

Morphological, Electrical, and Mechanical Properties of Multiwall Carbon Nanotube/Polysilsesquioxane Composite

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Received 10 May 2007; accepted 6 November 2007

DOI 10.1002/app.27660

Published online 6 May 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Multiwalled carbon nanotube (MWCNT) was modified with mixed acid. Diglycidyl ether of bisphenol A (DGEBA)-bridged polyorganosiloxanes was prepared. The multiwalled carbon nanotube/diglycidyl ether of bisphenol A-bridged polysilsesquioxane (MWCNT/DGEBA-PSSQ) composites was fabricated. The improvement of the affinity between MWCNT and the polymer matrix by acid modification was studied. SEM and TEM microphotographs confirm that acid-modified MWCNT exhibits better dispersion than the unmodified MWCNT in DGEBA-PSSQ. The mechanical and electrical properties of acid-modified MWCNT/DGEBA-PSSQ composites have been investigated. The tensile strength of the material increased 150.6% (with 1.0 wt % acid-modified MWCNT).

The flexural strength of the PSSQ increased 68.4% (with 0.6 wt % acid-modified MWCNT). The Young's modulus of the material increased 189.3% (with 1.0 wt % acid-modified MWCNT). The flexural modulus of the PSSQ increased 219.1% (with 0.8 wt % acid-modified MWCNT). The surface and volume electrical resistivities of MWCNT/DGEBA-PSSQ composites decreased 6 orders when 2.0 wt % of unmodified MWCNT was added to the PSSQ matrix. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2000–2007, 2008

Key words: polysilsesquioxane; multiwalled carbon nanotubes; electrical properties; mechanical properties; scanning electron microscopy

INTRODUCTION

Numerous investigations on the carbon nanotubes (CNTs) have been conducted as their structures have been identified since 1991.¹ Because of their excellent electrical,² mechanical,³ thermal and magnetic properties,⁴ low density, high surface area, flexibility and chemical stability,⁵ CNTs show great potential for use in polymer composites. Applications of carbon nanotube modified polymers have been extensively examined.⁴ Polymeric matrices such as polyethylene (PE),⁶ polypropylene (PP),⁷ poly(methyl methacrylate) (PMMA),⁸ poly(vinyl-carbazole), polyamide,⁹ and epoxy^{10,11} for CNT/polymer composites have been studied.^{6–11} Multiwalled carbon nanotube (MWCNT) can be modified with strong acid or strong oxidation agent. Xiong et al.¹⁰ modified SWCNT with strong acid (H₂SO₄/HNO₃) and then grafted with polypropylene glycol. The modified SWCNTs were then mixed with the monomer of polyurethane. Yang et al.¹¹ grafted hyperbranched poly(urea-urethane)s on acid-modified MWCNT.

Bridged polysilsesquioxanes (PSSQs) are a family of hybrid organic–inorganic materials, which can be prepared via sol–gel processing that contain an organic bridging group and two or more trifunctional silyl groups.¹²

Most bridged PSSQs possess excellent thermal stability in inert atmospheres or under normal atmospheric conditions; however, their mechanical properties are less well characterized than their thermal stability.¹² Thermal and mechanical properties of the bridged PSSQs depend strongly on their bridged structures and the preparation methods.

In this research, acid-modified CNTs were added to diglycidyl ether of bisphenol A-bridged polysilsesquioxane (DGEBA-PSSQ) and their effect on the mechanical properties was studied. The influence of acid modification of CNT on the electrical conductivity of composites will be discussed.

