Strain measurement of carbon nanotubes in aligned multi-walled carbon nanotubes/epoxy composites under tensile load using Raman spectroscopy.

Ayaka Aoki[1], Toshio Ogasawara[1], Yoshinobu Shimamura[2], Yoku Inoue[2]

[1]Department of Mechanical Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei-shi, Tokyo 184-8588, Japan
Email: s183398u@st.go.tuat.ac.jp, Web Page: https://www.tuat.ac.jp
[2]Faculty Engineering, Shizuoka University, 3-5-1, Jyohoku, Naka-ku, Hamamatsu-shi, Shizuoka 423-8561, Japan

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Abstract

Aligned multi-walled carbon nanotube (MW-CNT)/ polymer-based composites exhibit high Young's modulus and excellent tensile strength compared with randomly oriented MW-CNT/polymer composites processed by conventional mixing method. On the other hand, the strength of aligned-CNT/polymer composites is still lower than the theoretical estimations. This study examined the strain of MW-CNTs in aligned-MW-CNT/epoxy composites subjected to uniaxial tensile load using Raman spectroscopy to elucidate the load-transfer mechanism between MW-CNTs and epoxy. Regarding the composites with orientation directions of 0°, 30°, 45° and 90°, the G' band shift of MW-CNTs corresponded to the strain along the major material axis. It suggests revealed that the MW-CNT longitudinal strain could be directly measured using Raman spectroscopy. However, the measured peak shift per strain was much smaller than those of SW-CNTs, and carbon fibers reported in previous papers. The result implies that the load transfer between MW-CNT and epoxy and/or between MW-CNT inner layers is not sufficient.

1. Introduction

Carbon nanotubes (CNTs) found by Iijima in 1991 [1] have outstanding mechanical properties. Thus, it has been attempted to apply CNTs as reinforcement of polymers. As a composite material using CNTs, there is a dispersed CNT composite material in which powdered CNT is mixed with a resin [2-5]. In addition, a technique for fabricating a polymer-based composite using an aligned multi-walled(MW)-CNT sheet prepared by spinning vertically oriented MW-CNTs which is grown on a quartz has been established [8]. It has been reported that aligned MW-CNT composites exhibit higher elastic modulus and strength compared with conventional randomly oriented MW-CNT composites [9-12]. On the other hand, the strength of aligned-MW-CNT/polymer composites is still lower than the theoretical estimations. It is supposed to be the weak load transfer between CNT and epoxy. The load transfer mechanism at the MW-CNT/matrix interface in aligned MW-CNT composite has not yet been sufficiently elucidated.

Raman spectroscopy is an effective method for the characterization of CNTs, therefore many researches have been reported [13-17]. It is known that the peak wavenumber appearing in the Raman spectrum of CNT shifts toward the lower wavenumber side or the higher wavenumber side depending on tensile or compressive strain, that is, crystal lattice distortion [18, 19]. Many attempts have been made to evaluate the strain of CNT utilizing this property and the CNT / resin interfacial dynamics characteristics in the composite, and in each case, it is necessary to measure the deformation of the CNT in the composite material via the Raman spectrum succeeded in [20-24]. However, as for the above

mentioned aligned MW-CNT composite, as a research using Raman spectroscopy, the research example of aligned MW-CNT bundle embedded in resin by Yashiro et al is the only one [21].

In this study, experiments using Raman spectroscopy were conducted in order to clarify load transfer mechanism to MW-CNTs in aligned MW-CNT/Epoxy composite. Raman spectrum of MW-CNTs in composite under tensile load were measured by a Raman microscope and the peak shift rate corresponding to strains were studied.

2. Experimental procedure

2.1. Materials and processing of CNT/Epoxy composites

Aligned MW-CNT sheets were produced by winding multi-walled carbon nanotube (MWCNT) spun yarns up to Teflon cylinder (d=30 mm) [11]. That yarns were pulled out from vertically aligned MW-CNT array (forest) synthesized on a quartz using chemical vapor deposition (CVD) [25]. The MW-CNTs had 1.3 mm in length and 50 nm in diameter. B-stage cured epoxy resin with release paper was obtained for matrix. The epoxy resin consists of bisphenol-A type epoxy, novolac type epoxy, and aromatic diamine curing agent. The recommended cure condition is 130 °C for 1.5 h. The areal weight of epoxy resin film is well controlled as 30 g/m^2. The Prepreg was produced by Hot-melt method [9]. Aligned CNT sheet was covered with epoxy resin film. Epoxy resin was impregnated into the CNT sheet at 90 °C for 3 min in a hot press. Then, the prepreg sheet was cured at 130 °C for 90 min under 2 MPa in s hot press again. Using this method, 4 kinds of aligned MWCNT/Epoxy composites were produced, these have 0°, 30°, 45°, 90° in fiber orientation angles.

