

# Mechanical and physical properties of epoxy composites reinforced by vapor grown carbon nanofibers

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## Abstract

Epoxy/vapor grown carbon nanofiber composites (VGCF) with different proportions of VGCF were fabricated by the in situ process.

The VGCFs were well dispersed in both of the low and high viscosity epoxy matrices, although occasional small aggregates were observed in a high viscosity epoxy of 20 wt.%. The dynamic mechanical behavior of the nanocomposite sheets was studied. The storage modulus and the glass transition temperature ( $T_g$ ) of the polymer were increased by the incorporation of VGCFs.

The electrical and mechanical properties of the epoxy–VGCFs nanocomposite sheets with different weight percentages of VGCFs were discussed. The results were that both had maximum tensile strength and Young's modulus at 5 wt.% for both materials and reduced the fracture strain with increasing filler content. The electrical resistivity was decreased with the addition of filler content. Mechanical, electrical and thermal properties of low viscosity epoxy composites were resulted better than that of the high viscosity composites.

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## 1. Introduction

Vapor grown carbon nanofibers (VGCFs) are widely interesting because they possess very high mechanical and excellent physical properties. Therefore, VGCFs are being used for reinforcing polymer matrices to improve the mechanical, thermal and electrical properties [1–5]. However, to develop high performance nano-filler/polymer composites, a homogeneous dispersion must be achieved of the fillers in the polymer matrices as well as a strong interface interaction between the polymer and the fillers so as to affect efficient load trans-

fer from the polymer matrices to the VGCFs. Therefore, uniform dispersion within the polymer matrices and improved VGCF/matrices wetting and adhesion are important issues in the processing of composites.

Most commonly, filler/polymer composites were prepared with well dispersed fillers in a polymer matrix by using solution casting [6–8], spin casting [7], melt spinning and extrusion processing. Several research teams have studied dispersion processing to improve the mechanical properties i.e., PP/VGCF [9], PP/CNT [10], PPS/VGCF [11] and PEEK/VGCF [12]. Some researchers also obtained well dispersed carbon nanotubes (CNTs) in a polymer by high energy sonication of a solution of polymers containing dispersed CNTs followed by a solvent-evaporation method which successfully achieved homogeneous composites [6,9,13].

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Furthermore, it is very important to understand the polymer morphology due to the presence of a nano-phase in order to perfectly analyze a nanocomposite.

This article deals with the preparation of the VGCF/epoxy composites by the in situ process and the investigation of the influence of the dispersion processing state and the analysis of the mechanical, electrical and thermal properties of nanocomposite sheets. The thermal decomposition, dynamic, tensile and friction mechanical analyses were conducted.

## 2. Experimental

### 2.1. Nanocomposite sheets processing

Presently work is being done to reinforce the VGCFs with a homogenous dispersion state in a polymer matrix as well as the composite sheet interface between the fillers and epoxy matrix. The mechanical properties of the composites were measured and characterized.

Carbon nanofibers called VGCF<sup>TM</sup> were obtained from Showa Denko Japan company with diameters of 150 nm and lengths of 10–20  $\mu\text{m}$  with high crystalline carbon nanofibers synthesized by the gas phase method and they are highly entangled and randomly organized. The matrix used in this study is an epoxy polymer based Bisphenol A resin (Epikote 825), supplied from Japan Epoxy Resin Co. Ltd. and an aromatic hardener (Triethylenetetramine). The epoxy matrix was mixed with an aromatic hardener; the proportion was 20 parts of resin to 1.5 parts aromatic hardener by volume.

To prepare the sample, two methods of epoxy resin/VGCF composites were performed. The first method used the low viscosity epoxy resin diluted in acetone to make a lower viscosity epoxy.

Before utilizing the VGCF, VGCFs were dried at 120 °C in a vacuum for 24 h to remove the water. Prior to the dispersion processing in an epoxy matrix, a sieve was used at 106 and 53  $\mu\text{m}$  in order to reduce the diameter of clumps. Then the VGCFs were dispersed in an acetone beaker by sonification and the stirring process at room temperature, 1000 RPM for 15 min. Next the epoxy resin was added to the mixture. Sonification and stirring processes continued at room temperature, 1000 RPM for another 15 min. In order to evaporate the acetone, the mixtures were placed in a vacuum oven at 80 °C for 3 h.

After complete evaporation of acetone, the mixture was placed in a vacuum oven to remove the voids at 60 °C for 30 min. After adding the hardener, the mixtures were manually mixed at room temperature for 10 min. Next, the mixture was put in a vacuum oven to remove the voids at room temperature for 10 min. When the mixture reached a gelling state, a small amount of mixture was placed between two metal plates

under pressure to try to reduce the residual voids. The metal plates were pressed to reduce voids and kept a constant uniform thickness between 0.12 and 0.17 mm. The nanocomposite sheets were prepared with various contents of VGCF. Subsequently, the samples were then post-cured at room temperature for 16 h and at 120 °C for 3 h to completely cure the materials.

