

The Effect of Crack Orientation on Ethanol-Induced Crack Healing in Poly (Methyl Methacrylate)

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Abstract

The line- and the cross-crack healing of Poly(methyl methacrylate) (PMMA) under the ethanol treatment at 40 °C~60 °C have been studied. The cross-crack means that the crack plane is vertical to the crack plane of the line-crack. The effective glass transition temperature of PMMA is reduced after the ethanol treatment. Both crack healings only occur at the effective glass transition temperature lower than the transport temperature. Both crack closure rates are constant. The closure rate of the cross-crack is higher than that of the line-crack. The analyses of the surface morphology and mechanical strength show that there are also two stages for crack healing which is wetting and diffusion. The tensile fracture stress of the healed specimen increases with a rise in volume fraction of the absorbing ethanol. The tensile fracture stress of healed PMMA with cross-crack only can be recovered to the virgin material. The tensile fracture stress of healed PMMA with cross-crack is larger than that with the line-crack.

Key Words: Line- and Cross-Crack Healing, Poly (Methyl Methacrylate), Ethanol

1. Introduction

In this few years, crack healing in polymeric materials has been investigated by many researchers, which is related to various polymer engineering problems. Joining or crack healing two pieces of material may be divided into four categories: thermal healing, mechanical healing, adhesive healing, and solvent healing. The last kind was found in polymers such as poly (methyl methacrylate) (PMMA) by Lin et al. [1] and Wang et al. [2] Jud and Kausch [3] proposed to test a series of poly (methyl methacrylate) (PMMA) specimens of different molecular weights and degrees of copolymerization for their crack healing behavior. A theory of crack healing proposed by Wool and O'Connor [4] is widely accepted which includes five stages: surface rearrangement; surface approach; wetting; diffusion and randomization.

Kim and Wool [5] proposed a microscopic model of the diffusion and randomization stages based on the reptation model of chain dynamics. Skewis [6] obtained the data of tack strength vs $t^{1/4}$ for several polymer-polymer pairs. Wool et al. [4,7] and Voyutskii [8] pointed out that the healed fracture stress is proportional to $t^{1/4}$ for polybutadiene and polyisobutylene, where t is the healing time, respectively. Wool [9] described the thermal healing in polymers in details. The phenomena of crack healing in polymeric materials reported in literature were carried out at temperatures above the glass transition temperature T_g . In contrast to thermal healing, solvent healing is undertaken at the treated temperature below the glass transition temperature. The solvent is introduced to a polymer until healing and then removed. Solvent healing was observed in poly (methyl methacrylate) (PMMA) using ethanol and methanol [1,2].

Wool and O'Connor [10] pointed out the crack heal-

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ing temperature below the glass transition temperature of the virgin polymer but they ignored the lowering of T_g by organic solvent treatment in craze or crack zone. Lin et al. [1] suggested two distinctive stages for crack healing based on the recovery of mechanical strength.

The line-crack healing is defined as the crack was induced by a sharpened blade to form a line-crack and then immersed into ethanol treatment to heal. The cross-crack healing is defined as a line-crack healed specimen was cracked again at its vertical direction to become a cross-crack and immersed into ethanol treatment to heal. In this study the change about intersection between line and cross-crack healing is investigated.

2. Experimental

PMMA was obtained from NITTO JUSHI KOGYO Co, LTD. S-O Type in form of a 1 mm thick cast acrylic sheet. Two types of specimens were cut from the sheet. Size of sample is 2 cm \times 1 cm \times 1 mm for crack healing experiment, and piece of 1 cm \times 1 cm \times 1 mm for mass transport experiment.

Heat the specimens to the mass transport temperature and put them into the ethanol system from 40 °C to 60 °C immediately. After a period, take the specimens out from the ethanol system, weigh them using a kern 870 digital balance, and return them to the solvent immediately for continuing the mass transfer process until the amount of absorbed ethanol by PMMA stop changing. The crack healing process contains two types: (1) Line-crack healing process: Before cleaving the specimen, make a groove using a utility knife. Then a crack was induced by a sharpened blade as shown in Figure 1 and propagated along the groove until the ligament length was approximately 1 mm as shown in Figure 2(a) Preheated the specimens with cracks to the desired temperature for ethanol treatment and put them into the ethanol, filled glass bottles which were kept in a thermostaturated water bath at 40 °C–60 °C. (2) Cross-crack healing process: Before cleave the specimens healed from the line-crack, make a groove which is perpendicular to the healed line-crack by using a utility knife as shown in Figure 2(b). Then a crack was induced by a sharpened blade and propagated along the groove until the ligament length was approximately 1 mm. Preheated the specimens with cracks to the desired temperature for ethanol treatment

and put them into the ethanol-filled glass bottles which were kept in a thermostaturated water bath at 40 °C–60 °C. Observe the healing process in the healing time by event capture. Put the healed specimens into vacuum oven at the same temperature as ethanol treatment until there is no residual ethanol in the PMMA.

To prepare a tensile test specimens, remove the place without cleaving by CNC and the specification for tensile test plates is shown in Figure 2(c). The tensile specimen was mounted on a tensile test machine (HUNG TA INSTRUMENT, CO, LTD. TYPEIGHT 9102) and tested at a cross-head speed of 0.001 mm/s at room temperature. The fracture load was recorded and the fracture area equivalent to the healed area was measured using a Nikon Co. OPTIPHOT-100 optical microscope (OM). A continuous set of pictures of progressive healing during the ethanol transport was conducted using a camera of PENTAX Optio 750Z. From the recession of the crack surface with respect to the time interval, we measured the crack closure rate at temperature range 40 °C–60 °C. The crack closure length was obtained by averaging data over three specimens at each temperature. Fractography was also studied using a Nikon Co. OPTIPHOT-100 optical microscope (OM). A series of fracture morphology micrographs for different healing periods were taken. A comparison of fracture surfaces of healed and virgin materials was made.

