THE SYNTHESIS, THERMAL AND STRUCTURAL CHARACTERIZATION OF POLYVINYLCHLORIDE/GRAPHENE OXIDE (PVC/GO) COMPOSITES

Assist. Prof. Dr. F. Mindivan¹
Büşüyük Vocational College, Bilecik S.E. University, Bilecik, Turkey¹
ferda.mindivan@bilecik.edu.tr

Abstract: In this study, the thermal and structural changes were observed in polyvinylchloride / graphene oxide (PVC/GO) composites in different amounts of 0.1, 0.3, 0.5 and 1 wt.% To this aim, GO was prepared from natural graphite by Hummers method. XRD results of GO indicated that the interlayer distance increased from 0.33 nm to 0.88 nm. Energy Dispersive Spectroscopy (EDS) analysis results showed that oxygen content increased from 22.59 % to 47.95 % after the oxidation process. These features suggested that the GO sample, mainly oxygen-containing functional groups, was oxidized. PVC/GO composites were prepared by colloidal blending. XRD results of all composites indicated the GO layers well-dispersed in polymer matrix. SEM analysis revealed that the composites with 0.1 and 0.5 wt. % GO filler exhibited a uniform composite with highly porous and micro porous morphology respectively. TGA and DSC analysis showed that the use of minimum amount of GO in PVC matrix did not provide an important improvement on the thermal stability of the examined composites.

Keywords: COMPOSITE, GRAPHENE OXIDE, PVC.

1. Introduction

The innovations in modern technology pave the way for growing demand on advanced polymer-composite materials. Especially PVC is a universal polymer due to its easy processing, low cost, good physical, chemical and corrosion properties. Today, the annual production volume of PVC is more than 30 million worldwide and more than 50 % of this material is used in construction sector. In recent years, PVC has taken the place of wood, concrete and clay. In addition, it has some additional application areas such as flooring, cable insulation, roof tiles, packaging material, bottle and medical products [1]. However, PVC has several disadvantages such as poor processability, thermal stability and weatherability. Moreover, PVC without plasticizers or fillers is typically brittle and is not suitable for use in many fields [2-3]. Commonly, graphene derivatives such as graphene oxide (GO), reduced graphene oxide (RGO), modified graphene oxide (MGO) and multi-layer graphene (MLG) are widely used as fillers for polymer composite materials. The easy synthesis and solution processability of GO as an inexpensive filler material is used to produce polymer composites [4]. Recently, the improvement in thermal, electrical and mechanical properties of PVC matrix with graphene derivatives has been reported in many literatures [2, 5-8]. However, studies on the PVC/GO composite are scarce. Deshmukh and Joshi (2014) prepared PVC/GO composite films with an interconnected network of macro-pores morphology by using colloidal blending method, and they reported that the strong interaction between PVC and GO increased thermal stability of the composites [4].

The objective of this work is to synthesis, thermal and structural characterization of PVC/GO composites with the use of minimum amount of fillers. The present study examines the structural properties and thermal behavior of PVC/GO composites in the minimum amount of filler.

2. Experimental Details

All chemicals and reagents were of analytical grade in the experiments. All solutions were prepared using deionized (DI) water. GO was prepared from natural graphite (45μm nominal particle size) by the Hummers method [9]. Graphite (1 g) was mixed with 69 mL of concentrated H2SO4 and the mixture was stirred in an ice bath for around 30 min. After homogeneous dispersion of the graphite powder in the solution, K2MnO4 (8 g) was added slowly to the solution in an ice bath and the reaction mixture was stirred for 15 min. under a reaction temperature of 20°C. Then the ice bath was removed and the mixture was stirred at 35°C overnight to form thickened paste. Afterward 70 mL of de-ionized water was added slowly into the reaction solutions to avoid the reaction temperature rising to a limit of 98 °C. After 2 h of vigorous stirring, 12 mL of 30 % H2O2 was added and the color turned golden yellow immediately (Fig. 1 a). Finally, the mixture was then filtered and washed several times with 3 % HCl and DI water until pH 7 and dried at 65°C for 12 h to obtain GO powder. There are plenty of oxygen-containing functional groups in its graphitic backbone: carboxyl (COOH) and carbonyl (-C=O) groups at the sheet edges and epoxy (C-O-C) and hydroxyl (-OH) groups on the backbone [10] (Fig. 1 b).