The second method used a highly viscous epoxy resin. To fabricate the high viscosity epoxy nanocomposite sheets, the same process was performed as previously mentioned but without the acetone processing.

### 2.2. Thermal properties analysis

Thermal gravimetric analysis (TGA) was carried out using a DTG-50 instrument. The epoxy composites of 10 mg were placed in to a platinum crucible and heated up in air. The heating rate was 10 °C/min from room temperature to 800 °C under a constant air flow of 20 l/min. Dynamic mechanical thermal analyzer (DMTA) was used in air from room temperature to 200 °C using ITK DVA-225 instrument. All runs were performed using a frequency 10 Hz and heating rate of 5 °C/min. The sample size was 20  $\times$  4  $\times$  0.15 mm<sup>3</sup>. From this test, the storage modulus ( $E'$ ) and loss factor ( $E''$  or  $\tan \delta$ ) were obtained in the tensile mode.

### 2.3. Volume electrical resistivity property testing

Volume electrical resistivity measurements were taken by the standard four point technique. The volume electrical resistivity,  $\rho_v$ , was calculated using the following equation:

$$\rho_v = \frac{\Omega A}{L} \quad (1)$$

where  $\Omega$  is the electric resistance,  $A$  is the area of electrode and  $L$  is the distance between electrodes. Volume electrical conductivities were measured for all samples after remove the epoxy resin.

### 2.4. Mechanical properties testing

To be more precise about the critical point of 5 wt.% nanocomposite sheets were fabricated at 3 and 7 wt.% for both materials.

The tensile test samples were prepared 50  $\times$  10  $\times$  0.15 mm<sup>3</sup> in size. The tensile strength and Young's modulus were obtained from the tensile test, performed according to ISO 527-3, and was carried out using a Shimadzu tensile tester (AGS-J) at a cross-head speed of 1 mm/min.

The coefficient of friction was obtained by a friction test which was performed with a pin on a sample disc at 25 °C and 40% relative humidity. This friction test consisted of a rectangular nanocomposite pin sliding

against nanocomposite sheets. The sliding speed of friction test was of 0.5 mm/s. After running in at a load of 10 N and 5 cycles, then the friction coefficient was measured.

### 2.5. Scanning electron microscopy observation (SEM)

Scanning electron microscopy samples were taken of the dispersed of the VGCFs in an epoxy and were fractured after the tensile testing. All samples were gold coated to prevent charging.

## 3. Results and discussion

### 3.1. Microstructure

We found the best mixing time was between 30 and 40 min. This indicated that the fibers were not aggregated and had no breakage. Because, lower time gave adequate mixing and dispersion of the VGCFs in the polymer. While, higher times resulted in VGCF breakage which means that the VGCFs became about 20% shorter than the initial fiber length.

Fig. 1 shows the micrographs of the epoxy/VGCF composite sheets with VGCF content of 5 wt.% with and without pressure processing. In Fig. 1(a), we observed some voids in the composite that did not undergo pressure processing and no voids were noticed in the composite with the pressure processing (Fig. 1(b)).

The nanocomposite sheets were examined in a scanning electron microscope in order to determine the quality of the structure. Typical SEM images of the composites are shown in Fig. 2. They showed a high level of dispersion for all materials, although occasional small aggregates were observed in the high viscosity epoxy of 20 wt.% (Fig. 2(d), arrow). Comparing the high and low viscosity epoxy composites showed that the dispersion of low viscosity epoxy composites was better than the high viscosity epoxy composites due to the different polymer viscosity.

Fig. 3 shows SEM images of voids on the fracture surfaces of nanocomposite sheets after the tensile test. We observed that the voids and voids size increased with increasing VGCFs loading for both materials. Comparing both composites, there are more amount of voids, as can be seen from Fig. 3(a) and (b) due to the high viscosity epoxy polymer.

We also measured the void of the composites as a function of VGCF content. It is seen that the void increases with the fiber content for both composites (Fig. 4). This indicates that the infiltration of liquidized epoxy becomes more difficult with increasing VGCF loading.

Comparing both composites, the void content of low viscosity epoxy composites was lower than the high viscosity epoxy composites due to the different viscosity polymer. So poorer dispersion occurs, indicating the filler aggregates can act as defects which can lead to the formation of voids within the fibers. Therefore, the porosity could be under the influence of mechanical properties [14]. On the other hand, the low viscosity composites were dispersed well and had fewer voids which should improve the high mechanical properties more than the high viscosity epoxy composites.

### 3.2. Electrical property

The influence of VGCF concentration on volume electrical resistivity was measured for the high and low viscosity epoxy nanocomposite sheets which are shown in Fig. 5. In Fig. 5, both composite sheets are similar in terms of the electrical resistivity versus fiber concentration and show that the electrical resistivity decreases with increasing VGCFs loading.

