[Edge-functionalized graphene-like platelets as co-curing agents and nanoscale additives to epoxy resin]

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[Edge-functionalized graphene-like platelets as co-curing agents and nanoscale additives to epoxy resin]

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___________________________
Major Advisor
[Jong-Beom, Baek]
[Edge-functionalized graphene-like platelets as co-curing agents and nanoscale additives to epoxy resin]

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Abstract

Epoxy or polyepoxide is a thermosetting polymer formed from reaction of an epoxide "resin" with polyamine "hardener". Epoxy has a wide range of applications, including fiber-reinforced plastic materials and general purpose adhesives. In general, epoxies are known for their excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties and very good electrical insulating properties. Exfoliation of graphite, including into individual layers (graphene), is of great interest due to the exceptional properties. Graphite can be exfoliated into graphene sheets by physical and chemical methods, and graphene can also be grown by chemical vapor deposition on metal substrates as well as from single crystal silicon carbide. In this work, the method for edge-functionalization of ‘pristine’ graphite through “direct” Friedel-Crafts acylation in polyphosphoric acid/phosphorous pentoxide medium has been developed. Reactive 4-aminobenzoyl-functionalized graphite (AB-graphite) could be produced from the reaction between 4-aminobenzoic acid and ‘pristine’ graphite. The AB moiety at the edges of graphite played a role as molecular wedge to exfoliate the AB-graphite into graphene-like platelets, which was used as co-curing agents as well as nanoscale additives to epoxy resin. The physical properties of resultant epoxy/AB-graphite composites were improved due to efficient load transfer from graphene-like platelets to epoxy matrix through covalent links between the additives and matrix resin. Finally, the tensile strengths at break for pure epoxy and epoxy/AB-graphite with 4 wt% load were 61 MPa and 79 MPa, respectively. The value was approximately 30 % improved. In the case of Young’s modulus, the composite with 4 wt% of AB-graphite load displayed maximum average modulus 983 MPa, whose value was more than 40 % improvement. The remarkable improvement of tensile strength and Young’s modulus should be attributable to the covalent links between AB-graphite and epoxy matrix.
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I. Introduction

Epoxy or polyepoxide resin is the most widely used commodity thermosetting polymer, which forms the reaction between epoxide ‘resin’ and polyamine "hardener". Epoxy has a wide range of applications, including fiber-reinforced composites, general purpose adhesives and coatings. In general, epoxies are known for their excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties and very good electrical insulating properties.

Since their discovery, carbon nanomaterials (CNMs) have attracted great attention due to their unique chemical and physical properties. Carbon is the most versatile element that can be bonded in many ways to construct new structures, such as graphite, diamond, fullerene and carbon nanotubes that range from three to zero dimensions at the nanoscale (Scheme 1). These materials tend to possess several unique chemical, physical, and electronic properties, making them very attractive for a range of advanced technological applications.

Graphite, an allotrope of carbon, consists of superimposed lamellae of two-dimension (2D) carbon-carbon covalent networks, referred to as graphene, which stack along the c-axis as a result of strong van der Waals forces, and the separation of these layers is a considerable challenge.

Graphene nanoplatelets have exceptional mechanical strength (~1,100 GPa), thermal conductivity (~5,000 W m\(^{-1}\) K\(^{-1}\)), specific surface area (calculated value, ~2630 m\(^2\) g\(^{-1}\)) and electronic property (200,000 cm\(^2\) V\(^{-1}\) s\(^{-1}\)). Graphene is very attractive material for potential applications in composite, energy...

Scheme 1. This schematic diagram shows the different allotropes of carbon.

The exfoliation of graphite, including into individual layers (graphene), is undoubtedly the hottest research topic in condensed matters due to the exceptional properties of graphene. Graphene nanoplatelets have exceptional mechanical strength (~1,100 GPa), thermal conductivity (~5,000 W m\(^{-1}\) K\(^{-1}\)), specific surface area (calculated value, ~2630 m\(^2\) g\(^{-1}\)) and electronic property (200,000 cm\(^2\) V\(^{-1}\) s\(^{-1}\)). Graphene is very attractive material for potential applications in composite, energy...
related systems, sensors, electronics, photonics, spintronics, and so on. There are two major approaches for the preparation of graphene. The one is the exfoliation of ‘pristine’ graphite into graphene, which involves physical and chemical methods. The other is graphene can be grown by chemical vapor deposition (CVD) on metal substrates as well as from single crystal silicon carbide.

Many research efforts have been carried out to overcome the various barriers to accomplishing reinforcement by nanofiller in polymer composites, including the use of ultrasonication, high shear mixing, aid of surfactants, alignment, chemical modification, and polymer chain wrapping. They most likely benefit from easily accomplished dispersion and good chemical interaction between nanofillers and these specific polymers. Especially, functionalization enables interactions with the polymer matrix to be controlled through a variety of organic groups attached to the nanofillers, and commonly amine groups used the hardener of epoxy. The functionalization onto the surface of carbon nanomaterials could provide chemical affinity for both efficient dispersion and interfacial interactions.