The CNT volume fraction V_f[vol%] of composites was measured using TGA (Thermo-Gravimetric Analysis) in Ar. Under a constant heating rate of 10 °C/min, the weight change, between 150 °C and 700 °C of each sample was obtained. V_f was calculated using and below.

$$M_f = \frac{\Delta W_{Epoxy} - \Delta W_{Comp}}{\Delta W_{Epoxy} - \Delta W_{CNT}} \quad (1)$$

$$V_f = \frac{M_f}{M_f + \rho_{CNT}(1-M_f)/\rho_{Epoxy}} \quad (2)$$

The suffix represents each material, and M_f is the mass content. The density on CNT was 2 g/m^3, and the density of Epoxy resin was 1.2 g/m^3.

2.2. Tensile test

Fig.1 shows the shape of the specimen. A specimen was prepared by cutting out 3 mm width and 30 mm length and aluminum tabs of 1 mm thickness were bonded on both sides. The distance between tabs was 10 mm. A small tensile test rig fitted on the stage inside the Raman spectroscope was prepared and measured Raman spectrum of the specimen surface under tensile loading to the longitudinal direction of the specimen. The test rig is a feedforward control system using a stepping motor. The load was measured using a load cell with a maximum capacity of 200 N (TLCS-20L, Toyo Keiki), and the displacement was measured by a contact type displacement sensor (GT2-P12, Keyence).

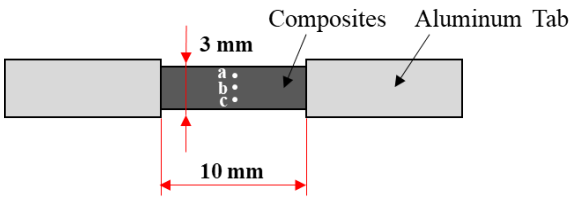

Fig.1 Illustration of tensile test specimen.

2.3. Raman spectroscopy measurement

The Raman spectra of the MWCNT/Epoxy composite specimens were obtained using a Raman microscope (LabRAM Evolution, HORIBA). In order to prevent the influence of heating on the surface of the specimen by the laser, ND filter was used and the exposure time was adjusted. As a result, measurement conditions were set such that downshift of the wavelength of Raman spectra, and damage of the specimen did not occur. The incident laser light was polarized at right angles to the specimen pulling direction. However, since the analyzer was not installed on the spectroscope, the influence of polarized light was relaxed, and it is considered that there was no big influence on the peak position of the Raman spectrum.

The Raman spectrum of aligned CNT/Epoxy composite, aligned CNT sheet, and Epoxy is showed in Fig.2. CNT has some characteristic peaks in spectrum, nevertheless, D-band (1350 cm^{-1}) and G-band (1580 cm^{-1}) overlapped with peaks of Epoxy. Therefore, in this experiment, we focused on the Raman spectrum in the range near the G'-band (2700 cm^{-1}). Table 1 shows the measurement conditions used for Raman microscope.

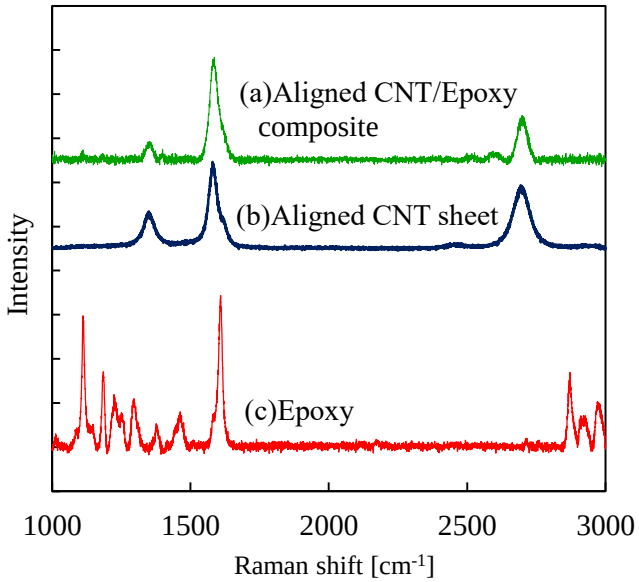

Fig.2 Typical Raman spectra of (a)Aligned CNT/Epoxy composite, (b)Aligned CNT sheet, (c)Epoxy.

Table 1 Measurement conditions for Raman spectroscopy.

