Thermal characterization of ABS-Graphene blended three dimensional printed functional prototypes for electro chemical energy storage

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Abstract: This study highlights the thermal characterization of ABS-Graphene blended three dimensional (3D) printed functional prototypes by fused deposition modeling (FDM) process. These functional prototypes have some applications as electro-chemical energy storage devices (EESD). Initially, the suitability of ABS-Graphene composite material for FDM applications has been examined by melt flow index (MFI) test. After establishing MFI, the feedstock filament for FDM has been prepared by an extrusion process. The fabricated filament has been used for printing 3D functional prototypes for printing of in-house EESD. The differential scanning calorimeter (DSC) analysis was conducted to understand the effect on glass transition temperature with the inclusion of Graphene (Gr) particles. It has been observed that the reinforced Gr particles act as a thermal reservoir (sink) and enhances its thermal/electrical conductivity. Also, FT-IR spectra realized the structural changes with the inclusion of Gr in ABS matrix. The results are supported by scanning electron microscopy (SEM) based micrographs for understanding the morphological changes.

Keywords: Fused deposition modeling, ABS, Graphene, Thermal characterization, Differential scanning calorimeter.

1. Introduction

Nano composites have been developed for the enhancement of thermal, mechanical and electrical characterizes of polymeric based materials without altering their processing conditions. Among the various materials, graphene (Gr) has a honeycomb, two-dimensional (2D) lattice structure in which carbon atoms are sp²-bonded, with promising mechanical, thermal, chemical, and electrical properties [1-3]. Due to its exciting electronic/ optoelectronic properties, it gains the attention of many researchers recently and becomes the focus of research in basic and applied science. Among its various properties, electrical and thermal conductivity are its interesting features.

Several distinguished properties of Gr make it exceptionally suitable for its applications in sensors. Having a pure 2D system, Gr symbolize the ultimate electromechanical system having all its atoms on the surface [4]. The emergence of a single adsorbed molecule on its surface, makes its conductance relatively sensitive to the ambient and its electrical characteristics can be significantly modified [5-6]. For making an effective sensor, there is a requirement of interface accessibility, good mechanical as well as electrical properties, ease of preparation and integration into presently available technologies. So, in this case, Gr seems to a successful candidate and has a great potential to appear as the sensor material [7]. Besides, Gr and chemically modified Gr, the composites of Gr with metal, their oxides, ceramics, and polymers emerge as a sensor materials [8-12]. Gr based sensors are smaller and lighter with variable design possibilities. They will likewise be more sensitive and ready to distinguish smaller changes, works rapidly and in the long run even be more affordable than conventional sensors.
Graphite is the utmost and cost-effective source for the extraction of graphene. The study highlighted that oxidative treatment of graphite, leads to the formation of graphite oxide (GO) which further extracted a graphene [13-14]. The mechanisms such as oxidation and exfoliation for the production of GO were explained by researchers [15-17]. The synthesis of Gr by exfoliation of natural graphite in ortho-dichloro benzene (ODCB) can be carried out by the process called “sonication” [18]. The specific properties (such as mechanical, optical and thermal) of Gr depends upon the extraction techniques [19-20]. Due to its highly sensitive behavior regarding thermal and electrical conductivity, Gr makes it self-eligible for various applications such as fabrication of bio-sensing devices, electronic circuits charge storage devices and medical bio-sensors [21-23].

Unfortunately, the use of these composite materials for FDM applications is rarely discussed. In the present work, the composite material has been developed to fabricate in-house ABS-Gr blended feedstock filament that can be further used for the 3D printing of electrochemical energy storage devices (EESD). The mechanism of reinforcement in ABS-Gr composite material is investigated through Melt flow index (MFI), differential scanning calorimeter (DSC) and Fourier transform infrared spectroscopy (FTIR).

2. Experimentation

2.1 Materials

The graded ABS was provided by Batra Polymers, India having melt flow index (MFI) of 2.92g/10min. The graphite in powder form having thermal conductivity 3–92 W/m K was supplied by Bharat Graphite Pvt. Ltd. (India). N-methylpyrrolidone (NMP) and acetone were purchased from Saiteja Chemicals, India. In the present case, acetone acts as a polar aprotic organic solvent to solvate ABS. This solvent can make a dilute ABS solution that can use the intermolecular forces for the bond formation of ABS and Gr. So, for making the polymeric based composite material, the Gr was reinforced in ABS matrix.

