

Manufacturing and characterisation of PMMA-graphene oxide (GO) nanocomposite sandwich films with electrospun nano-fibre core

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ABSTRACT

Purpose: Nanocomposite materials, comprising of polymer matrices and nano-sized reinforcements, exhibit significantly enhanced mechanical and functional properties at extremely low filler loading. In recent years, graphene oxide (GO) has emerged as a new class of low cost nano-filler with high mechanical strength and stiffness, and alterable electrical properties. For nano-fillers with layered structure like GO, complete exfoliation and uniform dispersion of filler in the polymer matrices is essential to enhance the matrix-filler interaction and in turn the mechanical and/or functional property improvement. Conventional nanocomposite manufacturing methods including in-situ polymerisation and solvent processing encounter the problem of agglomeration of GO films. Additionally, its low bulk density presents difficulties in handling, and the energy requirement for mechanical mixing and extrusion processes is very high. In this work, we report manufacturing of poly(methyl methacrylate)-graphene oxide (PMMA-GO) nano-fibre mat using relatively novel approach of employing electrospinning technique. The manufactured electrospun core was inserted between plain polymer layers to prepare a robust and easy to handle sandwich film. Morphology and structure of the PMMA-GO nano-fibre cores was evaluated with scanning and transmission electron microscopy and X-ray diffractometry. The manufactured nano-fibre mat samples exhibited uniform diameter and dispersion. The functional parameters including thermal stability and gas barrier were evaluated with differential scanning calorimetry and oxygen permeation testing, and these functional properties were observed to be superior to that of monolithic polymer counterparts.

Keywords: Nanocomposite; Graphene oxide; Electrospinning; Nano-fiber; Sandwich films

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1. Introduction

Polymer nanocomposites have attracted considerable attention in the field of advanced materials due to their superior mechanical

and functional properties, achieved at relatively lower filler loading. The improvement in properties is mainly attributed to the very high aspect ratio (in the range of 100-1000) of nano sized fillers [1], yielding light-weight composites with alterable

multifunctional properties [2]. However, the composite properties are highly influenced by the level of exfoliation of the nano-filler and its uniform dispersion in polymer matrix.

In recent years, significant research work has been conducted to exploit the excellent mechanical and functional properties of graphene by employing it as a nano-filler [2-6]. Additionally, graphene oxide (GO), an intermediate product in graphene synthesis process, has also emerged as a novel class of potential nano-fillers. Synthesis of GO is relatively easier than graphene and its layered structure, high mechanical strength and stiffness, superior fire retardancy and excellent gas barrier properties are similar to those of graphene [4,7,8]. Although GO is intrinsically an insulator, the electrical conductivity can be improved by chemical and/or thermal treatment. Such tunability of electrical properties of GO presents an interesting area of investigation and potential use of GO as a conducting nano-filler in optoelectronic and electromagnetic interference shielding devices in addition to structural and automotive components, memory devices, biomedical and gas sensors, etc. [5].

The conventional form of "GO paper" [9] consists of individual micron-sized sheets stacked on top of each other, obtained through filtration of the oxidized graphite flakes' dispersion in water. Though the process facilitates mass production of relatively thin sheets (1-100 μm), it is limited by the size of the dispersion media. Further exfoliation of graphite oxide sheets, to manufacture nano-scale, mono-layer GO sheets, can be achieved through ultrasonication or magnetic stirring of colloidal suspension in water or organic solvents [10-13] and/or rapid thermal heating in furnace [6,14] under inert atmosphere. While sonication and magnetic stirring methods produce exfoliated GO sheets with no change in chemical structure, the thermal methods lead to reduction of graphite oxide to some extent due to removal of oxygen and have crumpled morphology.

The established methods of manufacturing continuous polymer nanocomposites are in-situ polymerization, solvent processing and melt blending. GO sheets are relatively easily functionalized with either the monomer or polymer chains due to larger interlayer spacing compared to graphite and the presence of reactive functional groups [15]. However, the nanocomposite morphology of in-situ polymerised nanocomposites was observed to be intercalated in X-ray diffraction studies [16]. In solvent processing, the polymer and exfoliated GO nano-sheets are mixed in a solvent by mechanical stirring or shear mixing followed by removal of the solvent through chemical precipitation, drying or vacuum filtration, but this may result in aggregation of GO sheets in the polymer matrix. [2,3,17]. Melt blending requires prior exfoliation of GO nano-fillers in order to achieve level of filler dispersion similar to preceding methods. Besides, GO is susceptible to chemical reduction during melt blending due to its thermal instability [18]. Thus, complete exfoliation and uniform dispersion of GO sheets is difficult to achieve with these methods.