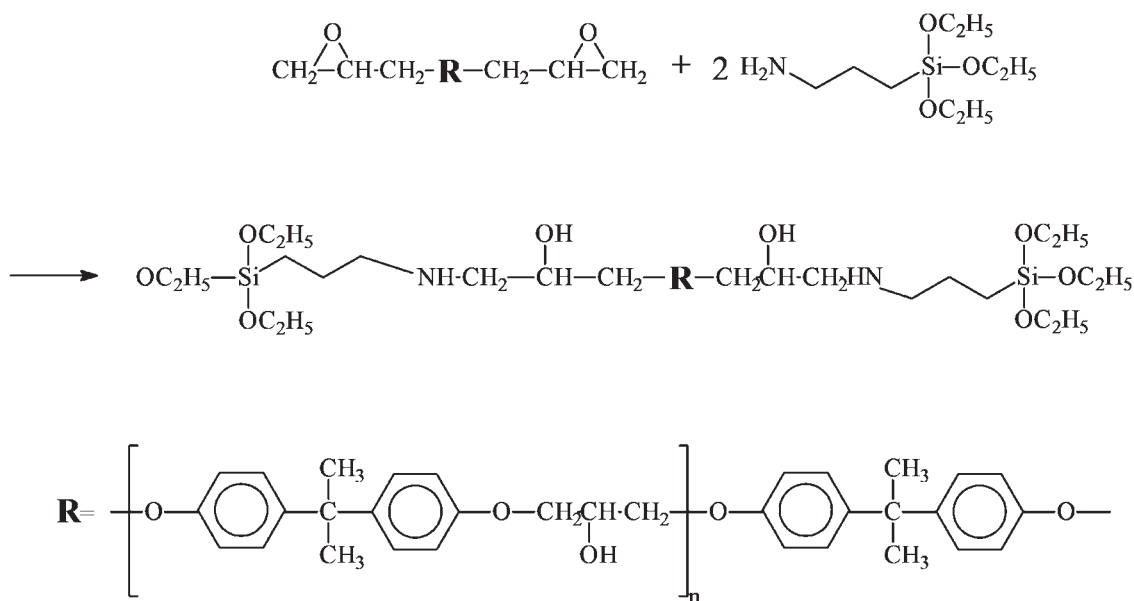
EXPERIMENTAL

Preparation of diglycidyl ether bisphenol A-bridged polyorganosiloxane precursors

DGEBA type Epoxy resin, Epon 828, was obtained from Nan Ya Plastics Corp. Taiwan, (3-aminopropyl)triethoxysilane (APTES) was obtained from Lancaster Synthesis, Morecambe, England. Epoxy and

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Contract grant sponsor: National Science Council, Taiwan, R.O.C.; contract grant number: NSC 93-2216-F-007-022.



Scheme 1 Synthetic method of DGEBA-PSSQ precursors from Epon 828 Epoxy.

APTES were mixed in the mole ratio of 1 : 2 and then the precursors of DGEBA-PSSQ will be formed at 15°C for 10 h (Scheme 1).

Modification of MWCNT

MWCNT was obtained from the Nanotech Port Company, Shenzhen, China. The diameters of the carbon nanotube were 40–60 nm. The lengths were 0.5–40 μm . The specific surface areas were 40–300 m^2/g . MWCNT was functionalized by with a mixture of $\text{H}_2\text{SO}_4\text{--HNO}_3$ (3 : 2 by weight) for 24 h, at 50°C.¹³

Preparation of MWCNT/DGEBA-PSSQ nanocomposites

Diglycidyl ether bisphenol A-bridged polyorganosiloxane precursors were mixed with the unmodified and acid-modified CNTs without solvent. The MWCNT was dispersed using an ultrasonic vibrator until no phase separation was observed (about 2 h). 0.02 g of dibutyltindilaurate (obtained from Tokyo Chemical Industry, Tokyo, Japan) was used as a catalyst, and was added to the mixture of the precursor DGEBA-PSSQ and MWCNT. The mixture was put on a plastic plane and heated at 60°C for 10 h, then placed between two flat plastics to reduce warp of the composites. Then they were heated at 60°C for another 62 h and to 120°C at a heating rate of 10°C/h. Scheme 2 describes the reaction of the mixture of CNT and the precursor to form CNT/DGEBA-PSSQ nanocomposites. The silyl ethoxy group may react with --OH group on the epoxy 828 [Scheme 2(b)], the polar group on acid-modified

MWCNT surface (--COOH or --OH) [Scheme 2(c)] and moisture in air [Scheme 2(d)]. The silyl ethoxy group also will react with dibutyltindilaurate catalyze, which also serves as a catalyst.

