International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
IJCS 2018; 6(5): 2517-2520
© 2018 IJCS
Received: 14-07-2018
Accepted: 16-08-2018

Vijay Kumar
M.Tech, Department of Plastics Engineering, Central Institute of Plastics Engineering and Technology, Bhubaneswar, Orissa, India

Correspondence
Vijay Kumar
M.Tech, Department of Plastics Engineering, Central Institute of Plastics Engineering and Technology, Bhubaneswar, Orissa, India

To study the morphological properties of graphene based polymer nanocomposite for food packaging

Vijay Kumar

Abstract
Polyethylene terephthalate (PET) is a widely used thermoplastic polymer. The addition of small amounts of nanofillers into a polymer matrix has proven an efficient method of improving the properties of the neat polymer. In the current project PET and PET nanocomposites reinforced with exfoliated graphene layers were prepared by melt compounding. In this project the morphological properties i.e (XRD, SEM, TEM) of PET by adding grapheme were studied. PET/Graphene blend have been prepared by melt blending process using a co-rotating twin-screw micro compounder (X pore 15, Netherlands) attached with a mini injection molder. The processing temperature has been kept as 240, 260 and 270 ^{0}C for the three successive zones of the extruder with a screw speed of 40 rpm (acceleration rate: 50 rpm). Injection molding parameters were fixed as mold temperature at 120 ^{0}C, melt temperature at 245 ^{0}C Injection time as 4 min and injection pressure 10 bar.

Keywords: Graphene, polymer, polyethylene terephthalate (PET)

Introduction
In the food industry polymers are the most frequently used for packaging of food products. Their purpose is to keep the food fresh for as long as creating a controlled atmosphere and to prevent its deterioration. Polyethylene terephthalate (PET) is a widely used thermo plastic polymer. The addition of small amounts of nanofillers into a polymer matrix has proven an efficient method of improving the properties of the neat polymer. In the current project PET and PET nanocomposites reinforced with exfoliated graphene layers were prepared by melt compounding. The polymers used for packaging because of the ease in manufacturing, chemical stability, inertness in contact with food, light sterilization, aesthetic design and low weight. Membranes made from graphene and its chemical derivative called graphene oxide (GO) (Chua, C. K. *et. al.,* 2014; Nair, R. R. *et. al.,* 2012) [1-6] show a range of unique barrier properties (Joshi, R. K. *et al* 2014; Mueller, K. *et al.,* 2012) [3-5]. Defect-free monolayer graphene is impermeable to all gases and liquids (Joshi, R. K. *et al* 2014) [5] and, similar to graphite, shows high chemical and thermal stability with little toxicity. These characteristics are believed to provide graphene with a competitive edge over the existing barrier materials (Li, Y.-Q., *et al.,* 2012) [4]. The HI reduction leaves fewer structural defects and little deformation so that the mechanical strength increases, becoming even higher than that for initial GO laminates that are known to be already exceptionally strong (Chua, C. K. *et. al.,* 2014) [1].
Unfortunately, prospects of using graphene as a protective coating are hampered by difficulties of growing large area defect-free films. For example, it is shown that grapheme films grown by chemical vapour deposition (CVD) possess many defects and grain boundaries and do not protect copper against oxidation but, to the contrary, speed up its corrosion (Tian, Y. *et. al.,* 2013) [8]. To improve barrier performance, we have developed a new process that combines solution blending and isothermal recrystallization techniques to prepare a PET/Graphene composite with improved gas barrier properties and good transparency.

Materials and Methods
Natural flake graphite has been purchased from Sigma Aldrich (USA). Sulfuric acid, hydrochloric acid, ethanol, hydrogen peroxide and potassium Hydroxide (KOH) were purchased from MERCK, India Ltd.

Potassium permanganate (oxidizing agent) and Hydroiodic acid (HI) (reducing agent) have been purchased from Sigma Aldrich (USA). All conventional chemicals were of analytical grade and were used without further purification. Ultra-pure water (18 MΩ cm) was used throughout the experiments.

Preparation of reduced graphene oxide (rGO)

In this work, we prepared mildly oxidized graphene oxide (MOGO) by following procedure which is based on modified Hummers method (Hummers, W. S. 1958) [2] involving a single chemical exfoliation of graphite powders within 4 h. The MOGO showed both excellent dispersibility in water (1 mg mL^{-1}) and high graphitic crystallinity. Chemical reduction of GO by HI acid was carried out through the procedures reported by Cheng and co-workers. Briefly, GO powder was prepared by vacuum filtration of GO dispersion through a membrane filter**.** Then the GO Powder was immersed into HI acid (55%) and the reaction system was kept at 100°C for 1 h. The obtained reduced graphene oxide (r-GO) was washed with ethanol and acetone and dried at room temperature. The electrical conductivity of reduced graphene oxide (r-GO) was measured to be 424 Scm^{-1}. The significantly improved electrical property of r-GO is attributed to its low degree of oxidation and low-defect structure.

