

STRESS CORROSION CRACK GROWTH IN ENGINEERING PLASTICS

Byoung-Ho Choi¹, Zhenwen Zhou¹, Kalyan Sehanobish² and Alexander Chudnovsky¹
1 FMMD Lab., Dept. of Civil & Materials Eng., University of Illinois at Chicago, IL 60607, U.S.A.
2 Dow Chemical Company, Auburn Hills, MI 48326, U.S.A.

ABSTRACT

Stress Corrosion Cracking (SCC) is the process of brittle crack growth in a normally ductile material exposed to a combination of a corrosive environment and relatively low constant or intermittent stresses. There is a specific atomic level pathway of SCC for each material-environment system. At the same time, there is also a striking commonality of the phenomena in different material-environment systems, when the problem is considered on a continuum level. In this paper we present a mathematical model of SC individual crack growth. A process zone (PZ), occupied by crazing, shear banding and/or other forms of strain localizations, are commonly observed in front of a crack in engineering thermoplastics. The growth of the crack is strongly coupled with the evolution of PZ. Thus, it is convenient to consider a crack with PZ as one system referred to as “Crack Layer” (CL), i.e., a crack with finite, variable thickness. Crack Layer (CL) formalism is employed here modeling of slow stress corrosion crack growth. There are thermodynamic forces X^C and X^{PZ} associated with crack and PZ evolution respectively. The forces X^C and X^{PZ} are conventionally expressed as the derivative of Gibbs potential with respect to crack and PZ sizes, and are presented as the difference between the driving and resisting parts. The driving part of X^C is the elastic energy release rate G_I due to crack extension into PZ. The resisting part of X^C is the specific fracture energy 2γ of PZ material. The distinction of corrosive environment on CL is a reduction of the resisting part 2γ due to chemical degradation of PZ material. It leads to a noticeable acceleration of an average crack growth rate, reduction of the lifetime as well as a change in the slope in Paris-Erdogan plot of crack growth rate vs. stress intensity factor. A modification of CL formalism that accounts for the presence of aggressive environment and an algorithm for evaluation of stress corrosion CL (SCCL) growth is proposed in this work. Examples of numerical simulation of SCCL are also presented.

1 INTRODUCTION

Stress corrosion cracking (SCC) results from strongly coupled chemical and thermo-mechanical processes, and sensitive to material composition and morphology. We distinguish four stages of SCC: 1) microcracks initiation; 2) slow growth of individual cracks; 3) strong interaction of cracks and formation of clusters of cracks; and 4) clusters growth and instability. The initiation stage of SCC is associated with mechano-chemical degradation of polymer, where chemical degradation plays the leading role. It was recently modeled in (Choi et al [1]).

A well-developed SC crack colony formed at the end of stage three of SCC in an accelerated testing of plastic pipe is illustrated in Figure 1 (Zhou et al [2]). An appearance of SC crack colony on the

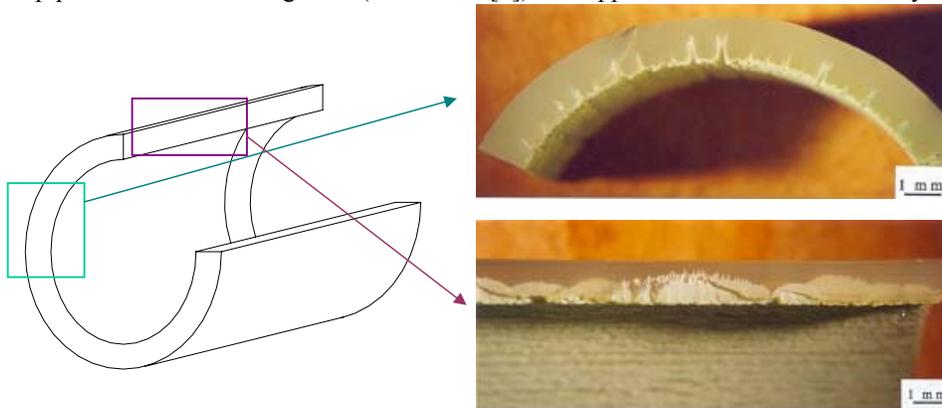


Figure 1: Schematics of cross sections and two micrographs of SC crack colony formed in an accelerated testing of a plastic pipe

