

# The Effect of Crack Orientation on Methanol-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 methanol 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 methanol 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 methanol. The tensile fracture stress of healed PMMA with line- or cross-crack 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), Methanol

## 1. Introduction

In recent years, crack healing in polymeric materials has been investigated by many researchers, which is related to various polymer engineering problems. Jud and Kausch [1] examined 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 [2] is widely accepted which includes five stages: surface rearrangement; surface approach; wetting; diffusion and randomization. Kim and Wool [3] proposed a microscopic model of the diffusion and randomization stages based on the reptation model of chain dynamics. Skewis [4] obtained the data of tacky strength vs  $t^{1/4}$  for several polymer-polymer pairs. Wool and O'Connor [2,5] and Voyutskii [6] 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 [7] described the thermal healing in polymers in details. 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 methanol and ethanol [8,9].

Wool and O'Connor [10] pointed out the crack healing 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. [11] observed the crack healing in PMMA by methanol treatment at 40 °C ~60 °C. A model proposed by Harmon et al. [12,13] was applied to analyze the methanol transport by Lin et al. [11]. Lin et al. [11] suggested two distinctive stages for crack healing based on the recovery of mechanical strength.

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These observations prompt us to investigate crack healing with line and cross type in PMMA by methanol treatment. The line-crack healing is defined as the crack was induced by a sharpened blade to form a line-crack and then immersed into methanol 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 methanol 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 × 1 cm × 1 mm for crack healing experiment, and piece of 1 cm × 1 cm × 1 mm for mass transport experiment.

Heat the specimens to the mass transport temperature and put them into the methanol system from 40 °C to 60 °C immediately. After a period of mass transportation time, take the specimens out from the methanol 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 methanol 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 methanol treatment and put them into the methanol-filled glass bottles which were kept in a thermostated 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 methanol treatment and put them into the methanol-filled glass bottles which were kept in a thermostated 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 to be desorption at the same temperature as methanol treatment until there is no residual methanol 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. TYPE:HT 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 methanol 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 ma-

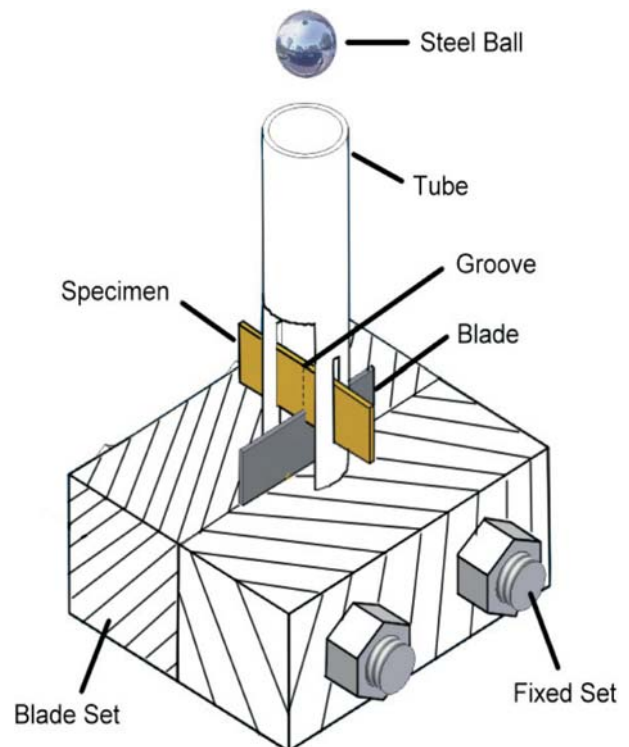
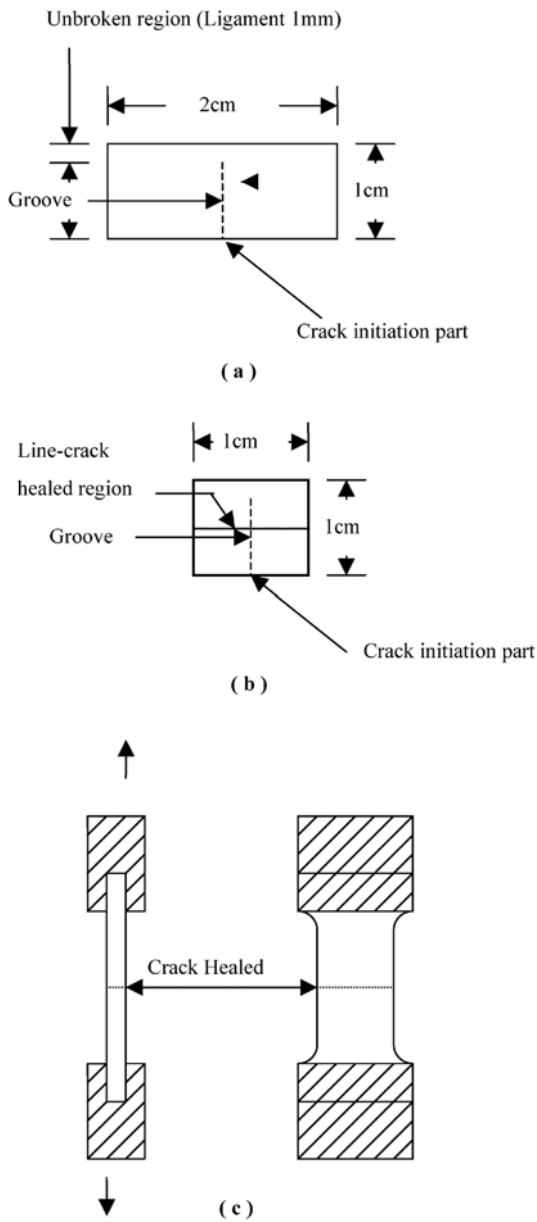


