PREPARATION AND PROPERTIES OF ALIGNED MWCNT-REINFORCED THERMOPLASTIC POLYIMIDE COMPOSITES

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ABSTRACT

Horizontally aligned 100-ply multi-walled carbon nanotube (MWCNT) sheets were produced from vertically aligned MWCNT arrays using drawing and press-winding techniques. Composites based on thermoplastic polyimide (TPI) resin and the aligned MWCNT sheets have been fabricated using hot-melt processing method. Effects of processing temperature and hot stretching on the mechanical properties of the aligned MWCNT/TPI composites were examined. The heating temperature of 410 ^{o}C can be regarded as a reasonable temperature for the aligned MWCNT/TPI composite fabrication in this study. Hot-stretched MWCNT/TPI composite showed greater tensile strength and elastic modulus than those of the non-stretched one. The enhancement in the tensile strength and elastic modulus of the aligned MWCNT/TPI composites caused by hot stretching is attributable to the increase of the MWCNT alignment and enhancing the MWCNT volume fraction. The experimental results suggest that the aligned MWCNT/TPI composites with high CNT volume fraction can be used as lightweight and high heat resistance materials for aerospace applications.

1 INTRODUCTION

Carbon nanotubes (CNTs) are regarded as the potential reinforcements for high-performance composites because of their high aspect ratio, high surface area available for stress transfer, and excellent mechanical properties [1]. The high-performance composites used for aerospace structures comprise a high volume fraction of aligned stiff fibers embedded in high-performance polymers. Recently, vertically aligned CNT arrays have been developed for the production of high volume fraction CNT-reinforced polymer composites [2–4]. Long-aligned CNT sheets have been created from vertically aligned CNT arrays using solid-state drawing and winding techniques [5–7]. Highly oriented aligned CNT sheets have been particularly promising for the development of high volume fraction CNT composites with high performance.

Thermoplastic polyimides (TPIs) are a class of thermally stable high-performance polymers that are used in many applications, such as adhesives, coatings, fibers, films, membrane, liquid crystalline displays, insulation, and composite matrices [8]. They have exhibited low moisture absorption, excellent thermal stability and chemical resistance, flexibility, high toughness and damage tolerance, and good mechanical properties both at room temperature (RT) and elevated temperatures [9]. In addition, TPIs have the ability to be re-melted and re-processed and thus the damaged structures made of TPIs are repairable by applying heat and pressure. Moreover, TPIs could be recycled and combined with other recycled materials to make new products. Recently, great efforts have been devoted to develop high-performance melt-processable TPIs which can be used as high-temperature matrix resins for advanced composites [10].

For this paper, composites made of TPI resin and highly aligned multi-walled CNT (MWCNT) sheets have been developed using hot-melt processing method. Effects of processing temperature on the mechanical properties of the composites were studied. In addition, hot stretching of the aligned MWCNT/TPI composites was conducted to improve the mechanical properties of the composites. The MWCNT volume fraction was estimated through thermogravimetric analysis (TGA) data. Field emission scanning electron microscopy (FE–SEM) (SU8030; Hitachi Ltd., Tokyo, Japan) was used to investigate the microstructural morphologies of the MWCNT sheets and their composites.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

Vertically aligned MWCNT arrays were grown on a bare quartz substrate using chloride-mediated chemical vapor deposition [2]. As-grown MWCNTs used in this study have mean diameter of 22 nm. Horizontally aligned 100-ply MWCNT sheets were produced from vertically aligned MWCNT arrays using drawing and press-winding techniques [6]. Figure 1 portrays a processing of a horizontally aligned MWCNT sheet from a vertically aligned MWCNT array. FE–SEM micrographs showing horizontally aligned MWCNTs drawn from the array and MWCNT sheet morphology were inserted in Figure 1. A scanning transmission electron microscopy (STEM) image showing the MWCNTs was also inserted in Figure 1. TPI resin film Midfil NS-31 used in this study was supplied by Kurabo Industries Ltd. (Osaka, Japan) with a glass transition temperature of 320 ^{o}C and a melting temperature of 388 ^{o}C. Thickness and density of the TPI film are approximately 6 μm and 1.43 g/cm^{3}, respectively.