Preparation of PET/Graphene blend and its composites and Specimen preparation

Prior to mixing, PET and Graphene were respectively dried in vacuum at 120 ^{0}C and 200 ^{0}C for4hrs. 0%, .5%, 1%, 1.5%, 3%, 5%, And 10%wt percentage of graphene were prepared in a co–rotating twin screw micro- compounder X-Plore 15mL DSM Netherland and a screw speed of 40RPM. The mixing was carried out at a temperature of 270 ^{0}C and the specimen were injection molded into ASTMD-638 Type I tensile bars and ASTMD-25606 impact bars using an Proface injection machine, with a maximum pressure of 10bar.Tensile properties of various compositions of PET- graphene nanocomposites were determined.

Morphological studies

X-ray Diffraction (XRD)

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. Before the geometrical constraints for x-ray interference are derived the interactions between x-rays and matter have to be considered. There are three different types of interaction in the relevant energy range. In the first, electrons may be liberated from their bound atomic states in the process of photo ionization. Since energy and momentum are transferred from the incoming radiation to the excited electron, photo ionization falls into the group of inelastic scattering processes. In addition, there exists a second kind of inelastic scattering that the incoming x-ray beams may undergo, which is termed Compton scattering. Also in this process energy is transferred to an electron, which proceeds, however, without releasing the electron from the atom. Finally, x-rays may be scattered elastically by electrons, which is named Thomson scattering. In this latter process the electron oscillates like a Hertz dipole at the frequency of the incoming beam and becomes a source of dipole radiation. The wavelength λ of x-rays is conserved for Thomson scattering in contrast to the two inelastic scattering processes mentioned above. It is the Thomson component in the scattering of x-rays that is made use of in structural investigations by x-ray diffraction.

Scanning Electron Microscopy

Introduction

The development of Scanning Electron Microscopy (SEM) in the early 1950's brought with it new areas of study in the medical and physical sciences because it allowed examination of great variety of specimens. As in any microscope, the main objective is magnification and focus for clarity. An optical microscope uses lenses to bend an electron beam, which is used to bend the light waves, and the lenses are adjusted for focus. In the SEM, electromagnets are used to bend an electron beam, which is used to produce the image on a screen. By using electromagnets an observer can have more control in how much magnification it obtains. The electron beam also provides greater clarity in the image produced. The SEM is designed for direct studying of the surfaces of solid objects. By scanning with an electron beam that has been generated and focused by the operation of the microscope, an image is formed in much the same way as a TV.

The SEM is a type of electron microscope capable of producing high-resolution images of sample surface. Due to the manner in which the image is created, SEM images have characteristic three-dimensional appearance and are useful for judging the surface structure of the sample. SEMs are patterned after reflecting light microscopes and yields similar information

Topography: The surface features of an object.

Morphology: The shape, size and arrangement of the particles makin upthe object that are lying on the surface of the sample.

SEM Specification

Test Procedure

In the present investigation the morphology of the nanocomposites was observed using SEM-JSM-6390 (JEOL Ltd, Japan) with 15 kV accelerating voltage at 5μm resolution. Specimens are platinum coated at low temperature. Ultra thin specimens of 100μm thickness were cut from fractured surface of tensile specimen.

Transmission Electron Microscopy (TEM)

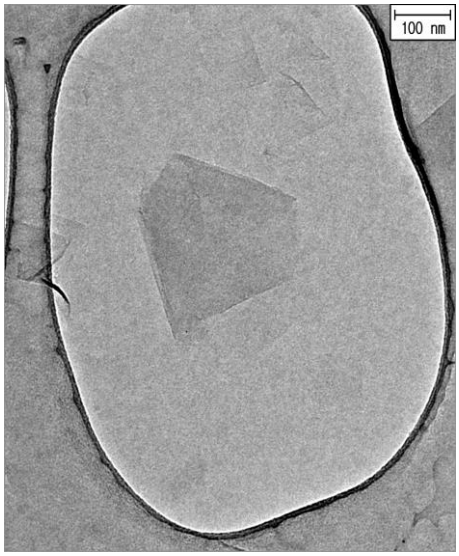
Transmission electron microscopy was performed in order to obtain visual images displaying the extent of the montmorillonite or organoclay dispersed in polymer matrix. The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. What we can see with a light microscope is limited by the wavelength of light. TEM uses electrons as "light source" and their much lower wavelength make it possible to get a resolution thousand times better than that with a light microscope. We can see objects to the order of a few angstroms (10^{-10} m). For example, we can study small details in the cell or different materials down to near atomic levels. The possibility for high magnifications has made the TEM a valuable tool in both medical, biological and materials research.