2.2 Synthesis of composites

The various techniques for the production of graphene are mechanical exfoliation from graphite, epitaxial growth on SiC and chemical vapor deposition (CVD) on Ni thin film. Figure 1 depicts the detailed procedure, followed in this work, for the extraction of Gr. The process starts with the treatment in the ultrasonic bath followed by centrifugation with a magnetic stirrer, which causes separation of graphite flakes from Gr. Aging of Gr dissolution contributed for stabilization of Gr layers in solutions then graphite flakes are removed to get Gr through pipetting. The present study presents an effective and efficient method to prepare Gr based polymer by a direct exfoliation of graphite in organic solvents with the addition of naphthalene.

Figure 1 Production method for Gr.
The Gr concentration of the dispersion in N-methylpyrrolidone (NMP) is as high as 0.15 mg/ml. Naphthalene serves as a molecular wedge to intercalate into the edge of graphite, which plays a key role during sonification and remarkably enhances the production of Gr. The extracted Gr flakes and their SEM image are shown in Figure 2a and 2b respectively.

![Gr flakes](image1)

![SEM image of extracted Gr](image2)

Figure 2 (a) Gr flakes (b) SEM of extracted Gr

It should be noted that Gr synthesized by the present method can be used for the production of conducting polymeric composites. In this work, the blending of ABS and Gr were carried out by two methods (Chemical blending and mechanical blending). For chemical mixing, Gr was dispersed in ABS by dissolving in acetone solution. Subsequently, the composite slurry was dried in vacuum oven at 70°C for 1-2 hr or until any possible residual moisture/solvent was removed. The resulting lump of the composite material was crushed mechanically. In case of mechanical blending, the mixture of Gr and ABS were directly fed into the hopper of twin screw extruder (TSE). For this method, initially, ABS granules was crushed to powder size (500-800µm) with the cryogenic grinding process then proportions of various ingredients were mixed in tumbler mixture by rotating at the speed of 250 rpm for 3 hours.

2.3 Melt Flow Index

The MFI values of composite materials were recorded by using MFI tester (Shanta Engineering, India). The MFI test was carried out by maintaining cylinder temperature of melt flow tester at 230°C and weight 3.8Kg as specified in ASTM D 1238-73 standard. The mean value of ‘5’ observations was measured for each composition. Table 1 shows the weight loading of Gr in ABS matrix and their respective MFI values by mechanical/chemical blending.

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight Proportion (g) ABS</th>
<th>Weight Proportion (g) Gr</th>
<th>Blending Method</th>
<th>MFI (g/10min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>75</td>
<td>25</td>
<td>Chemical</td>
<td>3.20</td>
</tr>
<tr>
<td>B</td>
<td>75</td>
<td>25</td>
<td>Chemical</td>
<td>2.20</td>
</tr>
<tr>
<td>C</td>
<td>90</td>
<td>10</td>
<td>Mechanical</td>
<td>4.12</td>
</tr>
<tr>
<td>D</td>
<td>90</td>
<td>10</td>
<td>Mechanical</td>
<td>2.51</td>
</tr>
<tr>
<td>ABS</td>
<td>100</td>
<td>0</td>
<td>---</td>
<td>2.92</td>
</tr>
</tbody>
</table>

As shown in Table 1, the experiments were conducted with two proportions, i.e. 25g Gr blended with 75g ABS, and 10g Gr blended with 90g ABS. As already mentioned above that acetone is only used in chemical mixing. Therefore resulting weight proportion of Gr has been calculated as:

\[ \text{w/w\%} = \left( \frac{25g (Gr)}{75g (ABS)+40g (Acetone)} \times 100 \right) \]

w/w% = 21.7%
Similarly for 90g ABS and 10g Gr dispersed in 40g acetone, the resulting weight proportion of Gr is 7.69%.

2.4 Differential Scanning Calorimeter

DSC analysis of composite materials and commercially available ABS material were performed on DSC1 (Mettler Toledo) with HSS8 sensors and Huber TC intercooler (Refrigerated cooling). The samples were not pre-treated and weighted about 4-9 mg sample for the measurements. Apart from this 40µl Al standard crucible with a pinhole on Mettler Toledo, 5 decimal balance was used. For the first cycle, the samples were heated from 30°C to 250°C with 1 min isothermal curing at 250°C and cooled to 30°C. Second heating and a cooling scan were then performed with the same set of input conditions. Both heating and cooling cycles were carried out at a rate of 10K/min. The DSC curves during the second cycle depict the peak whose area corresponds to the enthalpy involved in the process. The DSC curves highlight typical thermal effects during the heating and cooling of the amorphous material. The measurements were recorded under a constant nitrogen flow of 50ml/min.

