PREPARATION AND CHARACTERIZATION OF ATBN-FUNCTIONALIZED GRAPHENE NANOPLATELETS AND THE EPOXY NANOCOMPOSITES

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1. Introduction
Recently, graphene nanoplatelets, referred to as exfoliated graphite nanoplatelets (xGnP), have been paid attractive attention as promising carbon nanoparticles [1-5]. The incorporation of functionalized graphite nanoplatelets into a polymer resin results in the improved dispersion of the nanoplatelets in a polymer resin providing increased mechanical, electrical and thermal properties. Epoxy resins have been widely used in many plastics and composites applications. They have excellent mechanical, thermal, chemical and adhesion properties but they have low impact toughness like other thermosetting polymers [6]. Therefore toughening may be needed for it to enhance the performance and to extend the application. Liquid rubbers like amine-terminated poly(butadiene-co-acrylonitrile) (ATBN) have been used to improve the impact toughness of epoxy [7,8] but the contents were often high. The aim of the present work are primarily to characterize ATBN-functionalized xGnP by means of ATR-FTIR, XRD, XPS, and EDS in order to demonstrate the grafting of ATBN elastomeric molecules to xGnP prepared through a series of synthetic routes. The ultimate objective of the study is to increase the impact toughness of epoxy by fabricating epoxy nanocomposites with ATBN-functionalized graphene nanoplatelets. In this paper a number of analytical results demonstrating the functionalization of xGnP grafted with ATBN are given. The effect of functionalized xGnP on the properties of xGnP/epoxy nanocomposites will be discussed in the presentation.

2. Experimental
2.1 Materials
Graphite intercalation compound (GIC 3772) was supplied from Asubury Graphite Mills, Inc., NJ, USA. Fuming nitric acid, sodium chlorate, thionyl chloride, pyridine, chloroform, and ATBN (Hypro™ ATBN 1300x21, Hycar, USA) were used in the present work.

2.2 Preparation of ATBN-functionalized xGnP
Exfoliated graphene nanoplatelets prepared from intercalated graphite compound by microwave processing were oxidized by the Brodie’s method. A mixture of xGnP, fuming nitric acid and sodium chlorate was stirred for at room temperature for 24 h. It was neutralized until it reached near pH7. Then it was stirred with thionyl chloride and pyridine at 70°C. The acyl chloride-functionalized xGnP was reacted with a solution of chloroform and ATBN at 70°C. The excess solution was washed out with chloroform ten times and then the chloroform was removed in a vacuum oven. Finally, ATBN-functionalized xGnP was obtained.

2.3 Characterization
Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy (Jasco 6100) was performed to analyze the functional groups in the surfaces of xGnP, carboxylated xGnP and ATBN-functionalized xGnP. The X-ray diffraction patterns of the xGnP samples were observed using a wide-angle X-ray diffractometer (Rigaku, X-MAX 2000-PC) scanning
between 5° and 30° at 2°/min. All of samples were of powder state.

Raman spectroscopy was carried out using a Micro-Raman spectrometer (Renishaw, system 100, UK) in the range of 2000 to 500 cm⁻¹. The laser spot size was 0 to 250 μm and the excitation was 514 nm. An integration time of 30 s was chosen for each measurement to achieve spectra with good counting rates. The laser power was kept at 28.2 mW to prevent irreversible thermal damages of the specimen surfaces.

In order to assess the surface functional group, X-ray photoelectron (XPS) spectroscopy was performed using a Thermo Fisher Scientific (UK) Multilab-2000 XPS spectrometer. The X-ray source was Al-Kα radiation. The lens mode and energy step size were LAXPS and 0.1 eV, respectively. The photoelectron peaks (narrow scan spectra) were fitted by Fityk program made by M. Wojdyr and the peaks intensity was obtained from the Gaussian relation.

