Theory for the rate of crack closure

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The theory for the constant rate of crack closure was investigated. The aim of this theory is to explain why the rate of crack closure is constant during the wetting stage of healing. Assuming that a surface crack in a material is treated by compression or with solvent, its crack closes up at a constant rate and its shape is independent of time. This approach was based on the Gibbs energy of an atom near the boundary between healed and unhealed zones. The results are in satisfactory agreement with experimental data in the literature. © *1995 American Institute of Physics.*

I. INTRODUCTION

Crack healing or joining two pieces of material may be divided into four categories: thermal healing, mechanical healing (or cold welding), adhesive healing, and solvent healing (or solvent welding). Healing of the first three types was discussed by Jang and Lee.[1] The last type is found in polymers such as poly(methyl methacrylate)[2,3] and polycarbonate.[4] In solvent healing the solvent is introduced to a polymer until healing and then removed. No solvent is expected to remain in the polymer after healing; solvent welded specimens are similar to those that have undergone thermal healing and mechanical healing. Gupta[5] found four stages during thermal healing: (a) continuous regression of the coarse crack from the crack tip or discontinuous pinching off of the crack, (b) cylindrization of the crack, (c) breakup of cylindrical voids into rows of isolated pores, and (d) shrinkage of isolated pores. Dutton[6] observed two steps in thermal healing including stages (a) and (d) reported by Gupta.[5] When copper was annealed, the shrinkage of the grain-boundary cavity was found to be proportional to the reciprocal of the square of the crack length.[7] Roberts and Wrona[8] proposed that the rate of crack healing in UO_2 annealed at temperatures 1600–2000 °C was proportional to the square of the crack length. The distance of void shrinkage was observed to have a linear dependence on the annealing duration in LiF crystals.[9]

Wool and O'Connor[10] discussed thermal healing in polymers in terms of five stages: (a) surface rearrangement, (b) surface approach, (c) wetting, (d) diffusion, and (e) randomization. Kim and Wool[11] proposed a microscopic theory of the diffusion and randomization stages based on the reptation model of chain dynamics described by de Gennes.[12] Prager and Tirrell[13] predicted the number of bridges per unit area spanning the original junction surface as a function of time based on this reptation model.[12] Skewis[14] obtained the tacky strength proportional to $t^{1/4}$ for several polymer-polymer pairs, with t the healing period. Wool and O'Connor,[10] Wool,[15] and Voyutsaskii[16] found that the recovery of fracture stress is proportional to $t^{1/4}$. The mechanical strength is proportional to $t^{1/4}$ during the diffusion stage.

Mechanical healing has been extensively investigated. Conrad and Rice[17] investigated the cohesion of previously fractured metals in ultrahigh vacuum. Hockey[18] observed interfacial mismatch dislocations arising from spontaneous crack healing in brittle materials. Inagaki et al.[19] investigated the energy principle for soda-lime-silica glass to determine the work of fracture related to crack healing. Healing in ionic crystals was observed by Wagner, Lee, and Li,[20] Jang and Lee,[1] Wei, Lee, and Yu,[21] and Bhattacharya.[22] When a single crystal of KCl was subjected to compression, the crack closure was found to be linear with healing duration.[1,21] There are two stages in mechanical healing: (a) the recession of the crack tip and then (b) enhanced mechanical strength. Stage (a) includes wetting and atomic diffusion and stage (b) is attributed to atomic diffusion. This process differs from that of thermal healing proposed by Gupta.[5]

The time independence of the rate of crack recession was observed for single crystals of KCl,[1,21] for poly(methyl methacrylate),[2–3] and for polycarbonate.[4] They have similar initial crack shapes and constant rates of crack closure. These results prompted us to propose a theory of a constant rate of crack closure. The aim of this work is to describe the wetting stage during healing and to compare the theory with experimental results in the literature.

