

# Improving mechanical properties of multi-walled carbon nanotube/epoxy composites through a simple stretch-drawing method

- **Tran Huu Nam**
- **Vu Minh Hung**
- **Pham Hong Quang**

Petrovietnam University

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## ABSTRACT

Horizontally aligned multi-walled carbon nanotube (CNT) sheets were produced from vertically aligned CNT arrays using drawing and winding techniques. Composites based on epoxy resin and an aligned 100-ply CNT sheet have been developed using hot-melt prepreg processing. However, wavy and poor-packed CNTs in the sheets have limited reinforcement efficiency of the CNTs in the composites. In this study, a new simple stretch-drawing method was used to modify the structures of the aligned CNT sheets for improving the composite properties. The stretch-drawing of the CNT sheets enhanced the composite properties considerably. The improved properties of the composites originated

from straightening of the wavy CNTs and increasing the CNT dense packing in the composites. With a 3% stretch ratio, the aligned CNT/epoxy composites achieved their best mechanical properties in this study. The 3% stretched composites exhibit increased tensile strength by 113% and enhanced elastic modulus by 34% compared to non-stretched ones. Results show that the simple stretch-drawing is effective to produce highly aligned CNT sheets for the development of high-performance CNT composites. Compared to our previous stretching method, the stretch-drawing method in this study is more effective in improving the mechanical properties of aligned CNT/epoxy composites.

**Key words:** carbon nanotubes, prepreps, composites, stretching, mechanical properties.

## 1. INTRODUCTION

Carbon nanotubes (CNTs) have been regarded as the reinforcing agents for polymer composites because of their high aspect ratio, high surface area available for stress transfer, and excellent mechanical properties [1]. However, most CNT-reinforced polymer composites have been composed by unorganized CNTs dispersed in polymer matrices [2]. Those

composites could not fully take advantage of the excellent properties of CNTs because of low volume fraction and easy agglomeration in the dispersion of CNTs. Therefore, recent studies have focused on developing vertically aligned CNT arrays [3] and horizontally aligned CNT sheets [4]. The aligned CNT sheets have been used to create aligned CNT/epoxy composites. Although the composites contain the aligned

CNTs, their mechanical properties are low partly because of wavy and poor-packed CNTs in the composites [5]. Therefore, a mechanical stretching of the aligned CNT sheets has been applied to reduce wavy and poorly packed CNTs [6,7]. However, the handling of the CNT sheets without resin for the stretching is generally difficult because of static electricity [5]. To overcome this difficulty, a simple stretch-drawing method was proposed in this study to straighten the wavy CNTs and to reduce the poor-packed CNTs for improving their composite properties. Effect of the stretch-drawing on the mechanical properties of aligned CNT/epoxy composites was examined.

## 2. EXPERIMENTAL PROCEDURES

### 2.1. Materials

A B-stage epoxy resin film covered with release paper and plastic film was obtained from Sanyu Rec Co. Ltd. (Osaka, Japan) with the recommended cure condition of 130°C for 2 h. The areal weight of the B-stage epoxy resin film with density of 1.2 g/cm<sup>3</sup> was controlled to approximately 12 g/m<sup>2</sup>. Vertically aligned CNT arrays with about 0.8 mm height were grown on a bare quartz substrate using chloride-mediated chemical vapor deposition [3]. As-grown CNTs examined have mean diameter of 38 nm [6,7].

### 2.2. Processing of aligned CNT sheets

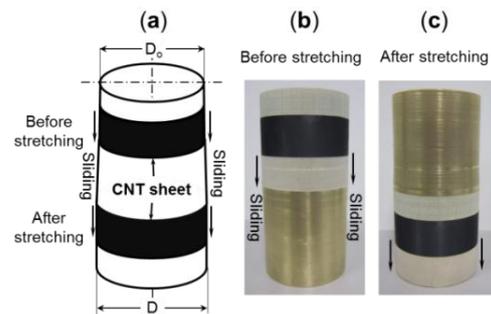
Pristine aligned and multiply CNT sheets were produced from the vertically aligned CNT arrays using drawing and winding processes. Detailed procedures were presented in several reports [4–7]. The stacked 100-ply aligned CNT sheets were used for composite fabrication.