The chemical composition of xGnP, carboxylated xGnP and ATBN-functionalized xGnP investigate by EDS (Energy dispersive X-ray spectroscopy, JEOL 6500F scanning electron microscope; INCA EDS). The thermal stability of xGnP, carboxylated xGnP and ATBN-functionalized xGnP was measured using a thermogravimetric analyzer (TA Instruments, Q500) in nitrogen atmosphere. The heating rate was 5°C/min. A scanning electron microscope (SEM, Tescan, VEGA ll MLMV) was used to observe the surface of xGnP, carboxylated xGnP and ATBN-functionalized xGnP.

3. Results and Discussion

Fig. 1 shows the ATR-FTIR spectra of xGnP and carboxylated xGnP (24 h acid treatment). Before acid treatment, the characteristic absorption peaks were not detected from the xGnP because it has no specific functional groups on the surfaces. The xGnP is mostly composed of carbon atoms and a tiny amount of residual unreacted intercalant may also be existed. As can be seen, the spectrum from carboxylated xGnP exhibited a broad peak around 3491 cm⁻¹, which was derived from O-H stretching vibration of carboxyl and hydroxyl groups. The other characteristic peaks appeared at 1738 cm⁻¹ and 1365 cm⁻¹ were due to C=O stretching vibration of carboxyl groups and to C-O stretching vibration of carboxyl groups, respectively. The result indicated that a lot of carboxyl groups were formed on the xGnP surfaces through the acid treatment by the Brodie’s method. The functionalization of ATBN to xGnP has been supported from the following analytical results.

Fig. 1. ATR-FTIR spectra for (A) xGnP, (B) carboxylated xGnP.

Fig. 2 displays the XRD patterns of xGnP, carboxylated xGnP, and ATBN-functionalized xGnP. The pristine xGnP (a) has a large and sharp 2θ peak at 26.48° and the d-spacing was found to be 3.36 Å. This value is very close to the d-spacing of pure graphite. The carboxylated xGnP (b) exhibited the 2θ peak at 13.32° and the d-spacing was 6.65 Å. The intensity of 2θ peak was notably reduced. The result indicated that the crystallinity of xGnP was decreased leading to structural disorder or defects due to the oxidation of xGnP by the acid treatment. The ATBN-functionalized xGnP (c) showed the 2θ peak at 24.58° with the much reduced intensity. The
$d$-spacing was 3.68 Å, which is close to the value of pristine xGnP. This may be explained by that the structural order in the xGnP nanoplatelets, which were destructed by the oxidation, was recovered to some extent by self-assembling during the ATBN functionalization. The decrease of the peak intensity may be ascribed to the loss of the crystalline structure by amorphous ATBN molecules grafted to the xGnP.

![Fig. 2. XRD patterns of (a) xGnP, (b) carboxylated xGnP, and (c) ATBN-functionalized xGnP.](image)

Fig. 2. XRD patterns of (a) xGnP, (b) carboxylated xGnP, and (c) ATBN-functionalized xGnP.

Fig. 3 depicts Raman spectra of xGnP, carboxylated xGnP, and ATBN-functionalized xGnP. The D-band of carboxylated xGnP at 1357 cm$^{-1}$ was largely increased, compared with xGnP. This is ascribed to the disordered or defect structure of carboxylated xGnP by the acid treatment. The G-band, which is corresponding for graphitic structure, became broaden, compared with that of xGnP. This spectral change resulted in the increase of $I_D/I_G$ ratio from 0.05 to 0.80. In the case of ATBN-functionalized xGnP, the D-band and G-band became sharper than those of carboxylated xGnP but they were still broader than those of xGnP, resulting in the $I_D/I_G$ ratio of 0.61, which was smaller than the ratio of carboxylated xGnP. This implies that the defected or disordered structure was not completely returned to the platelet structure of pristine xGnP after the ATBN functionalization of xGnP. This indicates that the grafted ATBN molecules were located in between the graphene nanoplatelet galleries.