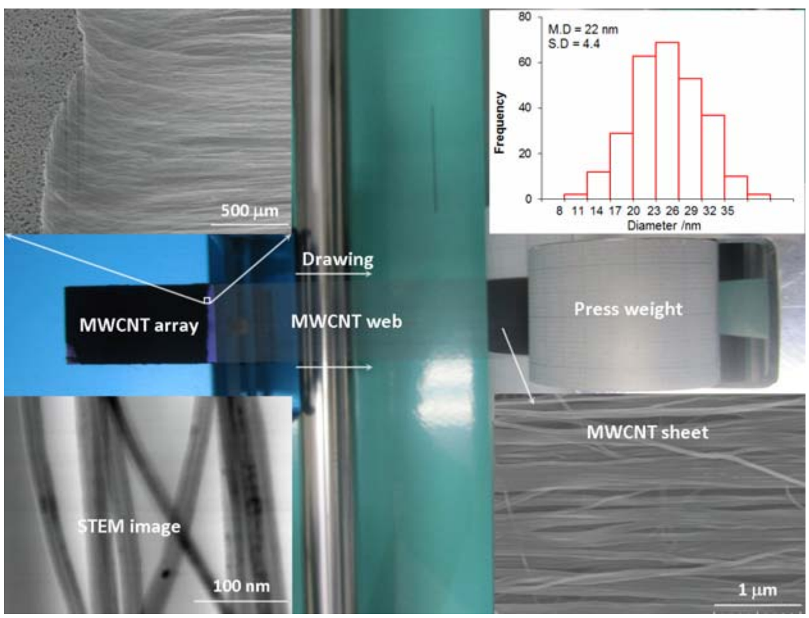

Figure 1: Processing of a horizontally aligned MWCNT sheet from a vertically aligned MWCNT array using drawing and press-winding techniques

2.2 Aligned MWCNT/TPI composite fabrication

High temperature composites based on TPI resin and aligned MWCNT sheets have been developed using hot-melt processing method. To begin with, an aligned MWCNT sheet with 20 mm width and 60 mm length was placed between two TPI resin films to develop aligned MWCNT/TPI composites. The stacking MWCNT sheet and TPI films was set between two UPILEX films supplied by UBE Industries Ltd. (Tokyo, Japan). To determine a most reasonable temperature for the composite processing, the stacking were pressed at the processing temperatures of 400, 410, and 420 ^{o}C for 10 min without pressure and followed by 10 min under a pressure of 2 MPa using a test press (MP-WNL; Toyo Seiki Seisaku-sho Ltd., Tokyo, Japan). Finally, the composites were cooled naturally by air under 2 MPa pressure for creating crystallinity in the TPI composites. The thickness of pristine 100-ply MWCNT/TPI composites is 14–17 μm.

2.3 Hot stretching of aligned MWCNT/epoxy composite

In this study, the 100-ply aligned MWCNT/TPI composite samples were hot-stretched at a temperature of 350 ^{o}C until maximal tensile load using a hydraulic servo testing equipment (Servopulser EHF-F1; Shimadzu Corp., Kyoto, Japan). The composite samples with 10 mm width and 60 mm length were used for hot stretching. The images showing the testing equipment with a mounted sample were depicted in Figure 2. The UPILEX film end tabs were bonded on both sides of the sample grip portions. The distance between the clamped end tabs of the samples was 40 mm. After hot stretching the composites were re-processed at a temperature of 410 ^{o}C for 10 min under 2 MPa pressure using the test press above. The obtained thickness of hot-stretched 100-ply MWCNT/TPI composites is 14–16 μm.

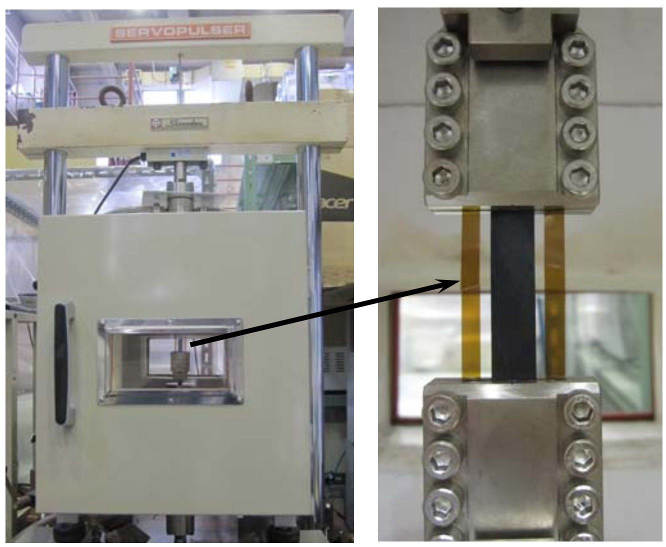

Figure 2: Images showing the hot stretching equipment with a mounted composite sample.

