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Graphene Endowed Nanocomposite Sheet: Synthesis, Characterization and Thermal Stability

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Abstract. Graphene oxide/polyimide nanocomposites, expect that these properties increase. That's why by the incorporation of modified graphene oxide into polyimides, graphene oxide polyimide nanocomposite can be achieved with excellent properties as compared to the parent material and may perform better than polyimide in different applications like in batteries and nano-platelet fillers etc. The aim of this research project is to enhance the thermal conductivity of graphene oxide (GO)/PI nanocomposite films. These polyimide nanocomposite films will be analyzed and characterized using X-rays diffractions (XRD), Fourier transform infrared spectroscopy (FTIR). We will measure the thermal stability of polyimide nanocomposites films by using gravimetric analysis (TGA).

Keywords: nanocomposite, graphene oxide, XRD, FTIR, TGA

Introduction

Nanocomposites are particular class of materials originating from particular mixing of two or more such nanoparticles objects in various suitable methods, resulting in materials having exceptional physical properties and applications in different field. As a result of successful mixing of parent components into single material new properties of nanocomposites derived. Materials scientists frequently hold such nanocomposites, formed by successful mixing of two or more inorganic nanoparticles. Afterward scientists are more interested in other forms of the nanocomposites, the course of thermal and electrical properties also used in practical applications. Hence, successful mixing of different properties of the core material in the course of the magnetic, catalytic, electronic and optical properties, etc., along with accessible properties of conducting polymers become the purpose of researchers.

Enhancement in unique physical properties of conducting polymers have been a topic of concern for scientists (Gangopadhyay and De, 1999; Bhattacharya *et al*., 1996). At the start dielectric properties of nanocomposites were studied with the use of testing a barium-titanate-PPy (polymer polypyrrole) nanocomposite. Percentage (%) of this compound is extremely small among the nanocomposites as a result of this small dc strength was observed as compared to pure PPy (103 S/cm) and new nanocomposites (Miyauchi *et al*., 1989).

In the beginning, first commercial nanocomposite was polyamide developed by Toyota Central Research and Development. The above indicated element is established lying on in-reactor regarding Caprolactam as well as Motmorillonite which has been ion exchanged among the hydrochloride salt of aminolauric acid (12-amino-decanoic acid) (Liu *et al*., 2022; Collister, 2002; Fornes *et al*., 2001). Enhancement in the electrical strength is achieved through the addition of a graphite platelet within polystyrene. It mainly showed the sharp transition of the polymer from an electrical insulator to an electrical semiconductor among the addition of a graphite nanoplatelet (Bilisik *et al*., 2022; Chen *et al*., 2001).

Material and Methods

All the material used was of analytical grade purchased from Sigma Aldrich which were used without further purification. All the glassware used were washed with detergent, dried in oven and was rinsed with ethanol before its usage.

Synthesis of graphene oxide (GO). In the preparation of improved method, mixture used ratio of intense mixture of sulphuric acid as well as phosphoric acid (180:20) mL was added towards graphite flakes (2 g,

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1 weight equivalent) in three necked round bottoms flasks. A mechanical stirrer was used for the homogenous mixing of mixture present in round bottom flask and it was stirred for 30-35 min as shown below in Fig. 1.

Then 12 g of potassium permanganate was divided into several parts and then added to mixture very slowly. Before its addition temperature was maintained at 4-5 °C using an ice bath so that no vigorous reaction would take place. At start only 0.5 g of $KMnO_4$ was added and so, on all the quantity was added in the mixture at the start while being stirred. By the addition of $KMnO_4$, the reaction was started to form a slight exotherm toward 35-40 °C with bumping to some extent. The mixture was continuously stirred, heated at low temperature as well as maintained the temperature for 2 h for the oxidation purpose of graphite. Distilled water (200-300 mL) w as added slowly into the oxidized suspension and temperature was increased to 60-70 °C with continuously stirring and mixing for 4-5 h. Solution was cooled to room temperature and was kept onto ice bath 400 mL. Reaction was terminated the reaction 30% H_2O_2 (3 mL) and distilled water were poured in cooled reaction mixture.

