

CRACK INITIATION IN ENGINEERING THERMOPLASTICS RESULTING FROM CHEMICAL DEGRADATION

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ABSTRACT

Stress Corrosion Cracking (SCC) in thermoplastics usually appears as a microcrack network within a layer of degraded polymer adjacent to the surface exposed to combine action of mechanical stress and chemically aggressive environment. The stage of crack initiation is primarily controlled by chemical degradation. Degradation of polymers is usually manifested in a reduction of molecular weight, increase of crystallinity in semicrystalline thermoplastics, increase of material density, a subtle increase in yield strength, and a dramatic reduction of toughness, i.e., specific fracture energy. An increase in material density, i.e., shrinkage of the degraded layer is constrained by adjacent unchanged material. It results in a buildup of tensile stress within the degraded layer and compressive stress in the adjacent unchanged material due to increasing incompatibility between the two. These stresses sum up with manufacturing and service stresses leading to an increase of the strain energy. At a certain level of degradation, a combination of toughness reduction and increase of the stored elastic energy results in fracture initiation (FI). From an energy consideration, SCC starts, when the release of the stored strain energy due to microcrack network formation compensates the required specific fracture energy. Considering a chain of micro-events leading to fracture initiation on macro scale, the probability of FI is evaluated using the formalism of Statistical Fracture Mechanics (SFM). A critical level of degradation is determined as the degradation at which FI takes place with certainty. The kinetics of the degradation process and the critical level of degradation then determine the time of fracture initiation. Experimental observations and a mathematical model of the described above processes are presented in this work.

1 INTRODUCTION

We distinguish four stages of stress corrosion cracking (SCC): 1) microcracks initiation resulting from polymer degradation; 2) slow growth of individual cracks; 3) strong interaction of cracks and formation of clusters; and 4) individual cracks and/or clusters growth and instability (Choi et al [1]). In this communication, we consider only the first stage, i.e., the fracture initiation process. The general problem of degradation related fracture initiation (FI) in engineering thermoplastics is considered here on example of plastic pipes in water distribution systems for specificity. FI in pipes employed in water distribution, is usually observed in form of a microcrack network within a degraded layer of material on the inner surface of the pipe exposed to flowing water. There is a specific molecular level pathway of material degradation for each material-environment system. At the same time, there is also a striking commonality of the phenomena in different material-environment systems, when it is considered on a continuum mechanics level. In this paper, we develop a model of FI driven by a combination of oxidative degradation and stresses. The chemical degradation plays a leading role in the fracture initiation process, whereas the mechanical stresses control the orientation of initial fracture.

2 STATISTICAL APPROACH TO FRACTURE INITIATION

According to numerous observations, the orientation of fracture and kinetics of fracture growth obey deterministic laws, whereas the time and location of individual microcrack initiation site are essentially random events. Thus, we consider an alternative to classical nucleation theory approach in modeling of fracture initiation by means of Statistical Fracture Mechanics (Chudnovsky [2], Chudnovsky and Kunin [3]). We define Fracture Initiation (FI) as an event of spontaneous expansion to a macroscopic scale of a brittle fracture (a microcrack) triggered by a random defect formed on a sub-microscopic scale. We consider oxidative degradation driven FI in polybutylene (PB) tubing for specificity, since detailed analysis of degradation process and resulting deterioration of mechanical properties has been reported. Certain disinfectants added to the water create a chemically aggressive

