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Effect of Atmospheric Plasma Treatments on Mechanical Properties of VGCF/Epoxy

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Abstract

Vapor grown carbon fibers (VGCF) were treated with atmospheric plasma enhancing the surface area in order to improve the bonding to the matrix in epoxy composites. The changes in the mechanical properties of VGCF/epoxy nanocompostes, such as tensile modulus and tensile strength were investigated in this study. VGCF with and without atmospheric plasma treatment for surface modification were used in this investigation. The interdependence of these properties on the VGCF contents and interfacial bonding between VGCF/epoxy matrix were discussed. The mechanical properties of atmospheric plasma treated (APT) VGCF/epoxy were compared with raw VGCF/epoxy. The tensile strength of APT VGCF/epoxy nanocomposites showed higher value than that of raw VGCF. The tensile strength was increased with atmospheric plasma treatment, due to better adhesion at VGCF/epoxy interface. The tensile modulus of raw VGCF and APT VGCF/epoxy matrix were of the similar value. The dispersion of the VGCF was investigated by scanning electron microscopy (SEM), SEM micrographs showed an excellent dispersion of VGCF in epoxy matrix by ultrasonic method.

Keywords
VGCF, atmospheric plasma treatments, ultrasonic method, mechanical properties

1. Introduction

Using VGCF as reinforcement for epoxy matrix has aroused interest as a means of improving composite properties. VGCFs can be produced at lower price than the conventional carbon fibers and they are expected to allow the adjustment of the thermal, electrical and mechanical properties of polymers [1–6]. It has especially been demonstrated that VGCF/epoxy nanocomposites provide high to excellent in-

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crease of modulus and strength. Also, Park *et al.* have reported that a small amount (1–2 vol%) of VGCF greatly increased the tensile modulus and tensile strength of epoxy matrix [7]. In addition to these facts, the bonding at the VGCF/epoxy interface is extremely important for the improvement of mechanical properties with increasing amount of VGCF. Surface modification of VGCF has been studied for many years. Several methods using plasma treatment with some materials coating such as oxygen, water, carbon dioxide, ammonia gas or formic acid have been attempted. Thereby, oxygen and nitrogen containing groups may be introduced onto the surface of VGCF [8–11]. Moreover, for good bonding to a polymer matrix, high surface energies are necessary. This can be achieved by modifying their surface in atmospheric plasma treatment. Furthermore, using atmospheric plasma treatment increased the roughness and surface area of VGCF, and accordingly increased the interface area between VGCF and epoxy matrix [12–14].

In the present work, the nanocomposites were prepared *via* ultrasonic technique using raw VGCF and atmospheric plasma treated VGCF, respectively. The ethanol was used as dispersion solution for VGCF. The uniform dispersion of the VGCF was observed by SEM. The changes of the tensile modulus and tensile strength of the VGCF/epoxy with varying VGCF contents were obtained by tensile strength test.

2. Experimental

2.1. Materials

2.1.1. Raw VGCF and Atmospheric Plasma Treated VGCF

Commercially available VGCF (VGCF®-H, manufactured by Showa Denko KK) was used in this study. VGCF®-H is the VGCF specifically designed to enhance the electrical and thermal properties of high performance materials. VGCF®-H is specially processed to improve dispersion and homogeneity (Table 1).

Table 1.
Typical properties of VGCF (Showa Denko, Japan) [15]

Fiber diameter	nm	150
Fiber length	μm	10–20
Real density	g/cm^3	2.0
Bulk density	g/cm^3	0.04
Specific surface area	m^2/g	13
Aspect ratio	Fiber length/diameter	60
Electrical resistivity	Ω cm	1×10^4
Conductivity	Powder resistivity: Ω cm	0.013
Dispersion	Good	

Atmospheric plasma treatment was applied to modify the surface of VGCF in order to increase the surface area and roughness. As a result, the adhesion at the interface between VGCF and epoxy would be improved.

