Effect of Graphene Oxide (GO) Dispersion on Basic Properties of Polycarbonate/GO Composites

Bom Yi Lee, Youn Cheol Kim

Kongju National University, lby49@kongju.ac.kr
Kongju National University, younkim@kongju.ac.kr

Abstract

The basic properties such as chemical structure, thermal and rheological properties of polycarbonate (PC)/graphene oxide (GO) composites, prepared by two methods: In-situ polymerizations and twin screw extruder was compared. A modified GO with COCl, GO-COCl was synthesized and the chemical structure of PC/GO-COCl and PC/GO was confirmed using FT-IR spectrum. GO, the hydroxyl (-OH), carbonyl (-C=O), ether (-CO-, C-O-C) bonds, is clearly identified by the peaks at 3395, 1724 and 1621cm⁻¹ respectively. Complex viscosities showed that the PC/GO composites by in-situ polymerization have larger shear thinning effect and this may be because of better dispersion of GO confirmed by scanning electron microscope (SEM).

Keywords: In-situ polymerization, Polycarbonate, Graphene Oxide, Dispersion

1. Introduction

Pencil that is commonly used, is constituted of an inexpensive graphite. Graphite are formed as a layered structure in which several folds of superimposed layers of benzene ring becomes honeycomb layers coupled at a distance of about 3.34 Å by van der Waals forces [1]. The layer consists of a weak van der Waals forces, and one layer of graphite can be removed, referred as graphene by chemical modification of the layer or by physical impact from the outside. In recent years, chemically modified graphite, one of which is acid treatment is gaining attention of researcher [2-8]. Among the basic structure of carbon nanostructure, graphite is three dimension structure, one dimensional graphene rounded into cylindrical form is carbon nano tube and soccer shaped round is fullerene .

With the introduction of graphene separation technique unique and excellent electrical properties and physical properties were actively researched. Graphene as being the collection of countless benzene ring has the very high electrical mobility of 200000 cm²V⁻¹s⁻¹ [9]. In addition, graphene is known to show optical transparency as 98% of visible light is transmitted. Graphene shows similar mechanical and physical properties to single walled CNT but graphene has a large surface area of 2630 m²/g [10][11]. Graphene as a filler is very useful in polymer composites [12][13]. Graphene also has many problems, of which first is chemical vapor density (CVD). Graphene prepared by CVD is of high purity compared to other method and also of desirable size, but amount of graphene produced is very little. Secondly, the two-dimensional graphene carbon to be used as nanocomposites for polymer aggregates with polymer matrices.

However, pure carbon materials is widely known, because it has a characteristic that melt, undissolved, physical modification or chemical modification in order to apply the polymer nano-composite carbon materials are have the need to increase the compatibility with the polymer through[14].

The purpose of this study is to prepare Polycarbonate and graphene oxide complex and compare their physical properties. Basic characteristics and rheological properties such as shear thinning of melt mixing complex and in-situ composites prepared by polymerization was analyzed. Before measuring electrical characteristics and identifying the degree of dispersion and predicting the characteristics of the electrical conductivity.

2. Materials and Measurements

In this study, 2,2-bis (4-hydroxyphenyl) propane (Bisphenol A), diphenyl carbonate (DPC) and GO (obtained by acid treatment of graphite) were used without further purification. GO-COCl was prepared by using the dimethylformamide and thionyl chloride.
GO and DPC was put in a four mouth 500 ml beaker where mechanical stirrer, temperature controller, reflux tube was fixed. After removing air and moisture, the temperature of the reactor was set to 120 °C and stirred for 30 minute in nitrogen condition and BPA was added to mixture. After the addition of BPA temperature was raised to 220 °C and reactor pressure was reduced by using vacuum pump. After one hour of reaction at reduced pressure, refluxing condenser was removed and strong vacuum was applied for two hours to remove phenol. The reaction was continued for 3 hours and temperature was allowed to rise from 220 to 270 °C at 750 mmHg before the reaction was terminated. The molar ratio of DPC and BPA was fixed to 1.08. The PC-GO blend composite was also prepared by twin screw extruder. The temperatures of extruder at different zone were 230/280/280/270/270/260 °C , and rpm was 150.

