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IMPROVED ELECTRICAL PRPERTIES OF NEW TERPOLYMER BY COMPOSITE FORMATION

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Abstract
Improvement in the electrical properties of a newly obtained terpolymer(AOTMNA) derived from aniline(A), ortho toluidine(OT) and m-nitroaniline(MNA) after its conversion into nano composite material by incorporation of graphene oxide (GO) in the polymer matrix have been reported in the present research paper. The composite under present investigation has shown significant improvement in its electrical properties as compared to terpolymer alone. AOTMNA terpolymer was obtained by condensation polymerisation of the starting materials and its structure has been proved 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 AOTMNA-GO composite. The results prove that composite formation improves the electrical properties of the terpolymer to a great extent.
Key words: graphene oxide, terpolymer, composite, electrical properties, Hummers method.

Introduction

Polyaniline is one of the most studied conducting polymers because of its high stability, enhanced conductivity and processability[1]. Terpolymers occupy the pivotal position in the field of polymer science. Their use in all spheres has been abundantly increased in recent years because of their novelty and versatility. 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[2-7]. 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[8,9]. Graphene is a two-dimensional carbonaceous material with sp^2-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[10-12]. For composite applications, the significant van der Waals force of pure graphene such as CNTs presents an obstracle while attempting to disperse them in both organic and inorganic solvents[13]. 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[14-19]. 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 [20-22]. Application of terpolymer composite as an excellent adsorbent for removal of carcinogenic Cr (VI) from polluted water has been reported in the literature[23]. In the present investigation, composite containing a low content of GO was prepared to study the improvement in mechanical & electrical properties of newly synthesized terpolymer. AOTMNA-GO composite containing 5 % of GO was prepared via a conventional solution-casting method. The structure of the polymer is supported by Fourier transform-infrared spectroscopy.

Experimental and Experimental Techniques

Chemicals

All the chemicals used were of Analytical reagent or chemically pure grade

Preparation of Terpolymer (AOTMNA), synthesis and purification of graphene oxide (GO) and composite fabrication has been done by methods which have already been published[24].

Characterization

The terpolymer and its composite have been characterised & the results obtained have already been published[24]. Electrical conductivity measurement of the terpolymer and its composite was done using digital multimeter (model DT 92080L.) 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

On the basis of physicochemical and spectral evidences[24] the most probable structure have been suggested and given in Fig.1

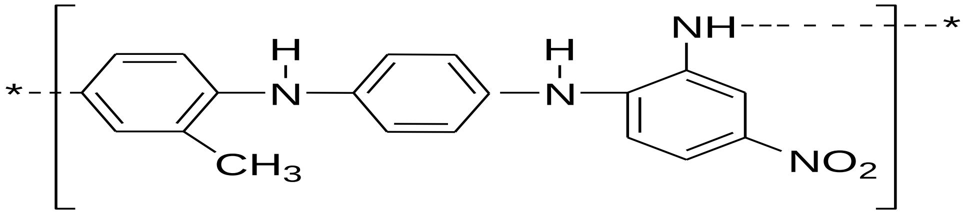


Fig.1. Structure of Terpolymer (AOTMNA)

DC-Conductivity measurement

The conductivity of polymers depend on number of parameters such as temperature, oxidation state, level of protonation, moisture content, and counter ion. The effect of temperature on electrical conductivity of metallic conductors and semiconductors is quite different.

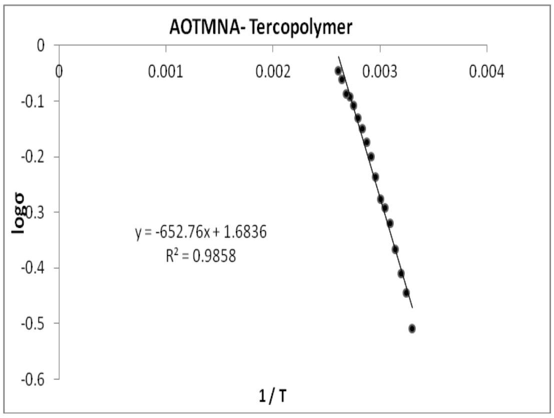
The results of electrical conductivity of AOTMNA-tercopolymer and its composite material at room temperature and at 150⁰C are listed in Table 1

