Electrically Conductive Epoxy/Clay/Vapor Grown Carbon Fiber Hybrids

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1. Introduction. Many electronic components and devices are being made from polymer-based composites. For polymer-based composites being used in these applications, a high electrical conductivity is required to provide electrostatic discharge (ESD) and electro magnetic interference (EMI) shielding. As electronic devices become smaller and faster, their sensitivity to static discharge increases and the need for an increased rate of ESD becomes vital. Conventionally, conductive fillers such as carbon black are incorporated into polymers in order to achieve electrical conductivity above the required order of 10^{-6} S m^{-1} for ESD.[1] However, a large amount of carbon black, usually 15−20 wt % or more, needs to be mixed into polymers to achieve the required level of conductivity, which leads to poor surface finishing of the components. Contaminations caused by the poor surface finishing have limited the applications of the carbon black-based polymer composites.

The key factors to achieve high conductivity in polymer-based composites are primarily the conductivity and dimension of fillers, followed by the filler dispersion, i.e., an effective filler dispersion to achieve high conductivity. Recently, carbon nanotubes (CNT) have been incorporated into polymers based on the first factor due to their excellent electrical property and high aspect ratio. Sandler et al. have achieved a volume conductivity around 10^{-2} S m^{-1} with a CNT volume fraction as low as 0.1 vol % in epoxy matrix.[1] Allaui et al. achieved a volume conductivity of 10^{-3} S m^{-1} with CNT content of 4 wt %.[2] A conductivity of 10^{-2} S m^{-1} was obtained with CNT content of 10 wt % by Shaffer et al.[3] The percolation threshold was different in each case, although multiwalled carbon nanotubes (MWNT) were used in all the studies. It suggests that not only the conductivity and dimension of CNT but also the CNT dispersions in polymers are critical to achieve a high conductivity with a low percolation threshold.

Vapor grown carbon fibers (VGCF) have been also used in polymer composites for the applications in ESD and EMI shielding. The electrical property of VGCF although is not as high as that of CNT, the cost of VGCF is much more inexpensive compared with that of CNT. Xu et al. reported that a vinyl ester resin-based composites with 8 wt % VGCF showed a resistivity of 10^2 Ω m and a percolation threshold of 2−8 wt %.[4] Lozano et al. reported that 15−20 wt % VGCF was required in PP matrix to achieve a volume resistivity of 10^6 Ω m.[5] Gordeyev et al. reported that the percolation threshold for PP/VGCF composites was about 4−5 vol %.[6] It has been found that relatively large amount of VGCF is needed to achieve a high conductivity/low resistivity compared to CNT.

A few studies have been reported so far on the effect of filler dispersion on electrical properties. Sumita et al. described that the preferential VGCF dispersion could be achieved using a blend of at least two incompatible polymers as the matrix, and VGCF dispersed predominantly in the polymer having a better affinity with VGCF.[7] In this approach, two or more polymers are needed to form a polymer blend in which the polymers selection are based on two criteria; the miscibility between each polymer, and the affinity of conductive fillers to a polymer.

In this study, effects of highly exfoliated clay layers on electrical properties of epoxy/clay/VGCF hybrids were studied. VGCF was chosen as the conductive fillers because of its low cost compared to CNT and the excellent electrical properties. The objective of this study was to propose new approach to develop electrically conductive polymer-based materials with minimum conductive filler content and without sacrificing other properties as cost-effective conductive materials for practical applications, especially for the ESD materials. VGCF-based epoxy hybrids with thermoplastic polymer particles were also prepared and investigated in this study to gain better understanding of the mechanism of a low percolation threshold observed in epoxy/clay/VGCF hybrids system.

2. Experimental Section. Two types of VGCF (VGCF and VGCF−H, Showa Denko) with different fiber length were mixed with a bisphenol A diglycidyl ether (DGEBA) type of epoxy (DER332, Dow Plastics) using a Thinky Mixer AR-250 (Thinky Corporation) for 10 min. The VGCF and VGCF−H have a fiber diameter of 150 nm and lengths of 10−20 and 5−10 μm, respectively. VGCF content was varied in a range from 1 to 10 wt %. The epoxy-based composite sheets with 0.5 mm in thickness were cured with a curing agent (Ethacure 100-LC, Albemarle Corporation) at 100 °C for 2 h and 180 °C for 5 h.