2.5 Fourier transform infrared spectroscopy

For FT-IR spectra, initially, the samples were dried at 75°C for five hours and then chamber was purged with nitrogen flow for five min. Infrared absorption spectra were collected on a Nicolet 5SXC FT-IR Spectrometer.

3. Results And Discussion

3.1 MFI Analysis

The most desirable condition of a new filament material for FDM is the judiciary selection of the proportions of polymeric materials and fillers materials [24-25]. A part of above, successful processing of a new filament material on FDM depends upon the fabrication of a strong and spoolable feedstock filament, having required consistent diameter. To understand the flow properties of the newly developed material, it is necessary to characterize the rheological behavior of the composite material. The understanding of flow properties concerning temperature and feed rate during processing in liquefier head of FDM facilitates the selection of input parameters for part building process [26]. The reinforcement of filler in Nylon6 modified its structure, and properties and it is necessary to investigate the effect, particularly for the analysis and design of processing operations [27]. Shenoy et al. [28] carried out MFI test of polymer composites to generate curves, which highlights the relationship between viscosity, temperature, and shear rate. Table 1 shows the MFI of ABS/Gr composites with different content of Gr and different blending method. The MFI of ABS/Gr composites were lower than that of virgin ABS. This is because the addition of Gr can cause amide exchange reactions with the ABS matrix resulting in an increase in the molecular weight of ABS.

As the molecular weight of ABS/Gr composites was steadily increasing with increasing content of Gr, the flowability of ABS/Gr composites was constantly decreasing. As we know the MFI is the measurement of flowability for comparative purpose and it is weight in ‘g’ of polymer extruded through standard die at a specified load and temperature (depends upon selected polymer). As already reported, with the increase of Gr content in ABS matrix, MFI value decreases (MFI of material ‘B’ is less than ‘D’ and MFI of material ‘A’ is less than ‘C’). Moreover, it is also observed that MFI is also affected by the blending process. For the same weight proportions, mechanical blended materials (B and D) have less MFI value than chemical blended materials (A and C). The increase in MFI during chemical blending may be due to the
entrainment of acetone in the ABS/Gr composite matrix. Further, with the increase of Gr content from 10g to 25g in ABS matrix, the effect of blending process on MFI reduces. For ‘C’ and ‘D’ materials difference in MFI is 1.61 but, for ‘A’ and ‘B’ it is 1.0. In mechanical blending, as the weight proportion of Gr increases from 10g to 25g, MFI reduces from 2.51 to 2.20g/10min but in chemical blending, it reduces from 4.12 to 3.20g/10min. With the loading of Gr, the occupancy of Gr increases and little space is available for acetone. On the contrary, the reinforcement of Gr in ABS causes the decrease in free volume and flow of the macromolecular chains ceases. The compatibility of chemical blended samples is more than mechanically blended samples. The incorporation of acetone improves fluidity of material and thus reduces the energy consumption during processing.

3.2 DSC analysis

The successive cycles of heating and cooling have been run on DSC. Figure 3-4 shows the DSC heating and cooling curves of ABS and ABS/Gr composites. The glass transition temperatures ($T_g$), can be determined from Figure 3-4, are shown in Table 2. The virgin ABS has a slightly higher melting temperature than in ABS/Gr composites. The difference in melting temperature is attributed to the incorporation of Gr into ABS matrix. Although the Gr has poor compatibility with ABS it can cause amide exchange reactions with ABS structure during its polymerization process to some extent. This resulted in the ABS having higher molecular weight and lower MFI (Table 1). Moreover, the melting temperature of ABS/Gr composites became lower with increasing of Gr content, due to the decrease of the molecular weight with the increase of Gr content [29]. Additionally, the addition of acetone to chemical blended ABS/Gr composites also resulted in a decrease in melting temperature. Because carboxylic groups on the surface of Gr will react with the amino terminal groups of ABS, this can terminate the chain propagation resulting in a further increase in the average molecular weight of the ABS and grafting of the ABS chains to the Gr surfaces.

Table 2. Summary of data from DSC measurements.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_g$(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>99.13</td>
</tr>
<tr>
<td>B</td>
<td>98.32</td>
</tr>
<tr>
<td>C</td>
<td>98.50</td>
</tr>
<tr>
<td>D</td>
<td>95.52</td>
</tr>
<tr>
<td>ABS</td>
<td>105.0</td>
</tr>
</tbody>
</table>

