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Effect of Different Types of Nano/Micro Fillers on the Interfacial Shear Properties of Polyamide 6 with De-Sized Carbon Fiber

Mohamed H. Gabr, Kiyoshi Uzawa

***Abstract*—**The current study aims to investigate the effect of fillers with different geometries and sizes on the interfacial shear properties of PA6 composites with de-sized carbon fiber. The fillers which have been investigated are namely; nano-layer silicates (nanoclay), sub-micro aluminum titanium (ALTi) particles, and multiwall carbon nanotube (MWCNT). By means of X-ray photoelectron spectroscopy (XPS), epoxide group which defined as a sizing agent, has been removed. Sizing removal can reduce the acid parameter of carbon fibers surface promoting bonding strength at the fiber/matrix interface which is a desirable property for the carbon fiber composites. Microdroplet test showed that the interfacial shear strength (IFSS) has been enhanced with the addition of 10wt% ALTi by about 23% comparing with neat PA6. However, with including other types of fillers into PA6, the results did not show enhancement of IFSS.

***Keywords*—**Sub-micro-filler, nano-composites, interfacial shear strength, polyamide.

I. Introduction

THERE are increasing interests recently in using thermoplastics matrices to replace thermosets for composite materials due to several advantages such as high toughness, shorter manufacturing cycles, and reprocessing possibilities [1].

The incorporation of various types of fillers is one of the ways to produce multifunctional composites which has been proved to be an effective way to improving the physical and thermal properties [2]. However, few disadvantages associated with nanofiller incorporation has concerned toughness, impact performance [3] and IFSS with carbon fiber[4].

The influence of the interphase that formed between the matrix and the carbon fiber can affect the properties of composites. [5]. Optimum interfacial adhesion, which plays a key role in determining the mechanical properties of the composites, can efficiently transfer stresses from the matrix to the fibers [6]. The goal of this research is to explore the effect of different kinds of fillers with different geometries, and sizes such as nanoclay, MWCNT, and ALTi on the IFSS with de-sized CF.

Mohamed H. Gabr is with the Innovative composite center (ICC), Kanazawa Institute of Technology, 〒924-0838, Japan (Corresponding author: +81-76-276-3170; fax: +81-76-276-3101; e-mail: mgabr@neptune.kanazawa-it.ac.jp), also he is with Faculty of Industrial Education, Sohag University, 〒611111, Egypt

Kiyoshi Uzawa is with the ICC, Kanazawa Institute of Technology, 〒924-0838, Japan (e-mail: uzawa@neptune.kanazawa-it.ac.jp).

Commercially available carbon fibers are normally coated by a sizing layer on the surface, which usually presents as solution or emulsion consisting of polymeric components [6]. The sizing can alter the handle-ability of carbon fiber which includes fiber protection, fiber alignment, and fiber wettability. Cao et al. [7] have investigated sizing agent composed of polyimide and epoxy for PAN-based carbon fiber. The sized fibers were reported to possess an improved wear resistant and 97% improvement of IFSS by comparing the unsized fibers. However, not all kinds of sizing could improve interfacial adhesion between fibers and matrix. Dilsiz [8] found that polyimide and polyurethane (PU) sized fibers in epoxy matrix show lower IFSS than unsized fibers by single fiber fragmentation test, which is attributed to the effect of surface chemical changes on the fiber/matrix adhesion.

The objective of this study is to evaluate the influence of nanoclay, MWCNT, and ALTi particles on the interfacial properties of PA6 composites with de-sized CF.

II. Experimental Work

A. Material

Polyamide (cm1006 with MFR 15 g/10 min at 230 °C) was purchased from Toray Co. Aluminum50%-Titanium50% (ALTi), RECOMAX, was purchased from Eco Earl Co., Ltd. Japan. ALTi particles were received in powder form with white to gray color. According to the technical data sheet; pH: 4~10, melting point: 1730 °C, and specific gravity: 3.2 kg/l.T300S carbon fibers were purchased form Toray, Japan. Montmorillonite clay, Nanomer® I.30E, containing 25-30 wt. % octadecylamine with bulk density 200-500 kg/m^3 was purchased from Sigma Aldrich Japan MWCNT, with average diameter 30nm, was purchased from Nanocyl Co.

