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Surface amination and hydrolyzation of carbon fibers treated with triethylene tetramine in supercritical water/ethanol system

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ABSTRACT

To improve the interfacial properties between carbon fibers and epoxy matrix, the fibers were treated by an ammoniac medium, which consisted of supercritical water, ethanol and triethylene tetramine. The images of atomic force microscopy and scanning electron microscope indicate that coating layers are formed on the surfaces of treated fibers. The results of X-ray photoelectron spectroscopy demonstrate that N content on the surfaces of carbon fibers increases and the main ammoniac groups of the coating layers are amino and imino groups. The mechanical measurements indicate that both interlaminar and interface shear strength of carbon fibers are significantly increased after amination.

1. Introduction

Carbon fibers combine exceptional mechanical properties and low weight, acting as ideal reinforcements for polymer matrix composite materials [1]. It has long been recognized that carbon fiber is essentially graphitic in nature, when untreated and unsized, and therefore possesses a chemically inert surface [2,3]. The interaction of carbon fiber surfaces with matrix material is of paramount importance to the ultimate mechanical properties of a carbon fiber reinforced polymer [4].

Surface treatments for carbon fibers are usually divided into two categories: oxidation and non-oxidation style [5]. Amination treatment that aims to improve the interfacial bonding of carbon fibers' surfaces by increasing nitrogen groups on it, is one attracting method in non-oxidation styles. This is the reason that nitrogen groups, such as amino and imino group, act as crosslinking centers for epoxy matrix [6,7]. Therefore, amination treatment is particularly suitable for the manufacture of carbon fiber/epoxy composite materials.

Amination in supercritical environment may bring about three considerable advantages. Firstly, high diffusion coefficient and penetration ability of supercritical fluid can fairly ensure full contact between the amination agents and the surfaces of treated carbon fibers [8,9]. Secondly, coating layer is firmly combined into carbon fiber's surface at the condition of high temperature and pressure within supercritical environment [10–12]. Lastly, after amination, using supercritical drying as separation step can avoid the effect of capillary force on the tows, which usually causes over cementation to carbon fibers [13,14].

This work represents an amination method performance within supercritical water/ethanol systems and using triethylene tetramine (TETA) as amination agent. In general, amination is more like "coating" rather than "grafting", so it is usually conducted combining with preoxidation steps. But in this work, we aimed at characterizing the properties of such an amination process, so preliminary oxidizing treatment for carbon fibers was not carried out before amination.

2. Experiment

2.1. Materials and experimental methods

PAN-based carbon fibers (3×10^3 single filaments per tow with an average diameter of 6.5 μm and a density of 1.76 g cm^{-3}, while linear mass was 0.161 g m^{-1}) were obtained from the Jilin Carbon Co. (Jilin, China) and used as received. The used matrix was E-618 epoxy resin system consisting of diglycidyl-ether of bisphenol-A (supplied from Yue-Yang Chem. Co. of China), and imidazole (curing agent, supplied from the First Factory of Chemical Agents) at 100/6 by weight. Analytically pure ethanol was purchased from the First Factory of Chemical Agents (Tianjin, China).

Carbon fibers (3 g) were bound on stainless steel frames and cleaned by supercritical water at 693 K for 20 min, then dried in