### 2.3. A simple stretch-drawing of CNT sheets

The simple stretch-drawing was applied to the aligned CNT sheets with round tube shaped using a cylinder with different top and bottom diameters (Figure 1). The stretch ratio  $\Delta$  was calculated using the following equation.

$$\Delta = \frac{D - D_o}{D_o} \quad (1)$$

Therein,  $D_o$  and  $D$  are the top and bottom diameters of the cylinder used for stretch-drawing the CNT sheets with round tube shaped, respectively. The top diameter  $D_o$  is 50 mm and the bottom diameters are 51 mm and 51.5 mm corresponding to the respective stretch ratios of 2% and 3%. Efforts to carry out 4% stretching corresponding to the bottom diameter of 52 mm were not successful because of sheet breakage.



**Figure 1.** (a) A schematic diagram of the stretch-drawing processes. The images showing the processes (b) before stretching and (c) after stretching.

### 2.4. Fabrication of CNT/epoxy composites

Composites made of an epoxy resin film and a 100-ply CNT sheet were developed using hot-melt prepreg processing with a vacuum-assisted system (VAS). First, the CNT sheet with round tube shaped was spread into a flat sheet. Next, a flat CNT sheet with 20 mm width and 50 mm length was covered with an epoxy resin film and was set between two release films

(WL5200; Airtech International Inc., CA, USA) to create an aligned CNT/epoxy prepreg. The prepreg was fabricated under 0.5 MPa pressure for 5 min at 100 °C using a test press (MP-WNL; Toyo Seiki Seisaku-sho Ltd., Tokyo, Japan). Finally, the prepreg was placed on the VAS and was cured at 130 °C for 2 h under 2 MPa in the test press to produce an aligned CNT/epoxy composite. The pristine and stretched CNT/epoxy composites were fabricated for comparative assessments.

### 2.5. Thermogravimetric analysis

The thermal degradation of epoxy resin, the CNTs, and their composites was analyzed up to 800°C in argon gas at a flow rate of 300 ml/min using a thermogravimetric analyzer (DTG-60A; Shimadzu Corp., Kyoto, Japan). About 5 mg of each specimen was loaded for each measurement at a heating rate of 10°C/min. The respective mass losses of epoxy resin, the CNTs, and the composites were recorded.

### 2.6. Characterizations and testing

Field emission scanning electron microscopy (FE-SEM) (SU8030; Hitachi Ltd., Tokyo, Japan) was used to investigate the microstructural morphologies of the CNT sheets and their composites. Polarized Raman spectra were measured to determine the degree of CNT alignment in the sheets and their composites using Raman spectroscope (XploRA-ONE; Horiba Ltd., Kyoto, Japan). Tensile testing was conducted for the composites in a laboratory environment. Tensile specimens with 10 mm gauge length were tested on a testing machine (EZ-L; Shimadzu Corp., Kyoto, Japan) with a crosshead speed of 0.1 mm/min. Widths of specimens were measured using an optical microscope (SZX12; Olympus Corp., Tokyo,

Japan), whereas their thickness was measured using a micrometer (102-119; Mitutoyo Corp., Kanagawa, Japan). The fracture strain was measured using a non-contacting extensometer (TRViewX; Shimadzu Corp., Kyoto, Japan) with two targets. Mean tensile properties were obtained from at least five specimens.

