



SURFACE MORPHOLOGY AND THERMAL PROPERTIES OF NEW AOTMNA-GO NANOCOMPOSITE

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Abstract

Initially Aniline(A), O-toluidine(OT) & m-Nitroaniline(MNA) terpolymer was synthesized in the laboratory employing free radical oxidative polymerisation technique. Nanocomposite based on graphene oxide (GO) and AOTMNA terpolymer have been obtained using molecular dispersion doping method. Uniformly dispersed terpolymer in solution phase got incorporated into the composite. The new nanocomposite obtained was characterised by FTIR & SEM studies. Thermal properties were investigated to understand the thermal stability of the newly synthesised nanocomposite. The composite have shown higher thermal stability in comparison with pure terpolymer. SEM studies proved the dispersion of graphene oxide nanotubes in the polymer matrix. Such terpolymer composite may be investigated for its various applications in light of toxic metal ion abatement and photocatalytic activities.

Keywords : terpolymer, composite, thermal properties, graphene nanotubes

Introduction

Graphene is a monolayer of sp^2 bonded carbon atoms that can be viewed as an individual atomic plane extracted from graphite. Graphene can be converted to its oxide employing Hummers method(1). Graphene has been attracting great interest due to its unique structure and properties(2). To take full advantage of its properties for applications, except for electronic devices, integration of individual graphene in polymer matrices to form advanced multifunctional composites is one of the most promising routes, because polymer composites usually have



exceptional specific modulus, specific strength, and wide application in aerospace, automobile and defence industries, etc. Moreover, polymer composites can be easily processed and fabricated into intricately shaped components with excellent preservation of the structure and properties of graphene using conventional processing methods. This is very important to make full use of the outstanding properties of graphene. Graphene has a higher surface-to-volume ratio because of the inaccessibility of the inner nanotube surface to polymer molecules(3). This makes graphene potentially more favourable for improving the properties of polymer matrices, such as the mechanical, electrical, thermal, and microwave absorption properties. More importantly, graphene is much cheaper than carbon nano tubes, because it can be easily derived from a graphite precursor in large quantity. Therefore, graphene-based polymer composites are of great importance. Recent advances (4,5) in the production of bulk quantities of exfoliated graphene from graphite have enabled the synthesis of graphene polymer composites. Such composites show tremendous potential for mechanical properties enhancement due to their combination of high specific surface area, strong nanofiller-matrix adhesion and the outstanding mechanical properties of the sp^2 carbon bonding network in graphene. Graphene oxide nanotubes are a new form of carbon, consisting of concentric cylinders of graphene oxide (GO) layers. Since its discovery(6), extensive studies have been devoted to the use of carbon/GO nanotubes as nanofillers to improve the performance of a matrix or to achieve new properties. Graphene oxide contains a range of reactive oxygen functional groups, which renders it as a good material for use in the aforementioned applications through chemical functionalizations(7). Chemical methods have been reported to produce chemically modified graphene via established colloidal suspension methodologies(8). In recent years emulsion polymerization of aniline has come to the forefront(9-11). Inverted emulsion polymerization method(12,13) have been reported for the synthesis of polyaniline



composites using an isooctane-toluene mixture and water to form the emulsion employing ammonium persulfate as the oxidant. Emulsion polymerization is essentially a compartmentalized polymerization reaction taking place in a large number of loci dispersed in a continuous external phase. Electrically conducting polyaniline has also been synthesized by using the microemulsion method with sodium dodecylbenzenesulfonate acting as both a surfactant and a dopant(14). Various polymers have been used as matrices to fabricate graphene/polymer composites(15). Recently TiO₂-2-HABT composite functional materials with excellent photocatalytic properties have been reported in the literature(16). Scanty references are available on nanocomposites derived from terpolymers and graphene oxide. In the present investigation a new AOTMNA-GO nanocomposite have been successfully synthesized and its morphological as well as thermal properties are reported.

Materials and methods

All the chemicals and solvents used in the present investigation were of analytical reagent (AR) grade. The solvents were double distilled prior to their use. DI water was used throughout the investigation.

