



RESEARCH ARTICLE

MECHANICAL AND MORPHOLOGICAL STUDIES OF NEW TERPOLYMER COMPOSITE

¹Bahekar, V. R., ^{*3}Rahangdale, P. K., ¹Thakare, S. R. and ²Shende, S. S.

¹Institute of Science, Nagpur 440010, India

²NPW college Lakhani, India

³Bhawabhuti Mahavidyalaya Amgaon-441902, India

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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 sp²-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.

*Corresponding author: Rahangdale, P. K.
Bhawabhuti Mahavidyalaya Amgaon-441902, India.

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 (KMnO₄, 99.0%), hydrogen peroxide (H₂O₂, 30 wt %), Sulphuric acid (H₂SO₄, 97%) and NaNO₃ 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 H₂SO₄ and this was stirred for 1 hrs. 15 grams KMnO₄ 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 H₂O₂ 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 cm⁻¹ and at 1510–1450 cm⁻¹ is due to aromatic ring stretching. Appearance of band at 3130-3070 cm⁻¹ is due to aromatic C-H stretching and 1225-950 cm⁻¹ is due to aromatic C-H bending (in the plane). Appearance of band at 900-670 cm⁻¹ may be because of asymmetric aromatic C-H bending (out of plane). Bands at 770-735 cm⁻¹ and 860-800 cm⁻¹ is indicative of ortho and para substitution in aromatic ring. Very strong absorption band at 3744 cm⁻¹ proves the presence of aromatic secondary amino linkage. Presence of aromatic nitro group is evident by appearance of bands at 1498 cm⁻¹ and 1547 cm⁻¹ respectively for asymmetric and symmetric stretching. Comparatively weak absorption band at 3618 cm⁻¹ indicates the presence of CH₃ group (C-H stretching). On the basis of physicochemical and spectral evidences the most probable structure have been suggested and given in Fig.2

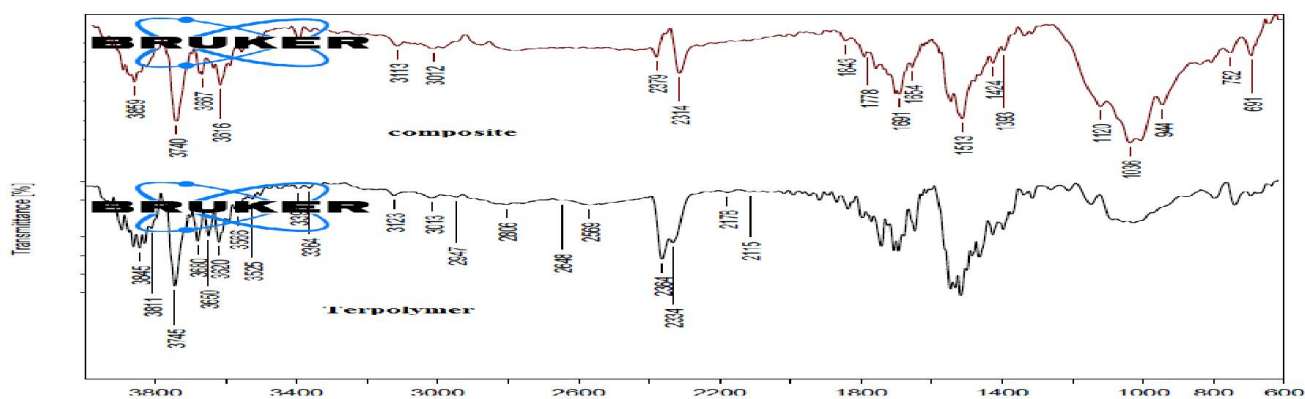


Fig. 1. FTIR spectra of terpolymer and its composite

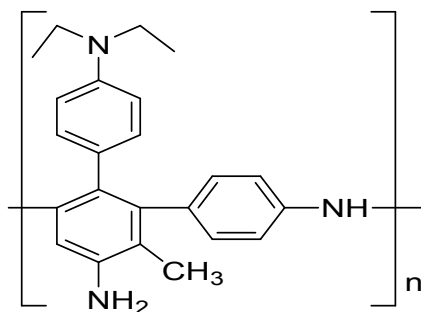


Fig. 2. Structure of terpolymer (AOTDEA)

In the FT-IR Spectrum of the composite the additional absorption bands at 1716 cm^{-1} (C=O symmetric stretching), 1393 cm^{-1} (C-N stretching) and 723 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 $3.5 \times 10^{13}\ \Omega\cdot\text{m}$ and $6.0 \times 10^8\ \Omega\cdot\text{m}$ respectively.