## 3. RESULTS AND DISCUSSION

### 3.1. Evaluation of the simple stretch-drawing on alignment of CNTs in the sheets

FE-SEM images showing microstructural morphologies of the pristine and stretched CNT sheets are presented in Figure 2. The pristine CNT sheets in Figure 2a showed many wavy and poor-packed CNTs. After the simple stretch-drawing (Figure 1), the wavy CNTs in the sheets decreased considerably (Figures 2b-2c). Besides, the stretch-drawing enhances the dense packing of CNTs in the sheets. Moreover, the 3% stretched CNT sheets showed more straight CNTs and greater CNT alignment than the 2% stretched CNT sheets (Figures 2b-2c).

The alignment and straightening of the wavy CNTs after stretch-drawing were examined using polarized Raman spectroscopy [7-9]. Polarized Raman spectra with Raman shift between 1000-2000  $\text{cm}^{-1}$  were measured using incident laser light with a wavelength of 532 nm normal to the CNT sheet samples (Figure 3). The incident light was polarized parallel and perpendicular to the CNT alignment (see Figure 3 inset). Polarized Raman spectra for all samples show two main peaks located at approximately 1350  $\text{cm}^{-1}$  and 1580  $\text{cm}^{-1}$ , which are attributed respectively to the disorder-induced D band and the graphite-structure derived G band. The Raman shift of the CNT sheets does not change significantly after stretch-drawing.

Moreover, the G-band intensity ratio  $R$  in

the parallel configuration to the perpendicular configuration was estimated to examine the degree of CNT alignment [7-9]. The higher CNT alignment produces the higher G-band intensity ratio because Raman scattering is more intense when the polarization of the incident light is parallel to the axis of a CNT [9]. The G-band intensity ratio  $R$  of the pristine CNT sheets was 1.67. After 2% stretching, the  $R$  value of the

CNT sheets was enhanced to 2.44. Particularly, the  $R$  value of the CNT sheets with 3% stretch ratio increased drastically to 3.03. Results show that the G-band intensity ratio of the 3% stretched samples is greater than that of the 2% stretched ones. The enhancement in the  $R$  is attributed to the better alignment of CNTs in the stretched sheets (Figure 2) caused by higher stretch ratio.

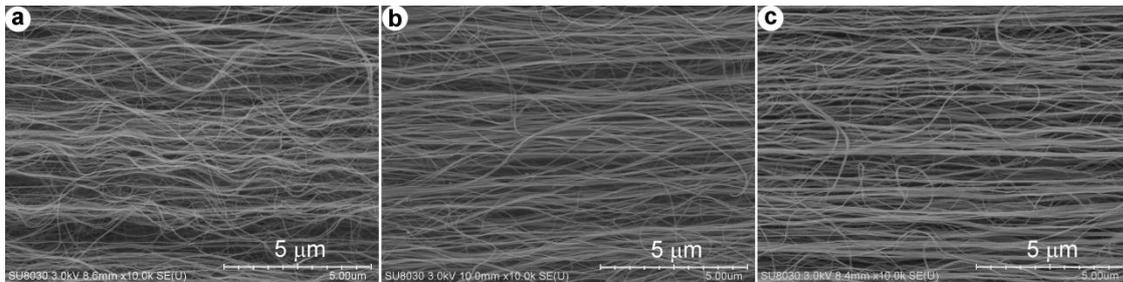


Figure 2. FE-SEM micrographs showing microstructural morphologies of (a) pristine, (b) 2% and (c) 3% stretched CNT sheets.

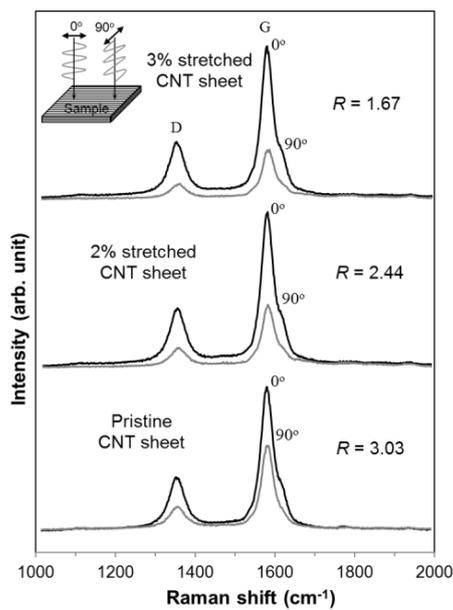


Figure 3. Polarized Raman spectra of pristine and stretched CNT sheets at 0° and 90° (0° and 90° directions correspond to configurations where the polarization direction of the laser light are, respectively, parallel and perpendicular to the direction of CNTs).