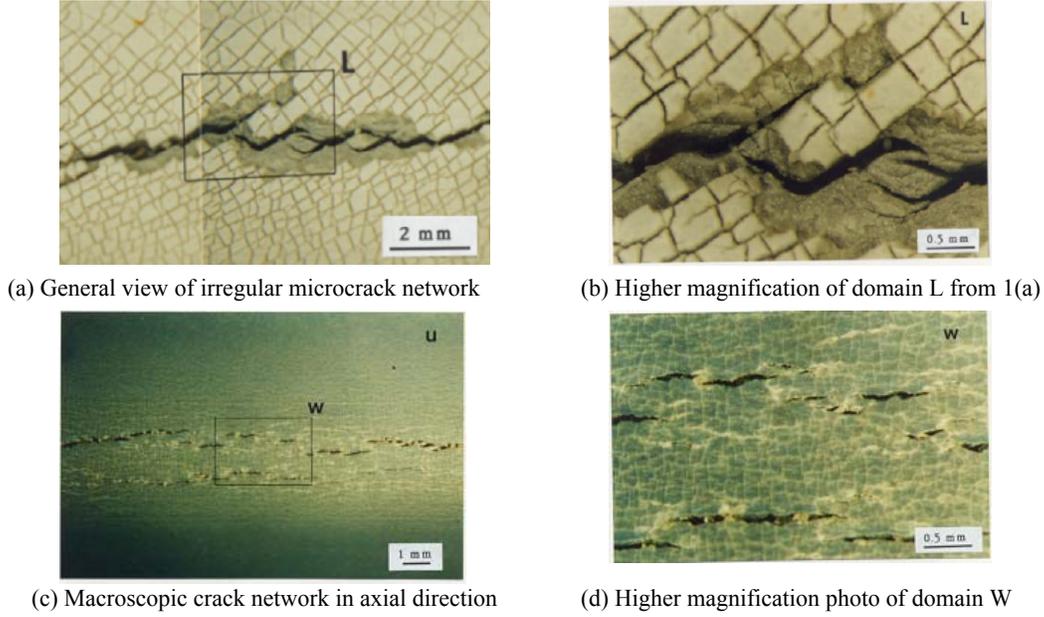


Figure 1: Microcrack network on the inner surface with irregular cell pattern

for PB environment, which with time results in formation of a layer of degraded material of thickness l_0 adjacent to the inner surface. The degradation process affects the fracture initiation in two ways: it causes a significant decay of specific fracture energy $\gamma(\omega)$ and a buildup of degradation related stress σ_ω as a significant part of total stress, σ_{tot} . The fastest rate of degradation in this case takes place at the inner surface of the tubing, which is in direct contact with the flowing water. Therefore the first, sub-microscopic defect that triggers FI is, most likely, located at the inner surface. A small domain of a circumferential cross section of PB tubing is shown on the micrograph in Figure 1(a). The micrograph displays a layer of degraded polymer adjacent to the inner surface of the tubing. A boundary that separates the degraded and original materials is also well visible due to the differences in color. Multiple fractures initiated at the inner surface of the tubing and extended through the degraded layer are also well visible. Figure 1(b) is a schematic representation of a sample set Ω of random fracture paths, that may be constructed considering a large number of cracks shown in Figure 1(a) shifted toward one origin, \underline{x}_0 . It can be seen on Figure 1(a) that only one particular path $w(\underline{x})$ from the set Ω of virtual paths is realized at each particular location. Moreover, the stress release resulting from fracture formation determines almost regular spacing between individual fractures. It is readily observable on Figure 1(a).

Let consider a fracture path $w(\underline{x})$ that starts at a point \underline{x}_0 on the inner surface and terminates at a point \underline{X} on the interface between degraded and undegraded material. The condition of fracture extension from \underline{x}_0 to \underline{X} along $w(\underline{x})$ is the requirement that Griffith condition $G_1 \geq 2\gamma(x)$ is met at every point of fracture trajectory $w(\underline{x})$. Here G_1 is the conventional in Linear Fracture Mechanics notation for the energy release rate (ERR), and the specific fracture energy $\gamma(x)$ is considered to be a random field that reflects a random variation of material composition, morphology and the extend of degradation on microscopic and sub-microscopic scales. Pointwise distribution of γ -field along the fracture path $w(\underline{x})$ follows Weibull distribution (with shift γ_{min} , scale γ_0 and shape α factors

respectively), since the crack “selects” the weakest direction at each step of its advance. The above condition of FI, i.e., fracture extension from x_0 to X along $w(x)$ is a natural generalization of Griffith condition for a heterogeneous media. A method to compute a probability of FI ($Pr\{FI\}$), i.e., a probability of spontaneous crack propagation from $x_0 = 0$ to $X = l_0$ along $w(x)$ has been proposed in (Chudnovsky [2], Chudnovsky and Kunin [3]). In the first approximation (the roughness of fracture path is ignored) $Pr\{FI\}$ can be expressed as:

$$Pr\{FI\} = \exp\left[-\int_0^{l_0} \exp\left\{-\left[\frac{G_1(x, \sigma_{tot}) - 2\gamma_{min}}{2\gamma_0}\right]^\alpha\right\} \frac{dx}{r}\right], \quad (1)$$

where r is the correlation distance of γ -field, and a dimensionless shift parameter $q = \gamma_{min} / \langle \gamma \rangle$ representing the shift factor normalized by the mathematical expectation $\langle \gamma \rangle$ of statistically homogeneous γ -field, is introduced here for further analysis.

