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Study on permeation behavior and chemical degradation of PA66 in acid solution

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Abstract

In many polymers under corrosive liquids, degradation followed after permeation of environmental solution for a long period. The permeation rate of environmental solution, in many cases, is very low in corrosion-resistant polymeric materials. Therefore, the observation of the permeation of environmental solution and degradation of polymeric materials are very difficult in practical application. A simulation of permeation of solution is required in order to understand the permeation behavior of environmental solution and polymer degradation. A detailed analysis of the permeation behavior of solution accompanied by chemical reaction is important to study for improving the lifetime of polymers. Polyamide 66 (PA66) and sulfuric acid solution were used to investigate the quantitative study of permeation of environmental solution and its relation to degradation of polymeric materials. Correlation between diffusion process and degradation of PA66 related to the decrease of weight average molecular weight was defined. The diffusion rate of sulfuric acid solution was found to increase by decreasing weight average molecular weight of PA66 due to the established chain scission by hydrolysis reaction. The permeation of sulfuric acid solution that affected the decomposition reaction was modeled and quantitative evaluation of permeation of sulfuric acid was established.

Keywords: Diffusion; Molecular weight; Polyamide; Chemical degradation; Sulfuric acid

1. Introduction

Polymeric material application has encountered in almost every area of modern life in this few decades. It has been used for micro-electronics, manufacturing of industrial equipments, composite applications, implanted components in human bodies, etc. This is attributed to the fact that polymeric materials offer good mechanical properties, low dielectric constant and good chemical resistance. The use of polymeric materials in increasingly demanding applications requires a profound understanding of their durability and underlying ageing phenomena. This statement is particularly true for applications where polymeric materials play a vital role in the security or safe functioning of an installation, a machine or others [1−3].

The lifetimes of materials are directly related to the environments to which they are exposed. Not only UV or thermal attack but also corrosive solution may affect. Permeants may enter a polymer−substrate system via permeation (absorption, diffusion and sorption) through the polymer bulk. Once a permeant penetrates into a system, it causes a variety of chemical and physical changes in the material, some of which include the influence on plasticization and swelling of the material and/or creation of a weak boundary layer between the adhesive and substrate. These changes may affect its performance [4−6].

The diffusion of single permeant into polymeric materials has been largely studied based on well-known theoretical models. Many scientists have carried out the research that focused on the diffusion of solution into unreacted (undegradable) polymeric materials, including the swelling effects or

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relaxation. There is a lack of data related to the permeation of solution into polymeric materials, which produces a chemical reaction during the diffusion process, especially under corrosive environment. The research that reported the kinetic study for permeation (defined by ASTM F739) of environmental liquids with chemical degradation is insufficient [7–15]. The behavior of environmental solution passing through the polymer followed by chemical reaction is one of the critical factors, especially for lining with polymeric material under corrosive environment. In many cases in corrosion-resistant polymeric material, permeation of environmental liquids is very slow and difficult to be observed. Therefore, we need to choose the case where the diffusion and reaction rate of environmental solution in polymeric materials are rapid and in comparable level,as in polyamide [16]. In the corrosion of a polymeric material, to evaluate both permeation of environmental solution and chemical degradation of polymeric materials are very important. Although it is an important factor how environmental solution passes through the polymer and how it influences on the degradation of polymer, there is not enough information about this topic until now. Therefore, in this research, quantitative study of the diffusion and kinetics of chemical degradation were carried out as the objective. We divided this topic into two parts. The work presented here deals with the diffusion of sulfuric acid solution into PA66 and its kinetic study. Simulation of the permeation behavior of acid solution and degradation of PA66 in various conditions will be presented in other paper.

2. Theoretical background

Many literatures reported about the diffusion of environmental solution into polymeric materials. The classical simple limiting case of diffusion is expressed by Fick's equation [17–24]:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{1}$$

where C is the concentration of solution in unit polymer volume at specific location from the surface x and time t. If the diffusion coefficient D is constant, the diffusion process will follow the Fickian type diffusion. In some cases, D depends on concentration or other factors.

In general, at the initial stage of sorption process, the weight change in polymer–permeant systems has been demonstrated to follow a power law expression of time of the form:

$$\frac{W_t}{W_\infty} = Kt^m \tag{2}$$

where W_t and W_∞ are the experimental weight change or mass uptakes at time t and equilibrium time ∞, respectively, K is a constant dependent upon the structural characteristics of the polymer and its interaction with the solvent, and an exponent m is related to the transport mechanism as follows:

$m = 0.5 \Rightarrow$ Fickian transport
$m = 1.0 \Rightarrow$ case II transport
$0.5 < m < 1.0 \Rightarrow$ anomalous transport

In case of Fickian diffusion, K is approximately defined as $4(D/\pi)^{1/2}/L$.

$$\frac{W_t}{W_\infty} = \frac{4}{L\sqrt{\pi}}\sqrt{Dt} \tag{3}$$

where L is the thickness of specimen. For example, this simplified solution can be applied for the initial stage of sorption process, that is, the plot of W_t/W_∞ vs $t^{0.5}$ should be linear up to $W_t = 0.6W_\infty$ with less than 2% deviation for true Fickian diffusion. Hence, the diffusion coefficient, D, can be calculated from the initial linear slope of the curves [8–10,17–20].

Other scientists have observed that when acid solution diffuses into polyamide (PA), degradation of PA occurred and reduced the weight average molecular weight and mechanical properties [12–14,16,25,26,28]. Degradation based on the chemical reaction between environmental solution and PA chains could be generally formulated as follows [16]:

$$-\frac{dM}{dt} = kC^\alpha M^\beta \tag{4}$$

where M is defined as the weight average molecular weight of PA66, C is the concentration of environmental solution at specific position, k is the reaction rate constant, α and β are constants, respectively. In case of constant concentration of environmental solution at the surface, Eq. (4) can be simplified to be

$$-\frac{dM}{dt} = k_1 M^\beta \tag{5}$$

where $k_1 = kC^\alpha$. The relationship between diffusion of solution and PA66 degradation was obtained quantitatively. We have done simulations on diffusion of solution and chemical reaction under corrosive environment in our previous work by assuming the constant diffusion coefficient, but the result is not yet quite satisfactory. The simulation results do not show a good agreement with experimental data [16]. This is because the diffusion coefficient of solution is not constant but molecular weight-dependent. In this paper, a detail study on the quantitative relationship between permeation of solution and chemical reaction was performed and clarified. Furthermore, the kinetic discussion for degradation under other conditions of diffusion and reaction rate was attempted to simulate in order to understand the transport behavior of solution into degradable polymer.

3. Experimental

3.1. Materials and conditions

In this research Polyamide 66 (PA66) was used as test material in the environment of sulfuric acid solution. PA66