Polypropylene-Polycarbonate composites with graphene oxide nanosheets: synthesis and characterization

Santosh K. Tiwari1,*, Andrzej Huczko1, Michal Bystrzejewski1, Nannan Wang2
1Department of Chemistry, Warsaw University, Warsaw, Poland
2Key Laboratory of New Processing Technology for Nonferrous Metals and Materials, Ministry of Education, School of Resources, Environment and Materials, Guangxi University, Nanning, China
ismgraphene@gmail.com

Abstract: Herein the effect of graphene oxide nanosheets (GOSs) on the thermo-mechanical stabilities of polypropylene (PP)/polycarbonate (PC), polymer blend nanocomposites (PNCs) fabricated via melt compounding has been explored. The comparison of properties of pure blend with PNCs, pointed out whether the mixing sequences have any effect on thermo-mechanical stabilities of PNCs. The PP/PC/GO nanocomposite exhibited an excellent increment in tensile strength and melting temperature as compared to the neat blend. In contrast, the PC/GO/PP nanocomposite, prepared by mixing the GOSs with PC first and then PC/GO with PP, has lower thermo-mechanical stability than PP/PC/GO. Interestingly, PP/GO/PC nanocomposite prepared by mixing the GOSs with PP first and then PP/GO with PC, showed the highest improvement in thermo-mechanical stability as compared to pure blend, PP/PC/GO, and PC/GO/PP. We attribute this trend of stabilities for PNCs due to the different extent of GOSs distributions within the polymer matrix. For PP/PC/GO, the GOSs were effectively dispersed in the PP phase due to low viscosity. In the case of PC/GO/PP, only small amount of GOSs was localized in PP and most of GOSs remain in PC phase. However, in case of PP/GO/PC, almost all GOSs were dispersed homogeneously in both phases resulting in a distinct increment of thermo-mechanical stabilities.

Keywords: GRAPHENE OXIDE NANOSHEETS, MIXING SEQUENCE, MELT COMPOUNDING AND THERMO-MECHANICAL PROPERTIES

1. Introduction

Polymers play a very crucial role in every part of our lives and it is very difficult to imagine present advancements without polymeric products. Polymer composites, because of their outstanding properties, like super toughness, lightweight, high elasticity, low cost, transparency and easy processing make them an excellent class of materials for the modern innovations [1-2]. The demand for polymeric materials is increasing steadily, mainly due to its extensive applications in healthcare, entertainment, clothing, food, communication and transportation industries [3]. Polycarbonate (PC) is an efficient and most commonly used amorphous engineering thermoplastic polymer. It is transparent and shows outstanding toughness up to the temperature of 140 °C [4]. The excellent toughness and tensile strength of PC is due to the existence of molecular dissipation (a sub glass transition temperature). However, it exhibits high notch sensitivity, high melts viscosity, hygroscopy and is prone to cracking with time. To avoid aforementioned shortcomings of PC, several modification have been reported [4, 5]. Among the various modifications, blending is an efficient technique in the polymer processing industries not only for the creation of new materials but also for hands-on recycling [6-7]. The melt compounding of PC with suitable polymers such as PMMA, Polyethylene, PP, and Nylons have been explored for the challenging applications as discussed in review papers [8-11]. PP is also engineering thermoplastic and commonly used for textiles, packaging stationery, automotive components and for laboratory equipment. However, most of the reported work to improve the toughness of PP/PC blend with fillers are acquired at the cost of tensile strength and thermal resistance [12]. Therefore, numerous strategies have been applied to avoid phase separation and weak interfacial adhesion due to the aggregation of fillers selectively in one of two polymer matrices [13, 14]. Often used facile routes to improve the quality of PP-PC blend was reviewed by Tchoudakov et. al. where different approaches have been explored to create a network like covalent bonding at the interfaces of blending partners [14, 15]. Hanim et. al. reported adsorption of nanofiller on the surface of PP chains and then melt compounding of PP-nanofiller with butadiene styrene to achieve desired thermomechanical stability [16]. Šupová et al. and few other workers recently have reviewed the effect of functionalization, size, and quantity of most frequently used fillers on polymer blend nanocomposites to improve physical properties of PP based polymer composites [17]. Hsieh et al. and Balazs et. al., reported homogeneous dispersion of layered silicate nanoclay in PC to increase stiffness, heat resistance and Young’s modulus, which makes a persuasive case for exploring PC nanocomposites, predominantly if toughness is wanted to be preserved. Thus, ample of works have been performed to achieve desired properties of PP/PC blend [18, 19].

