

A study on Crack Healing of Various Glassy Polymers
(part I)
-theoretical modeling-

Ouk Sub Lee

유리질 중합체의 균열 Healing에 관한 연구
(제 1 보)
- 이론 모델링 -

이 역 섭

1. Introduction

Crack, craze and void are common defects which may be found in the bulk of polymeric materials such as either thermoplastics or thermosets. The healing phenomena, autohesion, of these defects are known to be a intrinsic material property of various polymeric materials. However, only a few experimental and theoretical investigations on crack, void and craze healing phenomena for various polymeric materials have been reported up to date [1, 2, 3]. This may be partly due to the complications of healing processes and lacking of appropriate theoretical developments.

Recently, some investigators have been urged to study the healing phenomena of various polymeric materials since the significance of the use of polymer based alloys or composites has been raised in terms of specific strength and energy saving. In the earlier published reports [1, 2, 3, 4], the crack and void healing velocity, healing toughness and some other healing mechanical and physical properties were measured experimentally and compared with predicted values by utilizing a simple model such as the reptation model under some reasonable assumptions. It seems, however, that the general acceptance of the proposed modeling analyses is yet open question.

The crack healing processes seem to be complicate and highly dependent on the state of virgin material in terms of mechanical and physical properties. Furthermore, it is also strongly dependent on the histories of crack, craze and void development including fracture surface morphology, the shape of void and the degree of disentanglement of fibril in the craze.

The rate of crack healing may be a function of environmental factors such as healing temperature, time and pressure which gives different contact configurations between two separated surfaces.

It seems to be reasonable to assume that the crack healing processes may be divided in several distinguished steps like stress relaxation with molecular chain arrangement, surface contact (wetting), interdiffusion process and complete healing (to obtain the original strength). In this context, it is likely that we no longer have to accept the limitation of cumulative damage theories and fatigue life if it is probable to remove the defects such as crack, craze and void and to restore the original strength of polymers or polymer based composites by suitable choice of healing histories and methods.

In this paper, we wish to present a very simple and intuitive theoretical model for the prediction of healed fracture toughness of cracked or defective polymeric components. The central idea of this investigation, thus, may be the modeling of behavior of chain molecules under healing conditions including the effects of chain scission on the healing processes. The validity of this proposed model will be studied by making comparisons between theoretically predicted values and experimentally determined results in near future and will be reported elsewhere.

2. Theoretical

Actually, crack healing phenomena inclusive of molecular kinetics seems to be very complicated. It is, thus, useful and necessary to introduce some assumptions based on preliminary experimental observations and intuitions for crack healing processes of fractured surfaces in a polyester cross-linked thermoset resin and an uncross-linked thermoplastics, polymethylmethacrylate (PMMA). Some assumptions which have been used and made in this paper are presented in the following.

- 1) The wetting and interdiffusion processes appear to be equivalent through the whole domain of the fractured surfaces as shown in Figure 1. Our observation of crack healing in some polymers indicated that a surface mode rather than a point mode of healing was favored.
- 2) The actual fracturing processes in polymeric materials may be differentiated such as chain stretching, plastic deformation, microcrack deformation, chain disentanglement and chain scission. Some molecular chains, however, are assumed to be scissored in half of the original length of the molecular chain along the fractured surfaces as shown in Figure 2.