FT-IR (Perkin Elmer spectrum1000) was used to investigate the chemical structure of the polymers synthesized. Infrared was passed through the synthesized polymer to obtain 24 scans between frequency of 4000 ~ 400 cm⁻¹. Interlayer distance of functionalized graphene was measured by X-ray diffractometer (Rigaku Corporation Miniflex 600) by using the Cu-Kα Target, in the range of 5 ~ 40 °. XRD was conducted at room temperature at the rate of 2°/min. In order to determine the glass transition temperature, DSC (TA instrument DSC Q20) was done by heat/cool/heat procedure between temperature -50 ~ 300 in nitrogen atmosphere. The rate of cooling and heating used was 10 °C/min. TGA was measured under a nitrogen atmosphere at a heating rate of 10/min to 800 °C from room temperature using the TAG analyzer. To investigate the rheological properties Anton Paar's parallel plate rheological device having a diameter of 25mm was used with strain 10%, and frequency between 0.05 - 500Hz. Operating temperature was 280 °C and the gap size was 0.9mm. The specimens used were dried for 10 hours in a vacuum oven at 140 and hot pressed before measuring the rheological properties. Dispersivity of the complex was measured by SEM(TESCAN, MIRA3).

3. Result and Discussion

Characteristic graphite, GO and GO-COCI peak can be seen in figure 1. In case of graphite no specific characteristic peak can be seen but in figure 1(a), GO, the hydroxyl (-OH), carbonyl (-C=O), ether (-CO-, C-O-C) bonds, is clearly identified by the peaks at 3395, 1724 and 1621 cm⁻¹ respectively[15]. Oxygen reaction with graphite can also be seen. In GO-COCI, the OH absorption peak near 3500cm⁻¹, disappears from the -O=C-Cl peak and 1737cm⁻¹ is seen appearing on the surface of grapheme carbonyl chloride (-COCI) group confirmed that the surface was modified. Synthesized PC was compared with linear PC to determine composite and synthesis. Benzene and methyl sp³ and sp² C-H stretching vibration near 3000cm⁻¹, also carbonyl group (C=O) stretching vibration and the skeletal vibration of the compound and the phenyl ring stretching in 1778cm⁻¹, 1500cm⁻¹ confirms synthesis of PC[16].
X-ray diffraction analysis is done to confirm the interlayer distance between modified graphene as shown in figure 2. Bond between the layers of natural graphite is formed by van der Waals force and distance between the layers is $d = 3.37 \, \text{Å}$. When oxidized the interlayer distance due to van der Waals increased to $d = 8.23 \, \text{Å}$ suggesting addition of oxygen molecule in the layers\[17\][18]. In case of functionalized graphene two oxygen molecules are substituted by -Cl or -COCl as the hydrogen bond is not present. Therefore, interlayer distance further increased and also crystal structure did not show any diffraction peaks. The substitution of oxygen molecule by -Cl or -COCl is similar to the reduction process of GO because the combination of graphite van der Waals and the GO-COCl disappears and so no peak is observed. Diffraction peak of all the functional groups are seen near $2\theta = 23.7$, this can be the effect of diffraction peak graphite. For PC / GO_COCI complex, a peak is observed at $2\theta = 24.7$ near interlayer distance of functionalized graphene, and it is seen to be greatly affected by the chain size.