For epoxy/clay/VGCF hybrids, clay was first mixed into the epoxy resin by a “slurry compounding” approach.[8] The clay used is sodium montmorillonite (PGW) from Nanocor Inc., with a cation exchange capacity (CEC) of 145 mequiv/100 g, an aspect ratio of 200−400, a d001 spacing of 12.5 Å and a specific density of 2.6 g/cm3. The pristine clay (4 g) was dispersed into 120 mL of deionized water to form a suspension, which was stirred at room temperature for 24 h and sonicated for 30 min. The suspension was poured in 800 mL of ethanol and stirred vigorously for 5 min. A white precipitate formed, which was filtered and washed three times with ethanol. The wet product was added to 80 mL of ethanol to form a clay/ethanol slurry. 3-Glycidoxypropyltrimethoxysilane (GPTS) (0.2 g) was added into the slurry. The slurry was stirred for 10 h and sonicated for 30 min at room temperature. Afterward, the slurry was mixed with specific quantities of epoxy resin at 50 °C and stirred for 2 h. Ethanol was evaporated by drying in a vacuum oven at 50 °C, 3 mmHg, for 48 h. VGCFs were then mixed into the epoxy/clay system using a Thinky Mixer for 10 min. The clay content was varied from 1 to 5 wt %.

Poly(vinylidene fluoride) (PVDF, 301F, Atofina) powders of spherical shape with about 100 μm in diameter were used as

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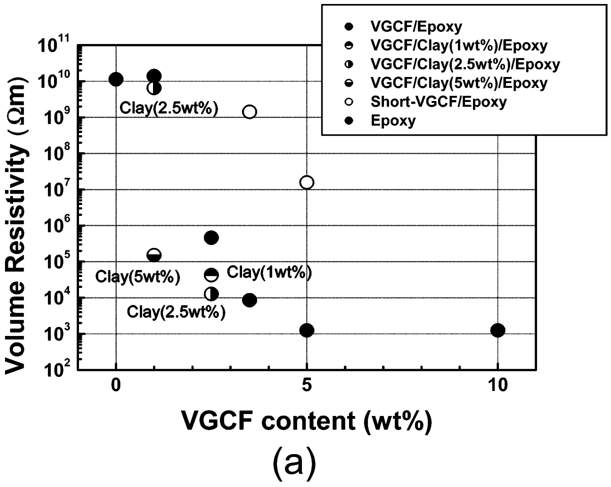


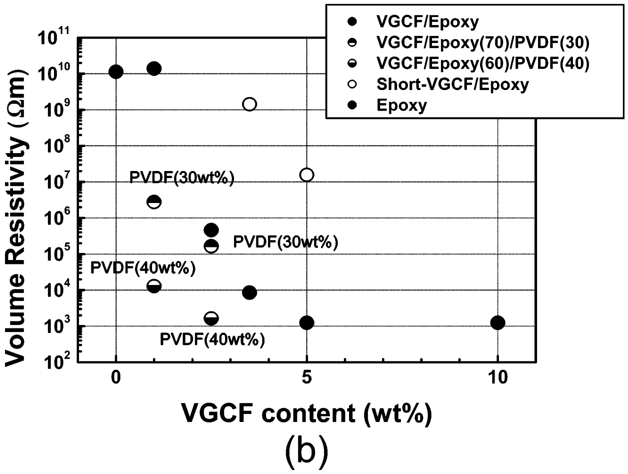
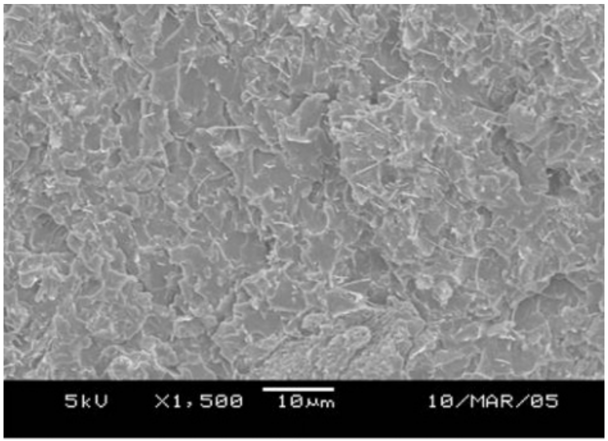


Figure 1. Relationship between volume resistivity and VGCF content: (a) epoxy/clay/VGCF hybrids and (b) epoxy/PVDF/VGCF hybrids.