Figure 1. Sample preparation for methanol treatment.



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

terials was made.

The effective glass transition temperature of PMMA arising from the methanol was conducted using a SEIKO I-200 differential scanning calorimeter (DSC). The specimens were immersed in methanol until saturated at temperatures of 40 °C–60 °C. Each specimen saturated with methanol, 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 methanol 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 Methanol Transport

The data of methanol 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. [12,13]. Assuming that methanol 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 methanol is in inside the PMMA, then the weight gain  $M_t$  based on one-dimensional model [25] can be written as

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

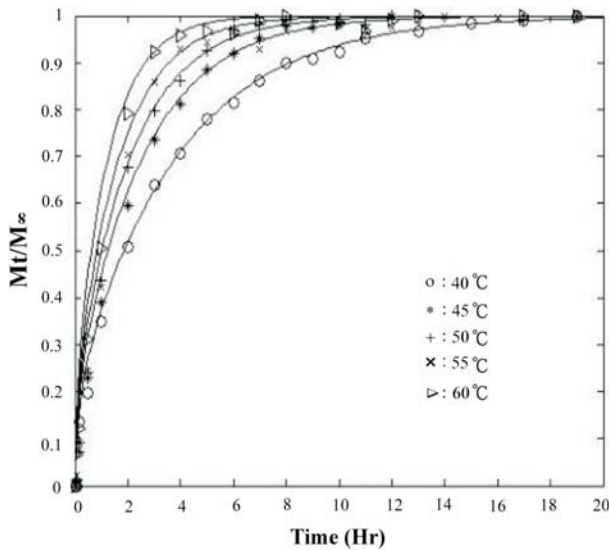
where

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

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

And  $2l$  is the total length of specimen.  $M_\infty$  is equal to the 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 14.85 kcal/mole and 8.81 kcal/mole, respectively. The solubility ESC is defined as mass of saturated methanol in the specimen divided by mass of specimen before methanol uptake. The solubility as a function of temperature is listed in Table 1. The solubility satisfies van't Hoff's equation