Nanocomposites in fibre forms have found increased usage in the past few decades in filtration and chemical processing, due to their comparatively larger surface area. Carbon based nano-fillers including MWCNTs have been successfully incorporated into polymer fibres [19] with electrospinning. This paper presents manufacturing of polymer-GO nano-fibres, using electrospinning, in order to achieve uniform distribution of GO sheets in nano-sized polymeric fibres. The produced nano-fibres were characterised with optical microscopes to assess their structure and morphology and

differential scanning calorimetry to evaluate the thermal stability. Additionally, the electrospun nano-fibres were inserted as core between thin, plain polymer layers to produce sandwich films, with vacuum assisted compression moulding. Oxygen permeation tests were conducted for these sandwich films to investigate their suitability for intended application as high barrier packaging material.

2. Experimental

2.1. Materials

Graphite flakes were bought from Sigma-Aldrich and were pulverized to fine powder with an average particle size of 30 μm . 95-97% sulfuric acid (H_2SO_4) used in the GO synthesis was purchased from Merck Group, Germany, and potassium permanganate (KMnO_4) was purchased from Ajax Chemicals, Australia. Sodium nitrate NaNO_3 and 30% hydrogen peroxide (H_2O_2) were purchased from Ajax Finechem Inc., Auckland, and was used in "as-procured" condition.

The solvents viz., N, N - dimethylformamide (DMF, Anhydrous, 99.8%) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich and ECP Ltd (Romil, UK), respectively. The polymer poly(methyl methacrylate) was procured from Chi Mei Corporation and used after drying as recommended in the manufacturer's datasheet.

2.2. Electrospinning technique

Electrospinning is an efficient way to produce nano-fibres from the polymers either in solvent solution or in molten form. The technique employs very high voltage across the needle of solvent containing syringe and a conducting collector to generate a nano-fibre mat on the collector surface. A typical set-up consists of a high voltage supply, syringe, needle, metal collector and flow rate controller, as shown in the schematic diagram in Fig. 1.

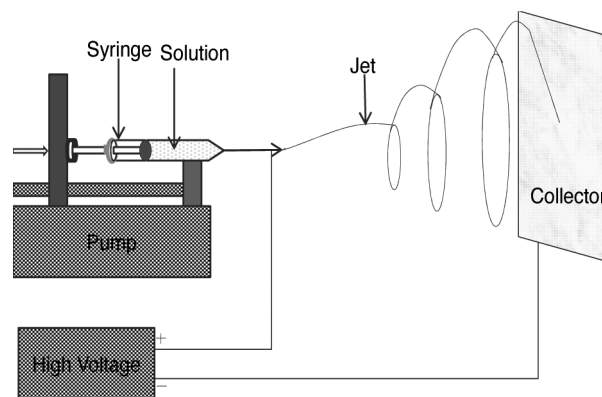


Fig. 1. Schematics illustrations of (a) FSLW and (b) material flow up-lifting un-welded lap thus hooking during FSLW and (c) forces applied to a welded joint during subsequent mechanical testing

The solution in the syringe is fed at a controlled rate by the pump through the needle. Due to the potential difference applied across the needle and conducting collector, the solution is polarised. As a result of the polarisation and surface tension, the solution particles form a conical arrangement, termed as “Taylor cone” [20], and travel towards the metallic collector. The solvent evaporates during the movement of solution particles from the needle to the collector, leaving an interconnected web of nano-fibres on the surface of the collector [21]. Morphology of the generated nano-fibre mat is governed by the viscosity of the solution, relative humidity, ambient temperature, and polarity [22].

2.3. GO synthesis

GO was synthesized from graphite using modified Hummers’ method [23], with increased quantity of acidic media. The GO sheets dispersed in water were subjected to ultrasonication up to 20 hours to achieve exfoliation. After drying, the films were ground to fine particles (325 mesh) using a centrifugal shear mixer so that it could be well dispersed in the solvent.

