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**RESEARCH ARTICLE**

**MECHANICAL AND MORPHOLOGICAL STUDIES OF NEW TERPOLYMER COMPOSITE**

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**ABSTRACT**

The present research article reports the mechanical and morphological properties of a new nano composite material derived from aniline - ortho toluidine - diethylaniline terpolymer (AOTDEA) and graphene oxide (GO). The composite under present investigation has shown significant improvement in its mechanical properties and morphological characters as compared to terpolymer alone. AOTDEA terpolymer was obtained by condensation polymerisation of the starting materials and its structure has been assigned by physicochemical and spectral evidences. GO was prepared from graphite using a modified Hummers method. GO was used as a nano-filler for the fabrication of AOTDEA-GO composite. It is evident that addition of 5% by weight of GO led to significant enhancement in tensile strength of the composite. It is supported by the drastic decrease in the Young's modulus values of terpolymer and its composite with GO that is 3.9 GPa and 2.3 GPa respectively. It is further supported by increased elongation at break values. The decrease in volume resistivity values suggests that incorporation of GO during composite fabrication served as a conducting filler material to form electrical percolation networks in the composites. The improved morphological properties are supported by scanning electron microscopy (SEM) images.

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**INTRODUCTION**

The use of terpolymers in all spheres of life has been abundantly increased in recent years because of their novelty and versatility. They occupy the pivotal position in the field of polymer science. The progress in this field has been extremely rapid, as they are generally useful in packaging, adhesives and coatings in electrical sensors, ion-exchangers, organometallic semiconductors, activators, catalyst and thermally stable materials (Masram *et al.*, 2010; Katkamwar *et al.*, 2009; Singru and Gurnule 2009; Hiwase *et al.*, 2010; Shah *et al.*, 2008). Although carbon nano tubes (CNTs) are effective fillers to enhance the mechanical and electrical properties of polymers, they cannot be dispersed easily in a solvent or a polymer matrix due to the van der Waals forces (Verdejo *et al.*, 2011; Vaia and Wagner 2004). Graphene is a two-dimensional (2D) carbonaceous material with sp<sup>2</sup>-bonded carbon atoms which has attracted much attention since its experimental discovery in 2004 due to both, its high aspect ratio and high surface area (Novoselov *et al.*, 2005; Castro Neto *et al.*, 2009; Compton and Nguyen 2010). For composite applications, the significant van der Waals force of pure graphene such as CNTs presents an obstacle while attempting to disperse them in both organic and inorganic solvents (Lee *et al.*, 2012). In contrast,

graphene oxide (GO) obtained by chemical oxidation of graphite, can meet this demand. It is well dispersed in organic solvents due to presence of functional groups on its basal planes and edges, such as epoxides, hydroxyls, ketones, diols and carbonyl groups (Cai *et al.*, 2008; Lerf *et al.*, 1998; Park and Ruoff 2009; Dikin *et al.*, 2007; Luong *et al.*, 2011; Kim *et al.*, 2012). In addition, GO is a highly cost-effective material compared to graphene or CNTs because it can be obtained from graphite, which is still abundant in nature, by simple preparation treatment (Hummers method). GO has been chemically modified to improve degree of dispersion in a solvent and a small amount of GO has been incorporated into a polymer matrix by a solution-casting method (Kuilla *et al.*, 2010; Hummers and Offeman 1958; Luong *et al.*, 2011). Application of terpolymer composite as an excellent adsorbent for removal of carcinogenic Cr (VI) from polluted water has been reported in the literature (Rahangdale *et al.*, 2013). In this article, composite containing a low content of GO was prepared to study their mechanical properties. AOTDEA-GO composite containing 5 % of GO has been prepared via a conventional solution-casting method. The structure of the polymer is supported by Fourier transform-infrared spectroscopy (FTIR). The volume resistivity and tensile properties were measured by a four-point probe unit and a universal tester, respectively. After the tensile test, the fractured surface of the composite has been interpreted by a scanning electron microscopy (SEM) images.