At present, nanocomposites employing carbon-based reinforcement materials are dominated by carbon nanotubes (CNTs). However, the development of CNT-reinforced composites has been impeded by their difficult dispersion in matrix and their higher costs have been hampering their application. Compared to carbon nanotubes, graphene continue to attract considerable attention because of their outstanding mechanical and electrical properties as well as high aspect ratio and low density, which results in one of the ideal candidates for developing functional and structural graphene-reinforced composites. Incorporation of graphene into ceramics or polymer matrices remarkably improves the properties of the materials. Wakabayashi et al. employed a solid-state shear pulverization (SSSP) to produce polypropylene-graphite nanocomposites, revealing a 100 % increase in Young’s modulus and a ∼60 % increase in yield strength as a function of the addition of 2.5 wt% graphite. Liang et al. prepared a nanocomposite of graphene/polymer with a 76 % increase in tensile strength and a 62 % improvement of Young’s modulus at a loading of 0.7 vol% graphite oxide. Wang et al. reported that a freestanding and flexible graphene/polyaniline composite paper gave a favorable tensile strength of 12.6 MPa. Therefore, more attention has been drawn to graphene as a potential reinforcement material in the next generation of composite materials. Meanwhile, the electrically conductive property can be obviously improved via adding the nanosheets into a matrix. Graphene nanosheet-based polystyrene composites synthesized by a liquid-phase blend route exhibited extraordinarily low electrical percolation threshold of 0.1 vol%. Composite films of noncovalent functionalized graphene sheets/sulfonated polyaniline revealed improved conductivity of 0.2 S cm⁻¹, good electrocatalytic activity, and stability, reported by Bai et al.

One of the key points to the successful development of graphene-based nanocomposites and to
the improvement of their performance is the dispersion of nanofillers in a polymer matrix. Because of their high specific surface area, graphene tends to form irreversible agglomerates or even restack due to van der Waals interactions. Full utilization of graphene nanosheets in polymer nanocomposite application will inevitably depend on their abilities to achieve full exfoliation and complete dispersion in the polymer matrix. Moreover, the good dispersion of these nanosheets in the polymer matrix is an important aspect to exhibit good interfacial strength with the matrix. Stankovich et al. treated graphene oxide with organic isocyanates, and these isocyanate-treated graphene oxides were then exfoliated into functionalized graphene oxide nanoplatelets, exhibiting a stable dispersion in polar aprotic solvents. So molecular-level dispersion of individual, chemically modified graphene sheets within polymer hosts could be formed. This group also reported a stable aqueous dispersion of graphitic nanoplatelets by coating reduced graphene oxide nanoplatelets with an amphiphilic polymer, so that it improved the ability to achieve good dispersion of the nanofiller component in the polymer matrix of choice.

In this work, the edges of ‘pristine’ graphite was selectively functionalized with 4-aminobenzoic acid to produce 4-aminobenzoyl-functionalized graphite (AB-graphite) by using ‘direct’ Friedel-Crafts acylation in polyphosphoric acid (PPA)/phosphorous pentoxide (P2O5) medium. The exfoliation of AB-graphite into graphene-like platelets as a simple and scalable approach was challenged, expecting that the AB-moiety played a role as ‘molecular wedges’. The AB-graphite was dispersed well into solvent and used as co-curing agents as well as nanoscale additives to epoxy resin. The physical properties of resultant epoxy/AB-graphite nanocomposites were enhanced due to the formation of covalent links between AB-graphite and epoxy resin, allowing an efficient load transfer possible.

The concept of this work is described in (scheme 2). One of the key points to the successful development of AB-graphite based nanocomposites and to the improvement of their performance is the dispersion of nanofillers in a polymer matrix. Polymer nanocomposites are plastic materials with small amounts of nanofiller added to them. The nanofiller must be mixed into the plastic at the nanometric scale. Specifically, pristine graphite is stacked with many layers of graphene due to van der Waals interaction. As a result, conventional graphite composite could not expect enhanced properties because the interface between filler and polymer is not connected and graphene has different properties with graphite.
Scheme 2. Concept of difference between ‘pristine’ graphite and AB-graphite composite.
Π. Experiment

2.1 Materials

All reagents and solvents were purchased from Aldrich Chemical Inc. and used as received, unless otherwise specified. Graphite (Aldrich Cat#: 7782-42-5, type: powder, particle size: < 45μm, purity: 99.99+%) was also obtained from Aldrich Chemical Inc. Epoxy resin used as matrix material was diglycidyl ether of bisphenol A (DGEBA) and was supplied by Kukdo Chemical Co. A curing agent 4,4’-diaminodiphenylmethane (MDA) was obtained from Alfa Aesar, USA.

2.2 Instrumentations

Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker Fourier-transform spectrophotometer model Spectrum 100. Elemental analysis was performed with a Thermo Scientific Flash 2000. The field emission scanning electron microscopy (FE-SEM) used in this work was NanoSem 230 (FEI, USA). High resolution transmission electron microscopy (HR-TEM) was JEM-2100F (JEOL, Japan). Thermogravimetric analysis (TGA) was conducted both in air and nitrogen atmospheres with a heating rate of 10 °C/min using a Q200 (TA Ins., USA). Dynamic mechanical analysis (DMA) was conducted using a Q800 (TA Ins., USA) with a frequency of 1 Hz using film tension clamp. The samples were ramped from room temperature (RT) to 250 °C with a ramping rate of 5 °C/min. The storage modulus and tangent delta (δ) were measured. The sample films were cut into rectangular shaped specimens with length, width and thickness of 30.0, 6.0 and (0.3 ~ 0.4) mm, respectively. Mechanical tests were performed using an Instron 3344 (ITW Co., USA) under a 100 N load cell with a cross-head speed of 10 mm/min. The dog-bone shaped tensile specimens were prepared according to the recommendation of ASTM D638 (Type V). All specimens were cut by using laser cutter. The length, width and thickness of working dimension was of 9.53, 3.18 and (0.3 ~ 0.5) mm, respectively.