In this work, we demonstrate the use of GOSs as a nano compatibilizer as well as a reinforcement to achieve better thermo-mechanical properties of PP/PC blend. The GOSs are single layered sp2 (predominantly) and few sp3 hybridized carbon sheets [20]. They are decorated with –OH and ─COOH groups at the edges while epoxy and ketonic groups are on its surface [20]. Several methods have been coined for the synthesis of GOSs and discussed in details elsewhere [21-22]. However, GOSs can be easily obtained from graphite powder as reported by Marcano et al [22]. During the last two decades GOSs have been widely studied in the context of several challenging applications, such as energy storage, separation of heavy ions from water, drug delivery and also as nanofiller for polymer blends [20, 23]. Many workers have proved that the thermo-mechanical characteristics, chemical inertness, gas barrier and electrical properties of the polymer composites can be enhanced by the incorporation of a minute amount GOSs [20]. Herein we report the role of mixing sequence on selective migration of GOSs into PP/PC blend that can offer an opportunity for the production of large-scale, high-quality blend nanocomposites. Rheological, mechanical and thermal properties of the as prepared PNCs are examined and discussed regarding their phase morphology and the selective distribution of GOSs in polymer matrices.

2. Experimental

2.1 Materials

Commercially available pure isotactic PP (grade LG SR20NS) was supplied by Bayer Materials Science, Thailand. Polycarbonate (grade LG 28) was also obtained from same source. We have not determined the molecular weight of these polymers because of its proper solubility in a particular solvent. For the synthesis of GOSs, we have used graphite powder, 98% H2SO4, 88% H3PO4, KMnO4 and 30% H2O2 from Sigma Aldrich (India).

2.2 Preparation of GOSs and Polymer blend nanocomposites

Prior to compounding, GOSs, PP, and PC were well dried in a vacuum oven at 50 °C for about 72 hours to remove moisture. The idea of mixing sequence was employed to produce three PNCs filled with GOSs and the neat blend. These PNCs and the neat blend were prepared by melt blending compounding using twin screw extruder at the working temperature 230 °C and 15 rpm and the mixing was performed for 15 minutes. Neat blend and PNCs was assembled in a definite shape using compression molding, at ~230°C and 12 MPa pressure for the mechanical property analysis, consequently the samples were cooled to room temperature. The composition and the
3. Characterization

Differential scanning calorimetry (DSC) analysis of neat blend and PNCs was performed in nitrogen gas environment with a DSC instrument (Model: NETZSCH DSC 200 PC instrument). The standardizations of heat flow and temperature were based on a run in which pure indium was heated through its melting point. The neat blend PNCs having a mass of about 30 mg were used for the study up to 200 °C at the heating rate 10 °C/min. The tensile test of the neat blend and PNCs were carried out on a dumb-bell shaped samples using a UTM instrument (Model No. Hounsfield HS 10 KS) operated at room temperature. The values of mechanical parameters reported in the present work are the average of the result for the test run on five samples. Dynamic mechanical analysis (DMA) was accomplished with a DMA analyzer (model No. 2980) for pure blend and PNCs. The test sample dimensions were approximately 50.0 x 13.0 x 3.5 mm. Liquid N$_2$ was used to attain the low temperatures and was also used to precisely control temperatures during the experiment. For TEM (JEM -2100 HRTEM, Make-JEOL, Japan) analysis, neat blend and PNCs were cut properly respective to their length axis using a ultramicrotom under cryogenic conditions with a thickness of around 70-100 nm for analysis. The cuts were taken from a middle and edge positions of the samples and then suitable sections were selected for the analysis. The instrument for analysis was operated at 100-120 kV and the micrographs were collected using an energy filter in zero loss mode for an optimal contrast of the GOSs.