![Oxidation of graphite to graphene oxide and (b) chemical structure of graphene oxide]({attachment:image.png})

PVC/GO composites were prepared by a colloidal blending method. PVC (1gr) was first dissolved in Tetrahydrofuran (THF) at 70 °C and was cooled to room temperature. GO powder was separately dispersed in THF at 25°C. The two solutions were stirred for 2 h at 60°C. The resulting homogeneous dispersion was poured into glass petri dish and kept in an oven at 60 °C for slow evaporation of the solvent to get PVC/GO composite. The GO content in the PVC/GO composite was varied from 0.1–1 wt. % (Table 1).

<table>
<thead>
<tr>
<th>Samples</th>
<th>GO Content (in weight %)</th>
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<tbody>
<tr>
<td>PVC/GO-0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>PVC/GO-0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>PVC/GO-0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>PVC/GO-1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 1: Ratios and codes of GO in the composites

Structural analyses of the composites were carried out by FTIR spectra (Spectrum 100, Perkin Elmer) in the range of 4000–400 cm⁻¹ and X-Ray Diffraction (XRD, PAN analytical, Empyrean) in the range of 10–60°. The surface morphology was examined by a Scanning Electron Microscopy (SEM, Supra 40VP, Zeiss). Thermogravimetric analysis (TGA, STA 409, Netzsch) was performed by heating the samples from 25°C to 800°C at a rate of 1°C min⁻¹ in a nitrogen atmosphere. Differential Scanning
Calorimetry (DSC, STA 409, Netzsch) analysis was performed by heating the samples from 20°C to 600°C.

3. Results and Discussion

FTIR spectra of GO and PVC/GO composites were represented in Fig. 2. The broad peak at 3214 cm⁻¹ and a peak at 1720 cm⁻¹ in the FTIR spectrum of GO could be assigned to O-H stretching vibration and the carbonyl (C=O) stretching vibration, respectively. The peaks located at 1160 cm⁻¹ and 1040 cm⁻¹ belong to epoxy C-O stretching vibration and the stretching vibration of alkoxy C-O functional groups, respectively [12-13]. These results suggested that the GO sample was oxidized and presented mainly oxygen-containing functional groups. For the PVC/GO composites, the characteristic C-H in phase and out of phase stretching vibrations bands can be observed at 2911 cm⁻¹ and 2859 cm⁻¹, respectively. The peaks at 1426, 1252, 956, 834, 611 cm⁻¹ in the FTIR spectra of PVC/GO composites were attributed to the CH₂ deformation, CH-rocking, trans CH wagging, C-Cl stretching and cis CH wagging vibration, respectively [8-14]. Obviously, there was no marked difference in the FTIR spectra for all composites (Fig. 2). This result was attributed to the low amounts of added GO. Deshmukh and Joshi [4] reported that FTIR spectra of PVC/GO composites exhibited an increase in the broadness of the peak in the region 1000–1500 cm⁻¹ at higher loading of GO (2.5 wt.%).

Fig. 2 FTIR spectra of GO and PVC/GO composites

Fig. 3 showed XRD patterns of the pristine graphite (GF) and prepared GO and PVC/GO composites. The crystalline GF had a sharp characteristic peak at 2θ=26.4º. The corresponding interlayer distance was observed to be 0.33 nm. After oxidation, the diffraction peak shifted to 9.9° indicating that the interlayer space increased to 0.88 nm [13]. The increase in the interlayer distance from 0.33 nm to 0.88 nm was due to oxygen-containing functional groups intercalated within the layered structure. The results show that the reflection shape of PVC/GO composites is almost exactly the same because of the low X-ray diffraction intensity of PVC and low amounts of added GO [6]. These results of all composites indicated the GO layers well-dispersed in polymer matrix, as shown in Fig 3.

