# COMBINED TEMPERATURE AND MOISTURE EFFECT ON THE STRENGTH OF CARBON NANOTUBE REINFORCED EPOXY MATERIALS

Yi-Ming Jen[1] and Chien-Yang Huang[2]
[1]*Department of Mechanical and Mechatronic Engineering, National Taiwan Ocean University, Keelung, Taiwan*
[2]*Department of Mechanical Engineering, Chung Hua University, Hsinchu, Taiwan*
*E-mail: ymjen@mail.ntou.edu.tw*

ICETI 2012-J1082_SCI
No. 13-CSME-61, E.I.C. Accession 3519

## ABSTRACT
This study experimentally analyzed the hygrothermal effect on the static and fatigue strengths of multi-walled carbon nanotubes (CNTs)/epoxy composites. The results show that the static and fatigue strengths decreased slightly at 25°C/85% RH environments compared with those tested under the 25°C/60% RH condition. However, the strengths decreased substantially under the 40°C/85% RH condition, indicating that the combined temperature and humidity environments weaken the interfacial adhesion between the CNT surfaces and the epoxy matrix.

**Keywords:** carbon nanotube; fatigue strength; hydrothermal; nanocomposite; static strength.

# L'EFFET COMBINÉ DES TEMPÉRATURES ET DE L'HUMIDITÉ SUR LA RÉSISTANCE DES MATÉRIAUX D'UN NANOTUBE DE CARBONE EN EPOXY RENFORCÉ

## RÉSUMÉ
Cette étude analyse au moyen d'expériences l'effet hygrothermique sur la statique et la résistance à la fatigue de nanotubes multiparoi en composites de résine d'expoxy. Les résultats montrent que la statique et la résistance à la fatigue décroît légèrement dans des environnements de 25°C/85% RH comparé à ceux testés sous une condition de 25°C/60% RH. Toutefois les résistances décroissent substantiellement sous la condition de 40°C/85% RH indiquant que dans un environnement dont la température et l'humidité combiné diminue l'adhésion interfaciale entre les surfaces CNT et la matrice en résine d'expoxy.

**Mots-clés :** nanotube de carbone ; résistance à la fatigue ; nanocomposite ; résistance statique.

## 1. INTRODUCTION

Because of the properties of high strength, high modulus, low density, and high aspect ratio, carbon nanotubes (CNTs) have been considered excellent reinforcements for embedding in polymer-based composites. Consequently, studies of the mechanical strengths of CNT/polymer nanocomposites have received considerable attention. Several studies have investigated the effect of CNT contents [1–4], CNT functionalization [5–8], and CNT alignments [9, 10] on the mechanical strengths of CNT reinforced nanocomposites. Static tensile tests were frequently used in these studies to evaluate the strength of the CNT/polymer composites. In addition to the static studies of CNT-based nanocomposites, it is crucial to study the fatigue strength and behavior of CNT/polymer composites, because the engineering materials are frequently subjected to cyclic service loading. A number of studies [11–13] found that embedding CNTs in the polymer matrix can increase the fatigue strength of the neat polymer materials effectively, and the bridging and pullout of CNTs are the main observed mechanisms of the fatigue failure of the related nanocomposites. Furthermore, the fracture mechanics approach was used to model the crack propagation behavior near the crack-tips of the carbon nano-fiber/epoxy composites [14–16]. However, the static and fatigue tests in prior strength-related studies of CNT/polymer composites were performed at room temperature. Because the strengths of polymer materials are sensitive to the environmental variables, understanding the environmental effects on the mechanical strengths of the CNT/polymer composites can extend the application of such novel nanocomposites at hygrothermal environments.

Hence, the static and fatigue strength of the CNT/epoxy composites at various hydrothermal environments were experimentally investigated to study the combined influence of the temperature and humidity on the mechanical properties of the nanocomposites. In addition, the effect of CNT contents on the static and fatigue strengths of the CNT/epoxy composites under various hygrothermal conditions was also studied. The facture surfaces of the studied specimens were examined after the tests to distinguish between the characteristics of the fracture surfaces obtained at various hygrothermal environments.