two cross sections is depicted in two micrographs on the right side of Figure 1. The multiplicity of cracks emanating from a thin degraded layer of material, almost regular spacing between the individual cracks, and random distribution of crack depth are well reflected in the circumferential cross section. A thumbnail shape and a variation of sizes of the individual cracks are well visible on the axial cross section. A ragged front of thumbnail crack in the center of axial cross section illustrates fingering, a typical mechanism of progression of SCC by localized degradation of polymer in an immediate vicinity of the crack front. In the present work, the chemical degradation of polymers is characterized by a degradation parameter, $\omega(t) = 1 - M_w(t)/M_w(0)$, which is directly proportional to the reduction of molecular weight, M_w (Niu et al [3]).

A typical time dependence of the degradation parameter on the dimensionless time $\tau = t/t_{OIT}$ is depicted by solid line in Figure 2. Here t_{OIT} stands for oxidation induction time (OIT). k is the rate of degradation parameter growth for the time interval $t_{OIT} \leq t \leq t_*$, and t_* is the time of complete degradation $\omega = 1$, ($t_* = t_{OIT} + k^{-1}$). For the modeling purpose the degradation parameter evolution at a given point of material, \underline{x} , is approximated as

$$\omega(\underline{x}, t) = k\{t - t_{OIT}(\underline{x})\} \cdot [H\{t - t_{OIT}(\underline{x})\} - H\{t - t_*(\underline{x})\}] + H\{t - t_*(\underline{x})\}, \quad (1)$$

where $H\{t - a\} = \begin{cases} 0 & \text{if } t < a \\ 1 & \text{if } t \geq a \end{cases}$ is a Heaviside step function. The approximation of eq. (1) is indicated by the dotted line on Figure 2.

2 MODELING OF SC CRACK GROWTH

Crack growth in engineering thermoplastics is usually preceded by a process zone (PZ), a zone of highly localized large deformation in a vicinity of crack front. Depending on loading, material and environment, PZ may consist of crazing, shear banding, voiding, microcracking etc. The crack growth and an evolution of PZ are closely coupled irreversible processes. The thermodynamic force (TF) responsible for PZ evolution is defined as the variational derivative of Gibbs potential with respect to an infinitesimal displacement vector δX_i of PZ boundary ∂V_{PZ} (Chudnovsky [4]).

$$X_i^{PZ} = - \left. \frac{\delta G}{\delta X_i} \right|_{a=const.}; \quad \text{where} \quad \delta G = \int_{\partial V_{PZ}} \delta X_i [P_{ij} - P_{ij}^{PZ}] d\Sigma \Big|_{a=const.} \quad (2)$$

Here, P_{ij} and P_{ij}^{PZ} stand for the energy momentum tensors (EMT) for the material outside of PZ and PZ material respectively, and V_{PZ} designates the PZ domain. In high and medium density polyethylenes, PZ is observed as a narrow strip of crazed (cold drawn) material as shown in Figure 4

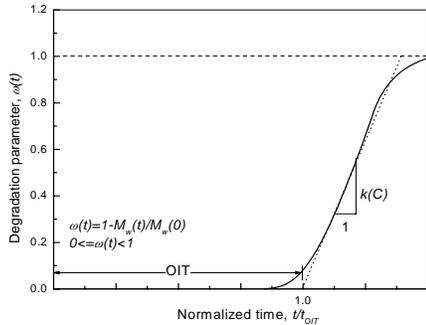
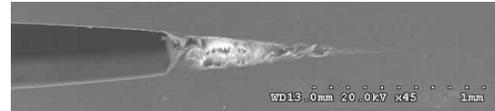
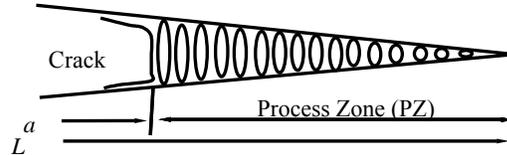