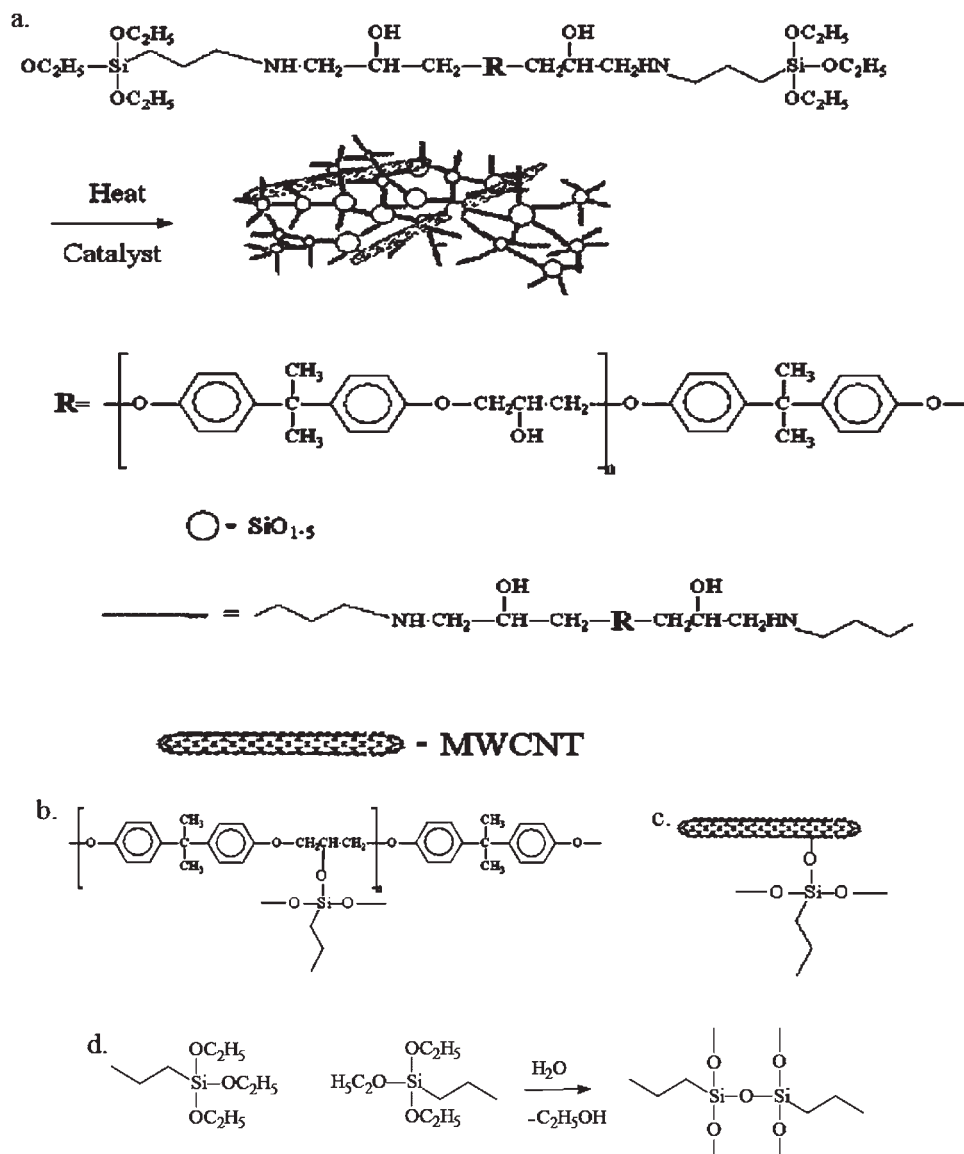
Properties measurement

Morphological properties were evaluated by a scanning electron microscope Hitachi, FE-SEM (S-4200). Composite film for scanning electron microscope (SEM) investigation was 3 mm \times 3 mm \times 1 mm. The cross section of the samples was studied. A transmission electron microscope (TEM) was performed by a JEOL-2000EX. A composite layer of 100 nm thick was microtoned and then was deposited on 200 mesh copper nets for TEM observation.

Tensile strength test was carried out by using an Instron machine Model 4488 at room temperature. Test procedure followed the ASTM-D638. Dimensions of test specimen are 120 mm \times 13 mm \times 3 mm. The crosshead speed was 2 mm/min.

Flexural strength test was carried out by using an Instron machine Model 4488 at room temperature. Test procedure followed the ASTM-D790. Dimensions of test specimen are 120 mm \times 13 mm \times 3 mm. The crosshead speed was 1 mm/min. Surface and volume electrical resistivities were measured by a ULTRA Mesohmeter SM-8220, DKK TOA Corporation, Tokyo, Japan.

The surface and volume electrical resistivities were measured with a thin film of 40 mm \times 40 mm \times 0.1 mm and contacted with carbon paste. The test was conducted with a voltage of 100 V, charge of 30 s, temperature at 25°C, and at 50% relative humidity.



Scheme 2 Cured MWCNT/DGEBA-PSSQ composites from the mixture of the DGEBA-PSSQ precursors and MWCNT (a) Curing of DGEBA-PSSQ with MWCNTs content, (b) silyl ethoxy group reacted with $-\text{OH}$ group on epoxy 828, (c) silyl ethoxy group reacted with polar group on acid-modified MWCNT surface, and (d) silyl ethoxy group reacted with moisture.

RESULTS AND DISCUSSION

Characterizations of MWCNT/PSSQ nanocomposites with FTIR and Raman spectra have been reported in our previous articles.¹³⁻¹⁵

Morphology of MWCNT composites

Figure 1(a-c) illustrate the SEM microphotographs of the cross section of unmodified CNT/DGEBA-PSSQ composites. Figure 1(a) presents the SEM microphotograph of the cross section of neat DGEBA-PSSQ. The polymer matrix shows homogeneous phase. Most of the MWCNT was embedded in the DGEBA-PSSQ composites when the unmodified CNT content

is 0.2 wt % [Fig. 1(b)]. Figure 1(c,e) show the SEM microphotographs of the cross section of unmodified CNT/DGEBA-PSSQ [the content of unmodified MWCNT in Figure 1(c) is 1.0 wt % and 4.0 wt % in Figure 1(e)]. A few clusters can be found in the unmodified MWCNT, suggesting that the unmodified MWCNT is not well dispersed in the composite materials, but embedded in the polymer matrix. Figure 1(d,f) present the SEM microphotographs of the cross section of acid-modified MWCNT/DGEBA-PSSQ. When the content of acid-modified MWCNT was 1.0 wt %, the carbon nanotube was not observed in the polymer matrix from the SEM microphotograph [Fig. 1(d)]. One can see the acid-modified MWCNT was well dispersed in the polymer matrix