Then the fully oxidized suspension was set aside in this condition for 24 h (shown in Fig. 2). Second day, the solution was centrifuged at 1500 rpm for 4-5 min. Heavy particles were settled down, while a suspension was separated. Then the suspension and settled both of these were washed with water and then with 30% HCl. Mixture was passed out through multiple washings about 5-6 times and centrifuged in order to obtain pH 5-6. Slurry of graphene oxide was obtained which was spread out in a Petri dish. Finally GO sheets were obtained after drying for 2-3 days in vacuum oven for 3 days.

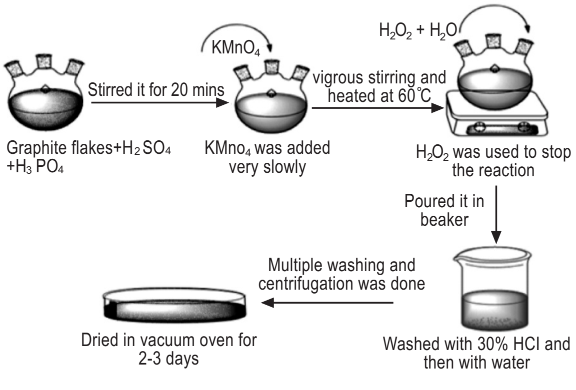

Fig. 1. Formation of graphene oxide sheet.

Synthesis of blank solution of polyimide. For the formation of polyimide (PI), firstly the poly amic acid (PAA) in two step method discovered by Dr. A. Endrey was formed. In the first step PAA is prepared by poly-condensation reaction between aromatic diamine and a dianhydride as well as in the other method cyclo-dehydration of PAAs was done to form polyimide (Ghosh, 1996; Sroog, 1976).

Formation of PI by two step method. Two step procedure of polyimide synthesis included firstly the preparation of the solution regarding aromatic diamine (ODA) in a polar aprotic solvent like pyromellitic dianhydride toward 4,4′-diamiondiphenyl ether solution at ambient temperature. Time requirement of solution preparation depend upon monomer reactivity. PAAs are fully soluble in the reaction which having high molecular weight then the solution spread into a film on appropriate substrate. Then after this imidization process in which heat the film at elevated temperature by adding dehydrating agent as shown in the Fig. 3 (Gohlke, 1987; Walter, 1965).

Preparation of GO/PI nanocomposite film. In the formation of pure polyimide and reduced graphene oxide/PI composite layer, ODA was added to the GO slurry and subsequently stirred at 80 °C for 8 h under nitrogen atmosphere. The solution is filtered as well as washed with NMP solvent considering many times to remove extra quantity of ODA. The GO-ODA sample is collected subsequent to drying. PI/GO-ODA solutions are formed with several GO-ODA loads. A resulting polymerization is according to that the: GO-ODA will first be scattered in NMP solution through sonication regarding 2 h a 250 mL) round bottom prepared along a nitrogen cove as well as magnetic stirrer will be exciting along distilled N-methylpyrolidine and suitable

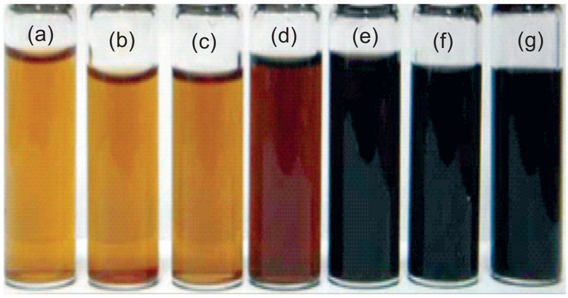

Fig. 2. Graphene oxide suspension under different conditions.

