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Hydrostatic pressure-dependent corrosion behaviour of polytetrafluoroethylene composites in the deep sea

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ABSTRACT

The effect of hydrostatic pressures up to 40 MPa on the corrosion behaviour of neat polytetrafluoroethylene (PTFE) and two fibre-reinforced PTFE composites exposed to seawater was studied. The results reveal that the hydrostatic pressure promotes seawater permeation into the PTFE materials, deteriorates the crystallinity of the PTFE matrix and causes an incompletely reversible loss of mechanical strength. The corrosion mechanisms of PTFE and its composites are discussed based on the crystalline structure transformation and the effect of the fibre/matrix interface.

1. Introduction

Polymeric materials often experience degradation in a series of properties, such as mechanical properties, electrical properties, and thermal properties, when they are affected by specific physical or chemical factors (e.g. stress, light, heat, oxygen, water and other media) in service environments. The environmental degradation processes are known as the corrosion of polymers, also called “aging”. Polymers are totally different from metals in terms of their corrosion mechanism. For example, in seawater, the corrosion of polymers is induced and dominated by the permeation of water molecules and ions from the seawater to the polymer interior [1], while the corrosion of metals is induced by electrochemical reactions, and is characterized by the dissolution of metals and the diffusion of metal ions [2,3].

Due to their excellent corrosion resistance, polymers and polymer-based composites have been widely used as a substitute for metals in some marine engineering applications. To diminish the seawater corrosion as much as possible, high-performance polymer materials serving in seawater environments, such as PTFE, ultra-high molecular weight polyethylene (UHMWPE), polyetheretherketone (PEEK), and polyimide (PI), often exhibit very low water absorption. They seem not to be influenced by corrosion in seawater, and have been called “non-corrodible materials”. Accordingly, the corrosion behaviour of such polymer materials has received little attention. To date, the available knowledge of the seawater corrosion behaviour of polymers has been established mainly based on a normal pressure seawater environment and without consideration of the effect of hydrostatic pressure. However, with an increase in the ocean depth, the hydrostatic pressure

of seawater greatly increases. Every 100 m increase in seawater depth is associated with a 1 MPa increase in hydrostatic pressure. Thus, under high hydrostatic pressure of seawater in the deep sea, is the corrosion behaviour of a polymer material still the same as that in normal pressure seawater?

PTFE, well known for its ultra-low water absorption and ultra-high chemical stability, has proven to be nearly unaffected by seawater, and therefore is widely used as a corrosion-resistant material in marine engineering. Recently, however, the authors have discovered the phenomenon that PTFE suffers from accelerated corrosion under a simulated high-pressure deep-sea environment, especially under hydrostatic pressure greater than 20 MPa. This finding suggests that there exists some dependence between the seawater hydrostatic pressure and the corrosion behaviour of PTFE or other polymers. The corrosion behaviour of polymers needs to be specifically examined in the high-pressure deep-sea environment.

In fact, some studies have been conducted to evaluate the effect of hydrostatic pressure on the mechanical properties of PTFE [4–6]. It was found that both the strength and modulus of neat PTFE can be greatly improved by applying high hydrostatic pressure of an inert medium. Moreover, the high hydrostatic pressure of an inert medium even induced a phase transformation in PTFE. However, in these studies, the effective hydrostatic pressure was often greater than 500 MPa [7,8]. The referred liquid media, such as kerosene and castor oil, were non-polar and inert and differed greatly from seawater in the properties of permeability and corrosivity. Therefore, these available results are not well correlated with our test findings in high-pressure seawater.

In this paper, the corrosion behaviour of PTFE and two fibre-

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reinforced PTFE-based composites are comparatively investigated in seawater with different hydrostatic pressures ranging from atmospheric pressure to 40 MPa. We focus on the correlation between hydrostatic pressure generated by seawater and the corrosion behaviour. The corrosion mechanism of PTFE and its composites are discussed based on the aggregation structure transformation of macromolecules and the effect of the fibre/matrix interface. Moreover, the corrosion-induced changes in the mechanical properties of PTFE and its composites are also investigated.

2. Materials and methods

2.1. Materials

PTFE powders (FR104-4, density of 2.16 g/cm³, average particle size of 25 μm) were supplied by Shanghai 3F New Materials Co., Ltd., China. Milled polyacrylonitrile-based carbon fibre (CF) powders (density of 1.83 g/cm³, diameter of 7 μm, length-diameter ratio of 4–8) and milled glass fibre (GF) powders (density of 2.60 g/cm³, diameter of 13 μm, length-diameter ratio of 5–10) were provided by Nanjing Fiberglass R&D Institute, China.