2.4. Solution preparation

The solvent selected for PMMA and GO was a 2:1 mixture of N, N-dimethylformamide (DMF) and tetrahydrofuran (THF). Mixture analysis was conducted and validated with the experimentally observed nano-fibre morphology and dispersion to determine the optimum level for the three constituents of the electrospinning solution [24], viz., PMMA, GO and DMF+THF. Three levels of %weight loading were selected for PMMA as 20, 22 and 23 and for GO as 1, 2 and 5, respectively.

The weight proportion ratio for the solvents DMF and THF was maintained as 2:1. The solvents were mixed for 15 minutes in an ultrasonication bath before adding pulverised GO sheets, as per the sample %weight ratio of PMMA and GO. The solution was subjected to 15 minutes of ultrasonication followed by stirring at room temperature for 8 hours. PMMA pellets, weighed according to the sample specification, were transferred to the beaker containing the GO-solvent solution mixture. This solution was mixed using a magnetic stirrer for 5 hours.

2.5. Electrospinning of composite nano-fibres

The electrospinning solution was filled in a 5 ml syringe and fed at controlled uniform rate of 2 ml/hour. An aluminium foil, connected to ground, was used as a collector. The needle of the syringe was connected to positive terminal to charge the solution with applied voltage 15.0 kV. This resulted in an accelerated jet of fluid from the needle to the aluminium foil over the spinning distance of 100 mm. The temperature and humidity in the electrospinning chamber were maintained in the range of 15-20°C and 50-60%.

2.6. Sandwich film formation

The electrospun nano-fibre mat was inserted as core between plain PMMA facings to form a sandwich film with vacuum assisted compression moulding.

3. Characterisation

The structure and morphology of PMMA-GO nano-fibres obtained through electrospinning was investigated with optical techniques of scanning and transmission electron microscopy.

3.1. Structure and morphology

The diameter, dispersion and porosity of the electrospun nano-fibres were examined by performing scanning electron microscopy (SEM). SEM samples were prepared by mounting the nano-fibre mat on the SEM stubs and coating with platinum for 300 s to make it conductive. The typical images obtained by scanning electron microscopy of samples with 23%weight PMMA, and 1 and 2%weight GO are shown in Figs. 2, 3, respectively.

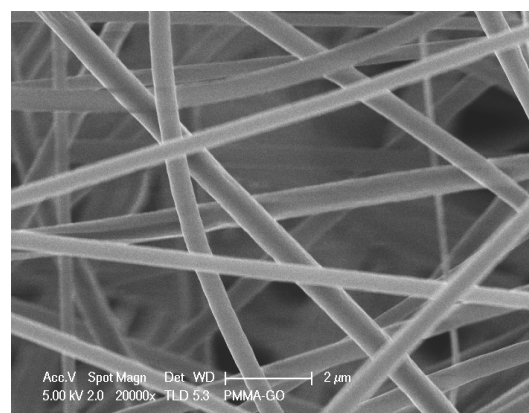


Fig. 2. SEM image of electrospun nano-fibre mat with 1%weight GO

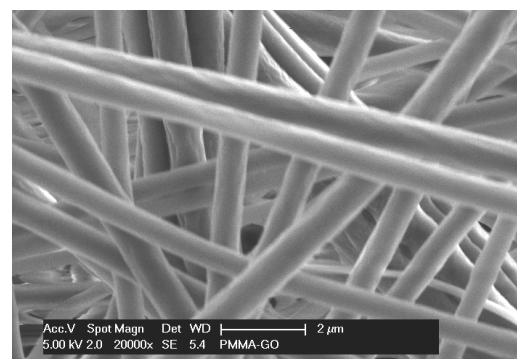


Fig. 3. SEM image of electrospun nano-fibre mat with 2%weight GO

The SEM images show that the nano-fibres formed with electrospinning are uniform and with no beads, indicating that the manufacturing parameters employed are suitable for a low-cost and efficient production of composite PMMA-GO nano-fibres. It was observed that the solutions with higher concentration of PMMA-GO yielded nano-fibres with larger diameter due to the reduction in amount of stretching with increased viscosity. The samples with 23% PMMA and 2% GO were observed to yield the most uniform fibre diameter and dispersion (Fig. 3)

To examine an individual nano-fibre, transmission electron microscopy (TEM) was conducted. The TEM samples were prepared by using copper grid for collecting electrospun nano-fibres. The images obtained could capture the wrinkled GO thin sheet aligned in the length direction of the composite nano-fibre with 1.2 μm visible length, as depicted in Fig. 4.