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

Sample	Terpolymer (AOTDEA)	AOTDEA-GO composite
Volume resistivity ($\Omega\cdot\text{m}$)	3.5×10^{13}	6.0×10^8
Young's modulus (GPa)	3.9 ± 0.3	2.3 ± 0.3
Tensile strength (MPa)	38 ± 2	53 ± 2
Elongation at break (%)	7.4 ± 0.5	16.2 ± 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 104 MPa 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.

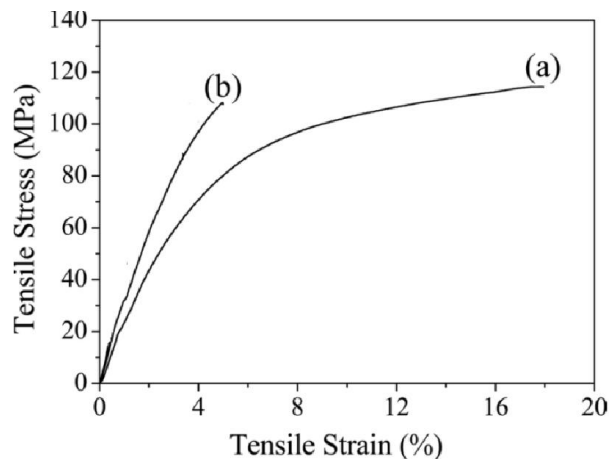
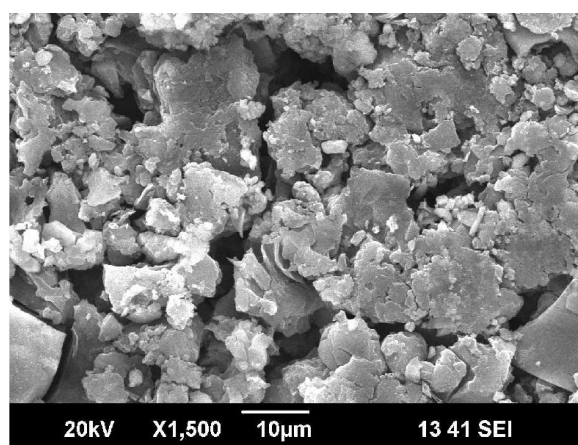
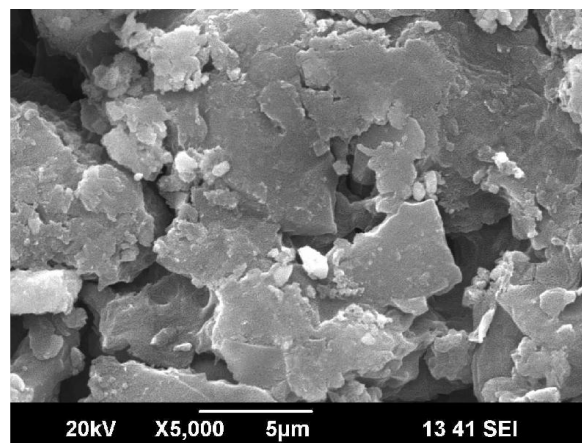


Fig. 3. Stress-strain curves of (a) terpolymer-GO composite, (b) pure terpolymer



(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 modulus 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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REFERENCES