## 2. EXPERIMENTAL

### 2.1. Materials and Specimen Preparation

The purity of the multi-walled CNTs was approximately 93%. The corresponding length and diameter were 10–200 nm and 30–50 nm, respectively. The received CNTs were acid-treated using nitric acid. The acid treatment helps to remove metal catalysts used in the synthesis of carbon nanotubes and carbon-impurities generated by high temperature. It also helps to produce more functional groups along the interface between the CNT surfaces and the epoxy matrix. The received multi-walled CNTs were mixed with nitric acid first and heated at 120°C with magnet stirring for 1 h. The mixture was subsequently filtered using a vacuum system associated with the PVDF filter. The filtered mixture was refluxed using deionized water with magnetic stirring and ultra-sonication. The cleaning, dispersion, and filtering steps were repeated five times to completely remove nitric acid from the CNTs, and the acid-treated CNTs were subsequently obtained.

The epoxy matrix was composed of the epoxy resin and hardeners with a ratio of 4 : 10. The acid-treated CNTs were mixed with the epoxy resin and the nonionic surfactant Triton X-100 first. Subsequently, the mixture was mechanically stirred for 30 min. The mixture was subsequently sonicated at 60 °C for 30 min to achieve superior dispersion in the epoxy resin. The mixture was vacuumed for 1 h to remove air bubbles produced by stirring. The mixture was sonicated at 25°C for 30 min. The hardener was added to the mixture with some deformer to remove the bubbles. Subsequently, the mixture was mechanically stirred for 10 min and sonicated at 25°C for 10 min. The mixture was then vacuumed for 1 h.

The mixture was poured into a stainless steel mold with the required specimen shape and dimensions, and vacuumed for 1 h to obtain bubble-free specimens. The mold was heated at 100°C for 5 min and

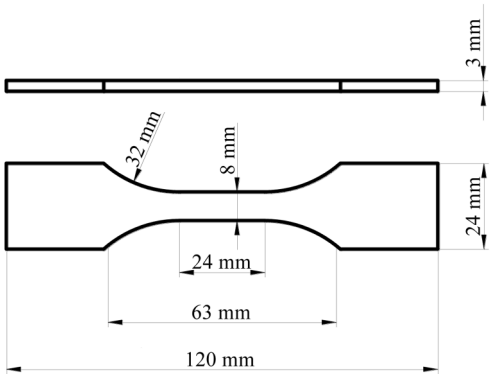


Fig. 1. Shape and dimensions of the studied CNT/epoxy specimen.

subsequently vacuumed for 30°min. The heating and vacuuming processes were repeated. Then the mixture was hot-pressed in a mold at 300 psi and 120°C for 30 min to obtain the specimens. The specimens were polished with sandpaper to obtain the smooth shape after releasing from the mold. The specimens with three CNT contents, that is, 0, 0.5, and 1.0 wt.%, were prepared to study the effect of CNT content on the static and fatigue strength of the CNT/epoxy composites at hygrothermal environments. The shape and dimensions of the specimens are shown in Fig. 1.

### 2.2. Static and Fatigue Tests

The tensile static and fatigue tests were performed using an Instron 8872 servo-hydraulic material testing system with a temperature-humidity control chamber. Two hygrothermal conditions (25°C/85% RH, and 40°C/85% RH) were selected as the experimental variables to study the hygrothermal effect on the static and fatigue strengths of the CNT/epoxy composite materials. The experimental data reported in the authors' previous study [17], in which the static and fatigue tests were performed at room temperature and moderate humidity (25°C/60% RH), were also considered herein for comparison purpose. For convenience, the three environmental variables, that is, 25°C/60% RH, 25°C/85% RH, and 40°C/85% RH, were denoted by the room-temperature/moderate-humidity (RT/MH), room-temperature/high-humidity (RT/HH), and high-temperature conditions (HT/HH), respectively. The specimens were placed at controlled environments for 30 min before the static and fatigue tests to reach the thermal and humid equilibrium. The static tests were performed by controlling the cross-head speed set at 0.01 mm/s. The fatigue tests were conducted by controlling the applied loads with a stress ratio of 0.1. The stress ratio is defined as the minimum applied stress $\sigma_{\min}$ divided by the maximum applied stress $\sigma_{\max}$ in the fatigue test. The stress was obtained by dividing the applied load by the original cross sectional area. The waveform of the fatigue tests was sinusoidal with a frequency of 5 Hz. The loading levels of the fatigue tests were determined based on the ultimate strength of the specimens with the same CNT content, $\sigma_{\text{ult}}$, which was obtained in the static test under the same hygrothermal conditions. The fatigue life $N_f$ is defined as the number of cycles corresponding to the specimen separation. After the tests, the fracture surfaces of the specimens were observed using a scanning electron microscope (SEM) to study the failure mechanism of the static and fatigue tests for the studied nanocomposite materials. The advantage of the proposed experimental method is that the actual environmental factors were replicated in the laboratory using the temperature-humidity control chamber, while the disadvantage is that the duration effect in the controlled environment was not considered in the experimental program.

