

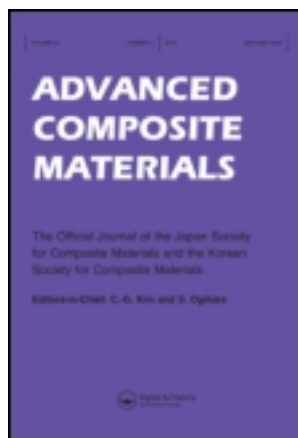
This article was downloaded by: [Siauliu University Library]

On: 17 February 2013, At: 06:52

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954

Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Advanced Composite Materials

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tacm20>

Influence of Allylamine Plasma Treatment Time on the Mechanical Properties of VGCF/Epoxy

Nguyen Quang Khuyen ^a, Jin Bong Kim ^b, Byung Sun Kim ^c & Soo Lee ^d

^a Composite Materials Laboratory, Korea Institute of Materials Science (KIMS) 66 Sangnam-dong, Changwon, Gyeongnam, 641-010, Korea

^b Composite Materials Laboratory, Korea Institute of Materials Science (KIMS) 66 Sangnam-dong, Changwon, Gyeongnam, 641-010, Korea

^c Composite Materials Laboratory, Korea Institute of Materials Science (KIMS) 66 Sangnam-dong, Changwon, Gyeongnam, 641-010, Korea

^d Department of Chemical Engineering, Changwon National University, 9 Sarim-dong, Changwon, Gyeongnam, 641-773, Korea

Version of record first published: 02 Apr 2012.

To cite this article: Nguyen Quang Khuyen, Jin Bong Kim, Byung Sun Kim & Soo Lee (2009): Influence of Allylamine Plasma Treatment Time on the Mechanical Properties of VGCF/Epoxy, *Advanced Composite Materials*, 18:3, 221-232

To link to this article: <http://dx.doi.org/10.1163/156855109X428835>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-

licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Influence of Allylamine Plasma Treatment Time on the Mechanical Properties of VGCF/Epoxy

Nguyen Quang Khuyen^{a,*}, Jin Bong Kim^a, Byung Sun Kim^a and Soo Lee^b

^a Composite Materials Laboratory, Korea Institute of Materials Science (KIMS) 66 Sangnam-dong, Changwon, Gyeongnam, 641-010, Korea

^b Department of Chemical Engineering, Changwon National University, 9 Sarim-dong, Changwon, Gyeongnam, 641-773, Korea

Received 23 April 2008; accepted 12 June 2008

Abstract

The allylamine plasma treatment is used to modify the surface properties of vapor grown carbon fibers (VGCF). It is to improve the interfacial bonding between the VGCF and epoxy matrix. The allylamine plasma process was performed by batch process in a vacuum chamber, using gas injection followed by plasma discharge for the durations of 20, 40 and 60 min. The interdependence of mechanical properties on the VGCF contents, treatment time and interfacial bonding between VGCF/ep was investigated. The interfacial bonding between VGCF and epoxy matrix was observed by scanning electron microscopy (SEM) micrographs of nanocomposites fracture surfaces. The changes in the mechanical properties of VGCF/ep, such as the tensile modulus and strength were discussed. The mechanical properties of allylamine plasma treated (AAPT) VGCF/ep were compared with those of raw VGCF/ep. The tensile strength and modulus of allylamine plasma treated VGCF40 (40 min treatment)/ep demonstrated a higher value than those of other samples. The mechanical properties were increased with the allylamine plasma treatment due to the improved adhesion at VGCF/ep interface. The modification of the carbon nanofibers surface was observed by transmission electron microscopy (TEM). SEM micrographs showed an excellent dispersion of VGCF in epoxy matrix by ultrasonic method.

© Koninklijke Brill NV, Leiden, 2009

Keywords

Vapor grown carbon fibers, allylamine plasma treatment, ultrasonic method, interfacial bonding, mechanical properties

1. Introduction

Epoxy resin is one of the most widely used polymer matrix for advanced composite materials. During recent years, micro- and nano-scaled particles have been considered as suitable filler material for epoxy to produce high-performance com-

* To whom correspondence should be addressed. E-mail: nqkhuyen@yahoo.com

Edited by KSCM

posites with enhanced properties. Park *et al.* have reported that the small amount (1–2 vol%) of VGCF greatly increased the tensile modulus and strength of epoxy matrix [1]. Chisholm *et al.* have observed 39% enhancement in flexural strength by infusing 1.5 wt% SiC nanoparticles in carbon/ep composite [2]. Also, Zhou *et al.* have reported 11% and 22.3% enhancement in the tensile and flexural strengths by adding 2 wt% carbon nanofibers/ep, respectively [3].