2.2. Preparation of PTFE and PTFE-based composites

The PTFE-based composites reinforced by carbon fibres and glass fibres were prepared. First, the PTFE powders were mechanically mixed with fibre powders at a volume fraction of 25%. The mixing duration was 20 min, and the rotor speed was 200 rpm. Then the mixtures were filled in a mold and compressed under a pressure of 50 MPa for 5 min at room temperature, followed by sintering at 380°C for 4 h in a furnace and then by natural cooling in the furnace. Finally, the bulk composite in the form of a plate with a diameter of 120 mm and a height of 4 mm was generated. Neat PTFE plates were prepared using the same procedure. According to different test requirements, the PTFE and PTFE-based composite plates were machined into different test specimens.

2.3. Seawater absorption test

The seawater absorption of PTFE and its composites under specific hydrostatic pressure was tested in a stainless vessel integrated with a water pump. The composition of natural seawater varies with the sea area, depth and season. Therefore, to improve the reproducibility of the test, the seawater used in this study was not natural seawater, but artificial seawater prepared according to the ASTM D 1141-98 standard [9]. The chemical composition of the seawater is listed in Table 1. The pH value of the seawater was adjusted to 8.2 using 0.1 mol/L NaOH solution. Before the absorption test, both the vessel and the pump were filled with the artificial seawater. The hydrostatic pressure of the seawater ranging from atmospheric pressure to 40 MPa can be simulated with an accuracy of 1 MPa. The seawater absorption tests were conducted at different hydrostatic pressures according to the ASTM D 570-

Table 1

Chemical composition of artificial seawater.

Component	Concentration (g/L)
NaCl	24.53
MgCl ₂	5.20
Na ₂ SO ₄	4.09
CaCl ₂	1.16
KCl	0.695
NaHCO ₃	0.201
KBr	0.101
H ₃ BO ₃	0.027
SrCl ₂	0.025
NaF	0.003

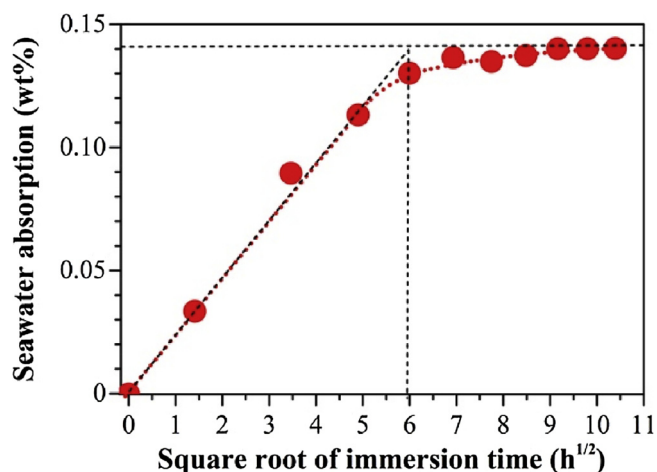


Fig. 1. Determination method of the permeation coefficient of seawater. The permeation coefficient is determined from the gradient of the initial region using Eq. (2). (The seawater absorption curve is taken from the CF/PTFE composite immersed in seawater at a hydrostatic pressure of 40 MPa seawater for 108 h).

98 standard [10]. The specimens, which were 4.0 ± 0.5 mm in thickness, 10 ± 0.5 mm in width and 80 ± 0.5 mm in length, were immersed in the seawater with different hydrostatic pressures at 23 °C, and weighed every 12 h to determine the weight-gain with an accuracy of 0.1 mg. The seawater absorption was expressed as the percentage of the weight-gain to the original mass of the tested specimen [11]:

$$m_t = \frac{M_t - M_0}{M_0} \times 100\% \quad (1)$$

where m_t is the seawater absorption at immersion time t , wt%; M_t is the weight of specimens at immersion time t , g; M_0 is the initial weight, g. The weighings were repeated until the increase in weight per 12 h period was less than 0.2 mg, and the specimen was then considered to be substantially saturated. For each type of polymer, the average seawater absorption of five specimens was reported.

The seawater permeation coefficient can be obtained by drawing the curve of the specimen seawater absorption versus the square root of the immersion time, as shown in Fig. 1. If the permeation process of seawater complies with Fick's law, the relative absorption should be linearly correlated with the square root of the immersion time at the initial stage of seawater absorption. The value of permeation coefficient k' can be calculated by the following relation [11,12]:

$$k' = \pi \left(\frac{z}{4m_\infty} \right)^2 \left(\frac{m_2 - m_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad (2)$$

where k' is the permeation coefficient of seawater, mm²/h; z is the sample thickness, mm; m_∞ is the saturated seawater absorption, wt%; t_1 and t_2 are arbitrary times chosen from the initial linear region of the curve, and m_1 and m_2 are the seawater absorption, related to t_1 and t_2 , respectively.

Taking into account the edge effect, the permeation coefficient obtained from Eq. (2) can be further amended as follows [13]:

$$k = \left(1 + \frac{z}{a} + \frac{z}{b} \right)^2 k' \quad (3)$$

where k is the amended permeation coefficient of seawater; z is the sample thickness, mm; a is the sample length, mm; and b is the sample width, mm.

2.4. Mechanical tests

The mechanical properties of PTFE and its composites subjected to

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