2.4 TGA and mechanical testing

Thermal degradation of TPI resin, MWCNTs, and MWCNT/TPI composites was analyzed up to 1000 °C in argon gas at a flow rate of 100 ml/min using a thermogravimetric analyzer (STD Q600; TA Instruments, Delaware, USA). About 5 mg of each specimen was loaded for each measurement at a heating rate of 10 °C/min. The respective mass losses of TPI resin, MWCNTs, and the composites were recorded.

Tensile tests were conducted for the aligned MWCNT/TPI composites in a laboratory environment at RT. Tensile specimens with 10 mm gauge length and 3 mm width were tested on a testing machine (EZ-L; Shimadzu Corp., Kyoto, Japan) with a crosshead speed of 0.1 mm/min. Samples width was measured using an optical microscope (SZX12; Olympus Corp., Tokyo, Japan), whereas their thickness was measured using a digital micrometer (IP65; Mitutoyo Corp., Kanagawa, Japan). The longitudinal strain of tensile samples was measured using a non-contacting video extensometer (TRIViewX; Shimadzu Corp., Kyoto, Japan) with two targets. Mean tensile properties of the composites were obtained from at least five specimens.

3 RESULTS AND DISCUSSION

3.1 Estimation of MWCNT volume fraction

MWCNT volume fraction of the composites was determined through TGA data. The respective mass loss of the MWCNTs, TPI resin and the composites were measured between 150 ^{o}C and 850 ^{o}C. The MWCNT mass fraction (m_f) of the composite was calculated from mass loss of the MWCNTs (Δm_f), TPI resin (Δm_m) and the composite (Δm_c) as follows [11–14].

$$m_f = \frac{\left(\Delta m_m - \Delta m_c\right)}{\left(\Delta m_m - \Delta m_f\right)} \tag{1}$$

The MWCNT volume fraction (V_f) was finally determined from the mass fraction of the MWCNTs, TPI resin density (ρ_m), and density of the composite (ρ_c), as

$$V_f = 1 - \frac{\left(1 - m_f\right)\rho_c}{\rho_m} \tag{2}$$

The MWCNT volume fractions of the pristine and hot-stretched MWCNT/TPI composites are 11.6% and 13.4%, respectively. Results show that hot stretching enhanced slightly the MWCNT volume fraction of the composites. The enhancement in the MWCNT volume fraction is attributed to the slight decrease of the composite thickness after hot stretching.

3.2 Influence of processing temperatures on the composite properties

The processing temperature for fabrication of TPI composites was recommended being between 400 ^{o}C and 420 ^{o}C. Therefore, the mechanical properties of the 100-ply MWCNT/TPI composites fabricated at the temperatures of 400, 410, and 420 ^{o}C were examined to determine a most reasonable temperature for the composite processing. The thickness, density, and MWCNT volume fraction of the composites are given in Table 1. Effects of the processing temperature on the tensile strength and elastic modulus of the composites are presented in Figure 3. Mean fracture strain of the composites fabricated at different processing temperatures did not change significantly between 0.64% and 0.65%.