The VGCF is produced by the pyrolysis of hydrocarbon gas, such as benzene and methane, in the presence of hydrogen at temperatures ranging from 950 to 1200°C [4, 5]. Due to the very small diameter of the VGCF particles, the reinforcement was known to be more effective compared with the particles or fiber reinforcement to enhance the mechanical properties of composite. These fibers have been characterized in terms of highly preferred orientation of their graphitic basal planes parallel to the fiber axis, with an annular ring texture in the cross-section. This structure improves the mechanical properties, electrical and thermal conductivities for high graphitization degrees of the fibers. Due to their physical properties and potentially low production cost, these fibers are quite useful for reinforcements. Therefore, polymer matrix composites are the main application of carbon fibers [6–11]. Although the thermal, electrical and mechanical properties of these composites can be improved, the success critically depends on the bonding of the fibers to the matrix [12–19]. Carbon nanofibers are currently grown from the vapor phase and have an essential graphitic surface with low surface energy in as-grown state [20, 21].

Surface modification of carbon fibers has been studied for many years as a high surface energy is necessary for good bonding to the polymer matrix. Therefore various methods have been reported to modify the surface of carbon fibers, such as chemical treatment [22, 23], thermal treatment [24, 25] and plasma treatment [26–33]. Miyagawa and Drzal have reported that the Izod impact strength of VGCF/ep was decreased by oxygen plasma treatment, due to better adhesion at VGCF/ep interface [26]. Bruser *et al.* have reported that the water contact angles of nanofibers were decreased by the low temperature plasma treatments in NH_3 , O_2 , CO_2 , H_2O and formic acid [27].

Furthermore, Bubert *et al.* have reported that the fiber changes the surfaces by forming a layer with a thickness of the order of one nanometer mainly consisting of functional groups like hydroxyl, carbonyl and carboxyl by the oxygen plasma treatment [28]. The chemistry of carbon fiber surfaces can be modified by using the low power plasma, which affects only the first few layers of the fiber surface. Nitrogen and ammonia gas plasmas can both be used to introduce amines onto the fiber surfaces, which will bond with epoxy resins and hopefully improve the fiber/resin adhesion [29].

The plasma surface treatment can also assist in creating chemically active functional groups such as amine, carbonyl, hydroxyl and carboxyl to improve the interfacial adhesion [28–33]. Obviously, the plasma surface treatment technology can be applied for carbon nanofibers.

The aim of the present work is to investigate the mechanical properties of VGCF/ep using VGCF with allyamine plasma treatment with variable treatment time, expecting that the AAPT may enhance the mechanical properties of obtained VGCF/ep.

2. Experimental

2.1. Materials

2.1.1. Carbon Nanofibers

Commercially available VGCF (VGCF[®]-H, manufactured by Showa Denko KK) was used as a raw material in this study. VGCF[®]-H has specific surface areas of 13 m²/g, the diameter and the length of VGCF[®]-H are 150 nm and 10–20 μm, respectively. The real and bulk densities of VGCF are 2.0 g/cm³ and 0.04 g/cm³, respectively.

2.1.2. Allylamine Plasma Treated VGCF

The atmospheric glow discharge (AGD) was developed with industrial plasma sources by using high voltage radio frequency excitation at kHz frequency ranges. The AGD plasma surface treatment can be used to modify the surface properties of VGCF, and to improve the interfacial bonding between the VGCF and the epoxy matrix. AGD was created by evacuating a reaction chamber and then refilling it with a low-pressure gas. The gas is then energized by one of the following types of energy: radio frequency, microwaves, and an alternating or a direct current. A wide variety of parameters can greatly affect the physical characteristics of plasma, which will subsequently influence the surface chemistry of fibers obtained by the plasma modification. Processing parameters, such as gas types, treatment power, treatment time and operating pressure, can be varied by the operator. However, system parameters, such as electrode location, reactor design, gas inlets and vacuum are set by the design of the plasma equipment.

Allylamine plasma treatment was applied to modify the surface of VGCF in order to increase the interfacial bonding between VGCF and epoxy. Allylamine was inserted into the reactor, using helium as a carrier gas. The electrodes were inductively connected around the tube and the frequency and the voltage were 20 kHz and 3 kV, respectively (Fig. 1).