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



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

where  $ESC_0$  and  $\Delta H$  are pre-exponent factor and heat of mixing, respectively. Using Eq. (4) with Table 1, we calculate the heat of mixing  $\Delta H = -4.54$  Kcal/mole. The negative sign of  $\Delta H$  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 methanol system at 60 °C. The time interval between two successive pictures is 5 min, 10 min, 20 min, 30 min, and 40 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 methanol 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 1.33) of methanol. 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 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 methanol system at 60 °C. The time interval between two successive pictures is 5 min, 10 min, 20 min, 30 min, and 40 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(g). The slope of inward concave curve decreases with time until the two sharp front meet at the center before methanol is saturated in PMMA, and left the healed line-crack which is shown in Figure 5(f). 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.

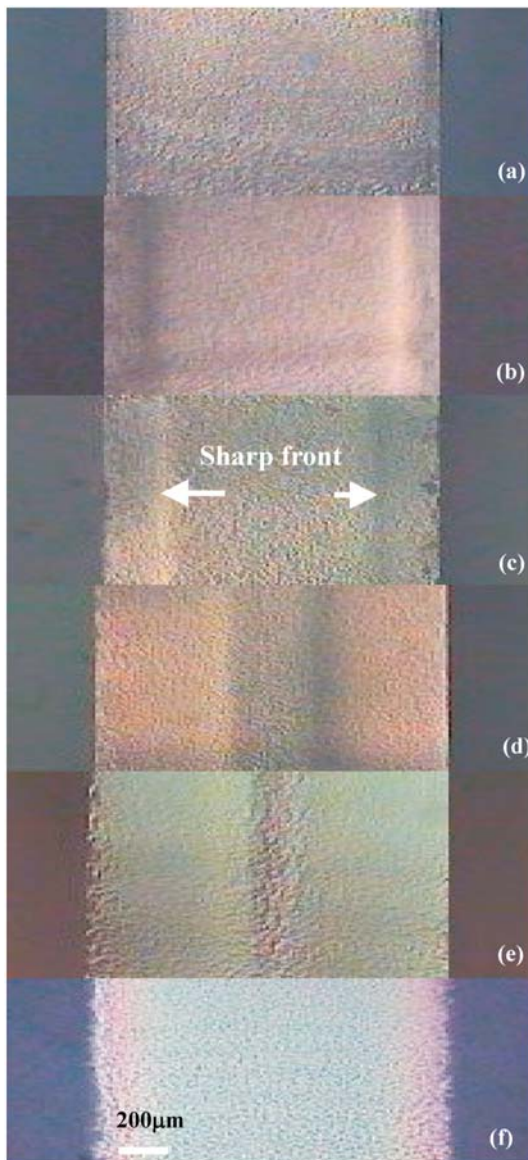
### 3.3 Crack Closure Rate

The line- and cross-cracked specimen with ligament

**Table 1.** The effective glass transition temperatures,  $D$  and  $v$  for the methanol 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  $\Delta H$  for the heat of mixing, respectively