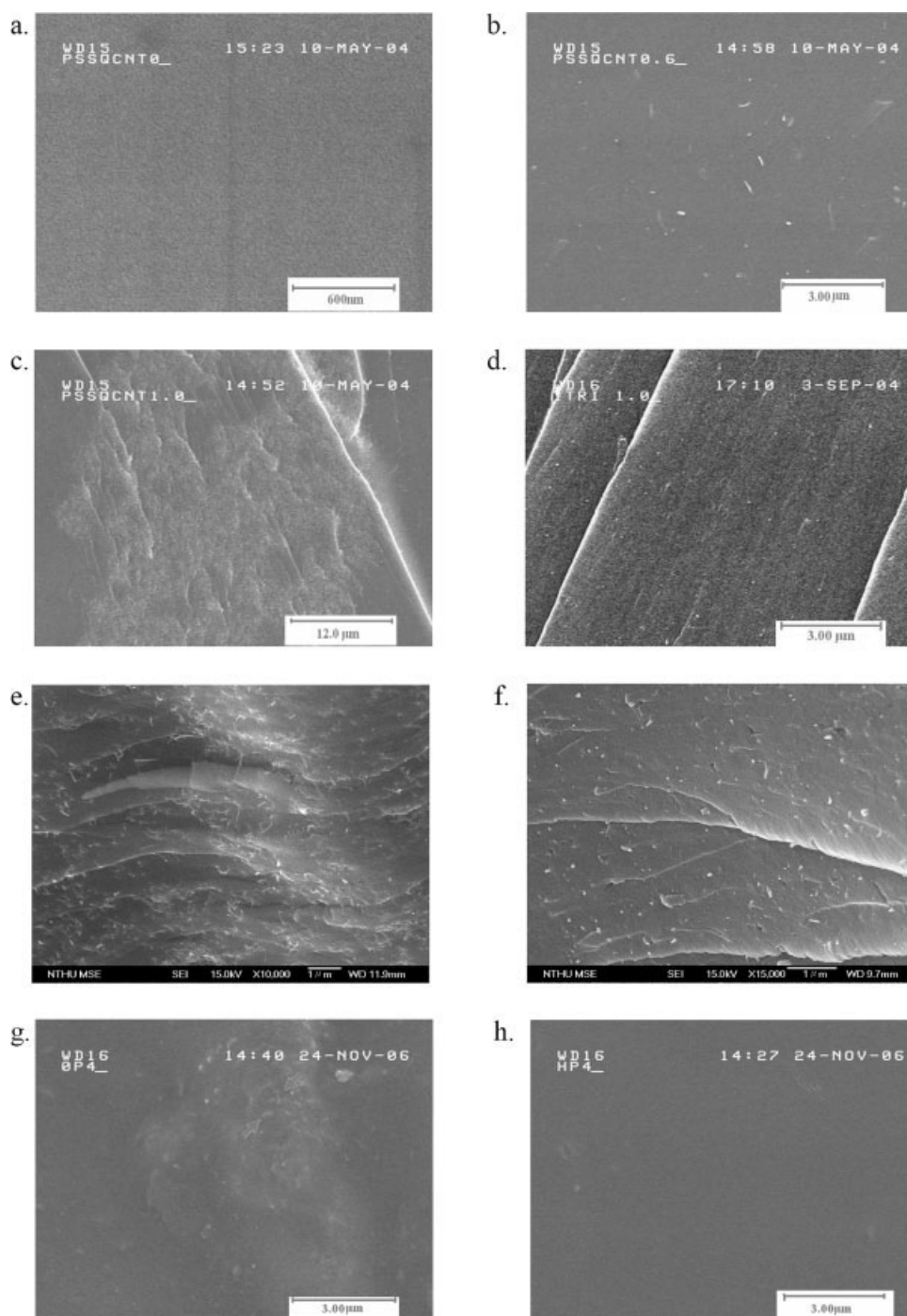


Figure 1 SEM microphotograph of the DGEBA-PSSQ nanocomposite cross section of (a) neat DGEBA-PSSQ with (b) 0.2 wt % unmodified CNT, (c) 1.0 wt % unmodified CNT ($\times 2500$), (d) 1.0 wt % acid-modified CNT, (e) 4.0 wt % unmodified CNT, (f) 4.0 wt % acid-modified CNT, and surface of (g) 4.0 wt % unmodified CNT, (h) 4.0 wt % acid-modified CNT.