2.1.2. Epoxy Matrix

Raw VGCF and APT VGCF were applied, respectively, for system Epoxy YD 128 (Kukdo Chemical) processed with the anhydride curing agent methyl tetrahydro phthalic anhydride, MTHPA, Kukdo®, KBH-1089 (Kukdo Chemical). The mixing ratio of epoxy and curing agent was 100/90 (wt/wt) [16].

2.2. VGCF/Epoxy Nanocomposites by Sonification

To produce the VGCF and APT VGCF/anhydride-cured epoxy (YD 128) nanocomposites (up to 3 wt% VGCF), respectively, the VGCF were sonicated in ethanol for 30 min by using a Sonic Mater® sonicator (The Sonic Tech, Co. Ltd.). 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. One hour later, the mixture was divided into two layers (the separated upper layer was ethanol). The ethanol was poured out and the remaining portion was removed by the vacuum extraction at 85°C for 2 h. Following that, the curing agent was blended in the mixture with mechanical stirring for 1 h. The air bubbles are removed by vacuum at 70°C for 30 min. The epoxy matrix was injected into metal mould with vacuum. The specimens were cured at 80°C for 30 min and then for 3 h at 120°C. The block diagram for manufacturing of VGCF/epoxy nanocomposite is shown in Fig. 1.

2.3. Dispersion

Using ethanol as dispersion solution, the raw VGCF and APT VGCF, respectively, were well dispersed in ethanol using the ultrasonic method for 30 min. Furthermore, the ethanol was easily separated from epoxy, so the ethanol was easily removed after mixing with epoxy resin and dried out. Obviously, the ethanol is less harmful than another organic solution.

The magnification SEM showed an excellent dispersion of raw VGCF and APT VGCF in epoxy matrix with ultrasonic method (Figs 2 and 3).

2.4. Tensile Test

The specimen was prepared in accordance with ASTM D638. The specimen thickness was 3.0 mm, 12.0 mm of width, total specimen length was 160.0 mm and the strain gauges length used was 5.0 mm. The Instron 5567 was used for tensile test. The machine was run under the displacement control mode with 2.00 mm/min of speed and all the tests were performed at room temperature. Six specimens were prepared from each panel for each condition.

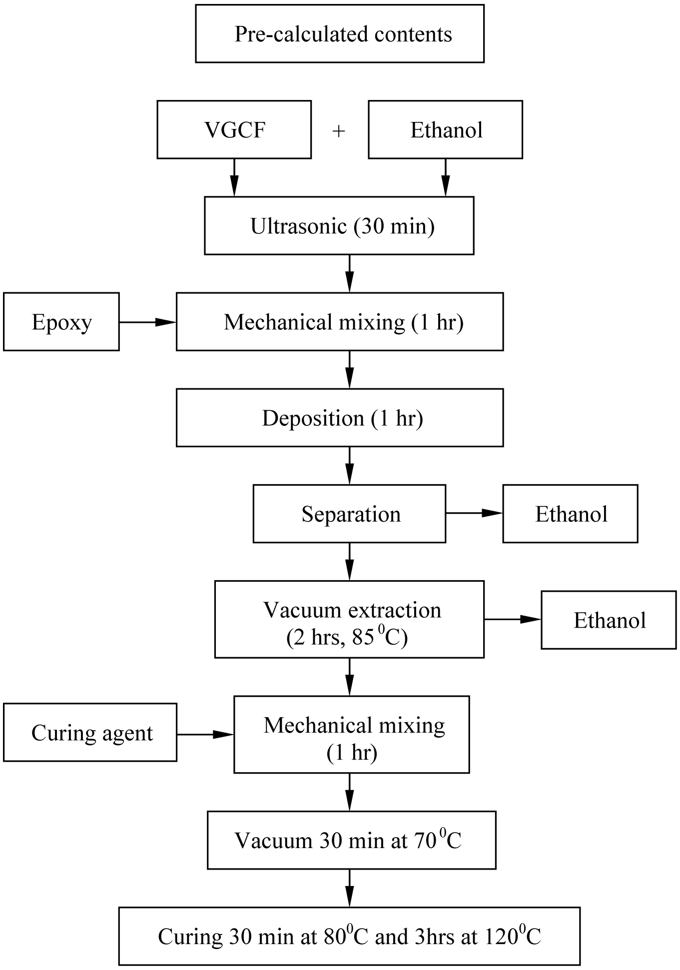

Figure 1. Processing of VGCF/epoxy nanocomposite.