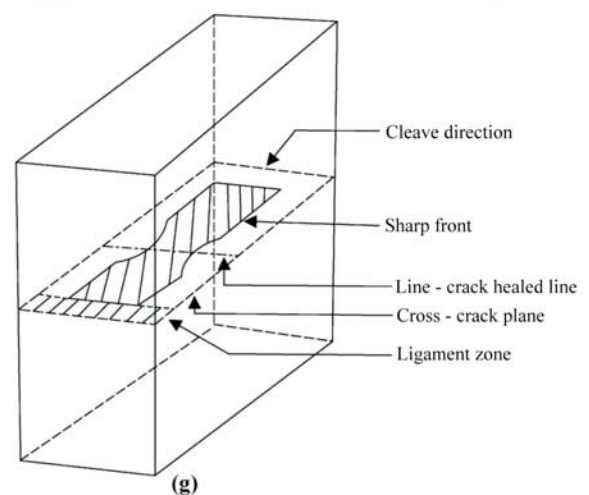
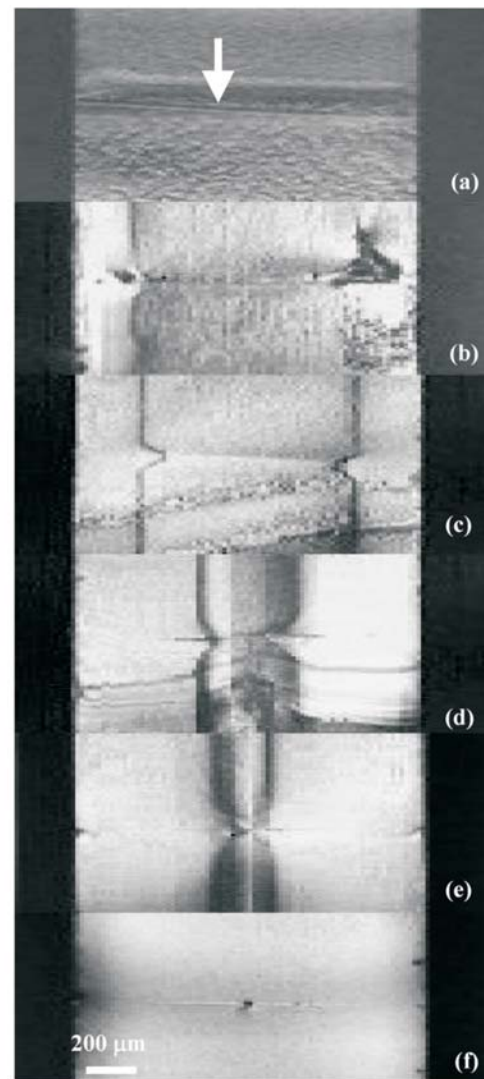
T (°C)	40	45	50	55	60
$T_{geff}$ (°C)	39.5	33.6	30.3	25.5	22.8
$D \times 10^8$ (cm <sup>2</sup> /s)	3.6	7.5	9.2	11.5	15.1
$V \times 10^6$ (cm/s)	4.1	5.4	6.5	8.5	9.6
$m_L$	0.7612	0.7516	0.5113	0.2477	0.1336
$m_C$	0.3622	0.3545	0.3401	0.2201	0.1329
$t_L$ (sec)	720	480	240	120	90
$t_C$ (sec)	630	360	192	90	72
$E_D$ (kcal/mole)			14.14		
$E_V$ (kcal/mole)			8.81		
$\Delta H$ (Kcal/mole)			-4.54		



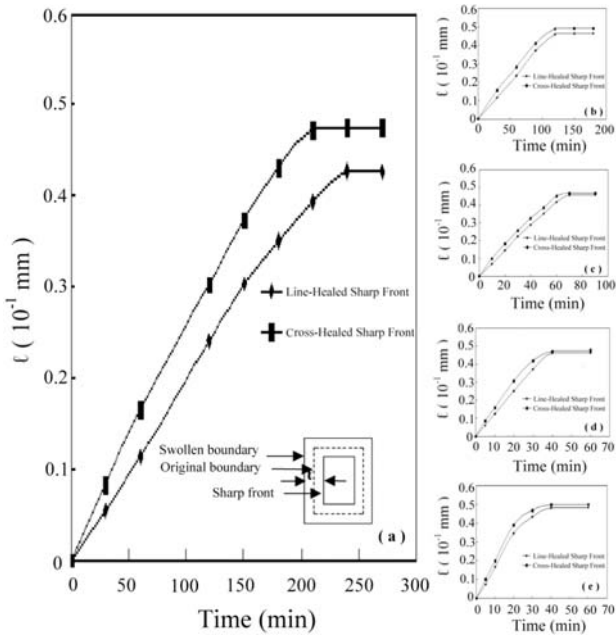


**Figure 4.** A set of continuous micrographics of sharp front in PMMA at 60 °C for periods of (a) 0 min (b) 5 min (c) 10 min (d) 20 min (e) 30 min (f) 40 min.

