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TENSILE PROPERTIES OF HYBRID THERMOSET NANOCOMPOSITE REINFORCED WITH MULTI-WALLED CARBON NANOTUBES

CƠ TÍNH CHỊU KÉO CỦA VẬT LIỆU NANOCOMPOSITE NHIỆT RẮN LAI ĐƯỢC GIA CƯỜNG BẰNG CÁC ỐNG NANO CARBON ĐA VÁCH

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ABSTRACT

The final objective of this study was to investigate the effect of various contents of muti-walled carbon nanotubes (MWCNTs) on the strength of a novel hybrid thermoset material. Besides, the influence of the hybrid matrix stiffness (epoxy/polyester blend) on the reinforcement role of MWCNTs were also studied. Specifically, this paper studied and evaluated the effects of weight percentages of MWCNT on the tensile strength of fabricated specimens. In addition, the morphology of the fracture surfaces of the resulting nanocomposites was examined by a field emission scanning electron microscope (FESEM). Experimental results indicated that the tensile strength of the novel nanocomposite material increases to 86.3 % with the addition of a 1% ratio of MWCNTs. Furthermore, FESEM analysis revealed that excellent adhesion and interfacing between the matrices and the fillers are the main reasons for optimum improvement of properties. The unique contribution of this study is the discovery that novel hybrid thermoset material reinforced with nano-filler (MWCNT) can be applied in making low cost, high strength and light weight components as automobile parts, transportation systems and biomedical devices.

Keywords: *Multi-walled Carbon Nanotubes (MWCNTs); Epoxy/Polyester Blend; Nanocomposite; Tensile Strength; Field Emission Scanning Electron Microscope (FESEM).*

TÓM TẮT

Mục đích chính của nghiên cứu này là để khảo sát ảnh hưởng của hàm lượng thay đổi của các ống nano carbon đa vách (MWCNTs) vào độ bền kéo của một vật liệu polymer nhiệt rắn lai mới. Bên cạnh, ảnh hưởng của độ cứng nền lai (của hỗn hợp trộn epoxy và polyester) vào vai trò gia cường của MWCNTs đã được thực hiện. Đặc biệt, bài báo này đã nghiên cứu và đánh giá ảnh hưởng của phần trăm trọng lượng của MWCNTs vào độ bền kéo của các mẫu thí nghiệm chế tạo. Thêm vào đó, hình thái của bề mặt các mẫu composite sau khi phá hủy được kiểm tra bằng kính hiển vi điện tử quét có độ phân giải cao. Kết quả thí nghiệm chỉ ra rằng độ bền kéo của vật liệu nanocomposite mới tăng đến 86.3% với việc thêm 1% hàm lượng MWCNTs. Hơn nữa, phân tích FESEM cho thấy rằng độ bám dính và kết hợp tuyệt vời giữa các vật liệu nền và chất độn là những lý do chính để cải thiện tối ưu các tính chất. Đóng góp độc đáo của nghiên cứu này là phát hiện ra vật liệu polymer nhiệt rắn lai mới được gia cố bằng chất độn nano (MWCNT) có thể được áp dụng trong việc chế tạo các phụ tùng có trọng lượng nhẹ, độ bền cao và chi phí thấp như các chi tiết trên ô tô, các hệ thống giao thông và thiết bị y sinh.

Từ khóa: *Ống nano carbon đa vách (MWCNTs); Hỗn hợp Epoxy/Polyester; Nanocomposite; Độ bền kéo; Kính hiển vi điện tử quét độ phân giải cao.*

1. INTRODUCTION

Carbon nanotubes possessing excellent mechanical, thermal and electrical properties were found by Iijima [1]. Particularly in the manufacture of composite materials, they serve as a superior filler material for enhancing the properties and strength of these hybrid materials.

Regarding the matrix, thermoset epoxy resins are universally and widely applied as matrix materials in the fabrication of advanced composites and electronic and electrical circuit boards as well as in hardware components [2,3,4]. In an effort to promote the performance of the thermoset matrix, modifications of epoxy using polyester matrix combinations are of interest [5,6]. Unsaturated polyester resin possesses very good mechanical, thermal and corrosion resistant properties and is also simpler to use and more economical than epoxy. They are used as the second phase of production, blended with epoxies to make the resin system of materials.