### 3.2. CNT volume fraction in the composites

The CNT volume fraction was ascertained via the TGA data. The respective mass losses of the CNTs, epoxy resin and the composites were measured at 150–750°C. The CNT mass fraction ( $m_f$ ) of the composite was calculated from the mass loss of the CNTs ( $\Delta m_f$ ), epoxy resin ( $\Delta m_m$ ) and the composite ( $\Delta m_c$ ) as below.

$$m_f = \frac{(\Delta m_m - \Delta m_c)}{(\Delta m_m - \Delta m_f)} \quad (2)$$

The CNT volume fraction ( $V_f$ ) was then estimated from the mass fraction of the CNTs, epoxy resin density ( $\rho_m$ ), and the density of the composite ( $\rho_c$ ) as follows.

$$V_f = 1 - \frac{(1 - m_f)\rho_c}{\rho_m} \quad (3)$$

The mass losses, CNT mass fractions, and CNT volume fractions of the composites are presented in Table 1.

**Table 1.** Properties of epoxy resin, the CNTs and the composites

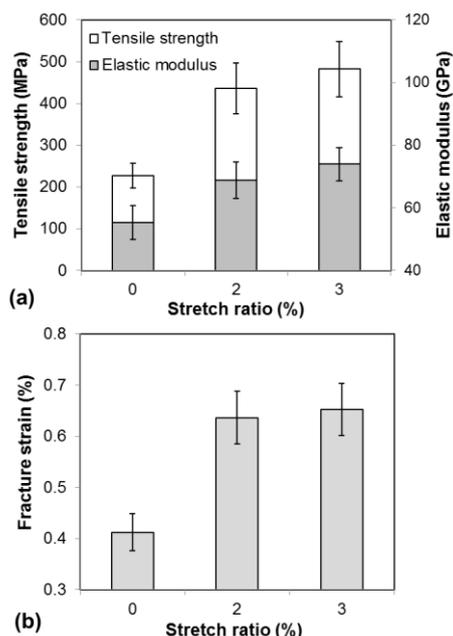
Materials	Thickness ( $\mu\text{m}$ )	Mass loss (%)	CNT $m_f$ (%)	CNT $V_f$ (vol. %)
Epoxy resin	8–10	87.9	–	–
CNTs	–	2.59	–	–
Pristine composites	16–19	47.1	47.8	35.5
2% stretched composites	14–16	45.4	49.8	37.3
3% stretched composites	14–16	44.1	51.4	38.8

The stretch-drawing of the sheets induced a slight enhancement of the CNT volume fraction in the composites. The increase of the CNT volume fraction was explained by the reduced composite thickness [6-7]. The reduced composite thickness is attributed to the straightening of wavy CNTs and increasing the dense packing of CNTs in the sheets. The 3% stretching engendered more straightening of wavy CNTs and denser packing of CNTs compared to the 2% stretching.

### 3.3. Effects of stretch-drawing on the mechanical properties of the composites

Mechanical properties of the pristine and stretched CNT/epoxy composites are presented in Figure 4. Mean tensile strength, elastic modulus, and fracture strain of epoxy resin respectively were 64.4 MPa, 2.6 GPa, and 4.8% [7]. FE-SEM micrographs showing in-plane distribution of CNTs in the pristine and

stretched CNT/epoxy composites are depicted in Figure 5.