Table: 1 Electrical conductivity of AOTMNA tercopolymer and composites

Properties	Conductivity (S/cm)	
	(30⁰C)	*(150⁰C)*
Tercopolymer (AOTMNA)	0.31	*1.19*
AOTMNA-GO (I)	27.3	*53.0*

The electrical conductivity of tercopolymer (AOTMNA) measured in the temperature range 30⁰ C to 150⁰ C. The electrical conductivity increases with temperature showing semiconducting behaviour and the conductivity at room temperature found to be 0.31 S cm^{-1} while at 150⁰ C has 1.19 S cm^{-1}. A plot of log σ vs. 1/T would be linear in given temperature range with a slope of (-Ea/2.303K). Using slope the activation energy Ea was calculated. The activation energy of electrical conduction of AOTMNA tercopolymer was found to be 2.074kJ $mole^{-1}$. The graph of log σ vs. 1/T of tercopolymer has shown in Fig.2. The experimental data revealed that electrical conductivity increases with rise in temperature have shown in Fig.3 Hence this tercopolymer shows semiconducting behaviour in the temperature range 303 to 423 K.

The electrical conductivities of the AOTMNA tercopolymer/GO composites are increased dramatically in comparison with that of pure tercopolymer. Such enhancement of the conductivity of the composite might be attributed to extended H-bonding between the tercopolymer and graphene oxide allowing extended p-conjugation in the polymer chains. The polymerization on the surface and pores of GO sheets restricts the twisting of the polymer backbone away from planarity, which plays a major role in enhancing the conductivity. Also there may have π–π stacking between the GO sheets and polymer backbone. Therefore, graphene oxide plays an effective role in enhancement of conductivity.



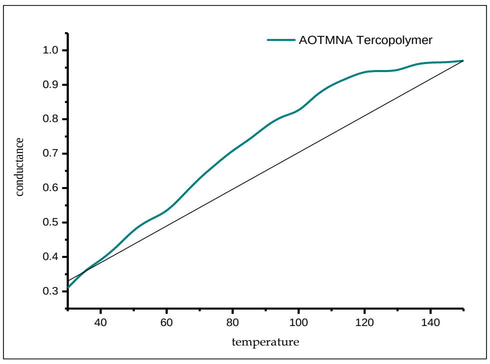


Fig.2 Plot of log σ Versus 1/T of AOTMNA-Terpolymer

Fig.3 Effect of temperature on conductivity of AOTMNA-Terpolymer

At high temperature, the mobility of the charge carrier increases with the increase in interchain and intrachain hopping. An increase in interchain and intrachain hopping results in high charge carrier mobility within the composite, which leads to an increase in conductivity at appropriate high temperature. The graph of log σ vs. 1/T of composite has shown in Fig.4. The experimental data revealed that electrical conductivity increases with rise in temperature have shown in Fig.5 of Hence this composite shows semiconducting behaviour in the temperature range 303 to 423 K. The conductivity values of the concerned composite are higher than that of pure tercopolymer.

Table: 2. Activation Energy of AOTMNA tercopolymer and composite

Properties	*'Ea' Activation Energy (kJ mole^{-1})*
Tercopolymer (AOTMNA)	2.074
AOTMNA-GO	1.00

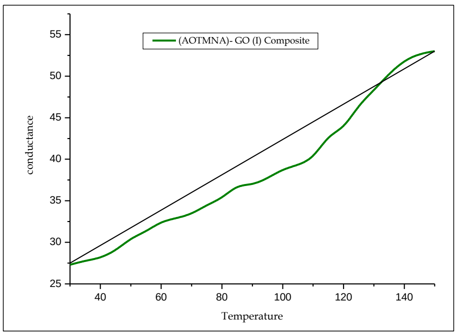


Fig.4 Effect of temperature on conductivity of (AOTMNA) - GO Composite.