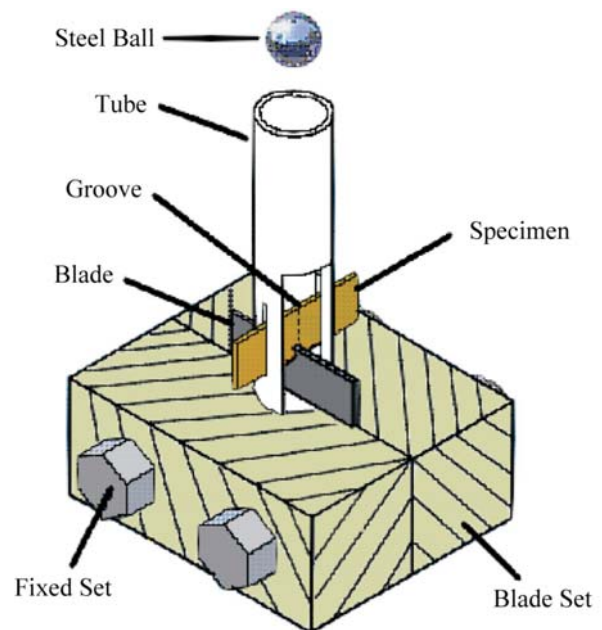


Figure 1. Sample preparation for ethanol treatment.

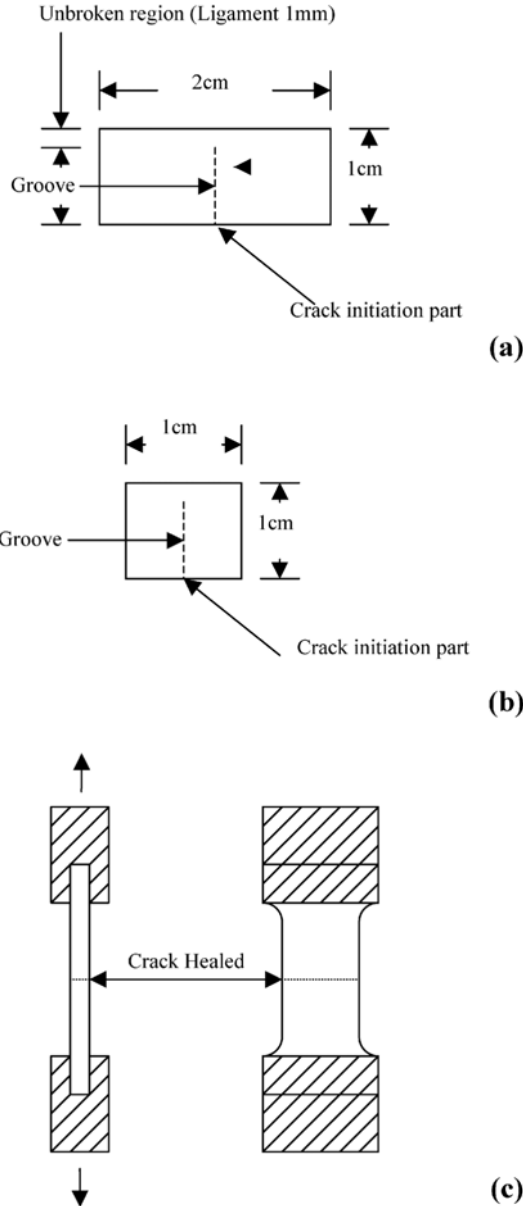


Figure 2. The specimen size for ethanol treatment tensile test: (a) Line crack healing. (b) Cross crack healing. (c) The specimen size for tensile test.

The effective glass transition temperature of PMMA arising from the ethanol was conducted using a SEIKO I-200 differential scanning calorimeter (DSC). The specimens were immersed in ethanol until saturated at temperatures of 40 °C–60 °C. Each specimen saturated with ethanol, having total weight of about 10 mg, was enclosed in a regular aluminum pan and moved into the DSC. The aluminum pan was sealed to keep the ethanol in the PMMA. The specimen was heated from 20 °C to 120 °C with a heating rate of 10 °C/min.

3. Results and Discussion

3.1 Ethanol Transport

The data of ethanol transport in PMMA in the absence of a crack are shown in Figure 3. These curves of weight gain versus transport time can be curve-fitted by a model proposed by Harmon et al. [11,12]. Assuming that ethanol transport is accounted for by case I, case II, and anomalous diffusion, the characteristic parameters corresponding to case I and case II are D for the diffusion coefficient and v for velocity, respectively. If the concentration at the boundary is constant at all diffusion times (t) and initially no ethanol is inside the PMMA, then the weight gain M_t can be written as

$$\frac{M_t}{M_\infty} = 1 - 2 \sum_{n=1}^{\infty} \frac{\lambda_n^2 [1 - 2 \cos \lambda_n e^{-v l / 2D}]}{\beta_n^4 \left[1 - \frac{2D}{v l} \cos^2 \lambda_n \right]} e^{-\beta_n^2 D t / l^2} \quad (1)$$