Table 1: Properties of aligned MWCNT/TPI composites at different processing temperatures

Processing temperature (^{o}C)	Thickness (μm)	Density (g/cm^3)	MWCNT volume fraction (%)
400	14–17	1.460	11.3
410	14–17	1.462	11.8
420	14–17	1.460	11.6

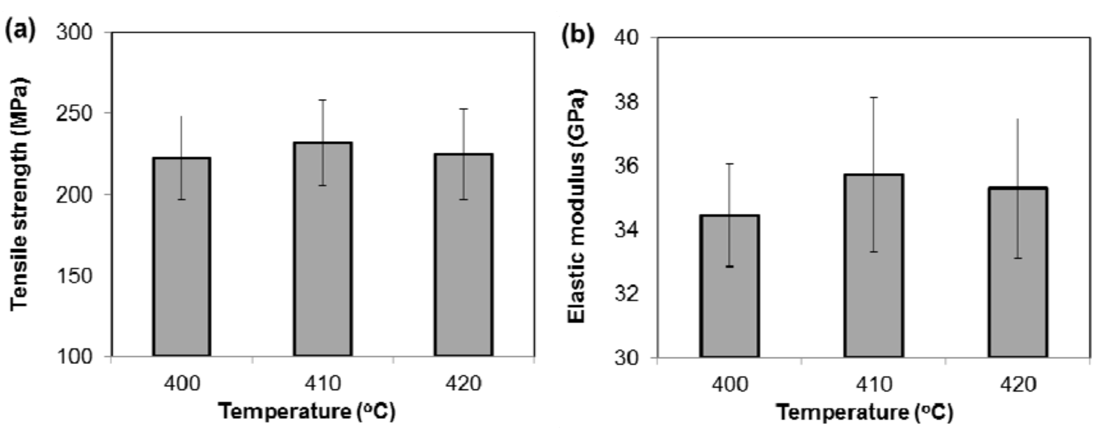

Figure 3: Effects of processing temperatures on (a) tensile strength and (b) elastic modulus of the aligned MWCNT/TPI composites.

As Table 1 and Figure 3 show, the properties of the composites nearly were unchanged with increasing the heating temperature from 400 °C to 420 °C. Nevertheless, the tensile strength and elastic modulus of the 100-ply MWCNT/TPI composites fabricated at 410 °C shows slightly higher than those at other processing temperatures. Therefore, the most reasonable temperature for production of the aligned MWCNT/TPI composites can be considered as 410 °C in this study.

3.3 Influence of hot stretching on the composite properties

Hot stretching of the aligned MWCNT/TPI composites was conducted at the temperature of 350 °C up to maximal tensile load. This temperature is above the TPI glass transition temperature and below its melting temperature. The mean stretch ratio of the composite samples for three measurements up to maximal load at 350 °C is 7.8%. The density of the hot-stretched composites is 1.466 g/cm^3. Influence of hot stretching on the tensile strength and elastic modulus of the aligned MWCNT/TPI composites fabricated at 410 °C is presented in Figure 4.

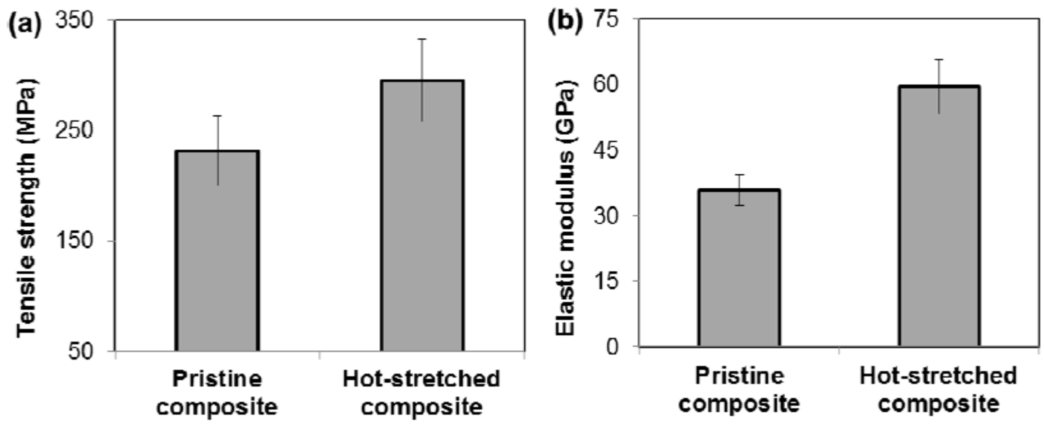

Figure 4: Influence of hot stretching on (a) tensile strength and (b) elastic modulus of the aligned MWCNT/TPI composites.