B. Preparation of PA6 Composites

PA6/ALTi

PA6/ALTi masterbatch with 40wt% ALTi was produced by melt-blending using a kneading twin-screw extrusion machine (Misoshino, NT-16-29) at 250 °C, and 100 rpm. The masterbatch pellets were mixed with specified contents of PA6 into twin screw extruder machine in order to receive the composites with various contents 5, 10 and 20 wt% ALTi. The pellets were dried at 80 °C for 48 hr; then samples were fabricated using hand-truder injection machine. Injection temperature was 245 °C, and the mold temperature was 90 °C.

PA6/clay

PA6/clay masterbatch with 10 wt.% clay was produced by melt-blending using a kneading twin-screw extrusion machine (Misoshino, NT-16-29) at 250 °C, and 100 rpm. The masterbatch pellets were mixed with specified contents of clay into twin screw extruder machine in order to receive the nanocomposites with various contents 1, 2, and 3 wt.% clay.

PA6/MWCNT

The process of preparation was performed in a special ultrahigh-shear extruder (HSE3000mini, Imoto Co. Japan), which a feedback-type screw was used. The L/D ratio of the screw was about 1.78. The screw rotation speed used in this study was 500 rpm, which corresponds to an average shear rate of 1470 s^{-1} in the region of the top part of the screw. The sample feeds to the top of the screw then returns to the root of the screw through the feedback path. The chamber capability is about 5 ml. The resulting sheet-like product was extruded from a T-die. The resulting sheets (10 wt% MWCNT) were pelletized in order to use them as a masterbatch for the nanocomposites. The masterbatch pellets were mixed with specified contents of MWCNT into twin screw extruder machine in order to receive the nanocomposites with various contents 0.05, 0.1, 0.3 wt. % MWCNT. The pellets were dried at 80 °C for 48 hr, then samples (including 10 wt.% MWCNT) were fabricated using hand-truder injection machine.

C. Characterization

IFSS of composites with desized carbon fibers were measured by a microdroplet pull-out test as shown in Fig. 1. Microdroplets of the composites were formed on each fiber, in the liquid state. Pellets were held by a helical spring inside the oven attached to the microdroplet machine (Tohei-sangyo Co.). Then, the pellets were heated up to 230 °C. Then, carbon fibers were embedded into the molten resin. The IFSS was calculated from the measured pullout force, F, using the equation:

$$IFSS = \frac{F_{max}}{\pi d.2r} \quad (1)$$

where; F is the load to debond the microdroplet, d is the fiber diameter, and 2r is the length of the fiber embedded in the matrix.

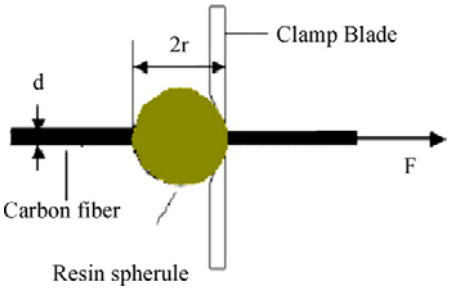

Fig. 1 Micro-droplets adhered on a carbon fiber filament

XPS was used to evaluate the chemical compositions on the carbon fiber surfaces. A Physical Electronics K-Alpha (KA1148) surface analysis system provided by Thermo Scientific with a concentric hemispherical analyzer and a monochromatic Al Ka X-ray source (1486.6 eV) was operated in an evacuated chamber at approximately 5.0E10−9mbar. An electron take-off angle of 45◦ with respect to the sample plane was employed. A spot of 400 µm in diameter, 150 eV of pass energy for survey scan and 30 eV for high-resolution scan were used in all the measurements. A seven-parameter curve fitting was conducted for the C 1s spectra by taking 284.6 eV as the reference peak.