In addition, the effect on reinforcing polymer by the addition of MWCNTs was also studied. The results showed that adding MWCNTs at low weight fractions improved the tensile and flexural properties of polyester resin [7,8]. More recently, amino functionalized MWCNTs were used to reinforce the mechanical and thermo-mechanical properties of e-glass/epoxy composites [9,10,11]. Ruban *et al.* [12] implemented the mechanical and thermal studies of unsaturated polyester-toughness epoxy composites filled with amino-functionalized nanosilica. Vizureanu *et al.* [13] investigated the dependence between thermal conductivity and reinforcing elements. Their researches were structurally, chemically and thermally conducted, and the final results confirmed that the effective thermal conductivity increases with the concentration of CNT. Giorcelli *et al.* [14] studied a wide-band microwave characterization of nanocomposites based on commercial MWCNTs and epoxy resin. Lavorgna *et al.* [15] investigated the effects of Silanization and silica enrichment of multi-walled carbon nanotubes on the thermal-mechanical properties of epoxy nanocomposites. They found that in the rubbery region, the storage modulus of composites with silanized and silica enriched carbon nanotubes were about 240% and 285% higher than modulus of neat epoxy system, respectively. Most studies on polymeric composites with functionalized CNTs focus on elastic properties. Among the various studies incorporating CNTs, some researchers [16] studied the effect of a matrix with different stiffnesses on the reinforcement role of CNT. Mechanical tests indicated that the stiffness matrix affects the reinforcement role of carbon nanotubes.

In recent years, composite materials have found common application in automotive industries, electronic circuit board production and aerospace and customer products. This is attributed to their light weight, high strength, corrosion resistance and ability to reduce manufacturing and maintenance costs. In particular, reinforced polymer composite materials using various methods in processing and for improving material strength will receive increasing interest in the future. The final objective of this study was to investigate the effect of various contents of muti-walled carbon nanotubes (MWCNTs) on the strength of a novel hybrid thermoset material. Besides, the influence of the hybrid matrix stiffness (epoxy/polyester blend) on the reinforcement role of MWCNTs were also studied. Specifically, this paper studied and evaluated the effects of weight percentages of MWCNT on the tensile strength of fabricated specimens. In addition, the morphology of the fracture surfaces of the resulting nanocomposites was examined by a field emission scanning electron microscope (FESEM). The unique contribution of this study is the discovery that novel hybrid thermoset material reinforced with nano-filler (MWCNT) can be applied in making low cost, high strength and light weight components as automobile parts, transportation systems and biomedical devices.

2. MATERIALS AND METHODS

2.1 Materials

The Multi-walled carbon nanotubes (MWCNTs) (Figure 1) fabricated by chemical vapor deposition with a purity of > 95%, outer diameters between 35 to 55 nm and lengths between 15 and 25 µm, were purchased from Cheap Tubes Inc. (USA). The matrix material is made by mixing of epoxy 6620, hardener AH150 and unsaturated polyester resin (UPR) supplied by Golden Company (Taiwan). For UPR, in the curing process, cobalt naphthenate (6%) was used as an accelerator and methyl ethyl ketone peroxide (MEKP) as a catalyst. An indispensable agent for separating and dispersion of the fillers in the resin is methyl ethyl ketone (MEK).

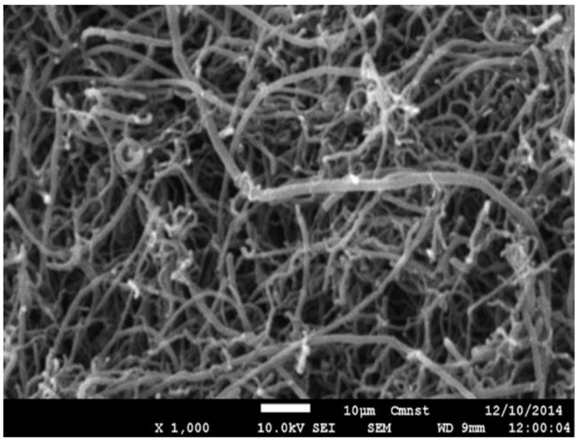


Figure 1. *Scanning Electron Microscopy graph of primary MWCNT.*

2.2 Manufacturing Process

In this study, MWCNTs with different weight percentage, respectively, were evenly mixed with the epoxy/polyester solution before casting. Nanocomposite specimens were fabricated by the hot compress molding process as illustrated in Figure 2.