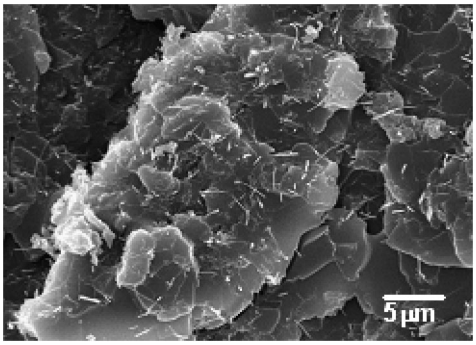

Figure 2. SEM micrographs revealing fracture surfaces with 2.0 wt% raw VGCF contents.

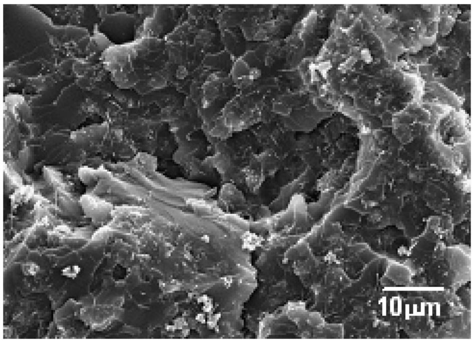

Figure 3. SEM micrographs revealing fracture surfaces with 3.0 wt% APT VGCF contents.

2.5. *Scanning Electron Microscopy*

The fracture surfaces of VGCF/epoxy nanocomposites were observed by SEM following the tensile test. An Au coating of a few nanometers in thickness was applied to fracture surface.

3. Results and Discussion

3.1. *Tensile Modulus of Raw VGCF and APT VGCF/Nanocomposites*

The relationship between tensile modulus and nano carbon fiber contents are graphically presented as filled graphs (Fig. 4). The tensile modulus of nano carbon fiber/epoxy matrix increases with increasing nano carbon fiber contents up to 3.0 wt%. The tensile modulus of raw VGCF/epoxy nanocomposites increased by 10.5%, 24.9% and 37.5% with the addition of 1.0 wt%, 2.0 wt% and 3.0 wt% of raw VGCF, respectively. The modulus of APT VGCF/epoxy nanocomposites increased 13.7%, 24.5 and 36.4% with the addition of 1.0 wt%, 2.0 wt% and 3.0 wt% of APT VGCF, respectively.

The tensile modulus was a slope of the tensile strength between 1000–3000 µm of strain. Indeed, the tensile modulus was not affected by interfacial bonding between VGCF and epoxy matrix with small strain. Therefore, the surface area of APT VGCF was increased, without further influence on tensile modulus.

The tensile modulus of APT VGCF/epoxy and the raw VGCF/epoxy nanocomposites had a similar value with the same VGCF contents. Thus, the atmospheric plasma treatments have no effect on tensile modulus (Fig. 4).

3.2. *Tensile Strength of Raw VGCF and APT VGCF/Nanocomposites*

Adding raw VGCF and APT VGCF, respectively, to epoxy matrix may increase the mechanical properties. Indeed, a number of VGCF properties, such as roughness, surface energy and surface area are important factors for improving the bonding strength with epoxy matrix. In the case of VGCF without surface modification, the poor adhesion at the interface was obtained as a result of the lack of physi-