Laser power [mW]	50
Laser wavelength [nm]	532
Spot size [μm]	2
Grating [gr/mm]	1800
ND filter [%]	3.2
Exposure time [s]	30
Integration count	3
Measurement range [cm^{-1}]	2550~2850

Stepwise tensile load was subjected to each specimen. The displacement increment was approximately 10 μm, which was controlled using a stepping motor. The Raman spectrum was measured for 5 times, for three points along a line perpendicular to the specimen longitudinal direction. The peak wavenumber of the Raman spectrum was obtained by the Gaussian curve fitting method using a data reduction software for analysis equipment (Labspec6, HORIBA).

3. Result and discussion

The Young's modulus E [GPa] and the CNT volume fraction V_f [vol%] of each specimen are presented in Table 2. E was obtained in the strain range of 0.1 to 1 % using linear regression. Here, V_f of the 30° specimen is significantly different from those of other specimens. Therefore, symbol (*) was added at values of that specimen as a reference value.

Table 2 Young's modulus and CNT volume fraction of CNT/Epoxy composites.

Specimen	E [GPa]	V_f [vol%]
0°	21.2	9.58
30°*	3.38	4.15
45°	4.89	8.67
90°	3.16	10.1

Fig.3 shows the relation between the peak wavenumber of the G'-band and the strain applied in the load direction of each specimen. There was great variability in the data, therefore the average value was presented in Fig. 3. The peak wavenumbers downshift linearly as increase in tensile strain. Therefore, the relation between the peak wavenumber κ [cm^{-1}] and the strain ε [%] is approximately represented using the following equation.

$$\kappa = v\varepsilon + v_0 \tag{3}$$

In the Eq. (3), v_0 [cm^{-1}] and v [cm^{-1}/%] are the peak wavenumber and the peak shift rate each at no load.

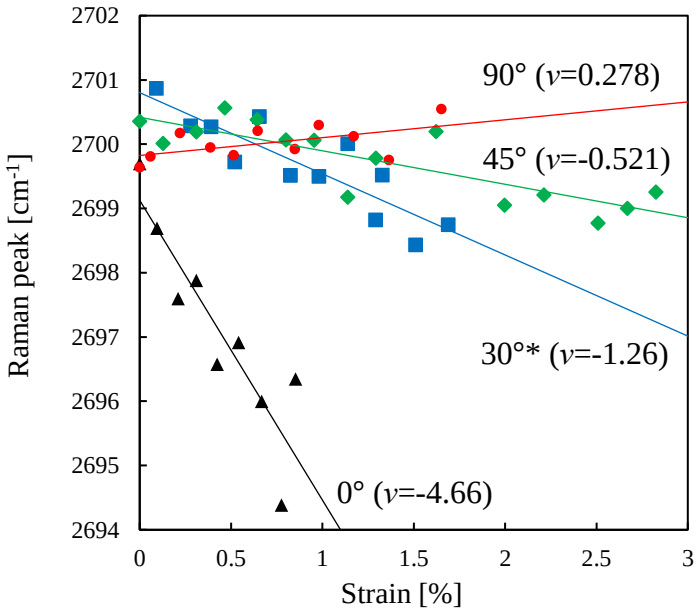

Fig.3 Relationship between the peak wavenumber of G' band and the longitudinal strain of CNT/epoxy composites.

Cooper et al. reported a value of -3.4 cm^{-1}/% as v of the random oriented MWCNT composite [20]. Yashiro et al. also reported -4.56 cm^{-1}/% as v of the aligned MWCNT bundle embedded in the epoxy resin [21]. Considering these facts, it is likely that the peak shift rate of 0° specimen obtained in this study is quite reasonable. The peak shift rate of the aligned CNT composites seems to be slightly higher compared with the random oriented MW-CNT [20].

On the other hand, the peak shift rate of the randomly oriented SWCNT composites are much higher than those of MW-CNT composites, for example -13 cm^{-1}/% [20], and -14.0 cm^{-1}/% by Qiu et al [24]. It is suggested that the peak shift rate as a whole is greatly reduced due to little deformation of inner layers of MW-CNT, expect for the outermost layer [26]. There is a possibility that the load transfer between the layers inside the MW-CNT is insufficient.

In the case of carbon fiber, it is known that the peak shift rate corresponding to the strain under tensile load has a linear relationship with the elastic modulus [18.19]. The relation between the peak shift rate and the elastic modulus E [GPa] of carbon fiber is written as follows.

$$\nu = E\nu_E \tag{4}$$

Cooper et al. measured the peak shift rates for some kinds of pitch-based carbon fibers exhibiting different elastic modulus and reported that the proportionality constant ν_E in Eq. (4) was -0.05 cm^{-1}/(%·GPa) [20]. It has been believed that the Young's modulus of MW-CNT is from 500 to 1000 GPa. Using the analogy of carbon fibers, the peak shift rate ν of CNT is estimated to be from -50 to -25 cm^{-1}/%. However, the peak shift rate ν of MW-CNT composites obtained in this research was much smaller than the expected values. As a cause, there is a possibility that MW-CNTs in the composite were not theoretically deformed, that is, the load transfer between matrix resin and MW-CNT is not sufficient, which is due to the sliding at the interface between the resin and MW-CNT, or between the layers inside the MW-CNT.