The hot-stretched MWCNT/TPI composite indicated higher mechanical properties than those of the pristine one. The hot-stretched MWCNT/TPI composite showed an increase in the tensile strength by 27.4% and in the elastic modulus by 66.4% compared to the pristine one. Nevertheless, the percentage enhancement in the stiffness of the hot-stretched MWCNT/TPI composite is greater than that in its strength. The increase in the tensile strength and elastic modulus of the aligned MWCNT/TPI composite caused by hot stretching is attributable to the increasing the MWCNT volume fraction of the composite. In addition, the enhancement of the tensile strength and elastic modulus of the hot-stretched composite can be attributed to the increase of MWCNT alignment. The enhancement in the MWCNT alignment is ascribable to the reduction in the microscopic waviness of MWCNTs resulting from hot stretching [11]. Moreover, Cheng et al. [15] showed that the decrease in the microscopic waviness of MWCNTs by hot stretching made the strength enhancement even more notable.

FE-SEM images showing fractured surfaces of the pristine and hot-stretched MWCNT/TPI composites are depicted in Figure 5. High-magnification FE-SEM micrographs in Figure 5 showed that the TPI resin was infiltrated well between individual and bundled MWCNTs, resulting in effectively load transfer between the MWCNTs and TPI resin in the composites. The dense packing of MWCNTs is visible on the fractured surfaces of the composites. The MWCNTs were either broken or pulled out from the TPI matrix during tensile testing. The pulled-out MWCNTs with a few micrometers length are apparent on the fractured surfaces of the composite specimens. The hot-stretched MWCNT composites showed larger MWCNT bundles than the pristine ones. The existence of the MWCNT bundles created by pressing the MWCNT webs was evidenced on the surface morphologies of the MWCNT sheet (see Figure 1 inset). In general, FE-SEM observations of composite fractured surfaces showed that the hot-melt processing method is useful for fabrication of the aligned MWCNT/TPI composites.

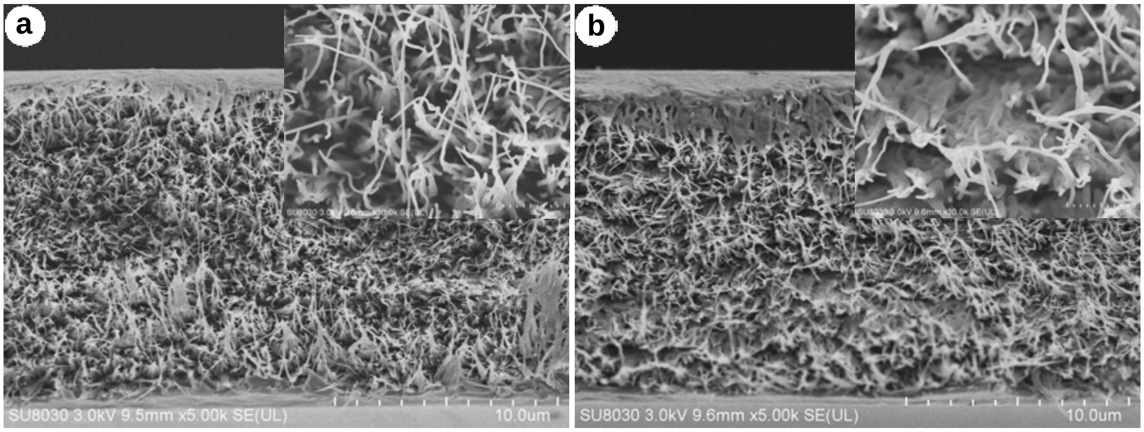

Figure 5: FE-SEM micrographs showing fracture surfaces of (a) pristine and (b) hot-stretched 100-ply MWCNT/TPI composites.

4 CONCLUSIONS

The aligned MWCNT/TPI composites have been fabricated successfully using hot-melt processing method. The heating temperature of 410 ^{o}C can be regarded as a reasonable temperature for the aligned MWCNT/TPI composite fabrication in this study. Hot stretching at the temperature of 350 ^{o}C improved the strength and stiffness of the aligned MWCNT/TPI composites considerably. The surface morphologies of the composites showed a good MWCNT impregnation in the TPI matrix. The experimental results suggest that the aligned MWCNT/TPI composites with high MWCNT volume fraction can be used as lightweight and high heat resistance materials for aerospace applications.

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