length of about 1 mm was immersed into methanol at temperatures of 40 °C~60 °C. The healed crack closure length 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 40 and 32 second, respectively. Figure 8 shows the plot of  $\text{Log}(V_{\text{LH}}T)$  and  $\text{Log}(V_{\text{CH}}T)$  versus  $1/T$ .  $V_{\text{LH}}$  and  $V_{\text{CH}}$  represents healed line- and cross-crack closure speeds. In Table 2, the crack closure speed is constant with methanol system at 40 °C~60 °C. Then  $t_{\text{LC}}$  and  $t_{\text{CC}}$  mean the fully healing time



**Figure 5.** A set of continuous micrographics of sharp front in crack healed PMMA at 60 °C for periods of (a) 0 min (b) 5 min (c) 10 min (d) 20 min (e) 30 min (f) 40 min (g) the change of Cross-crack healed of PMMA in methanol.



**Figure 6.** The displacement  $\ell$  of sharp front as a function of mass transport time at (a) 40 °C (b) 45 °C (c) 50 °C (d) 55 °C (e) 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.

of line-crack and cross-crack, respectively. According to the study of Wu [14], the surface energy density of PMMA ( $\gamma$ ) does not change significantly in the range of temperature from 40 °C~60 °C. Thus, the crack length  $l_c$  can be expressed as a function of time  $t$  [15],

$$l_c = l_o - \frac{Dra}{kT}t = l_o - V_H t \tag{5}$$

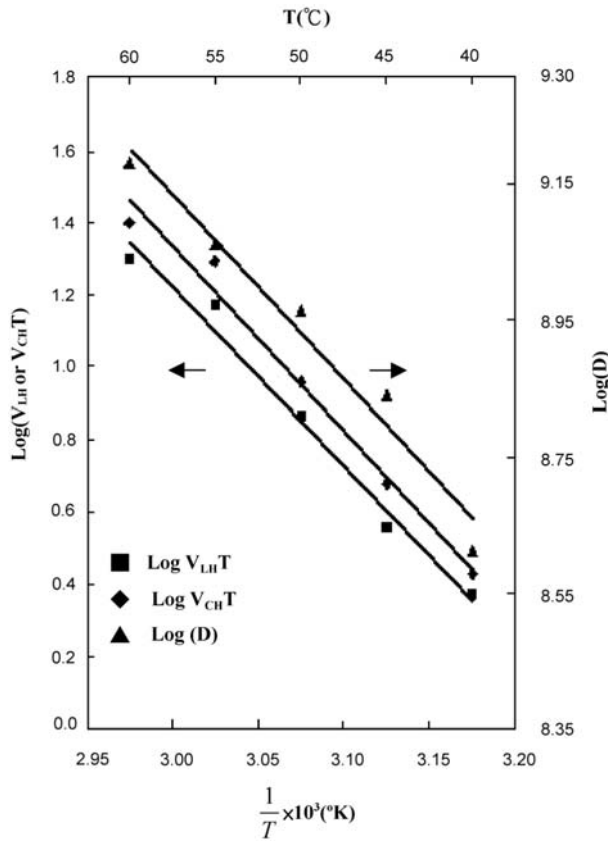
Where  $l_o$  is the original crack length,  $a$  is characteristic length of methanol penetrating into PMMA,  $V_H$  is the crack closure speed and satisfies the modified Arrhenius equation:  $V_H = (U/T) \exp(-E_H/RT)$ , where  $U$  and  $E_H$  are the pre-exponent factor and activation energy. The corresponding activation energy ( $E_H$ ) of the line-and cross-crack healing is equal to 10.25 kcal/mole and 10.58 kcal/mole, respectively and comparing to PMMA sample with methanol system at 40 °C~60 °C, we could know that the crack healing is contributed by case I and case II from  $E_D = 14.14$  kcal/mole and  $E_v = 8.81$  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 Ein-



**Figure 7.** Plot (a) and (b) to show the continuous pictures of healed line- and cross-crack during mass transfer at 50 °C.

stein 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. [11]. Under an ideal condition, perfect material could be healed without any extra force. Thus the surface energy density,  $\gamma$  of PMMA is proportional to the crack closure rate.