when the acid-modified MWCNT content is 4.0 wt % [Fig. 1(e)]. When MWCNTs were modified with acid, they were dispersed more uniformly in the polymer matrix than unmodified MWCNT. Figure 1(g) shows SEM microphotograph of the surface of 4.0 wt % unmodified MWCNT/DGEBA-PSSQ composites, some of MWCNTs were exposed and aggregated. Figure 1(h) shows the SEM microphotograph of the surface of 4.0 wt % acid-modified MWCNT/

DGEBA-PSSQ composites. Few MWCNT could be found on the surface of 4.0 wt % acid-modified MWCNT/DGEBA-PSSQ composites. All of the acid-modified MWCNTs were dispersed in the polymer matrix. Figure 2(a,b) exhibit the TEM microphotographs of MWCNT/DGEBA-PSSQ composites. Both carbon nanotube and particles (as shown in arrows) can be seen in TEM microphotographs of unmodified MWCNT/DGEBA-PSSQ composites [Fig. 2(b)].

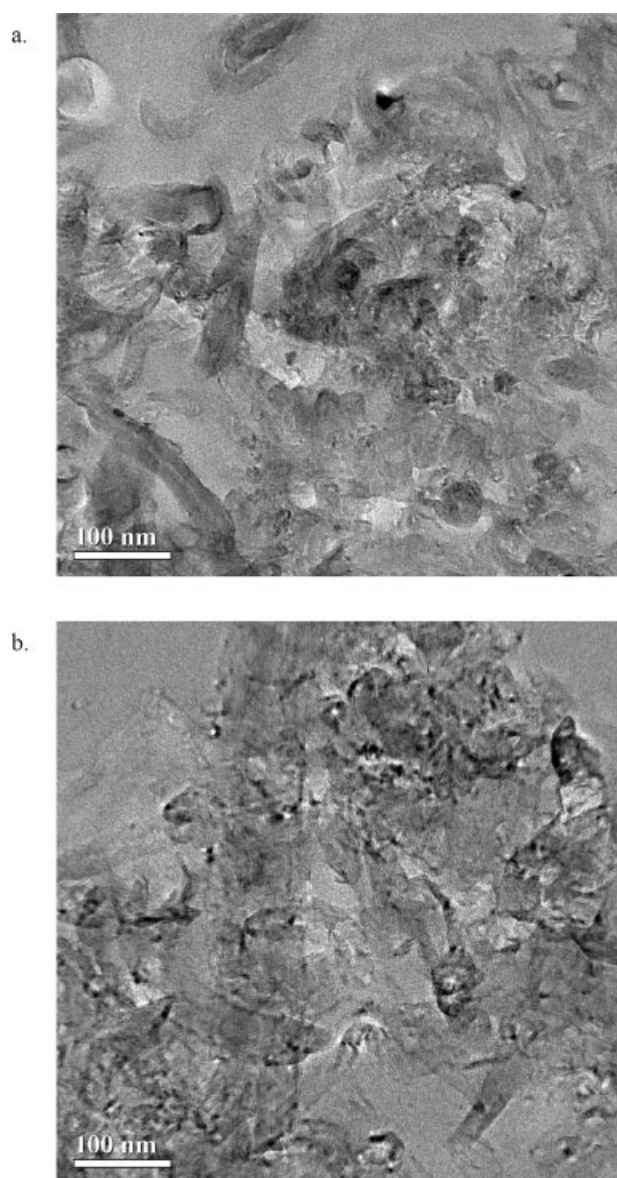


Figure 2 TEM microphotograph of the (a) 1.0 wt % unmodified CNT (b) 1 wt % acid-modified CNT/DGEBA-PSSQ nanocomposite.

The diameter of particle found in the unmodified MWCNT/DGEBA-PSSQ composites was 14–40 nm. The particle may be amorphous graphite clusters. However, only carbon nanotube was found in acid-modified MWCNT/DGEBA-PSSQ composites [Fig. 2(b)]. The amorphous carbon could be removed by oxidation.

Mechanical properties

Figure 3(a) reveals that the tensile strength of cured DGEBA-PSSQ composites increased from 5.82 MPa (the neat DGEBA-PSSQ) to 8.56 MPa (1.0 wt % unmodified MWCNT/DGEBA-PSSQ, increased 47.1%), and to 14.58 MPa (1.0 wt % acid-modified MWCNT/DGEBA-PSSQ, increased 150.5%). The improvement of

tensile strength of the DGEBA-PSSQ with acid-modified MWCNT is much higher than that with the unmodified MWCNT. Figure 3(b) indicates that the Young's modulus of cured DGEBA-PSSQ composites increased from 0.56 GPa (neat DGEBA-PSSQ) to 1.19 GPa (with 0.8 wt % unmodified MWCNT, increased 112.5%) and to 1.52 GPa (with 0.8 wt % acid-modified MWCNT, increased 171.4%), and to 1.62 GPa (with 1.0 wt % acid-modified MWCNT, increase 189.3%). Acid-modified MWCNT can improve the Young's Modulus of the DGEBA-PSSQ than unmodified MWCNT. The Young's modulus of composites depends on the affinity of the filler toward the polymer matrix. Acid-modified MWCNT exhibits greater affinity toward the polymer matrix since the functional groups were formed.