4. Result and Discussion

4.1 ATR (Attenuated total internal reflectance) FTIR spectroscopy

The ATR-FTIR spectrum of pure blend and PNCs showed several bands (Fig. 1), confirming structural entities which are present in the PP, PC and GOSs. The major spectral features correspond to the IR absorption in the pure blend and PNCs are listed in Table 2 [23, 24]. The neat blend showed all characteristic peaks of PC and PP as previously reported by Renaut and co-workers [25]. The incorporation of GOSs leads to a notable change in the band positions and the intensities for PNCs in comparison to the neat blend as shown in the magnified IR spectra. It is well established that PP and PC form an incompatible blend due to the large viscosity lag and unfavourable interactions between the same [24-25]. In the fabricated PNCs, PC has excess polar components and, therefore, it may easily interact with GOSs. We have also analysed the C=O stretching region of PC to access the possible interaction between PC and GOSs. As shown in Fig. 1, the C=O stretching frequency of PC is centred at around 1737 cm$^{-1}$ and shifts to higher wavenumber with the incorporation of GOSs. This shift can be attributed to the hydrogen bonding between oxygen functional moieties of GOSs and C=O of PC. This shift suggests the presence of GOSs in the PC phase which is due to the better interaction of GOSs with PC phase as compared to PP. However, hydrogen bonding between PC and GOSs could decrease the stretching frequency of C=O of PC but an increase in the wavenumber can be explained in terms of stacking of PC chains on GOSs [26]. The stacking of PC on the GOSs may be attributed to π-π interaction between the similar carbon skeleton of PC and GOSs. It is well known that any restriction on the vibration of bonds require higher energy to exert the vibrational deformation. Therefore, an increase in the wavenumber can be observed for the C=O of PC in the case of PNCs. Due to the better interaction between GO and PC, polymer chains of PC get wrapped over the GOSs driven by the hydrogen bonding and π-π stacking between graphic sheets and aromatic backbone of PC. This wrapping of polymer chains restricts the vibration of C=O and hence increased the wavenumber probably through thermal energy migration dynamics mechanism as discussed by Li et al. [27]. A similar shift was also observed when GOSs was added to the PC phase first then with PP matrix which is an indication of presence of GOSs in PC phase. Interestingly, when GOSs was added first to PP matrix followed by PC, then the peak shift was also observed but the band was broadened as compared to PC/GO/PP sample (magnified FTIR graph). It might be due to the incomplete migration of GOSs from PP phase to the PC phase. Moreover, when GOSs was mixed first in PP followed by PC, then due to the better nonbonding interactions between PC and GOSs, the GOSs started migration from the PP to PC matrix. This migration might not be completed during the mixing duration and hence some C=O of PC remained unaffected without any interaction with GOSs and possessed its characteristic peak at 1737 cm$^{-1}$ due to which the peak broadened. So, FTIR analysis explains why the mixing sequences of GOSs can affect the dispersibility of blending partners and influence the incompatibility. If this selective dispersion occurred during melt blending then it must affects its thermal stability. Hence, the thermal stabilities of PNCs were analysed with DSC in the next section.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Composition and mixing order</th>
<th>Sample Code</th>
<th>Processing Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PP (70%) + PC (30%)</td>
<td>PPC</td>
<td>Temp. 230 °C, mp. 15</td>
</tr>
<tr>
<td>2</td>
<td>PP (69.5%) + PC (29.5%) + GO (1%)</td>
<td>PP/PC/GO</td>
<td>Same</td>
</tr>
<tr>
<td>3</td>
<td>PP (69.5%) + GO (1%) + PC (29.5%)</td>
<td>PP/GO/PC</td>
<td>Same</td>
</tr>
<tr>
<td>4</td>
<td>PC (29.5%) + GO (1%) + PP (69.5%)</td>
<td>PC/GO/PP</td>
<td>Same</td>
</tr>
</tbody>
</table>

Table 1. Composition and corresponding codes of the studied samples

Fig. 1 ATR-FTIR spectra of as prepared neat blend and PNCs. Magnified section of FTIR graph showing impact of GOSs incorporation into PP/PC blend.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>rmp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>230°C</td>
<td>15</td>
</tr>
</tbody>
</table>