The Gr particles occupy the available free space in ABS structure, which causes the ABS chains to be more difficult to flow. Additionally, carboxylic groups on the surface of Gr can react with the amino terminal groups of ABS. So, the amide covalent bonds formed also restrict the free motion of the polymer chains. As shown in Figure 3, a small drop was observed for glass transition in the first heating cycle (104.37°C), while 105.77°C during the second heating cycle. Normally, the $T_g$ of virgin ABS is 105°C. Similarly for the chemical blended sample with proportion 75:25 a small drop occurred in the curve having value 97.76°C shows glass transition in the first heating cycle, while 99.13°C during the second heating cycle. The observed values in chemically blended samples are much closer to the $T_g$ of ABS, i.e. 105°C while in case of mechanically blended samples the temperature range is quite far. The Gr particles emerge as a nucleation agent which promotes the crystallization process but it seems to interfere the perfect crystallization of ABS/Gr composite material [29-30]. This resulted in the shift of $T_m$ to a lower temperature. The presence of acetone in chemical blended samples acts as an interface between ABS and Gr and thus improves its compatibility and bond formation. However, among these ABS/Gr composite materials, A is highly thermally stable and can be used for making FDM prints.
3.3 FT-IR Characterization

Fourier-transform infrared spectroscopy is a technique, generally used to generate an infrared spectrum of absorption or emission of a solid, liquid or gas. Basically, it measures the light absorbed at each wavelength. The commonly used instrument (spectrometer) has a range 4000 cm$^{-1}$ to 660 cm$^{-1}$, simultaneously collects high-spectral-resolution data and measures intensity over a narrow range of wavelengths at a time. In this work, spectra range from 2000 cm$^{-1}$ to 560 cm$^{-1}$ was selected. The spectra of material ‘A’ (75/25 chemical blended),
material ‘B’ (75/25 mechanical blended), material ‘C’ (90/10 chemical blended), material ‘D’ (90/10 mechanical blended) and virgin ABS are shown in Figure 5-9 respectively.

Figure 5. FT-IR spectra of material ‘A’.

Figure 6. FT-IR spectra of material ‘B’.

Figure 7. FT-IR spectra of material ‘C’.
Structural changes were visualized in FT-IR spectra after the reinforcement of Gr in ABS matrix (Figure 5-9). The vibrational band assignment confirms the molecular structure of ABS and ABS/Gr composite materials. There was some significant difference observed in ABS without Gr and ABS blended with various concentrations of Gr as shown in Table 3. The changes in peaks confirm the presence of Gr in ABS matrix as it affects the transmittance of that composition. This shows that the interfacial effect is a dominant factor in the binding of ABS/Gr composites. The FT-IR results showed the peak at 1701.12 in ‘A’, 1750.54 in ‘B’, and 1830.51 in ‘D’ due to characteristic band stretch of C = O of Gr but it is not visualized in ‘C’. Increase in intensity of characteristic band stretch of C = C in FTIR spectra of ‘A’ and ‘B’ sample showed the presence of Gr in ABS material (Table 3). The change in peaks of ABS and ABS/Gr composites confirms that reinforcement of Gr in ABS matrix affects the transmittance of ABS.
Table 3. FT-IR spectra and assignment of ABS/Gr composites and virgin ABS.

<table>
<thead>
<tr>
<th>Wavenumbers (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>1701.12</td>
<td>1750.54</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1577.43</td>
<td>1577.31</td>
</tr>
<tr>
<td>1448.52</td>
<td>1449.69</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1182.78</td>
<td>1181.70</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>964.00</td>
<td>963.84</td>
</tr>
<tr>
<td>767.26</td>
<td>766.26</td>
</tr>
<tr>
<td>697.49</td>
<td>698.41</td>
</tr>
<tr>
<td>---</td>
<td>558.33</td>
</tr>
</tbody>
</table>

4 Conclusion

In this work, ABS/Gr based composites were systematically characterized regarding Melt flow index (MFI), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimeter (DSC). The results revealed that ABS/Gr based composites could be used as filament material for the production of EESD with FDM process. The MFI confirmed that the flowability of ABS/Gr based composites was affected by the weight proportion and blending method. The MFI value decreases with the increase of Gr content in ABS matrix (MFI of material ‘B’ is less than ‘D’ and MFI of material ‘A’ is less than ‘C’). For the same weight proportions, mechanical blended materials (B and D) have less MFI value than chemical blended materials (A and C). The Gr particles loading act as a thermal reservoir (sink) which absorbs heat of crystallization and hinders the crystal nucleation and growth. The DSC results indicate the decreased of melting temperature and T<sub>g</sub> to 95.52°C, (approx.10.0%) with the inclusion of Gr fillers ABS matrix. Overall, ABS/Gr based material shows high potential for promising applications in the rapid manufacturing of energy storage devices. Thus, it can be concluded that ABS/Gr based feedstock filament can be used for the production of EESDs with FDM process.

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References