Figure 2: Evolution of degradation parameter in normalized time t/t_{OIT}



(a) Actual photo of PZ in PE



(b) PZ model with narrow strip shape

Figure 3: A micrograph and schematics of process zone in PE in front of crack

(Lu et al [5], Showaib and Moet [6], Stojimirovic et al [7], Kadota [8]). In such a case the PZ evolution is uniquely determined by the movement (in material coordinates) of PZ front (a tip of PZ cross section shown in Figure 4), and the thermodynamic force (2) for PZ evolution is reduced to

$$X_1^{PZ} = J_1^{PZ} - \gamma_c, \text{ where, } J_1^{PZ} = \int_{\Gamma_1} P_{1j} n_j d\Gamma, \quad (3)$$

where the driving part of TF, the energy release rate (ERR) due to PZ front movement in plain strain problem is expressed in terms a path invariant contour integral outside of PZ of EMT,. The resisting part of TF, γ_c , stands for specific energy of crazing (SEC) that includes cavitation energy, as a major part. Similarly, the thermodynamic force for crack growth is defined as the derivative of Gibbs free energy with respect to crack front movement.

$$X_{CR} = \left. \frac{\partial G}{\partial a} \right|_{V_{PZ}=\text{const.}} = J_1^{CR} - 2\gamma(\omega(x,t),t), \text{ where } J_1^{CR} = \int_{\Gamma_0} P_{j1}^{PZ} n_j d\Gamma, \quad (4)$$

where, Γ_0 is an arbitrary contour within a homogeneous PZ (Γ_0 dose not cross PZ boundary ∂V_{PZ}), and 2γ is the specific fracture energy (SFE) of the PZ material. SFE usually decays with time due to material aging (e.g. creep). This process is highly accelerated by chemical degradation of polymer. Thus, SFE at each point \underline{x} and time instance t is a function of degree of degradation $\omega(\underline{x},t)$ and the creep strain $\varepsilon^P(t)$ or time t . The existence of PZ significantly reduces the driving part of X^{CR} by providing stress shielding. The resistance to crack growth is determined by SFE of PZ material and the rate of its decay with creep and degradation. The kinetic equations for the crack and PZ growth follow conventional relations between thermodynamic forces and corresponding fluxes (Chudnovsky et al [5], Chudnovsky [9])

$$\begin{cases} \frac{da}{dt} = X^{CR}, & \text{for } X^{CR} \geq 0 \text{ and } 0 \text{ for } X^{CR} < 0 \\ \frac{dL}{dt} = X^{PZ}, & \text{for } X^{PZ} \geq 0 \text{ and } 0 \text{ for } X^{PZ} < 0 \end{cases}, \quad (5)$$

There are two types of solution of (5), which describe the continuous and discontinuous (stepwise) CL growth. According to the experiment data, the crack and PZ in PEs grow in a stepwise manner. It means zero crack growth rate and nonpositive thermodynamic force X^{CR} for most of the time, i.e. $J_1^{CR} \leq 2\gamma(\omega(x,t),\varepsilon(t),t)$ (see eq. (4) and the first eq. of (5)). However, with progression of

degradation, i.e., an increase of ω and ε^P , γ decreases. As an example, Figure 4 shows the decay of SFE of polybutylene (PB) due to chemical degradation (Niu et al [3]). In general, the SFE decays in one way (by creep, for instance) prior to the beginning of chemical degradation, and by another way, when the chemical degradation is in action. It can be expressed as follows:

$$\gamma(\omega(x,t),\varepsilon(t),t) = \begin{cases} \gamma_m(\varepsilon^P) & \text{for } t < t_{OIT} \\ \gamma_m(\varepsilon^P) + \gamma_0(1-\omega)^n - 1 & \text{for } t > t_{OIT} \end{cases}, \quad (6)$$