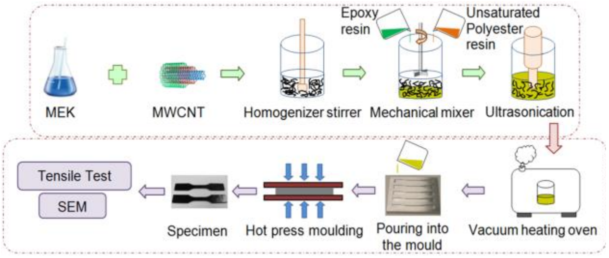
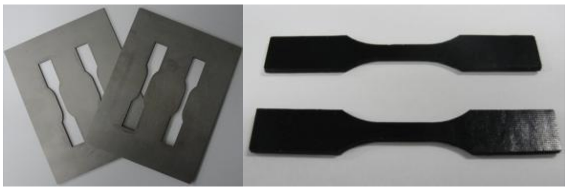


Figure 2. *Schematic diagram showing the preparation process of nanocomposite.*

The precalculated amount of MWCNTs and epoxy/unsaturated polyester were mixed together in a suitable beaker. MWCNTs were dispersed into an epoxy/polyester resin using ultrasonic energy in combination with high speed mechanical stirring. Ultrasonication was carried out at 40 ^{0}C in a bath sonicator (T490DH Transsonic Digital S) operated at 40 kHz and mechanical stirring was performed at 2000 rpm using a high speed mechanical stirrer. The beaker was then placed in a ultra-sonicator with a high intensity for one and half hour with pulse mode (9s on/9s off). External cooling system was employed by submerging the beaker containing the mixture in an ice bath to avoid temperature rise during the sonication process. When the process was finished, all agents including hardener, accelerator and catalyst with the weight ratio of 2:1/1/1 were mixed to the previous thermoset polymer solution. A aluminium mold (Figure 3(a)) with required dimensions was used for making samples on par with ASTM standard. The mold was covered with a mold releasing agent to remove the sample easily. The completed mixture was poured into the mold. The 2 parts casting mold was maintained under the pressure of 0.8 MPa for 24 h at ambience temperature. To eliminate the residual stress due to the heat and complete the curing process, experimental specimens were post cured at 90ºC for 2 h. The specimens of resulted nanocomposites are shown in Figure 3(b).



(a) *(b)*

Figure 3. *(a) Mold. (b) Tensile test specimens.*

In this study, the influence of different matrix stiffnesses on the reinforcement ability of nano-fillers was investigated. The resulted nanocomposite will become softer and more ductile when the addition of hardener is little. It can be conluded that the curing process is incomplete. The stiffness of matrix can be varied by the mixing ratios between the hybrid matrix and hardener. The mixing ratios 2:1, 1.5:1 and 1.3:1 between the epoxy and hardener were sequentially used to change the hybrid thermoset matrix stiffness.

With this analysis, a set of nanocomposite samples comprising various stiffnesses of matrix and different weight percentages of nano-fillers, was fabricated. The neat hybrid polymers were also made to compare with the nano-fillers reinforced composites samples.

2.3 Tensile Test

The experimental set up for tensile test was done on the tensile test machine (Instron 5566-CN2081) with a ASTM standard (D638 Type V). The following parameters were set up for the experiment: clamp length: 26.3 mm, tensile speed: 0.5 mm/min, room temperature: 25^0C. For each content of filler, the tensile test was carried out at least on 5 specimens and the result is the average value of 5 times of measuring.

2.4 Field Emission Scanning Electron Microsope (FESEM)

FESEM at 10 kV voltage was used to observe the distribution of the nano-fillers in the structure of nanocomposite system as well as evaluate the effective of nano-filler dispersion process and the adhesion among the phases. To not be affected by the heat of the laser beam during observation process, the samples were coated with a thin gold film in the vacuum chamber before being analysed.

3. RESULTS AND DISCUSSION

3.1 Tensile Properties

The stress-strain reponses of the nanocomposite specimens in tensile test are shown in Figure 4. This figure reveals that the tensile properties of the nanocomposites at different weight percentages of filler transform in the similar way. Initially, tensile stress increased with the linear style, exhibiting the period of elastic deformation of the resulting nanocomposites. Then, stress reached the maximum value and then rapidly decreased to the completely destroyed state. The results of tensile test shows that nanocomposite specimens have a elastoplasticity property and a rather brittle charateristic.

The analysis data of the 90 experiments, achieved by using Nexygen Plus 3.0 with a high reliability over 95%, have been presented in Tables 1 and 2 at the different mixing ratios of hybrid matrix and hardener.