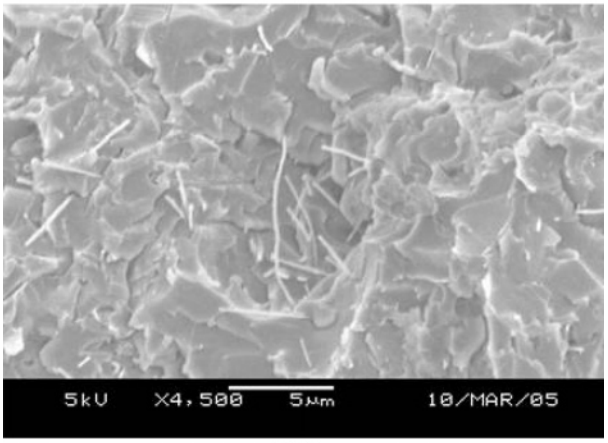
the alternate phase of clay. The PVDF powders were first mixed into epoxy resin using a Thinky Mixer for 10 min, followed by mixing VGCFs into the epoxy/PVDF system using a Thinky Mixer for 10 min. PVDF contents were varied as 30 and 40 wt %. The hybrid systems were cured under the same conditions as the epoxy/VGCF systems.

Volume resistivity of the VGCF-based nanocomposites were measured using resistivity test fixture (model 8009, Keithley) and electrometer/high resistance meter (model 6517A, Keithley) according to ASTM D257. The nanocomposites were mounted between two electrodes attached to the resistivity test fixture, and subjected to the applied voltage of 40 V for 30 min to measure a resistivity. Tensile tests were carried out using an Instron 8800 microforce tester at a crosshead speed of 1 mm/min according to ASTM D-638. Dog-bone bars (Type V, gauze size 7.62 × 3.18 × 3.0 mm) were machined with a Ceast contour cutter. The mode I critical stress intensity factor (K_{IC}) was measured using single-edge-notch 3-point bend (SEN-3PB) specimens with the geometry of 60 × 12.7 × 3.0 mm. The SEN-3PB tests were conducted using an Instron 8800 microforce tester at a crosshead speed of 0.5 mm/min.

3. Results and Discussion. Figure 1 a shows the relation between volume resistivity and VGCF content of epoxy/VGCF nanocomposites. Longer VGCF led to much lower volume resistivity compared to shorter VGCF. The longer VGCF nanocomposites achieved a volume resistivity lower than 10^6 Ω m with VGCF content of 2.5 wt % and an order of 10^3 Ω m with VGCF content of 5 wt %, but the shorter VGCF nanocomposiets showed only 10^7 Ω m with 5 wt % VGCF. It suggests that the aspect ratio of electrically conductive fillers is an important parameter to achieve low resistivity with small amount of conductive fillers. In contrast with the epoxy/VGCF binary systems, the volume resistivity was significantly decreased by incorporating small amount of clay. The clay contents of 1 and 2.5 wt % led to data on the order of 10^4 Ω m with a VGCF content of 2.5 wt %, and the addition of 5 wt % clay resulted in a volume resistivity as low as 10^5 Ω m with only 1 wt % VGCF. It has been found that a low volume resistivity in a range of ESD can be achieved with a relatively small amount of VGCF by incorporating a small amount of clay.



(a)



(b)

Figure 2. SEM micrographs of brittle fracture surface of epoxy/clay (2.5 wt %)/VGCF (2.5 wt %) hybrids.

Figure 2 shows SEM micrographs of the brittle fracture surface of epoxy/clay/VGCF hybrids. VGCFs were uniformly dispersed in epoxy matrix, but some clusters of VGCFs were still observed (Figure 2b). TEM micrographs of epoxy/clay nanocomposites and epoxy/clay/VGCF hybrids are shown in Figure 3. In the epoxy/clay nanocomposites, the clay layers were highly exfoliated in an epoxy matrix (Figure 3, parts a and b). A high degree of exfoliation of the clay layers was also observed in the epoxy/clay/VGCF hybrids (Figure 3, parts c and d); i.e., the addition of VGCF into the epoxy/clay nanocomposites did not affect the clay exfoliation in the hybrids. In the hybrids, VGCFs were not found in the exfoliated clay layers but were excluded by the clay layers (Figure 3d). The SEM and TEM