where

$$\lambda_n = \frac{v l}{2D} \tan \lambda_n \quad (2)$$

$$\beta_n^2 = \frac{v^2 l^2}{4D^2} + \lambda_n^2 \quad (3)$$

And $2l$ is the total length of specimen. M_∞ is equal to the

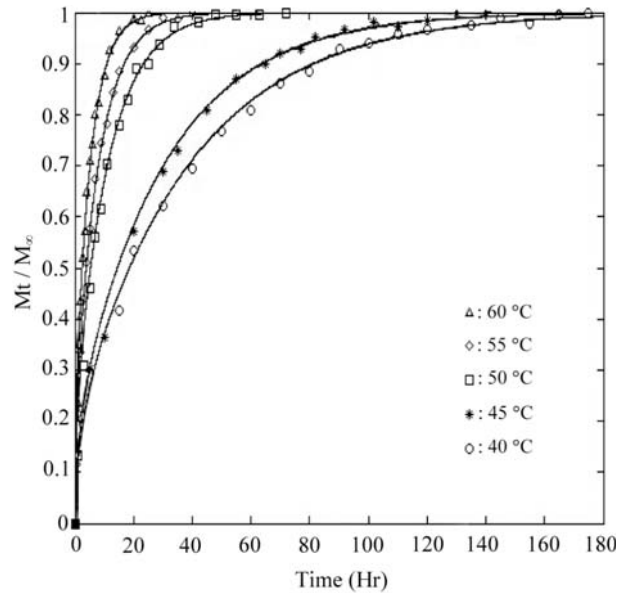


Figure 3. Ethanol transport uncracked at various temperatures (40 °C–60 °C).

equilibrium weight gain, obtained at time approaching infinity. The solid line is plotted using Eq. (1). It was found that the theoretical curve is in good agreement with the experimental results. Both D and v for different temperatures are listed in Table 1, Both D and v obey the Arrhenius equation [$D = D_0 \exp(-E_D/RT)$; $v = v_0 \exp(-E_v/RT)$] and their activation energies E_D and E_v are 21.12 kcal/mole and 23.59 kcal/mole, respectively. The solubility ESC is defined as mass of saturated ethanol in the specimen divided by mass of specimen before ethanol uptake. The solubility as a function of temperature is listed in Table 1. The solubility satisfies van't Hoff's equation

$$ESC = ESC_0 \exp(\Delta H/RT) \quad (4)$$

where ESC_0 and ΔH are pre-exponent factor and heat of mixing, respectively. Using Eq. (4) with Table 1, we calculate the heat of mixing $\Delta H = -13.12$ Kcal/mole. The negative sign of ΔH indicates the mass transport in PMMA is an exothermic process.

3.2 Sharp Front

Figure 4 is pictures of sharp fronts healed from line-crack with the condition of PMMA in the ethanol system at 60 °C. The time interval between two successive pictures is 0 min, 20 min, 40 min, 60 min, 80 min, 100 min, and 110 min, respectively. It is found that the displacement of the sharp front rises in time and both sharp fronts meet at the center before the saturated ethanol permeates the PMMA. The reason to form the sharp front is the change of optical density from the outer swollen zone to the inner glassy

zone. The refractive index n of swollen zone is lower than glassy zone ($n = 1.5$) which is resulted in the low refractive index (about 1.36) of ethanol. The optical density of glass-to-liquid transition changes greater than glass-to-rubber transition. Thus the optical density of the swollen zone is different from the glassy zone. In summary, the major mechanism of sharp front is glass-to-liquid transition.

Figure 5 is pictures of sharp fronts healed from cross-crack with the condition of PMMA in the ethanol system at 60 °C. The time interval between two successive pictures is 0 min, 20 min, 40 min, 60 min, 80 min, 100 min, and 110 min, respectively. As the pictures can be seen, chevron or inward concave shape appears at the healed line-crack on sharp front and the place far away from the healed line-crack remains straight line. The relationship between the sharp front and the healed cross-crack is shown in Figure 5(h). The slope of inward concave curve decreases with time until the two sharp front meet at the center before ethanol is saturated in PMMA, and left the healed line-crack which is shown in Figure 5(g). The sharp fronts of the healed cross-crack go forward faster than the healed line-crack and the sharp fronts meeting at the center happen faster than the line-crack as shown in Figure 6. For the reason of that the mass transfer type of superposition at the healed line-crack region is faster than any other areas. Additionally, the speed of the sharp front increases with the increasing transport temperature.

3.3 Crack Closure Rate

The line- and cross-cracked specimen with ligament length of about 1mm was immersed into ethanol at temperatures of 40 °C~60 °C The healed crack closure leng-

Table 1. The effective glass transition temperatures, D and v for the ethanol transport in PMMA, the initial time of stage II exponent m_L , m_C , E_D and E_V for activation energies of D and v , and ΔH for the heat of mixing, respectively

T (°C)	40	45	50	55	60
T_{geff} (°C)	14.63	12.38	10.22	9.11	8.31
$D \times 10^8$ (cm ² /s)	0.489	0.675	1.76	2.53	3.76
$V \times 10^6$ (cm/s)	0.286	0.656	1.356	2.36	2.79
m_L	1.9803	1.7418	1.5337	1.5285	1.5024
m_C	1.5209	1.4990	1.0284	0.7372	0.1564
t_L (sec)	7,560	5,400	4,320	1,800	720
t_C (sec)	5,040	3,960	3,240	1,296	648
E_D (kcal/mole)			21.12		
E_V (kcal/mole)			23.59		
ΔH (Kcal/mole)			-13.12		