2.3 Edge-functionalization of ‘pristine’ graphite with 4-aminobenzoic acid

Into a resin flask equipped with a high torque mechanical stirrer, nitrogen inlet and outlet, 4-aminobenzoic acid (2 g), graphite (2 g), PPA (83 % assay, 80 g), and P₂O₅ (20 g) were placed. The mixture was stirred under dry nitrogen purging at 80 °C for 1h. The reaction mixture was heated to 100 °C and stirred for 1 h. Then, it was heated to 130 °C and maintained for 72 h. At the end of reaction, the color of mixture was dark blue, and water was added into flask. The resulting precipitates
were washed with water and collected by suction filtration. The product was Soxhlet-extracted with methanol and water for each overnight and finally freeze-dried for 48 h to give 3.26 g (86.9 % yields) of dark black powder. Anal. Calcd. for C_{18.42}H_{6}NO (calculated on the basis of 100 % conversion): C, 85.98 %; H, 2.36 %; O, 6.22 %; N, 5.44 %. Found: C, 85.88 %; H, 1.94 %; O, 7.11 %; N, 5.08 %.

2.4 Representative procedure for the preparation of epoxy/AB-graphite composite

A stock solution of AB-graphite (1.0 g) dispersed in ethanol (1 L) was prepared by magnetic stirring with brief ultrasonication (5 min), which was applied to accelerate dispersion of AB-graphite. The AB-graphite solution (100 mL) was mixed well with epoxy resin (9.9 g). Then, ethanol was completely removed under reduced pressure (0.05 mmHg) at 50 °C. The curing agent MDA (27 wt% to epoxy resin) was added and homogeneously mixed at room temperature to be curable epoxy resin mixture. The mixture was cured as follows: persisting voids were further removed under reduced pressure prior to cast. Then, the mixture was poured on between leveled plates in a convection oven and pre-cured at 80 °C for 2 h and post-cured at 150 °C for 2 h to produce a cured film with approximate diameter of 10 cm.
### Results and discussion

#### 3.1 Functionalization of graphite

As describe in scheme 3, the edge aminobenzoyl-functionalized graphite (AB-graphite) was prepared from the reaction between 4-aminobenzoic acid and graphite in PPA/P₂O₅ as described in the literature procedure ⁴⁹. The elemental analysis (EA) data are summarized in Table 1. The ‘pristine’ graphite contains a significant amount of hydrogen (0.18 wt%) due to the sp²C-H at the edges of graphite. The value implies that the sp²C-H is present for every 45.8 carbon atoms. The sp²C-H is responsible for the edge-functionalization of 4-aminobenzoic acid by Friedel-Crafts acylation reaction. The reaction mixture was stepwise heated to 130 °C with mechanical stirring. Interestingly, the colors of the reaction mixture were changed from dark-black to deep brown. The initial color was due to the graphite dispersion and the final one was due to the functionalization and exfoliation of graphite into graphene and graphene-like platelets. The powder precipitates upon pouring into distilled water were collected by suction filtration and washed with water. To minimize unexpected variables, the powder product was transferred to an extraction glass thimble and Soxhlet extracted with water overnight to completely remove reaction media and with methanol overnight to get rid of unreacted 4-aminobenzoic acid. Finally, the samples were freeze-dried for 48 h to give 86.9 % yield of dark black powder. The resultant AB-graphite from EA showed that the carbon contents between the experimental and theoretical counts agreed well (Table 1).
Scheme 3. Edge-functionalization of ‘pristine’ graphite with 4-aminobenzoic acid in polyphosphoric acid (PPA)/phosphorous pentoxide (P\textsubscript{2}O\textsubscript{5}) medium to produce 4-aminobenzoyl-functionalized graphite (AB-graphite).

Table 1. Elemental analysis (EA) of ‘pristine’ graphite and AB-graphite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Analysis</th>
<th>C (%)</th>
<th>H (%)</th>
<th>O (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine graphite</td>
<td>Calcd.</td>
<td>100.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>98.22</td>
<td>0.18</td>
<td>BDL</td>
<td>0.00</td>
</tr>
<tr>
<td>AB-graphite</td>
<td>Calcd.</td>
<td>85.98</td>
<td>2.36</td>
<td>6.22</td>
<td>5.44</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>85.88</td>
<td>1.94</td>
<td>7.11</td>
<td>5.08</td>
</tr>
</tbody>
</table>

* BDL=Below detection limit.

3.2 FT-IR Study

The Fourier-transform infrared (FT-IR) spectroscopy has proven to be an important technique for studying functionalized carbon nanomaterials \textsuperscript{47}. While ‘pristine’ graphite shows featureless spectrum (Figure 1a), AB-graphite displays the characteristic bands for primary amines (-NH\textsubscript{2}) at 1603 cm\textsuperscript{-1}, which corresponds to N-H bending (Figure 1b). The C-N stretching band of the aromatic amine and N-H out-of-plane bending were appeared at 1313 and 846 cm\textsuperscript{-1}, respectively. Furthermore, AB-graphite clearly shows aromatic carbonyl (C=O) peak at 1651 cm\textsuperscript{-1}, which occurs at the covalent junctions between 4-aminobenzoyl group and graphite. As expected, 4-aminobenzoyl groups were covalently linked to graphite.
Figure 1. FT-IR (KBr pellet) spectra: (a) ‘pristine’ graphite; (b) AB-graphite; (c) 4-aminobenzoic acid