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## MATERIALS AND METHODS

### Preparation of Terpolymer (AOTDEA)

Equimolar mixture of monomers viz. Aniline(A), O-toluidine (OT) & diethylaniline (DEA) was dissolved in the organic solvent (chloroform) with constant stirring to obtain a gray coloured solution, followed by the dropwise addition of 100 ml of the dopant (1M HCl) and 100 ml of an aqueous solution of the oxidant (0.1M ammonium persulphate). The mixture was stirred for 48 hrs. The solution obtained was washed repeatedly with deionised (DI) water. 200 ml of acetone was then added in to the solution when the terpolymer (AOTDEA) was precipitated out. It was filtered, washed several times with acetone and dried in oven for 24 hrs.

### Synthesis and purification of graphite oxide (GO)

Graphite flakes (150 mesh, 99.5%) were obtained from SDFCL Mumbai, India. potassium permanganate ( $\text{KMnO}_4$ , 99.0%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 wt %), Sulphuric acid ( $\text{H}_2\text{SO}_4$ , 97%) and  $\text{NaNO}_3$  were procured from Merck, Mumbai, India. GO was synthesized by a modified Hummers method (Hummers and Offeman, 1958). 4 grams graphite flakes were added to a 250 ml round-bottom flask containing 120 ml  $\text{H}_2\text{SO}_4$  and this was stirred for 1 hrs. 15 grams  $\text{KMnO}_4$  was divided into 5 parts which were then added to the mixture at intervals of 20 min while being stirred. The mixture was slowly heated to 40°C and maintained for 5 hrs in order to oxidize the graphite. Subsequently, 150 ml of DI water was added to the mixture followed by addition of 15 ml  $\text{H}_2\text{O}_2$  solution with constant stirring for 30 min and then kept in this condition for 24 hrs. The mixture was centrifuged, washed several times with DI water. GO, so obtained, was finally dried in oven at 45°C for 24 hrs.

### Composite fabrication

Terpolymer (AOTDEA) was dissolved in DMF. Graphene oxide was added with constant stirring using magnetic stirrer for 2-3 hrs and dried in oven to evaporate the solvent. Composite fabricated was possessing of 5% by weight of graphene oxide concentrations

## Characterization

The terpolymer and its composite have been characterised using Fourier transform Infrared spectroscopy (FT-IR Spectrophotometer, BRUKER). The volume resistivity was measured using a resistivity meter and a super megohmmeter. The tensile testing of the composite was carried out using an tensile strength tester with a cross head speed of 5 mm/min. The length and width of the specimen were 2.5 cm and 0.5 cm, respectively, and at least 5 specimens were prepared for each test. Surface morphology has been studied from Scanning electron microscopy (JEOL-JSM-5200 microscopy, STIC Cochin). An acceleration voltage of 15 kV was used to observe the morphology of the fractured surfaces of pure terpolymer and it's composite.

## RESULTS AND DISCUSSION

### Characterization of the Terpolymer and its composite

The FT-IR spectra of terpolymer and its composite are shown in Fig. 1.

FTIR Spectrum of AOTDEA terpolymer shows a band at 1615–1580  $\text{cm}^{-1}$  and at 1510–1450  $\text{cm}^{-1}$  is due to aromatic ring stretching. Appearance of band at 3130–3070  $\text{cm}^{-1}$  is due to aromatic C-H stretching and 1225–950  $\text{cm}^{-1}$  is due to aromatic C-H bending (in the plane). Appearance of band at 900–670  $\text{cm}^{-1}$  may be because of asymmetric aromatic C-H bending (out of plane). Bands at 770–735  $\text{cm}^{-1}$  and 860–800  $\text{cm}^{-1}$  is indicative of ortho and para substitution in aromatic ring. Very strong absorption band at 3744  $\text{cm}^{-1}$  proves the presence of aromatic secondary amino linkage. Presence of aromatic nitro group is evident by appearance of bands at 1498  $\text{cm}^{-1}$  and 1547  $\text{cm}^{-1}$  respectively for asymmetric and symmetric stretching. Comparatively weak absorption band at 3618  $\text{cm}^{-1}$  indicates the presence of  $\text{CH}_3$  group (C-H stretching). On the basis of physicochemical and spectral evidences the most probable structure have been suggested and given in Fig.2