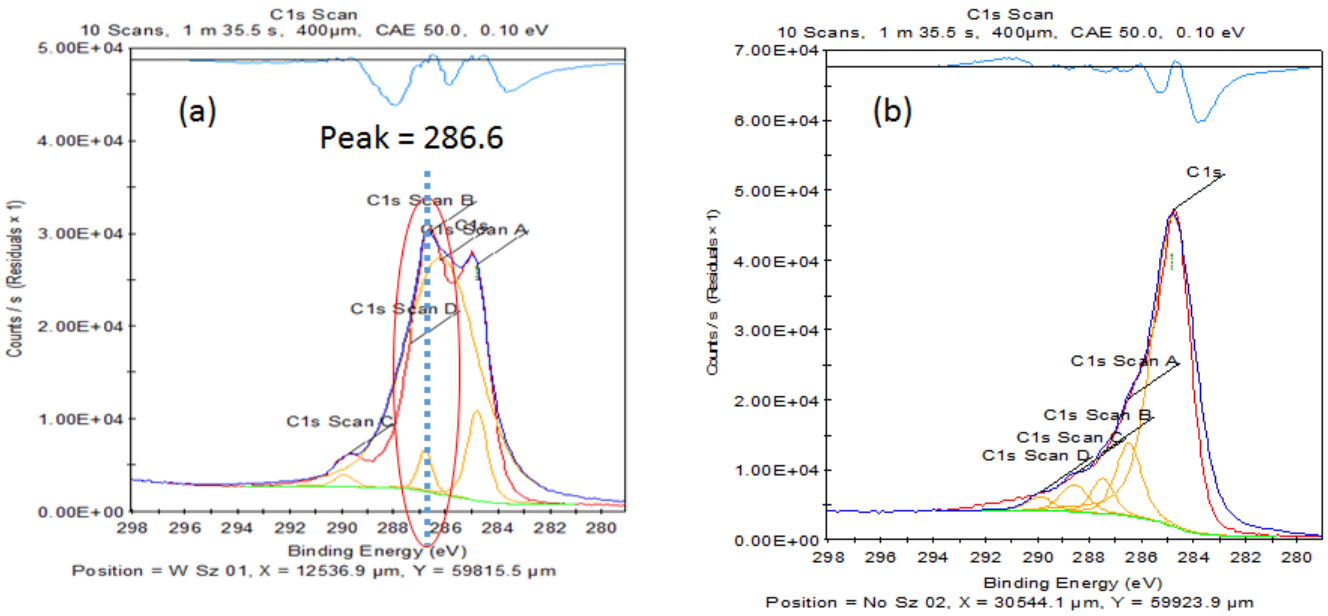

Fig. 2 C 1s spectra of (a) T300S showing the peak of epoxy group at 286.6, and (b) desized T300S showing disappearing the peak after heat treatment

III. Results

A. Surface of Carbon Fiber

The surface composition of each carbon fibers was determined by XPS, and the results of C 1s are given in Fig. 2, which shows that the spectra shape of the desized fibers has significant differences with the sized ones. As shown in the figure that the peak at 286.6 which represent sizing agent was almost disappear after heating treatment at 450 ºC. The disappearing of the peak are mainly caused by removing or decreasing C-O-C=O as represent the epoxy group.

In order to confirm whether the heating treatment has a negative effect on the surface of carbon fiber or not, the surface was observed by SEM (Fig. 3). SEM photos did not show any obvious damage on the surface of carbon fiber after heat treatment which proves that heating treatment at the specified temperature was safe for the CF.

