Journal of Materials and Electronic Devices 4 (2022) 40-44

JOURNAL OF MATERIALS AND ELECTRONIC DEVICES
FYTRONIX JMED http://dergi-fytronix.com/

Physiochemical Modification of Graphene Nanosheets to tailor Electrical Properties of Graphene based PMMA Composites

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In the present work, a series of modified reduced graphene oxide (m-rGO) based poly methyl methacrylate (PMMA) composite by solution mixing method using chloroform as solvent have been synthesized. Here, reduced graphene oxide (rGO) has been modified by using Friedal-Craft acylation reaction. For this purpose, 4-bromobenzoic acid was used as a reagent in the above mentioned reaction to introduce an acyl group at the surface of rGO, which may increase the homogeneity of the synthesized composites of m-rGO and PMMA (m-rGO/PMMA). Series of composites having different wt. % of filler (m-rGO) was prepared. FTIR and UV-Vis spectroscopic techniques were employed for confirmation of the synthesis of GO and rGO and modification of the rGO. Significant improvement in electrical properties has been observed because of the surface modification of the rGO. An interesting frequency dependence relationship between conductivity and dielectric constant has been obtained. A lower percolation threshold was observed for these nanocomposites because of enhanced interfacial interaction of m-rGO with PMMA. Above mentioned results encourage the modification of the rGO for its incorporation in PMMA for composite formation..

Keywords: *PMMA, GO, Composites, Electrical conductivity, Dielectric Constant.*

Submission Date: 26 October 2022
Acceptance Date: 08 December 2022

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1. Introduction

Polymers are a unique class of materials and have widespread application because of their low weight, ease in processing, and remarkable finishing [1]. Polymers, being inherently less electro and thermally conductive and weak in tensile strength, are widely used after the synthesis of the polymer composites [2, 3]. For this purpose, some organic and inorganic based materials are potentially used as fillers to boost the electrical, thermal, and mechanical properties of polymers [4, 5]. Among the inorganic based fillers, metal nanoparticles are leading at the front and are widely used for the synthesis of polymer composites. Such inorganic based polymer composites exhibit excellent electrical, remarkable mechanical, and brilliant thermal properties. However, processing such

polymer composite is difficult. Among the organic based fillers, single-walled carbon nanotubes, double walled carbon nanotubes, multi-walled carbon nanotubes, graphene oxide and reduced graphene oxides are considered as best choices for the synthesis of polymer composites [3]. Such above mentioned organic fillers based polymer composites also exhibit excellent features as far as conductivity and stability are concerned along with ease in processing. Such electro-active polymer composites are extensively employed in energy storage devices, sensors and membranes used for purification.

Here in the present work, modified reduced graphene oxide (m-rGO) based poly methyl methacrylate (PMMA) composite have been synthesized aiming to have materials with good electrical features. For this purpose, graphite has been converted to graphene oxide followed by reduction to have reduced graphene oxide (rGO). This reduced graphene oxide has been further modified by Friedal-Craft acylaton reaction. For this purpose, 4-bromobenzoic acid was used as a reagent in the above mentioned reaction to introduce acyl group at the surface of rGO, which may increase homogeneity of the synthesized composites of m-rGO and PMMA (m-rGO/PMMA). The synthesis process of the GO and rGO and modification of rGO (m-rGO) have been monitored by UV-Visible and FTIR spectroscopy. The effect of the modification of the rGO has been explored by using the electrical properties of the synthesized composites.

2. Experimental

2.1 Instruments and chemical

Chloroform, PMMA, graphite, P2O5, polyphosphoric acid, and other chemicals have been used as obtained. UV-Visible of PG Instrument (T90+) and FTIR spectrometer of Agilent Tech (Cary 63) have been used for the monitoring of the synthesis process of composites and modification of the filler. LCR meter of Keysight (Pvt) Limited (E4980 AL) has been used to measure the electrical properties of the synthesized composites.

2.2 Synthesis of reduced graphene oxide

Synthesis of reduced graphene oxide from the graphite is a two-step process. First, graphite has been converted into graphene oxide by modified Hummer's method [6] and followed by a reduction of the graphene oxide to reduced graphene oxide [7]. Synthesis of the graphene oxide and reduction of the graphene oxide has been monitored by UV-Visible and FTIR spectroscopy.

2.3 Modification of the reduced graphene oxide

Modification or functionalization of reduced graphene oxide is the most important part of this research work and is done by the method reported in the literature with slight modification [8]. For this purpose, 20mg of the synthesized product of the last step, reduced graphene oxide, has been taken in a three-neck round bottom flask along with the calculated amount of 4-bromo benzoic acid, phosphorous penta oxide, and polyphosphoric acid. A temperature of 1300C was maintained for 72 hours in an inert environment with the help of a reflux condenser. This inert environment was maintained by the continued supply of nitrogen gas. After the completion of the reaction, the synthesized product has been washed properly with water and alcohol to remove all unreacted impurities. Finally, the dark brown colored synthesized product was dried in the oven at 600C and stored for further use.