Figure 3(c) demonstrates that the flexural strength of DGEBA-PSSQ composites increased from 40.62 MPa (neat DGEBA-PSSQ) to 52.04 MPa (with 0.8 wt % unmodified MWCNT, increased 28.11%) and to 68.41 MPa (with 0.6 wt % acid-modified MWCNT, increased 68.4%). Acid-modified MWCNT mixed with the DGEBA-PSSQ exhibits better flexural strength than that of the unmodified MWCNT. Figure 3(d) shows that the flexural modulus of DGEBA-PSSQ composites increased from 0.94 GPa (neat DGEBA-PSSQ) to 1.71 GPa (with 0.8 wt % unmodified MWCNT, increased 81.9%) and to 3.00 GPa (with 0.8 wt % acid-modified MWCNT, increased 219.1%). Acid-modified MWCNT mixed with DGEBA-PSSQ exhibits better flexural modulus than that with unmodified MWCNT.

In this work, acid-modified MWCNT significantly improves the mechanical properties of the composites materials, especially Young's modulus and flexural modulus. Adding a small quantity of acid-modified MWCNT can improve the Young's modulus and flexural modulus significantly. Although acid treatment may shorten MWCNT length and increase their defects,¹⁶ the affinity between MWCNT and polymer matrix was increased because of the functional group was formed on MWCNT. MWCNT becomes shorter and forms —COOH functional group during acid modification. The —COOH functional group may form hydrogen bonding with —OH and —NH— groups of the DGEBA-PSSQ molecule.¹⁷ However, unmodified MWCNT only forms Van der Waals force with the polymer matrix and it was much weaker than that of the hydrogen bonding. SEM microphotograph also shows unmodified MWCNT are aggregated in the polymer matrix and acid-modified MWCNT are well dispersed. Acid-modified MWCNT was attracted to DGEBA-PSSQ resin more strongly than that of unmodified MWCNT, consequently, considerable improvement on tensile strength, Young's modulus, flexural strength, and flexural modulus can be achieved.