To reveal the load transfer mechanism in detail, we have to obtain the relation between the strain of the MW-CNT and the Raman peak shift rate directly. In addition, as described above, since laser polarization is not taken into consideration in our experiment, there is possibility that the intensity and the shape of spectrum were not sufficiently accurate.

In the cases of the results of specimens having different CNT orientation, each stress component in the major material axis (x,y) direction with respect to the loading direction (X,Y) is given by the following equation,

$$\begin{aligned} \sigma_x &= l^2\sigma_X \\ \sigma_y &= m^2\sigma_X \\ \tau_{xy} &= -lm\sigma_X \end{aligned} \tag{5}$$

Where $l=cos\theta$, and $m=sin\theta$, respectively. The stress-strain relationship in the major material axis direction (0°) is written by;

$$\varepsilon_x = S_{11}\sigma_x + S_{12}\sigma_y \tag{6}$$

Here, the elastic compliance $S_{11}$and S_{12} are given as follows;

$$\begin{aligned} S_{11} &= 1/E_1 \\ S_{12} &= \nu_{12}/E_1 \end{aligned} \tag{7}$$

Since the CNT volume fraction, V_f of each specimen was slightly different, the Young's modulus E_1 [GPa] in the major material axis direction was normalized as the elastic modulus of the 0° specimen (E_1=21.7 GPa) using the rule of mixtures. The value of E_{CNT} [GPa] obtained by the rule of mixtures from the result of the 0° specimen, and as E_m [GPa], an actual measurement value of 2.5 GPa was used. Using E_1 and Eq.(5)-(7), the strain of the main material axis direction for each specimen when the strain of the longitudinal axis direction of each specimen was calculated.

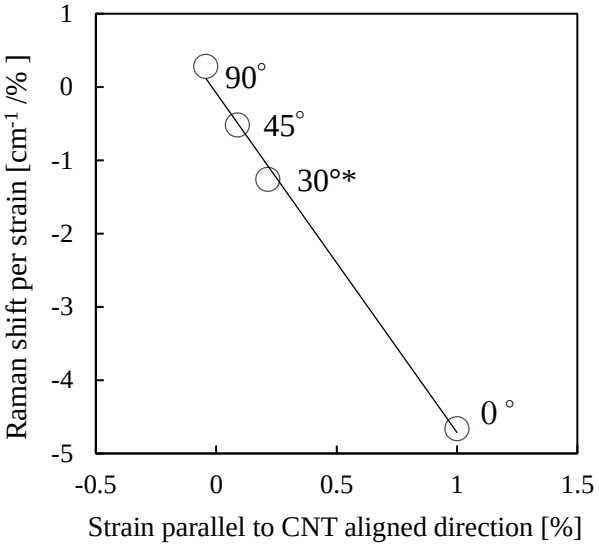

Fig.4 Peak wavenumber shift of G' band versus tensile strain
parallel to major material axis (CNT aligned direction) of CNT/epoxy composites.

Fig.4 presents the relationship between the peak shift rate of the longitudinal axis direction, and the strain along the major material axis. For the calculations, the Poisson's ratio (ν_{12}) was assumed to be 0.3, which is the value of general unidirectional CFRP. Since the relationship in Fig.4 is linear, it was confirmed that the peak shift rate reflects the strain of the longitudinal axis direction of each specimen. However, not only for the 0° specimen but also for the 30°, 45° and 90° specimens, it can be said that the peak shift rates were quite small as CNT, so it is required to clarify the detailed cause.

4. Conclusion

This study examined the strain of MW-CNTs in aligned-MW-CNT/epoxy composites subjected to tensile load using Raman spectroscopy to elucidate the load-transfer mechanism between CNTs and epoxy. As a result, regarding the composites with orientation directions of 0°, 30°, 45° and 90°, it was clarified that the G' band shift of CNTs corresponded to the strain along the major material axis. It suggests that the MW-CNT longitudinal strain could be directly measured using Raman spectroscopy. However, the measured peak shift rate was much smaller than those of SW-CNTs, and carbon fibers reported in previous papers. The result implies that the load transfer between MW-CNT and epoxy and/or between MW-CNT inner layers is not sufficient.

5. Acknowledgments

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