Fracture behavior of degraded polyethylene thin films for solar thermal applications

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Abstract

Thin polymer films and tubes are under consideration as materials for use in roof top mounted solar thermal collectors. When polymer components are exposed to chlorinated water or UV light, degradation can lead to diminished mechanical performance and premature failure from rupture. In this paper, fracture toughness and crack growth of degraded polyethylene (MDPE) are investigated. Thin film PE samples (0.3mm thick) are degraded through exposure to 80°C chlorinated water (8 ppm chlorine) for up to 45 days. The extent of degradation is quantified by carbonyl index, a nondestructive measure of the chemical byproduct of degradation, such that a high carbonyl index indicates significant degradation. Single edge notched specimens are prepared from the degraded samples and mode I fracture tests are performed. In one set of tests, samples are loaded at a constant rate and the fracture toughness of the film samples is evaluated by the essential work method. In another set of tests, samples are loaded under a constant load and the crack growth rate is measured. The data can be used to inform design of polymeric components for solar applications. For designs that use thin films, the fracture toughness can be used to obtain a conservative estimate of the critical stress $\sigma_c$. Hence, an appropriate film thickness can be selected to ensure that stresses do not exceed the design stress value during the lifetime of the component. For designs that use tubes, the rate of crack growth can be used to estimate the time to rupture. Tube thickness can be selected to extend the lifetime.

Keywords: Fracture behavior; degradation; polyethylene; fracture toughness; crack growth rate

1. Introduction

Polymeric materials have been considered for low temperature solar thermal applications. Traditionally, glass and metal have been used for constructing domestic hot water (DHW) solar collectors. These materials are expensive and susceptible to corrosion. In addition, the heavy weight of
these materials greatly increases the installation costs. Polymeric materials can provide a low cost, light weight option for solar collectors [1].

Several commercially available solar thermal collectors utilize polymeric absorbers comprised of many thin walled polymeric tubes. Tube geometries are selected to satisfy the competing requirements of strength and thermal resistance: thicker tubes are desirable for satisfying strength requirements while thinner tubes are desired to minimize the conductive thermal resistance across the tube wall. Polymeric film absorbers fabricated from PE and/or PP films (with additives for UV resistance) are also under development [2]. As with multi-tube absorbers, the polymer film thickness must be selected to meet both strength and thermal requirements. Commodity thermoplastic polymers such as PE and PP are often selected for these applications because these low cost materials have good fabrication properties and excellent compatibility with hot water. When compounded with antioxidant stabilizers, polymer lifetime can be extended. However exposure to chlorinated potable water, UV and high temperature depletes the anti-oxidant stabilizers over time and places the polymer at risk of degradation. As the polymer degrades, the tube or film becomes brittle. Cracks initiate due to the inner pressure, thereby jeopardizing the component strength. Increasing the tube/film thickness might lessen the degradation effects; however, it also has a negative impact on the component thermal performance. Hence, it is important to characterize the mechanical durability over the component lifetime.

In the present study, methods for evaluating crack growth and fracture toughness as a function of degradation are presented. Fracture data are obtained for MDPE samples that have been degraded (formation of carbonyl groups) in chlorinated water.

2. Background

2.1. Crack growth in polymers

The basic mechanism of crack growth in polymeric materials can be described as a stepped process. After a small, micro scale, initial crack forms, a process zone develops ahead of the crack tip. Large localized deformation occurs in the process zone [3]. As shown in Figure 1 the process zone is comprised of fibrils and voids. When a crack opening load is applied, voids are created within the process zone and these voids elongate into a “fiber-like” network. These fibers break and the crack extends through the process zone. This process is repeated: formation of the process zone, voids, and propagation of the crack through the zone.