**Figure 4.** Mechanical properties of the pristine and stretched CNT/epoxy composites.

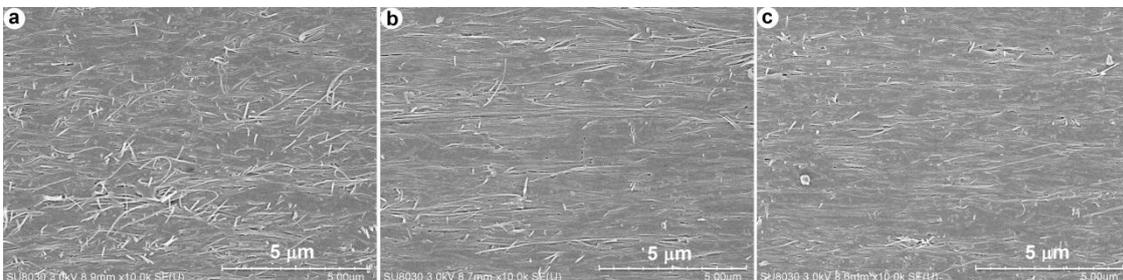
The measured mechanical properties of the epoxy resin and the composites show that the aligned CNTs greatly enhanced tensile strength and elastic modulus of epoxy resin. Compared to the epoxy resin, the pristine CNT/epoxy composite showed increased tensile strength by 252.6%, enhanced elastic modulus by 207.6%, and decreased fracture strain by 91.5%. The improvement in the tensile strength and elastic modulus of the composites is explainable by the fact that the aligned CNTs in the composites carry the load along the length of CNTs and provide strength and stiffness in the loading direction [5–7]. As seen in Figure 2, most CNTs in the sheets are aligned in the drawing direction. In addition, the CNT alignment in the composites was maintained during resin impregnation using hot-melt prepreg processing (Figure 5). As observed in Figure 5a, the wavy

and poor-packed CNTs are apparent in the pristine composites. After stretch-drawing, the wavy CNTs were straightened and the dense packing of CNTs was enhanced (Figures 5b–5c). The reduction in the fracture strain of the composites is mainly attributable to the addition of high CNT contents, resulting in the decrease in the amount of epoxy matrix available for the elongation, as presented in earlier reports [5–7].

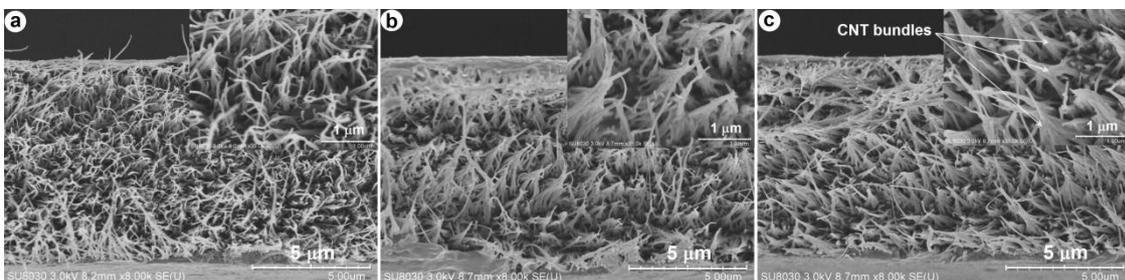
Furthermore, the stretch-drawing of the CNT sheets improved the mechanical properties of the aligned CNT/epoxy composites considerably (see Figure 4). The mechanical properties of the composites increased concomitantly with the increase of the stretch ratio up to 3%. Compared with the pristine composite, the 2% and 3% stretched CNT/epoxy composites respectively showed an increase in tensile strength by 92.5% and 112.7%, an improvement in elastic modulus by 24.3% and 33.6%, and an enhancement in fracture strain by 54.4% and 58.4%. The increase in the

mechanical properties of the composites is attributed to the straightening of the wavy CNTs (Figure 2 and Figure 5) and a slight increase of the CNT volume fraction (Table 1). The aligned CNTs are self-assembled and are straightened along the CNT direction during the stretching. Consequently, the packing of CNTs in the stretched sheets (Figures 2b–2c) became more compact than that in the pristine sheets (Figure 2a). The straightening of the wavy CNTs caused by stretch-drawing was proved by the better alignment of CNTs in the sheets through the G-band intensity enhancement, as presented above.