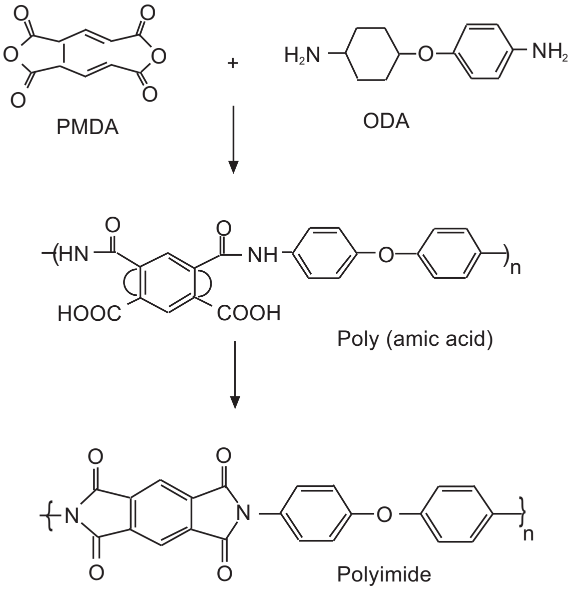

Fig. 3. Preparation scheme of PI.

amount of graphene oxide-ODA/NMP solution. Behind ODA is run, the equal amount of dianhydride (PMDA) would be supplementary. The solution is stirred at room temperature regarding 3 h. Mixture was then combining at high temperature regarding 10 h as well as water formed through imidization was constantly removed among flow regarding nitrogen (N). In this way, whirling solution contain 0.5% through weight of graphene oxide-ODA in polyimide is obtain. We are expecting that an increase in the thermal stability of GO/PI nanocomposite films. This is analyzed and characterized by XRD and FTIR technique.

Results and Discussion

UV/VIS spectrophotometer analysis. The UV/VIS spectroscopy used the light in the visible as well as in adjacent ranges. In the visible region the absorption directly affects the colour of the chemicals involved. Also, electronic transition of the atoms and molecule take place in the electromagnetic spectrum. It is corresponding to fluorescence spectroscopy which measures the transitions from excited to ground state but in absorption it deals with transition from lower to higher state. It is also used for the structure determination of highly conjugated organic compound, transition metal ions and biological macro-molecules. The degree of conjugation in UV/VIS can be determined by ëmax and the value of ëmax increase when the conjugation is higher than less energy is used for the electronic transition. We obtained UV/Vis spectra which explained the peak at 232 nm of improved graphene oxide. The absorption shows that the improved graphene oxide has more aromatic rings.

The $\lambda_{\max}$ value indicates to facilitate that the aromatic rings are not in absolute conjugation. Blank solution which is the PI its UV/VIS spectra explain that if the quantity of graphene is higher in the mixture, then peak is lower but when the graphene amount is less than it shows higher peak. But in UV/VIS spectra of PI/GO nanocomposite shows that when the graphene oxide is present in higher quantity then the cut off wavelength is observed because we add graphene oxide in three different concentrations. When the quantity of GO is less in GO/PI nanocomposite than the peak shows higher transmittance. We use three different concentrations of graphene oxide when the concentration is 0.5% than GO/PI nanocomposites shows lower transmittance but when the graphene oxide concentration is 1% than transmittance is increased than first. When the concentration of graphene oxide is 1.5% than a high transmittance is observed as shown in graph which is approximately 232 nm as shown in Fig. 4.

Transmission electron microscopy. It is known as conventional transmission electron microscopy in which image is formed when an electron beam is transmitted through a specimen. Mostly the specimen is an ultrathin section which is less than 100 nm thick. When the beam is transmitted through the specimen and interact the electrons with sample than image is formed. The image is than focused on a charged coupled device, fluorescent screen and a layer of photographic film. This property allowed the instrument to give confine

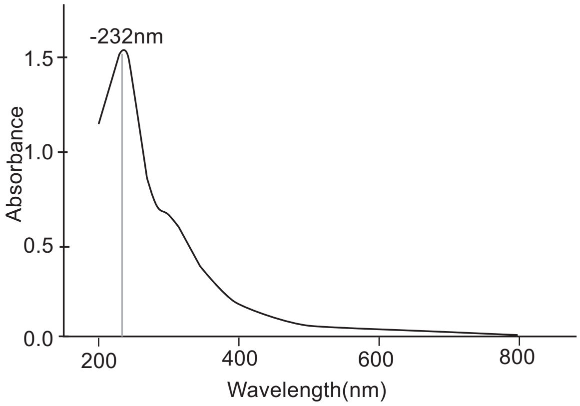

Fig. 4. UV/VIS spectra of GO.