We compared both composite sheets and the high electrical resistivity was measured for the high viscosity epoxy composites. It is estimated that the dispersion of VGCF was not good using the manual mixing process because of the high viscosity of the epoxy polymer. Therefore the creation network of fibers in high viscosity epoxy nanocomposite is weaker than low viscosity epoxy composites (see Fig. 2).

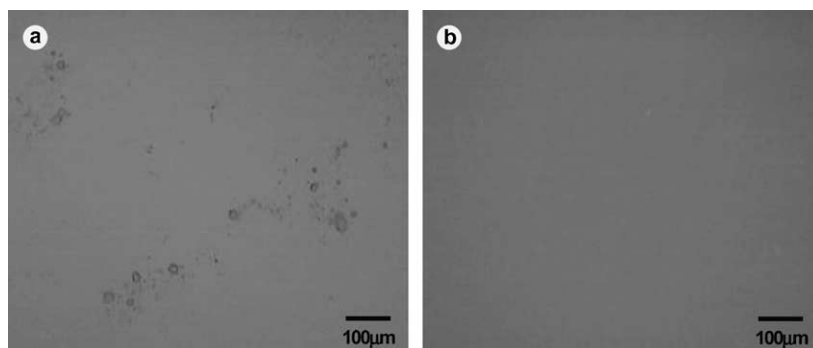


Fig. 1. Optical microscopy of VGCF content of 5 wt.% composites, without (a) and with (b) pressure processing.

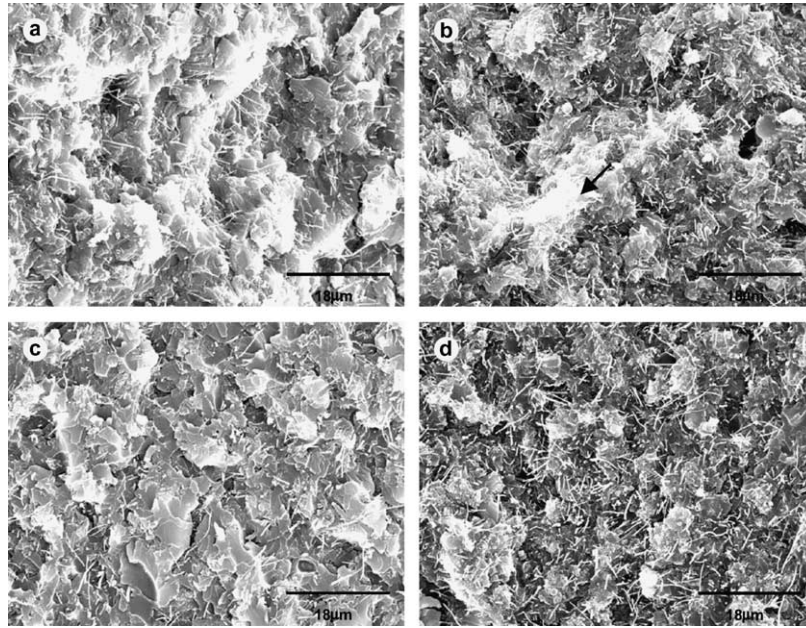


Fig. 2. SEM micrographs of dispersion of VGCF in an epoxy matrix: (a) 5 wt.% and (b) 20 wt.% high viscosity, (c) 5 wt.% and (d) 20 wt.% low viscosity.

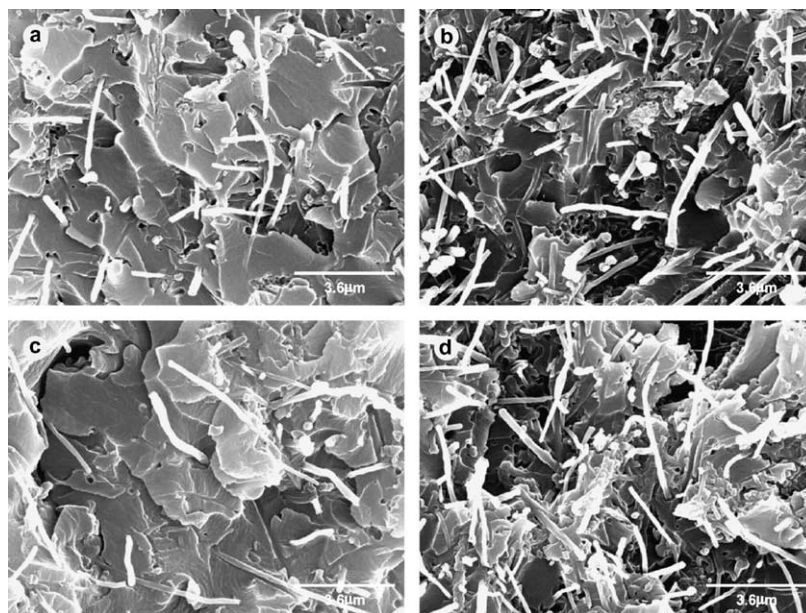


Fig. 3. SEM micrographs of voids of composites: (a) 5 wt.% and (b) 20 wt.% high viscosity, (c) 5 wt.% and (d) 20 wt.% low viscosity.