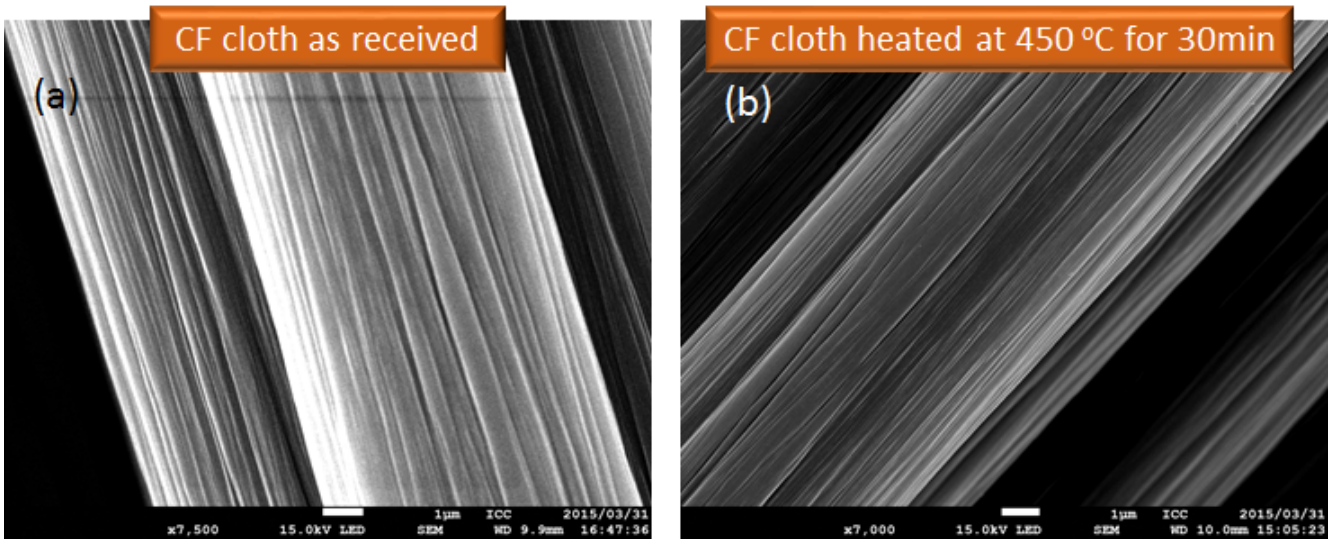

Fig. 3 SEM photos for (a) T300S CF, and (b) desized T300S CF showing there is no damage for both cases

B. Interfacial Adhesion of Carbon Fiber Reinforced PA6/ALTi Composites

The microbond test used in this study provides a simple and effective way to measure carbon fiber/PA6 *IFSS* values. The *IFSS* of the carbon fibers with PA6 composites is shown in Fig. 4 (a). The embedded length of the microdroplets was approximately 90 µm for all samples. The pull-out force for microdroplets of 5 wt% ALTi composite to cause the debonding was about the same as the neat PA6 microdroplets. The pull-out force for microdroplets of 10 wt% ALTi composite to cause the debonding was higher than that needed to cause debonding of the neat PA microdroplets, indicating that the IFSS between a carbon fiber and PA6/ALTi composites was significantly higher than that for neat PA matrix.

The schematic sketch of the microdroplet pull-out test specimen is shown in Fig. 4 (b). The amplified schematic might help in the explanation for the improvement of adhesion in the composite. There is an improvement in adhesion due to an increase in the interfacial friction at the interface. Additionally, the more rigid nature of the PA6/ALTi composite, compared to neat PA6, likely contributes to better interfacial adhesion.

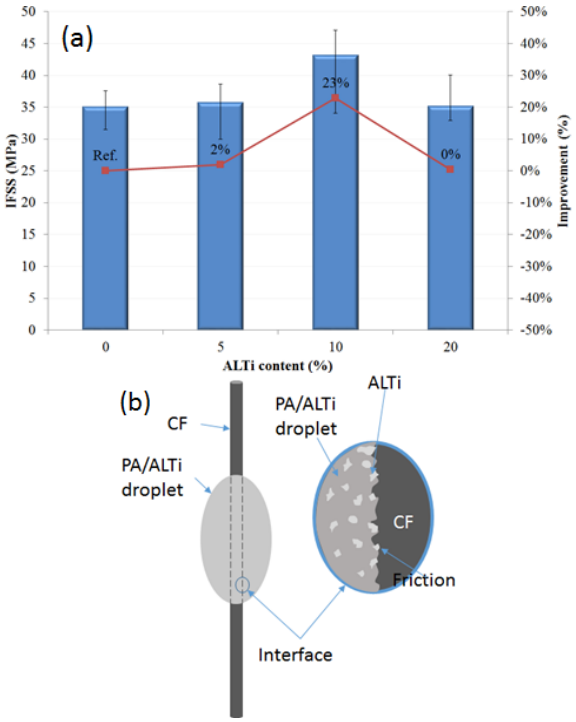

Fig. 4 (a) IFSS of PA6/ALTi composites, (b) Schematic sketch of the microdroplet pull-out test specimen