57 YEAR XV, ISSUE 2, P.P. 56-61 (2021)
4.2 DSC Analysis

DSC analysis of polymeric samples was carried out and the respective graphs are shown in Fig. 2. It is established that glass transition temperature of PC, melting temperature of PP and melting temperature of neat PP/PC is around ~140-145 °C, ~158-160°C and ~158 °C, respectively [14,28]. The melting temperatures of each sample can be derived from the derivative DSC curve. In the present work each of studied samples shows a broad peak corresponding to the melting temperature and melting temperature of the as-prepared pure blend as reported elsewhere by Laoutid et al. [14]. The reason for the appearance of melting peak rather than glass transition temperature for the PP/PC based composites is outlined in [14]. A significant increment in melting temperature for the as-fabricated PNCs can be observed due to the incorporation of GOSs as nanofiller. This feature may be attributed to the function of GOSs as a nucleating agent as well as a nano compatibilizer during the crystallization process of PNCs. As expected, the melting temperature of PP/GO/PC system is significantly higher than that of other PNCs fabricated on the basis of mixing sequence. The greater thermal stability of PP/GO/PC is in accord with previous work [14] and depends on homogeneous dispersion of GOSs in the blend components as discussed in ATR-FTIR section. Remarkably, melting temperature of PP/PC/GO is of ~4°C higher than PC/GO/PP. This indicates that most of the PP chains were not covered by GOSs due to their aggregation in the PC phase and therefore a free movement of PP chains leads to an easy chain loosening process. This observation offered us another very strong evidence that the mixing sequence of GOSs played a crucial role in uniform distribution GOSs in both polymer matrices of PNCs.

4.3 TEM Analysis

The TEM images of the pure blend and PNCs are presented in Fig. 3a-d. The TEM images of the neat blend (Fig.3a) clearly show phase separation and droplets of PC domains. The droplets of PC are quite prominent and depict incompatible behavior of neat blend. This result is in agreement with our previous investigations [29]. The phase of the neat blend is indicated by the red circles in TEM micrographs of PP/PC (Fig.3a). The incorporation of 1% of GOSs provides a notable improvement in compatibility between PP & PC due to the nanosizing effect and nucleation effect of GOSs and it can be seen in the TEM micrographs of PNCs in Fig. 3b-d. However, the contribution of mixing sequence of GOSs on the same cannot be denied. The TEM micrograph of PC/GO/PP (Fig.3b) shows a huge agglomeration of GOSs mainly in PC domains as explained in FESEM section in our previous work [29]. For the sake of clarity we have heightened aggregation of GOSs in the Fig. 3b. Such selective dispersion of GOSs mainly in the PC phase is due to the lucid interaction between PC and GOs as discussed in the FTIR section. The PP/PC/GO showed better surface morphology and proper dispersion of GOs in PC and PP in comparison to the PC/GO/PP (Fig. 3c). However, in this case the accumulation of GOs can be observed at the interfaces of PP and PC instead of a homogenous distribution. This aggregation of GOs at interfaces is highlighted in TEM image of PC/GO/PP (Fig. 3c). The TEM micrograph of PP/GO/PP (Fig. 3d) shows a very uniform dispersion of GOs in the PP and PC. For PP/GO/PC, when GOs was mixed with PP first then with PP, the chains were adsorbed properly on the graphene oxide nanosheets and consequently strong hydrogen bonding and intense π-π interaction between GOs and PC resulted in excellent thermo-mechanical stability as compare to other fabricated systems.