FE–SEM images showing fracture surfaces of the composites are presented in Figure 6. As Figure 6 shows, the CNT bundles caused by the stretch-drawing are visible on the composite fracture surfaces. The existence of the CNT bundles is evidenced by the surface morphologies of the CNT sheets (see Figures 2b–2c).



**Figure 5.** FE–SEM micrographs showing CNT distribution of (a) pristine, (b) 2% and (c) 3% stretched composites.

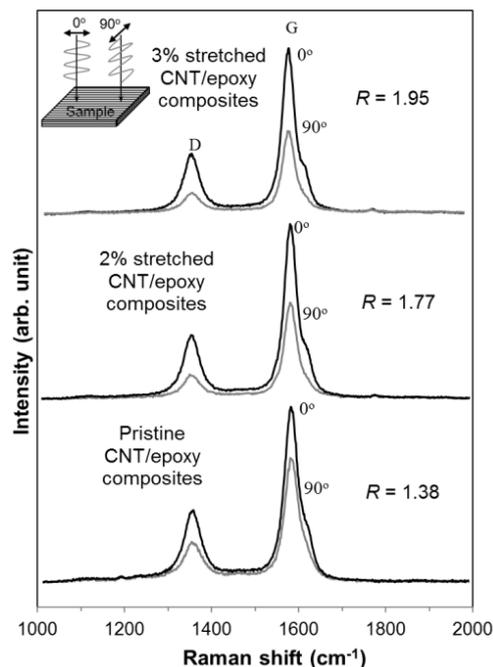


**Figure 6.** FE–SEM micrographs showing fracture surfaces of (a) pristine, (b) 2% and (c) 3% stretched composites.

As presented in our previous studies [6,7], stretching of the flat CNT sheets was effective for improving the mechanical properties of aligned CNT/epoxy composites. With the stretch ratio of 3%, the 100-ply aligned CNT/epoxy composite showed the high tensile strength of 448.6 MPa and high elastic modulus of 67.4 GPa [6]. With the same CNT diameter and stretch ratio of 3%, mean tensile strength (482.5 MPa) and elastic modulus (73.9 GPa) of the stretched CNT/epoxy composite in this study respectively are higher than those of the one presented in the report [6]. Therefore, the stretch-drawing of the CNT sheets with round tube shaped in this study is more effective than the stretching of the flat CNT sheets described in our earlier reports.

### 3.4. Evaluating the increase of CNT alignment in the composites caused by stretch-drawing

The straightening of the wavy CNTs after stretch-drawing resulted in higher alignment of CNTs in the composites (Figure 5). The higher degree of the CNT alignment in the composites was examined using polarized Raman spectroscopy [7]. Typical polarized Raman spectra of the composite samples in the range of 1000-2000  $\text{cm}^{-1}$  are presented in Figure 7. Raman spectroscopic measurements were conducted with incident light normal to the specimens, which was polarized parallel and perpendicular to the CNT alignment (see Figure 7 inset). Compared with the pristine samples, the stretched ones showed a lower D and G band peaks at  $90^\circ$ . The G band peaks decreased greatly for the stretched composites at the angle of  $90^\circ$ , thereby increasing the CNT alignment in the stretched composites.



**Figure 7.** Polarized Raman spectra of pristine and stretched CNT/epoxy composites at  $0^\circ$  and  $90^\circ$  ( $0^\circ$  and  $90^\circ$  directions correspond to configurations where the polarization direction of the laser light are, respectively, parallel and perpendicular to the direction of CNTs).