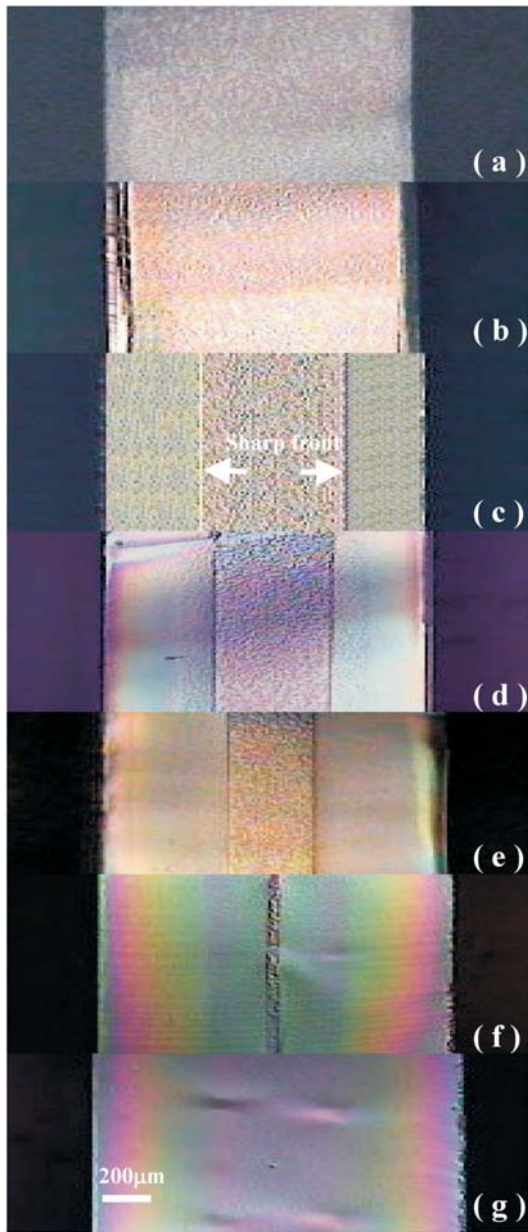


Figure 4. A set of continuous micrographics of sharp front in PMMA at 60 °C for periods of (a) 0 min, (b) 20 min, (c) 40 min, (d) 60 min, (e) 80 min, (f) 100 min, (g) 110 min.

th is decreased with increasing time. Figures 7(a) and 7(b) show the continuous pictures of healed line- and cross-crack during mass transfer at 50 °C. The time interval between two successive pictures is 12 and 9 min, respectively. Figure 8 shows the plot of $\text{Log}(V_{\text{LH}}T)$ and $\text{Log}(V_{\text{CH}}T)$ versus $1/T$. V_{LH} and V_{CH} represents healed line- and cross-crack closure speeds. In Table 1, the crack closure speed is constant with ethanol system at 40 °C~60 °C. Then t_{LC} and t_{CC} mean the fully healing time of

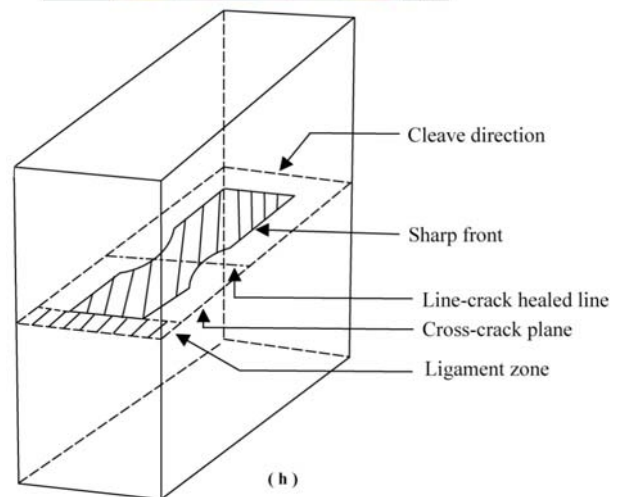
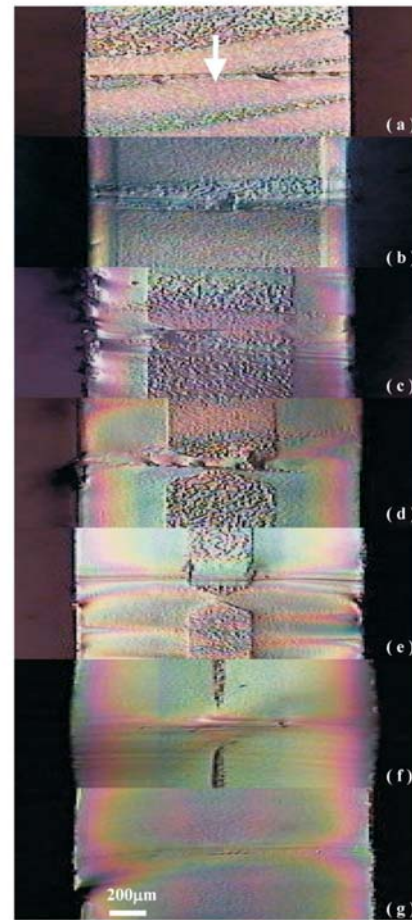


Figure 5. A set of continuous micrographics of sharp front in crack healed PMMA at 60 °C for periods of (a) 0 min, (b) 20 min, (c) 40 min, (d) 60 min, (e) 80 min, (f) 100 min, (g) 110 min, (h) the change of Cross-crack healed of PMMA in ethanol.

line-crack and cross-crack, respectively. According to the study of Wu, the surface energy density of PMMA (γ) does not change significantly in the range of temperature