Table 1. *The relationship between the weight percentage of tensile strength and MWCNT filler at the mixing ratio of 2:1.*

Content of MWCNTs	0%	0.2%	0.5%	1%	1.5%	2%
Tensile strength (MPa)	17.01	27.17	28.73	31.69	30.64	25.62

Table 2. *The variation of tensile property of MWCNT reinforced nanocomposites at different mixing ratios.*

wt% of MWCNTs	Tensile strength (MPa)		
	2:1	*1.5:1*	*1.3:1*
0	17.01	15.45	13.29
0.2	27.17	22.71	16.85
0.5	28.73	24.95	19.48
1	31.69	27.51	22.77
1.5	30.64	23.37	17.39
2	25.62	18.18	15.36

Figure 5 shows the relationship between the weight percentage of filler (MWCNT) and the tensile strength of the nanocomposite at the mixing ratio of 2:1. The figure indicates that the tensile strength of nanocomposite specimens increases rapidly as the weight percentage of MWCNTs increases from 0% to 0.2%. The tensile strength changes slightly in the range of MWCNT content from 0.2% to 1.5%. The maximum value of tensile strength achieved at the MWCNT content of 1%. This value increases approximately 86.3% as compared with that of the specimens without added fillers. As the weight percentage of MWCNT increases to over 1.5%, the tensile strength of nanocomposites decreases rapidly.

To create different stiffnesses of matrix, a range of mixing ratios between the hybrid matrix and hardener was proposed consisting of 2:1, 1.5:1 and 1.3:1. Figure 6 presents the relationship between the tensile strength of MWCNT reinforced hybrid polymer nanocomposite in different mixing ratios and the filler content of 0%, 0.2%, 0.5%, 1%, 1.5% and 2%. The tensile strength value of the composite decreased from 31.69 MPa to 13.29 MPa when the mixing ratio runs from 2:1 to 1.3:1. The composites with the low stiffness matrix (mixing ratio 2:1) had an increase of tensile strength to 86.3% in 1% MWCNT weight percentage. The composites with the medium stiffness matrix (mixing ratio 1.5:1) had a 77.9% increase of tensile strength in 1% MWCNT weight percentage. The composites with the high stiffness matrix (mixing ratio 1.3:1) had a 71.4% increase of tensile strength in 1% MWCNT weight percentage.

The results proved that the nano-fillers (MWCNTs) show an extremely significant and clear reinforcement ability in a soft matrix rather than a hard matrix. The reinforcement role of these two categories of nano-fillers decreases when the stiffness of matrix increases.

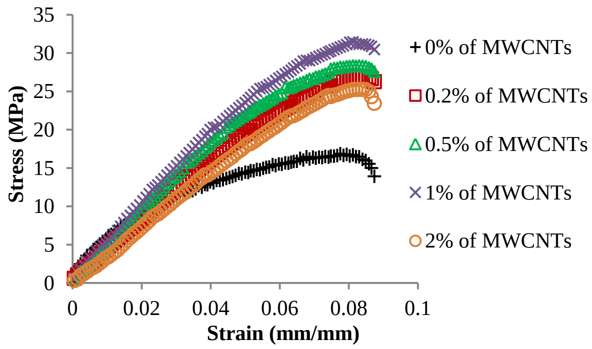


Figure 4. *Stress-strain curve in tensile test of MWCNT reinforced composite.*

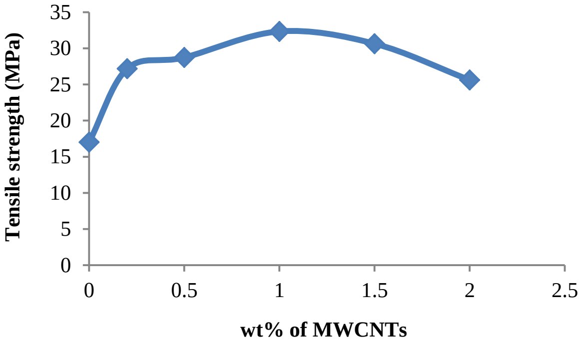


Figure 5. *The relationship between tensile strength and wt%* of MWCNT.