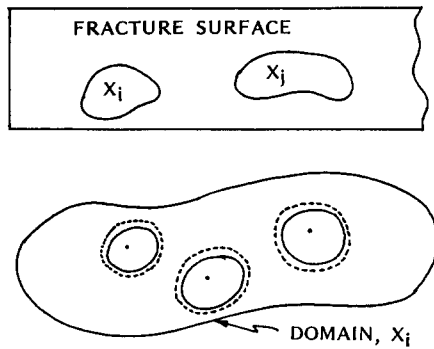


Fig. 1. Surface Mode of Wetting Distribution and Its Growth

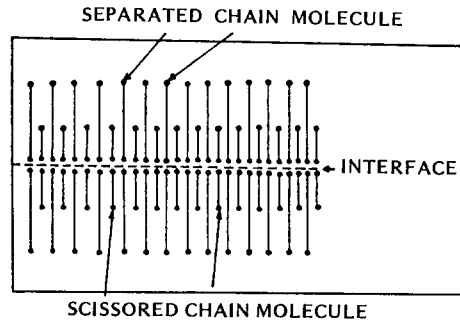


Fig. 2. Scissored and Separated Molecular Chains along Interface

- 3) On the other hand, the half of total number of molecular chains are not scissored but simply separated along the fractured surfaces as shown in Figure 2. Recently, Kramer computed the number of scissored chains per unit area by using geometric statistics and for example 28×10^{15} for a PMMA were obtained [5].
- 4) If the time, say t_3 , required for wetting of whole fractured surface is short enough comparing with total time for crack healing, the interdiffusion differences during wetting period may be negligible. If t_3 appears to be long, different degree of entanglement of molecule chains over the healing surfaces during this period may be expected. We may need to apply some pressures onto the healing surfaces in order to shorten the wetting period.
- 5) The entanglement numbers of molecular chains are proportional to the interpenetration distance of molecular chain, x . And x would be proportional to healing strength.
- 6) The toughness contribution of the interpenetration distance of molecular chains may be sum of effects obtained from short and long molecular chains.
- 7) The chain mobility may be increased inversely proportional to the chain length and double increases of chain mobility may result an increase of entanglement numbers in proportion to the square of entanglement numbers of original molecular chain without scission.

3. Useful Function

Some useful functions regarding to theoretical modeling of crack healing can be defined based on physical phenomena and assumptions observed and made through preliminary

experiments and some published theoretical developments as the following.

a) Macroscopic Recovery Function, R [3]

Defining an intrinsic healing function, R_h , and a wetting distribution function, $\phi(X,t)$, which will be appeared in this section later, we may represent a macroscopic recovery function, R, as the following.

$$R = \int_0^{t=t} R_h(t-\tau) \frac{d\phi(\tau, X)}{d\tau} d\tau \dots\dots\dots (1)$$

where;

- R = f (t_h, T_h, C_h), $C_h = f(P_h, R_h)$
- t_h = the duration of healing processes
- T_h = the healing temperature
- C_h = the index of surface contact morphology
- P_h = the healing pressure
- R_s = the index of roughness of crack surface
- R_h = the intrinsic crack healing function
- $\phi(X, t)$ = the wetting distribution function

b) Intrinsic Healing Function, $R_h(t)$

It seems reasonable to introduce an intrinsic healing function in terms of healing strength or healing toughness since we are interested in mechanical properties which may be recovered through the healing processes. The interdiffusion phenomena of a chain molecule between two fractured surfaces should be modeled to introduce healing function. For long chain polymer melts, each chain may be imagined to move slowly within a long, curved pipe line formed by the constraints of all other neighboring chains. It is, thus, assumed that the self diffusion of coil chain molecules may be simulated by adopting the tube model (reptation model) in which each network is confined within a tube as shown in Figure 3. The chain P is free to move only between the fixed obstacles,

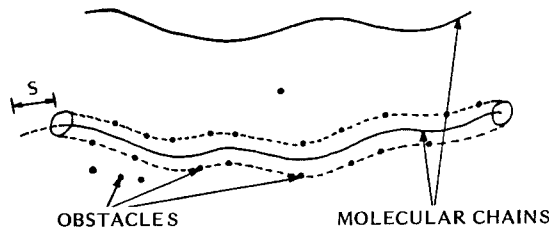


Fig. 3. Schematic Diagram of the Tube Model

O, but it cannot cross any of them. Actually, it seems to be trapped in a tube which may be topological constraints on its motion imposed by the other chains in the neighbor-

hood. This may be simulating the molecular diffusion between the fracture surfaces. The curvilinear motion, S , of one end of chain as shown in Figure 3 is given by

$$S^2 = 2D_c t \quad \dots\dots\dots (2)$$

where;

- D_c = the curvilinear diffusion coefficient
- t = the healing time

The effective number of entanglement of molecular chain, N_0 , can be represented by [6]

$$N_0 \propto \left[\frac{\text{density} \cdot l}{m} \right]^{\frac{1}{2}} \cdot L \quad \dots\dots\dots (3)$$

where;

- L = the total length of polymer chain molecules present
- l = the effective length of the submolecules
- m = the effective mass of the submolecules

The following relations may be established regarding to the assumption (5) and eqs. (2) and (3).

$$N_0 \propto x \quad \dots\dots\dots (4)$$

$$\sqrt{l} \propto \sqrt{N_0} \quad \dots\dots\dots (5)$$

Now, it seems likely that the curvilinear motion, s , may be related to the effective length of the submolecules, l , in terms of entanglements through the reptational movement. Thus, we can express as

$$\sqrt{l} \propto \sqrt{s} \propto N_0 \quad \dots\dots\dots (6)$$

It may be noted that average distance of curvilinear motion which commuted either from one surface to another surface or vice versa would be expressed as \sqrt{s} rather than s itself. We may, thus, obtain the following.

$$\sqrt{s} \propto N_0 \propto x \propto (2D_c t)^{\frac{1}{2}} \quad \dots\dots\dots (7)$$

This relationship may be for separated chain molecules with original chain length which were disturbed by deformation in itself and neighborhood by the fracture. Therefore, we may obtain a relation between the penetration distance, x and healing time, t , such as

$$x = K_1 t^{\frac{1}{2}} \quad \dots\dots\dots (8)$$

where;

- x = the penetration distance for long molecular chain
- K_1 = the interpenetration constant for separated molecule chain

Eq. (8) is similar to those obtained by other investigators [1, 2].