II. THEORY

Crack closure is a wetting phenomenon in which a crack tip moves backward to the location of crack initiation. From a microscopic point of view, healing occurs when an atom jumps from the unhealed area to the healed area across a boundary. Assume that the Gibbs energy of an atom near the crack tip between the healed and unhealed zones is as shown in Fig. 1. In crossing the boundary (or crack tip), the atom must overcome an energy barrier $\Delta G_u (= G_m - G_u)$. After reaching the healed zone, the atom has a low Gibbs energy. The minimal energies of an atom in the unhealed and healed
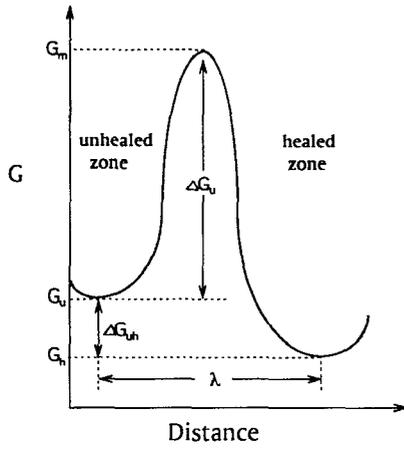
FIG. 1. Gibbs energy diagram of an atom near the boundary between healed and unhealed regions.

zones are G_u and G_h, respectively. That is, the difference in energy between healed and unhealed zones is $\Delta G_{uh}(=G_u-G_h)$.

The atomic flux ($\equiv$ net number of atoms per second) from the unhealed region to the healed region is equal to the difference in the atomic movement to and from the healed zone, which is written as

$$I = Sfe^{-\Delta G_u/kT} - Sfe^{-(\Delta G_u + \Delta G_{uh})/kT}, \tag{1}$$

where S is the number of atoms facing the boundary, f is the atomic vibration frequency, and I is the atomic flux from the unhealed region to the healed region. The parameters k and T are the Boltzmann constant and absolute temperature, respectively. When the atoms jump, they move an average distance λ. The rate of crack closure is defined as

$$v_H = \lambda I/S, \tag{2}$$

where I/S is the average number of jumps per second per atom facing the boundary. Assume ΔG_{uh} is much smaller than kT. Substituting Eq. (1) into Eq. (2), one obtains

$$v_H = \lambda f \frac{\Delta G_{uh}}{kT} e^{-\Delta G_u/kT}. \tag{3}$$

ΔG_{uh} is assumed to be equal to the difference in chemical potential between healed and unhealed zones,

$$\Delta G_{uh} = \mu_h(t) - \mu_u(t), \tag{4}$$

where t is the healing time. The unhealed zone corresponds to the crack surface,[23]

$$\mu_u = -\Omega \gamma_s K, \tag{5}$$

where Ω is atomic volume, γ_s is surface energy density, and K is curvature of the crack surface near the tip. Assume that the recession of the crack tip is self-similar. K is independent of time but not equal to zero. In contrast, μ_h depends on the healing treatment. Two healing methods are considered, as follows

(1) Crack closure due to compression, observed by Jang and Lee:[1] The major contribution to the chemical potential at the healed zone is

$$\mu_h = \sigma_0 \Omega, \tag{6}$$

where σ_0 is the normal compressive stress at the healed zone. During crack closure, σ_0 is independent of time and approximately equal to the remote applied load divided by the instantaneous healed area.[21] Substituting Eqs. (5) and (6) into Eq. (4) one obtains

$$\Delta G_{uh} = \Omega(\gamma_s K + \sigma_0), \tag{7}$$

which is a constant. Substituting Eq. (7) into Eq. (3), one obtains

$$v_H = \frac{\lambda f \Omega(\gamma_s K + \sigma_0)}{kT} e^{-\Delta G_u/kT}. \tag{8}$$

(2) Crack closure due to the polymeric material treated by a solvent:[2–4] Crack closure occurs for a brief duration during solvent treatment, then the hydrostatic stress σ_h at any point is proportional to the concentration of solvent C,[24] according to

$$\sigma_h = -\frac{2}{9} \frac{E\bar{V}}{1-\nu} C, \tag{9}$$

where E and ν are Young's modulus and Poisson's ratio, respectively. $\bar{V}$ is the partial molal volume. The chemical potential of an atom in the healed zone for this case is

$$\mu_h = \frac{2}{9} \frac{E\bar{V}^2}{1-\nu} C. \tag{10}$$

As the concentration depends on the period of polymer immersion in the solvent, μ_h [Eq. (10)] is small compared to Eq. (5). As a result, ΔG_{uh} in the solvent-crack system is written as

