4} & (t < t_{\infty}) \\ \sigma \sim M^{-1/4} & (\text{constant } t) \\ \sigma_{\infty} \sim M^{1/2} & (t > t_{\infty}) \\ \sigma \sim \dot{\gamma}^{1/2} & (\text{rate effect}) \end{array}$$

These results are demonstrated for several polymers in Figs. 3, 4, and 5.

The fracture of glassy polymers (healed above the glass transition temperature) is more complex due to the role of bond rupture and the mechanism of a crack propagating through a craze-like zone.

Molecular fracture in amorphous polymers produced by a crack propagating through a craze microstructure was simulated by a microtome slicing method. A GPC analysis of the polystyrene slices gave exact measures of  $N_f$ , the number of broken bonds per  $\text{cm}^2$ .  $N_f$  was found to be

$$N_f = \frac{7 \times 10^{17}}{\text{m}^2} M^0$$

At room temperature,  $N_f$  was independent of  $M$  but at higher fracture temperatures, major effects of temperature and  $M$  were observed.

The topology of entangled amorphous polymers was investigated and a description for the onset of entangled behavior at the critical entanglement



molecular weight,  $M_c$ , was obtained as:

$$M_c = \frac{30.89 C_\infty M_0}{\alpha^2 j c}$$

where  $C_\infty$ ,  $M_0$ ,  $\alpha$ ,  $j$  and  $C$  are the characteristic ratio for random-coil chains, the monomer molecular weight, the ratio of the contour length to the chain bond length, the number of bonds per monomer and the concentration of chains, respectively. This relation for  $M_c$  was found to be in remarkably good agreement with experimental values for  $M_c$ . The entangled structure suggested by this theory has many consequences for microscopic aspects of fracture and rheological behavior of polymer melts.

Wedge-Cleavage methods were used to study the time and molecular weight dependence of welding. For mixed mechanism (chain pullout and bond rupture) we find that the Dugdale fracture mechanics model predicts,

$$\begin{array}{ll} G_{IC} \sim t^{1/2} M^{-x} & 1/2 < x < 1 \\ G_{IC} \sim (M - M_c) & M_c < M < M^* \\ G_{IC} \sim M^0 & M > M^* \\ \left( \frac{\partial a}{\partial N} \right)_{\Delta K} \sim M^{-5/2} & \end{array}$$

where  $M^* \approx 2 \times 10^5$  for polystyrene. Since  $K_{IC} \sim G_{IC}^{1/2}$ , the dependence of the critical stress intensity factor on  $t$  and  $M$  can be readily derived.

Experimental support for these relations is given in Figures 6-8. We are continuing to study the fracture mechanics and dynamics of strength development at polymer-polymer interfaces. References and details of the results contained in this report are given in the ARO publication list below.

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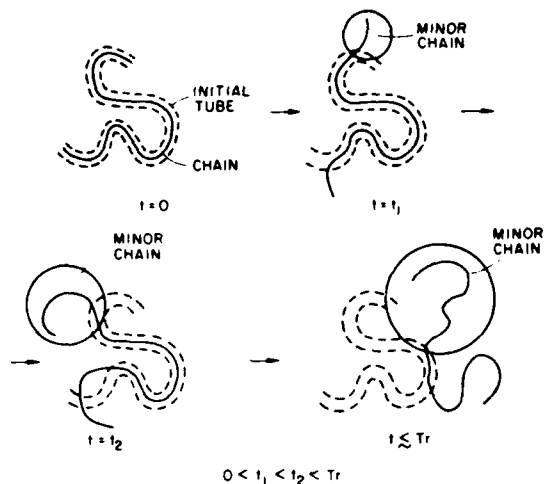
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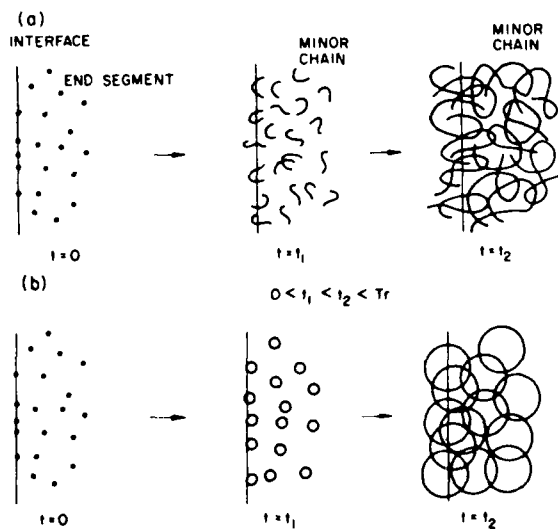
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**Figure 1.** The reptation model for a chain in an entangled melt is shown relaxing from its "tube" at several times  $t < t_{\infty}$ , where  $t_{\infty}$  is the reptation time. That part of the chain which has relaxed from the original tube (at  $t = 0$ ) is termed the minor chain and is shown in its most probable random-coil spherical envelope.