### 3.3. Thermal properties

Fig. 6 shows the TGA curves of low viscosity pure epoxy and various filler contents composites. All samples started to decompose at around 260 °C (first stage) and are completely decomposed at about 640 °C, 720 °C, 730 °C and 735 °C (third stage) for pure epoxy, epoxy/5 wt.%, 10 wt.% and 20 wt.% VGCF composites, respectively. Comparing with the TGA curves of pure epoxy and epoxy/VGCF blending composites, the decomposi-

tion of materials shifted to a high temperature with increasing VGCF content (from second stage). This means that the incorporation of VGCFs into epoxy offers a stabilizing effect against the decomposition. Similar effects have been observed in nanotube composites based on other polymers, and are thought to relate to radical capture by the nanotube surface and by the interactions between the carbon fibers [15–17].

The tensile storage ( $E'$ ) and loss modulus ( $\tan \delta$ ) properties of the composites were characterized



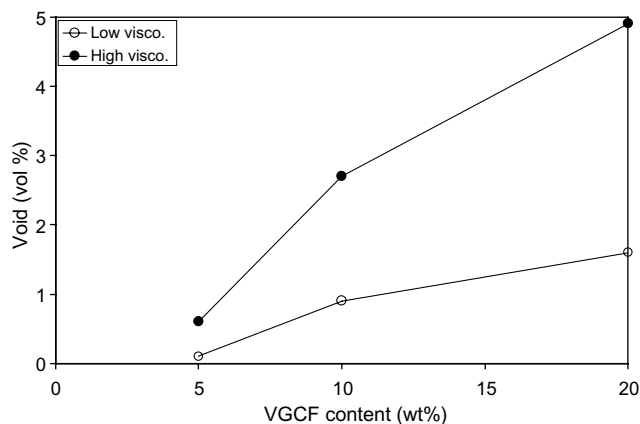


Fig. 4. Composites void as a function of fiber loading.

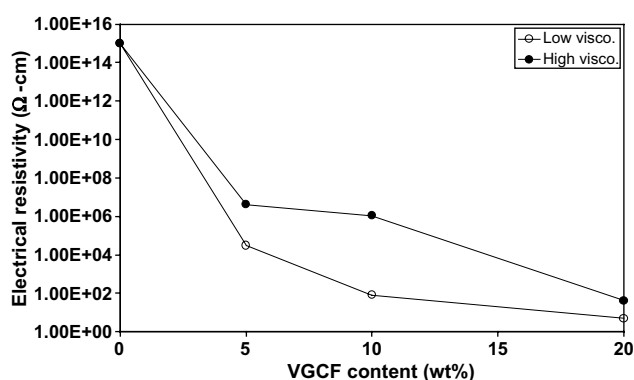


Fig. 5. Electrical resistivity of epoxy/VGCF as a function of the fiber loading for high and low viscosity epoxy nanocomposite sheets.

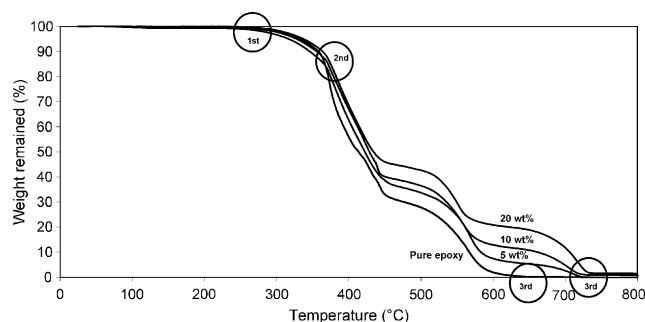


Fig. 6. TGA curves of low viscosity pure epoxy and various nanocomposite sheets.

by DMTA as a function of VGCF loading and temperature. Fig. 7 shows that the storage modulus decreased corresponding to the glass transition temperature ( $T_g$ ). This modulus drop is therefore ascribed to an energy dissipation phenomenon involving cooperative motions of the polymer chain. We also estimated an increase in the storage modulus of both materials above the glass transition temperature with increasing filler content. Particularly, the temperature close to the glass transition temperature of nanocomposite and the effect being

more pronounced around the softening point of the matrix. Therefore, more filler is able to enhance greater stiffness in the polymer matrix.

For instead at around 80 °C, the storage modulus of composite with 20 wt.% filler content is 14 and 27 times for the high and low viscosity epoxy composites, respectively compared to that without filler. Similar observations had been made from Shaffer and Windle [18,19]. For comparison, the storage modulus of the low viscosity epoxy composite was higher than the high viscosity epoxy composite. Because the VGCF of low viscosity epoxy composite was well dispersed there was good interaction with the epoxy matrix and fewer voids in composites.