and the mechanical degradation due to creep, $\gamma_m(\varepsilon^P) = \gamma_0 / (1 - (t/t_c)^\alpha)$, γ_0 , t_c (a characteristic time scale) and α are constants. Figure 5 present the normalized SFE decay due to creep and chemical degradation in normalized time t/t_{OIT} . The solid line in Figure 5 depicts SFE decay due to creep for $t \leq t_{OIT}$. For $t > t_{OIT}$, the chemical degradation takes over, since it progresses much faster. The SFE decay due to chemical degradation is shown by dotted line. It is also assumed that the rate SFE reduction due to chemical degradation does not depend on the SFE reduction by the creep. Thus, for a given external load and fixed CL geometry, the thermodynamic force, X^{CR} , increases and becomes positive with time due to the decay of SFE. $X^{CR} = 0$ corresponds to unstable crack

equilibrium, which is the starting point for crack growth inside PZ. There is a corresponding critical value ω^* of degradation parameter ω , which is calculated from eq. (4) and (6) for time $t > t_{OIT}$:

$$\omega^* = 1 - \left(\frac{2 - J_1(\sigma_\infty, a) - 2\gamma_m(\varepsilon^P)}{2\gamma_0} \right)^{\frac{1}{n}} \quad (7)$$

Finally, the total time of building up the critical level of degradation, ω^* , can be obtained using equations (1) and (7). For the example of a single edge notch (SEN) specimen and a given external load considered below, J_1^{CR} increases with crack length. Therefore, the critical level of degradation ω^* decreases with an increase of crack length, and thus it shortens the duration of stationary crack configuration. It is illustrated in Figure 5, by three levels of ERR, J_1^{CR} corresponding to three different crack sizes, a_1 , a_2 and a_3 indicated. The crack starts to grow, when SFE 2γ decays to the level of the current J_1^{CR} . It determines the duration of the stationary crack configuration. Apparently, this duration $\Delta t(a)$ decreases with increase of the crack size, i.e., an increase of J_1^{CR} . Since the resisting part of X^{CR} is reduced by degradation of PZ material, the crack, when it starts to grow, propagates relatively fast to the end of PZ according to the first equation of (5). Then it gets arrested due to high SFE, γ_0 , of undegraded, fresh material outside of PZ. Thus, the increment of crack length Δa is controlled by the size of PZ at the time, when crack starts to grow inside of PZ. It happened at the end of the stationary stage of the discontinuous CL growth, during which both the crack and PZ thermodynamic forces are negative and both rates of the crack and PZ growth, according to (5) equal 0. The equilibrium size of PZ is determined by condition of vanishing ($X_1^{PZ} = J_1^{PZ} - \gamma_c = 0$). Since for the narrow strip, $J_1^{PZ} = (K^{tot})^2 / E$, the equation for PZ size can be written as:

$$(K^{tot})^2 - E\gamma_c = 0, \quad (8)$$

where the total stress intensity factor (SIF) K^{tot} is the difference between SIF K_∞ at the PZ tip due to externally applied load and SIF K_d at PZ tip due to drawing stresses acting along PZ boundary:

$$K^{tot} = K_\infty - K_d \quad (9)$$

E in (8) stands for the Young's modulus for plain strain problem, and γ_c is SEC introduced in (3). According to our previous study (Kadota et al [8]), SEC in PEs is related to the thickness of the layer of original material, which is transformed into craze, i.e., undergoes cavitations followed by cold drawing. This thickness is proportional to the crack opening displacement (COD) δ at the root of PZ with the coefficient of proportionality $(\lambda - 1)^{-1}$, where λ is the natural draw ratio. COD is computed for CL with the cutoff of the craze domain V_{PZ} and substitution of craze material by traction along the boundary ∂V_{PZ} . Based on our previous analysis of the equilibrium PZ size, a power type relation between SEC γ_c and COD δ is assumed as $\gamma_c = \gamma_{c0}\delta^b$, and γ_{c0} and b are constants.

The driving part of the PZ thermodynamic force increases with crack movement inside PZ and reaches maximum value, when crack reaches the tip of PZ. Apparently, at a certain point it triggers PZ growth, following the second of (5). However, with an increase of PZ size, the thermodynamic force of PZ decreases and PZ reaches an equilibrium state, $X^{PZ} = 0$. It completes one step of the discontinuous CL growth. This process is repeated until the final instability, $J_1^{CR} \geq \gamma_0$.