Allylamine is an organic amine with the molecular formula of C₃H₇N. The allylamine plasma treatments of VGCF were conducted for 20, 40 and 60 min (designated as AAPT VGCF20, AAPT VGCF40, AAPT VGCF60), respectively.

2.1.3. Epoxy Matrix

The epoxy used is diglycidyl ether of bisphenol A (epoxy YD-128, Kukdo Chemical), which is a standard epoxy with epoxide equivalent weight = 190 g/eq. When cured with an appropriate curing agent, it demonstrates excellent mechanical, chemical, electrical and adhesive properties in a cured state. Raw VGCF, AAPT VGCF20, AAPT VGCF40 and AAPT VGCF60 were applied to the epoxy system

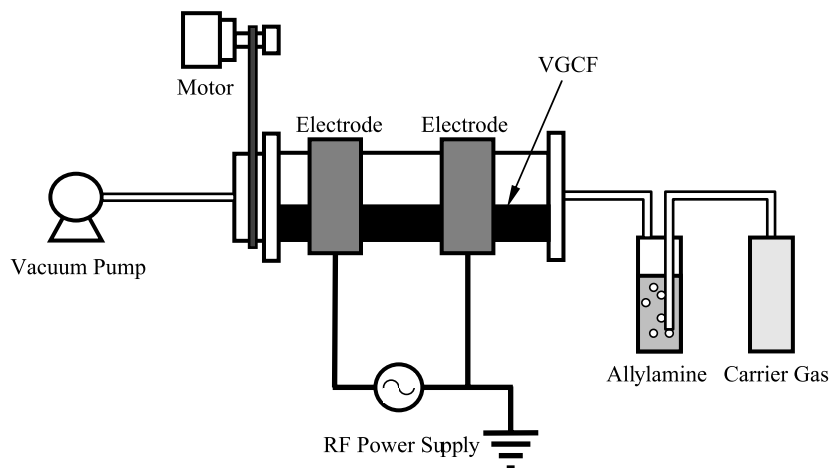


Figure 1. Schematic diagram of the allylamine plasma treated VGCF.

and processed with the anhydride curing agent MTHPA (methyltetrahydro phthalic anhydride, KBH-1089, Kukdo Chemical). The mixing ratio of epoxy and curing agent was 100/90 weight ratio.

2.2. Processing of VGCF/Ep

To produce VGCF/ep (up to 3 wt% nanofibers), the VGCF was sonicated in ethanol for 30 min using the Sonic Mater[®] sonicator. The solution contained more than 100 ml of ethanol per 1 g of VGCF. The epoxy was then added and mixed under continuous mechanical mixing for an additional hour, and the mixture was divided into two layers (the separated upper layer was ethanol) after 1 h. The ethanol was decanted and the remaining portion was removed by the vacuum extraction at 70°C for 9 h. After extraction, the curing agent was blended to the mixture with mechanical stirring for 1 h. The air bubbles were removed by vacuum at 70°C for 30 min. The epoxy matrix was injected into a metal mould with the vacuum pump. The specimens were cured at 80°C for 30 min and at 120°C for 3 h.

2.3. Effect of Dispersion

When using ethanol as a dispersion solution, raw VGCF and AAPT VGCF were well dispersed in ethanol by the ultrasonic method for 30 min. Furthermore, the ethanol was easily removed after mixing with the epoxy resin and drying.

The magnified SEM micrograph revealed an excellent dispersion of VGCF in epoxy matrix with ultrasonic method (Fig. 2).

2.4. Tensile Test

The specimen was prepared in accordance with ASTM D638. The specimen's dimensions were $3.0 \times 12.0 \times 160.0 \text{ mm}^3$. Instron 5567 was used for tensile test and the extensometer length was 25.0 mm. The machine was operated under the dis-

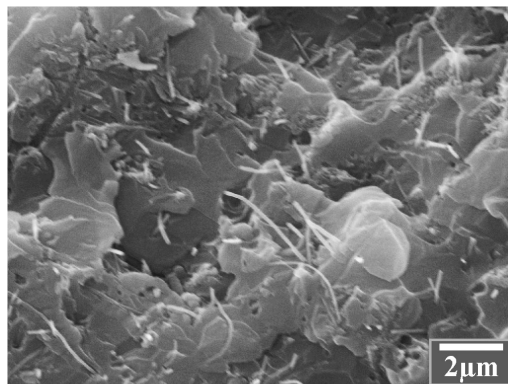


Figure 2. SEM micrographs revealing fracture surfaces with 3.0 wt% raw VGCF contents.

placement control mode with 2.00 mm/min of speed. A total of six specimens were prepared from each panel for each condition.