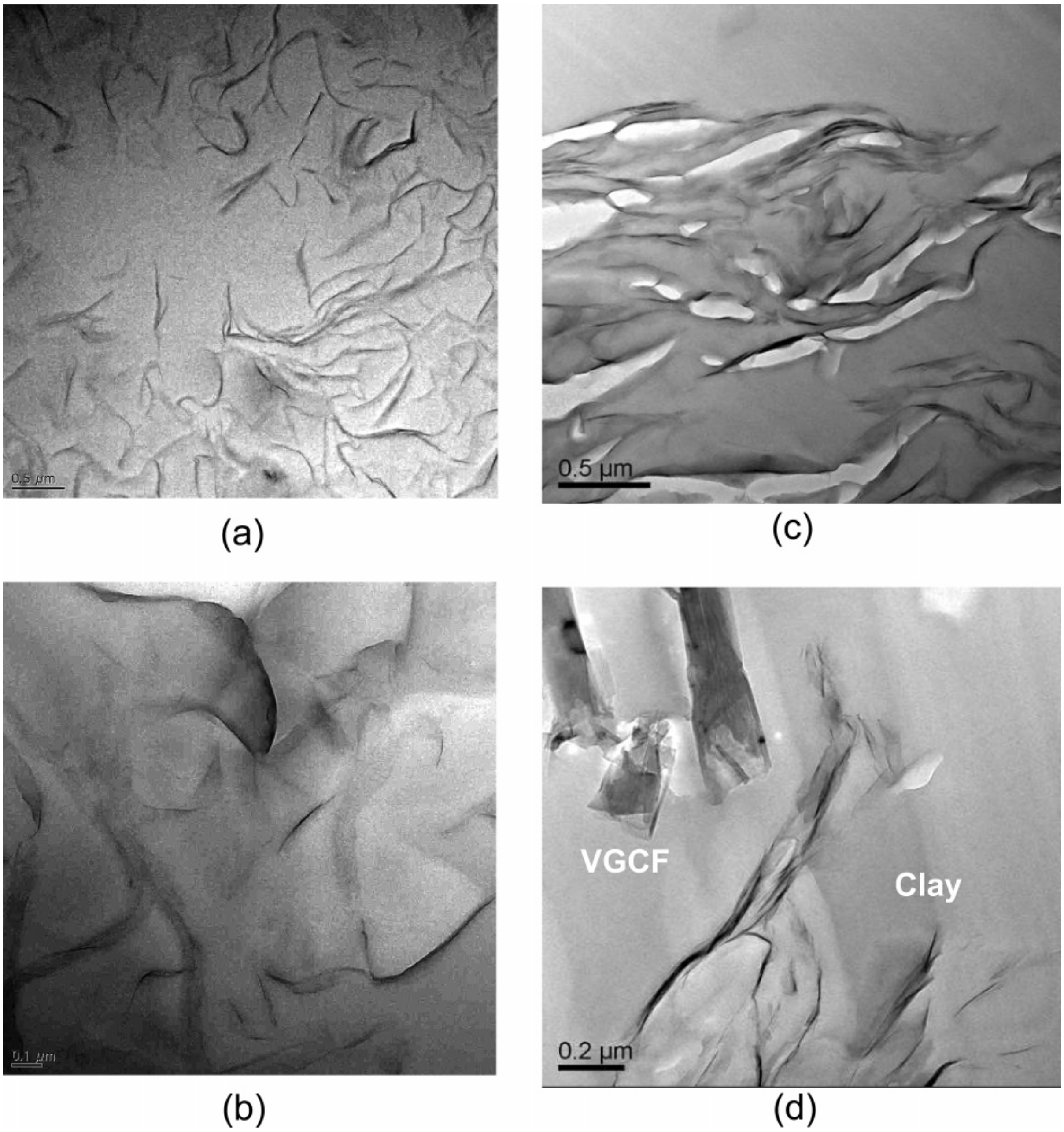


Figure 3. TEM micrographs of (a, b) epoxy/clay (2.5 wt %) nanocomposites and (c, d) epoxy/clay(2.5 wt %)/VGCF(2.5 wt %) hybrids.

micrographs suggest that an effective VGCF dispersion of electroconductive network is developed by the highly exfoliated clay layers, in which the VGCFs are excluded from clay dominated areas.