We also introduced here a degradation parameter ω , which is discussed in more details in the following section. Energy release rate (ERR) G_1 for the problem at hand can be expressed as $G_1 = (1.12\sigma_{tot})^2 \pi x E^{-1}$, where $E' = E(\omega)/(1 - \nu^2(\omega))$, E and ν stand for the Young's modulus and Poisson's ratio weakly dependent on degradation parameter, and the total stress σ_{tot} comprises of residual (manufacturing related) stresses, service stresses σ_0 , and degradation induced stresses σ_ω . Thus, G_1 as well as the parameters of Weibull distribution depend on the degradation parameter ω .

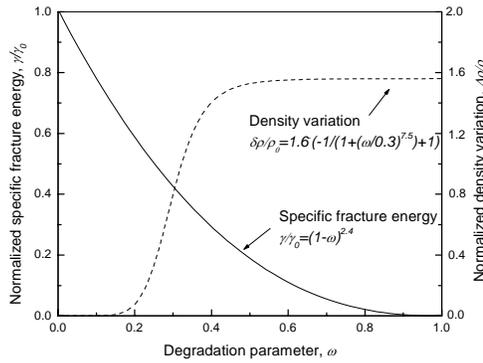


Figure 2: Normalized toughness, γ/γ_0 , and density change, $\Delta\rho/\rho_0$ (in %)

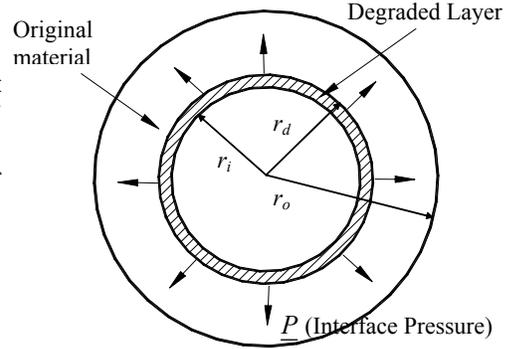


Figure 3: A sketch of polymer tubing cross section with inner degraded layer

Therefore $Pr\{FI\}$ depends on ω and can be rewritten as $Pr\{FI, \omega\}$. A critical level of degradation, ω^* , can be defined as the value of the degradation parameter at which fracture initiation takes place with certainty. Then cumulative distribution as well as the statistical moments of ω^* can be obtained.

$$F(\omega^*) = Pr\{FI, \omega\} \Big|_{Pr\{FI\} = 1} ; \langle \omega^* \rangle = \int_0^1 \omega^* dF(\omega^*), \sigma^2(\omega^*) = \int_0^1 (\omega^* - \langle \omega^* \rangle)^2 dF(\omega^*), \quad (2)$$

The original PB has sufficient toughness $2\gamma_0$ to make the crack nucleation practically an impossible event. However, there is a decrease of $\gamma(\omega)$ and an increase of σ_{tot} with progression of degradation (increasing ω). Thus, the probability of crack nucleation increases to the certainty ($P = 1$) with ω approaches a critical value. The kinetics of the process of degradation in time $\omega(t)$ together with the value of ω^* allows one to determine the time t_i of fracture initiation.

3 CHEMICAL DEGRADATION AND MECHANICAL PROPERTIES VARIATION.

Chemical degradation is the name for detrimental changes in chemical makeup and/or molecular structure of polymer caused by chemical interaction with the environment. It leads to a deterioration of useful properties of the material. Degradation by oxidation directly results in a reduction of molecular weight, which in turn leads to an increase of crystallinity in semicrystalline polymer as well as density, a subtle increase in yield strength, and a dramatic reduction in toughness. Chemical degradation of polymers is usually linked to the molecular weight reduction. An easy measurable degradation parameter expressed in terms of current $M_w(t)$ and initial $M_w(0)$ weight average molecular weights, $\omega(t) = 1 - M_w(t)/M_w(0)$ has been recently proposed (Niu et al. [4]). In that study, the relationships between $\omega(t)$ and crystallinity, density and toughness variations have been observed using a UV accelerated oxidation technique. The molecular weight of PB was measured by solution viscosimetry, density was measured using density gradient column, and the tensile toughness was evaluated from standard tensile test (ASTM D 638). An increase of degradation parameter as a function of UV exposure time has been reported in (Niu et al. [4]). The changes in crystallinity, density and toughness vary in time following $\omega(t)$. The material properties variation in terms of the degradation parameter $\omega(t)$ (a state parameter), rather than in time are presented below based on data reported in (Niu et al. (4)). Both, the relative density $\delta\rho/\rho_0$ (in %) and normalized toughness parameter γ/γ_0 variations with degradation parameter ω are shown in Figure 2. Simple relations of the experimental data, $\gamma = \gamma_0(1 - \omega)^n$ and $\delta\rho/\rho_0 = 1.5\{1/(1 + 0.2\omega)^m\}$, are used. As seen in Figure 2, the most variation of the material properties occurred prior to ω reaching 0.5.