description due to smaller de Broglie wavelength of electrons that's why this technique possesses greater resolution of images than light microscope. It is major analytical technique in chemical, biological and physical sciences. When magnification power of TEM is less it shows variation in images due to differential absorption of electrons. But at higher magnification complex wave interaction change the intensity of images. TEM gives us information about structural composition, crystallinity and width of synthesized graphene oxide. Width of graphene oxide is about 0.2 µm. TEM shows image of graphene in which the layered as well as wrinkle structure observed. It is due to the rapid removal of intercalated functional (C-O) groups from GO during exfoliation. Appearance of layered structure in the compounds is due to uniform dispersion of graphene sheets in the polymer matrix as well as the strong connection between remaining oxygen functional (C-O) groups. The image reveals the random scattering of graphene oxide sheets in the polymer matrix with a few restacking which may affect the thermal and other properties of the composite. TEM image of GO/PI nanocomposite shows that the GO sheets are not dispersed well and aggregated in the polymer matrix as shown in the Fig. 5.

FTIR analysis. The sharp and intense peak at 1730/cm is carbonyl(C=O) group of graphene oxide. The peak at 1670/cm is functional group peak. The peak 3 in the graph is at 1400/cm is the carboxyl group peak also at 1228/cm the epoxy group shows peak. But in GO/PI nancomposite the imide group show peak at 3490/cm as shown in Fig. 6.

Thermogravimetric analysis. Thermogravimetric analysis is used to examine the thermal conductivity of the GR based matrix. TGA is a powerful tool to discover out the number of the grafted organic substance because in GR the linkage between the atoms is covalent also the substituent attach on the atoms in graphene sheet are able to possess high temperature ranges as a result TGA indicate the weight reduction and thermal conductivity of functionalized GO matrix. As a result of removal of water, the temperature is gradually reduced and also the decomposition of functional group (C-O) takes place. Evaluation regarding thermal decomposition behaviour of graphene oxide and also modified GO-ODA exhibits a different weight loss curve. At low temperature the properties of graphene oxide are different like ODA change the surface properties of GO. We use TGA to analyzed the thermal conductivity, stability of GO and also the modified graphene oxide with ODA. TGA method is useful to determine the thermal properties of the GO/PI nanocomposites.

Interpretation of the nature of the polyimides that the Tg values of PIs depend upon the tructure of the dianhydride (PMDA) component, consequently, reduce with increasing elasticity of the PI backbones. The polyimide is containing the ether linkage show low peak of Tg, while which contain phthalimide molecule shows higher peak. When graphene oxide modified with ODA it shows lower peak due to ether linkages between the molecules. But in case of PMDA the pyromellitimide element is present as a result it shows higher peak. If graphene oxide containing the amine group in less quantity the resultant peak from TGA is

Fig. 5. TEM image of GO/PI nanocomposite.

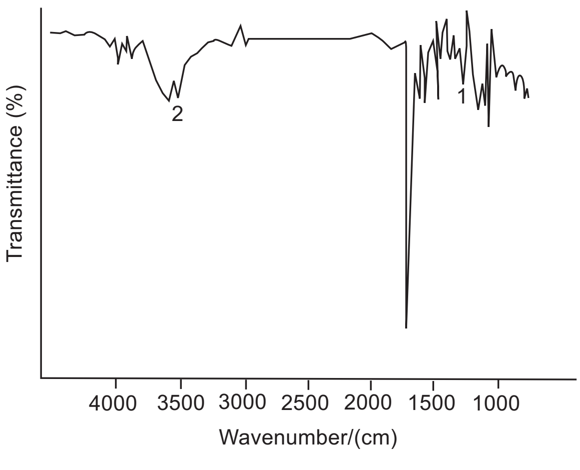

Fig. 6. FTIR spectra of GO/PI nanocomposite.

low if it contains more quantity of amine group then peak is higher as shown in Table 1.