We find that the sample of cross-crack has a shorter healing time than line-crack in Table 2. This is because superposition of the mass transfer along with line-crack



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

**Table 2.** Crack closure rates  $V_{\text{LH}}$  and  $V_{\text{CH}}$ ; and the fully healing time  $t_{\text{LC}}$  and  $t_{\text{CC}}$  at various transport temperature  $T$

$T$ ( $^\circ\text{C}$ )	40	45	50	55	60
$V_{\text{LH}}$ (mm/s)	0.0075	0.0113	0.0225	0.0450	0.060
$V_{\text{CH}}$ (mm/s)	0.0086	0.0150	0.0281	0.060	0.075
$t_{\text{LC}}$ (sec)	1200	800	400	200	150
$t_{\text{CC}}$ (sec)	1050	600	320	150	120

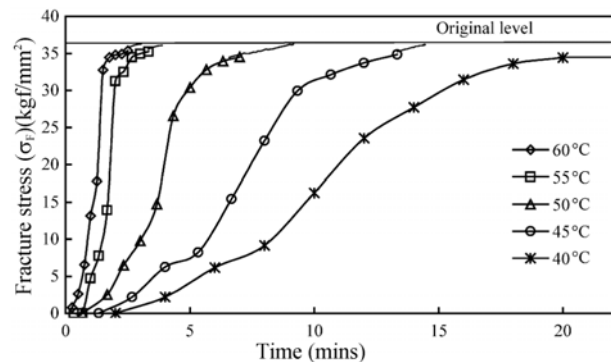
during the process of cross-crack healing. The mass transfer of cross-crack induced stress is higher than the stress induced during mass transfer of line-crack. PMMA sample in the methanol system at  $40^\circ\text{C}$ – $60^\circ\text{C}$  performs a healing mechanism by lowering the glass transition temperature. Due to the activated molecular chain on crack surface during methanol treatment, the effective glass transition temperature is lower than the mass transporting temperature as shown in Table 1. It is derivable that self-diffusion of molecule chain would happen when the effective glass transition point of methanol treatment transporting temperature is lower than the mass trans-

porting temperature. Crack self-healing in PMMA is produced immediately after methanol mass transfer finished and self-diffusion of molecule chain near the crack surface is active [1], and this active surface is called solvent affected zone (SAZ). Owing to reptation of molecule, interdiffusion happens to cause crack self-healing [3]. On the other hand, molecular chain self-diffusion would not happen when the effective glass transition temperature is higher than the mass transport temperature.

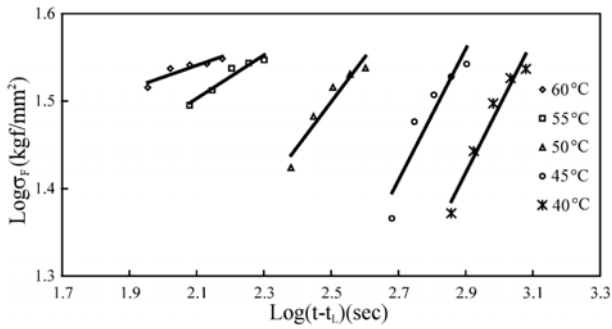
### 3.4 Recovery of Tensile Fracture Strength

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 interdiffusion, which enhances the quality of healing behavior, begins when the crack is completely closed. Wool and O'Connor [2] 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  $\sigma_{\text{F}}$  as a function of healing time at different temperatures of methanol treatment is shown in Figure 9 and Figure 11.