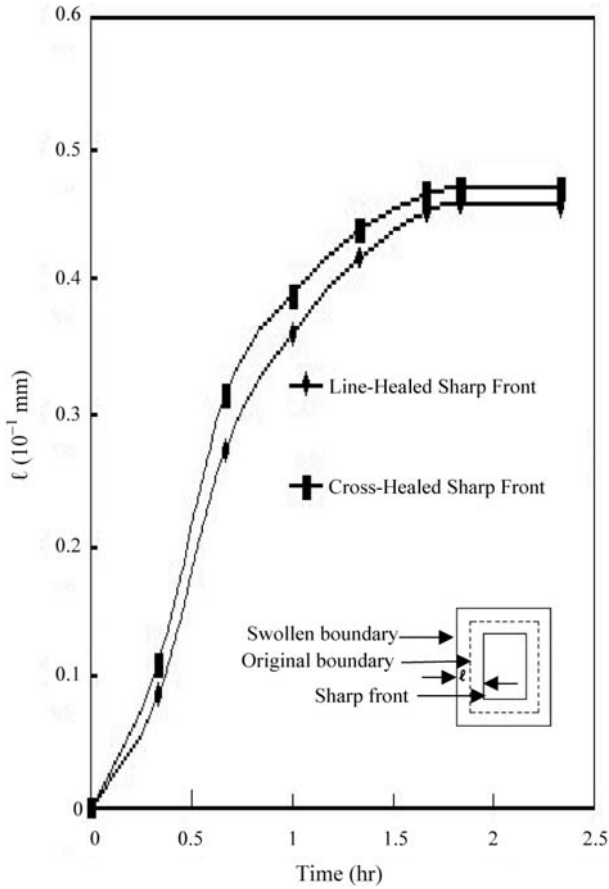


Figure 6. The displacement of sharp front as a function of mass transport time at 60 °C. A schematic of the sharp front in the specimen is shown in the inset where the dashed line is the boundary of specimen before mass transport. Outer and inner coarse lines stand for the boundary of specimen and the sharp front at time t , respectively.

from 40 °C~60 °C. Thus, the crack length l_c can be expressed as a function of time t [13],

$$l_c = l_o - \frac{Dra}{kT}t = l_o - V_H t \quad (5)$$

Where l_o is the original crack length, a is characteristic length of ethanol penetrating into PMMA, V_H is the crack closure speed and satisfies the modified Arrhenius equation: $V_H = (U/T)\exp(-E_H/RT)$, where U and E_H are the pre-exponent factor and activation energy. The corresponding activation energy (E_H) of the line- and cross-crack healing is equal to 20.06 kcal/mole and 20.22 kcal/mole, respectively and comparing to PMMA sample with ethanol system at 40 °C~60 °C, we could know that the crack healing is contributed by case I

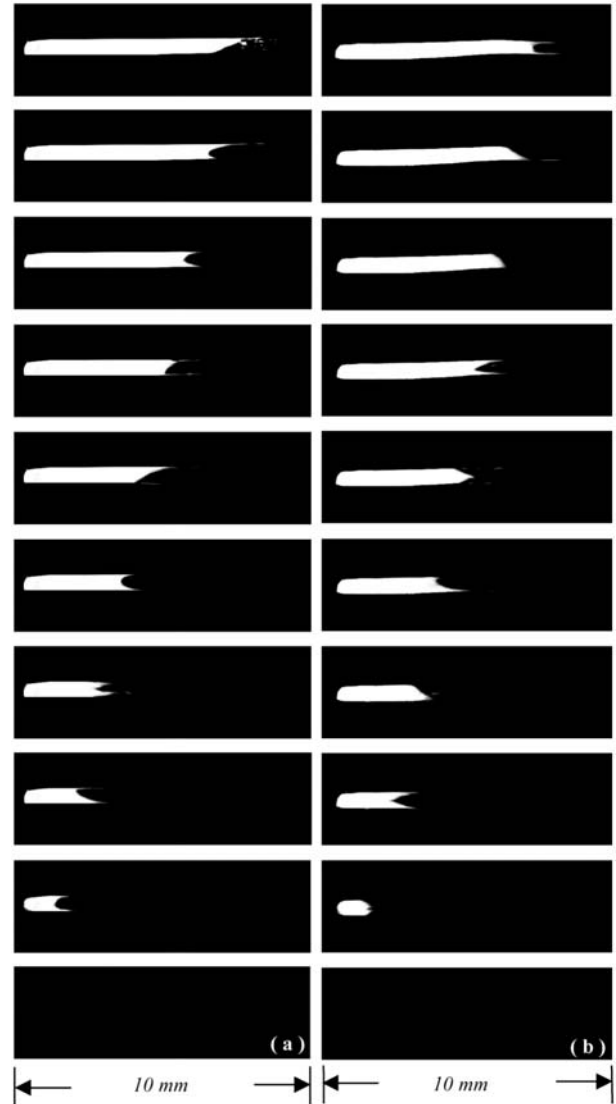


Figure 7. Plot (a) and (b) to show the continuous pictures of healed line- and cross-crack during mass transfer at 50 °C. The time interval between two successive pictures is 12 mins and 9 mins, respectively.

from $E_D = 21.12$ kcal/mole. Comparing slopes of $\text{Log}(V_{LH}T)$ and $\text{Log}(D)$ to $1/T$, it is found that V_{LH} is proportional to (D/T) . Note that based on the Einstein relation, the mobility is equal to D/kT , where k is the Boltzmann constant. This implies that the crack closure rate is determined by the unusual mass transport. These results differ from the healing equation proposed by Lin et al. [1]. Under an ideal condition, perfect material could be healed without any extra force. Thus the surface energy density, γ of PMMA is proportional to the crack closure rate.