**Figure 2.** (a) The behavior of the minor chains at the polymer-polymer interface (one side is shown for convenience) is shown at times,  $t$ , less than the reptation time,  $t_{\infty}$ . (b) The behavior of the spherical envelopes of the minor chains is shown during the interdiffusion process.

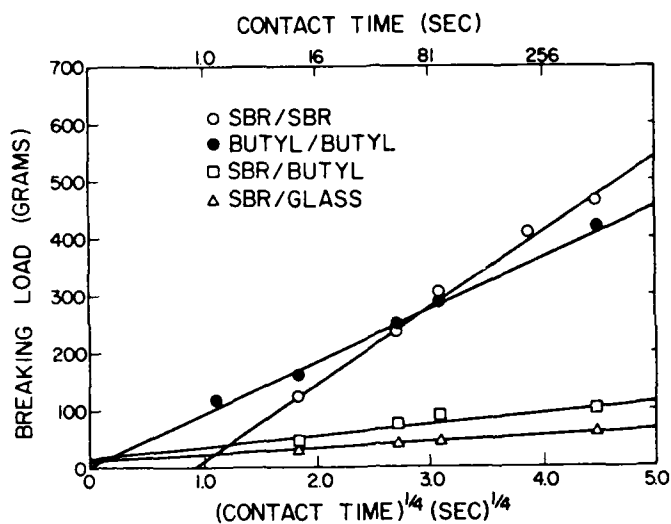


FIG. 3.—The tack or breaking load versus  $t^{1/4}$  for several polymer-polymer uncured pairs as investigated by Skewis<sup>11</sup>. Tack measurements were done with a contact load of 1000 g. and a contact area of 0.40 cm<sup>2</sup>. The viscosity average molecular weight of the SBR was 260,000 and 225,000 for the butyl rubber.

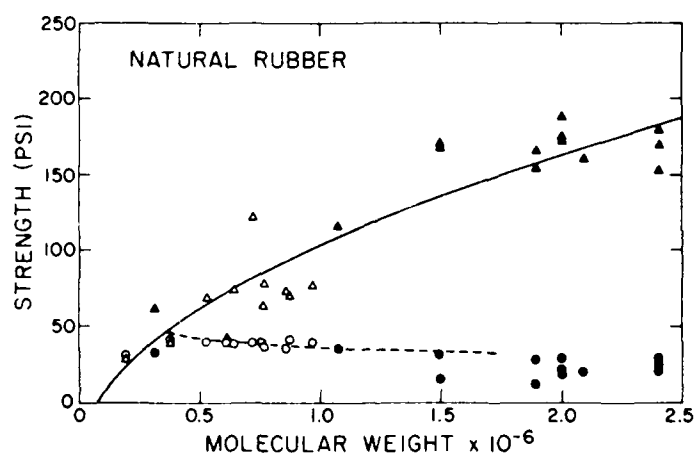


FIG. 4.—Tack (circles) and green strength (triangles) as a function of viscosity average molecular weight for fractionated samples of natural rubber (Forbes and McLeod<sup>12</sup>). The solid line for green strength was theoretically obtained using Equation (49) and the dashed line for tack using Equation (50). The green strength was evaluated at a uniaxial test speed of 26.67 cm/min at 25°C. and the tack was evaluated at a contact time of 30 s for each sample.