4.4 DMA Analysis

The tan delta value is a good measure of the leather-like midpoint between the rubbery and glassy region for the polymeric materials and therefore it is an important parameter to evaluate the thermo-mechanical stability of polymeric materials [34]. A typical tan delta curve of the neat blend and PNCs is shown in the Fig.4. Herein, tan delta curves do not show any sharp and intense T_g peaks, because the neat blend and PNCs chains are not arranged in ordered crystals and are just strewn around in random fashion, even though they are in the solid state [35]. Thus, the shape and height of the tan delta peak changes spontaneously with a degree of amorphous content present in the PNCs. A broad peak between 60-160 °C in tan delta curves can be seen for the neat blend and PNCs. This tan delta peak is a signature for the presence of major amorphous portions in the studied samples. This is why the studied samples could not have any high-pitched glass transition temperature and melting temperature peaks. The neat blend showing a broad tan delta peak at around 66 °C depicts the high degree of incompatibility between PP and PC, which promoted micro-crack formation at the interface as well as non-uniform stress transfer due to unfavorable morphology (as shown in TEM images of the neat blend). However, a noteworthy shift in tan delta peak can be seen for the PNCs due to the incorporation of GOSs (Fig. 4) indicating

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>996, 971</td>
<td>-CH₃ rocking vibration of PP&amp;PC and</td>
</tr>
<tr>
<td>1045</td>
<td>-C=O and C-O groups from PC</td>
</tr>
<tr>
<td>1170</td>
<td>-CH₃ symmetric deformation vibration of PP</td>
</tr>
<tr>
<td>1268</td>
<td>Epoxide linkage of GO</td>
</tr>
<tr>
<td>1374</td>
<td>-CH₂ bending vibration of PP&amp;PC</td>
</tr>
<tr>
<td>1455</td>
<td>-CH₃ bending vibration of PP&amp;PC</td>
</tr>
<tr>
<td>1605</td>
<td>-C=C stretching from aromatic</td>
</tr>
<tr>
<td>1732</td>
<td>-C=O stretching of PC</td>
</tr>
<tr>
<td>2748</td>
<td>-C=O stretch carbonylic acid of GO</td>
</tr>
<tr>
<td>2918, 2863, 2833</td>
<td>-C=H stretching vibration of PP&amp;PC</td>
</tr>
<tr>
<td>3200-3400</td>
<td>-OH group of GO</td>
</tr>
</tbody>
</table>

Table 2. FTIR peaks corresponding to the functional groups present in the studied samples

![Fig. 2 DSC plot of fabricated PNCs and neat blend showing its melting point](image-url)
an increase in the thermo-mechanical stabilities of PNCs. The tan delta peak for PP/GO/PC was noted at the highest temperature among all the PNCs owing to homogeneous dispersion of GOSs in both phases of PNCs. On other hand either due to the aggregation of GOSs or due to its selective dispersion of GOSs in PC phase, both PP/PC/GO and PC/GO/PP shows reduced thermo-mechanical properties as comparisons to PP/GO/PC.

![Fig. 3 TEM images of neat blend (a: PP/PC) and PNCs (b: PC/GO/PP, c: PP/PC/GO and d: PP/GO/PC) showing the dispersion of GOs in polymer matrices](image)

4.5 Rheological Analysis

The rheological properties of the neat blend and PNCs were investigated to understand the microstructural change occurring due to the incorporation of GOSs in light of the mixing sequence methodology. **Fig. 5** displays the typical melt viscosity Vs shear rate graph for the PNCs and the neat blend. One can observe that the introduction of GOSs to the neat blend induced an apparent change in the melt viscosity and it can also be noticed that mixing sequence of GOSs plays an important role to define the viscoelastic properties of PNCs. The largely increased viscosity is obtained at low frequencies when GOs were first added to PP, then PP/GO to PC (i.e. in the case of PP/GO/PC). This is a good agreement with the thermal and morphological investigations as discussed in the previous sections. The high viscosity of PP/GO/PC is due to nucleating effect and homogeneous distribution of GOSs in PP/PC matrix which reduced the mobility of melts (polymeric components) possibly due to the cross-linking effect of GOSs as discussed in the FTIR section. However, it is worth to note that at the relatively higher shear rate, the difference in melt viscosity for PC/GO/PP and PP/PC becomes much smaller in comparison to PP/GO/PC and PP/PC/GO. This signifies that under the condition of high shear rate PC/GO/PP due aggregation of GOSs and neat blend due to the high degree of interfacial slippage between the blend components leads to phase separation. In other words, we can say that the only incorporation of GOSs to neat blend does not apparently affect the viscoelastic behavior of PNCs but it also depends on mixing sequence of GOSs.