The tangent of the ratio of the complex to real modulus ( $\tan \delta$ ) is a measure of damping, and in this case, the peak in  $\tan \delta$  corresponds to the glass transition (Fig. 8).

We estimated that the presence of the nanofillers weakly influenced the peak position in the case of the pure matrix and the 5 wt.% of VGCF content for both materials. While, both the VGCF content 10 and 20 wt.% composites significantly affected the peak position. Evidently, VGCFs restrict the segmental motions of the polymer chains in the composites, resulting in a higher  $T_g$ . Furthermore, in the glass transition region, the VGCFs act as resistance to viscous flow of the polymer chains.

The decreasing height of the peak with increasing VGCF loading is to be related to crosslinking densities as fillers loading goes up especially loading of 20 wt.%. We also noted the presence of the VGCF, there was a broadening of the peak due to the unconstrained segments of the polymer molecules retained the  $T_g$ . But those segments close to the nanofiller surface were less mobile which lead to an increase in  $T_g$ . Similar effects have been observed in other polymer systems filled with finely divided materials [20].

From Figs. 7 and 8, we concluded that VGCF reinforcing effect at high temperature improves the thermal stability of the nanocomposite materials. Indeed, the stiffness of the non-reinforced matrix decreases with temperature.

Fig. 9 describes the relation between the glass transition temperatures ( $T_g$ ) as a function of the VGCF content. The glass transition temperature was assigned as the temperature at peak maximum of  $\tan \delta$  as shown in Fig. 8. These results show that  $T_g$  of the both VGCF/epoxy composites are higher than that of the pure epoxy. This means that a molecular mobility is restricted due to the presence of VGCF reinforcement, it results in enhanced the  $T_g$ .

For example, in VGCF/epoxy of low viscosity epoxy nanocomposite at 20 wt.% VGCF loading, the glass transition temperature increased about 26 °C comparing with pure epoxy. While the glass transition temperature decreased at 20 wt.% VGCF loading for high viscosity

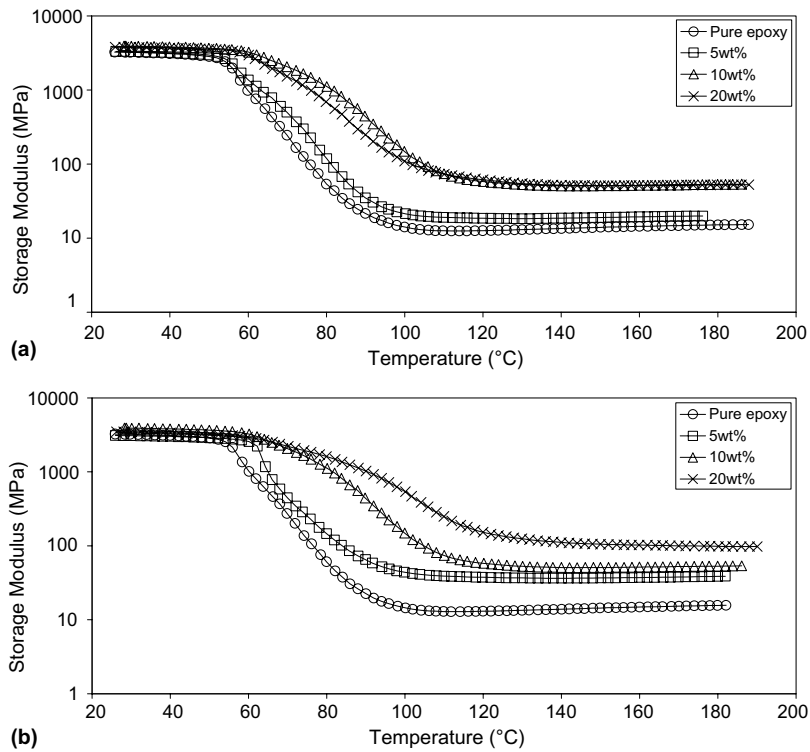


Fig. 7. Dynamic mechanical thermal analysis of epoxy composites as a function of temperature with logarithm of the storage modulus (a) high and (b) low viscosity epoxy.