Table 1. Experimental results of the ultimate strengths the studied specimens obtained in the monotonic tests.

| CNT content | 0 wt.% | | 0.5 wt% | | 1.0 wt.% | |
|---|---|---|---|---|---|---|
| Testing condition | 25°C 85% RH | 40°C 85% RH | 25°C 85% RH | 40°C 85% RH | 25°C 85% RH | 40°C 85% RH |
| Ultimate strength $\sigma_{ult}$ (MPa) | 64.84 | 56.43 | 66.43 | 58.95 | 61.15 | 56.82 |

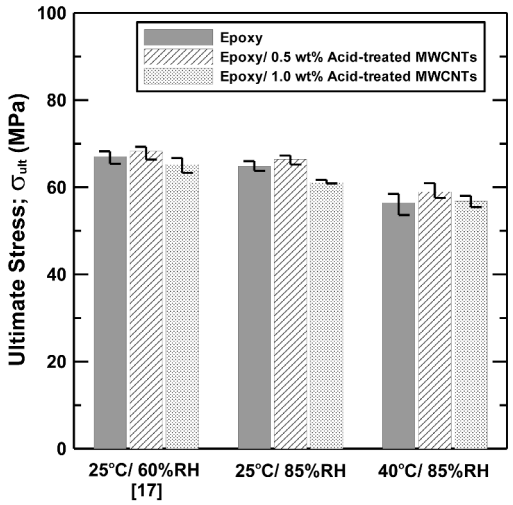


Fig. 2. Effects of hydrothermal conditions and CNT contents on the ultimate strengths of the CNT/epoxy composites.

## 3. RESULTS AND DISCUSSION

### 3.1. Static Strength Study

The experimental results of the ultimate tensile strengths obtained from the static tensile tests at various hygrothermal environments for the studied CNT/epoxy composites with various CNT contents are listed in Table 1. The comparison of the ultimate strengths of the studied specimens with various CNT contents tested at various hygrothermal conditions is shown in Fig. 2. At RT/HH environments, the average ultimate tensile strengths for CNT/epoxy composite specimens were slightly lower than those at RT/MH environments. This indicates that humidity had a slight influence on the tensile strength of the studied nanocomposites at room temperature. Under the HT/HH conditions, the average static tensile strengths of the CNT/epoxy composite specimens were considerably lower than those tested under RT/HH conditions. This indicates that the combined effects of combined temperature and humidity on nanocomposite specimens are greater than that of only humidity. Bao and Tjong studied the temperature effect on the mechanical behavior of the polypropylene/carbon nanotube nanocomposites [18], and the static strength was found to decrease with increasing of the temperature. The tendency between the static strength and the temperature of the CNT-reinforced polymer material observed in the present study is similar to that reported in [18].

The experimental results of the static tests also show that the addition of 0.5 wt.% CNTs can improve the tensile strength of the neat epoxy material substantially, regardless of the hygrothermal condition. However, the tensile strength of the nanocomposite with 1.0 wt.% CNTs was lower than that with 0.5 wt.% CNTs. The stress concentration resulting from the aggregates of CNTs was detrimental to the tensile strength of the nanocomposites.