![Fig. 3. Raman Spectra of xGnP, carboxylated xGnP, and ATBN-functionalized xGnP.](image)

Fig. 3. Raman Spectra of xGnP, carboxylated xGnP, and ATBN-functionalized xGnP.

by means of a survey scan method. Table summarized their percent atomic compositions obtained from the area of the characteristic peaks of C1s, O1s and N1s. In xGnP and carboxylated xGnP, the carbon contents were much greater than those of the oxygen contents. The nitrogen content was not detected. The carbon content of xGnP was greater than that of carboxylated xGnP, as expected. It was pointed out that the oxygen content of carboxylated xGnP was markedly increased from 5.39% to 25.40% due to the acid treatment for 24 hours by the Brodie’s method. The presence of nitrogen in the ATBN-functionalized xGnP confirmed that the ATBN was grafted to the xGnP via oxidation, acylation and amidation, supporting other analytical results.

![Fig. 4. XPS spectra of xGnP, carboxylated xGnP, and ATBN-functionalized xGnP.](image)

Fig. 4. XPS spectra of xGnP, carboxylated xGnP, and ATBN-functionalized xGnP.
Table 1. Atomic compositions of xGnP, carboxylated xGnP, and ATBN-functionalized xGnP obtained from XPS analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon C1s</th>
<th>Oxygen O1s</th>
<th>Nitrogen N1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>xGnP</td>
<td>94.61</td>
<td>5.39</td>
<td>None</td>
</tr>
<tr>
<td>Carboxylated xGnP</td>
<td>74.60</td>
<td>25.40</td>
<td>None</td>
</tr>
<tr>
<td>ATBN-functionalized xGnP</td>
<td>85.87</td>
<td>12.41</td>
<td>1.72</td>
</tr>
</tbody>
</table>

Table 2 presents the chemical compositions of xGnP, carboxylated xGnP, and ATBN-functionalized xGnP obtained by means of EDS analysis during a scanning electron microscopic observations. The result shows that the xGnP has the carbon content about 90%, the oxygen about 10%, and no nitrogen. After carboxylation, the carbon content was decreased to about 64% whereas the oxygen content was increased about 36%, as shown with a similar tendency in Table 1. It was confirmed that the oxygen content was resulted from the oxygen-containing groups like carboxyl, ether and/or epoxide groups in the carboxylated xGnP. After ATBN-functionalization, the carbon content was increased again and the oxygen content was decreased as well. Also the nitrogen of 4.6% was found therein. It is obvious that the nitrogen founding was attributed to the nitrogen in the amine group and acrylonitrile moiety of ATBN.

Table 2. Chemical compositions of xGnP, carboxylated xGnP and ATBN-functionalized xGnP observed by means of EDS

<table>
<thead>
<tr>
<th>Element</th>
<th>xGnP Atomic %</th>
<th>Carboxylated xGnP Atomic %</th>
<th>ATBN-functionalized xGnP Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>89.9</td>
<td>64.3</td>
<td>79.3</td>
</tr>
<tr>
<td>O</td>
<td>10.1</td>
<td>35.7</td>
<td>16.1</td>
</tr>
<tr>
<td>N</td>
<td>0</td>
<td>0</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Fig. 5 displays the variation of the weight change of xGnP, ATBN, carboxylated xGnP and ATBN-functionalized xGnP as a function of temperature. The xGnP was thermally stable to 800°C and a small loss of the weight of about 1-2% was due to the removal of the intercalant remaining in the xGnP even after the expansion process. In the carboxylated xGnP, the abrupt weight drop down to about 74% at about 316°C implies that the content of oxygen-containing groups mainly including carboxyl groups was approximately 26% and the large portion of xGnP was grafted with oxygen-containing groups. ATBN exhibited an abrupt weight drop down to roughly 0% above about 440°C. The thermal stability of ATBN-functionalized xGnP was lower than that of xGnP but higher than carboxylated xGnP in the range of 300-600°C, showing a gradual weight loss as a function of temperature. It seemed that it exhibited the thermal stability combined with xGnP, carboxylated xGnP, and ATBN.

4. Conclusions

Graphene nanoplatelets were successfully functionalized with ATBN rubber molecules by grafting through oxidation, acylation and then amidation and the grafting was demonstrated by means of multiple analytical methods such as ATR-FTIR, XRD, Raman, XPS, EDS, TGA and SEM. It was investigated that the incorporation of ATBN-functionalized xGnP influenced the impact and thermal properties of xGnP/epoxy nanocomposites.

References