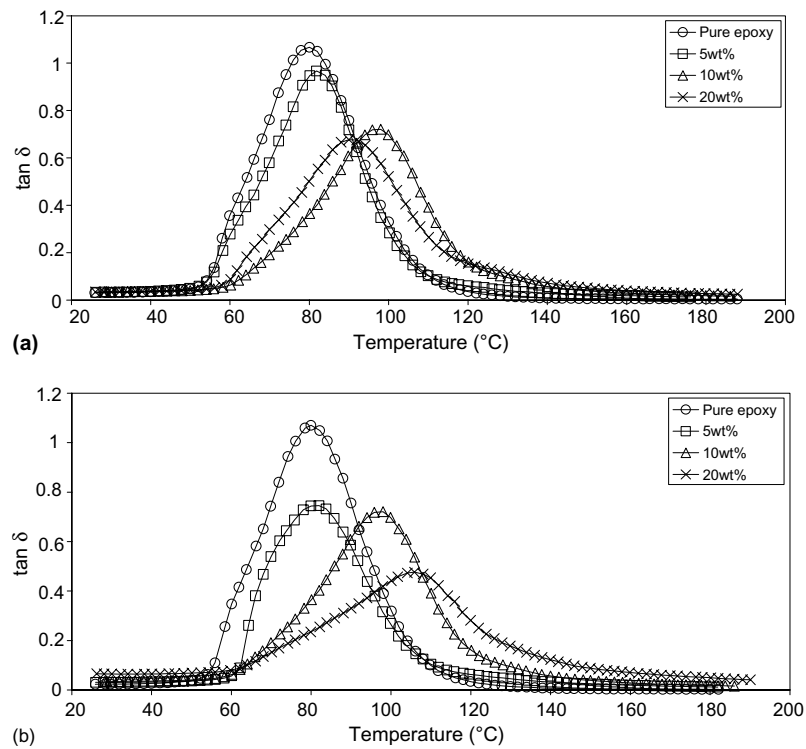


Fig. 8. Dynamic mechanical thermal analysis of epoxy composites as a function of temperature of the tangent  $\delta$  (a) high and (b) low viscosity epoxy.

epoxy nanocomposite. This decrease is probably due to less interaction between the fillers and epoxy because of

the presence of voids and poor dispersion of VGCF in the composites.

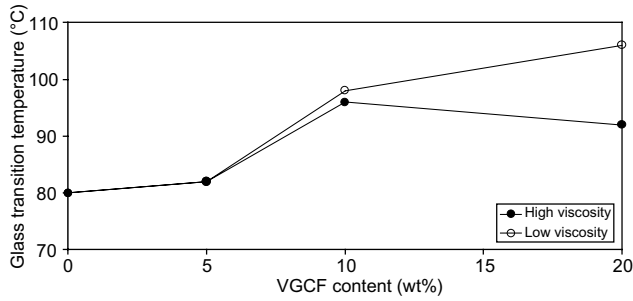


Fig. 9. Glass transition temperature of epoxy and various composites versus VGCF content.

3.4. Mechanical properties

The stress–strain curves of the matrix and of the composite containing 0, 3, 5, 7, 10, and 20 wt.% VGCFs of high and low viscosity epoxy composites are depicted in Fig. 10(a) and (b). These results showed that the maximum strain to failure was about 2.8% and 2.5% for high

and low viscosity pure epoxy composites, respectively and their mechanical behaviors were almost the same. While the stain to failure point decreased both composites when the VGCFs content increased. This result is in contrast to previous studies in which the addition of VGCFs reduced the impact and tensile strength properties of polycarbonate [21,22] and the strain to failure of polypropylene [23]. In case of our results, this effect were well pronounced for the 20 wt.% of both composites, which showed brittle fracture behaviors.

The tensile strength and Young’s modulus for both materials plotted in Fig. 11(a) and (b). It showed that the reinforcement effect reaches a maximum for tensile strength and Young’s modulus at 5 wt.%. At higher contents, the mechanical properties decreased with filler loading, common in both materials. There are three main reasons concerning this decreasing effect:

First, the dispersion of VGCF is more homogeneous in the 5 wt.% composite.

Second, as the VGCF content increased, the plastic range decreased considerably. This can be attributed in