3.3 Thermal Properties

Since different structural forms of carbon nanomaterials will exhibit different thermooxidative stability, thermogravimetric analysis (TGA) was utilized to investigate the stability between pristine-graphite and AB-graphite. In addition, the degree of functionalization could be quantitatively estimated. For pristine-graphite, there is almost no weight loss up to 600 °C in air (Figure 2a). On the other hand, AB-graphite shows stepwise weight losses starting from 488 °C in air (Figure 2a). This early weight loss should be attributed to 4-aminobenzoyl (AB) moiety that covalently attached to the edges of graphite. The amount of weight loss was approximately 47 wt% at 750 °C. The result strongly implied that a large amount of AB moiety was covalently attached to the AB-graphite. In nitrogen, the ‘pristine’ graphite was stable enough to 900 °C and AB-graphite showed approximately 23 wt% of weight loss at 750 °C (Figure 2b). The difference in weight loss between in air and in nitrogen is due to some portions of aromatic AB pendants are carbonized under inert condition and remained as thermally stable char.
Figure 2. TGA curves of pristine graphite and AB-graphite with heating rate of 10 °C/min: (a) in air; (b) in nitrogen.

3.4 Morphology of pristine graphite and AB-graphite

The scanning electron microscopy (SEM) image of pristine-graphite shows that their surfaces are smooth and clean (Figure 3a), while the surfaces of AB-graphite are rough and furry because of the attachment of AB moieties (Figure 3b), which further assures the reaction between 4-aminobenzoic acid and ‘pristine’ graphite to produce AB-graphite.

To further assure, AB-graphite was dispersed in ethanol and then holes carbon grid was dipped into the solution. The grid was dried in vacuum oven. Typical TEM image of the AB-graphite at low magnification is shown in (Figure 3c), showing exfoliated graphene and graphene-like platelets. The ‘edge-on’ view image at high magnification (Figure 3d) and selected area electron diffraction (SAED) pattern (Figure 4d, inset) shows the presence of individual graphene with high crystallinity. Further survey with TEM indicated that significant portions of graphene consist of single layer and bilayer (Figure 4a-c), while some portions are graphene-like platelets with the number of graphene layers as many as 15 layers (Figure 4d).
Figure 3. SEM images: (a) pristine graphite; (b) AB-graphite. Scale bars are 5 μm. TEM images of AB-graphite; (c) low magnification; (d) high magnification. The inset is selected area electron diffraction (SAED) pattern from the basal area of (d).
Figure 4. TEM images of AB-graphite: (a) single layer; (b) single layer; (c) bilayer; (d) fifteen layers.

3.5 Dynamic Mechanical Analysis

The homogeneous dispersion of nanofillers into supporting matrices and their interfacial interaction should have a significant effect on the mechanical properties. Analysis of storage modulus (E’) and tan δ curves obtained by dynamic mechanical analysis (DMA) is common tool to assess the role of nanofillers under stress and temperature. DMA specimens were prepared as described in the experimental section. As AB-graphite loads were increased, the transmittance of specimens is decreased (Figure 5). The temperature dependence of the storage modulus is shown in Figure 6a and the data are summarized in Table 2. The storage modulus of the composites at room
temperature was increased as AB-graphite load was increased to 2.0 wt%. The storage modulus of the composite with 2.0 wt% of AB-graphite load was 2.52 GPa, while that of the pure-epoxy composite is 1.98 GPa. The storage modulus increased as much as 21% and the trend was saturated beyond 2 wt% load. For the composite with 4 wt% AB-graphite load, the initial storage modulus is slightly decreased compared to the sample with 2 wt% load, but the modulus was stable above 100 °C.

Figure 6b shows the temperature dependence of tan δ for the epoxy/AB-graphite composites. The loss factor tan δ is defined as the ratio of the loss modulus to the storage modulus (E’’/E’), which is very sensitive to solid structural transformation in materials. The tan δ peak positions determine the glass transition temperatures (T_g) of the composites and are presented in Table 2. The T_g's of composites were slightly shifted to lower temperature region by increasing AB-graphite loads. It is possibly because the existence of the graphite reduces the density of crosslinks and increases the mobility of the epoxy matrix 51.

Figure 5. (a) Photograph of dynamic mechanical analysis (DMA) specimens; (b) optical transmittances of specimens with respect to AB-graphite loads.
Figure 6. Dynamic mechanical analysis of epoxy/AB-graphite composites: (a) Storage Modulus \((E')\); (b) Tan \(\delta\).
Table 2. Thermomechanical Properties of AB-graphite/epoxy composites.