X-ray diffraction spectroscopy. We analyzed the sample and obtained results through XRD. When analyzed the graphene oxide by XRD it shows less intense peak and smaller wavelength because of the oxidation while pure graphite shows intense peak than graphene oxide. But in case of GO/PI nanocomposite intensity depends upon the graphene oxide concentration. If the concentration of graphene oxide is lower in GO/PI composite than XRD shows less intense peak. We use three different concentrations of GO. When concentration of GO is 0.5% than the peak is less intense and having less wavelength according to XRD. But when concentration of graphene oxide is increase in GO/PI from 0.5 to 1% than the peak is intense from the first peak of containing 0.5% concentration. The more intense peak of GO/PI is obtained when the concentration of graphene oxide is 1.5% also the wavelength is increased by increasing the concentration.

Table 1. TGA analysis data for the synthesized nanocomposite sheet

Sample	Td5	Td10
Pure PI	490	545
PI/GO 0.25wt%	495	548
PI/GO 0.5wt%	510	555
PI/GO 0.25wt%	530	565

Fig. 7. Synthesized graphene oxide sheet.

Synthesis of GO-ODA. In the synthesis of graphene oxide after several time washing the material with acid and water when PH is maintained at 5-6. GO dry and isolate it with anhydrous DMAc solution by sonicating which lead to the homogeneity of the graphene oxide sheets. Then took a 100 mL round bottom flask which is set on magnetic stirrer. After this ODA added into GO suspension and then stirred at 80 °C for 24 h under nitrogen atmosphere. The mixture is filter and washed with NMP for several times to remove the excess ODA. GO-ODA will firstly disperse in anhydrous N-methylpyrrolidone through sonication for 2 h as shown in Fig. 7, after the formation of graphene oxide-ODA and characterize through FTIR, XRD and XPS.

X-ray photoelectron spectroscopy. Analysis by the XPS spectra gives indication that the graphene oxide particles are synthetically modified. The GO-XPS spectrum explain important oxidation range as various oxygen containing groups, such as alcohol, epoxides and carbonyl are examined. The intensity and binding energy is having direct relation in XPS spectra of GO. According to XPS spectra the graphene oxide shows higher intensity and binding energy due to the presence of epoxy group. But the modification of graphene oxide with ODA shows less intense peak because it having less epoxy group. Therefore, the XPS results of graphene oxide/ODA agree that predictable structure of 4,4-oxydianaline compounds are effectively implant at GO epoxy group (C-O-C-).

Synthesis of polyimide film (blank solution). In a typical two-step method of aromatic PIs synthesis, first step is to prepare the mixture regarding aromatic diamine within polar aprotic solvents like N- methylpyrrolidone or dimethylacetamide and then add tetra-carboxylic acid in it. At higher temperature the intermediate is formed that is PAA. Time requires for the reaction mostly depend upon the monomer reactivity. The PAA is completely soluble in solvent that have high molecular weight so, the solution might ejection into a layer on suitable substrate. In the imidization process heat the film at high temperature.

Synthesis of GO/PI nanocomposites. In the formation of graphene oxide/PI nanocomposites we use round bottom flask for the dissolvation of ODA in solvent like dimethyl acetamide. The different temperature conditions require for the reaction to proceed mostly at high temperature also magnetic stirrer and nitrogen gas used in this procedure. The prepared GO sheet is first modified with ODA by the help of ultrasonic vibration which convert the layer of GO into suspension form. Then add PMDA in the solution by means of ODA to obtain a sticky solution of poly (amic acid) that act as transient catalyst. Consequently GO/PAAs solution is obtained when all the quantity of PMDA was added into the mixture. After this the solution of graphene oxide/PAA is converted into GO/PI layer when GO/PAAs solution deposited on the surface of glass substrate by medical doctor blade as well as thermal imidization. Then for the purpose of drying the sheet place it in oven for 2-3 days and the resulting thickness of the sheet is approximately 20 micro meters.

As a result, the values of inherent viscosity are determined by the Ubbelohde viscometer at 25 °C by the use of solvent DMAc and copoly (amic acid) and the concentration of solution is 0.5 g/DL. Inherent viscosity of PAA is measured in dimethylacetamaide solution at 25 °C as well as present in the table XXX. Measurements of inherent viscosity of PAAs show that molecular weight of PAA is high which allows the ejection of flexible and hard PAAs films. The inherent viscosity of PMDA-ODA is 0.82 dL/g.