Fig. 5 shows photographs of the microdroplet pull-test specimens after loading to failure. These photographs further

illustrated differences in the microdroplet failure patterns. These pullout patterns are consistent with the pull-out force results just discussed. For the PA6/ALTi composite, the increase of the amount of the resin attached to the carbon fiber surface after debonding in comparison with the neat PA was observed which could be attributed to the higher interfacial adhesion between the composite and the CF. The increase in IFSS is believed to be mainly attributable to improvement in interface roughness between the PA6/ALTi composite and the carbon fiber.

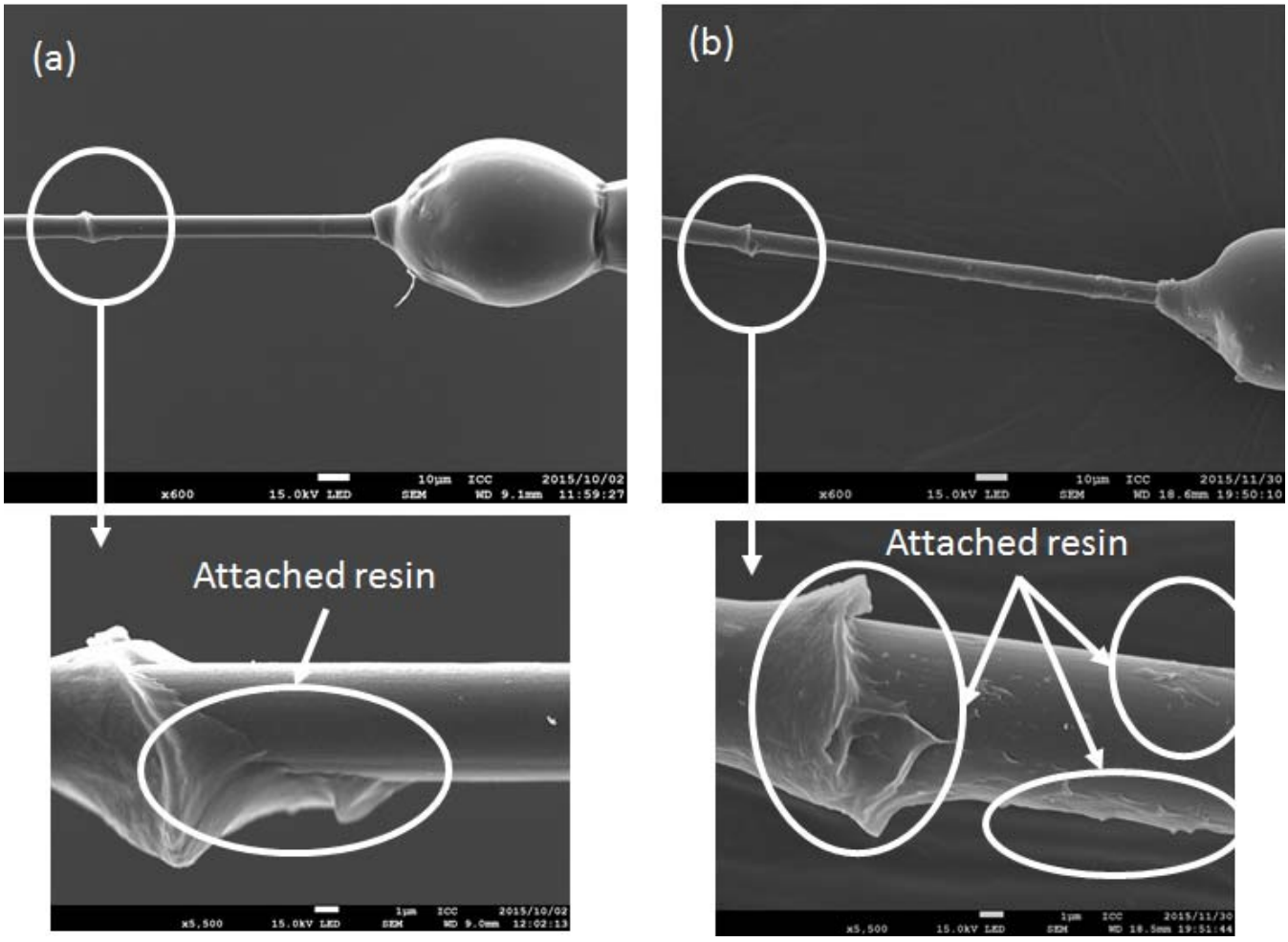

Fig. 5 SEM photomicrographs of a microdroplet after debonding; (a) neat PA6, and (b) 10 wt% ALTi.