2.5. Scanning Electron Microscopy (SEM)

The fracture surfaces of raw VGCF, AAPT VGCF20, AAPT VGCF40 and AAPT VGCF60/ep were observed by SEM after the tensile test. Au coating of a few nanometers thickness was applied to fracture surface.

2.6. Transmission Electron Microscopy (TEM)

The surfaces of raw VGCF, AAPT VGCF20, AAPT VGCF40 and AAPT VGCF60 were observed by TEM. The samples were prepared by ultrasonic dispersion of nanofibers in ethanol before applying a few drops of the solution to a holey carbon copper grid.

3. Results and Discussion

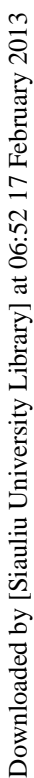
3.1. Effect of Allylamine Plasma Treatment

Most amines are reactive at room temperature with the epoxy resin (Scheme 1). The amine-epoxy reaction is an exothermal reaction, and the reaction will proceed faster as the temperature increases [34, 35].

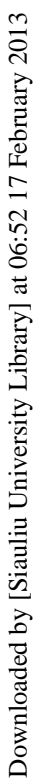
Kim *et al.* have claimed that the properties of the amine plasma treated carbon nanotubes/ep composites were improved due to the modification of carbon nanotubes resulting in enhanced dispersion and interaction between the carbon nanotubes and the epoxy resin [36]. Also, Lu *et al.* have reported that the allylamine plasma treatment was conducted on the activated carbon fibers for the immobilization of amine groups in the surface of carbon fibers [37].

The adhesion between raw VGCF and the epoxy was relatively weak; therefore, the raw VGCF was easily pulled-out without breakage under the tensile test (Fig. 3).

Allylamine plasma treatment increased the interfacial bonding between the carbon nanofibers and the epoxy. The amine group of allylamine remained on the



Downloaded by [Siauliu University Library] at 06:52 17 February 2013



Downloaded by [Siauliu University Library] at 06:52 17 February 2013

Downloaded by [Siauliu University Library] at 06:52 17 February 2013

Downloaded by [Siauliu University Library] at 06:52 17 February 2013

Downloaded by [Siauliu University Library] at 06:52 17 February 2013

Downloaded by [Siauliu University Library] at 06:52 17 February 2013

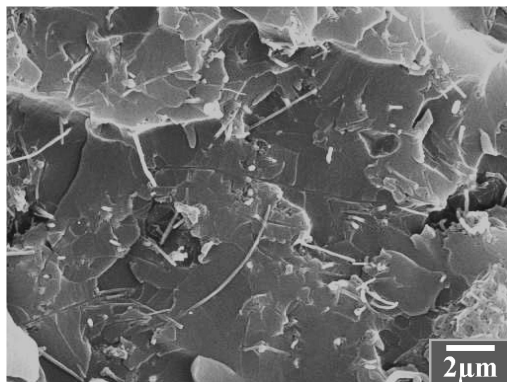


Figure 4. SEM micrographs revealing fracture surfaces with 3.0 wt% AAPT VGCF40 contents.

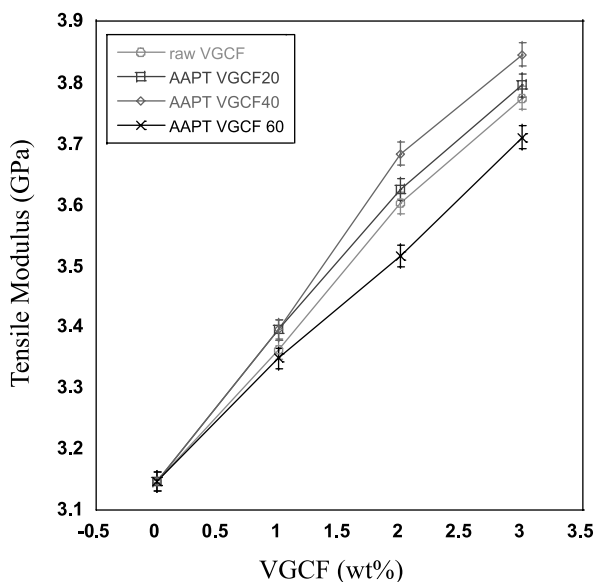


Figure 5. The tensile modulus of raw VGCF, AAPT VGCF20, AAPT VGCF40 and AAPT VGCF60/ep.

contents. However, in the 60 min plasma treated case, VGCF60/ep, the modulus showed a lower value than that of raw VGCF. Thus, the allyamine plasma treatment had effects on the tensile modulus of VGCF/ep.