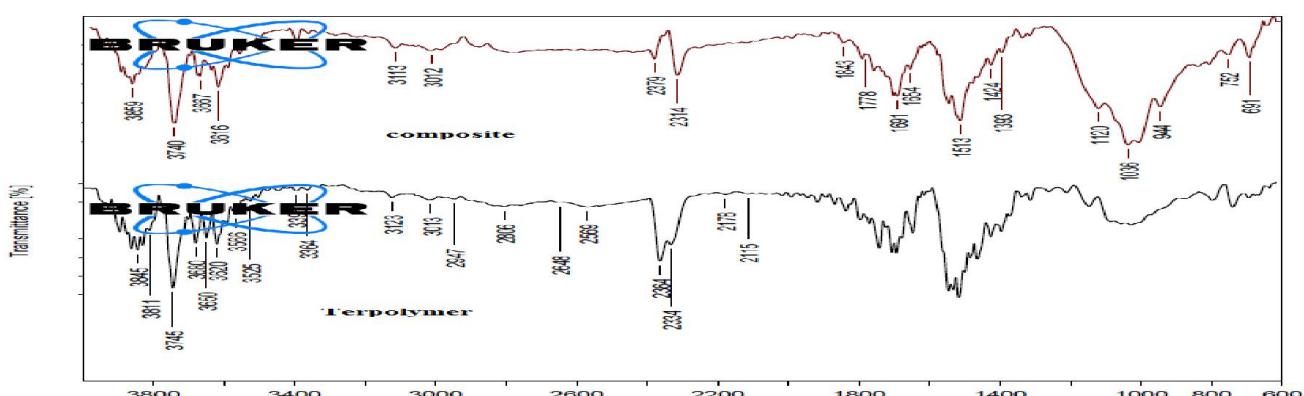
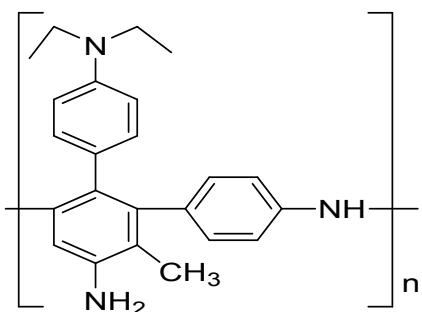


Fig. 1. FTIR spectra of terpolymer and its composite



**Fig. 2. Structure of terpolymer (AOTDEA)**

In the FT-IR Spectrum of the composite the additional absorption bands at  $1716\text{ cm}^{-1}$  (C=O symmetric stretching),  $1393\text{ cm}^{-1}$  (C-N stretching) and  $723\text{ cm}^{-1}$  (C=O bending of imide) can be clearly noticed, which confirms the successful fabrication of AOTDEA-GO composite.

#### Volume resistivities of pure Terpolymer (AOTDEA) and AOTDEA-GO composite

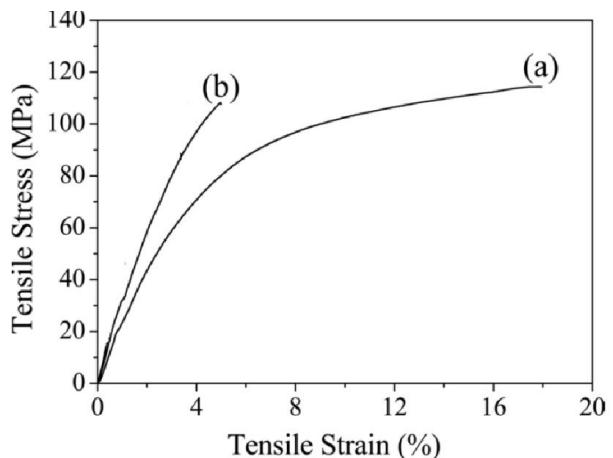
The volume resistivities of pure Terpolymer and Terpolymer-GO composite were measured by four-point probe unit (Table 1). The volume resistivity of pure terpolymer and terpolymer-GO composite(5 wt% GO) was found to be  $3.5 \times 10^{13}\text{ }\Omega\cdot\text{m}$  and  $6.0 \times 10^8\text{ }\Omega\cdot\text{m}$  respectively.