The IFSS for the microdroplets of 1wt.% clay composite to cause the debonding was about the same as neat PA6 microdroplets. The IFSS values for 2 and 3wt. % of clay filled PA6 were dramatically smaller than that neat PA6 (Fig. 6). It seems that octadecylamine treated clay platelets have weakened the bonding with carbon fiber with increasing the contents of the clay. Treated clay platelets by octadecylamine can facilitate good clay dispersion and can achieve effective intercalation due its low molecular weight, which allows its highly mobilized short chains to interact actively with a great number of clay platelets in large clay surface areas. Meanwhile, the most of the octadecylamine was incorporated at the interlayer of clay, thereby reducing the adhesion between carbon fiber and PA6. Arao et al. [9] reported that clay has negative effects on the interfacial properties of other material systems. They suggested that intercalation, which has a traction force into the interlayer of clay platelets, also possibly reduces the interfacial strength between the fiber and the matrix.

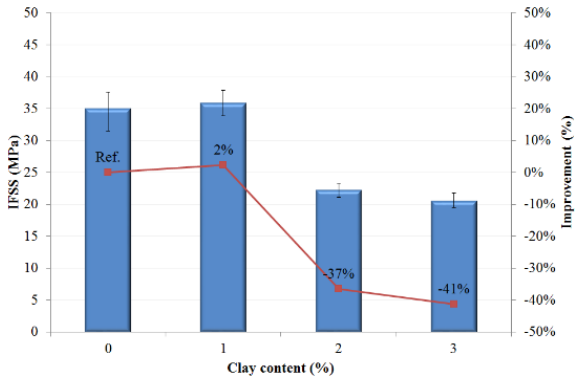

Fig.6 IFSS of PA6/Clay nanocomposites

Fig. 7 shows photographs of the microdroplet specimens after loading to failure. These photographs further illustrated differences in the microdroplet failure patterns for neat PA6 and 3wt% nano-clay which consistent with the IFSS results just discussed. For the neat PA6, resin attached to the fiber was shown at the end of the separated part of microdroplet. In Fig. 7 (b), for 3wt% clay, clear fiber surface was shown with no resin attached to the fiber surface indicating adhesive fracture at the interface.