Conclusion

In summary, we have determined a simple and efficient HGO+ for the preparation of graphene oxide. Improved method used for the formation of GO has important advantages over Hummers' method. The improved method yields advanced fraction of well-oxidized water loving carbon matrix. Prepared GO was used as nano filler to form high performance polyimide (PI) nano-composites GO/PI with enhance the properties *via* in situ polymerization. Characterization was done by UV/Vis analysis which provided the information about the maximum absorbance at 232 nm of GO/PI nano-composites. Also, the characterization by the XRD shows that the GO/PI nanocomposite show intense peak and wavelength when GO concentration is increased to 1.5% and the XPS spectra shows that the modification of graphene oxide shows the less intense peak due to less epoxy groups, while transmission electron micro-scopy is recommended that well-dispersed exfoliated morphology of GO film in a Polyimide matrix. Further-more, the addition of GO increased the thermal properties of GO/PI nanocomposites as compared to pure PI. GO-based polyimide composite materials show promise for a wide range of applications. The characterization of GO/PI nanocomposites through XRD, FTIR, TEM, XPS and TGA results shows the enhancement in the thermal conductivity of GO/PI than GO and GO-ODA.

Conflict of Interest. The authors declare that they have no conflict of interest.

References

Baig, U., Gondal, M.A. 2016. Facile synthesis of polypyrrole-ziconium (IV) oxide ethanolamine anion exchange nano-composite its utilization in membrance electrode development of sensing and quantitative direction of AS(III) in water. *Nano-Science and Nano-Technology Letters*, **V(8):** 998-1006.

Bhattacharya, A., Ganguly, K., De, A., Sarkar, S. 1996. A new conducting nano-composite-PPy-zirconium (IV) oxide. *Materials Research Bulletin*, **31:** 527-530.

Bilisik, K., Akhter, M. 2002. Polymer nano-compsites based on graphite nanoplatelets (GNPs): a review on thermal-electrical conductivity, mechanical and barrier properties. *Journal of Material Science*. DOI: 10.1007/s/10853-22-07092-0

Chen, G.H., Wu, D.J., Weng, W.G., Yan, W.L. 2001. Preparation of polymer/graphite conducting nano-composite by intercalation polymerization. *Journal of Applied Polymer Science*, **82:** 2506-2513.

Collister, J. 2002. Commercialization of polymer nano-composites. *ACS Publications*.

Fornes, T., Yoon, P., Keskkula, H., Paul, D. 2001. Nylon 6 nano-composites: the effect of matrix molecular weight. *Polymer*, **42:** 09929-09940.

Gangopadhyay, R., De, A. 1999. Polypyrrole-ferric oxide conducting nano-composites: I. synthesis and characterization. *European Polymer Journal*, **35:** 1985-1992.

Ghosh, M. 1996. *Polyimides: Fundamentals and Applications*, CRC Press, pp. 912, Boca Raton, Florida, USA. DOI.org/10.1201/9780203742945

Gohlke, U. 1987. *Advances in Polymer Synthesis. Hg. Von Bm Culbertson Je Mcgrath (Polymer Science and Technology Series*, Plenum Press, vol. **34,** New York, USA.

Liu, Y., Wei, M., Liu, X., Sheng, S. 2022. Influence of the matrix molecular weight on the morphology and properties of (poly ethylene terephlhalate)/poly(ethylene-octome) blends. *Journal of Macromolecular Science, Part-B*, **61:** 871-881.

Miyauchi, S.N., Abiko, H., Sorimachi, Y., Tsubata, I. 1989. Preparation of barium titanate-polypyrrole compositions and their electrical properties. *Journal of Applied Polymer Science*, **37:** 289-293.

Sroog, C. 1976. Polyimides. *Journal of Polymer Science: Macromolecular Reviews*, **11:** 161-208.

Walter, M.E. 1965. *Polyamide-acids, Compositions there of and Process for their Preparation*. Google Patents.