**Table 1. Tensile properties of (AOTDEA) terpolymer and AOTDEA-GO composite**

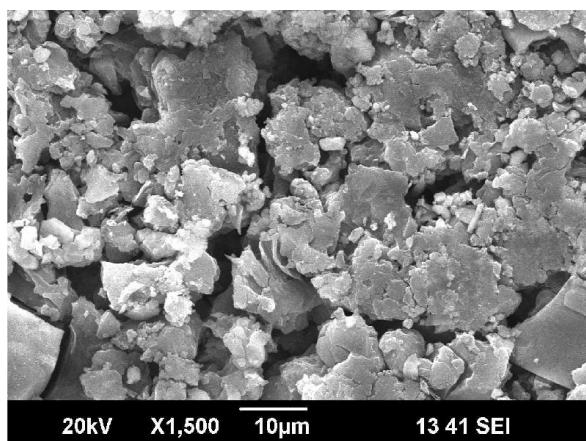
Sample	Terpolymer (AOTDEA)	AOTDEA-GO composite
Volume resistivity ( $\Omega\cdot\text{m}$ )	$3.5 \times 10^{13}$	$6.0 \times 10^8$
Young's modulus (GPa)	$3.9 \pm 0.3$	$2.3 \pm 0.3$
Tensile strength (MPa)	$38 \pm 2$	$53 \pm 2$
Elongation at break (%)	$7.4 \pm 0.5$	$16.2 \pm 0.5$

#### Mechanical properties of pure terpolymer and its composite

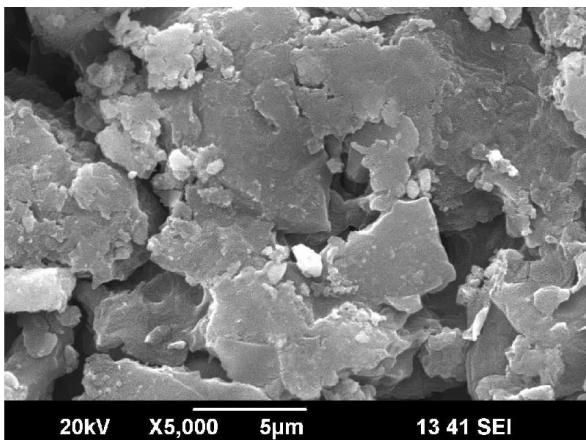
The typical stress-strain curves of pure terpolymer and its composite have shown in Fig.3. The values of the tensile properties are summarized in Table 1. The Young's modulus increased significantly with the addition of GO. The Young's modulus with regard to the GO-terpolymer composite containing 5 wt% GO drastically decreased from 3.7 GPa to 2.1 GPa most likely due to the non-covalent and molecular level interaction between GO and terpolymer. Also, the corresponding tensile strength increased from 104MPa to 111 MPa owing to the fillers in the composite, which led to the phase separation of GO from the terpolymer matrix. It is well known that external stress on terpolymer composite is transferred from the continuous phase (polymer matrix) to the discontinuous phase (filler) and that the final properties depend on the extent of the bonding between the two phases, resulting in good mechanical properties. The fractured surfaces of the pure terpolymer and terpolymer-GO composite were observed by SEM (Fig. 4.) after tensile testing in order to understand the tensile properties of the GO-terpolymer composite, the fractured surfaces were relatively rough compared to that of the pure terpolymer.



**Fig. 3. Stress-strain curves of (a) terpolymer-GO composite, (b) pure terpolymer**



(a)



(b)

**Fig. 4. SEM images of (a) AOTDEA-terpolymer, (b) AOTDEA-GO composite**

#### Conclusion

Following conclusions have been drawn on the basis of results obtained during the investigation.

- AOTDEA terpolymer have been successfully synthesised in the laboratory and characterised.
- Most probable structure for AOTDEA terpolymer has been proposed on the basis of physicochemical and spectral evidences.
- AOTDEA-GO composite has been successfully fabricated and characterised using FT-IR and SEM studies.
- AOTDEA-GO composite has superior properties than that of AOTDEA terpolymer.
- Improvement in the mechanical properties is supported by increased values of tensile strength and elongation at break while decreased Young's modules values respectively for pure terpolymer and its composite under present investigation.
- Decreased values of volume resistivity suggest that the terpolymer can be converted to semi-conducting /conducting polymer by composite fabrication.
- Improvement in the conducting behaviour is due to incorporation of GO during composite fabrication which might have created electrical percolation networks in the composites.
- The SEM images show roughing of the surface which led to increased surface area which favorable situation for the composite material if it used as an adsorbent.
- Thus the composite fabrication is fruitful for improvement of superior mechanical and morphological properties of terpolymers.

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