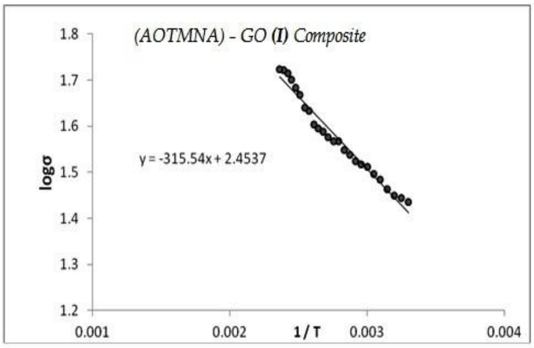


Fig.5 Plot of log σ Versus 1/T of AOTMNA-GO Composite

Conclusions

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

- Synthesis of AOTMNA terpolymer, fabrication of AOTMNA-GO composite is and their characterisation is successful.
- Most probable structure for AOTMNA terpolymer has been proposed on the basis of physicochemical and spectral evidences.
- AOTMNA-GO composite has superior properties than that of AOTMNA terpolymer.
- Improvement in the conducting behaviour is due to incorporation of GO during composite fabrication which might have created electrical percolation networks in the composites.
- Thus the composite fabrication is fruitful for improvement of superior electrical properties of terpolymers.

Scope for future work

The studies can be extended to evaluate the improvement in other properties (mechanical, morphological etc.) of the terpolymer under investigation by way of composite formation.

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References

1) D.Li and R.B.Kaner, J. Am. Chemical Society, 128, 968 (2006).
2) D.T. Masram, K.P. Kariya, N.S. Bhave, (**2010**): Electrical conductivity study of resin synthesized from salicylic acid, butylenediamine and formaldehyde. *Arch. Apll. Sci. Res. vol.2 (2)*, pp. 153-161.
3) D.T. Masram, N.S. Bhave, 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.
4) S.S. Katkamwar, 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.
5) R.N. Singru, W.B. Gurnule, (**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.
6) V. V. Hiwase, 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.
7) B.A. Shah, A.V. Shah, B.N. Bhandaria, R.R. Bhatt, (**2008**): Synthesis, Charecterization and Chelation Ion-Exchange Studies of a Resin CopolymerDerived from 8-Hydroxyquinoline-Formaldehyde-Catechol. *J. Iran. Chem. Soc. 5(2)*, pp. 252-261.
8) R.Verdejo, 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.
9) R.A.Vaia, H.D.Wagner. **(2004),** Framework for nanocomposites. *Mater Today,* ***7***, 32 http://dx.doi.org/10.1016/s1369-7021(04)00506-1.
10) K. S.Novoselov, 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.
11) A. H. Castro Neto, F. Guinea, NMR Peres, K.S.Novoselov, A. K. Geim. **(2009),**The electronic properties of graphene. *Rev Mod Phys, 81*, 109
12) O.C. Compton, 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/ smll.200901934.
13) S. H.Lee, 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. jpcs.2012.01.015.
14) W. W. Cai, 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 .
15) A. Lerf, 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.
16) S. J. Park, R. S. Ruoff, **(2009)** Chemical methods for the production of graphenes. *Nat Nanotechnol, 4,* 217. http://dx.doi.org/10.1038/ nnano.2009.58.
17) D. A Dikin, S. Srankovich, 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.
18) N.D. Luong, 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.
19) G. Y. Kim, 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(amid acid) and graphene carboxylic acid. *Macromol Mater Eng, 297,* 303. http:// dx.doi.org/10.1002/mame.201100211.
20) T. Kuilla, 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.
21) W. S.Hummers, R. E.Offeman. **(1958)** Preparation of graphitic oxide. *J Am Chem Soc, 80*, 1339. http://dx.doi.org/10.1021/ ja01539a017.
22) N. D. Luong, 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.
23) P. K. Rahangdale, 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.
24) V. R. Bahekar, P. K. Rahagdale, S. R. Thakare. S. S. Shende **(2014)** Surface morphology and thermal properties of new AOTMNA-GO Nanocomposite, *Int. Journal of Research in Bio. Agri. &Technology vol.(1),* ISSN-2347-517X

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