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Ageing of a thermosetting polyurethane and its pultruded carbon fiber plates subjected to seawater immersion

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HIGHLIGHTS

- Polyurethane and its CFRP plates were studied on the resistance to seawater.
- The polyurethane-CFRP was slightly affected by seawater immersion.
- The polyurethane-CFRP exhibited better resistance to seawater than the epoxy-CFRP.

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ABSTRACT

Carbon fiber reinforced polyurethane (CFRPU) composites exhibit a high potential in infrastructure application due to their efficient manufacturing and excellent mechanical properties. In the present article, the resistance to seawater immersion of a thermosetting polyurethane (PU) and its pultruded CFRPU plates was investigated, which was compared to a commonly used epoxy resin as well as its pultruded plate. The ageing conditions were determined as immersion in artificial seawater for one year at 20 °C, 40 °C or 60 °C. The water absorption/desorption, glass transition temperature (T_g), fiber-matrix interfacial bond strength and the tensile properties were evaluated as a function of time. As indicated by the water uptake testing, the PU resin exhibits a relative high water uptake (~2.65%), while the CFRPU plates show a much lower value (~0.71%), illustrating the good seawater resistance of the PU resin and the CFRPU. The positive resistance results were further supported by the high retention of the fiber-matrix interfacial bond strength and glass transition temperature for the immersed samples. In addition, the seawater immersion brings in a very slight decrease in the tensile strength for the PU and CFRPU plates. In terms of the above tested performances, the PU and CFRPU are significantly superior to the epoxy and carbon fiber reinforced plates. This result is attributed to the PU-carbon fiber adhesion of high resistance to the seawater.

1. Introduction

Since the 1930s, polyurethane (PU) resins with the function group of —NHCOO— have been widely using as coatings [1], foams [2], rubbers [3], shape-memory polymers [4] and insulation materials [5], etc. In recent years, the polyurethane (PU) resin has been applied as resin matrices for FRP composites [6–11], due to its excellent processability and mechanical properties, e.g., toughness [12]. Such FRPs have been found wide applications in various industry fields and construction, such as marine structures. During their application in the marine structures, the long-term durability of the resin matrices and their composites subjected to seawater immersion is a concern.

As regards to the resin matrices, the ageing of the epoxy resins subjected to various harsh environments was investigated much more frequently [13–17]. The thermo-mechanical properties were affected significantly by plasticization, relaxation, swelling and hydrolysis, etc. On the contrary, much limited works were performed on the durability of the PU resins and the related FRPs [18]. Moreover, although some studies [19–23] were related to the durability of the PU resins, the most of the PU resins were the thermoplastic PU resins or one-component PU resins [19–21,23]. A two-component thermosetting PU was reported to have a saturated water

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uptake of 2.54% and diffusion coefficient of 4.09×10^{-7} mm^2/s immersed in water at 22 °C, respectively [22].

Similarly, the ageing of the epoxy-based carbon fiber reinforced polymer (CFRP) composites subjected to various harsh environments was also well studied [24–28]. As found, the water uptake can lead to the degradation of the thermo-mechanical properties of the epoxy-based CFRP. The degradation was largely reversible after drying due to plasticization. The irreversible degradation was attributed to the hydrolysis of the resin matrix, swelling, coalescence of voids, micro-cracks and the fiber-matrix interfacial debonding [26,27]. In contrast to the epoxy-based CFRP composites, much limited works have been done on the durability of the carbon fiber reinforced polyurethane (CFRPU) composites [7,29,30]. However, few works were performed on the glass fiber reinforced polyurethane (GFRPU) composites subjected to seawater [18]. As reported, the GFRPU composites showed worse long-term performances due to the hydrolysis of the matrix and the fiber-matrix interfacial debonding.

In the present study, ageing of a two-component thermosetting PU and its pultruded CFRPU plates subjected to seawater immersion at 20 °C, 40 °C or 60 °C for 1 year were investigated. The results were compared to a common epoxy resin and its CFRP plates. The water uptake, glass transition temperature (T_g), the fiber-matrix bond and the tensile properties were studied. The degradation mechanism was discussed with Fourier transform infrared (FTIR) spectra and the electron scanning microscopy (SEM) analysis. The study is expected to understand the feasibility of the application of the PU and CFRPU in infrastructures, especially for the marine structures.