![Fig. 5 Typical rheology graph of PNCs and neat blend showing viscoelastic properties](image)
4.6 Mechanical Properties

The effect of GOSs on the mechanical competency of the neat blend and PNCs were tested using an UTM instrument. Fig. 6 shows the graph of Young’s Modulus (Fig. 6a) and the tensile modulus (Fig. 6b) for the studied samples. The mechanical property of PNCs was greatly improved due to the incorporation of GOSs. The GOSs serve as not only the compatibilizers but also as the reinforcing negotiators due to their excellent mechanical properties. The mechanical properties of GOSs-compatibilized PNCs are substantially increased and this finding suggests that GOSs are desirable over the conventional nanofillers. This difference can be described in terms of homogeneous dispersion, nanosizing effect, and nonbonding interactions of GOSs with PC. The reason behind the homogeneous dispersion of GOSs and suitable crosslinking between filler and matrix in the case of PP/GO/PC was discussed in the FTIR section which created a situation for uniform stress transfer through GOSs present at the interface of PP and PC. Thus, the presence of GOSs at the interface of PP and PC can act as stress transferring medium and consequently high tensile modulus in the presence of GOSs at the interface of PP and PC can act as stress transfer through GOSs present at the interface of PP and PC. Therefore, a very little stress transfer between PP-PC and lowest tensile strength was observed. This reasoning was pointed out by many other researchers as discussed elsewhere [36]. Fig. 6a illustrates the Young’s modulus of the neat blend and PNCs. All PNCs showed increasing trend on Young’s modulus because the GOSs were quite rigid than the PP and PC. Therefore, the stiffness all nanocomposites increased with the incorporation of GOSs as expected and similar achievement has been reported by many researchers. This increase in Young’s modulus was also well supported by the increased thermal stability of PP/PC due to the addition of GOSs. Thus it seems that the presence of GOSs endorsed transcrysallization due to the nucleation effect of GOSs. As a result, the crystalline region in PNCs is increased, and it might increase the Young modulus of PNCs. The Young modulus of PP/GO/PC was significantly higher other PNCs as expected. The exceptional increase in tensile modulus of PP/GO/PC was due to the homogeneous interfacial bonding between the PP, GO and the PC as discussed in FTIR and TEM sections.

Fig. 6 Effect of mixing sequence and GOSs loading on (a) Young’s modulus and (b) tensile strength of PP/PC based PNCs produced via melt compounding

5. Conclusion

In this work the effect of graphene oxide nanosheets (GOSs) and their mixing sequence on thermo- mechanical stabilities of PP/PC blend and nanocomposites was studied. The best dispersion of GOSs was obtained for PP/GO/PC (among the other prepared blends e.g. PP/PC/GO, PC/GO/PP and PP/PC) after using melt compounding under the controlled temperature and pressure. It was found that the uniform distribution of GOSs resulted in excellent mechanical strength and thermal stability for PP/GO/PC comparing to poorly dispersed GOSs in cases of PP/PC/GO and PC/GO/PP. However, the significant increments in both mechanical and thermal properties were observed in contrast to the neat blend. The increases in the tensile strength values are ~50% and ~28% for the nanocomposites with 1% wt. of highly and poorly dispersed GOSs in comparison to the neat blend, respectively. Moreover, the homogeneously dispersed GOSs are much more operative in improving the melting temperature and the tensile modules of nanocomposites than the poorly dispersed GOSs and the neat blend. The TEM and rheological investigation showed that the mixing sequence are the key elements of the toughening effect in the PP/PC-based nanocomposites. It was also found that the aggregation of GOSs in polymer matrices results in a tremendous decrease in thermo-mechanical properties of nanocomposites.

Acknowledgement

Prof. G.C. Nayak (Dept. of Applied Chemistry, IIT Dhanbad, India) is greatly acknowledged for his suggestion and support during the experimental work. SKT would like to thank the Polish National Agency for Academic Exchange for the NAWA research grant (PPN/ULM/2019/1/00008/DEC/2).

References