3.3. Tensile Strength of Raw VGCF and AAPT VGCF/Ep

The stress–strain curves of the raw VGCF, AAPT VGCF20, AAPT VGCF40 and AAPT VGCF60/ep, containing 1.0 wt% of VGCF are shown in Fig. 6.

All specimens failed immediately when the tensile stress reached the maximum value; however, the stress–strain curves showed considerable non-linearity before

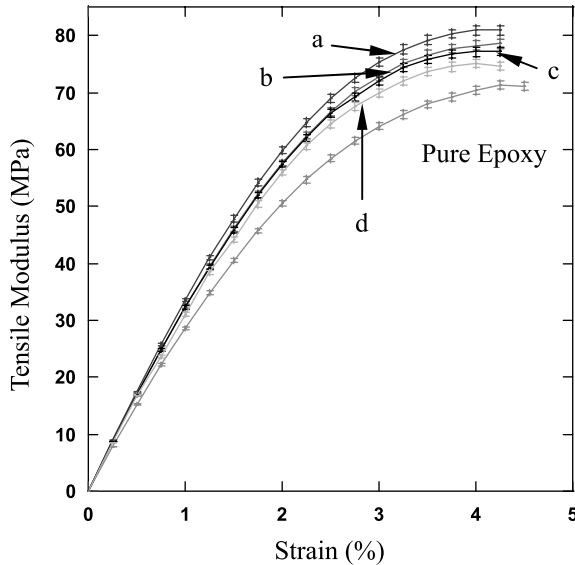


Figure 6. Tensile strength vs. strain with VGCF and AAPT VGCF with 1.0 wt% nanofibers: (a) AAPT VGCF40, (b) AAPT VGCF20, (c) raw VGCF and (d) AAPT VGCF60.

reaching the peak value. The tensile strength of AAPT VGCF40/ep with 1.0 wt% nanofibers contents at maximum point was 5.0% greater than that of raw VGCF. For AAPT VGCF60, the tensile strength was decreased by 3.3% compared with that of the raw VGCF/ep matrix, and the tensile strength of AAPT VGCF20/ep and the raw VGCF/ep showed similar values with the same VGCF contents (Figs 6 and 7).

The stress–strain curves of the VGCF, AAPT VGCF20, AAPT VGCF40 and AAPT VGCF60/ep, containing 2.0 wt% of nanofibers are shown in Fig. 7. The tensile strength with 2.0 wt% AAPT VGCF40 at the maximum point was 5.9% greater than that of raw VGCF. However, the tensile strength of AAPT VGCF60/ep was 3.8% lower than that of raw VGCF.

The stress–strain curves of the raw VGCF, AAPT VGCF20, AAPT VGCF40 and AAPT VGCF60/ep containing 3.0 wt% of nanofibers are illustrated in Fig. 8. The tensile strength AAPT VGCF40/ep matrix at maximum point was 4.8% greater than that of raw VGCF with 3 wt% nanofiber content. For AAPT VGCF20, the tensile strength was increased by 2.6% compared with that of raw VGCF/ep. Otherwise, the tensile strength of AAPT VGCF60/ep was 3.1% lower than that of raw VGCF.

The allyamine plasma treatment was applied to modify the surface of carbon nanofibers. As a result of the allyamine plasma treatment, a good bonding at the AAPT VGCF/ep interface was obtained; thus, the tensile strength of AAPT VGCF40/ep was greater than that of raw VGCF.