Increase of density, i.e., shrinkage of the degraded inner surface layer of plastic pipe is constrained by the outer layer of unchanged material. It results in an increase of incompatibility between the inner and outer layers and a buildup of tensile stress within the degraded layer and compressive stress in the outer layer. To evaluate the stresses it is convenient to consider an outward oriented traction \underline{P} along the interface between the inner (degraded) and outer (unchanged) layers that reflects the constrain applied to the shrinking inner layer (see Figure 3). Computation of interfacial traction \underline{P} and degradation related radial $\sigma_{\omega,rr}$; circumferential (hoop) $\sigma_{\omega,\theta\theta}$ and axial $\sigma_{\omega,zz}$ components of stress tensor follows from the solution of an axisymmetrical, plain strain elasticity problem for traction free thin bimaterial cylindrical shell with a time dependent density of the inner layer as shown on Figure 3. The compatibility equation (displacement continuity along the interface between inner and outer layers) together with the conventional equilibrium equations constitutes a complete set of equations for determination of stress tensor. All stress tensor components, hoop, axial and radial ones acting in the degraded layer are proportional to the interfacial traction \underline{P} , which explicitly depends on density variation, pipe dimensions and degraded layer thickness:

$$\underline{P} = \frac{E(\omega)(r_d^2 - r_i^2)(r_o^2 - r_d^2)}{4r_d^2(r_o^2 - r_i^2)} \cdot \frac{\Delta\rho}{\rho}, \quad (3)$$

where r_d , r_i , and r_o are indicated on Figure 6. For the problem at hand, the most important hoop stress $\sigma_{\omega,\theta\theta}$ can be expressed as:

$$\sigma_{\omega,\theta\theta} = \frac{\underline{P} \cdot r_d^2}{r_d^2 - r_i^2} \left\{ 1 + \left(\frac{r_i}{r} \right)^2 \right\}, \quad (4)$$

The stress $\sigma_{\omega,\theta\theta}$ is the dominant stress component induced by degradation. Dependence of the hoop stress $\sigma_{\omega,\theta\theta}$ on the degradation parameter ω is shown in Figure 4 for three values of degraded layer thickness l_0 : 1% (0.02 mm), 3% (0.06 mm) and 5% (0.1 mm) of wall thickness. It can be seen from Figure 4 that the degraded layer thickness has almost no effect on the magnitude of hoop stress. The

amount of degradation induced stresses due is approaching yield stress (σ_y is about 20 MPa) and at least comparable, but most commonly greater then the service stresses.

4 EVALUATION OF CRITICAL LEVEL OF DEGRADATION AND FRACTURE TIME

The total stress should be used for evaluation of the critical level of degradation according to the described above procedure (2). The total hoop stress σ_{tot} is the sum of hoop stress $\sigma_{0,\theta\theta}(p)$ due to applied internal pressure that does not depend on ω , and degradation induced $\sigma_{\omega,\theta\theta}$ expressed by (4) (here we ignore the processing related stresses). The hoop stress $\sigma_{0,\theta\theta}(p)$ in internally pressurized pipe is well known (e.g. Shames and Cozzarelli [5]):

$$\sigma_{0,\theta\theta} = p \frac{r_i^2}{r_o^2 - r_i^2} \left(1 + \frac{r_o^2}{r_i^2} \right), \quad (5)$$

Employing (4) and (5) for computation of ERR G_1 and taking $\langle \gamma \rangle$ dependence on ω the same as in Figure 2 into equations (1), we find the cumulative distribution $F(\omega^*)$, and the statistical moments of ω^* (eq. (2)) and their dependence on internal pressure p . The cumulative distribution $F(\omega^*)$ for three values of $q = \gamma_{min} / \langle \gamma \rangle$ are shown in Figure 5. The mathematical expectation of $\langle \omega^* \rangle$ dependence on internal pressure is depicted in Figure 6 for various values of q . Apparently,