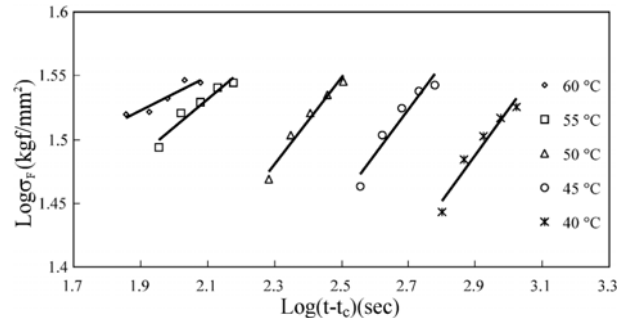
The tensile fracture stress is defined as the fracture load divided by the actually healing area. According to Figure 9 and Figure 11, First, at any transport temperature, the reactive incubation times,  $t_{\text{L}}$  and  $t_{\text{C}}$  of the line- and cross-crack, respectively always exist as shown in Table 1. The reactive time increases with decreasing healing temperature. Second, there are two stages for fracture stress at low temperatures, for instance,  $40^\circ\text{C}$  and  $45^\circ\text{C}$ . Stage I corresponds to the recession of the crack surface. Stage II is that interdiffusion of active molecule



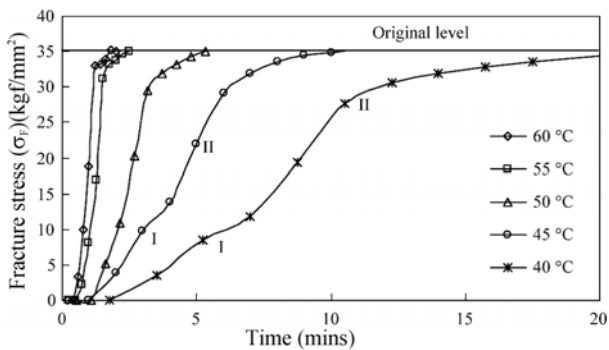
**Figure 9.** Plot of line-crack healing fracture stress versus healing time.



**Figure 10.** 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 11.** Plot of cross-crack healing fracture stress versus healing time.

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 methanol treatment at temperatures of 40 °C–60 °C. According to Jud et al. [16], 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. [16] have the common characteristics that the glass transition temperature was kept constant during the healing treatment. Therefore, the self-diffusion coefficient of molecule 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 10 (for line-crack healing) and Figure 12 (for cross-crack healing). It can be seen from Figure 10 (for line-crack healing) and Figure 12 (for cross-crack healing) that the recovery of fracture stress  $\sigma_F$  increases

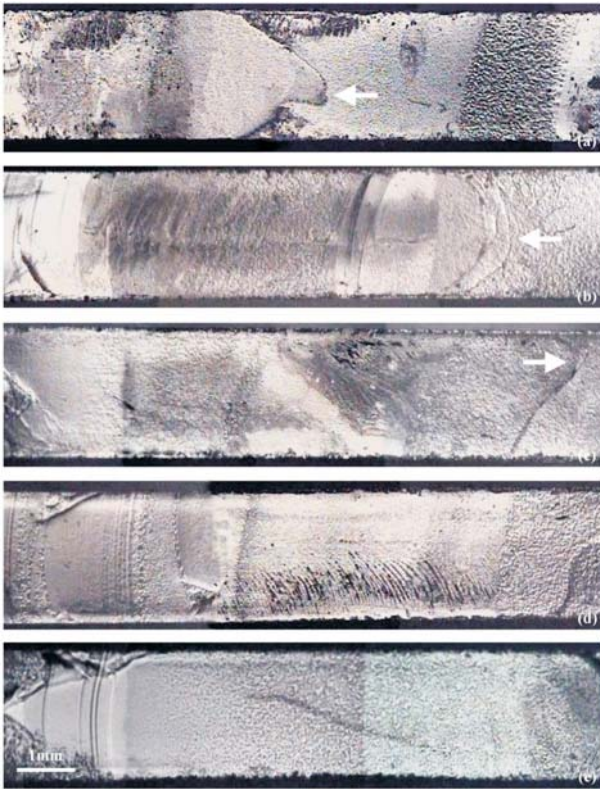
with healing time  $t-t_c$  as  $\sigma_F \propto (t-t_c)^m$ . The values of  $m$  and  $t_c$  for different temperatures are tabulated in Table 1. The value of  $m$  decreases with increasing temperature, However, just only values of 55 °C and 60 °C are smaller than  $1/4$ . This is because the effective glass transition temperature is a function of the amount of methanol at the same transport temperature in PMMA [17].

