Polymer Testing 55 (2016) 257–260

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Short Communication: Test Method

Mechanical mapping of the interphase in carbon fiber reinforced poly(ether-ether-ketone) composites using peak force atomic force microscopy: Interphase shrinkage under coupled ultraviolet and hydro-thermal exposure

Yi-Fan Niu*, Ying Yang, Sai Gao, Jia-Wei Yao

Sino-European Institute of Aviation Engineering, Civil Aviation University of China, Tianjin, 300300, China

ARTICLE INFO

Article history:
Received 23 July 2016
Accepted 7 September 2016
Available online 9 September 2016

Keywords:
Polymer matrix composites (PMCs)
Interphase
Atomic force microscopy (AFM)
Mechanical mapping
Shrinkage

ABSTRACT

The interphase size and properties of carbon fiber reinforced poly(ether-ether-ketone) composites (T300/PEEK) were quantitatively characterized using Peak Force Quantitative Nano-Mechanics (PF-QNM) with atomic force microscopy (AFM). The elastic modulus maps of the interfacial region were obtained, and the interphase dimension was determined based on the elastic modulus profile. The interphase thickness of T300/PEEK under coupled ultraviolet (UV) and hydro-thermal degradation decreased from 70.1 ± 8.6 to 18.3 ± 1.8 nm after 1560 h of exposure. The shrinkage of interphase size was attributed to the embrittlement of PEEK after crosslinking reactions induced by UV exposure. This technique shows a great potential in the quantitative measurement of nanomechanics relevant in polymer and polymer composites, where the structure and properties of the interphase are of special interest.

1. Introduction

Carbon fiber reinforced polymer composites (CFRPs) have been widely used in aeronautical and astronautic equipment due to their excellent mechanical properties such as high specific modulus and strength. The carbon fiber and resin matrix are the two main components in a CFRP system, while a region of finite thickness between the bulk fiber and bulk matrix exists and is defined as the interphase [1]. Both the frictional and physico-chemical adhesion between the fiber and matrix influences the load transfer capability of the interphase [2,3]. The structure and properties of the interphase play an important role in the mechanical behavior and environmental resistance of the integrated structure of composites [4–6]. Therefore, the quantitative measurement of the interphase structure, properties and its evolution are critical in determining the durability and damage mechanism of CFRPs.

Characterizing the interphase structure and properties quantitatively and directly is difficult using traditional methods since the thickness of interphase is generally less than 1 μm. Atomic force microscopy (AFM) becomes a useful tool to characterize each components in composites by tapping mode [4] and force modulation mode [5,7]. However, the quantitative nanomechanical results of the interphase region are still difficult to extract with the current AFM techniques. Nanoindentation and nanoscratching are common nanomechanical techniques and have been used in attempts to characterize the properties of interphases [8–10]. However, the lateral resolution is highly constrained due to the indentation depth, size and geometry of the indenter. Nanoscale dynamic mechanical analysis (nanoDMA) increases the spatial resolution by minimizing the indentation depth and was applied to identify the interphase region by mapping the storage modulus around the profile of the fiber [6]. Nevertheless, the measured moduli of carbon fiber and resin matrix were still obviously different from the bulk materials.

Recently, an expanded AFM technique, Peak Force Quantitative Nano-Mechanics (PF-QNM), has shown great potential in interphase identification with high lateral resolution and quantitative interpretation of data [11,12]. Compared with the atomic force acoustic microscopy (AFAM), the configuration and calibration of PF-QNM are much simpler and it does not need further update in hardware. In the present work, (i) we demonstrate the use of PF-QNM to map the elastic modulus on the cross-section surface of T300/PEEK and investigate the structure and properties of the

* Corresponding author.
E-mail address: yifan.niu@foxmail.com (Y.-F. Niu).

http://dx.doi.org/10.1016/j.polymertesting.2016.09.008
0142-9418/

corresponding interphase; (ii) the evolution of the interphase structures under coupled UV and hydro-thermal exposure are quantitatively characterized.

2. Experimental section

T300/PEEK composites were processed via vacuum infusion molding. The specimens were exposed to cycled UV light and water condensation in an accelerated weathering chamber (Q-Lab QUV/Spray) according to ISO 4892-3. A single exposure cycle included two steps: (i) 8 h of UV irradiation of 1.55 W m^{-2} at 70 °C, (ii) 4 h of water condensation at 50 °C. The total exposure times were 120, 240, 840 and 1560 h, respectively. In order to investigate the fiber/matrix interphase, the samples were mechanically ground perpendicularly to the fiber axis with 1200, 2500 and 5000 grit silicon carbide papers and polished with 0.04 μm alumina suspension on an automatic polish-grinding machine (Presi Mecatech-234). The surface morphology of the polished sample was analyzed using AFM (Bruker Dimension Icon) and the root mean square roughness (R_q) of the polished surface was less than 10 nm.