Several researchers have proposed modeling approaches to evaluate crack growth in polymers, and, in some cases, the effect of degradation on crack growth. Brown et al. [4] have proposed a theory for crack growth in polyethylene which relates the crack opening displacement rate with several factors including the yield point of polymer, stress intensity factor, intrinsic viscosity of fibrils in the craze, and Young’s Modulus. Choi et al. [3] have proposed a model for crack propagation in polyethylene based on Crack
Layer Theory [5] which considers chemical degradation along with mechanical degradation of polymer. Their model, which includes the simultaneous effects of chemical and mechanical degradation (creep) in the polymer, is based on energy methods. The thermodynamic forces that drive the crack ($X^{CR}$) and process zone ($X^{PZ}$) are considered to be directly proportional to the net energy release. The crack is stationary when the energy release rate is smaller than the specific fracture energy. Over time, the specific fracture energy decreases due to chemical and mechanical degradation of the material. When the energy release rate becomes greater than the specific fracture energy, the crack grows. The resulting crack propagation curve (crack length vs. time) shows steps corresponding to the progress of degradation through the thickness of the sample [3].

One commonly employed, “lab scale”, method for evaluating slow crack growth in polymers is the PENT test (Pennsylvania Edge-Notch Tensile Test, ASTM F1473). In the PENT test, a notched rectangular (25 x 8 mm cross section) specimen is subjected to uniaxial tensile loading. The load is selected to achieve a stress at the notch tip of 2.4 MPa, and tests are often performed at an elevated temperature to accelerate crack growth. The time to failure (i.e. rupture) or to achieve a separation of 1.25 cm (in the notched region) is recorded. PENT test results have been used to compare polymer materials for applications in which long term loading is expected, such as piping. Researchers affiliated with the polymer piping industry have recently noted, however, that the PENT test does not accurately reflect the failure modes associated with creep rupture testing (hydrostatic pressure testing) of polymer pipes [6]. In particular, the PENT test failure time is largely influenced by large scale, macroscopic ductile failure—which is inconsistent with brittle failure observed in piping burst tests. Frank et al. [7] have recently proposed a method for studying the crack growth kinetics in high density polyethylene pipes. The authors measured the crack kinetics in a 13.8 mm diameter cylindrical bar sample (Crack Rounded Bar) for several stress ratios and extrapolated the data to obtain creep crack growth. For either the PENT test or the CRB test, the sample size is relatively thick and degradation will not be uniform through the thickness. To evaluate the fracture behavior as a function of degradation, the ideal specimen will have uniform degradation throughout the thickness. A test procedure that requires thick specimens will not be well suited for studying the effect of degradation.

2.2. Fracture toughness

Resistance to crack growth is characterized by fracture toughness: A material with higher fracture toughness is more resistant to crack initiation. Fracture toughness is expressed in terms of the critical stress intensity factor $K_c$. For a film subjected to a tensile stress $\sigma$ with an initial crack length $a$ (Figure 2), the stress within the film must be less than the critical stress $\sigma_c$ that causes crack propagation:

$$\sigma < \sigma_c \quad \text{where} \quad \sigma_c = \frac{K_c}{Y\sqrt{a}}.$$  \hspace{1cm} (1)

Where $Y$ is a geometry factor. While $K_c$ has been characterized for many polymer films [3 p. 447], the property has not been characterized for degraded polymer films or as a function of the extent of the film degradation. Because the film will undergo degradation throughout the lifetime of the collector, a method to evaluate $K_c$ as a function of the extent of degradation is important to designing a polymeric collector.
The procedure for evaluating $K_c$ depends on the loading conditions (plane stress or plane strain) and the material failure mode (ductile or brittle). For the present application, plane stress loading conditions and a ductile failure mode apply [8] (note in this case ductile implies local yielding near the crack tip, but not at the macroscale). The essential work method (EWM) has been applied to evaluate fracture toughness (and $K_c$) of ductile materials. In the essential work method [9,10,11], the work required to initiate crack growth in single edge notched (SEN) film samples loaded in tension is evaluated. The total work in fracture $W_T$ is attributed to two sources: the essential work $W_e$ that results in tearing and forming a necked region, and the non-essential work $W_p$ expended in plastic deformation of the outer region. While there is also energy dissipation due to the viscoelastic nature of the polymer film, this work is considered small compared to $W_e$ and $W_p$ and therefore negligible. The specific fracture energy $w_T$ is further defined as the total work $W_T$ divided by the ligament efficiency, the product of the ligament length $L$ and sample thickness $t$:

$$w_T = W_T / Lt$$

Thus, the specific fracture energy is approximated as [12]:

$$w_T = w_c + \beta w_p L$$

where $\beta$ is a proportionality constant related to the non essential work. Equation (3) describes the linear relationship between the total specific energy of fracture and the ligament length. For the critical condition (at which the crack begins to propagate), $K_c$ can be found from the essential work of fracture [11]

$$w_c = \frac{K_c^2}{E}$$

To implement the essential work method, SEN samples are loaded in tension at a constant rate and the load as a function of crosshead displacement is recorded. The total fracture energy $W_T$ is calculated by integrating the load over the crosshead displacement and the specific fracture energy $w_T$ is evaluated by dividing the total energy by the ligament efficiency (equation (2)). The data are plotted as a function of the ligament length and fit with a line (equation (3)). The resulting intercept with the $L=0$ axis is the specific essential fracture work $w_c$ (Figure 3). It is anticipated that as the extent of degradation progresses the essential fracture work will decrease, as shown in Figure 3. Many samples, each with a different ligament length and degradation level, are required to determine $K_c$. 

![Fig. 2. Crack propagation in a thin film loaded in stress. $r_p$ represents the plastic zone at the crack tip.](image)
3. Objective

The goal of the present work is to develop test methods for evaluating fracture behavior (crack growth and fracture toughness) in polymer materials as a function of the extent of degradation. Polymer test specimen degradation must be controlled, uniform and quantifiable. The crack growth mechanism must also be consistent with that observed in polymer pipe burst tests: namely, microscopic fracture of fibrils in the process zone.

4. Experimental procedure

Thin film samples are well suited to study the effect of degradation, in that the samples, when exposed to an oxidative environment can be uniformly degraded through the thickness. In the proposed method, thin film polyethylene samples are uniformly degraded via oxidation in an 80°C water bath. The extent of degradation is characterized by FTIR. An initial crack is placed in the sample and crack growth under uniaxial loading is observed. Details of the test methods are as follows.

4.1. Sample preparation

Thin “plaque” samples of medium density polyethylene (MDPE), 32 mm by 44 mm by 0.3 mm thick, are prepared by compression molding. The unexposed material has a density of 0.936g/cm³, and a molecular weight $M_w = 200kg/mol$. The material was specially formulated with a minimum additive level so that degradation proceeds more rapidly than in commercially available materials. The samples are exposed to 80°C chlorinated water for up to 45 days. The water bath conditions are controlled such that the concentration of the chlorine is maintained at 8ppm and the pH is $6.8 \pm 0.2$. The ORP (oxidation reduction potential) is in the range of 700 - 750 mV. The extent of degradation in these samples is characterized by FTIR following the procedure described in [13]. These researchers showed that there is a correlation between the carbonyl index and the material strain at failure (Figure 4). In this case the carbonyl index is defined as the ratio of the area of the OX band (1690 – 1790 cm⁻¹) to the peak corresponding to polyethylene (2018 cm⁻¹). The carbonyl index for unexposed samples is less than 10. The carbonyl index for samples with the longest exposure time is greater than 50. By using FTIR, the extent of degradation of a sample can be characterized nondestructively, prior to evaluation of the fracture toughness. Moreover, because the samples are thin films, the extent of degradation can be assumed to be uniform through the thickness of the sample [14].
Exposed samples were removed from the bath at intervals ranging from days to week in order to achieve a range of degradation levels. The carbonyl index for each sample was measured by FTIR. SEN samples (Figure 2) were prepared by introducing an initial crack in the (degraded) plaque samples using an X-ACTO knife. The crack was oriented along the 32 mm width W of the specimen. For the crack growth experiments, the crack length $a$ is $5.5 \pm 1$ mm. For the fracture toughness experiments, the crack length was set such that the ligament length $L$ was $5.1 \pm 0.6$ mm.