$$\Delta G_{uh} = \gamma_s K\Omega. \tag{11}$$

Substituting Eq. (11) into Eq. (3), one finds

$$v_H = \frac{\lambda f \Omega \gamma_s K}{kT} e^{-\Delta G_u/kT}. \tag{12}$$

Both Eqs. (8) and (12) have a common form,

$$v_H = \frac{B}{T} e^{-\Delta G_u/kT}, \tag{13}$$

where

$$B = \lambda f \Omega(\gamma_s K + \sigma_0)/k \tag{14a}$$

for mechanical healing,

$$B = \lambda f \Omega \gamma_s K/k \tag{14b}$$

for solvent-induced crack healing.

According to Eq. (13) v_H has a more complicated expression with temperature than a simple Arrhenius equation. By means of Eq. (13), the activation energy of the rate of crack closure is obtained by plotting $\log(v_H T)$ vs $1/T$.

III. COMPARISON WITH EXPERIMENTAL RESULTS

Cracked specimens of amorphous polymers with small ligament length treated by solvent can be healed without external force in the temperature range 40–60 °C. For example, when the cracked specimen was immersed in carbon
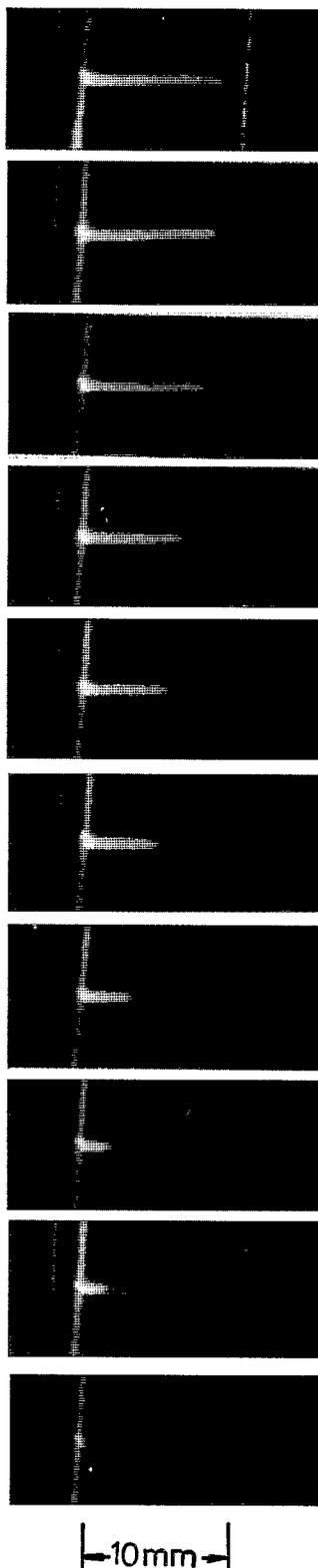
FIG. 2. Continuous pictures of crack healing in polycarbonate treated by carbon tetrachloride. The interval between successive pictures is 20 s.

TABLE I. Rates of crack closure for poly(methyl methacrylate) immersed in methanol v_{HM}, poly(methyl methanylate) immersed in ethanol v_{HE}, and polycarbonate immersed in carbon tetrachloride v_{HC}.

T (°C)	40	45	50	55	60
v_{HC} (10^{-3} mm/s)	9.3	17.8	35.6	91.4	142
v_{HC} (10^{-3} mm/s)	5.2	10	33.7	76.1	165.3
v_{HC} (10^{-2} mm/s)	5	8	16	25	45

crack tip and the rate of crack closure is constant. Similar pictures were observed for the poly(methyl methacrylate)-methanol system[2] and the poly(methyl methacrylate)-ethanol system.[3] During recession of the crack tip, the healing front looks similar regardless of healing duration. That is, the curvature of the crack surface is independent of time. The rate of crack closure as a function of temperature for various polymer systems is listed in Table I. According to Eq. (13) with Eq. 14(b), the curves of $\log(v_H T)$ vs $1/T$ are replotted in Fig. 3. They satisfy the Arrhenius equation and their activation energies are 24, 30, and 38 kcal/mol for polycarbonate-carbon tetrachloride, PMMA-methanol, and PMMA-ethanol systems, respectively. Based on the model of mass transfer derived by Harmon, Lee, and Li,[25] the activation energies of the diffusion coefficient for case I are 30.2 and 40 kcal/mol for methanol and ethanol in PMMA, respectively; the activation energy of velocity for case II is 22 kcal/mol for carbon tetrachloride in polycarbonate. Compared to both activation energies of $(v_H T)$ and mass transfer, the crack closure is controlled by case I transport in PMMA and by case II transport in polycarbonate. The expression for crack length as a function of healing duration obtained by dimensional analysis yielded the same conclusion for the rate-controlling mechanism.