There is a following computational procedure of the proposed model. Starting from the initial crack size a_0 we compute PZ thermodynamic force, according to (3), and PZ size growth according to the second equation of system (5). The equilibrium PZ size for a given crack length a_0 and external load

follows from equation (8). It determines the first stationary configuration of CL. The duration of CL stationary state is determined by the reduction of SFE γ given by (6) and depicted in Figure 5, and critical level of degradation (7). Then the crack grows inside PZ according to the first equation of system (5) until it reaches the tip of PZ and stops there. Then, the above computations are repeated again for the new crack length $a_0 + \Delta a$, and for the following steps of the discontinuous CL growth until J_1^{CR} reach the initial value of SFE γ_0 . There is a transition at that point from discontinuous to a continuous CL growth, which corresponds to the solution of the system (5) with always-positive thermodynamic forces X^{CR} and X^{PZ} . An average crack growth rate during the step-wise CL growth is defined as the ratio of the equilibrium PZ size and the duration of the corresponding stationary configuration.

3. ILLUSTRATIVE EXAMPLES

The major factors determining the rate of SC crack propagation and the severity of SCC in general are stress concentration, creep and chemical degradation of PZ material. Here we consider applications of the outlined above model of SC crack growth to pipe grade PE. The numerical simulation of SC crack growth is performed for SEN specimen, of 10 mm width with the initial crack size of 0.5 mm. The Young's modulus E , drawing stress σ_{dr} , is the normalized value, SFE γ_0 over cavitation energy γ_{c0} of the model material (γ_0 / γ_{c0}) are selected as $2.2GPa$, $20MPa$, and 1. Three levels of applied stresses, σ_∞ are considered, $0.3\sigma_{dr}$, $0.4\sigma_{dr}$, and $0.5\sigma_{dr}$, and the rate of degradation, k , is considered as a variable parameter. Figure 6 represents numerical simulations of CL growth according to the system of equations (6) and displays the crack and CL lengths (vertical axes) vs. time. We consider two scenarios of CL growth: one with SFE decay due to creep only, and another one is SCC, i.e., SFE decay caused by a combination of creep and chemical degradation. Apparently, the lifetime of SCC is noticeably shorter than that for mechanically (creep) driven crack. There is also smaller number and shorter duration of individual steps in SCC in comparison with that for creep driven crack. The same time the critical CL configuration at the transition point from discontinuous, step-wise growth to continuous (much faster) propagation is the same for both cases. It is common in crack growth analysis to express the crack growth rate in terms of SIF (Hertzberg and Manson (16)). Figure 7, displays the relationship between crack growth rate da/dt and SIF $K_I(a, \sigma_\infty)$ for SCC with various OIT as well as for mechanically driven crack. In case of mechanically driven crack, the results of numerical simulation agree very well with empirical Paris-Erdogan power equation (a linear relation in $\log \sim \log$ scale). However, there is a different slope in $\log(da/dt) \sim \log(K_I)$ relations and noticeably higher values of da/dt for the same K_I in case of SCC. These differences decrease with increase of SIF K_I and completely disappear at a certain level of SIF. After that point, the crack growth rates of mechanically driven crack and SC crack are