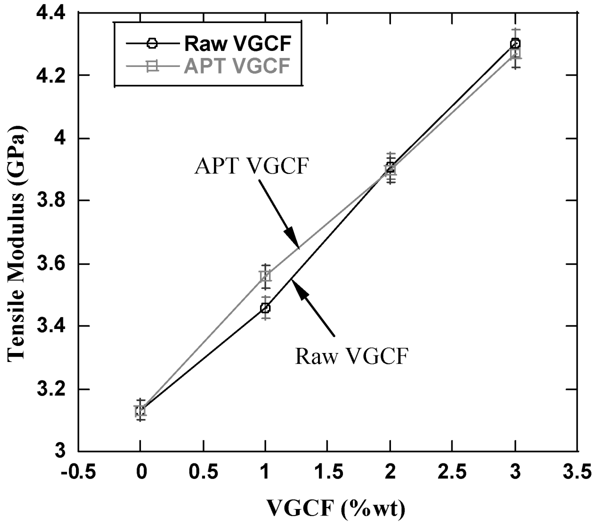

Figure 4. The tensile modulus of raw VGCF and APT VGCF/epoxy matrix.

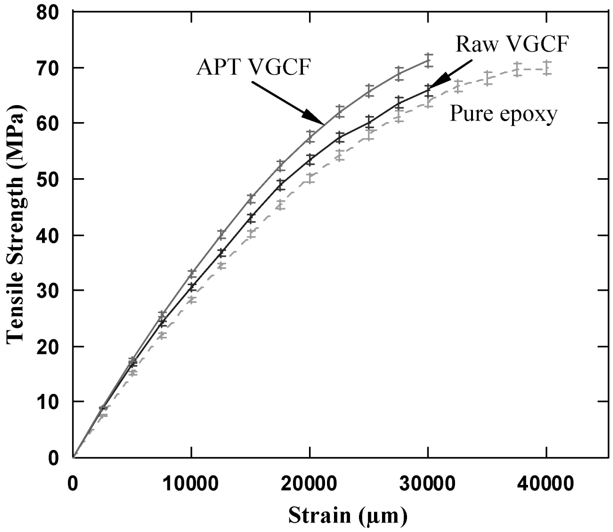

Figure 5. The stress *vs* strain with raw VGCF and APT VGCF with 1.0 wt% VGCF, respectively.

cal property on the VGCF surface to enhance the bonding with the epoxy matrix. The VGCF were stretched and pulled-out under low tensile strength. Atmospheric plasma treatment was applied to modify the surface of VGCF in order to increase the surface energy. As a result of atmospheric plasma treatment, good bonding at the APT VGCF/epoxy interface was obtained, and APT VGCF stretched, but broken under the loading.

The tensile strength–strain curves of the nano carbon fiber/epoxy matrix containing 1.0 wt% raw VGCF and 1.0 wt% APT VGCF are shown in Fig. 5. The tensile

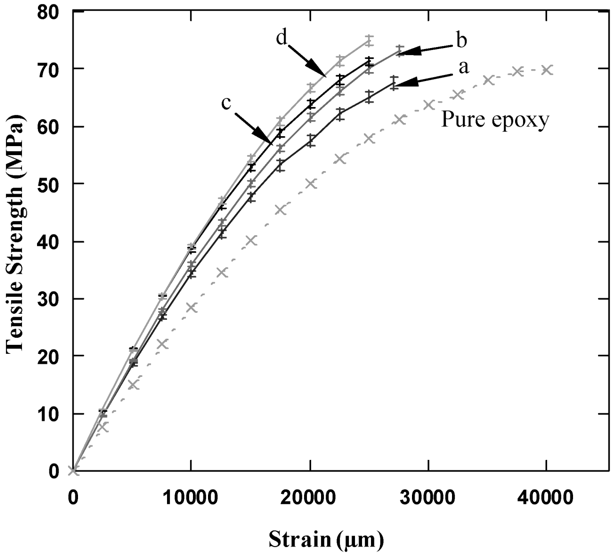

Figure 6. The tensile strength *vs* strain with (a) 2.0 wt% raw VGCF; (b) 2.0 wt% APT VGCF; (c) 3.0 wt% raw VGCF; (d) 3.0 wt% APT VGCF.

strength with 1.0 wt% APT VGCF at maximum point is 2.0% greater than that of pure epoxy with the same VGCF contents. For raw VGCF, the tensile strength was decreased by 5.8% compared with that of pure epoxy. At 20 000 μm of strain, the tensile strength of APT VGCF/epoxy matrix was increased by 14.7% and for raw VGCF, the tensile strength was increased by 6.8% compared with pure epoxy.