Figure 3 shows the typical SEM images of the fracture surface of the studied nanocomposite specimens with 0.5 wt.% CNTs, obtained after the static tests performed at various hygrothermal environments. The

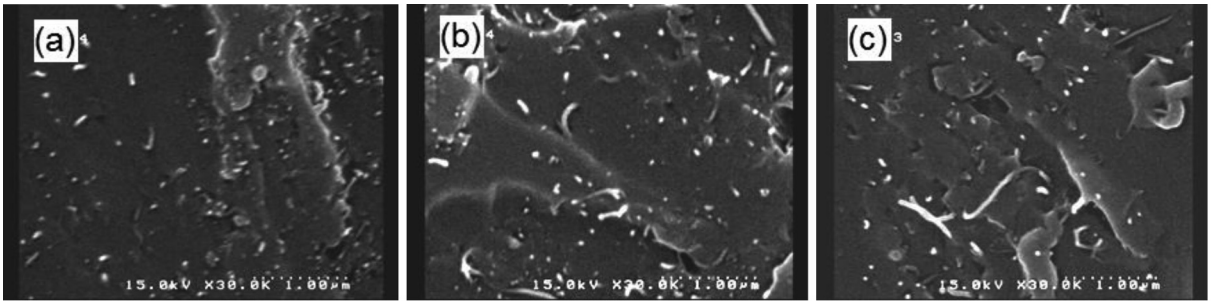


Fig. 3. SEM images of the fracture surfaces for the specimens with 0.5 wt.% CNTs statically tested at (a) RT/MH, (b) RT/HH, and (c) HT/HH environments (×30,000).

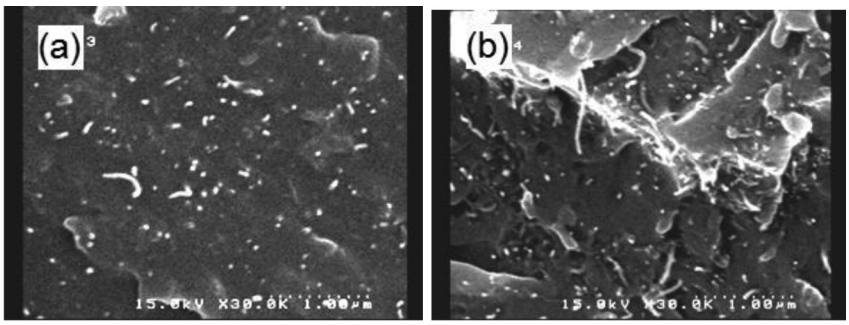


Fig. 4. SEM images of the fracture surfaces for the specimens with (a) 0.5 and (b) 1.0 wt.% CNTs statically tested at RT/MH environments (×30,000).

fracture surfaces were similar under RT/MH and RT/HH conditions, as shown in Figs. 3a–b, which show that the CNTs were pulled out on the fracture surfaces. However, the fracture surface under the HT/HH environment demonstrated that longer CNTs were pulled out from the matrix than those observed after the static tests under RT conditions (Fig. 3c). The difference in the length of pulled-out CNTs indicates that the adhesive strength between the CNT surfaces and the epoxy matrix under HT/HH conditions is considerably lower than that under RT conditions. Figure 4 shows the effect of CNT content on the fracture surface characteristics of the studied nanocomposites. The CNTs were evenly dispersed in the matrix material at a CNT amount of 0.5 wt.% (Fig. 4a). However, the agglomerates of CNTs were clearly observed when the added CNT amount was 1.0 wt.%, which resulted in the decrease of static strength because of the stress concentration effect (Fig. 4b).

### 3.2. Fatigue Strength Study

Table 2 lists the experimental results of the fatigue lives for the studied specimens tested at various hygrothermal conditions. Figure 5 shows the hygrothermal effect on the experimental fatigue life curves of the studied CNT/epoxy composites with various CNT contents. The relationship between the maximum applied stress $\sigma_{\max}$ and the fatigue life $N_f$ can be expressed using the power-law model:

$$\sigma_{\max}\ (\text{MPa}) = aN_f^b, \tag{1}$$

where $a$ and $b$ are material constants that depend on the hygrothermal conditions and the CNT contents. The material constants were obtained by fitting the experimental data points. The obtained fatigue life curves are shown in Fig. 5. These fatigue-related constants are listed in Table 3. As shown in Fig. 5, the fatigue strengths for the specimens tested under the RT/MH environment decreased slightly compared with that tested under the RT/HH condition, regardless of the employed CNT content.