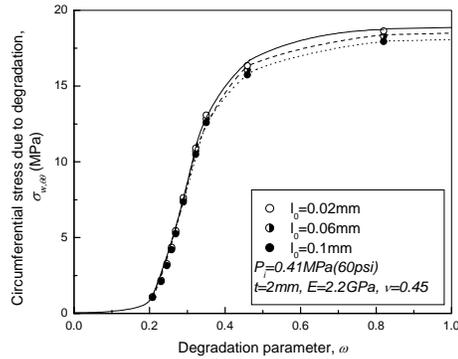


Figure 4 Maximum hoop stress dependency on degradation level

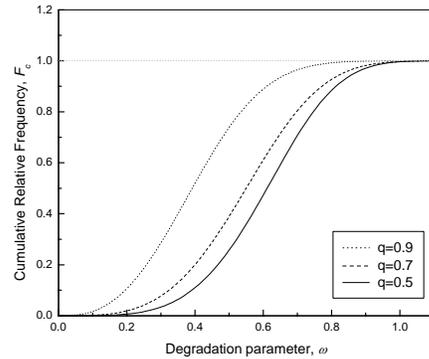


Figure 5 Cumulative distribution $F(\omega^*)$ for three values of q

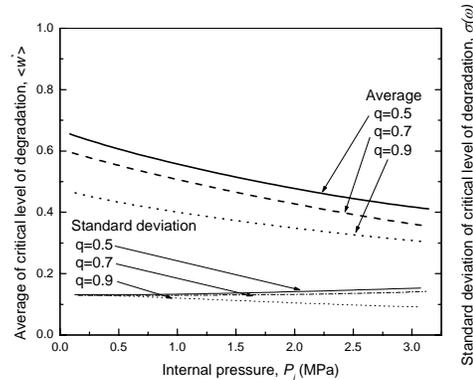


Figure 6 Critical degradation level dependence on internal pressure

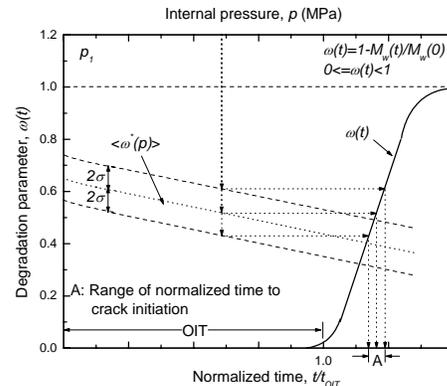


Figure 7 Schematic diagram for determination of fracture initiation time

the greater is the applied pressure p , the lesser level of degradation is required to initiate fracture.

The kinetic equation for the degradation parameter $\omega(t)$ combined with a critical level ω^* of degradation at the onset of fracture leads to determination of time to FI. A simple procedure for evaluation of time to fracture initiation as the result of polymer degradation is presented in Figure 7. The solid line on Figure 7 represents the progression of degradation $\omega(t)$ with time. The oxidation induction time t_{OIT} at normal service conditions is taken as the time scale for horizontal axis. There is very little degradation for dimensionless time, $\tau = t/t_{OIT} < 1$. Beginning from $\tau = 1$ the degradation process rapidly progresses ($\omega(t) \rightarrow 1$). The dotted line represents $\langle \omega^* \rangle$ dependence on applied pressure p . The internal pressure p is indicated on the upper horizontal axis. Two values of applied pressure are selected for the illustration of the procedure. The corresponding two levels of the average critical degradation parameter are marked on the dotted line of $\langle \omega^* \rangle \sim p$ dependence by vertical arrows. The horizontal arrows indicate $\langle \omega^* \rangle$ levels on the $\omega(t)$ curve. Vertical arrows from these points to the time axis indicate the corresponding time to fracture initiation. The schematic diagram of Figure 7 for evaluation of the time to fracture initiation suggests that the onset of fracture in PB is primarily controlled by the degradation process and weakly dependent on applied load. At the same time, one should keep in mind that the stresses may affect OIT that is used as a time scale for normalization.

5 CONCLUSIONS

The initiation stage of SCC is primarily controlled by the kinetics of chemical degradation. The degradation significantly affects the specific fracture energy and creates a noticeable buildup of degradation related stresses. The applied pressure may affect the critical level of degradation at the onset of fracture. However, it has a relatively small effect on the time of fracture initiation. The applied load starts to play an increasingly important role with stress corrosion crack growth, crack interaction and formation of clusters (the second and third stages of SCC). Finally, the external load becomes a dominant factor in SCC colony instability and ultimate failure.

There is a challenge to formulate an accelerated test conditions that would be relevant to the observed phenomena. Conventional acceleration by an elevated temperature disturbs the similarity conditions by changing material morphology (crystallinity), and mobility of aggressive agent. Moreover, the processes of AO extraction, consumption, and diffusion as well as various stages of fracture all have different temperature acceleration factors. It appears that different scaling laws operate on various stages of fracture process. The theoretical modeling allows one to sort out the abovementioned factors and formulate an appropriate accelerated testing for different fatigue stages.

6 REFERENCES

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