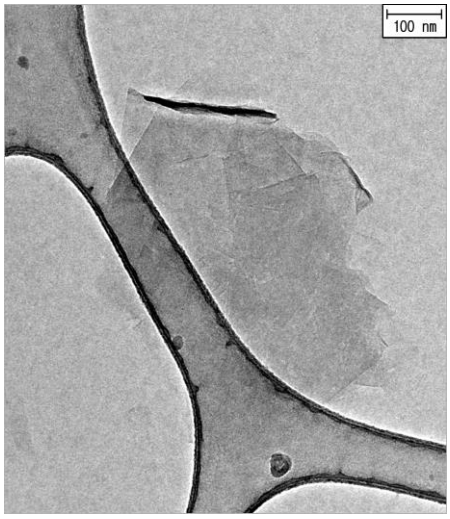
Results and discussion

TEM, XRD and Raman Spectroscopy, were used to characterize the morphology and microstructure of as-made

GO and rGO sheets. It shows that TEM image of the rGO nanosheets, which demonstrates that the rGO sheets were efficiently exfoliated to form thin nanosheets with typical wrinkled structure (Z-S. Wu. *et al.*, 2009) [9]. The wrinkles observed were probably caused by the presence of oxygen-containing functional groups and the resultant defects during the preparation of rGO (S. Korkut *et al.*, 2011) [7]. It also reveals from the Figure that the prepared rGO are transparent and maintain substantial stability under the high energy electron beam.