The stress–strain curves of the nano carbon fiber/epoxy matrix containing 2.0, 3.0 wt% raw VGCF and 2.0, 3.0 wt% APT VGCF are shown in Fig. 6.

For 2.0 wt% of VGCF content, the tensile strength of APT VGCF/epoxy nanocomposite at 20 000 μm of strain was increased by 22.7% and for raw VGCF, the tensile strength was increased by 14.7% compared with that of pure epoxy.

At the maximum point, the tensile strength of 3.0 wt% APT VGCF/epoxy nanocomposite was 7.1% greater than that of pure epoxy. With the same VGCF contents, for raw VGCF, the tensile strength was increased by 2.0% compared with that of pure epoxy. Correspondingly, the APT VGCF had excellent interfacial bonding with epoxy matrix.

From these results, it can be deduced that the atmospheric plasma treatment on VGCF has improved the interfacial boding between VGCF and epoxy matrix. Thereby, the tensile strength of nanocomposites with APT VGCF was higher than that of raw VGCF at the same amount of VGCF contents.

3.3. Effect of Atmospheric Plasma Treatment

The adhesion between raw VGCF and epoxy matrix was weak; therefore, the raw VGCF was easily pulled-out without breakage under tensile test (Fig. 7).

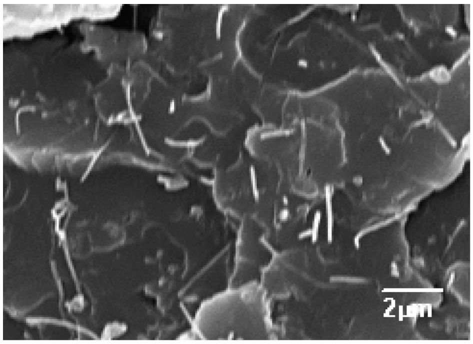

Figure 7. SEM micrographs revealing fracture surfaces with 2.0 wt% raw VGCF contents.

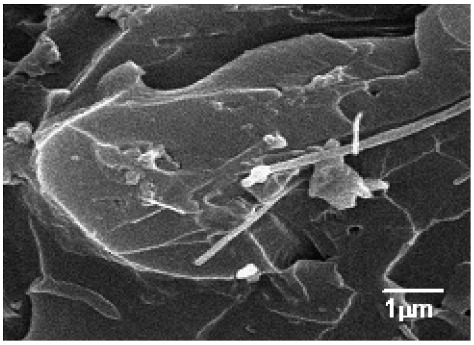

Figure 8. SEM micrographs revealing fracture surfaces with 2.0 wt% APT VGCF contents.

Atmospheric plasma treatment increased the roughness and surface area of carbon nanofibers. This implies that the APT VGCF had an excellent interfacial bonding with epoxy matrix by improving the area of adhesion at the interface between VGCF and epoxy. Correspondingly, the APT VGCF was broken under tensile test, since this is where the tensile strength of APT VGCF/epoxy was the greatest (Fig. 8).

4. Conclusions

In this study, the mechanical properties of epoxy nanocomposites reinforced by raw VGCF and APT VGCF were discussed. The effect of dispersion methods for VGCF in epoxy matrix was investigated.

Atmospheric plasma treatment of raw VGCF increased roughness and surface area. Thereby, atmospheric plasma treatment appears to have a positive effect by improving the interfacial bonding between VGCF and epoxy matrix. As a result, the tensile modulus of raw VGCF/epoxy matrix and APT VGCF/epoxy matrix showed similar values, but the tensile strength of APT/epoxy matrix was higher than that of raw VGCF/epoxy matrix with varying VGCF contents.

With ethanol as a dispersion aid solution, the ultrasonic method has provided well-dispersed raw VGCF and APT VGCF in the anhydride-cured epoxy matrix.

Acknowledgement

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