Synthesis of terpolymer

The AOTMNA terpolymer was synthesise by continuous stirring of equimolar mixture of the starting materials i.e Aniline, O-toludine and m-nitroaniline which were dissolved in required amount of chloroform(solvent) followed by dropwise addition of 1M HCl and 0.1 M ammonium persulphate. The stirring was continued for 24 h at room temperature. The terpolymer obtained was filtered, washed several times with DI water followed by washing with acetone. The AOTMNA terpolymer obtained was dried in oven at 60°C for 48 h.



Preparation of AOTMNA-GO composite

AOTMNA terpolymer was dispersed in N-N Dimethylformamide using mechanical stirrer for 75 min at room temperature. Then GO was added and stirring was continued for 6 hrs. The temperature of the system was raised to 65°C and kept overnight so that the solvent was evaporated completely. Equimolar terpolymer / GO composition was taken in the composite. The solid AOTMNA-GO composite was characterised by FTIR, SEM & TGA Studies. The morphological properties were investigated from SEM picture and thermal properties from TG analysis.

Results and Discussion

Characterisation of AOTMNA-terpolymer

FTIR Analysis

Figure 1 shows FTIR spectrum of AOTMNA terpolymer with its characteristic bands. 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 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 CH_3 group (C-H stretching).

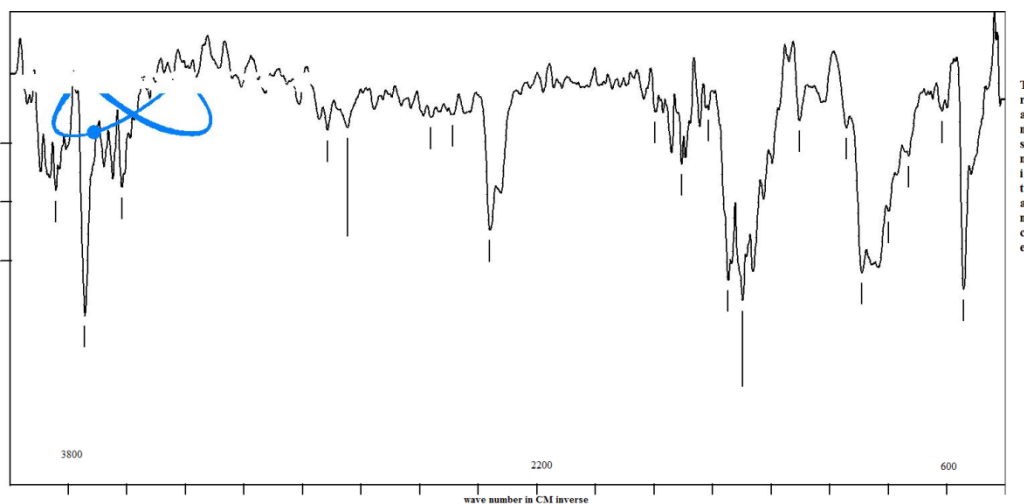


Fig.1 FTIR of AOTMNA terpolymer

On the basis of physicochemical and spectral evidences the most probable structure (17) for AOTMNA terpolymer have been assigned which is shown in Fig.2

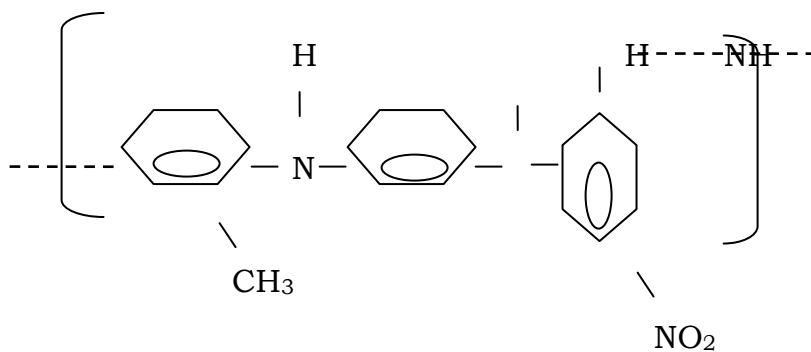


Fig.2 Srtucture of AOTMNA-terpolymer

Characterisation of AOTMNA-GO composite

FTIR analysis

Fig. 3 represents the FTIR spectrum of AOTMNA-GO composite. It can be observed that both, the FTIR for AOTMNA terpolymer and AOTMNA-GO composite are almost similar. The noticeable difference is appearance of strong sharp absorption band at 1690 cm^{-1} which is indicative of C=O group (reactive oxygen functional groups). It proves the incorporation of Graphene oxide (possessing C=O surface group) in the terpolymer matrix during composite formation.