DSC and TGA were used to determine the thermal properties. When the number average molecular weight is 10000 or more, the glass transition temperature ($T_g$) of all the synthesized polycarbonate had a value of about 150 °C. When the molecular weight is not high the glass transition temperature is about 140 °C for synthesized PC as shown in Figure 3. It is believed that the addition of GO during the
course of synthesis acted as the inhibitor of polymerization. The glass transition temperature ($T_g$) and decomposition temperature ($T_d$) of the samples are listed in table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$(°C)</th>
<th>$T_d$(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-Graphite</td>
<td>146.43</td>
<td>439.58</td>
</tr>
<tr>
<td>PC-GO blend</td>
<td>140.71</td>
<td>456.99</td>
</tr>
<tr>
<td>PC-GO in-situ</td>
<td>141.45</td>
<td>458.64</td>
</tr>
<tr>
<td>PC-GO COCl in-situ</td>
<td>138.70</td>
<td>436.21</td>
</tr>
</tbody>
</table>

Thermal gravimetric analysis of graphite, GO, GO-COCl is shown in figure 4(1). In case of natural graphite there was almost no weight loss until 650 °C but GO showed weight loss of about 49.4% at the same temperature. Water molecules present in hydrogen bond are gradually removed between 100 ~ 400 °C, epoxy group are so easily decomposed and thus maximum weight loss around 182 °C is seen. Slowly, after the temperature higher than 550 °C, the carbonyl group begins to evaporate. Carbonyl chloride group showed almost 24.6% reductions in mass. GO showed less mass loss compared to GO-COCl which indicated that GO is excellent to thermal stability than GO-COCl. Figure 4(2) shows the thermogravitric analysis of PC-composites. Thermal stability of PC with GO was found better than PC-graphite while PC-GO produced by in-situ process was the best.

In general linear polymer melt rheology is divided into lower area, middle area and higher area shear rate. Lower region of shear rate, referred as the lower Newtonian region, is heavily dependent to molecular weight, molecular structure, filler, etc. Addition of filler material to polymer will lead to significant change in polymer melt rheology. Viscoelastic properties in the melt increases during the elastic properties and as the effects of long-chain branches power law index is decreased significantly.

Figure 5 shows the plot of complex viscosity and $G'$-$G''$. Complex viscosity of PC composite prepared by melt mixing is higher compared to PC synthesized by in-situ polymerization. Complex viscosity of simple mixing composite of PC was higher in entire range of frequency but PC synthesized by in-situ showed significant change, i.e. decrease in complex viscosity with increase in angular frequency, and this phenomenon is known as shear thinning property [19]. Shear thinning property of in-situ polymerized PC composite was higher compared to melt mixed PC composite. In shear thinning phenomena the entangled polymer molecule moves freely by sorting the entanglement by shear in shear direction reducing the resistance phenomena with increasing frequency. Because of better dispersion of GO in PC, the occurrence of this phenomenon is higher in in-situ polymerization PC-GO composite compared to melt mixed PC. $G'$-$G''$ plot of the in-situ composites is seen to shift further to the left. Complex elastic property is seen to be dominant than simple elastic property.
The dispersibility of GO in simple mixing complex and in situ complex was analyzed by SEM, and result is shown in figure 6. In simple mixed composite filler stick together to form a bulk but in in-situ composite several layers of filler with 10nm are seen in PC matrix. This shows GO has been dispersed well. In-situ composite can be predicted to have better electrical conductivity, as it has better dispersed composite.

4. Conclusion

In this study, a simple mixed complex and in-situ polymerized composites prepared were tested for thermal properties, rheological properties and were evaluated for dispersion characteristics. Glass transition temperature were almost similar but the decomposition temperature of in-situ polymerization was higher thus thermal stability of in-situ polymerized complex was found to be superior. Rheological property of in-situ polymerization is better compared to simple mixing composite in term of shear thinning property where with the increase in frequency decreased resistance to flow. Well dispersion of GO in in-situ polymerization complex was confirmed. It can be evaluated by the dispersion characteristics that rheological properties of in-situ composite are better than simple mixing complex.

Acknowledgement

“This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(MEST) (No. 2012R1A1A22003989).”
5. References


