POLYMER TESTING

Property modelling

Observation and modeling of environmental stress cracking behaviors of high crystalline polypropylene due to scent oils

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A B S T R A C T

Environmental stress cracking (ESC) is a common phenomenon that affects commercially available polymeric materials exposed to liquid agents under external loading, and it is one of the most common causes of their unexpected long-term failure. In this study, ESC behavior of high crystalline polypropylene (HCPP) was studied through modified notched constant tensile load testing using two different scent oils as environmental agents. The relationship between total lifetime of the material and initial stress intensity factor was determined. Despite the similar molecular structures of the scent oils, they caused a remarkable lifetime difference for the material within a certain loading range. Swelling tests were also conducted in order to define diffusion coefficients for the scent oils without any loading. From these results, the diffusion coefficients for the two scent oils into the HCPP were modeled according to the initial stress intensity factor.

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1. Introduction

Environmental stress cracking (ESC) is a phenomenon that affects externally loaded polymers through diffusion of the surrounding liquid or gas agents into the material. Examples of ESC agents include detergents, oils, water and soaps. Since many engineering polymers are frequently exposed to such agents, environmental stress cracking resistance (ESCR) is an important long-term property of polymers. Sudden failure of these materials during practical applications is commonly caused by ESC [1–3]. Therefore, the mechanisms and prevention of polymer ESC have been widely studied and are of particular interest [1–7].

The main difference between ESC and stress corrosion cracking (SCC), another type of chemical-induced stress cracking, is whether a chemical reaction takes place or not. SCC involves the degradation by chemical reaction between the polymer chain and aggressive chemicals, which normally leads to chain scission, cross-linking and embrittlement [8]. However, ESC is limited to polymer cracking without any chemical reactions, and entails diffusion and sorption, which cause softening and plasticization of particularly the amorphous regions in the polymer [9,10]. The diffused agents ease the formation of crazes [7,11]. For the case of externally loaded

high-density polyethylene (HDPE) in contact with detergents, the diffused agent acts as a lubricant for the amorphous phase tie chains. These chains have a larger available free volume than the crystalline regions, thus reducing the inter-lamellar cohesive strength through a lubricating effect [12]. This may cause the unexpected failure of engineering polymers with an applied stress that is well below their strength threshold. Therefore, crystallinity and molecular weight (MW) are important factors for polymer ESCR.

Rose et al. [13] investigated long term durability of polyethylene based on a creep deceleration factor and proposed the single creep parameter, which can be used to model slow crack growth as well as associated ESC behaviors of polyethylene. Soares et al. [14] studied the relationship between ESCR and crystallinity and MW of HDPE using CRYSTAF and SEC characterization. Kurelec et al. [15] reported a strong correlation between the strain hardening modulus and ESCR of polyethylene. In fact, it is known that the tie chain concentration within lamellae is one of the important factors that controls crack initiation, and the stain hardening modulus correlates well with tie chain concentration [16,17]. The presence of a high MW HDPE increases the ESCR since the disentanglement of tie molecules is inhibited. Choi et al. [1] also studied the ESCR of HDPE in a detergent using the tie chain concentration with respect to permeability, which is a more specific factor, through bent strip tests. A linear dependency was obtained between ESCR of HDPE and this new factor. For design purposes, ESCR for a blow molded

polyethylene terephthalate (PET) container was tested in order to optimize the shape of beverage bottles [6].

Although research concerning ESC of polymers has been consistently performed, a complete understanding of ESC phenomena has not yet been achieved because of the combination of complex materials and environmental parameters, such as diffusion coefficients of agents, sorption and desorption, viscoelastic behavior of polymers, micro void formation and their coalescence, and crack propagation. Moreover, most studies have focused only on several grades of polyethylene (PE) and a limited number of glassy polymers [18–20]. Considering the increasing demand of engineering polymers due to their many advantages, such as design flexibility, light weight, and recyclability, more fundamental research on ESC of diverse polymers is necessary.

Basically, ESC occurs because of deterioration of resistance of loaded polymers to crack initiation and propagation, inherently due to the diffusion of surrounding agents. Thus, in order to understand the underlying physical mechanisms of ESC, knowledge of the diffusion behavior of the ESC agent into the loaded polymer medium must first be acquired. In this regard, there have been some studies on the stress dependence of the diffusion coefficient in polymeric materials and composites [21,22]. However, these studies focused on a mathematical derivation using the free volume theory because it is difficult to measure the actual diffusion coefficient. Neumann et al. tested water absorption in a graphite-epoxy composite material under an applied stress [23,24]. Nowadays, polymers are used in a variety of environments, and not just in water, therefore diffusion behavior due to a multitude of agents must be studied. Furthermore, a relationship between the stress-dependent diffusion coefficient and the ESC behavior of various polymeric materials must be established.