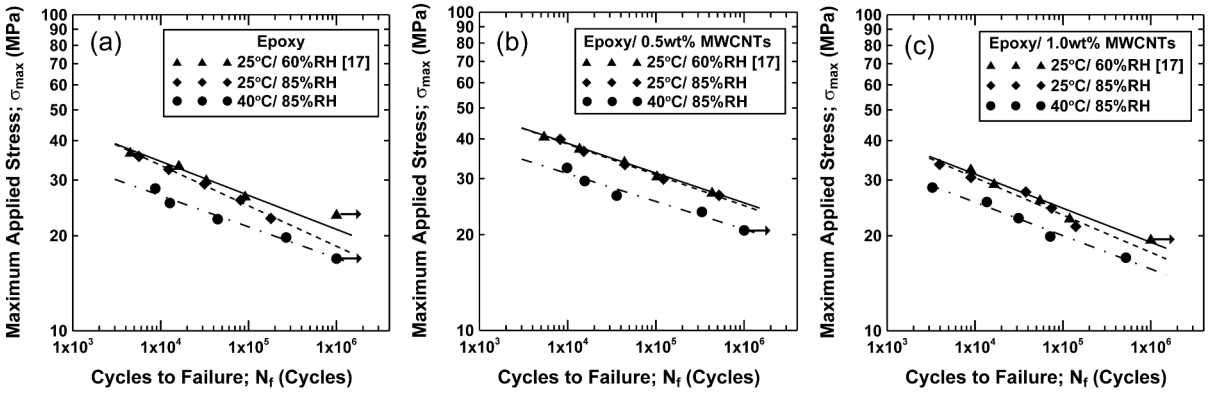


Fig. 5. Experimental results of the fatigue tests and corresponding stress-life curves for the CNT/epoxy composites with (a) 0, (b) 0.5, and (c) 1.0 wt.% CNT contents under various hydrothermal conditions.

Table 2. Experimental results of the fatigue lives of the studied specimens obtained in the fatigue tests.

| Loading level | Fatigue life (cycles) | | | | | |
|---|---|---|---|---|---|---|
| | 0 wt.% CNTs | | 0.5 wt% CNTs | | 1.0 wt.% CNTs | |
| $\sigma_{max}/\sigma_{ult}$ | 25°C | 40°C | 25°C | 40°C | 25°C | 40°C |
| | 85% RH | 85% RH | 85% RH | 85% RH | 85% RH | 85% RH |
| 60% | – | – 8,220 | – | – | – | |
| 55% | 5,652 | – | 15,189 | 9,806 | 3,944 | – |
| 50% | 12,322 | 8,674 | 44,455 | 15,575 | 8,965 | 3,264 |
| 45% | 31,510 | 12,687 | 121,602 | 35,887 | 37,765 | 13,592 |
| 40% | 81,132 | 44,451 | 518,870 | 331,872 | 74,201 | 31,208 |
| 35% | 179,295 | 267,454 | – | >1,000,000 | 139,881 | 71,575 |
| 30% | – | >1,000,000 | – | – | – | 520,034 |

Figure 6 shows the effect of CNT content on the fatigue strength of the CNT/epoxy composites tested at various hygrothermal environments. As shown in Fig. 6, the nanocomposite specimens with 0.5 wt.% of carbon nanotubes exhibited the highest fatigue strength among the specimens with various CNT contents. The fatigue strength of the nanocomposite specimens decreased considerably when the CNT content was 1.0 wt.%. The stress concentration caused by the excessive CNTs had an adverse effect on the fatigue strengths of the studied nanocomposites. The agglomerates resulting from the excessive CNTs induce the stress concentration effect. Moreover, many voids can be observed within the CNTs of the agglomerates. It is because the viscous epoxy resin cannot flow into the tiny spaces when solidification. The incomplete matrix foundation cannot provide sufficient adhesion between the CNT surfaces and the matrix, accordingly reduces the strength significantly.