We find that the sample of cross-crack has a shorter

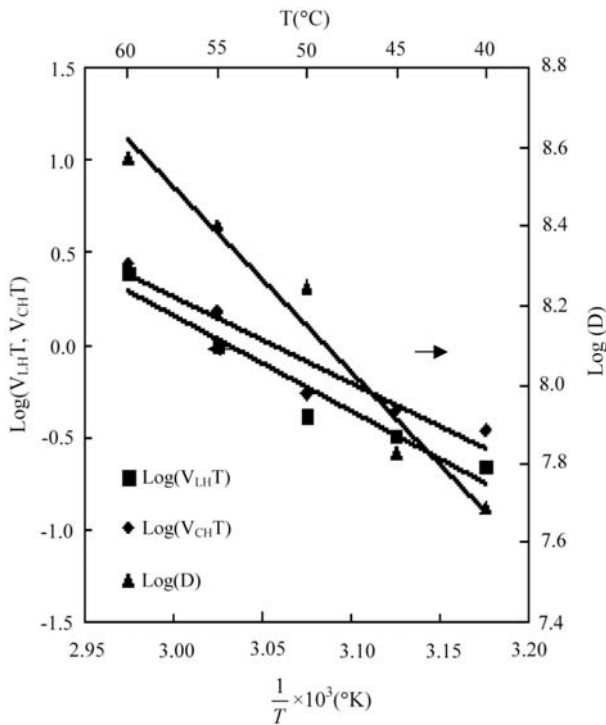


Figure 8. Plot of $\text{Log}(V_{LH}T, V_{CH}T)$ and $\text{Log}(D)$ as function of $(1/T)$. The units of $(V_{LH}T, V_{CH}T)$ and D are $\text{mm}^2/\text{s}^\circ\text{K}$ and cm^2/s .

healing time than line-crack in Table 1. This is because superposition of the mass transfer along with line-crack during the process of cross-crack healing. The mass transfer of cross-crack induced stress which is higher than the stress induced during mass transfer of line-crack. PMMA sample in the ethanol system at 40°C – 60°C performs a healing mechanism by lowering the glass transition temperature. Due to the activated molecular chain on crack surface during ethanol treatment, the effective glass transition temperature is lower than the mass transport temperature as shown in Table 1. It is derivable that self-diffusion of molecular chain would happen when the effective glass transition point of PMMA is lower than the mass transporting temperature. Crack self-healing in PMMA is produced immediately after ethanol mass transfer finished and self-diffusion of molecular chain near the crack surface is active [3], and this active surface is called solvent affected zone (SAZ). Owing to reptation of molecule, interdiffusion happens to cause crack self-healing [5]. On the other hand, molecular chain self-diffusion would not happen when the effective glass transition temperature is higher than the mass transport temperature.

3.4 Recovery of Tensile Fracture Strength

On the basis of the recovery of mechanical strength, the healing process is divided into two stages. The first stage (I) is the wetting occurring on two crack closure surfaces and the crack closure rate is constant during progressive healing process. The second stage (II) is that due to interdiffusion, which enhances the quality of healing behavior, begins when the crack is completely closed. Wool and O’Connor [4] stated that the extent of healing is defined by the recovery of mechanical strength which is affected by wetting and diffusion. The tensile fracture stress σ_F as a function of healing time at different temperatures of ethanol treatment is shown in Figure 9 and Figure 10.

The tensile fracture stress is defined as the fracture load divided by the actually healing area. According to Figure 9 and Figure 10, at any transport temperature, the reactive incubation times t_L and t_c of the line- and cross-crack, respectively always exist as shown in Table 1. The reactive time increases with decreasing healing temperature. Second, there are two stages for fracture stress at

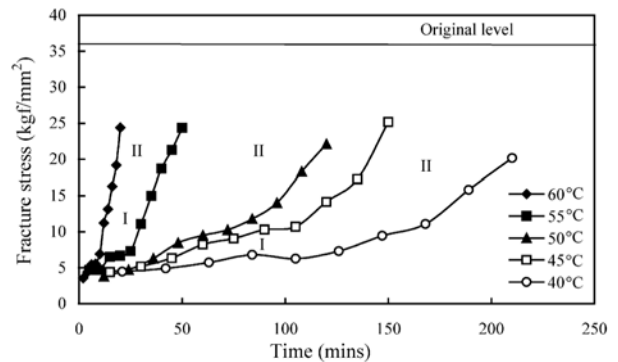


Figure 9. Plot of line-crack healing fracture stress versus healing time.

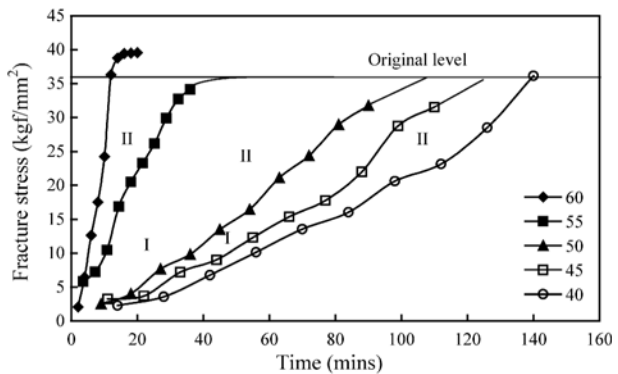


Figure 10. Plot of cross-crack healing fracture stress versus healing time.