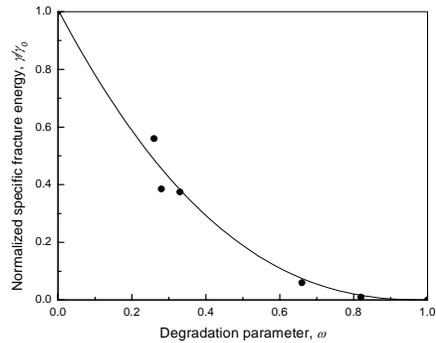


Figure 4: Decay of specific fracture energy with chemical degradation parameter

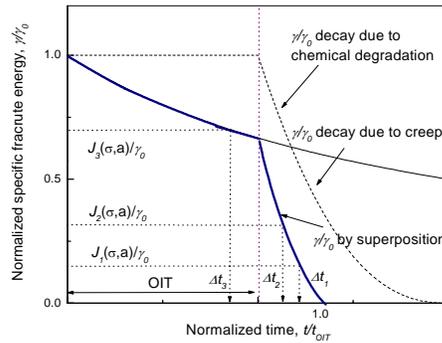


Figure 5: Schematics of specific fracture energy with chemical degradation

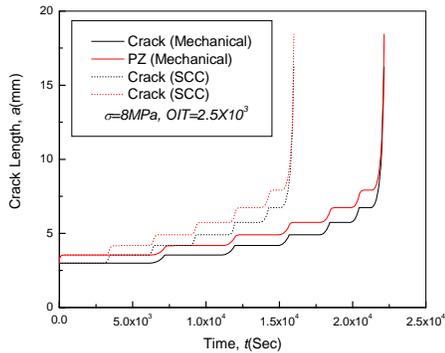


Figure 6: Comparison of SCC propagation with mechanically driven crack

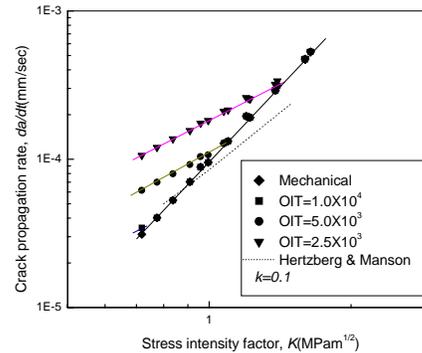


Figure 7: Relationship between crack growth rate and SIF for various OIT

almost same. It is also clear from Figure 7 that OIT affects noticeably the SC crack growth rate: reduction of OIT increases the average crack growth rate. An analysis of the effect of the rate of chemical degradation k (see Figure 2) on the rate of SCC has been also performed, but the effect of k is found to be much weaker than that of OIT: Both, the average crack growth rate and the duration of stable SC crack growth are not sensitive to the rate of chemical degradation, k , but highly dependent on OIT.

4 CONCLUSION

In this paper, formalism for quantitative modeling of SCC is developed. Stress corrosion crack growth is modeled by a system of highly nonlinear ordinary differential equations that calls for numerical solution. Numerical simulation and comparative analysis of stress corrosion crack growth with mechanically (creep) driven crack are performed. There is a step-wise crack growth pattern in both cases. However, there is a smaller number of steps and shorter duration of each step in SCC. There is also a higher average crack growth rate and shorter lifetime in stress corrosion cracking in comparison with that for mechanically driven crack. The numerical simulation of crack layer growth also reconstructs Paris–Erdogan equation for crack growth rate as a function of SIF. A parametric analysis suggests that the crack growth rate as well as the lifetime strongly depend on the oxidation induction time and is insensitive to the rate of chemical degradation after depletion of polymer stabilizing package. The proposed formalism and numerical simulation may serve as the foundation of an accelerated testing for SCC.

5 REFERENCES

- [1] B.-H. Choi, Z. Zhou and A. Chudnovsky, *International Journal of Solids and Structures*, accepted to publication.
- [2] W. Zhou, B. Zhang, A. Chudnovsky, P. Vibien, J. Couch and K. Oliphant, *Proceedings of Plastic Pipes XI*, Munich, Germany, 2001.
- [3] X. Niu, E. Martynenko, A. Chudnovsky, S.H. Patel and S.S. Stivala, *Proceedings of SPE/ANTEC 2000 III*, Orlando, Florida, 2000, pp. 3228-3232
- [4] A. Chudnovsky, *NASA Report*, N174634, 1984
- [5] X. Lu et al, *Journal of Materials Science*, 1991, 26, p. 918
- [6] E.A. Showaib and A. Moet, *Journal of Materials Science*, 1993.
- [7] A. Stojimirovic, K. Kadota and A. Chudnovsky, *Journal of Polymer Science*, 1992, 46(6), pp. 1051-1056
- [8] K. Kadota, *Ph. D. Thesis*, The University of Illinois at Chicago, 1992
- [9] A. Chudnovsky, V.A. Dunaevsky and V.A. Khandogin, *Archives of Mechanics*, 1978, 30(2), pp. 165-174