Fig. 3 X-ray diffraction patterns of GF, GO and PVC/GO composites.

Fig. 4 showed the SEM images of the GF, GO, PVC and PVC/GO composites. The SEM image of Fig. 4a that GF had a thin plate stacked structure [15]. GO presented a worm-like structure randomly aggregated [16-17] (Fig. 4b). According to EDS results of the GO and GF, oxygen content increased from 22.59 atom % to 47.95 atom %. When compared to the straight surface of neat PVC shown in Fig. 4c, the PVC/GO-0.1 composite with low doping amount (0.1 wt %) of GO showed continuous and compact structure with highly porous (Fig. 4d). As shown in Fig. 4e, the SEM image of the PVC/GO-0.3 composite showed that GO exhibited a crumpled structure in the form of thin sheets in a random manner closely associated with each other. Pores and cavities with 4-5 µm in size were observed on the PVC/GO-0.5 composite with 0.5 wt. % GO (Fig 4f) due to polymer growing in the pores and galleries of GO [4]. In Fig. 4g, the SEM image of PVC/GO-1 composite indicated a low degree of agglomeration of GO.

Fig. 4 SEM images of (a) GF, (b) GO, (c) PVC, (d) PVC/GO-0.1, (e) PVC/GO-0.3, (f) PVC/GO-0.5, (g) PVC/GO-1 (magnification 5000X).

TGA weight loss and derivative thermograms for the PVC and PVC/GO composites with different GO content were given in Fig. 5 and thermal parameters were summarized in Table 2.

Fig.5 TGA and DTG curves of (a) PVC, (b) PVC/GO-0.1, (c) PVC/GO-0.3, (d) PVC/GO-0.5 and (e) PVC/GO-1.
PVC started to degrade at low temperatures of about 153°C. PVC and its composites showed two stages of decomposition. The first weight loss was observed in 296°C for the neat PVC, corresponding to the loss of HCl [6] (Fig. 5 a). For the composites, the first weight loss (T1) in the range 292–276°C was attributed to the elimination of oxygen containing functional groups of GO [4] (Fig. 5 b - e). The decomposition temperatures of the PVC/GO-0.1, PVC/GO-0.3 and PVC/GO-0.5 composites were almost the same (Table 2) (Fig. 5 b-d). This means that the GO plays little role in improving the thermal stability of the PVC. When compared to the neat PVC, the first thermal decomposition temperature of the PVC/GO-1 composite in Fig. 5 a and e reduced to 276°C. It showed lower stability because the GO layers act as a reinforcing particulate filler attracting Cl. Therefore, the C–Cl bonds in PVC were weakened at this temperature [5-6]. The low thermal stability of the PVC/GO-1 composite was mainly attributed to the weak interactions between the GO and PVC [2]. As shown in Fig. 5 b-e, no weight loss from 290 to 470°C was observed, which indicates the stability of the composites at this temperature. The second major weight loss (T2) was observed between 457 and 470°C for all composites in Fig. 5 b-e, which was much shorter than the previous stage. For all PVC/GO composites, the mass loss during this degradation stage was little increased compared to the neat PVC (Table 2), which indicated that the dispersion of GO layers partially prevented the formation of volatile aromatic compounds along with a decrease of carbonaceous residue [6]. This result is consistent with those of the graphene/PVC composites reported in literature [2].

The resultant DSC thermograms were presented in Fig. 6 and the quantified results were summarized in Table 3. From the data, it could be observed that the neat PVC exhibited glass-transition temperature (Tg) at around 59°C. However, the PVC/GO composites showed a different behavior with the value of Tg shifted below 59°C (Table 3) [7]. Reducing of glass transition temperature provides an easier relaxation of molecular chain [18]. As shown in Fig. 6, DSC thermograms of the neat PVC and composites exhibited endothermic transition peaks. The peak temperature of melting occurred at about 300°C for all the PVC/GO composites, indicating that the addition of GO had little effect on the melting point of the composites (Table 3).