low temperatures, for instance, 40 °C and 45 °C. Stage I corresponds to the recession of the crack surface. Stage II is that interdiffusion of active molecule enhances recovery of tensile strength. It is found that the periods of both stages decrease with increasing healing temperature. When the healing temperature is equal to or larger than 50 °C, the incubation time covers stage I. As a result, only stage II is shown. Third, all samples can be recovered to the original mechanical strength by ethanol treatment at temperatures of 40 °C–60 °C. According to Jud, et al. [14], the fracture toughness K_{II} in the interface increases with healing time t , as $K_{II} \propto t^{1/4}$ as predicted by the diffusion model. Those healing phenomena reported by Jud et al. [14] have the common characteristics that the glass transition temperature was kept constant during the healing treatment. Therefore, the self-diffusion coefficient of molecular chains in the PMMA is constant at the transport temperature. In this paper, the curves corresponding to stage II arise from diffusion and it is notable that t_L and t_c is the initial time of stage II, as shown in Figure 11 (for line-crack healing) and Figure 12 (for cross-crack healing). It can be seen from Figure 11 (for line-crack healing) and Figure 12 (for cross-crack healing) that the recovery of fracture stress σ_F increases with healing time $t-t_c$ as $\sigma_F \propto (t-t_c)^m$. The values of m and t_c for different temperatures are tabulated in Table 1. The value of m decreases with increasing temperature. However, just only value of 60 °C for cross-crack healing is smaller than $1/4$. This is because the effective glass transition temperature is a function of the amount of ethanol at the same transport temperature in PMMA [15]. In the other words, effective glass transition temperature is not constant during the healing process. Also, wetting and diffusion are convoluted. During the healing treatment the amount of ethanol in PMMA increases with time. The self-diffusion coefficient of PMMA chains is dependent on the glass transition temperature. Therefore, the self-diffusion coefficient of PMMA chains is a function of time during the healing treatment. Thus, self-diffusion of PMMA chains is anomalous. It can be seen from Table 1. Thus, the slope of $\text{Log } \sigma_F$ versus $\text{Log } (t-t_c)$ corresponding to 60 °C is 0.1564 for cross-crack healing as listed in Table 1.

3.5 Fractography

It has been mentioned previously on above section

that the healing process consists of two stages based on recovery of mechanical strength. This section is confirmed the existence of both stages by means of fractography. The self-similar crack healing was along the opposite direction to the crack propagation, and serial pictures of optical microscopy prove that tensile fracture surface appears from the right wave front curve to the left. Figures 13 a–d (for line-crack healing) and Figures 14 a–e (for cross-crack healing) correspond to stage I of crack healing at 60 °C, respectively. This is due to pure wetting controlled by case I ethanol transport. From Figure 13 and Figure 14, tensile fracture surface at stage I is a co-planar with original fracture surface. Based on reptation model, the molecular chain near or on the crack interface would be activated by ethanol, so the second bond energy entangle with the interface freely. Thus the distance from stage of wetting healing to interdiffusion of molecular chain is short. It is found that the chevron shape of crack propagation is opposite to

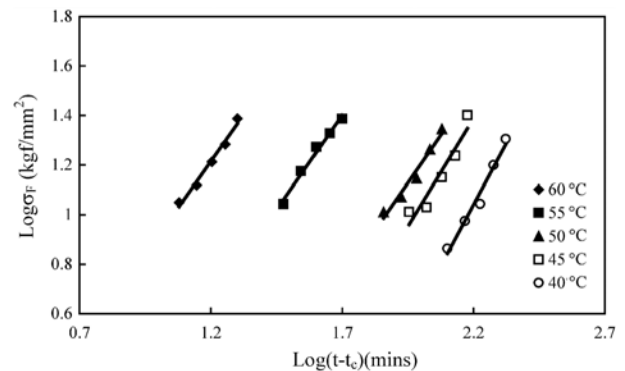


Figure 11. Plot of line-crack healing fracture stress versus healing time for stage II where t_c is the beginning time of stage II.

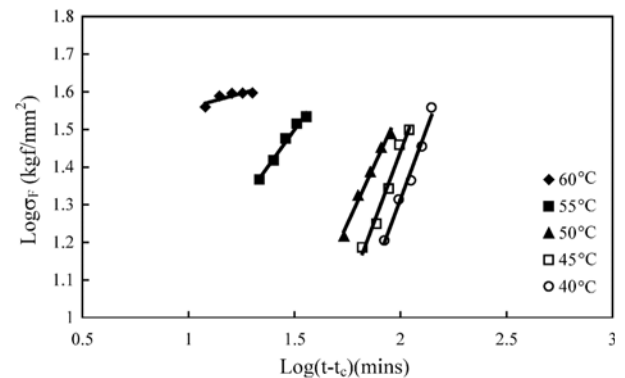


Figure 12. Plot of cross-crack healing fracture stress versus healing time for stage II where t_c is the beginning time of stage II.