3.4. Transmission Electron Microscopy (TEM)

The properties of nanofibers, such as roughness, surface energy and chemical group on the nanosurface are important factors to improve the bonding strength with the

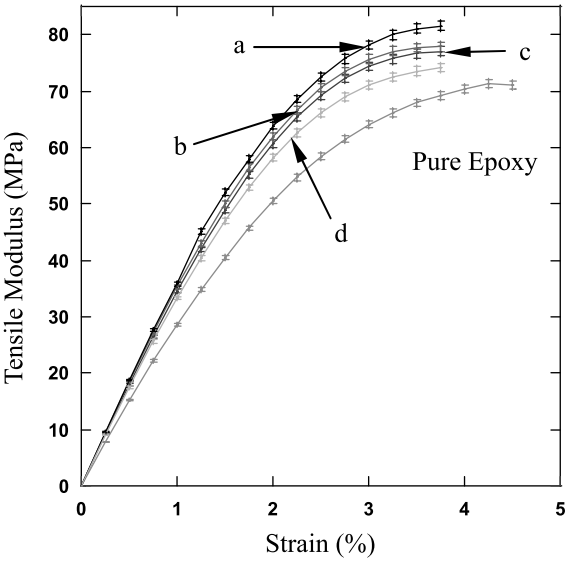


Figure 7. Tensile strength vs. strain with VGCF and AAPT VGCF with 2.0 wt% nanofibers: (a) AAPT VGCF40, (b) AAPT VGCF20, (c) VGCF and (d) AAPT VGCF60.

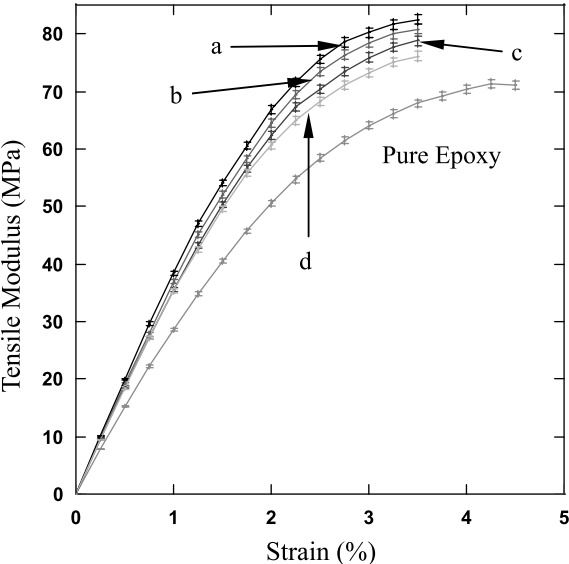


Figure 8. The tensile strength vs. strain with VGCF and AAPT VGCF with 3.0 wt% nanofibers: (a) AAPT VGCF40, (b) AAPT VGCF20, (c) VGCF and (d) AAPT VGCF60.

epoxy matrix. The surface of raw VGCF was smooth and inert, so poor adhesion at the interface was obtained due to the lack of physical properties on the nanofibers surface to enhance bonding with the epoxy matrix.

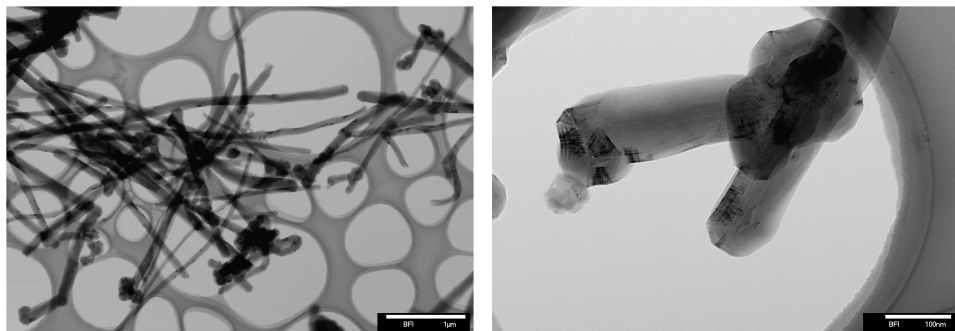


Figure 9. TEM images of AAPT VGCF60, scale bar = 1 μm and 100 nm, respectively.

AAPT VGCF had an excellent interfacial bonding with the epoxy matrix, which implies that an improvement of the adhesion at the interface between nanofibers and the epoxy matrix had been achieved. However, with longer allylamine plasma treatments, the VGCF appears to be broken (Fig. 9), and this may explain the lower values of tensile modulus and tensile strength of APT VGCF60/ep than those of raw VGCF.

From these results, it can be deduced that the allylamine plasma treatments on carbon nanofibers have improved the interfacial bonding between nanofibers and epoxy matrix. Thereby, the tensile modulus and strength of nanocomposites with AAPT VGCF40 were higher than those of raw VGCF with the same amount of nanofiber contents.

4. Conclusions

In the present work, the interfacial bonding between VGCF and the epoxy matrix and the mechanical properties of VGCF/ep reinforced by raw VGCF and AAPT VGCF were discussed. The effect of allylamine plasma treatment duration on mechanical properties of VGCF/ep matrix was investigated.