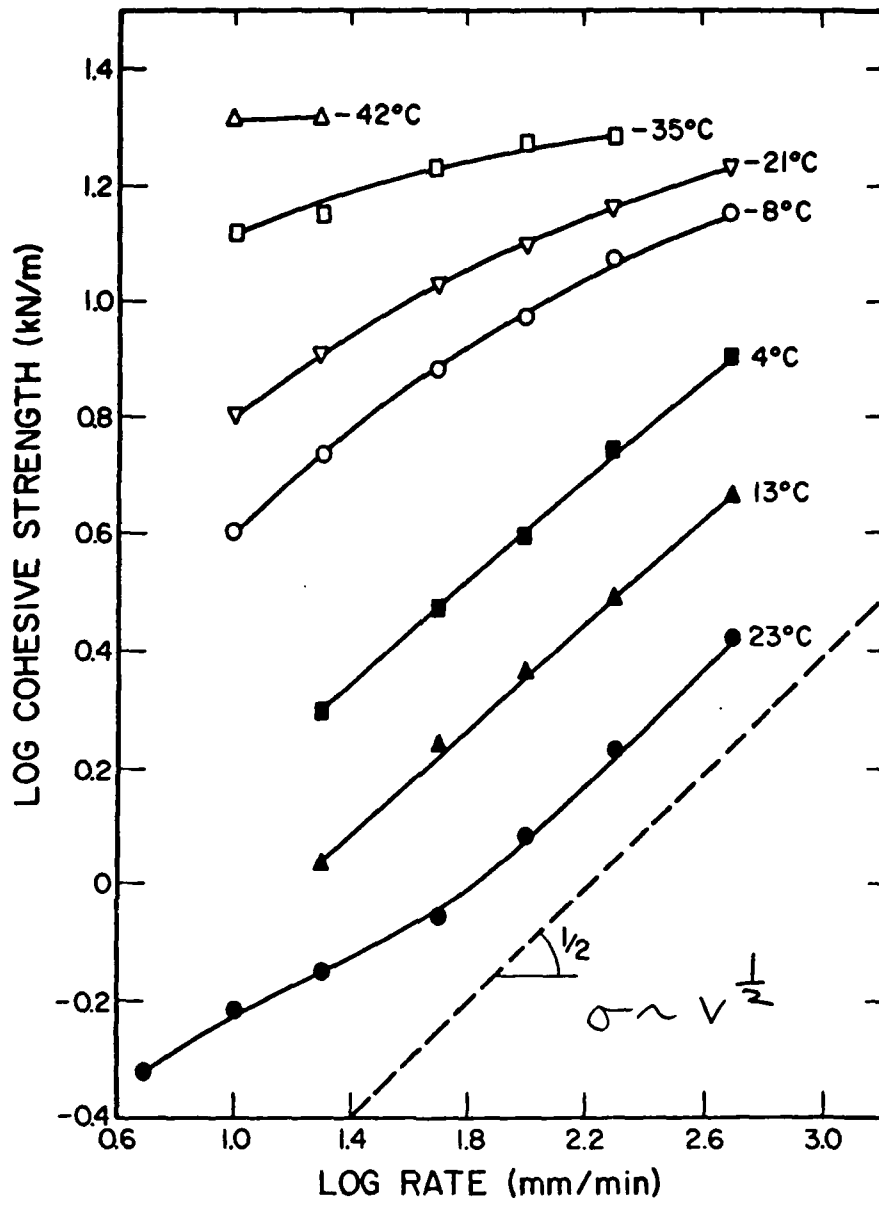


FIG 5 COHESIVE STRENGTH OF SBR RUBBER VS PEEL RATE (WOOL), HAMED DATA

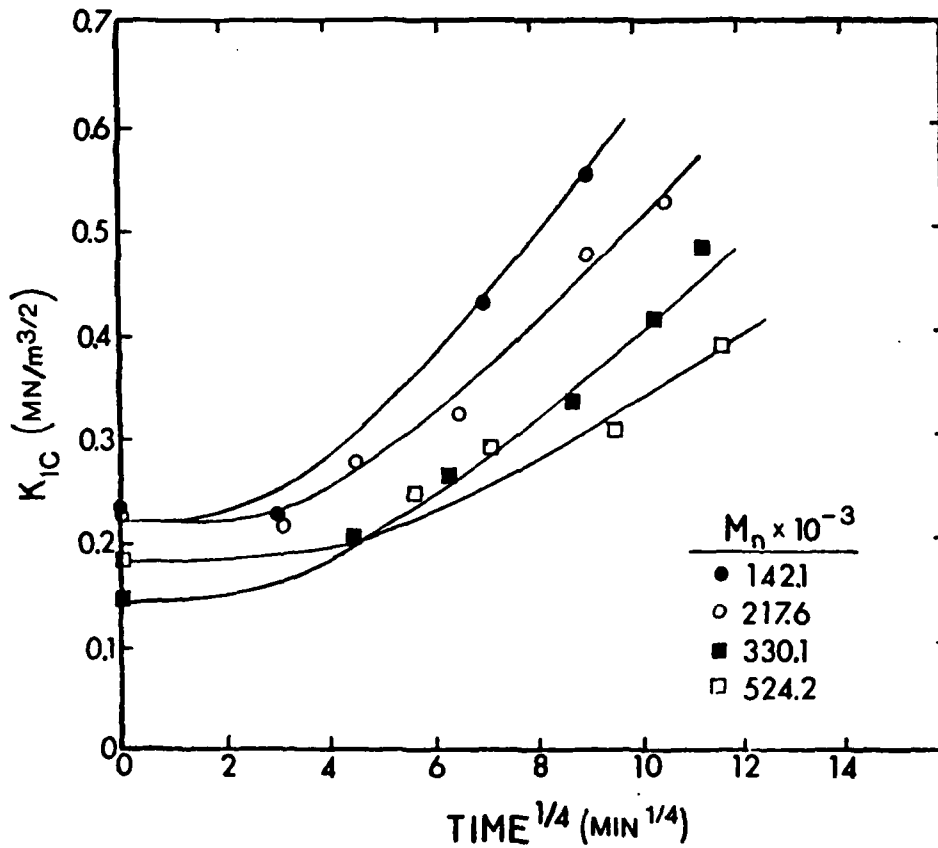
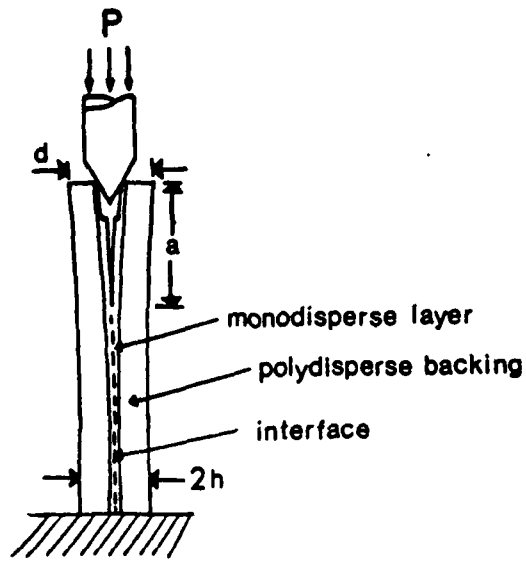


FIGURE 6 The Wedge Cleavage method (top) for determining strength of a healing interface is shown. Results of the critical stress intensity factor versus time to 1/4 power are shown (bottom) for several monodisperse polystyrene interfaces using the two step thermal history.