2.4 Synthesis of the modified reduced graphene oxide based composites

A series of m-rGO based PMMA composites have been prepared by varying the amount of m-rGO by solution mixing method [9]. For this, suspension of m-rGO in chloroform has been sonicated followed by magnetic stirring of 20 minutes each. Afterward, a calculated amount of PMMA has been added to the suspension of m-rGO and magnetic stirring is continued for further 20 minutes. This reaction mixture was taken in a petri dish and the petri dish is put in the oven at a temperature of 900C to dry the solvent. After the evaporation of the chloroform, a very bright and thin film of the m-rGO based PMMA composite (m-rGO/PMMA) has been obtained. Similarly, a series of the m-rGO/PMMA composites have been prepared by varying the amount of filler and matrix.

3. Results and Discussion

UV-Visible spectra of graphene oxide and reduced graphene oxide have been shown in figure 1. The absorption maximum for graphene oxide is observed at 235 nm and that of reduced graphene oxide is observed at 265nm. Reduction of graphene oxide results in a red shift in absorption maximum in VU-Visible spectra. Absorption maxima at similar positions for graphene oxide and reduced graphene oxide have also been reported in the literature[10, 11] which indicate the successful synthesis of GO and rGO.

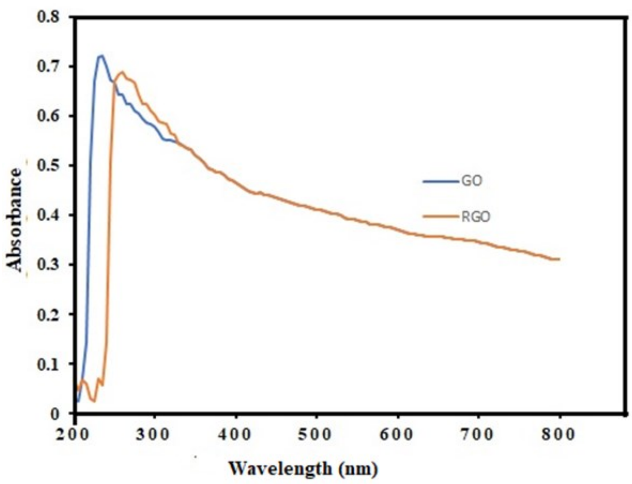

Figure 1 UV-Visible spectra of GO and rGO

FTIR spectra of graphene oxide and reduced graphene oxide have been shown in figure 2. Peaks present at 3300 cm-1 and 1380 cm-1 in the spectrum of graphene oxide correspond to –OH and C-O, respectively. It is reported in the literature that peaks corresponding to –OH and C-O are present in the same region [12, 13] which confirms the successful GO. FTIR spectrum of rGO showed no sharp peak belonging to any oxygen containing functional group. Moreover, the appearance of a small peak around 1650cm-1 points to the presence of – C=C-. These observations confirmed that the reduction process was successful as well.

FTIR spectrum of m-rGO has been given in figure 3. Well-established peaks at 1600cm-1 and 1720cm-1 present in the FTIR spectrum of m-rGO confirm the presence of benzene and acyl groups and at the same time repetition of peaks pattern of reduced graphene oxide confirm the modification of reduced graphene oxide by the introduction of acyl group via Friedel-Craft acylation. Peaks belong to C-X (x=halide) appear around 600-1000cm-1 in FTIR spectrum as per literature [14].Two prominent peaks appeared in the said range and it is assumed that these two peaks belonged to two types of C-Br.

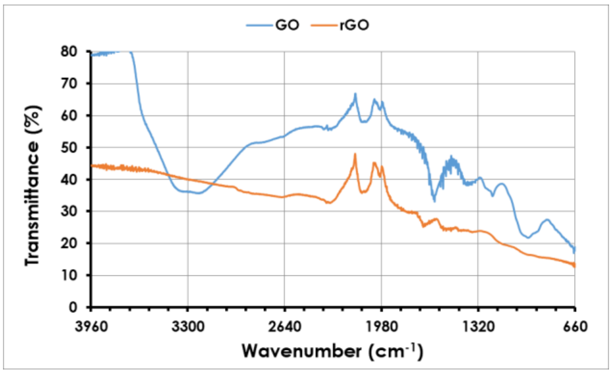

Figure 2 FTIR spectra of GO and rGO.