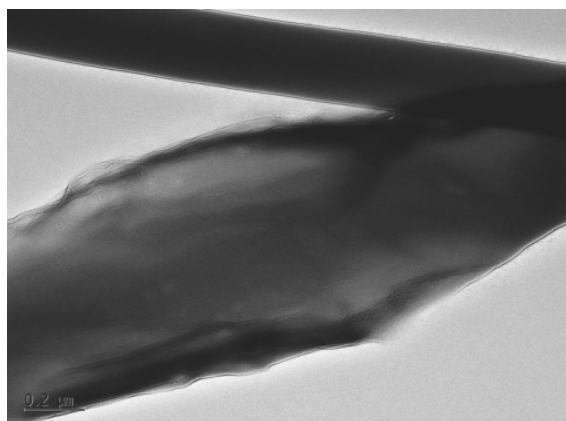


Fig. 4. TEM image of electrospun nano-fibre

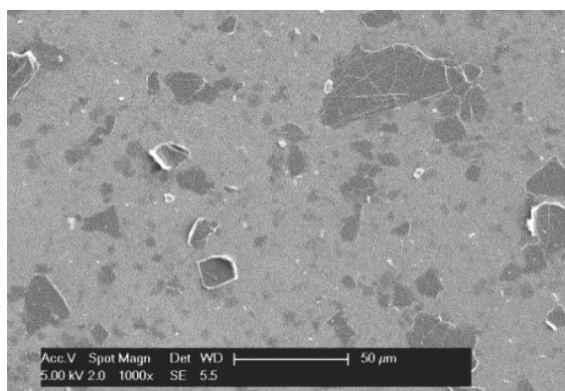


Fig. 5. SEM image of GO dispersion in water subjected to ultrasonication for 20 hours

Thus, it can be observed that electrospinning is an effective way of incorporating mono-layer GO sheets with very high aspect ratios, in polymer matrix. Electrospinning can overcome the problem of filler agglomeration observed in solvent casting route of preparing nanocomposites, as the polymer matrix is converted to a nano-sized fibre instead of a continuous sheet, thus facilitating better dispersion of exfoliated GO.

GO sheets were exfoliated with ultrasonication in this work, as it is comparatively more effective technique than mechanical stirring. However, excessive ultrasonication may result in damaged GO sheets with broken edges. This was investigated by subjecting the ultrasonicated suspension of GO to SEM. A few of the produced GO sheets were observed to have sharp, broken edges as depicted in Fig. 5. However, majority of the GO sheets were observed to have a similar range of lateral dimension. It may be noted though that these observations are highly localised in nature and cannot be established as a generic rule.

3.2. Filler dispersion

Wide-angle X-ray scattering (WXR) is an effective tool to characterise inter-layer distance of multi-layered materials, particularly intercalated/exfoliated morphologies. The intercalated arrangement of layered fillers results in a basal reflection peak at smaller diffraction angle, while the complete exfoliation is indicated by absence of a peak. The technique employs a scintillation counter to measure the angular distribution of scattered X-ray, reflecting the diffraction intensities in form of peaks. For this work, X-ray diffractometry was conducted with Cu-K α radiation at scan speed of 0.02 $^\circ$ /s, over 5-50 $^\circ$.

The XRD curves obtained for GO, PMMA pellets and PMMA-GO nano-fibres are illustrated in Fig. 6. The sharp peak at $2\theta = 10^\circ$ for GO indicates the effective oxidation of graphite and resultant increased inter-layer distance between graphene planes. The results observed for PMMA pellets and PMMA-GO nano-fibres are devoid of sharp peaks. The smooth curve for PMMA-GO nano-fibres suggests high level of exfoliation and dispersion of individual GO sheets in polymer matrix.