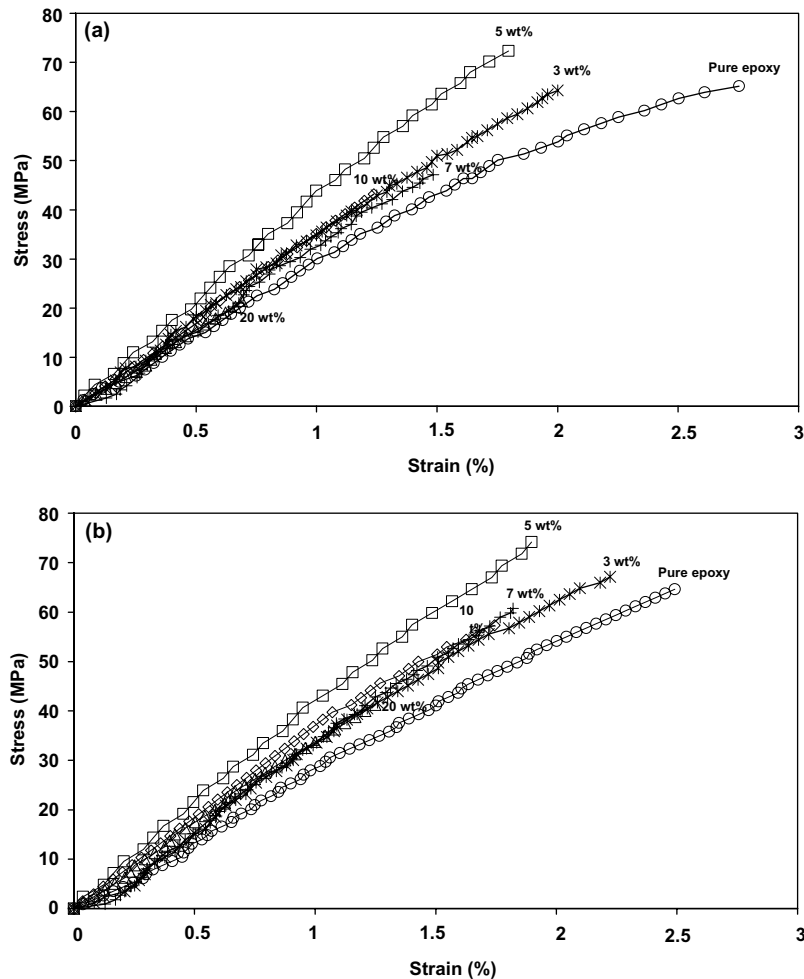


Fig. 10. Representative stress–strain curves as a function of VGCF loading for (a) high and (b) low viscosity epoxy composites.

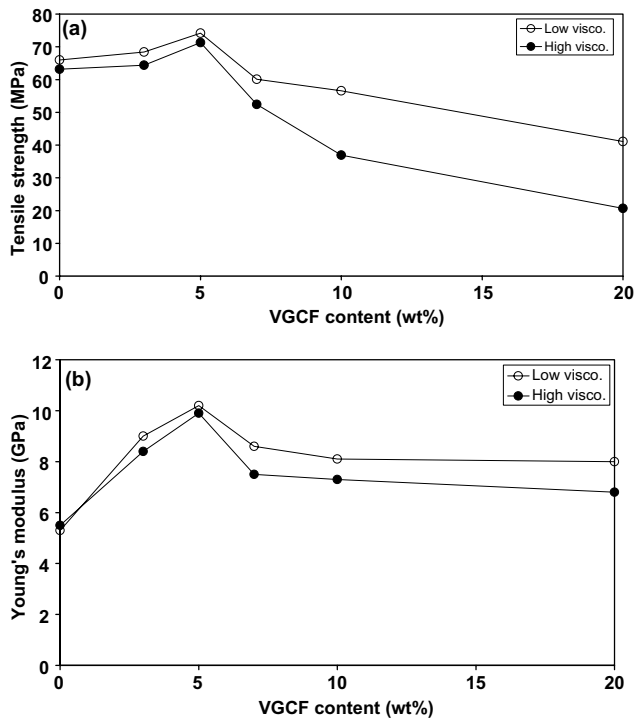


Fig. 11. Effect of VGCF loading on the (a) tensile strength and (b) Young's modulus of high and low viscosity epoxy composites.

part to modification of the crystalline fraction of the matrix. Therefore, it causes a decrease in ductility and an increase in brittleness.

Third, the voids may be also another effect for the decrease of the mechanical properties. In fact, we observed that few voids were produced during the curing process and the voids increased with the VGCF content increasing. These voids could be under the influence of mechanical properties.

Comparing the mechanical properties in both composites, the high mechanical properties resulted in a low viscosity composite. This may be due to well dispersed fillers and the number of porosities was much lower than the high viscosity composite. We also observed that the mechanical properties of high viscosity epoxy composites dramatically decreased after 5 wt.%. Because of the cracks appeared only for the high viscosity epoxy nanocomposite sheets with VGCF content at 10 and 20 wt.% (Fig. 12).

These cracks occurred at low VGCF density areas then propagated along the weak VGCF–epoxy interface of relatively low VGCF density regions. Some fibers pulled-out from the epoxy matrix and increases with the filler content. It is clear that the available resin was not sufficient to wrap all the remaining available volume. To avoid this problem, the fibers must possess a good functionalisation of the outer surface to make a low contact angle and high surface energies as well as create a strong interface interaction between the poly-