For the scissored chain molecules during fracturing, it may be expected that entanglement numbers would be increased since the shorter chain molecules can move much easier than the longer chain molecules may. If the mobility of the scissored chain molecules increases by the factor of two comparing with that of original length chain molecules, then the entanglement number of the shortened chain molecules, N_s , as mentioned in the earlier section, can be represented as

$$N_s = N_0^2 \dots\dots\dots (9)$$

Following the development for the original length chain molecule, we may express relations between the interpenetration distances and healing times such that

$$N_s \propto x_s \dots\dots\dots (10)$$

$$N_0^2 \propto x_s \propto S \dots\dots\dots (11)$$

$$X_s \propto 2D_c t^{\frac{1}{2}} \dots\dots\dots (12)$$

$$X_s = K_s t^{\frac{1}{2}} \dots\dots\dots (13)$$

where;

- K_s = the interpenetration constant for scissored molecule chains

The total penetration in terms of the average sensitivity and/or recovered strength, may be obtained by summing two interpenetration distances, x_1 and x_s up. It appears, thus, to be

$$x_T = x_1 + x_s = K_1 t^{\frac{1}{4}} + K_s t^{\frac{1}{2}} \dots\dots\dots (14)$$

It may be expected that K_1 would be small comparing to K_s since the equilibrium state is only little disturbed by deformation itself and fracturing of neighboring chain molecules. In the case of creep recovery, however, it should be emphasized.

Now, we define a entanglement index, N_E , such as

$$N_E = \frac{N_h}{N_v} \dots\dots\dots (15)$$

where;

- N_h = the entanglement number after healing
- N_v = the entanglement number of virgin material

Then, the constraint index, C_o , say, may be represented as

$$C_o \propto N_E \dots\dots\dots (16)$$

It is, thus, likely to relate the recovery stress by healing, σ_d , across the interface to C_o and x_T such as the following.

$$\sigma_d \propto C_o \propto N_E \propto x_T = K_1 t^{\frac{1}{4}} - K_s s^{\frac{1}{2}} \dots\dots\dots (17)$$

$$\sigma_d = Q_1 t^{\frac{1}{4}} + Q_s t^{\frac{1}{2}} \dots\dots\dots (18)$$

where;

$Q_1, Q_s =$ the constants

Considering the diffusion initiation phenomena referring to Wool's theory [3] and introducing a diffusion initiation function, $\psi(t)$, we obtain σ_d such as

$$\sigma_d = (Q_1 t^{\frac{1}{4}} + Q_s t^{\frac{1}{2}}) * \dot{\psi}(t) \dots\dots (19)$$

where;

* stands for convolution

It is expected that all the scissored and separated chains will be available for immediate reptation across the interface after average constant wetting time duration which appears to be very short comparing with whole healing period. It may be postulated such as

$$\dot{\psi}(t) = \delta(t) \dots\dots\dots (20)$$

where;

$\delta(t) =$ the Dirac delta function

Combining eqs. (19) and (20), we can obtain σ_d like

$$\sigma_d = Q_1 t^{\frac{1}{4}} + Q_s t^{\frac{1}{2}} \dots\dots\dots (21)$$

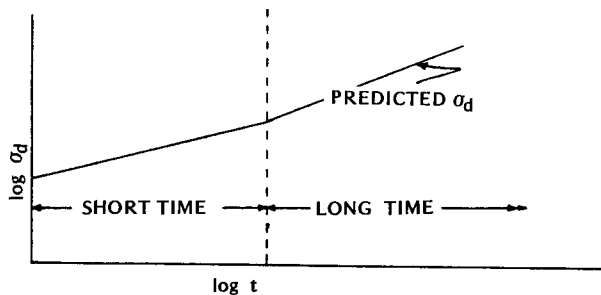


Fig. 4. Healing Stresses, σ_d , vs. Healing Time, t

Figure 4 shows a general relationship between healing stresses and healing time on the log-log scale. For short time period the slope of 1/3, say, is expected and the transition from this to 1/2 is anticipated for the long time duration of the crack healing although some ambiguity appears at the very initiation instant. The intrinsic healing function, R_h , in terms of recovered stresses, thus can be expressed such as

$$R_h(\sigma; t) = \frac{\sigma_w + \sigma_d * \dot{\phi}(t)}{\sigma_v} \dots\dots\dots (22)$$

where;