Figure 7 shows the SEM images of the fracture surface of CNT/epoxy composite specimens, obtained after the fatigue tests performed under various hygrothermal conditions. The fracture surface characteristics of the specimens that were fatigue-tested under the RT/MH and RT/HH conditions were similar (Figs. 7a–b). The pulled-out CNTs dominated the fracture surfaces. However, under the HT/HH condition, the length of pulled-out CNTs was longer than that obtained after performing the fatigue test at RT (Fig. 7c), which indicates that the combined high temperature and high humidity environments soften the carbon nanotubes/epoxy composite specimens and result in weak grasp between the CNT surfaces and the epoxy matrix.

Table 3. The fatigue-related constants for the studied nanocomposites tested at various hygrothermal conditions.

| Content of CNT (wt.%) | 0 | | 0.5 | | 1.0 | |
|---|---|---|---|---|---|---|
| Fatigue constant | *a* | *b* | *a* | *b* | *a* | *b* |
| Hygrothermal condition | | | | | | |
| 25°C/60% RH [17] | 92.51 | –0.108 | 91.52 | –0.093 | 84.57 | –0.108 |
| 25°C/85% RH | 108.50 | –0.128 | 93.63 | –0.097 | 90.70 | –0.118 |
| 40°C/85% RH | 66.58 | –0.099 | 69.53 | –0.087 | 67.47 | –0.106 |

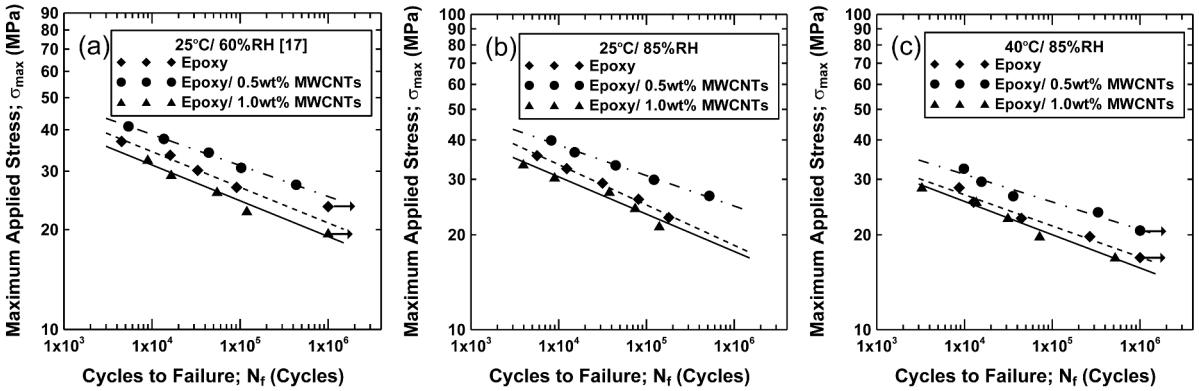


Fig. 6. Experimental results of the fatigue tests and corresponding stress-life curves for the CNT/epoxy composites with various CNT contents under (a) RT/MH, (b) RT/HH, and (c) HT/HH hydrothermal conditions.