<table>
<thead>
<tr>
<th>Loading (wt%)</th>
<th>Storage modulus (GPa)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure epoxy</td>
<td>1.98</td>
<td>179.3</td>
</tr>
<tr>
<td>0.25</td>
<td>2.08</td>
<td>174.0</td>
</tr>
<tr>
<td>0.5</td>
<td>2.25</td>
<td>173.8</td>
</tr>
<tr>
<td>1.0</td>
<td>2.46</td>
<td>173.7</td>
</tr>
<tr>
<td>2.0</td>
<td>2.52</td>
<td>170.5</td>
</tr>
<tr>
<td>4.0</td>
<td>2.35</td>
<td>170.9</td>
</tr>
<tr>
<td>8.0</td>
<td>2.39</td>
<td>179.5</td>
</tr>
</tbody>
</table>

3.6 Tensile Properties

The tensile properties of filler-reinforced composites depend on the interactions between fillers and supporting matrices. Based on the ASTM D638 (Type V), the epoxy/AB-graphite composite films were cut into dog-bone shapes. The dimensions of the specimens were 64 mm in length, 9.5 mm in width and ~ 0.5 mm in thickness. The representative stress-strain curves of specimens with different AB-graphite loads are presented in Figure 8a. The average values with standard deviations are also presented in Figure 8b and the results are summarized in Table 3. To ensure data accuracy and repeatability, a minimum of five and up to ten specimens from different batches of samples were tested. Compared to pure epoxy, both tensile strengths and Young’s moduli of epoxy/AB-graphite composites were increased in all compositions. The average tensile strengths at break for pure epoxy and epoxy/AB-graphite with 4 wt% load were 61 MPa and 79 MPa, respectively. The value was approximately 30 % improved as compared to neat epoxy. In the case of Young’s modulus, the composite with 4 wt% of AB-graphite load displayed maximum average modulus 983 MPa, whose value was more than 40 % improvement. The remarkable improvement of tensile strength and Young’s modulus should be attributed to the covalent links between AB-graphite and epoxy matrix. Further increasing AB-graphite load above 4 wt%, both tensile strength and Young’s modulus were decreased. It is assumed that the degree of AB-graphite dispersion is poor and thus, some aggregates may play as defects. As a result, it could be concluded that 4.0 wt% of AB-graphite load seems to be a critical concentration for the maximum enhanced properties. The results implicated that AB-graphite could be efficiently dispersed in epoxy matrix, when AB-graphite load was less than 4 wt%. Upon increasing AB-graphite load, aggregates could be formed by restacking of AB-graphite, reducing reinforcing efficiency of the composites.
Figure 7. Epoxy/AB-graphite dog-bone specimens according to ASTM D638 (Type V).
Figure 8. (a) Stress-strain curves of epoxy and epoxy/AB-graphite composite films; (b) the average tensile strengths and Young’s moduli of epoxy and epoxy/AB-graphite composites.
Table 3. Tensile properties of epoxy/AB-graphite composites

<table>
<thead>
<tr>
<th>Loading (wt%)</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure epoxy</td>
<td>61 ± 2</td>
<td>695 ± 70</td>
</tr>
<tr>
<td>0.25</td>
<td>63 ± 6</td>
<td>723 ± 50</td>
</tr>
<tr>
<td>0.5</td>
<td>66 ± 3</td>
<td>855 ± 60</td>
</tr>
<tr>
<td>1.0</td>
<td>67 ± 3</td>
<td>831 ± 85</td>
</tr>
<tr>
<td>2.0</td>
<td>66 ± 5</td>
<td>867 ± 20</td>
</tr>
<tr>
<td>4.0</td>
<td>79 ± 10</td>
<td>983 ± 70</td>
</tr>
<tr>
<td>8.0</td>
<td>71 ± 7</td>
<td>912 ± 60</td>
</tr>
</tbody>
</table>

3.7 SEM study of fracture surfaces

The degree of nanofiller dispersion in the polymer matrix directly correlates with its effectiveness for improving mechanical, electrical, impermeability, and many other properties. The origin of improved mechanical properties could be visually anticipated by microscopic observations. The SEM images were obtained from the fracture surfaces of epoxy film and epoxy/AB-graphite composite film with 2.0 wt% of AB-graphite load. The surface of pure epoxy film displays smooth fracture surface, indicating the material is fragile without ductility (Figure 9a and 9b). On the other hand, the surface of epoxy/AB-graphite film demonstrates that AB-graphite is uniformly distributed into epoxy matrix (Figure 9c and 9d). It is difficult to find AB-graphite aggregates due to the good dispersion of AB-graphite in the matrix. AB-graphite is embedded well in the matrix and held tightly by matrix, because covalent links could be formed from the reaction between amine groups of AB-graphite fillers and epoxide groups of epoxy matrix. The covalent bonding should provide strong interfacial adhesion between AB-graphite and epoxy matrix, resulting in efficient load transfer from AB-graphite to supporting epoxy matrix and vice versa.
Figure 9. SEM images obtained from fracture surfaces of tensile tested films: (a) pure epoxy; (b) magnified image of (a); (c) epoxy/AB-graphite composite with 2wt% AB-graphite load; (d) magnified image of (c).

3.8 Transmission Electron Microscopy

Furthermore, the epoxy/AB-graphite composite film with 2 wt% AB-graphite load was ultramicrotomed and placed on carbon coated grid. The Transmission electron microscopy (TEM) images show that AB-graphite is in the form of a few layer graphene platelets (Figure 10a). Due to the flexibility, thin graphene platelets appear to be crumpled and wrinkled in epoxy matrix. The graphene platelets were rolled into helical ribbon (Figure 10b, arrow).
Figure 10. TEM images obtained from epoxy/AB-graphite with 2 wt% of AB-graphite load after ultramicrotoming of the sample: (a) lower magnification; (b) higher magnification.
IV. Conclusions