- Cai W. W., R. D. Piner, F. J. Stadermann, S. J. Park, M. A. Shaibat, Y. Ishii, D. X. Yang, A. Velamakanni, An SJ, M. Stoller, An JH, D. M. Chen, R. S. Ruoff. 2008. Synthesis and solid-state NMR structural characterization of ¹³C-labeled graphite oxide. *Science*, 321, 1815. <http://dx.doi.org/10.1126/science.1162369>.
- Castro Neto A. H., F. Guinea, NMR Peres, K.S. Novoselov, A. K. Geim. 2009. The electronic properties of graphene. *Rev Mod Phys*, 81, 109
- Compton O.C., S.T. Nguyen. 2010. Graphene oxide, highly reduced graphene oxide, and graphene: versatile building blocks for carbon-based materials. *Small*, 6, 711 <http://dx.doi.org/10.1002/sml.200901934>.
- Dikin D. A, S. Srnkovich, E. J. Zimney, R. D. Piner, H. B. Dommett, G. Evmenenko, S. T. Nguyen, R. S. Ruoff. 2007. Preparation and characterization of graphene oxide paper. *Nature*, 448, 457. <http://dx.doi.org/10.1038/nature06016>.
- Hiwase V. V., A.B. Kalambe, K.M. Khedkar, S.D. Deosarkar, 2010. Ion exchange properties of resins derived from phydroxybenzaldehyde, resorcinol and formaldehyde. *E - J. Chem.* 7(1), pp. 287-294.
- Hummers W. S., R. E. Offeman 1958. Preparation of graphitic oxide. *J Am Chem Soc*, 80, 1339. <http://dx.doi.org/10.1021/ja01539a017>.
- Katkamwar S.S., A.B. Zade, S.S. Rahangdale, W. B. Gurnule, 2009. Terpolymer resin-III: Synthesis and characterization of 8-hydroxyquinoline-dithiooxamide-formaldehyde terpolymer resins. *J. Appl. Polym. Sci.* 113, pp. 3330-3335.
- Kim G. Y., M. C. Choi, D. Lee, C. S. Ha. 2012. 2D-aligned graphene sheets in transparent polyimide/graphene nanocomposite films based on noncovalent interactions between poly(amide acid) and graphene carboxylic acid. *Macromol Mater Eng*, 297, 303. <http://dx.doi.org/10.1002/mame.201100211>.
- Kuilla T., S. Bhadra, D. Yao, N. H. im, S. Bose, J. H. Lee. 2010. Recent advances in graphene based polymer composites. *Prog Polym Sci*, 35, 1350. <http://dx.doi.org/10.016/j.progpolymsci.2010.07.005>.
- Lee S. H., Y. J. Kim, D. H. Kim, B.C. Ku, H. I. Joh 2012. Synthesis and properties of thermally reduced graphene oxide/polyacrylonitrile composites. *J Phys Chem Solids*, 73, 741. <http://dx.doi.org/10.1016/j.jpccs.2012.01.015>.
- Lerf A., H. He, M. Forster, J. Klinowski, 1998. Structure of graphite oxide revisited II. *J Phys Chem B*, 102, 4477. <http://dx.doi.org/10.1021/jp9731821>.
- Luong N. D., N. Pahimanolis, U. Hippi, J. T. Korhonen, J. Ruokolainen, L. S. Johansson, J. D. Nam, J. Seppala, 2011. Graphene/cellulose nanocomposites paper with high electrical and mechanical performances. *J Mater Chem*, 21, 13991. <http://dx.doi.org/10.1039/C1JM12134K>.
- Luong N.D., U. Hipp, J. T. Korhonen, A. J. Soininen, J. Ruokolainen, L. S. Johansson, J. D. Nam, L. H. Sinh, J. Seppala. 2011. Enhanced mechanical and electrical properties of polyimide film by graphene sheets via in situ polymerization. *Polymer*, 52, 5237 <http://dx.doi.org/10.1016/j.polymer.2011.09.033>.
- Masram D.T., K.P. Kariya, N.S. Bhavé, 2010. Electrical conductivity study of resin synthesized from salicylic acid, butylenediamine and formaldehyde. *Arch. Appl. Sci. Res. vol.2 (2)*, pp. 153-161.
- Masram D.T., N.S. Bhavé, K.P. Kariya, 2010. Kinetics study of thermal degradation of resin derived from salicylaldehyde, ethylenediamine and formaldehyde. *E - J. Chem. vol.7(2)*, pp. 564-568.
- Novoselov K. S., A K Geim, S. V. Morozov, D. Jiang, M.I. Katsnelson, I.V. Grigorieva, S. V. Dubonos, A.A. Firsov, 2005. Two-dimensional gas of massless Dirac fermions in graphene. *Nature*, 438, 197. <http://dx.doi.org/10.1038/nature04233>.
- Park S. J., R. S. Ruoff, 2009. Chemical methods for the production of graphenes. *Nat Nanotechnol*, 4, 217. <http://dx.doi.org/10.1038/nnano.2009.58>.
- Rahangdale P.K., M.R. Lanjewar, S. S. Hunge, (2013) Application of new composite terpolymer adsorbent for removal of carcinogenic Hexavalent chromium, *J Nat. Sci. vol.1(1)*, pp.71-81. (ISSN -2320-4346)
- Shah B.A., A.V. Shah, B.N. Bhandaria, R.R. Bhatt, 2008. Synthesis, Characterization and Chelation Ion-Exchange Studies of a Resin Copolymer Derived from 8-

- Hydroxyquinoline-Formaldehyde-Catechol. *J. Iran. Chem. Soc.* 5(2), pp. 252-261.
- Singru R.N., W.B. Gurmule, 2009. Chelation ion-exchange study of copolymer resin derived from 8-hydroxyquinoline 5-sulphonic acid, oxamide, and formaldehyde. *J. Appl. Polym. Sci.* 116, pp. 3356–3366.
- Vaia R.A., H.D.Wagner. 2004. Framework for nanocomposites. *Mater Today*, 7, 32 [http://dx.doi.org/10.1016/s1369-7021\(04\)00506-1](http://dx.doi.org/10.1016/s1369-7021(04)00506-1).
- Verdejo R., M.M. Bernal, L.J. Romasanta, M.A.Lopez-Manchado. Graphene filled polymer nanocomposites. 2011. *J Mater Chem*, 21, 3301 [http:// dx.doi.org/ 10.1039/C0JM02708A](http://dx.doi.org/10.1039/C0JM02708A).