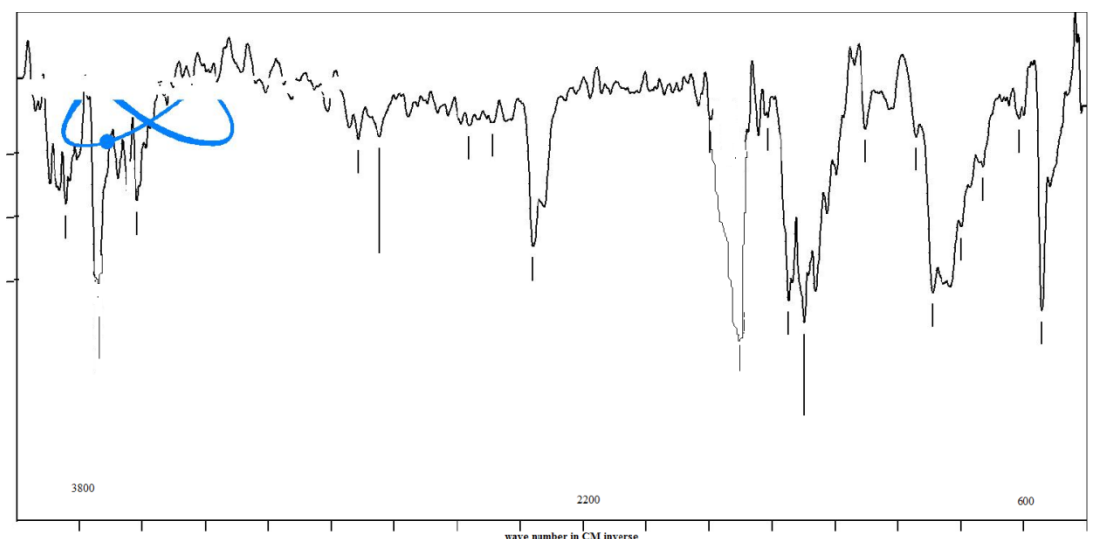


Fig.3 FTIR of AOTMNA-GO composite

SEM Analysis

SEM picture of AOTMNA-GO composite is given in Fig.4. It is evident from the SEM picture that the nanosized (about 150-200nm) GO tubes have been successfully incorporated in AOTMNA terpolymer matrix thus the synthesis of nanocomposite is fruitful. The SEM picture also proves highly porous nature of the composite under investigation which is suggestive of very high surface area. Thus this nanocomposite material may be of great use as excellent absorbent and a very good photocatalytic material.