We developed a method for edge-functionalization via “direct” Friedel-Crafts acylation in polyphosphoric acid (PPA)/phosphorous pentoxide (P₂O₅). Using this method, graphite was functionalized with 4-aminobenzoic acid (ABA) to afford 4-aminobenzoyl-functionalized graphite (AB-graphite), which was used as co-curing agents as well as nanoscale additives to epoxy resin. On the basis of characterizations, the ‘pristine’ graphite was functionalized well with 4-aminobenzoyl groups. AB-graphite was dispersible in many polar solvents and thus, it was dispersed in ethanol. Epoxy/AB-graphite composites were prepared and mechanical properties were tested. Based on DMA and UTM study, the tensile strength and Young’s modulus were improved according to AB-graphite homogeneously dispersed into epoxy matrix and the interfaces between AB-graphite and epoxy matrix were not discernable because of covalently links. The value of tensile strength was approximately 30 % improved. In the case of Young’s modulus, the composite with 4 wt% of AB-graphite load displayed maximum average modulus 983 MPa, whose value was more than 40 % improvement. The results indicated that AB-graphite played as co-curing agents and nanoscale fillers to improve mechanical properties and can be applicable for filler of many thermosetting or thermoplastic resins. Further study, we develop that the graphite functionalize with various monomer and the outstanding properties of graphene apply to various fields.
References


surfactant-improved dispersion of carbon nanotubes in polystyrene', *Polymer*, vol. 50, no. 24, pp. 5787-93.


Reinforcing efficiency of epoxy resin by 4-(aminophenoxy)benzoyl-functionalized carbon nanomaterials

I. Introduction

II. Results and Discussion

III. Conclusion
Reinforcing efficiency of epoxy resin by 4-(aminophenoxy)benzoyl-functionalized carbon nanomaterials

I. Introduction

One-dimensional, nanoscale carbon-based materials are generally divided into three categories according to the number of walls and their diameter dimensions: single-wall carbon nanotubes or SWNTs (0.7–3 nm); multi-wall carbon nanotubes or MWNTs (2–20 nm); carbon nanofibers or CNFs (40–100 nm). Carbon nanotubes (CNT) have received much attention due to their expected outstanding properties.

However, when they are used as nanoscale reinforcing additives, two issues are addressed first to effectively deliver their properties to supporting matrices. The one is the effective aspect ratio, which is mainly depending upon dispersion state. The other is interfacial adhesion, which is depending upon the chemical affinity between components.

Epoxy resin-based CNT composites have been extensively investigated due to the potential that these materials have in a number of industrial/technological applications. Effective utilization of CNT in epoxy resin composites with regards to enhancement of mechanical properties and electrical conductivity depends primarily on the ability to disperse the CNT homogeneously throughout the polymer matrix and tailor the interfacial interactions between the components of the composite. However, homogeneous dispersion of CNTs is difficult due to the intermolecular van der Waals interactions between CNTs, thus resulting in the formation of aggregates. This problem presents a major challenge in the field of CNT composites and can only be resolved by the chemical functionalization of CNT prior to the incorporation into the polymer matrices.

To covalently attach reactive functional groups onto the surface of carbon nanomaterials such as vapor-grown carbon nanofibers (VGCNF) and MWNT, 4-(4-aminophenoxy)benzoic acid was prepared via two reaction steps. The reaction between 4-fluorobenzonitrile and 4-aminophenol afforded 4-(aminophenoxy)benzonitrile, which was subsequently hydrolyzed to afford 4-(4-aminophenoxy)benzoic acid. VGCNF and MWNT, respectively, were functionalized with 4-(aminophenoxy)benzoic acid in polyphosphoric acid (PPA)/phosphorous pentoxide (P₄O₁₀) medium via “direct” Friedel-Crafts acylation reaction to afford 4-(aminophenoxy)benzoyl-functionalized VGCNF (AP-VGCNF) and MWNT (AP-MWNT). They were blended with epoxy resin by simple mechanical stirring in respectively dichloromethane and isopropyl alcohol, which was added to help efficient mixing. The physical properties of resultant epoxy/AP-VGCNF and epoxy/AP-MWNT nanocomposites are expected to display enhanced properties due to the formation of covalent network between epoxy and AP-VGCNF or AP-MWNT.
Materials.

All reagents and solvents were purchased from Aldrich Chemical Inc. and used as received, unless otherwise mentioned. Long vapor grown carbon nanofibers (VGCNF (l), Pyrograf III-19-PS with diameters of 100-200 nm and lengths of 30~100 μm) and short vapor grown carbon nanofiber (VGCNF (s), Pyrograf III-24-PS with diameters of 60-150 nm and lengths of ~5 μm) were obtained from Applied Science Inc., Cedarville, OH. Multi-walled carbon nanotubes (MWNTs, CVD MWNT 95 with diameters of 10−20 nm and lengths of 30−50 μm) were purchased from Hanhwa Nanotech Inc. Epoxy resin used as matrix material is diglycidyl ether of bisphenol A (DGEBA) were supplied by Kukdo Chemical Corporation. A curing agent 4,4’-diaminodiphenylmethane (MDA) was obtained from Acros Organics, USA.

Functionalization of VGCNF and MWNT with 4-(aminophenoxy)benzoic acid.