As given in Table 3, the addition of 0.1 wt. % GO produced an increase of 62.9 J/g in enthalpy. This could well be explained by the reinforcing effect of GO sheets leading to improved thermal stability. Moreover, this result demonstrated the compatibility of TGA and DSC curves of the PVC/GO-0.1 composite. When the GO content is increased to 0.3 and 0.5 wt. %, the melting enthalpy decreased to some extent. However incorporating 1 wt. % GO into PVC matrix led to a 29.81 J/g decrement in the value of enthalpy compared to the neat PVC and the composites with 0.1, 0.3 and 0.5 wt. %, which shows the existence of weak interaction between the polymer and the filler [18]. Also, TGA results (Table 2) and SEM images (Fig 4) supported the decrease in the enthalpy of the PVC/GO-1 composite.

### Table 2: Thermal parameters for the PVC and PVC/GO composites (20°C/min heating rate, under nitrogen atmosphere).

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C) range</th>
<th>Weight loss at 600°C (%)</th>
<th>Residue at 600°C wt. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>296</td>
<td>452</td>
<td>84</td>
</tr>
<tr>
<td>PVC/GO-0.1</td>
<td>292</td>
<td>464</td>
<td>86</td>
</tr>
<tr>
<td>PVC/GO-0.3</td>
<td>297</td>
<td>457</td>
<td>83</td>
</tr>
<tr>
<td>PVC/GO-0.5</td>
<td>293</td>
<td>469</td>
<td>86</td>
</tr>
<tr>
<td>PVC/GO-1</td>
<td>276</td>
<td>470</td>
<td>88</td>
</tr>
</tbody>
</table>

### Table 3: Glass-transition temperature and melting parameters of the neat PVC and PVC/GO composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Glass transition temperature (Tg, °C)</th>
<th>Melting temperature (Tm, °C)</th>
<th>Enthalpy (ΔH, J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>59</td>
<td>302</td>
<td>58.66</td>
</tr>
<tr>
<td>PVC/GO-0.1</td>
<td>56</td>
<td>299</td>
<td>62.49</td>
</tr>
<tr>
<td>PVC/GO-0.3</td>
<td>53</td>
<td>303</td>
<td>57.24</td>
</tr>
<tr>
<td>PVC/GO-0.5</td>
<td>54</td>
<td>294</td>
<td>55.41</td>
</tr>
<tr>
<td>PVC/GO-1</td>
<td>55</td>
<td>303</td>
<td>29.81</td>
</tr>
</tbody>
</table>

### Fig. 6 DSC curves of the neat PVC and PVC/GO composites.

4. **Conclusion**

In this study, FTIR, XRD and EDS results showed that GO was successfully synthesized from natural graphite by Hummers method. PVC/GO composites with dispersion in THF had been synthesized by colloidal blending method using minimum amount of GO. XRD results of all composites indicated the GO layers well-dispersed in PVC matrix. No changes was observed in XRD patterns and FTIR spectrums of all composites with addition of small amounts of GO to PVC matrix. However, the composites had a different morphological structure compared with the neat PVC. The SEM images showed that the composites with 0.1 and 0.5 wt. % GO filler exhibited a uniform composite with highly porous and micro porous morphology, respectively. TGA and DSC results showed that there was a good interaction between the GO and PVC. However, the addition of small amounts of GO into PVC matrix has not manifested an important improvement on thermal properties of the composites. All results of this study revealed that the structural changes of the PVC/GO composites must had influenced their mechanical properties. Therefore, the mechanical properties of these composites will be examined in a future work.

5. **Literature**


17. Li, D., B. Zhang, F. Xuan. The sequestration of Sr(II) and Cs(I) from aqueous solutions by magnetic graphene oxides, Journal of Molecular Liquids 209, 2015, 508–514.