Cracked samples of KCl single crystals with small ligament length were healed by compression at room temperature.[1,2] A set of pictures similar to Fig. 2 was observed to confirm the constant rate of crack closure. Rates of
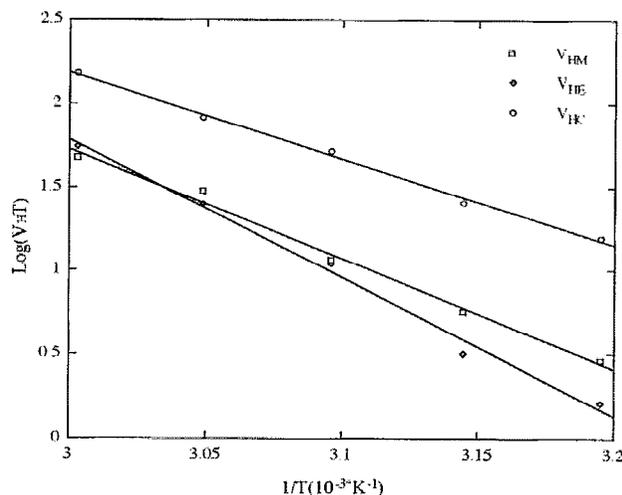

FIG. 3. Curves of rate of crack closure versus reciprocal of temperature in which □, ◇, and ○ represent the PMMA-methanol, PMMA-ethanol, and polycarbonate-carbon tetrachloride systems, respectively.

tetrachloride at 40 °C, a set of consecutive pictures of the recession of the crack tip appears in Fig. 2 for which the interval between successive pictures was 20 s.[4] According to Fig. 2 the nucleus of healing is invariably located at the

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TABLE II. Rate of crack closure v_H of a laser-induced internal crack in LiF crystals at temperatures 630–780 °C (Ref. 9).

T (°C)	630	658	691	712	733	756	780
v_H (10^{-5} μm/s)	1.36	3.23	6.58	12.38	15.70	25.68	49.35

FIG. 4. Plots of rate of healing of a LiF crystal versus the reciprocal of temperature in which □ and ○ correspond to internal and surface cracks measured by Wang et al. (Ref. 9) and Rai and co-workers (Ref. 26), respectively.

crack closure were 12.6×10^{-3} m/s for a cleavage crack and 6.57×10^{-4} m/s for a fractured surface at a crosshead speed 6×10^{-6} m/s, and the counterparts were 2.07×10^{-4} and 0.99×10^{-4} m/s for a cleavage crack and a fractured surface at a crosshead speed 6×10^{-7} m/s. Hence, the morphology of the crack surface has a significant influence on the jumping frequency, jumping distance, and energy barrier from the unhealed zone to the healed zone; the crosshead speed affects the internal stress distribution in the specimen. Because data are insufficient to prove the Arrhenius behavior, further study is necessary.