At first, the reaction between 4-fluorobenzonitrile and 4-aminophenol produced 4-(aminophenoxy)benzonitrile, which was subsequently hydrolyzed to afford 4-(aminophenoxy)benzoic acid. Into a 500 mL resin flask equipped with a high torque mechanical stirrer, nitrogen inlet and outlet, 4-(aminophenoxy)benzoic acid (3 g), VGCNF or MWNT (3 g), PPA (83 % assay, 120 g), and P₂O₅ (30 g) were placed and stirred with dried nitrogen purging at 80 °C for 1h. The reaction mixture was stirred and heated to 100 °C for 1h, and then reaction mixture was heated and maintained at 130 °C for 72 h. At the end of reaction, the color of mixture was dark blue, and water was added into flask. The resulting precipitate was washed with water and collected by suction filter. The product was Soxhlet-extracted with water and methanol for respectively 3 days and finally freeze dried for 24 h to give dark black powder. Anal. Calcd. for AP-VGCNF (C₃₉H₁₀NO₂): C, 93.82 %; H, 1.04%; N, 2.40 %. Found: C, 83.34 %; H, 1.80 %; N, 2.51 % and AP-MWNT (C₃₅H₁₀NO₂): C, 93.82 %; H, 1.04 %; N, 2.40 %. Found: C, 86.70 %; H, 2.07 %; N, 2.18 %.

Representative procedure for the preparation of epoxy/AP-VGCNF (1.0 wt% load) composite

The AP-VGCNF (0.1 g) was mixed with epoxy (9.9 g) by simple mechanical stirring in dichloromethane, which was used to aide dispersion of AP-VGCNF and help efficient mixing. After evaporation of dichloromethane in vacuum oven (80 °C), 2.673 g (27 wt% to epoxy) of MDA was added and mixed to get a homogeneous curable resin mixture. The resultant mixture was studied before and after cured. The cured resin prepared as follows: the curable mixture was degassed under a reduced pressure and was poured into mold and it was cured at 150 °C for 2 h.
II. Results and Discussion

Functionalization of CNTs

As shown in Scheme 1, functionalization of CNTs was carried out following the literature procedure and the products were fully characterized. The resultant AP-CNTs were decorated by 4-(aminophenoxy)benzoyl, which could enhance dispersion and be useful sites to react with epoxy. The resultant AP-CNTs from elemental analysis showed that the carbon contents between the experimental and theoretical counts agreed well (Table 1).

Scheme 1. The network structure of reaction between AP-CNTs and epoxy resin.
Table 1. Elemental analysis (EA) of pristine CNTs and AP-CNTs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Analysis</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VGCNF (l)</td>
<td>Calcd.</td>
<td>100.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>94.14</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>VGCNF (s)</td>
<td>Calcd.</td>
<td>100.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>92.95</td>
<td>0.50</td>
<td>0.58</td>
</tr>
<tr>
<td>MWNT</td>
<td>Calcd.</td>
<td>100.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>96.24</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>AP-VGCNF (l)</td>
<td>Calcd.</td>
<td>93.82</td>
<td>1.04</td>
<td>2.40</td>
</tr>
<tr>
<td>(Yield 71.7 %)</td>
<td>Found</td>
<td>85.34</td>
<td>1.80</td>
<td>2.51</td>
</tr>
<tr>
<td>AP-VGCNF (s)</td>
<td>Calcd.</td>
<td>93.82</td>
<td>1.04</td>
<td>2.40</td>
</tr>
<tr>
<td>(Yield 81.6 %)</td>
<td>Found</td>
<td>80.76</td>
<td>2.15</td>
<td>2.29</td>
</tr>
<tr>
<td>AP-MWNT</td>
<td>Calcd.</td>
<td>93.82</td>
<td>1.04</td>
<td>2.40</td>
</tr>
<tr>
<td>(Yield 84.4 %)</td>
<td>Found</td>
<td>86.70</td>
<td>2.07</td>
<td>2.18</td>
</tr>
</tbody>
</table>

FT-IR spectra

The progress of the reaction was conveniently monitored with FT-IR. AP-CNT samples showed aromatic carbonyl (C=O) peak at 1632 and 1660 cm⁻¹ and amine (N-H) peak at 1497 and 1554 cm⁻¹ and phenoxy (O-) peak at 1235 and 1278 cm⁻¹. Therefore, CNTs were successfully functionalized to AP-CNTs. (Figure 1)
Figure 1. FT-IR (KBr pellet) spectra of samples

Scanning Electron Microscopy (SEM)

For the comparison purpose, the SEM image of pristine VGCNF is presented (Figure 2a). It shows that the tube surfaces are seamless and smooth surfaces. The average diameter of pristine VGCNF is 60-150 nm. But the surfaces of functionalized VGCNF are clearly decorated with covalently bonded moieties (Figure 2b). And pristine MWNT is presented (Figure 2c). The average diameter of pristine MWNT is 10-20 nm. And the functionalized MWNT is presented (Figure 2d). The covalent bonding should provide strong interfacial adhesion between AP-CNTs and epoxy matrix, resulting in efficient load transfer could be possible from AP-CNTs to supporting epoxy matrix. The fracture SEM images of epoxy/AP-CNT nanocomposites display that AP-CNTs were homogeneously wrapped around epoxy matrix (Figure 3).
Figure 2. SEM images: (a) VGCNF(l) (x50,000); (b) AP-VGCNF(l) (x50,000); (c) MWNT (x100,000); (d) AP-MWNT (x100,000)
Figure 3. Fracture surfaces of epoxy/CNT composites (×50,000): (a) AP-VGCNF (l); (b) AP-VGCNF (s); (c) AP-MWNT