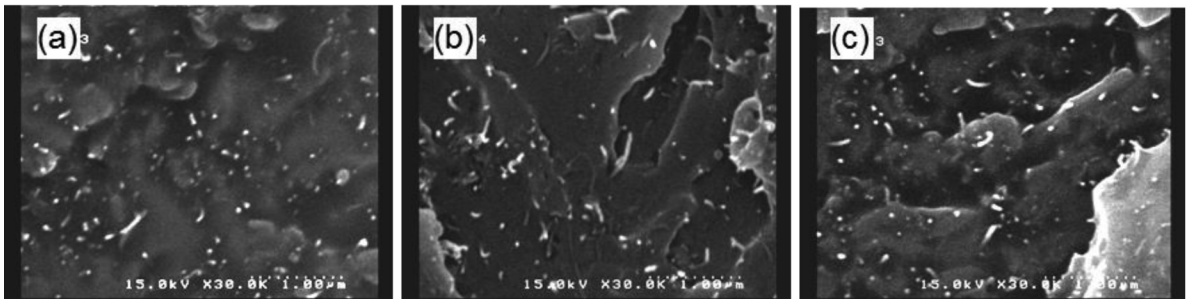


Fig. 7. SEM images of the fracture surfaces for the specimens with 0.5 wt.% CNTs fatigue-tested at (a) RT/MH, (b) RT/HH, and (c) HT/HH environments (×30,000).

## 4. CONCLUSIONS

The static and fatigue properties of CNT/epoxy composites with various CNT contents were experimentally studied under three hygrothermal conditions. The effects of the hygrothermal environment and the CNT content on the static and fatigue behavior were investigated, and the corresponding characteristics of the fracture surface were also examined. Several conclusions were summarized as follows:

1. Under the RT/HH environment, the static and fatigue strengths of the CNT/epoxy composite specimens were slightly lower than those obtained under RT/MH environments. However, the static and fatigue strengths of the studied nanocomposites under the HT/HH condition decreased considerably as compared to those tested under the RT conditions. The sole humidity has minor effect on the static and fatigue strengths of the studied nano-composites, while the combination effect of temperature and humidity has significant influence on the static and fatigue strengths of the CNT/epoxy composites.

Table 4. Hygrothermal effect on the mechanical behavior of the CNT/epoxy composites.

| Temperature (°C) | 25 | 25 | 40 |
|---|---|---|---|
| Moisture (RH) | 60% | 85% | 85% |
| Static/fatigue strength (compared with room temperature data) | – | slightly lower | significantly lower |
| The length of pulled-out CNTs | short | medium | long |

Table 4 summarizes the hygrothermal effect on the mechanical behavior of the CNT/epoxy composites.

2. The SEM images of the fracture surfaces indicate that the characteristics of the fracture surfaces obtained under the RT/MH and RT/HH conditions were similar. The pulled-out CNTs were the main characteristics of the fracture surfaces. However, under the HT/HH conditions, the nanocomposites were more ductile, and the length of the pulled-out CNTs on the fracture surfaces were relatively longer compared with those obtained under the RT condition.

3. The static and fatigue strengths of the studied nanocomposites with 0.5wt.% CNT content were higher than those of the neat epoxy specimens. However, when excessive CNTs (1.0 wt.%) are embedded in the matrix, the static and fatigue strengths of the studied nanocomposites cannot be improved effectively. From the SEM images of fracture surfaces obtained after the static and fatigue tests, the CNT aggregates were observed in the facture surface of the studied nanocomposites with 1.0 wt.%, indicating that the stress concentration resulting from the CNT aggregates is detrimental to the static and fatigue strength of the CNT reinforced nanocomposites. There is an optimum CNT content in the preparation of nano-composite specimens that makes the CNT-reinforced polymer material have the highest strength. The embedding of excessive CNTs in the epoxy matrix has adverse effect on the strength of the studied nano-composites.

## ACKNOWLEDGEMENT

The authors would like to thank the National Science Council of the Republic of China, Taiwan, for financially supporting this research under grant number NSC-99-2221-E-019-056.