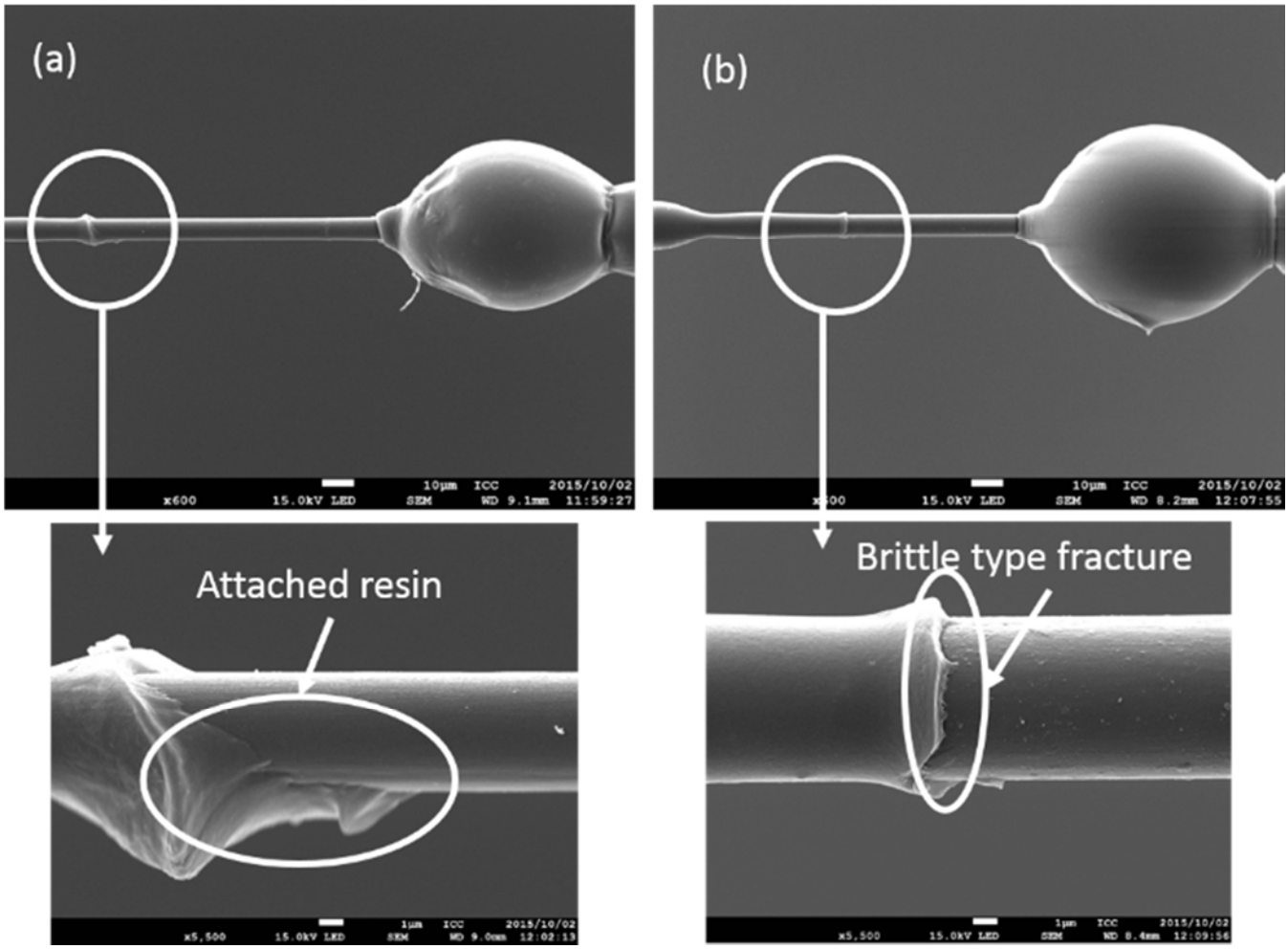

Fig. 7 SEM photomicrographs of a microdroplet after debonding; (a) neat PA6, and (b) 3% clay.

The IFSS for microdroplets of PA/MWCNT composites to cause the debonding were lower than the neat PA6 microdroplets. The IFSS values were decreased dramatically by about 37% (Fig. 8).

Fig. 9 shows photographs of the microdroplet specimens after loading to the failure of PA/MWCNT composites. These photographs further illustrated the brittle behaviors of PA/MWCNT which consistent with the IFSS results just discussed.

IV. Conclusion

This paper aimed to study the effect nanoclay, ALTi particles, and MWCNT on the IFSS of desized carbon fiber. IFSS has enhanced with 10wt% ALTi by about 23% comparing with neat PA6. The enhancement could be attributed to the interfacial friction at the interface between the carbon fiber and the particle. With addition of 1wt% nanoclay, IFSS was the same as the neat PA. However, with incorporating MWCNT into PA6, the IFSS has dramatically decreased.