Thermal Properties

The pristine-CNTs and AP-CNTs were subject to thermogravimetric analysis (TGA) with heating rate of 10 °C/min in air and nitrogen. All sample indicated that the temperatures at which 5% weight loss ($T_{d5\text{%}}$) occurred were at 643.96, 572.71, 595.82, 494.37, 433.97 and 434 °C in air, respectively (Figure 4a). Moreover, pristine-CNTs indicated that weight loss ($T_{d5\text{%}}$) occurred over 800 °C in nitrogen (Figure 4b). AP-CNTs commenced the weight loss at much lower temperature than pure-d-CNTs. Besides, it could be confirmed that organic pendants were covalently attached to the surface of AP-CNTs from change of inclination at around 520 °C in air.
Figure 4. TGA of samples with heating rate of 10 °C/min: (a) in air, (b) in nitrogen

Tensile Properties

The mechanical properties of filler-reinforced composites depend on the interaction between the matrix and fillers. Based on the ASTM D638 (Type V). Compared with pure epoxy, all filler-reinforced composites were significantly increased (Figure 5).
Figure 5. Universal tensile test results of dog-bone specimens with strain rate of 10 mm/min: black and red circles are tensile strength and Young’s modulus, respectively.

Dynamic Mechanical Analysis

The homogeneous composites and the stronger interfacial interaction between nanofillers and the polymer matrix should have a significant effect on the mechanical properties. Analysis of storage modulus (E’) and tan δ curves has been proven to be an effective tool to assess the reinforcing efficiency of AP-CNTs under stress and temperature (Figure 6). Temperature dependence curves of storage modulus and tan δ of different cured composites are shown in Figure 6 and are summarized in (Table 2 and 3). The storage modulus of all AP-CNTs composites at room temperature is higher than pure-epoxy. In this data, the storage modulus of the composite containing 4.0 wt% AP-VGCNF is 2.77 GPa, while that of the pure-epoxy is 1.98 GPa. The storage modulus increased by 140 % and the increasing trend is especially clear with lower loading. The composites of containing AP-MWNT are also higher non-filler epoxy sample (Figure 6a and c).

Figure 6b and d shows the temperature dependence of tan δ for the AP-CNTs/epoxy composite. The loss factor tan δ is defined as the ratio of the loss modulus to the storage modulus (E’’/E’’), which is very sensitive to solid structural transformation in materials. The highest tan δ peak values determine glass transition temperature (T_g) of the composites and presented in (Table 2 and 3). One can observe that glass transition temperature slightly shifted to a low temperature region by increasing the loading of AP-CNTs. It is possibly because that the existence of the graphite physically hindered the mobility of the epoxy monomers.
Figure 6. Dynamic mechanical analysis of epoxy/AP-VGCNF composites: (a) Storage Modulus ($E'$); (b) Tan δ; epoxy/AP-MWNT composites: (c) Storage Modulus ($E'$); (d) Tan δ.

Table 2. Thermomechanical Properties of AP-VGCNF/epoxy composites.

<table>
<thead>
<tr>
<th>Loading (wt%)</th>
<th>Storage modulus (GPa)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure epoxy</td>
<td>1.98</td>
<td>179.3</td>
</tr>
<tr>
<td>0.25</td>
<td>2.49</td>
<td>182.2</td>
</tr>
<tr>
<td>0.5</td>
<td>2.45</td>
<td>169.9</td>
</tr>
<tr>
<td>1.0</td>
<td>2.37</td>
<td>173.7</td>
</tr>
<tr>
<td>2.0</td>
<td>2.43</td>
<td>173.1</td>
</tr>
<tr>
<td>4.0</td>
<td>2.77</td>
<td>172.9</td>
</tr>
</tbody>
</table>

Table 3. Thermomechanical Properties of AP-MWNT/epoxy composites.
### Table 1: Storage Modulus and Glass Transition Temperature of the Epoxy-Graphene Composites

<table>
<thead>
<tr>
<th>Loading (wt%)</th>
<th>Storage modulus (GPa)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure epoxy</td>
<td>1.98</td>
<td>179.3</td>
</tr>
<tr>
<td>0.25</td>
<td>2.58</td>
<td>162.8</td>
</tr>
<tr>
<td>0.5</td>
<td>2.70</td>
<td>175.8</td>
</tr>
<tr>
<td>1.0</td>
<td>2.76</td>
<td>170.8</td>
</tr>
<tr>
<td>2.0</td>
<td>2.88</td>
<td>182.6</td>
</tr>
<tr>
<td>4.0</td>
<td>2.86</td>
<td>178.8</td>
</tr>
</tbody>
</table>

#### III. Conclusion

One of our continuous devotes on the development of chemical modification of carbon nanomaterials in polyphosphoric acid (PPA), which is effective but mild enough not to damage carbon framework. VGCNF and MWNT were successfully functionalized to afford AP-VGCNF and AP-MWNT, which can be used as co-curing agents for the epoxy resin. Based on UTM study, the tensile strength and Young’s modulus were improved according to AP-CNTs homogeneously dispersed into epoxy matrix and the interfaces between AP-CNTs and epoxy matrix were not discernable because of covalently links. The SEM study supported this result in the report.
Manuscript

International


Domestic

1. Kyung-Su Kim, In-Yup Jeon, Jong-Beom Baek “Reinforcing efficiency of epoxy resin by amine-functionalized graphite” The polymer Society of Korea 2010, 35(2), (Daegu, October 7-8).

2. Kyung-Su Kim, In-Yup Jeon, Jong-Beom Baek “Reinforcing efficiency of epoxy resin by 4-(aminophenoxy)benzoyl-functionalized carbon allotrope” The polymer Society of Korea 2010, 35(1), (Daejeon, April 8-9).


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