## REFERENCES

1. Ma, P.C., Kim, J.K. and Tang, B.Z., "Effects of silane functionalization on the properties of carbon nanotubes/epoxy nanocomposites", *Composites Science and Technology*, Vol. 67, No. 14, pp. 2965–2972, 2007.
2. Ma, P.C., Tang, B.Z. and Kim, J.K., "Effect of CNT decoration with silver nanoparticles on electrical conductivity of CNT-polymer composites", *Carbon*, Vol. 46, No. 11, pp. 1497–1505, 2008.
3. Kosmidou, T.V., Vatalis, A.S. and Delides, C.G., "Mechanical and electrical characterization of epoxy-amine/carbon black nanocomposites", *Express Polymer Letters*, Vol. 2, No. 5, pp. 364–372, 2008.
4. Ma, P.C., Liu, M.Y., Kim, J.K. and Tang, B.Z., "Development of electrically conducting nanocomposites by employing hybrid fillers of carbon nanotubes and carbon black", *ACS Applied Materials & Interfaces*, Vol. 1, No. 5, pp. 1090–1096, 2009.
5. Jiang, B., Liu, C., Zhang, C., Wang, B. and Wang, Z., "The effect of non-symmetric distribution of fiber orientation and aspect ratio on elastic properties of composites", *Composites Part B: Engineering*, Vol. 38, No. 1, pp. 24–34, 2007.
6. Sui, G., Zhong, W., Yang, H.X.P. and Yu, Y.H., "Curing kinetics and mechanical behavior of natural rubber reinforced with pretreated carbon nanotubes", *Materials Science and Engineering: A*, Vol. 485, No. 1, pp. 524–531, 2008.

7. Geng, Y., Liu, M.Y., Li, J., Shi, X.M. and Kim, J. K., "Effects of surfactant treatment on mechanical and electrical properties of CNT/epoxy nanocomposites", *Composites Part A*, Vol. 39, No. 12, pp. 1876–1883, 2009.
8. Yang, B.X., Shi, J.H., Li, X., Pramoda, K.P. and Goh, S.H.J., "Mechanical reinforcement of poly(1-Butene) using polypropylene-grafted multiwalled carbon nanotubes", *Journal of Applied Polymer Science*, Vol. 113, No. 2, pp. 165–172, 2009.
9. Steinert, B.W. and Dean, D.R., "Magnetic field alignment and electrical properties of solution cast PET-carbon nanotube composite films", *Polymer*, Vol. 50, No. 3, pp. 898–904, 2009.
10. Zhu, Y.F., Ma, C., Zhang, W., Zhang, R.P., Koratkar, N. and Liang, J., "Alignment of multiwalled carbon nanotubes in bulk epoxy composites via electric field", *Journal of Applied Physics*, Vol. 105, No. 5, pp. 054319–054326, 2009.
11. Ren, Y., Li, F., Cheng, H.M. and Liao, K., "Tension-tension fatigue behavior of unidirectional single-walled carbon nanotube reinforced epoxy composite", *Carbon*, Vol. 41, No. 11, pp. 2177–2179, 2003.
12. Ren, Y., Fu, Y.Q., Liao, K., Li, F. and Cheng, H.M., "Fatigue failure mechanisms of single-walled carbon nanotube ropes embedded in epoxy", *Applied Physics Letters*, Vol. 84, No. 15, pp. 2811–2813, 2004.
13. Yu, N., Zhang, Z.H. and He, S.Y., "Fracture toughness and fatigue life of MWCNT/epoxy composites", *Materials Science and Engineering: A*, Vol. 494, No. 1–2, pp. 380–384, 2004.
14. Zhang, W., Picu, R.C. and Koratkar, N., "Suppression of fatigue crack growth in carbon nanotube composites", *Applied Physics Letters*, Vol. 91, No. 19, pp. 193109, 2007.
15. Zhang, W., Hoshi, A., Wang, Z., Kane, R.S. and Korakar, N., "Creep mitigation in composites using carbon nanotube additives", *Nanotechnology*, Vol. 18, No. 18, pp. 185703, 2007.
16. Zheng, Q., Xue, Q., Yan, K., Gao, X. and Li, Q., "Influence of chirality on the interfacial bonding characteristics of carbon nanotube polymer composites", *Journal of Applied Physics*, Vol. 103, No. 4, pp. 044302, 2009.
17. Jen, Y.M. and Huang C.Y., "Fatigue characterization of acid-treated carbon nanotube/epoxy composites", *Journal of Composite Materials*, Vol. 47, No. 13, pp. 1665–1675, 2013.
18. Bao, S. P. and Tjong S. C., "Mechanical behaviors of polypropylene/carbon nanotube nanocomposites: The effects of loading rate and temperature", *Materials Science & Engineering A*, Vol. 485, No. 1–2, pp. 508, 2008.