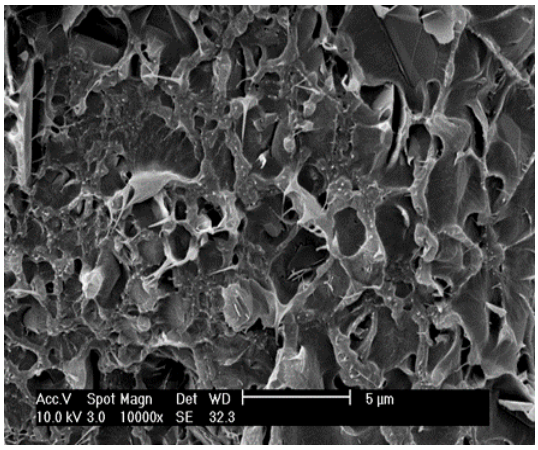
Images of reduced graphene Oxide



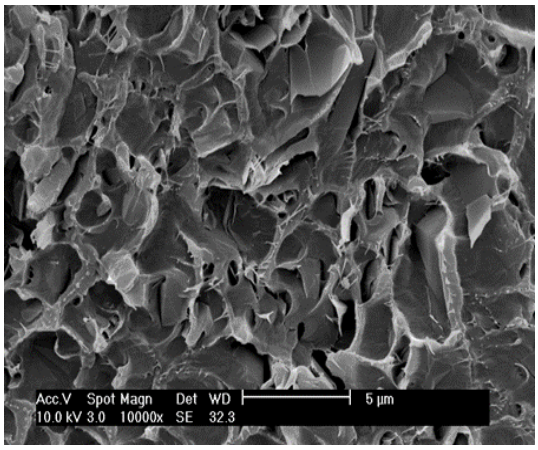


SEM Micrographs

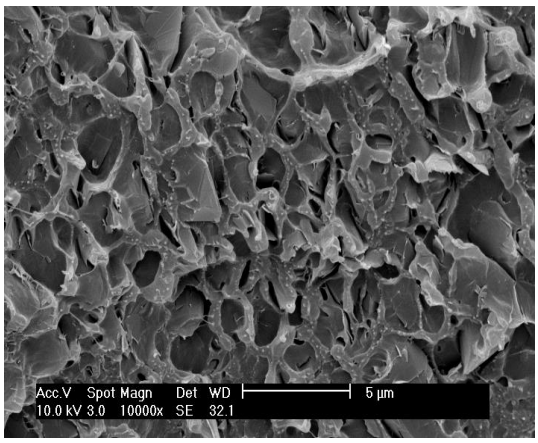
The SEM Micrographs were taken for different composition of PET/rGO and were analyzed. The fractured of the samples were used to for the analysis. The distribution of filler was uniform as the crack was not smooth. The fractured was rough so in the SEM fractograph has many relatively small dimples can be found on the fracture surface with addition of rGO. The formation of the dimples is accompanied by the creation of new fracture surfaces, and thus much fracture energy was likely dissipated. Normally, these dimples are initiated by the rGO which resist crack propagation by bifurcation to induce the formation of a large number of micro-cracks. This would result in more energy dissipation through the well-known pinning and crack tip bifurcation mechanisms. Similar phenomena were also observed in other composition.



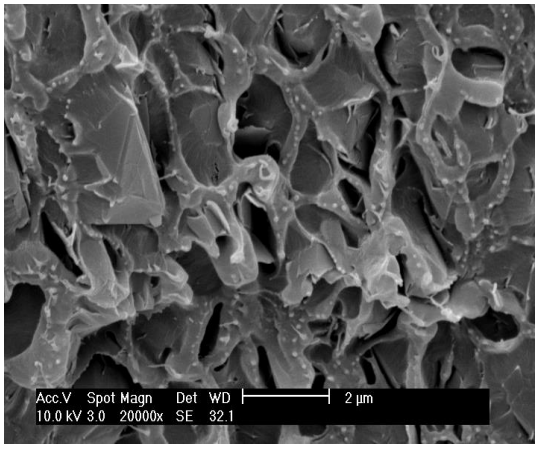
PET-rGO 1%



PET- rGO3%



PET-rGO5%



PET-rGO10%

Conclusion

Orientation has been used to modify the morphologies of the dispersed phase in polymer blending in order to decrease the oxygen gas permeability. The barrier properties of a final blend depend not only on the composition or the intrinsic barrier properties of the components butal so on the final morphology of the blend. Spherical morphology of any dispersed phase with high barrier properties only gives moderate permeability, however, laminar morphology drastically decreases the permeability. SEM fractograph has many relatively small dimples can be found on the fracture surface with addition of rGO. The formation of the dimples is accompanied by the creation of new fracture surfaces, and thus much fracture energy was likely dissipated. Normally, these dimples are initiated by the rGO which resist crack propagation by bifurcation to induce the formation of a large number of micro-cracks. TEM, XRD and Raman Spectroscopy demonstrates that the rGO sheets were efficiently exfoliated to form thin nanosheets with typical wrinkled structure. The wrinkles observed were probably caused by the presence of oxygen-containing functional groups and the resultant defects during the preparation of rGO.

References

1. Chua CK, Pumera M. Chemical reduction of graphene oxide: a synthetic chemistry viewpoint. Chem. Soc. Rev. 2014; 43:291-312.
2. Hummers WS, Offeman RE. Preparation of graphitic oxide. J Am. Chem. Soc. 1958; 80:1339-1339.
3. Joshi RK et al. Precise and Ultrafast molecular sieving through graphene oxide membranes. Science. 2014; 343:752-754.
4. Li Y-Q, Yu T, Yang T-Y, Zheng L-X, Liao K. Bio-Inspired Nacre-like Composite Films Based on Graphene with Superior Mechanical, Electrical, and Biocompatible Properties. Adv. mater. 2012; 24:3426-3431.
5. Mueller K, Schoenweitz C, Langowski HC. Thin Laminate Films for Barrier Packaging Application – Influence of down gauging and substrate surface properties on the permeation properties. Packaging Tech. Sci. 2012; 25:137-148.
6. Nair RR, Wu HA, Jayaram PN, Grigorieva IV, Geim AK. Unimpeded permeation of water through helium-leak-tight graphene-based membranes. Science. 2012; 335:442-444.
7. Korkut S, Roy-Mayhew JD, Dabbs DM, Milius DL, Aksay IA. ACS Nano. 2011; 5:5214-5222.
8. Tian Y, Cao Y, Wang Y, Yang W, Feng J. Realizing Ultrahigh Modulus and High Strength of Macroscopic Graphene Oxide Papers Through Cross linking of Mussel-Inspired Polymers. Adv. mater. 2013; 25:2980-2983.
9. Wu Z-S, Ren WC, Gao LB, Zhao JP, Chen ZP, Liu BL *et al*. Cheng, ACS Nano. 2009; 3:411-417.