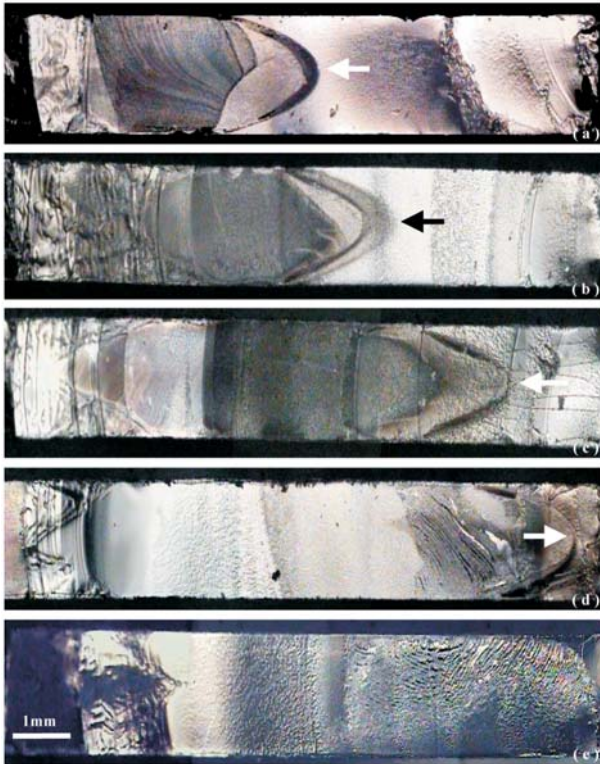


Figure 13. Line-crack healing with ethanol treatment at 60 °C. The time interval between two successive pictures is 2 mins.

the parabolic shape of crack healing. Tensile fracture surface and original fracture surface at stage I are coplanar.

Figure 13e (for line-crack healing) and Figure 14f (for cross-crack healing) show the fractography of healing PMMA at the beginning of stage II. There is no healing front at this stage. Comparing Figure 13a–d to 13e (for line-crack healing) and Figure 14a–e to Figure 14f (for cross-crack healing), the fracture surface morphology of stage II is completely different from stage I. The fracture surface of the healed specimen of stage II seems not to appear at the original crack surface, perhaps because the interpenetration distance of minor chains is large enough to destroy the original crack surface via diffusion. Comparing the fracture surfaces of healed specimens of stage II as shown in Figure 13e (for line-crack healing) and Figure 14f (for cross-crack healing) with that of virgin PMMA, both fracture surfaces have similar morphologies. This is indirect evidence that mechanical strength of the healed specimen of stage II could be recovered to that of the virgin PMMA by ethanol treatment and the tensile fracture stress of cross-

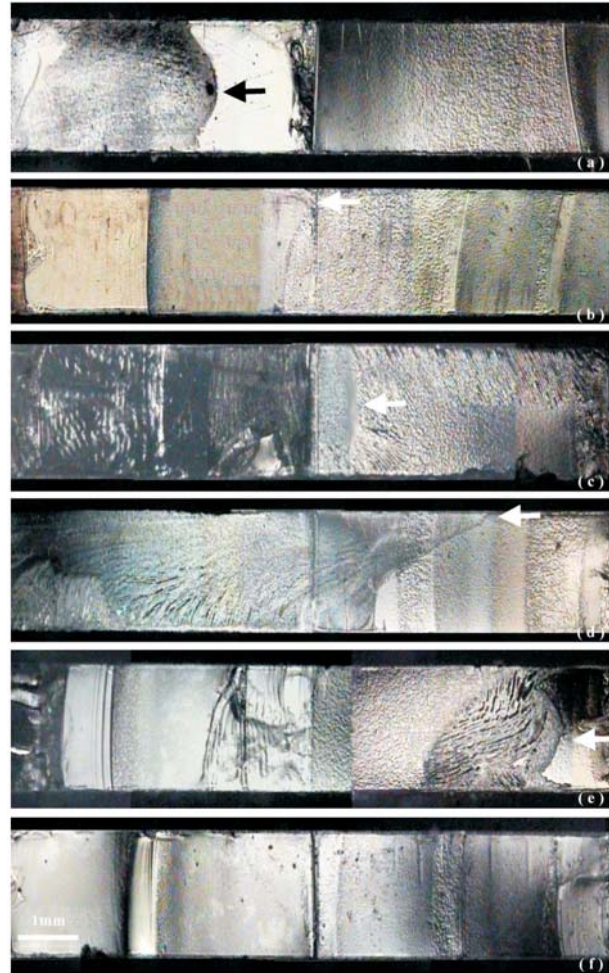


Figure 14. Cross-crack healing with ethanol treatment at 60 °C. The time interval between two successive pictures is 1min and 48 sec.

crack is higher than line-crack for the reason of interdiffusion and entanglement of twice healed molecular chain on crack surface and second surface higher than once.

4. Summary and Conclusion

The line-crack and the cross-crack healing in PMMA treated by ethanol treatment at 40 °C–60 °C have been investigated. Some important conclusions are summarized as follows:

- (1) Sharp front with straight line is observed after ethanol transport to PMMA with line-crack. On the contrary, shape of chevron or inward concave appears in PMMA with cross-crack.
- (2) The healing process can be divided into two stages

based on the recovery of mechanical strength. Stage I represents wetting. Stage II starts after the stage I ends and the activated molecular chain begins to interdiffuse, and enhances the mechanical strength of healing.

- (3) The crack closure rate of stage I observed by optical means is constant at a fixed mass transport temperature. The crack healing rate of cross-crack at stage I is faster than that of line-crack.
- (4) By comparing tensile fracture stresses, one finds that the fracture surface at stage I of crack healing is coplanar to the original crack closure surface. However, the fracture surface at stage II of crack healing occurs through a zone incorporating the original healed surface and appears like the virgin fracture surface.
- (5) Both stages of the healing process are confirmed by sequential pictures of crack surface morphology and fracture tests.
- (6) Only cross-crack healed specimen treated with ethanol can recover to the virgin material. The tensile fracture stress of cross-crack healed specimen is more than line-crack healed specimen.

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