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Imaging the interphase of carbon fiber composites using transmission electron microscopy: Preparations by focused ion beam, ion beam etching, and ultramicrotomy

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Abstract Three sample preparation techniques, focused ion beam (FIB), ion beam (IB) etching, and ultramicrotomy (UM) were used in comparison to analyze the interphase of carbon fiber/epoxy composites using transmission electron microscopy. An intact interphase with a relatively uniform thickness was obtained by FIB, and detailed chemical analysis of the interphase was investigated by electron energy loss spectroscopy. It shows that the interphase region is 200 nm wide with an increasing oxygen-to-carbon ratio from 10% to 19% and an almost constant nitrogen-to-carbon ratio of about 3%. However, gallium implantation of FIB tends to hinder fine structure analysis of the interphase. For IB etching, the interphase region is observed with transition morphology from amorphous resin to nano-crystalline carbon fiber, but the uneven sample thickness brings difficulty for quantitative chemical analysis. Moreover, UM tends to cause damage and/or deformation on the interphase. These results are meaningful for in-depth understanding on the interphase characteristic of carbon fiber composites.

1. Introduction

The use of carbon fiber composites has substantially increased in the fields of aerospace, transportation, and sports goods due to their excellent properties, such as high specific strength, high specific modulus, and the ability to be tailored for specific applications.[1–3] At the same time, a great deal of scientific efforts has been focused on the analysis of interfacial properties and the approaches to improve, since it is well recognized that the interphase significantly impacts the final behavior of

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composites.[4–6] At the core of these efforts lies in the need to understand the structure, mechanical, and physico-chemical properties of components, as well as their interactions at the interphase region across multiple length scales starting from nanoscale characterization. Based on this, nanomechanical techniques, such as dynamical modulus mapping,[7] atomic force microscopy,[8,9] nanoindentation and nanoscratch,[10,11] and fiber push-in and push-out tests,[12–15] have been developed to reveal the thickness and mechanical properties of interphase in specific composite systems. However, knowledge of the interphase morphology as well as the structure and chemical properties between carbon fiber and polymer is still lacking at the present time. Detailed studies of microstructure and physico-chemical properties are favorable to understand the interfacial functionary mechanism and the structure–property relationship, which are critical to optimize composite behaviors.

Transmission electron microscopy (TEM) provides the unique combination of analytical techniques, for example, electron energy loss spectroscopy (EELS) and energy dispersive X-ray (EDX), which is suited and able to characterize the structural and chemical information of a sample at the nanometer scale. However, such studies require the sample to be transparent (approximately 100–150 nm) to the electron beam and being much thinner is preferred for EELS analysis.[16,17] Preparation of such a sample, especially for the interphase of heterogeneous materials, is both a science and a challenge. Focused ion beam (FIB),[18–20] ion beam (IB) etching,[21–23] and ultramicrotomy (UM)[24–26] are three common preparation techniques. FIB uses a finely focused beam of ions to bombard a target so that site-specific milling or cutting can be performed.[17] IB etching is a sputtering process in which energetic neutral atoms or ions from a cathode impinge on a sample wafer, at an angle.[16] UM produces an ultrathin section with the thickness down to approximately 30 nm by creating a micro crack that progressively propagates into a sample.[27]

Since sample preparation techniques are very material-dependent, the selection of a suitable preparation technique is of great significance for TEM analysis. For carbon fiber reinforced resin composites, the challenge arises because of the huge mismatch in properties, such as modulus and hardness, between carbon fiber and resin. This brings great difficulty for preparing a thin TEM sample with an intact interphase. Based on this, herein, FIB, IB etching, and UM techniques were respectively used to prepare a TEM sample of a carbon fiber/epoxy composite. Our specific goals were to (1) identify the capabilities of these preparation methods for TEM analysis of the interphase in the carbon fiber/epoxy composite, (2) reveal the suitability and strength of each method for investigating which characteristic of the interphase, and (3) understand the microstructure, chemical components, chemical bonding states, and thickness of the interphase.

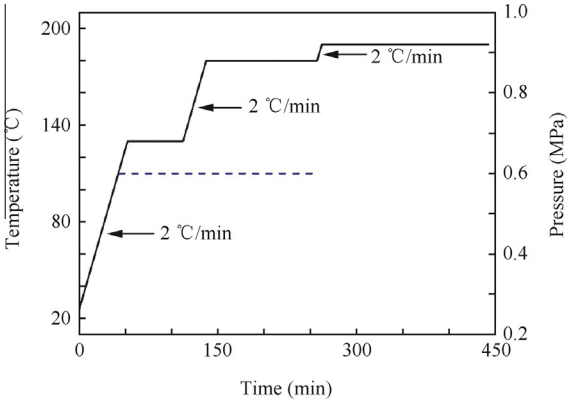
2. Experimental

2.1. Materials

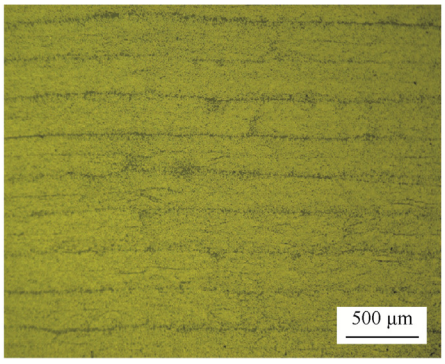
Unidirectional T300-3K-40B carbon fiber (7 μm in diameter, Toray Inc.)/epoxy (5228, Beijing Institute of Aeronautical Materials) prepreg was impregnated by the hot-melt method and cured in autoclave. The cure cycle and metallographic image of the prepared composite are shown in Fig. 1. The composite has a uniform distribution of carbon fibers and a low void content. The tensile modulus of the fibers is 230 GPa (from TORAYCA™ carbon fibers data sheet), and that for the epoxy matrix is determined to be about 3.5 GPa according to GB/T 2567–2008.

2.2. Preparation methods

FIB experiment was performed in an AURIGA 40 (Carl Zeiss, Germany) Dual Beam FIB-scanning electron microscope (SEM) system with a Ga^+ ion source at 30 kV. The preparation process is illustrated in Fig. 2. Firstly, the cross-section of the composite was identified and targeted as the region of interest (yellow rectangular box in Fig. 2(a)). Secondly, a 1 μm platinum (Pt) protective layer was deposited on the surface of the target milling area (see Fig. 2(b)), and then coarse and medium milling was performed (see Fig. 2(c)). 20 nA beam current was used for coarse milling until the sample was left with a 2 μm thickness, and then 4 and 1 nA beam current was for medium milling until a thickness of ~1 μm was reached. Water gas was used for fast material sputtering. Thirdly, the section was detached from the surrounding material and transferred to a TEM half-grid for fine thinning (see Fig. 2(d)). Fourthly, fine thinning was carried out only at the desired areas (two braces in Fig. 2(e)) until they became transparent at 3 kV (SEM mode), using 600 pA and 240 pA



(a) Cure cycle



(b) Metallographic image of the prepared T300/epoxy composite

Fig. 1 Cure cycle and metallographic image of the prepared T300/epoxy composite.