Relationship between volume resistivity and VGCF content of epoxy/PVDF/VGCF hybrids is shown in Figure 1b in a comparison with epoxy/clay/VGCF hybrids. PVDF particles with 40 wt % content were required to achieve a volume resistivity as low as that of epoxy/clay/VGCF hybrids with small amount of VGCF content. Figure 4 shows SEM micrographs of brittle fracture surface of epoxy/PVDF/VGCF hybrids. PVDF particles of spherical shape with about 100 mm in diameter was seen on the fracture surface as same shape/size as the raw materials, indicating that the PVDF particles were not fully melted during the post-curing process at 180 °C although it is close to the melting point of the PVDF. VGCFs located near by interface region between PVDF particles and epoxy matrix were seen; i.e., VGCFs were excluded by PVDF particles and developed an electrically conductive network by their effective dispersion. The enrichment of VGCF in the interfacial regions might be due to the high affinity of VGCF to PVDF and the partially melted PVDF particles in the interfacial regions during the post-curing process of the epoxy resin. The mechanism used to achieve a low volume resistivity with a small amount of VGCF is considered to be same as that of epoxy/clay/VGCF hybrids, i.e., a volume exclusion effect. However, it is noteworthy that the electrical properties of the VGCF-based hybrids can be enhanced by a much smaller content of the additional phase when highly exfoliated clay layers are incorporated. It suggests that highly exfoliated clay layers with 2.5 wt % in content are equivalent to PVDF particles with 30−40 wt % in terms of the volume exclusion effect on VGCF dispersion, i.e., the exfoliated clay layers leads to about 30−40% of clay-rich regions in volume with only 2.5 wt % of clay incorporation.

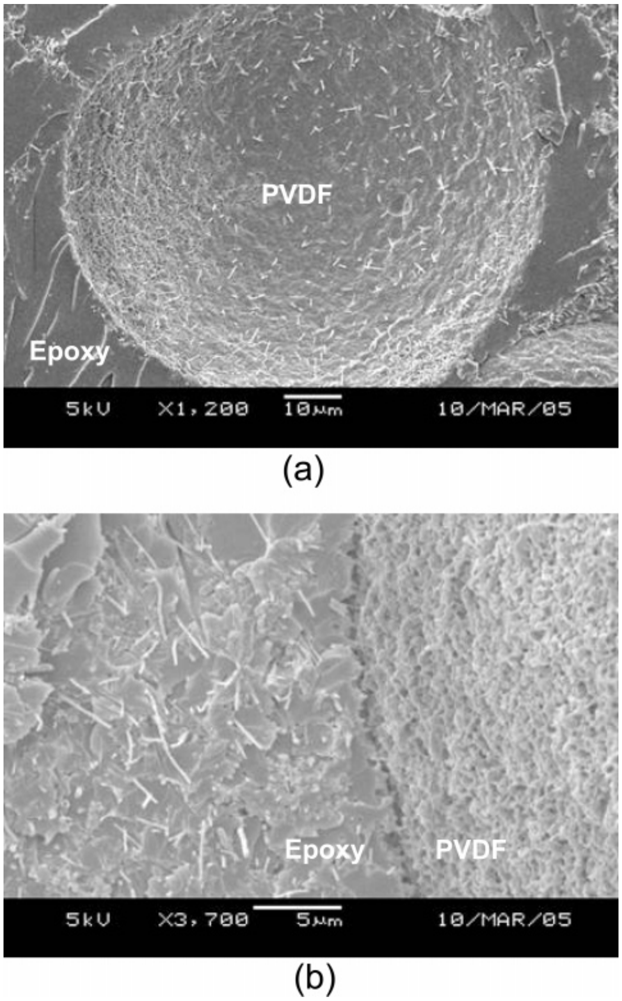


Figure 4. SEM micrographs of brittle fracture surface of epoxy/PVDF (40 wt %)/VGCF(2.5 wt %) hybrids.

Tensile tests and fracture toughness tests were conducted in order to investigate effect of clay addition on mechanical properties of the epoxy/VGCF nanocomposites. The addition of 2.5 wt % clay reduced tensile strength of the epoxy-based nanocomposites with 2.5 wt % VGCF by about 17%, but maintained the tensile modulus and significantly increased the fracture toughness by about 38%. It can be expected that other properties including barrier properties, flame retardancy, and thermomechanical properties are improved by incorporating exfoliated clay layers as the nature of clay layers. Hence, the epoxy/clay/VGCF hybrids developed in this study can be good candidates for many engineering applications where high conductivity and high mechanical and other physical properties are required.

4. Conclusions. Electrically conductive epoxy-based hybrids filled with VGCF and clay were developed. The VGCF-based hybrids with highly exfoliated clay layers have a low volume resistivity with a relatively low VGCF content, i.e., a low percolation threshold. The low volume resistivity was achieved by an effective VGCF dispersion of electroconductive network enhanced by highly exfoliated clay layers.

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