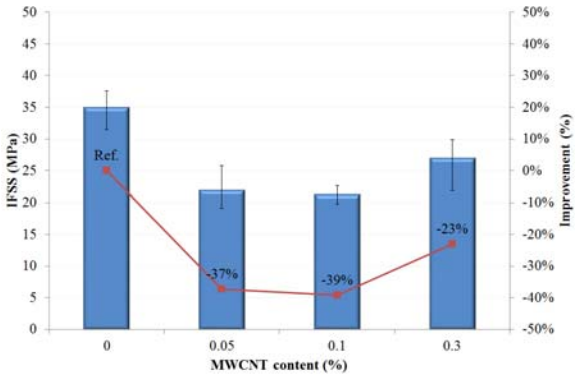

Fig. 8 IFSS of PA6/MWCNT nanocomposites

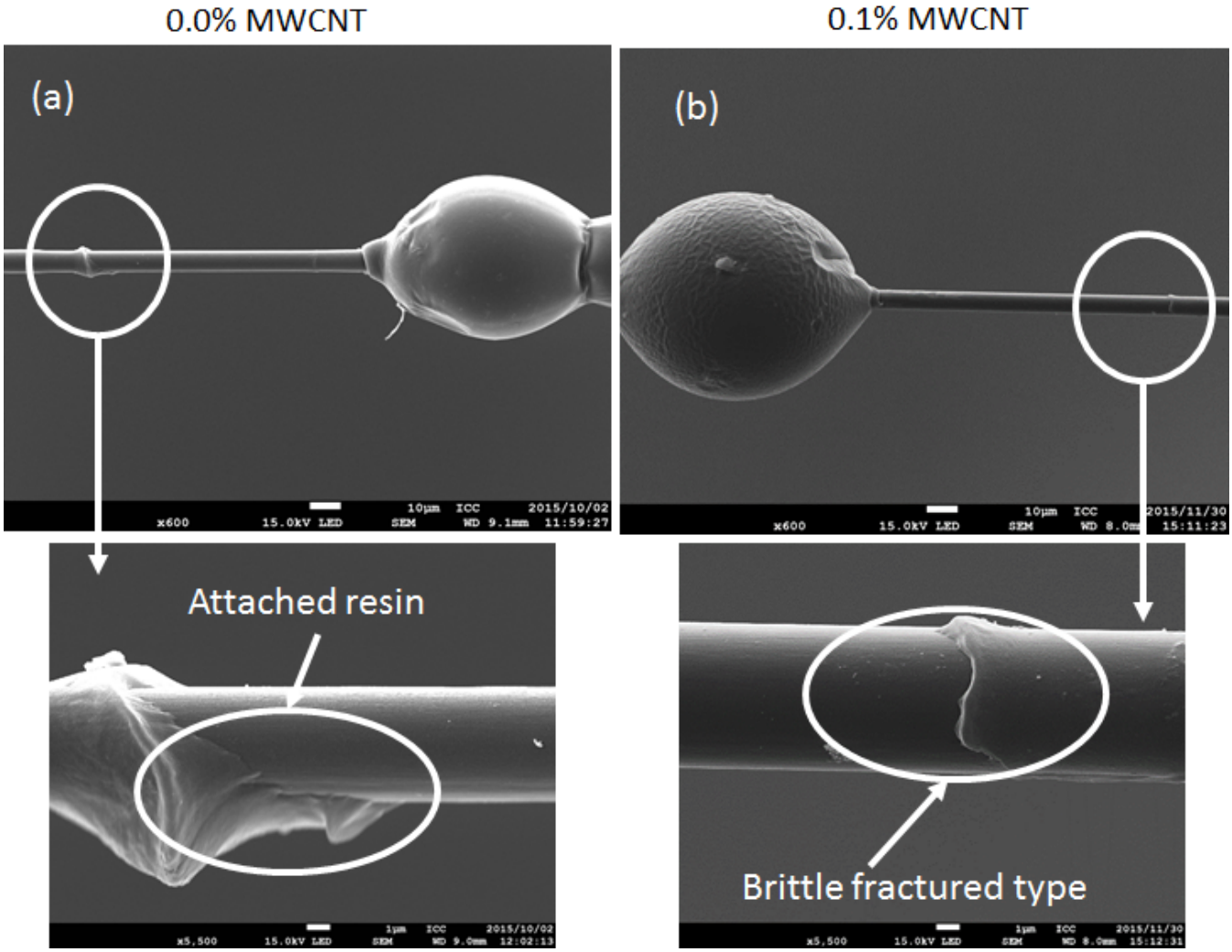

Fig. 9 SEM photomicrographs of a microdroplet after debonding; (a) neat PA6, and (b) 0.1% MWCNT

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