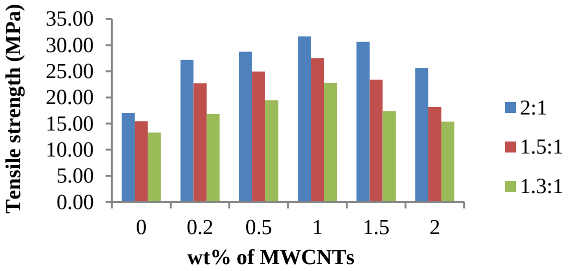
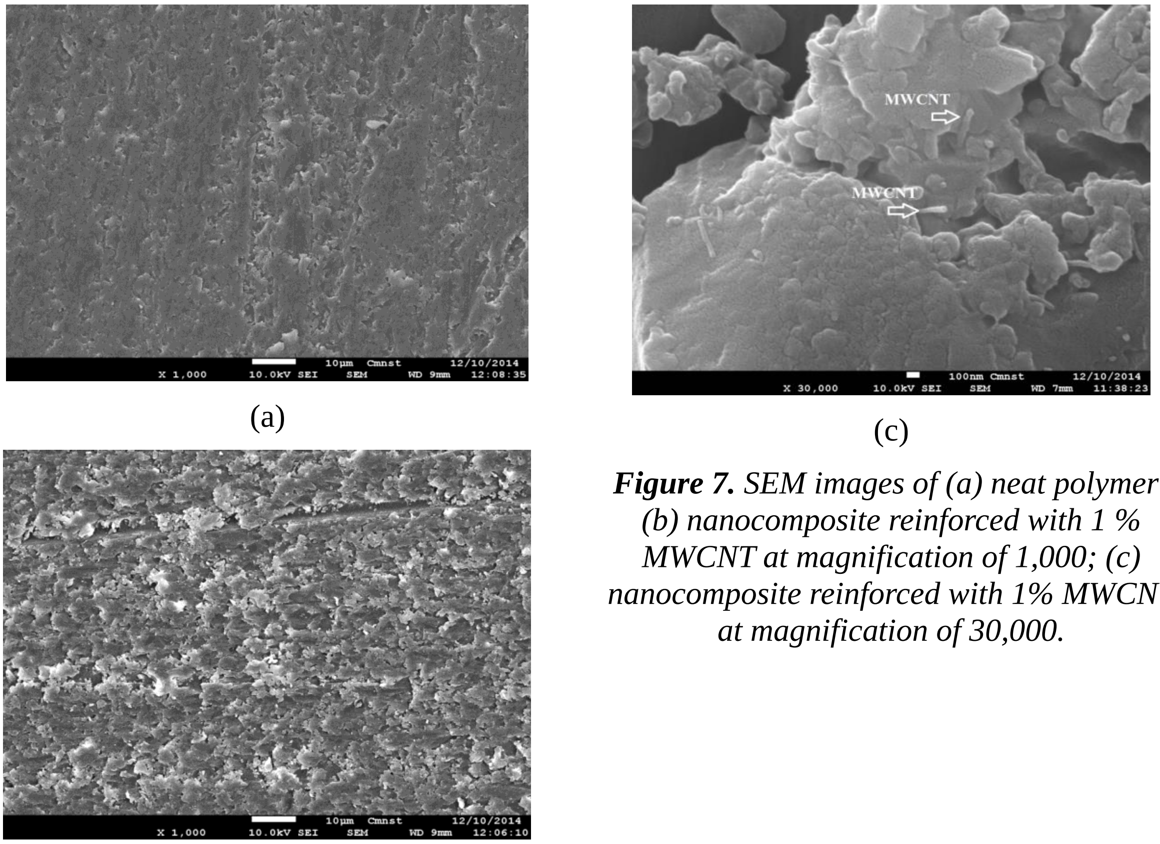


Figure 6. *The variation of tensile strength of nanocomposite with different mixing ratios.*

3.2 Fracture Surface Properties

Figure 7 shows the SEM graphs of the fracture surface in the tensile test. This observation is consistent with the experimental results of tensile strength shown in Figure 6. A pretty smooth surface can be seen in Figure 7(a) for the pure composite without nano-fillers. With 1% of MWCNTs, the fracture surface of nanocomposites is pretty rough, showing a brittle fracture kind, as indicated in Figure 7(b). In the SEM image with 30,000 magnification, the surface of nano-fillers are seen to be entirely covered by the hybrid polymer matrix as shown in Figures 7(c). This indicates a good adhesion between the matrix and reinforcement substance and the reliable results of the mechanical properties of the manufactured experimental specimens.



(a)

(c)

(b)

Figure 7. *SEM images of (a) neat polymer; (b) nanocomposite reinforced with 1 % MWCNT at magnification of 1,000; (c) nanocomposite reinforced with 1% MWCNT at magnification of 30,000.*

4. CONCLUSIONS

This paper studied and evaluated the effect of various contents of muti-walled carbon nanotubes (MWCNTs) on the tensile strength property of a novel hybrid thermoset material. Experimental results indicated that the tensile strength of the novel nanocomposite material increases to 86.3 % with the addition of a 1% ratio of MWCNTs. Furthermore, FESEM analysis revealed that excellent adhesion and interfacing between the matrices and the fillers are the main reasons for optimum improvement of properties. The unique contribution of this study is the discovery that novel hybrid thermoset material reinforced with nano-filler (MWCNT) can be applied in making low cost, high strength and light weight components as automobile parts, transportation systems and biomedical devices.

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