In this study, ESC behavior of high crystalline polypropylene (HCPP) immersed in two different types of scent oils was studied through modified notched constant tensile load (NCTL) testing based on ASTM D5397 methodology. Swelling tests were also conducted to compare the diffusion coefficients for each oil without any loading. Each scent oil has a different composition, which leads to a different lifetime of the polymeric material under the same loading conditions. Furthermore, a newly suggested concept for crack initiation criteria under the ESC condition was used for modeling the diffusion coefficient with respect to the applied load. This concept should be employed as a design parameter for polymer applications in environments that induce ESC.

2. Experimental methods

2.1. Test materials and scent oils

ESCR tests on an injection molded HCPP sample, with ASTM D1822 type L geometry, were conducted using two different scent oils. The HCPP in this study was a homo-polymer, with an HJ-4012 grade number, produced by Yuhwa Polypro Company. A summary of the key mechanical properties is shown in Table 1. The thickness of the sample was approximately 1.9 mm, and an initial notch of

Table 1
Summary of key material properties of the tested HCPP.

Material property	Unit	Value
Density		0.91
% Elongation	%	50
Flexural modulus	GPa	2.06
Yield strength	MPa	41.2
Rockwell hardness	HRC	110
Heat deflection temperature	°C	140

approximately 0.2 mm was used for the accelerated tests. Two non-reactive liquid agent scent oils, limonene and lavender, were used as shown in Table 2. These oils were produced by Charabot Company. These scent oils have very similar compositions, but the lavender oil has an additional large molecule, 1-octen-3-yl acetate, which has a MW of 170.25 g/mol. This large molecule was the main reason for the lifetime variation of the material, even under the same loading conditions.

2.2. Swelling tests

Swelling of block-shaped HCPP in scent oils was also studied at the same temperature through creep testing. The absorbed mass of oil with respect to immersion time was measured for 200 h, and using a 3-dimensional diffusion equation, the diffusion coefficients for the scent oils into HCPP without any loading were determined. Assuming a constant diffusion coefficient (D) and constant molecular weight (MW) for the oils, the distribution of the diffused oil concentration, $\rho(x,y,z,t)$, satisfies the following 3-dimensional diffusion equation:

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho \tag{1}$$

The boundary and initial conditions are defined as follows:

$$\rho(0,y,z,t) = \rho(L_1,y,z,t) = \rho_0 \tag{2}$$

$$\rho(x,0,z,t) = \rho(x,L_2,z,t) = \rho_0 \tag{3}$$

$$\rho(x,y,0,t) = \rho(x,y,L_3,t) = \rho_0 \tag{4}$$

$$\rho(x,y,z,0) = 0 \tag{5}$$

A separation of variables method that combines the above equations yields the generalized form for the distribution of diffused oil, defined as Equation (6).

$$\frac{\rho}{\rho_0} = 1 - \frac{64}{\pi^3} \cdot \left[\left\{ \sum_{n=0}^{\infty} \frac{\pi}{N} \sin\left(\frac{Nx}{L_1}\right) \cdot e^{-D\left(\frac{N}{L_1}\right)^2 t} \right\} \right.$$
$$\cdot \left\{ \sum_{m=0}^{\infty} \frac{\pi}{M} \sin\left(\frac{My}{L_2}\right) \cdot e^{-D\left(\frac{M}{L_2}\right)^2 t} \right\}$$
$$\left. \cdot \left\{ \sum_{k=0}^{\infty} \frac{\pi}{K} \sin\left(\frac{Kz}{L_3}\right) \cdot e^{-D\left(\frac{K}{L_3}\right)^2 t} \right\} \right] \tag{6}$$

Here, $N = (2n+1)\pi$, $M = (2m+1)\pi$, and $K = (2k+1)\pi$.

By using the oil density distribution at specific points in the HCPP medium, the increasing mass of oil in the HCPP block with time can be obtained using a volume integral. Comparing the swelling test results with the estimated results, the diffusion coefficients for the scent oils into HCPP may be determined.

2.3. ESCR tests

As shown in Figs. 1 and 2, each notched sample was loaded with a stress in the range of approximately 7–14 MPa while in contact with the scent oils. All tests were conducted at an elevated temperature of 50 °C until failure, according to ASTM D5397 methodology. During the tests, the weight displacement was recorded to obtain creep strain versus time plots. A stiff steel wire was used to minimize any additional elongation after deformation of the loaded