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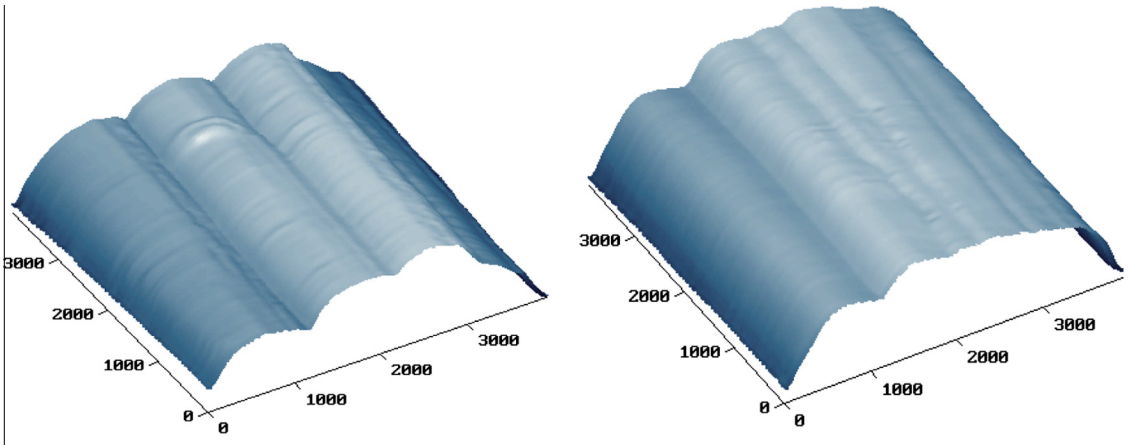
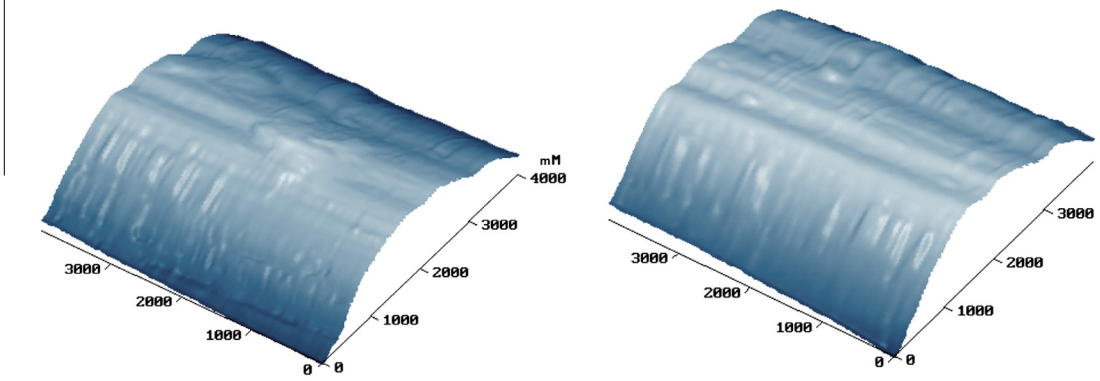
drying oven at 393 K for 24 h. In this work, the untreated carbon fiber means to the fibers cleaned by supercritical water. After cleaned, the coating layers on carbon fibers can be removed thoroughly. Accurately volume (0.4 ml, 0.8 ml, 2.0 ml, 4.0 ml) of TETA was poured into 50 ml volumetric flask, dissolved and made up to the mark with mobile phase which was composed of deionized water and ethanol with the volume ratio of 1:1. Then 25 ml solution mentioned above and pretreated carbon fibers were transferred into a stainless steel autoclave (95 ml) with a high pressure valve. The autoclave was heated to 673 K, hold for 30 min, then released the supercritical fluid slowly to normal pressure. After it, the autoclave was cooled to room temperature. By this separation step, dried carbon fibers were acquired.

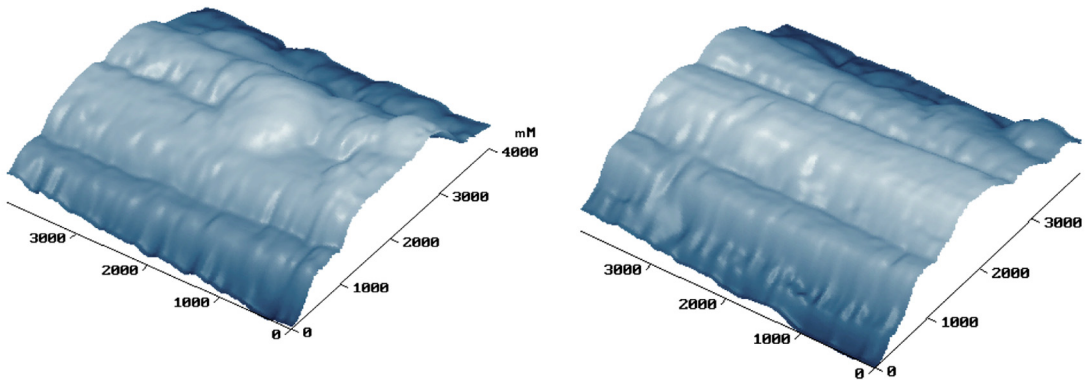
After treatments, unidirectional composite specimens were fabricated by combining carbon fibers with E-618 through a compression molding processing method and compared with an untreated specimen. The resin/hardener mixture was thoroughly stirred for 15 min and deposited in a vacuum oven with the temperature at 60 °C for half an hour in order to degas. The termination products were cut into 22 mm length, 6.5 mm width and 2.0 mm thickness. The ILSS of CFRP was determined according to ASTM D2344, with a crosshead speed 1.5 mm per minute and the span to thickness ratio greater than 5:1.



(a) Untreated



(b) Treated with 0.4 ml TETA



(c) Treated with 1.0 ml TETA

Fig. 1. AFM images of untreated and aminated carbon fibers.