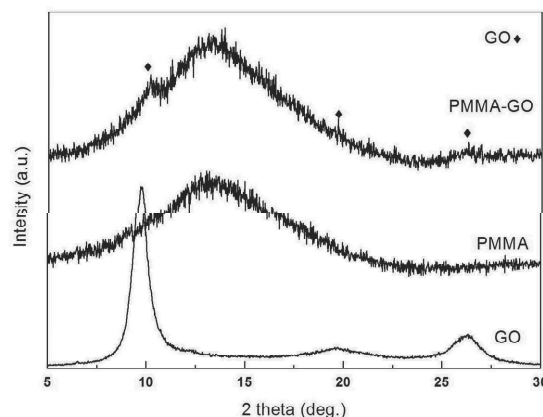


Fig. 6. XRD curves for PMMA, GO and PMMA-GO nano-fibres [25]

3.3. Thermal stability

The thermal behaviour of PMMA and PMMA-GO nano-fibres was investigated by conducting differential scanning calorimetry and the heat flow trend with temperature increase at the rate

of 10°C/min are illustrated in Fig. 7. The samples were prepared by encasing small quantity of fibres in sealed aluminium pans and subjecting it to thermal ramp. The heat flow curve obtained for PMMA nano-fibres exhibited a peak at ~120°C corresponding to a glass transition temperature, which is higher than the glass transition temperature of atactic PMMA (105°C) and in line with the glass transition temperature range of commercial PMMA varieties (85-165°C). The heat flux graph for PMMA-GO nano-fibres contains no visible peaks in the range of 0-200°C, indicating higher thermal stability of these in comparison with plain PMMA nano-fibres.

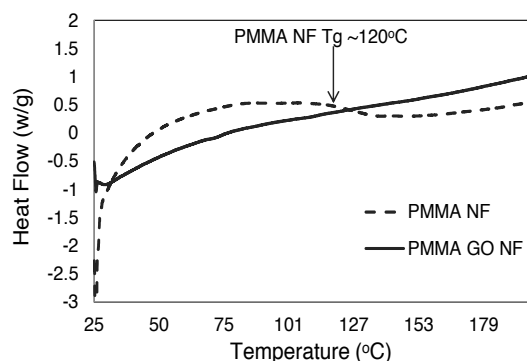


Fig. 7. DSC curves for PMMA and PMMA-GO nano-fibres

The observed thermal behaviour makes PMMA-GO nano-fibres suitable for further temperature assisted processing in order to incorporate the electrospun mats in realistic application devices. For this work, the electrospun mat was inserted between plain polymer facings to prepare a thin sandwich film with vacuum assisted compression moulding.

3.4. Resistance to oxygen permeation

With the electrospun nano-fibre core, impermeable GO fillers and layered structure, the manufactured sandwich films presented potential for significant resistance to permeation of gases. This was assessed by conducting oxygen permeation testing in laboratory (MOCON OX-TRAN 2/10).

The permeation values observed for sandwich films with electrospun core containing 1-2 %weight GO were in the range of $3.08\text{-}3.56\cdot 10^{-16}$ mol/m²·s·Pa, indicating that the films are practically impermeable for oxygen. The finite element numerical modelling of the fluid flow through these films depicted the major role played by electrospun core, compared to the polymer facings, in rendering the observed high gas barrier. The high resistance to permeation of environmental gases, displayed by the sandwich films suggest potential for application in food and beverage packaging

4. Summary

This paper presents the successful incorporation of a comparatively novel class of fillers, graphene oxide (GO),

into nano-sized polymeric fibres. The composite nano-fibres were manufactured by electrospinning the solution of poly(methyl methacrylate) and GO nano-fillers dissolved in a 2:1 mixture of solvents N, N - dimethylformamide (DMF) and tetrahydrofuran (THF).

The produced composite nano-fibres displayed uniform dispersion and diameter for 20-23 %weight range of PMMA and 1-5 %weight range for GO. The thermal stability of the PMMA-GO nano-fibres was observed to be superior to monolithic polymer fibres indicating better suitability for further processing and applications. The electrospun nano-fibre mats, when incorporated as core between plain, polymer facings to form a sandwich film, presented a nearly impermeable barrier to passage of oxygen gas indicating very high suitability in packaging and oxygen sensitive chemical processing applications.

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