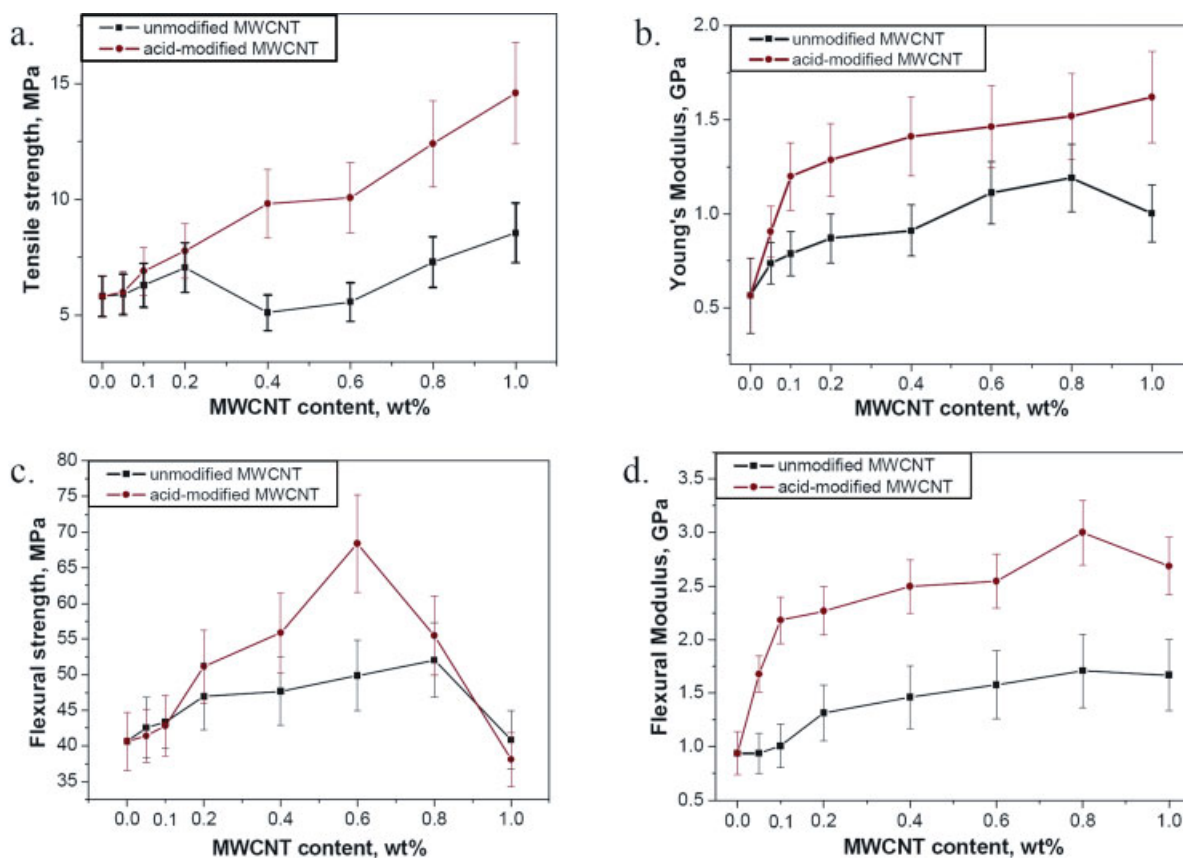


Figure 3 Effect of MWCNT content of the (a) tensile strength, (b) Young's modulus, (c) flexural strength, (d) flexural modulus of DGEBA-PSSQ composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Surface and volume electrical resistance and volume resistance

MWCNT possesses a high aspect ratio and contains many π -bonds (C=C bond). The electrons are transferred through the π -bond (C=C bond) of CNT. Adding a small quantity of MWCNT significantly improves the surface and volume electrical conductivity. However, acid-modified MWCNT shows less improvement on the surface electrical conductivity and volume conductivity than that of the unmodified MWCNT. Although the SEM microphotograph reveals that the acid-modified MWCNT was dispersed better in DGEBA-PSSQ than that of unmodified MWCNT, the aggregated MWCNT may provide a pathway for charge transfer, whereas fully dispersed MWCNT may be isolated each other in the polymer matrix. Additionally, acid treatment may shorten the MWCNT length and increases the number of defects. The Raman spectrum reveals that several π -bonds (C=C bond) of MWCNT was broken to form δ -bonds (C—C bonds) during acid treatment,^{13,15} which may reduce the electrical conductivity. Zhu et al. reported acid-modified MWCNT/Polyimide composites have less improvement on electri-

cal conductivity.¹⁷ Our previous work also showed similar result in electrical resistivity of acid-modified MWCNT/Polyimide composites.¹⁸

The surface electrical resistivities of acid-modified MWCNT/DGEBA-PSSQ composites were much higher than that of unmodified MWCNT/DGEBA-PSSQ composites with same quantity of MWCNT. SEM microphotograph of the surface of 4.0 wt % unmodified MWCNT/DGEBA-PSSQ composites shows a few MWCNTs were exposed and were aggregated. SEM microphotographs of the surface of 4.0 wt % acid-modified MWCNT/DGEBA-PSSQ composites show that MWCNTs could not be found on the surface of 4.0 wt % acid-modified MWCNT/DGEBA-PSSQ composites. All of the acid-modified MWCNTs were dispersed in the polymer matrix. However, some of the unmodified MWCNT could be migrated to the surface of the composites and they may provide pathways for charge transfer on the surface, while acid-modified MWCNT could not found on the surface of the material. The pathways for charge transfer are not easy to form on the surface of acid-modified MWCNT/DGEBA-PSSQ composites.