The interphase structure and properties were studied using a nanomechanical mapping technique operated in PF-QNM mode on AFM. The cantilever was modulated by a sinusoidal wave with a frequency of 1 kHz. The force on the probe was calculated by the deflection and the spring constant of the cantilever. Fig. 1a shows the force/distance curve during a single tapping cycle. The tip firstly approaches the surface and is attracted by the Van Der Waals force. Then, it is lowered continuously and changed to a repulsive effect, until the force on the probe reaches a maximum (peak force set point). Afterwards, the probe is pulled off with an adhesion effect and returned to the original position. The maximum deformation of the sample is the distance from the attractive point to the peak force point in the loading curve (Fig. 1a). The corresponding elastic modulus is fitted by the Derjaguin-Muller-Toporov (DMT) model [13] using the part of the unloading curve. The high speed and simultaneous capture of topography images and modulus maps are the main advantages of PF-QNM technique compared to previous nanomechanical techniques [14,15]. All quantitative measurements were performed with an MPP 13100-10 probe (Bruker) at 512 × 512 pixel resolution. The cantilever spring constant and tip radius were calibrated using a polystyrene film ($E = 2.7$ GPa, Bruker).

Fig. 1b illustrates the degradation condition by UV irradiation and hydro-thermal effect. The probe scanning direction was along the radius of fibers. At least 5 selected interphase regions were measured after each step of exposure, and all tested fiber/matrix interphases were relatively close to the surface of exposure (<10 μm).

3. Results and discussion

Fig. 2a shows the DMT modulus image of a pristine T300/PEEK sample. The contrast clearly illustrates that the elastic modulus of the PEEK matrix (blue) is much lower than that of the carbon fiber (red), and a transition region (white) exists around the profile of the fiber. In Fig. 2b, a line scan of the elastic modulus data in Fig. 2a reveals two obvious modulus gradients between the matrix and the fiber. Previous studies demonstrated that the mechanical properties and the elastic modulus of interphase were generally different from those of the matrix and fibers, thus the region of modulus change was defined as the interphase [6].

For measuring the interphase size accurately with sufficient values of modulus, the local modulus information (500 nm × 500 nm) was studied (Fig. 2c). The interphase region of T300/PEEK is easy to distinguish in white color for unaged sample and becomes quite narrow after 1560 h of exposure. The corresponding line scans of these two modulus maps are shown in Fig. 2d. The modulus distribution shows the similar trend in the interphase local area with respect to the position, presenting two steps in matrix and fiber region, as well as a modulus gradient in the transition area (Fig. 2b). After fitting the scattered modulus data, the interphase region can be determined according to the two inflection points in the fitting curve. The interphase thickness is 70.1 ± 8.6 nm for unaged sample and 18.3 ± 1.8 nm after 1560 h of exposure.

In order to obtain the modulus of each phase around the interphase, the values of elastic modulus were collected in a histogram with respect to the pixel counts. The histogram in Fig. 2e indicates the statistical DMT modulus data of the samples. Each curve contains a narrow peak and a wide peak, representing the modulus distribution of the matrix and fiber, respectively. The average elastic modulus of unaged PEEK matrix is 4.36 GPa, which is slightly higher than that of bulk materials (~3.8 GPa). This result can be explained by the surface hardening caused by mechanical grinding and polishing during the sample preparation, the tip sensitivity, material uniformity and calibration variation. The measured average modulus of 1560 h aged PEEK matrix is 6.23 GPa due to the embrittlement by chain scissions and crosslinking reactions from UV exposure. Thus, PF-QNM shows excellent applicability and reliability in the modulus measurement of polymer matrix. The modulus values of carbon fiber were in a range of

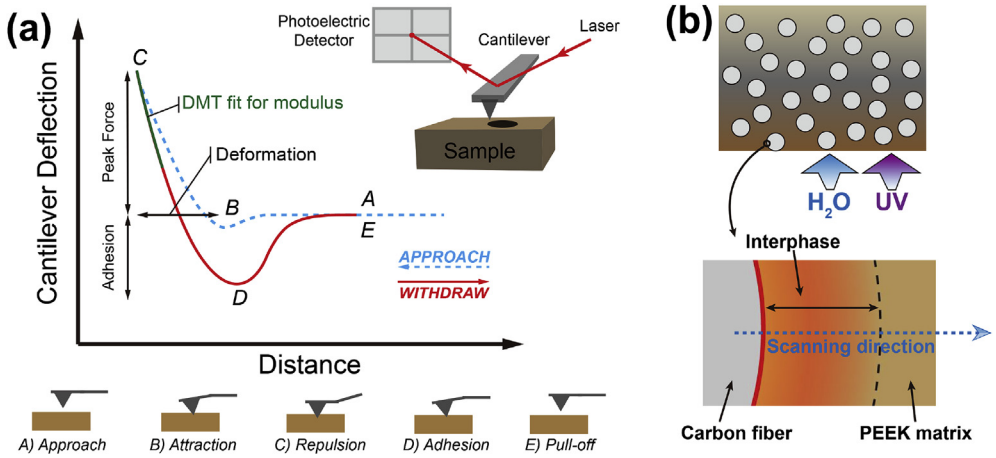

Fig. 1. (a) Schematic illustration of one cycle in PF-QNM technique, (b) tested regions and scanning direction of AFM probe.