4.2. Testing method

The SEN samples are loaded at a constant load (for crack growth experiments) or at a constant load rate (for fracture toughness experiments). Crack initiation and growth are recorded by a digital camera and a video capture card. The video recording apparatus consists of a Panasonic CCTV camera (WV-BP330), Navitar lens system, a tripod stand, a video capture card (HD 600 PCI Digital and Analog TV Tuner from ATI TV wonder), and a computer with video editing & processing software. The videos are separated into images at regular intervals of time and each image is filtered based on the pixel intensity using MATLAB. Images are then processed to evaluate the length of the crack and process zone. The images available for processing have the resolution of 96 dpi. The crack and process zone lengths as a function of time are obtained from the processed image data. The experimental set up is shown in Figure 5.

![Diagram](image1.jpg)

**Fig. 4.** Strain at failure data for polyethylene samples as a function of the carbonyl index [13].

**Fig. 5.** Crack propagation experimental setup, taken from [13]
5. Results and discussion

The carbonyl index data for plaque samples ranged from 10 to 90. Strain at break data for polyethylene plaque samples with similar carbonyl index values were published in [13] (see Figure 4). For less degraded samples, with a carbonyl index <10, the strain at failure can be as great as 700%. As the material degradation increases, to carbonyl index greater than 50, the strain at break asymptotically approaches 15%. Even at this highly degraded state, the sample strain at break is considered ductile. Because there is good correlation between strain at break and CI, the material ductility can be determined by FTIR without destroying the sample.

Data from video images recorded during testing of SEN samples further confirm that the degraded film exhibited ductile behavior. Figures 6 (a) and 6 (b) show video images of crack growth in moderately degraded (CI=23) and highly degraded (CI=52) SEN specimens, respectively. Zone A and zone A’ denote the corresponding plastic deformation areas on the two samples. Plastic deformation is much greater in the less degraded sample, indicating higher material ductility. For the highly degraded sample, ductile failure can still be observed, although in a less significant manner. In both cases, the surface of the fracture is fibrous, and voids grow in the vicinity of the crack tip. These are characteristics of ductile fracture.

Fig. 6. (a) Crack growth in a moderately degraded SEN polyethylene sample (CI=23). (b) Crack growth in a highly degraded SEN polyethylene sample (CI=52)

5.1. Crack growth rate

In the crack propagation experiments, SEN samples were subjected to stress levels ranging from 5.1 to 9.2 MPa. Seven samples in all were tested with CI ranging from 44 to 93. Table 1 summarizes the sample geometry, extent of degradation, loading condition and time to failure. Note failure time does not necessarily decrease with increasing CI. Failure time will depend on the initial crack length as well as the applied stress. Crack growth rate data are plotted in Figure 7. The plot axes correspond to the standard equation of crack growth from linear elastic fracture mechanics (LEFM)

\[ \frac{da}{dt} = C(D)(K/Y)^n \]

where Y is the geometry factor and K is the stress intensity factor (see equation 1).

The plot shows log (K/Y) as a function of the crack growth rate. The data are grouped into four levels of degradation: D1=44; D2=55; D3=62, 64; and D4=88, 93. By plotting the data as a function of K, the effects of stress and crack length are considered and data at a comparable degradation level are collinear. Lines were fit to each of the four degradation level data sets in the log(K/Y) vs log(da/dt) plot. The best-
fit lines are parallel ($R^2=0.88$), indicating that the exponent 'n', the inverse of the slope, is independent of the degradation. The linear fit corresponds to $n=30.3$. The intercepts of these trend lines, decrease with increasing degradation. Thus, the crack growth coefficient $C$ is a function of the extent of degradation. The relationship between the crack growth coefficient and the carbonyl index CI is found by a linear fit to the intercept data such that: $\log(C) = n[(0.0042)(CI)-6.54]$.