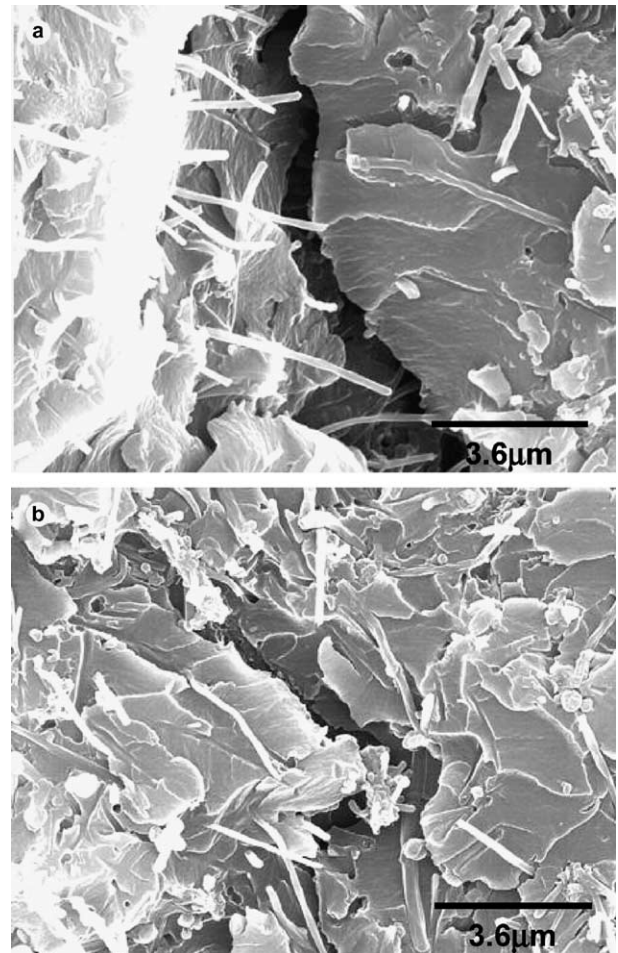


Fig. 12. Showing strengthening mechanisms in VGCF-based (a) 10 wt.% and (b) 20 wt.% for high viscosity epoxy composites of nanoscale reinforcement with a crack.

mers and the fillers so as to induce efficient load transfer from the polymer to the fibers. There are various common surface treatments of carbon fibers in previous work that involves oxidation, whereby oxygen containing functional groups are formed on the surface of the fibers. We can achieve the oxidation by heat treatment in air, oxygen, chemical treatment, plasma treatment and ozone treatment etc.

We compared the other research results concerning the pure epoxy and the around 4 wt.% of carbon nanofiller content [24] that our nanocomposite had approximately double the tensile strength and quadruple the Young's modulus of un-reinforced and reinforced materials. These different results are because the processing was different for the composites, especially the void removal process.

The variation of friction coefficients for pure epoxy and the composites with various VGCF content are shown in Fig. 13. The friction coefficient of both materials was obtained and the coefficient of friction of both materials decreased when the VGCF content



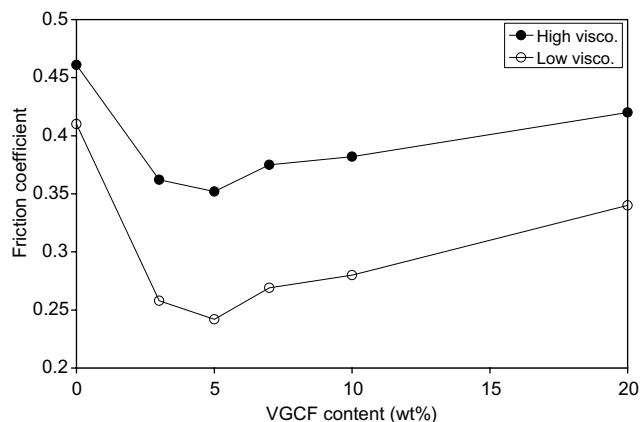


Fig. 13. Variation of friction coefficient with VGCF content.

was at 5 wt.%, then the variation of the friction coefficients increased when the VGCF loading surpassed 5 wt.%. We estimated that the filler was well dispersed for the small amount of VGCF content and the voids increased when VGCF content increased.

For comparison, the friction coefficient of the low viscosity epoxy composite was lower than the high viscosity epoxy composite. Because there were high void content and poor dispersion for high viscosity epoxy composites.

This study showed that the VGCFs were effective in reducing the coefficient of friction of epoxy when added in an amount of 5 wt.%. This weight comes to a critical point about mechanical and tribological properties of the nanocomposite sheets. The above observation agrees well with the results of the tensile test of the composites.

#### 4. Conclusions

This study has successfully explored the potential of various VGCFs loading for manual and mechanical reinforcements in high and low viscosity epoxy nanocomposite sheets. The vapor grown carbon nanofibers were dispersed well into the epoxy matrix but there were some aggregations of the VGCF in the 20 wt.% of high viscosity epoxy composites and the void and voids size increased with increasing VGCF loading. The addition of VGCF decreased the electrical resistivity for both materials.

The VGCFs delayed the decomposition of epoxy. The storage modulus and the glass transition temperature of the polymer significantly increased with increasing VGCF loading fraction.

Both maximum tensile strength and Young's modulus resulted at 5 wt.%. This indicates good fiber dispersion and less voids for both 5 wt.% of VGCF. We also observed; the mechanical properties of high viscous

composites dramatically decreased after 5 wt.%. This is due to cracks that appeared only in high viscosity epoxy nanocomposite sheets with VGCF content at 10 and 20 wt.%. The cracks were produced at low VGCF density areas and then propagated along the weak VGCF–epoxy interface.

The coefficient of friction of both materials obtained at 5 wt.% of VGCF content was good. We estimated this was because the filler was well dispersed and had fewer voids in composites. The 5 wt.% is a critical point for mechanical and tribological properties of the composites.

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