2. Experimental

2.1. Raw materials

The PU resin is a two-component thermosetting polyurethane (Elastocoat® CC6226/101) purchased from BASF Polyurethane Specialties (Shanghai, China). The ratio of the polyol component and isocyanate component is 1:1.259. The carbon fibers used in the present study are PAN-based carbon fibers (800 tex, 12 K) with the average diameter of 7 μm purchased from Sinopec Co., Ltd. (Shanghai, China). The tensile strength, modulus and elongation at break of single carbon fiber are 3.75 GPa, 210.2 GPa and 1.78%, respectively.

2.2. Sample preparation

To prepare the PU samples, the polyol component was dehydrated in a vacuum oven at 110 °C for 10 h and then cooled to the room temperature before mixing. After that, the two components were mixed in proportion, stirred for 5 min at room temperature and then poured into an aluminium mould, which was preheated at 140 °C for 30 min. At last, the aluminium mould with the PU resin mixture with size of 200 mm × 150 mm × 2.5 mm was cured in an oven at 200 °C for 15 min and then cooled to the room temperature. Note, to reduce the effect of water on the curing, the beakers and glass rods were pre-heated at 60 °C for 12 h before using. The density of the PU resin is 1.20 g/cm^3.

The CFRPU plates with a cross-sectional dimension of 25 mm × 1.46 mm were pultruded by our group (Lab for FRP Composites and Structures). The fiber volume content and density of the CFRPU plates are approximately 70.8% and 1.80 g/cm^3, respectively.

2.3. Experimental environments

The PU and CFRPU specimens were immersed in artificial seawater at 20 °C, 40 °C and 60 °C for 1 year, respectively. The artificial seawater was prepared without heavy metals according to ASTM D1141 (Standard Practice for the Preparation of Substitute Ocean Water).

2.4. Water uptake

The PU and CFRPU specimens were cut into the size of 25 mm × 25 mm × 2 mm and 50 mm × 25 mm × 1.46 mm, respectively. Before immersion, all the specimens were dried at 60 °C in an oven for 2 days. The weight of samples swiped off the surface water using tissue paper was measured with an electronic balance with an accuracy of 0.1 mg by periodically. Fifteen samples for each condition were weighted and the average value was calculated. The weight gain at time t (M_t) of each sample is defined as

$$M_t = \frac{W_t - W_0}{W_0} \times 100\% \quad (1)$$

where W_t is the wet weight at time t, and W_0 is the initial weight of the sample before immersion.

2.5. Water desorption

After immersion for 6 months or 1 year, five immersed specimens were removed from seawater for the desorption tests, respectively. Specimens were dried in an oven at 60 °C until a stable weight was achieved. During drying, the weights of the specimens were recorded periodically. The weights of the samples were recorded. The water desorption (M_{dt}) of specimens during drying at time t is defined as

$$M_{dt} = \frac{m_t - W_0}{W_0} \times 100\% \quad (2)$$

where m_t is the weight of the samples at drying time t.

2.6. FTIR test

The functional groups of the PU and CFRPU specimens after 1 year of immersion were detected using a Nicolet AVATAR 360 Fourier transform infrared (FTIR) spectroscopy. Tablet method was utilized to make samples, which consist of 1–2 mg specimens and 200 mg potassium bromide (KBr). The scanned wave-number ranges from 4000 cm^{-1} to 450 cm^{-1}.

2.7. DMTA test

Dynamic mechanical thermal analysis (DMTA) test (Q800, TA, USA) was conducted by periodically on the PU and CFRPU specimens with size of 40 mm × 8 mm × 2 mm and 38 mm × 10 mm × 1.46 mm, respectively. The DMTA tests for the PU specimens were performed with the tensile film mode, 1 Hz frequency heating from 25 °C and 200 °C at 5 °C/min. The DMTA tests for the CFRPU specimens were performed with the single cantilever mode, 1 Hz frequency heating from 25 °C and 220 °C at 5 °C/min.

2.8. In-plane shear strength test

In-plane shear strength (IPSS) [31] is defined as the debonding strength making the FRP composites stratified from the cross section (Seeing in Fig. 1) in the present study. The size of specimens for the IPSS test is 25 mm × 10 mm × 1.46 mm. To make sure the stability of IPSS, specimens were stratified at the middle position in the width direction (Seeing in Fig. 1). For each condition, five samples were repeated and the average results were reported. Speed of testing is 1 mm/min. The IPSS can be calculated by the following equation