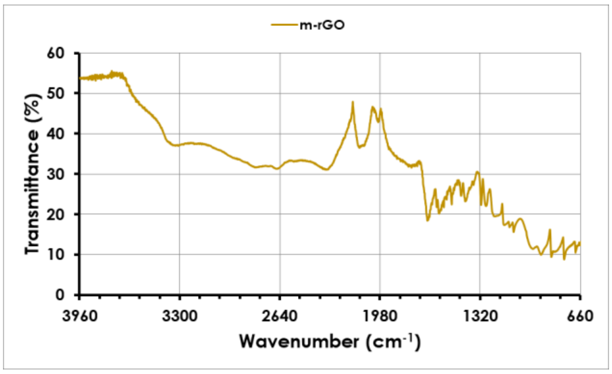

Figure 3 FTIR spectrum of m-rGO

The occurrence of these two types of peaks for C-Br can be associated with a difference in the relative intensity of D bond and G bond at the core of the graphene and edges of the graphene [15]. So results of the FTIR spectrum of m-rGO are strong evidence of the introduction of 4-bromo benzyl to rGO by Friedel-Craft acetylation.

A plot of values of conductivity as a function of wt% of m-rGO at different frequencies has been shown in figure 4. Some interesting and important facts have been observed from the frequency and wt% dependence of conductivity. Initially, a slow increase in conductivity as a function of the contents of m-rGO has been observed and that slow increase in conductivity is more prominent at a relatively lower frequency. On further loading of m-rGO, a sudden increase in conductivity has been observed which indicates the development of a percolation network. It can be seen in the graph that the value of the percolation threshold is between 0.1 to 0.2wt% of filler loading. Here, the achievement of such a low value of percolation threshold is made possible due to the modification of the rGO, which helps out in uniform dispersion of the filler by developing non-covalent interaction with the PMMA. Six order of increase in conductivity is obtained for composites with contents of m-rGO around 0.3 wt% at 100 kHz. The maximum value of conductivity observed is greater than 10 mS/m just at 2 wt% of m-rGO. The effect of the frequency on the conductivity is very prominent for composite with lower filler loading while after certain filler loading, beyond the percolation threshold; the effect of frequency on the conductivity values vanished. This specifies that the mechanism of the conductivity is not the same before and after the percolation threshold.

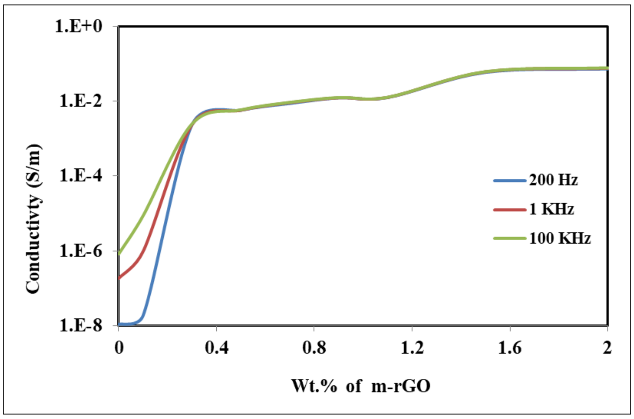

Figure 4 Plot of conductivity of m-rGO/PMMA composite as a function of m-rGO at different frequencies.

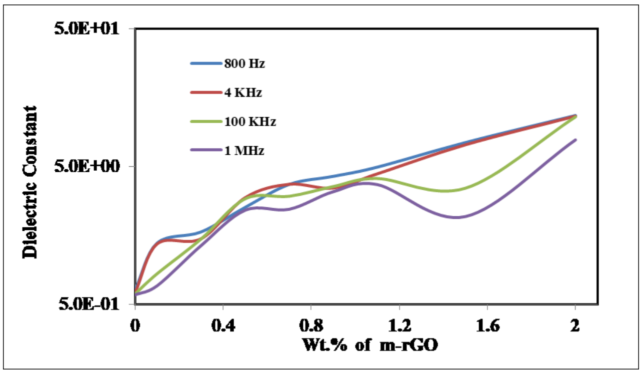

Figure 5 Plot of dielectric constants of m-rGO/PMMA composite as a function of m-rGO at different frequencies.

Trends of dielectric constant as a function of wt% of m-rGO at different frequencies have been shown in figure 5. The figure shows that the dielectric constant has been linearly increased with the increase in the amount of conductive filler in the non-conductive matrix even after the percolation threshold. The linear increase in the dielectric constant suggests that modification controlled the agglomeration of the filler particles and therefore, the tangent loss will be minimum. Results showed that there is no prominent effect of frequency on the dielectric constant has been observed.

4. Conclusions

The successful synthesis of GO and rGO followed by the modification of reduced graphene oxide has been accomplished. A Series of m-rGO/PMMA composites with different compositions have been prepared successfully by a simple solution mixing method. Results obtained from UV-Visible and FTIR spectroscopy hereby confirmed the synthesis of GO and rGO and the modification of rGO. Data of conductivity and dielectric constant as a function of wt % of m-rGO at different frequencies strongly recommend the use of rGO and such other fillers after the modification or treatment to enhance the interaction between filler and matrix to obtain desired results.

Acknowledgement

T.H woud like to thank University of the Punjab for providing travel grant to present this research work 9th MSNG 2022 held at Ankara, Turkiye on September 22-24, 2022

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