The allylamine appears to have a positive effect for improving the interfacial bonding between nanofibers and epoxy matrix. The tensile modulus and strength of AAPT VGCF40/ep showed higher values than those of raw VGCF/ep with varying carbon nanofibers contents.

The optimal allylamine plasma treatment time for VGCF was found to be 40 min, which provided the highest tensile modulus and strength as compared to the other samples.

References

1. J. Park, D. Kim, S. Kim, P. Kim, D. Yoon and K. DeVries, Inherent sensing and interfacial evaluation of carbon nanofiber and nanotube/ep composites using electrical resistance measurement and micromechanical technique, *Composites Part B* **30**, 847–861 (2006).

2. N. Chisholm, H. Mahfuz, V. Rangari, A. Ashfaq and S. Jeelani, Fabrication and mechanical characterization of carbon/SiC-epoxy nanocomposites, *Compos. Struct.* **67**, 115–124 (2005).
3. Y. Zhou, F. Pervin, S. Jeelani and P. Mallick, Improvement in mechanical properties of carbon fabric-epoxy composite using carbon nanofibers, *Mater. Proc. Technol.* **198**, 445–453 (2008).
4. J. Paredes, A. Alonso and J. Tasco'n, Oxygen plasma modification of submicron vapor grown carbon fibers as studied by scanning tunneling microscopy, *Carbon* **40**, 1101–1108 (2002).
5. J. Figueiredo, P. Serp, B. Nysten and J. Issi, Surface treatments of vapor-grown carbon fibers produced on a substrate: Part II: Atomic force microscopy, *Carbon* **37**, 1809–1816 (1999).
6. P. Serp, J. Figueiredo, P. Bertrand and J. Issi, Surface treatments of vapor-grown carbon fibers produced on a substrate, *Carbon* **36**, 1791–1799 (1998).
7. J. Kim, A. Sharma and Y. Lee, Demonstration of the formation of porous silicon films with superior mechanical properties, morphology and stability, *Mater. Lett.* **60**, 1166–1169 (2006).
8. J. Fidelus, E. Wiesel, F. Gojny, K. Schulte and H. Wagner, Thermo-mechanical properties of randomly oriented carbon/epoxy nanocomposites, *Composites Part A* **36**, 1555–1561 (2005).
9. Y. Iwahori, S. Ishiwata, T. Sumizawa and T. Ishikawa, Mechanical properties improvements in two-phase and three-phase composites using carbon nano-fiber dispersed resin, *Composites Part A* **36**, 1430–1439 (2005).
10. J. Xu, J. Donohoe and C. Pittman, Preparation, electrical and mechanical properties of vapor grown carbon fiber (VGCF)/vinyl ester composites, *Composites Part A* **35**, 693–701 (2004).
11. M. Inagaki, K. Kaneko and T. Nishizawa, Nanocarbons — recent research in Japan, *Carbon* **42**, 1401–1417 (2004).
12. S. Sihn, R. Kim, W. Huh, K. Lee and A. Roy, Improvement of damage resistance in laminated composites with electrospun nano-interlayers, *Compos. Sci. Technol.* **68**, 673–683 (2008).
13. V. Yudin, A. Feldman, V. Svetlichnyi, A. Shumakov and G. Marom, Crystallization of R-BAPB type polyimide modified by carbon nano-particles, *Compos. Sci. Technol.* **67**, 789–794 (2007).
14. B. Shim, J. Starkovich and N. Kotov, Multilayer composites from vapor-grown carbon nano-fibers, *Compos. Sci. Technol.* **66**, 1174–1181 (2006).
15. Y. Zhou, F. Pervin, V. Rangari and S. Jeelani, Fabrication and evaluation of carbon nano fiber filled carbon/epoxy composite, *Mater. Sci. Engng A* **426**, 221–228 (2006).
16. Y. Zhou, M. Baseer, H. Mahfuz and S. Jeelani, Monte Carlo simulation on tensile failure process of unidirectional carbon fiber reinforced nano-phased epoxy, *Mater. Sci. Engng A* **420**, 63–71 (2006).
17. F. Gojny, M. G. Wichmann, B. Fiedler, W. Bauhofer and K. Schulte, Influence of nano-modification on the mechanical and electrical properties of conventional fibre-reinforced composites, *Composites Part A* **36**, 1525–1535 (2005).
18. F. Pervin, Y. Zhou, V. Rangari and S. Jeelani, Testing and evaluation on the thermal and mechanical properties of carbon nano fiber reinforced SC-15 epoxy, *Mater. Sci. Engng A* **405**, 246–253 (2005).
19. T. Uchida, T. Dang, B. Min, X. Zhang and S. Kumar, Processing, structure, and properties of carbon nano fiber filled PBZT composite fiber, *Composites Part B* **36**, 183–187 (2005).
20. H. Lin, S. Shiue, Y. Chou, H. Lin and T. Wu, Effect of substrate temperature on the properties of carbon-coated optical fibers prepared by plasma enhanced chemical vapor deposition, *Thin Solid Films* **516**, 114–118 (2007).
21. H. Poche, J. Dijon and T. Monsabert, Radio-frequency plasma system to selectively grow vertical field-aligned carbon nanofibers from a solid carbon source, *Carbon* **45**, 2904–2916 (2007).
22. J. Zheng, X. Zhang, P. Li, X. Zhou, D. Chen, Y. Liu and W. Yuan, Oxygen reduction reaction properties of carbon nanofibers: effect of metal purification, *Electrochim. Acta* **53**, 3587–3596 (2008).