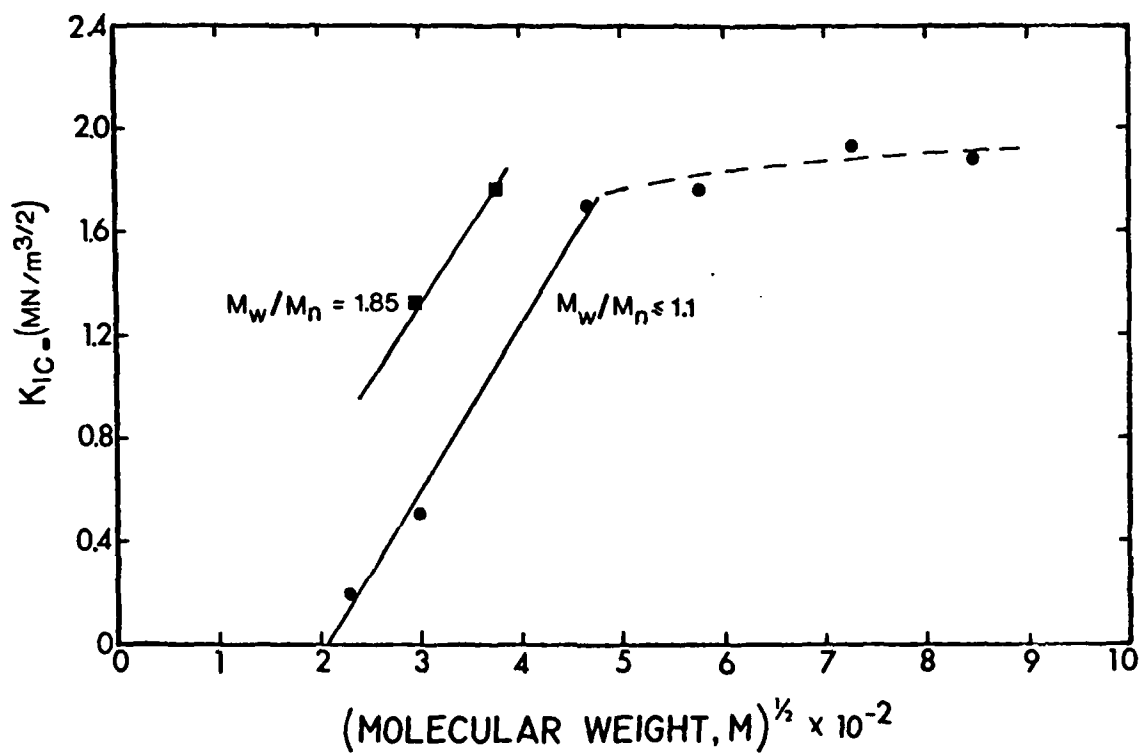


FIG 7 The virgin critical stress intensity factor,  $K_{IC}$ , versus the square-root of molecular weight is shown for compact tension experiments with monodisperse (circles) and polydisperse (squares) polystyrene. Results obtained by Wool and O'Connor.

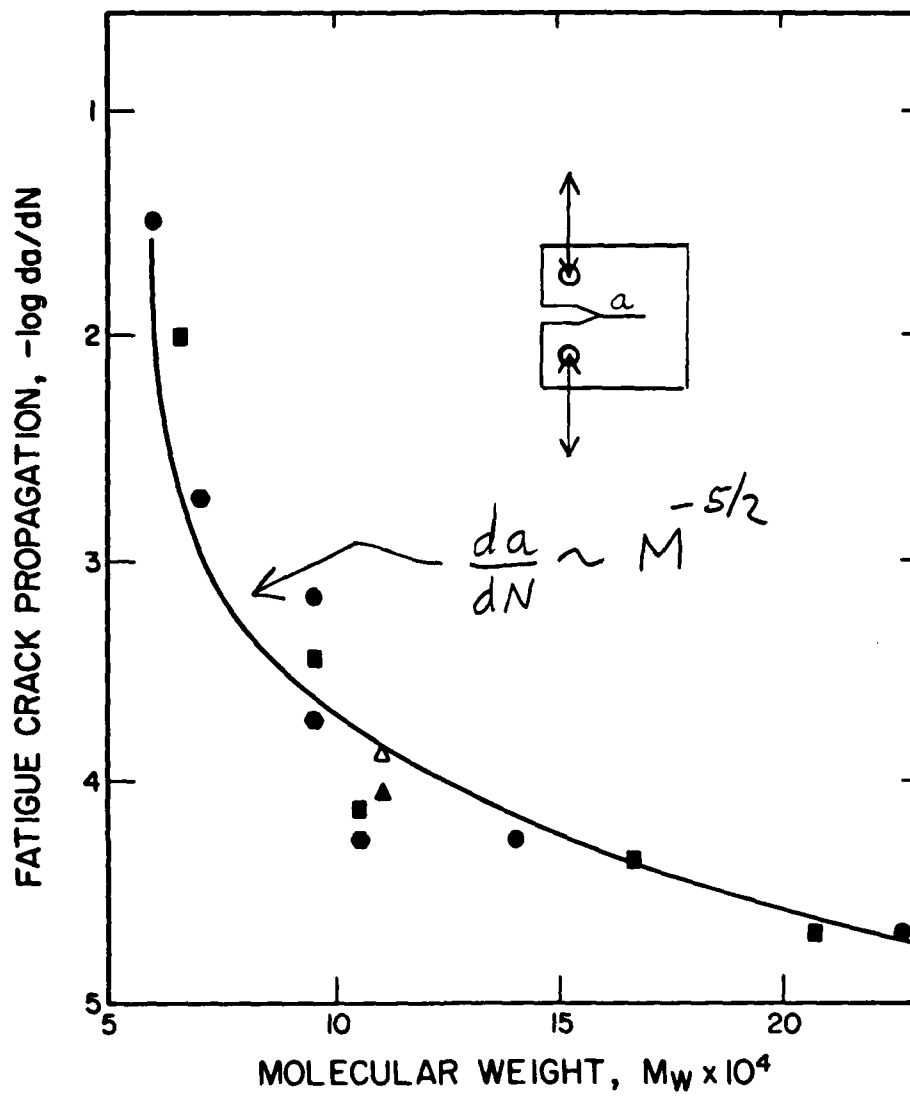


FIG 3 FATIGUE CRACK PROPAGATION RATE DEPENDENCE ON MOLECULAR WEIGHT OF PVC (WOOL), HERTZBERG DATA

Personnel Supported: J. L. Willett

O. J. McGarel

Degrees Granted: Kevin O'Connor, Ph.D.

D. B. Kline, M.S.

D. H. Klosterman, M.S.

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