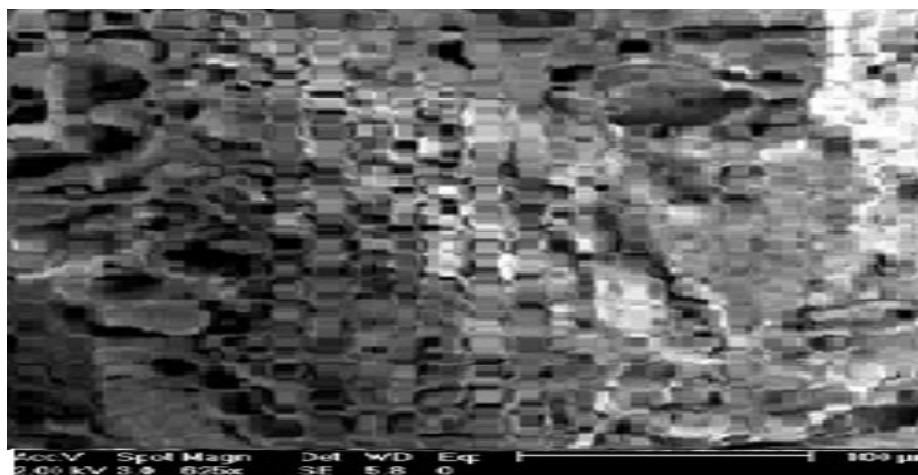


Fig. 4 SEM of AOTMNA-GO composite

Thermogravimetry analysis

TG curves for pure graphene oxide, pure AOTMNA terpolymer and AOTMNA-GO composite have been presented in Fig. 5. The thermal stability of AOTMNA-GO composite were analysed by TGA in presence of air. TG graph for pure graphene oxide (GO) clearly indicates that the material is almost stable up to 500 °C. It is evident that AOTMNA-GO composite is comparatively more stable as compared to pure AOTMNA terpolymer this reflects that addition of GO in to terpolymer can improve the thermal stability of terpolymer due to interaction of the terpolymer matrix with GO. The nanocomposite material is found to be thermally stable nearly up to 200°C which is a good sign towards its practical applicability.

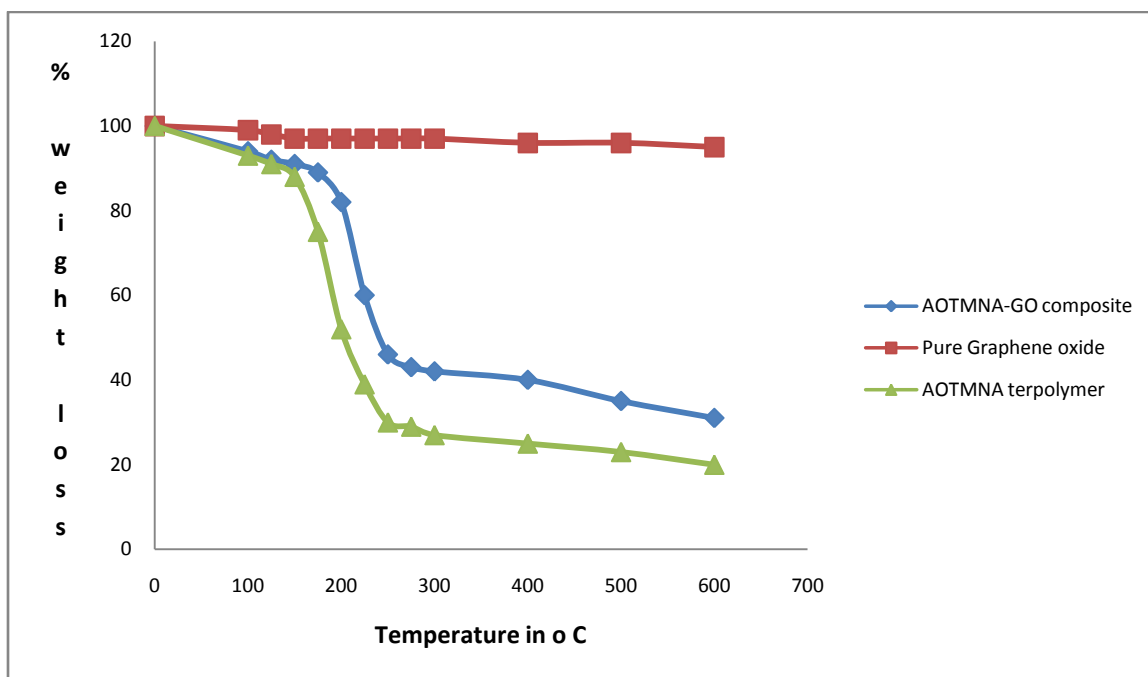


Fig.5 TG curves for pure graphene oxide, pure AOTMNA terpolymer & AOTMNA-GO Composite

Conclusions

- The AOTMNA terpolymer was successfully prepared and characterised.
- The composite based on AOTMNA & GO was synthesised and characterised.
- SEM studies proved highly porous morphological structure with very high surface area of the nanocomposite which indicates its suitability for various practical applications as an excellent adsorbent and a very good photocatalytic material. The nanotubing structure of the composite has also been proved by SEM analysis.
- The composite under present investigation is quite stable upto 200°C which is again a good symptom for its practical use in various applications.
- There is a scope for further studies to test the practical applicability of the nanocomposite material.



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