Table 1. Sample data for the crack growth experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbonyl Index (CI)</th>
<th>Stress level (MPa)</th>
<th>Initial crack length/Sample width (a/w)</th>
<th>Failure time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>44</td>
<td>9.2</td>
<td>0.203</td>
<td>0.24</td>
</tr>
<tr>
<td>B</td>
<td>55</td>
<td>7.7</td>
<td>0.218</td>
<td>1.39</td>
</tr>
<tr>
<td>C</td>
<td>62</td>
<td>7.0</td>
<td>0.194</td>
<td>1.83</td>
</tr>
<tr>
<td>D</td>
<td>64</td>
<td>6.3</td>
<td>0.166</td>
<td>180.5</td>
</tr>
<tr>
<td>E</td>
<td>76</td>
<td>5.8</td>
<td>0.144</td>
<td>171.6</td>
</tr>
<tr>
<td>F</td>
<td>88</td>
<td>5.1</td>
<td>0.178</td>
<td>163.8</td>
</tr>
<tr>
<td>G</td>
<td>93</td>
<td>6.3</td>
<td>0.131</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Fig. 7. Crack growth data for SEN samples at various levels of degradation

5.2. Fracture toughness

The specific work of fracture $w_T$ was evaluated for ten samples, each with a ligament length of 5.1 ±0.6 mm. The error in $w_T$ is caused by the variance in ligament length. Absolute error decreases with increasing degradation, but relative error remains almost constant (about 25%) for all specimens. For carbonyl index less than 30, $w_T$ ranges from 70-180 kJ/m² (Figure 8). As sample degradation increases (increasing carbonyl index), the specific work of fracture decreases. This trend is reasonable since it is expected that the fracture toughness will decrease as the material becomes less ductile. The specific work of fracture $w_T$ approaches a threshold value of approximately 25 kJ/m² for samples with a carbonyl index of 50 or greater.
The specific work of fracture data indicate that there is a threshold level of degradation: as the polyethylene film degradation exceeds a carbonyl index of 50, $w_T$ remains constant. Given the relationship between $w_T$, $w_e$ and $K_c$, it is expected that $K_c$ will also approach a minimum value. This minimum $K_c$ can guide designs in which degradation is expected. A conservative estimate of the critical stress (equation (1)) can be obtained by using the threshold value of $K_c$. For example, film thickness in a solar collector should be selected such that the stress is less than this conservative estimate of the critical stress.

![Graph](Fig. 8. Carbonyl Index plotted against $w_T$. The uncertainty in the essential work is a result of variability in the ligament length)

### 6. Summary and Future Work

When polymers are used in solar thermal applications, there is potential for material degradation from exposure to UV or chlorinated (potable) water. The particular failure mechanism in polymer components that have degraded (via oxidation) is fracture. In this study, we describe experimental techniques for evaluating the relationship between crack growth and the extent of degradation in polymers. The key to the proposed methods is to perform fracture experiments on samples that have been uniformly degraded. In this case, 0.3 mm thick film specimens are exposed to chlorinated hot water for up to 45 days. Degradation is uniform through the thickness of the film. Furthermore, the extent of degradation is nondestructively quantified by FTIR analysis. In this way, the samples used in the crack propagation study have a known, quantified extent of degradation.

The study of crack growth is critical to predicting lifetime in polymer tubes exposed to UV or potable water. The extent of degradation in a polymer tube (or other solar thermal components) will vary through the thickness. For example, if potable water flows through the tube, then degradation at the tube inner surface will be greater than at the tube outer surface. Crack growth, will proceed at rates that depend on the extent of degradation and the applied stress. This crack growth data must be obtained over a range of degradation states. A model based on crack growth through the thickness can guide the selection of an optimum tube wall thickness.

An essential work method is proposed to quantify the fracture strength/resistance of the film. The pilot study data are limited to a single ligament length $L_0$, but span a range of material degradation levels. This study, then, represents the case of a vertical line at $L=L_0$ through several sets of essential work data each at a single level of degradation (Figure 3). The effect of degradation on the critical stress intensity factor can only be determined by studying crack initiation and propagation over a range of ligament lengths. The study implies that $K_c$ approaches a minimum value as the degradation increases. In the future, only a set of samples, spanning a range of ligament lengths, degraded beyond the threshold degradation (CI=50) is needed to evaluate the minimum $K_c$. A conservative estimate of $\sigma_c$ can therefore be determined from this minimum $K_c$. 
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References


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