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 methanol 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 55 °C are 0.2477 for line-crack healing and 0.2201 for cross-crack healing as listed in Table 1. This value of  $m$  is very close to  $1/4$  as predicted by the diffusion model [5,6].

### 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

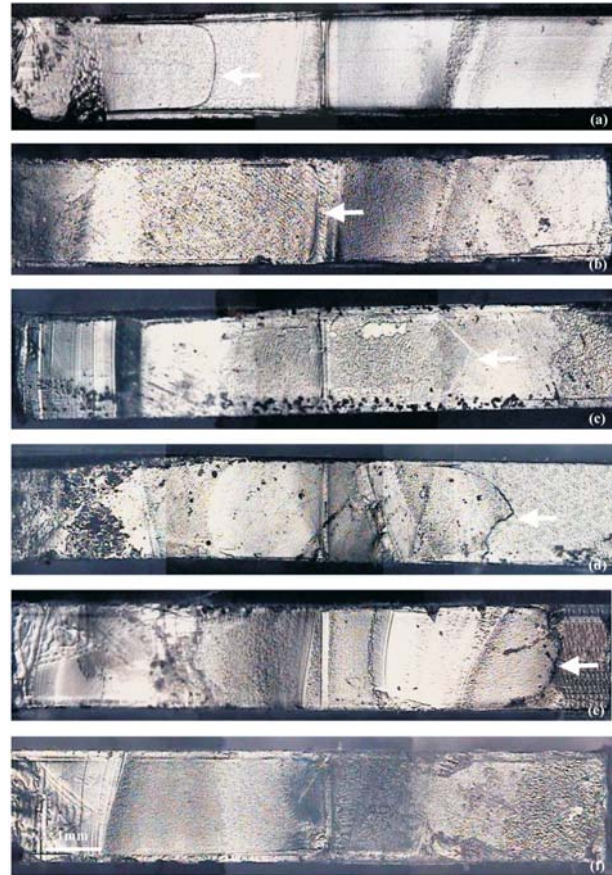




**Figure 13.** Line-crack healing with methanol treatment at 50 °C. The time interval between two successive pictures is 40 sec.

wetting controlled by case I methanol 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 methanol, so the second bond energy entangle with the interface freely. Thus the distance from stage of wetting healing to interdiffusion of molecule chain is short. It is found that the chevron shape of crack propagation is opposite to 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 lar-



**Figure 14.** Cross-crack healing with methanol treatment at 50 °C. The time interval between two successive pictures is 32 sec.

ge 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 methanol treatment and the tensile fracture stress of cross-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 Conclusions

The line-crack and the cross-crack healing in PMMA treated by methanol treatment at 40 °C–60 °C have been investigated. Some important conclusions are summa-

rized as follows:

- (1) Sharp front with straight line is observed after methanol transport to PMMA with line-crack. On the contrary, shape of chevron or inward concave is produced in PMMA with cross-crack at where the line-crack healed.
- (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 transporting temperature. The crack healing rate of cross-crack at stage I is faster than that of line-crack.
- (4) Both stages of the healing process are confirmed by sequential pictures of crack surface morphology and fracture tests.
- (5) 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.
- (6) The line- and cross-crack healed specimens treated with methanol can recover to the virgin material. The tensile fracture stress of cross-crack healed specimen is larger than line-crack healed specimen.

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