The healing behavior of rectangular internal cracks in laser-irradiated LiF crystals annealed at temperatures 630–780 °C was examined by Wang et al.[9] The shape of the internal crack was invariably rectangular when the shrinkage rate was constant. The shrinkage rate of the internal crack is tabulated in Table II and plotted in Fig. 4. They derived the formula for shrinkage rate as in Eq. (13) with another expression for B. Their B is related to the radius of the cylinder, but their void is rectangular. According to Fig. 4 the activation energy of the shrinkage rate is 46 kcal/mol. Compared to activation energies for the shrinkage rate and the volume diffusion coefficient of fluoride ion in LiF crystals (42–51 kcal/mol), the rate of healing is controlled by the volume diffusion of the fluoride ion. Rai, Pavinich, and Ahlquist[26] reported that, for a surface crack on single crystals of LiF, the rate of healing was constant and the shape of the surface crack remained the same during healing. The rate of healing as a function of temperature is relisted in Table III and replotted in Fig. 4. According to Fig. 4 the activation energies for rate of healing are 46 kcal/mol at $T > 700$ °C and 20 kcal/mol at $T < 700$ °C, respectively. Compared to activation energies of the rate of healing and volume (42–51 kcal/mol) and surface (25 kcal/mol) diffusion coefficients of fluoride ion in LiF crystals, the rate of healing (surface crack) is controlled by the volume diffusion of the fluoride ion at temperature $T > 700$ °C and by surface diffusion of the fluoride ion at temperature $T < 700$ °C. According to the above observation in thermal healing the location of crack has a significant influence on the rate of healing.

Wool and O'Connor,[10] Wool,[15] and Voyutskii[16] found that the fracture stress is proportional to $t^{1/4}$, t being the period of annealing. This result was well fitted by a model of chain dynamics proposed by Kim and Wool.[11] In their model
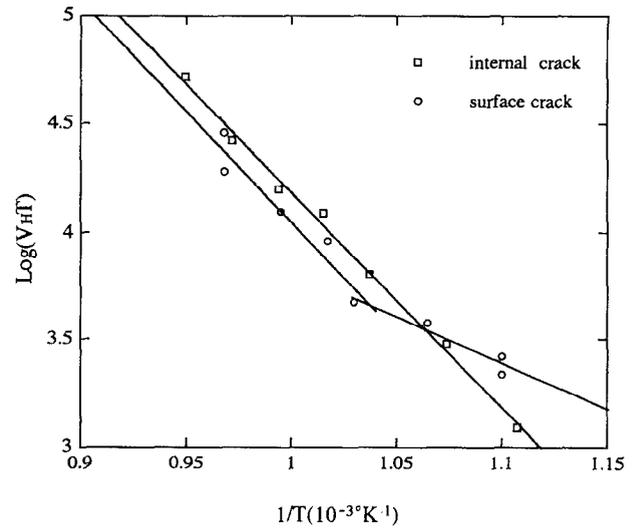
they assumed that the recovery of fracture stress occurs at the stages of diffusion and randomization, not at the stage of wetting. Roberts and Wrona[8] reported that fracture stress is proportional to the square root of time for UO_2 annealed at temperatures from 1600 to 2000 °C. Using their result, they proposed that the rate of healing is proportional to the square of the crack length, but no direct measurement was done. Their data seem to pertain to the second stage of mechanical healing in which the mechanical strength is enhanced. The model proposed by Roberts and Wrona[8] contradicts that proposed by Kim and Wool.[11]

IV. SUMMARY AND CONCLUSIONS

The theory of the constant rate of crack closure is proposed. This theory is used to describe the phenomenon of wetting during healing. When a cleavage crack is treated by compression or with solvent, its tip moves in reverse toward the crack initiation and its shape remains similar regardless of the duration of healing. Based on the Gibbs energy of an atom near the boundary between healed and unhealed zones, the rate of crack closure v_H as a function of temperature T is derived,

$$v_H = \frac{B}{T} e^{-\Delta G_u / kT},$$

where B is a constant independent of T, and ΔG_u is the activation energy or energy barrier. The results are in satisfactory agreement with experimental data from the literature.

TABLE III. Rate of crack closure v_H of a cleavage surface of width w in LiF crystals at temperatures 636–760 °C (Ref. 26). The value within brackets is the crack width w in units of μm.

T (°C)	636	666	698	710	732	760
v_H (10^{-5} μm/s)	2.4(0.48) 2.9(0.50)	4.0(0.44)	4.9(0.43)	12.3(0.48)	12.3(0.48)	27.8(0.32) 18.5(0.49)

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The experimental data were obtained in polycarbonate treated with carbon tetrachloride, poly(methyl methacrylate) treated with methanol and ethanol, single crystals of KCl to which was applied a compressive load, and single crystals of LiF annealed at temperatures 630–780 °C. This model can also predict the rate-controlling mechanism according to a comparison of the activation energy. Wetting is not necessary in conjunction with mechanical recovery.

ACKNOWLEDGMENT

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