23. K. Yamaguchi, M. Kitazawa, Z. Wang, Y. Sugita, J. Tanaka, M. Tanemura and Y. Hayashi, Room-temperature growth of ion-induced carbon nanofibers: effects of ion species, *Diamond and Related Materials* **17**, 525–528 (2008).
24. S. Lee, T. Kim, A. Ogale and M. Kim, Surface and structure modification of carbon nanofibers, *Synthetic Metals* **157**, 644–650 (2007).
25. S. Lee, S. Da, A. Ogale and M. Kim, Effect of heat treatment of carbon nanofibers on polypropylene nanocomposites, *J. Phys. Chem. Solids* **69**, 1407–1410 (2008).
26. H. Miyagawa and L. Drzal, Effect of oxygen plasma treatment on mechanical properties of vapor grown carbon fiber nanocomposites, *Composites Part A* **36**, 1440–1448 (2005).
27. V. Bruser, M. Heintze, W. Brandl, G. Marginean and H. Bubert, Surface modification of carbon nanofibres in low temperature plasmas, *Diamond and Related Materials* **13**, 1177–1181 (2004).
28. H. Bubert, X. Haiber, M. Heintze, V. Bruser, E. Pasch, W. Brandl and G. Marginean, Basic analytical investigation of plasma-chemically modified carbon fibers, *Spectrochimica Acta Part B* **57**, 1601–1610 (2002).
29. C. Jones and E. Sammann, The effect of low power plasmas on carbon fibre surfaces, *Carbon* **28**, 509–514 (1990).
30. B. Kim and S. Park, A simple method for the preparation of activated carbon fibers coated with graphite nanofibers, *Interface Sci.* **315**, 791–794 (2007).
31. A. Felten, C. Bittencourt, J. Colomer, G. Tendeloo and J. Pireaux, Nucleation of metal clusters on plasma treated multi wall carbon nanotubes, *Carbon* **45**, 110–116 (2007).
32. P. He, Y. Gao, J. Lian, L. Wang, D. Qian, J. Zhao, W. Wang, M. Schulz, X. Zhou and D. Shi, Surface modification and ultrasonication effect on the mechanical properties of carbon nanofiber/polycarbonate composites, *Composites Part A* **37**, 1270–1275 (2006).
33. H. Okuno, E. Grivei, F. Fabry, T. Gruenberger and J. Aguilar, Synthesis of carbon nanotubes and nano-necklaces by thermal plasma process, *Carbon* **42**, 2543–2549 (2004).
34. L. Burton, The thermooxidative stability of cured epoxy resins, *J. Appl. Polym. Sci.* **47**, 1821–1837 (1993).
35. E. Karayannidou, D. Achilias and I. Sideridou, Cure kinetics of epoxy–amine resins used in the restoration of works of art from glass or ceramic, *Eur. Polym. J.* **42**, 3311–3323 (2006).
36. J. Kim, D. Seong, T. Kang and J. Younm, Effects of surface modification on rheological and mechanical properties of CNT/epoxy composites, *Carbon* **44**, 1898–1905 (2006).
37. N. Lu, S. Tang, S. Ryu and H. Choi, Surface characterization of the activated carbon fibers after plasma polymerization of allylamine, *Carbon Sci.* **6**, 243–247 (2005).