Moreover, the higher degree of the CNT alignment in the composites engenders the higher G-band intensity ratio  $R$ . The G-band intensity ratio  $R$  for the two polarizations of the pristine, 2%, and 3% stretched composites respectively are 1.38, 1.77, and 1.95. These values show that the G-band intensity ratio of the composite samples is increased after applying the stretch-drawing of the CNT sheets. The enhancement of the G-band intensity ratio is ascribed to the better alignment of CNTs in the composites caused by stretch-drawing of the CNT sheets. The G-band intensity ratio of the 3% stretched composite exhibited the highest value among all the composites, thereby achieving the best mechanical properties of the aligned CNT/epoxy composites in this study.

#### 4. CONCLUSIONS

The simple stretch-drawing has produced highly aligned CNT sheets with dense packing of CNTs. Raman spectra measurements showed a higher alignment of CNTs in the sheets and their composites after the stretch-drawing. The stretch-drawing of the CNT sheets improved the mechanical properties of the composites considerably. The improved properties of the composites proceeded from straightening of the wavy CNTs and increasing the dense packing of CNTs caused by the stretch-drawing. The

mechanical properties of the composites increased gradually with the increase of the stretch ratio up to 3%. With a 3% stretch ratio, the aligned CNT/epoxy composites achieved their best mechanical properties in this study. In short, the simple stretch-drawing is effective to produce highly aligned and dense-packed CNT sheets for the development of high-performance CNT composites. Particularly, the stretch-drawing of the CNT sheets in this study is more effective than the stretching of flat CNT sheets presented in our previous studies.

# Cải thiện tính chất cơ học của vật liệu composit nền epoxy gia cường ống cacbon nano định hướng bằng phương pháp nong-kéo đơn giản

- **Trần Hữu Nam** - *E-mail: namth@pvu.edu.vn*
- **Vũ Minh Hùng**
- **Phạm Hồng Quang**

Trường Đại học Dầu khí Việt Nam

## TÓM TẮT

Các tấm mỏng ống nano cacbon (CNT) đa thành định hướng ngang đã được chế tạo từ các mảng CNT định hướng dọc bằng phương pháp kéo và quấn. Vật liệu composit nền epoxy gia cường các CNT định hướng đã được phát triển trên cơ sở tấm mỏng với 100 lớp CNT định hướng bằng phương pháp ép nóng chảy bán thành phẩm của chúng. Tuy nhiên, độ cong và sự sắp xếp không chặt của các CNT trong tấm mỏng đã làm giảm khả năng truyền lực của chúng trong composit. Do đó, một phương pháp nong-kéo đơn giản đã được sử dụng để biến đổi cấu trúc của các tấm mỏng CNT định hướng nhằm cải thiện các tính chất của composit. Kết quả đo trình bày trong bài báo chỉ ra rằng phương pháp nong-kéo đơn giản đã làm tăng đáng kể cơ tính của composit. Sự cải thiện các tính chất của

composit bắt nguồn từ sự duỗi thẳng của các CNT cong và từ sự tăng độ sắp xếp chặt của các CNT trong composit. Trong nghiên cứu này composit có tính chất cơ học cao nhất tương ứng với tỷ lệ nong-kéo là 3%. So với composit không nong-kéo thì composit nong-kéo 3% có độ bền kéo, và môđun đàn hồi cao hơn tương ứng là 113% và 34%. Nhìn chung, các kết quả nghiên cứu cho thấy hiệu quả của phương pháp nong-kéo đơn giản là tạo ra được các tấm mỏng CNT định hướng cao có thể sử dụng để phát triển các composit với đặc tính cao cấp. So với phương pháp kéo tấm mỏng đã trình bày trong một số nghiên cứu trước, phương pháp nong-kéo trình bày trong nghiên cứu này hiệu quả hơn trong việc cải thiện cơ tính của CNT composit.

**Từ khóa:** Ống nano cacbon, bán thành phẩm, composit, nong-kéo, tính chất cơ học.

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