- σ_w = the recovery stress during wetting period
- σ_v = the strength of virgin state

If $\sigma_w \ll \sigma_d$, then, eq. (22) becomes

$$R_h(\sigma, t) = \frac{Q_1 t^{\frac{1}{3}} + Q_s t^{\frac{1}{2}}}{\sigma_v} * \dot{\phi}(t) \dots\dots (23)$$

4. Healing Fracture Toughness, K_{IH}

The macroscopic recovery function, R , defined like eq. (1), can be rewritten by substituting for eq. (23) into eq. (1) i.e.,

$$R(\sigma, t) = \left[\frac{Q_1 t^{\frac{1}{3}} + Q_s t^{\frac{1}{2}}}{v} * \dot{\phi}(t) \right] * \dot{\phi}(t) \dots\dots\dots (24)$$

If the time duration of average constant wetting is short enough as observed at a preliminary experiment comparing with total healing time period, it is not unreasonable to be considered the wetting process as an instant wetting, and thus,

$$\dot{\phi}(t) = \delta(t) \dots\dots\dots (25)$$

$$R(\sigma, t) = \frac{Q_1 t^{\frac{1}{3}} + Q_s t^{\frac{1}{2}}}{v} \dots\dots\dots (26)$$

It is well-known that the fracture toughness is proportional to the fracturing stresses. In this context, it is quite natural to relate the fracture toughness of healed polymeric material with healing stresses such as

$$K_{IH} \propto \sigma_d \dots\dots\dots (27)$$

Therefore, K_{IH} can be expressed as the following.

$$K_{IH} \propto (Q_1 t^{\frac{1}{3}} + Q_s t^{\frac{1}{2}}) \dots\dots\dots (28)$$

$$K_{IH} = (q_1 t^{\frac{1}{3}} + q_s t^{\frac{1}{2}}) \dots\dots\dots (29)$$

where;

$q_1, q_5 =$ the constant

Figure 5 shows a general relationship between healed fracture toughness and healing time on the log-log scale.

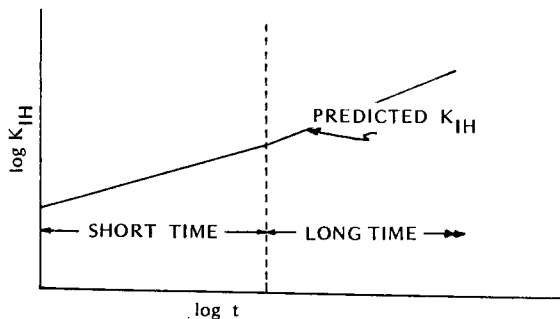


Fig. 5. Healing Toughness, K_{IH} , vs. Healing Time, t

5. Conclusion

A simple tube model for the crack healing of various polymeric materials was presented. The addition of the molecular chain scissoring effect on this model represented somewhat different recovery predictions from those of other investigators [1, 3]. A relationship of $R \propto t^{1/2}$ for long time healing duration was determined through a theoretical modeling analysis.

Acknowledgement

The work reported here has been supported by KOSEF. The author wishes to acknowledge the support and encouragement of KOSEF during the course of this investigation.

REFERENCES

1. J. Jud, H.H. Kausch and J.G. Williams, "Fracture Mechanics Studies of Crack Healing and Welding of Polymers", *J. of Material Science*, 16(1981), pp. 204-210.
2. R.P. Wool and K.M. O'Connor, "Time Dependence of Crack Healing", *J. of Polymer Science*, 20 (1982), pp. 7-16.
3. R.P. Wool and K.M. O'Connor, "A Theory of Crack Healing in Polymers", *J. of Applied Physics*, 52(10), October (1981), pp. 5953-5963.
4. J.O. Outwater and D.J. Gerry, "On the Fracture Energy, Rehealing Velo-

- city and Refracture Energy of Cast Epoxy Resin”, J. of Adhesion, October (1969), pp. 291-298.
5. E.J. Kramer, P. Green and C.J. Palmstrom, ‘Interdiffusion and Marker movement in concentrated Polymer-Polymer diffusion Couples’.
6. S.F. Edwards, ‘The Statistical Mechanics of Polymerized Material’, Proc. Phys. Soc., 1967, Vol. 92, pp. 9-16.
-