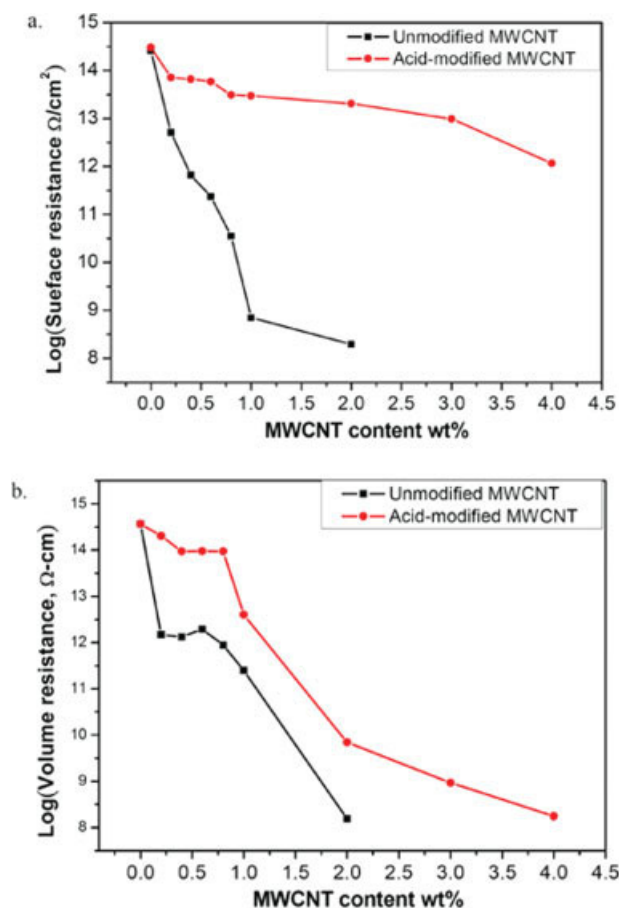


Figure 4 Effect of CNT content of the (a) surface electrical resistance (b) volume resistance of DGEBA-PSSQ composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4(a) reveals that the surface electrical resistivity of MWCNT/DGEBA-PSSQ decreased as the MWCNT content increased. The surface resistivity of neat DGEBA-PSSQ was $2.60 \times 10^{14} \Omega/\text{cm}^2$. When unmodified MWCNT was added, it decreased to $7.08 \times 10^8 \Omega/\text{cm}^2$ (with 1 wt % unmodified MWCNT, decreased 6 orders) and then to $1.95 \times 10^8 \Omega/\text{cm}^2$ (with 2 wt % unmodified MWCNT, decreased 6 orders). When acid-modified MWCNT was added, it decreases to $2.98 \times 10^{13} \Omega/\text{cm}^2$ (with 1 wt % acid-modified MWCNT, decreased 1 orders) and then to $1.17 \times 10^{12} \Omega/\text{cm}^2$ (4.0 wt % acid-modified MWCNT, decreased 2 orders). These results may owe to the charge transfer in acid-modified MWCNT/DGEBA-PSSQ composites is less efficient than that in unmodified MWCNT/DGEBA-PSSQ. The percolation threshold of the unmodified MWCNT at 1.0 wt % and of the acid-modified MWCNT is over 4.0 wt %.

Figure 4(b) shows that the volume electrical resistance of MWCNT/DGEBA-PSSQ decreased as the MWCNT content was increased. The volume electrical resistance of neat DGEBA-PSSQ was $1.60 \times 10^{14} \Omega\text{-cm}$, when unmodified MWCNT was added, it

decreases to $2.54 \times 10^{11} \Omega\text{-cm}$ (with 1 wt % unmodified MWCNT, decreased 3 orders) and then to $1.56 \times 10^8 \Omega\text{-cm}$ (with 2 wt % unmodified MWCNT, decreased 6 orders). When acid-modified MWCNT was added, it decreased to $3.99 \times 10^{12} \Omega\text{-cm}$ (with 1 wt % MWCNT, decreased 3 orders) and then to $1.76 \times 10^8 \Omega\text{-cm}$ (with 4.0 wt % MWCNT, decreased 6 orders). Acid-modified MWCNT shows less improvement in volume electricity conductivity for DGEBA-PSSQ composites than the unmodified MWCNT. The difference between the volume electrical resistivity of unmodified MWCNT/DGEBA-PSSQ and acid-modified MWCNT was not as significant as the differences between surface electrical resistivity.

CONCLUSIONS

A novel MWCNT/DGEBA-bridged PSSQ nanocomposite has been prepared successfully. SEM microphotographs indicate that unmodified MWCNT was aggregated in the polymer matrix and acid-modified MWCNT was dispersed thoroughly in the polymer matrix. The mechanical properties of MWCNT/DGEBA-PSSQ composites improved significantly with the MWCNT content. The tensile modulus of the material increased 189.3% (with 1.0 wt % acid-modified MWCNT). The flexural modulus of the PSSQ increased 219.1% (with 0.8 wt % acid-modified MWCNT). Acid-modified MWCNT have greater affinity than that of unmodified MWCNT toward the polymer matrix. This research suggests that the optimum MWCNT content for the MWCNT/PSSQ composites was 0.6 wt %, which has maximum flexural strength for acid-modified MWCNT/PSSQ composites. The unmodified MWCNT associated with DGEBA-PSSQ shows an improvement on surface and volume electrical conductivity of the composites, which exceeds those that are associated with acid-modified MWCNT. Surface electrical resistivity of the DGEBA-PSSQ decreased from $2.06 \times 10^{14} \Omega/\text{cm}^2$ (neat DGEBA-PSSQ) to $1.95 \times 10^8 \Omega/\text{cm}^2$ (2.0 wt % unmodified MWCNT content) and $1.17 \times 10^{12} \Omega/\text{cm}^2$ (4.0 wt % acid-modified MWCNT content). Volume electrical resistivity of the DGEBA-PSSQ decreased from $1.60 \times 10^{14} \Omega\text{-cm}$ (neat DGEBA-PSSQ) to $1.56 \times 10^8 \Omega\text{-cm}$ (2.0 wt % unmodified MWCNT content) and $1.76 \times 10^8 \Omega\text{-cm}$ (4.0 wt % acid-modified MWCNT content).

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