



PHYSICAL, THERMAL, AND DIELECTRIC PROPERTIES ENHANCEMENT IN GRAPHENE/POLY (VINYL ALCOHOL) NANOCOMPOSITE AS NOVEL MULTIFUNCTIONAL MATERIALS

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ABSTRACT

In this research, poly (vinyl alcohol)/ exfoliated graphite nanoplatelets® (PVA/xGnP) nanocomposites in the form of films were prepared by solution casting processing methods. The objective of this research was to investigate the thermal stability, physical, dynamic mechanical and dielectric properties of PVA/xGnP nanocomposites having different xGnP loading content (0.5, 1, 3, 5, 7wt %). The dynamic mechanical analysis (DMA) results indicated that the glassy-state storage modulus (at 30 °C) of PVA/xGnP nanocomposites at 0.5, 1, 3wt % xGnP loading increases about 230%, 200% and 180% beyond that of pure PVA sample, respectively. Furthermore, the good interaction of the xGnP nanofillers with the host PVA significantly increases the glass transition temperature (T_g) of nanocomposite with lower filler loading (0.5-3wt %). It can be clearly observed that the trend in dynamic mechanical properties (T_g) of the PVA/xGnP nanocomposite is in excellent agreement with that in the tensile characteristic. Thermogravimetric analysis (TGA) demonstrated an enhancement in thermal stability of the PVA/xGnP nanocomposite containing xGnP at loading 0.5 and 1wt%. The PVA/xGnP nanocomposites show an enhancement in dielectric properties upon the addition of xGnP fillers. The dielectric permittivity (ϵ') of the nanocomposites having filler content less than 3wt% show behaviour of weak frequency dependence. However, when the filler content was increased to a level 3wt% and above, the ϵ' of the nanocomposites exhibits strong frequency dependence and decreased sharply between the frequencies ranges from $10^6 - 10^7$ Hz.

Keywords: exfoliated graphite nanoplatelets, poly (vinyl alcohol), dynamic mechanical, thermal stability and dielectric.

INTRODUCTION

In recent years, multifunctional nanocomposites are increasingly needed for applications requiring prescribed sets of physical, thermal and electrical properties. Polymeric nanocomposites offer design engineers a wide range of tuneable materials properties that would enhance the polymer properties and extend their applications to new areas. The development of materials like graphene has revitalized nanocomposite science and technology which led to the evolution of a new generation of materials. Nanocomposite is one of the most promising approaches to enhance the polymer properties by combining the light weight and flexibility of polymers with the extraordinary mechanical and thermal properties of the nanofiller at far lower reinforcement concentrations than their conventional micro and macro counterpart. However, maximal mechanical enhancement can only be achieved when the nanofiller is dispersed homogeneously, or best at the molecular level, in the matrix and the external load is efficiently transferred via a strong interaction at the interface between the filler and the matrix [1].

Graphene-based materials have been extensively used to fabricate polymer nanocomposites because they combine the unique properties of carbon nanotubes (they have the same chemistry) and nanoclays (the platelet structure) providing thus reinforcement in 2D is leading to multifunctional polymer nanocomposites [2]. Graphite nanoplatelets (GNPs), also called graphite nanosheet (GN) or graphite nanoflake (GNF) is a type of 2D graphitic

nanofiller consisting of stacked graphene layers. The stacked graphene sheets with a typical d-spacing of 0.335nm are bonded to each other by weak Van der Waals forces [3]. The thickness of GNPs varies from several to dozens of nanometers, as compared to their diameter, usually in the microscale, which leads to the high specific surface area of GNPs. Therefore, layered materials such GNPs can be converted into high aspect ratio nano-reinforcements as the thickness and diameter of GNPs could be tuned by a variety of techniques, such as intercalation, oxidization, heat treatment, microwave irradiation, and ultrasonic treatment, etc. [4–7]. Compared with other classic 2D nanofillers, such as nanoclays, GNPs have lower mass density, and are highly electrically and thermally conductive, due to the sp² hybridized carbons in the monolayer graphenes within the GNPs [3]. Single crystal graphite also is one of the stiffest materials in nature with an elastic modulus of over 1 TPa, which is many times greater than nanoclay [8]. Therefore, GNPs are truly ideal for improving the properties of polymers and realizing multifunctionalities for applications in electrostatic discharge, electromagnetic interference shields, and thermal conductor [9]. However, due to the intrinsic van der Waals interactions, graphene/graphene derivatives usually easily re-agglomerate, which makes dispersion and exfoliation difficult [10]. Agglomeration reduces the interface and thus limits the stress transfer across it strongly impacting the mechanical properties [2]. In addition, agglomeration decreases the aspect ratio of the nanomaterial and can even alter its shape reducing



significantly its reinforcing efficiency. Interestingly, nano-size graphite flakes can be expanded and exfoliated followed by pulverization in order to enhance their reinforcing efficiency while maintains its pristine characteristics. During the last several years, a number of papers have claimed improvements in properties of polymer nanocomposites using GNPs. A compilation of selected properties data for nanocomposites filled with GNPs is shown in Table-1.

This study focuses on using Exfoliated graphite nanoplatelets® (xGnP) made by microwave exfoliation of acid intercalated synthetic graphite [11] as reinforcement in a polymer. The goals of this study are first to fabricate composites consisting of biocompatible polymer named polyvinyl alcohol (PVA) and xGnP by solution mixing. Second, the effect of xGnP content on the thermal stability, dynamic mechanical and physical properties of PVA/xGnP nanocomposite were investigated and characterized using thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and tensile testing. Finally, the dielectric properties of PVA/xGnP nanocomposite were investigated. Our aim was to produce multifunctional nanocomposites that would show enhancement in thermal, physical and dielectric properties without sacrificing one for the other.

Table-1. Graphene-based polymer nanocomposite.

Polymers	GNPs	Properties Studied	Ref.
Polyamide	xGnPs	Flexural, DMA, DSC	[2]
Vinyl Ester	GNPs	DMA, Impact	[12]
Poly (methyl methacrylate)	GNPs, EG	DMA	[7]
Epoxy	UV-GNPs	DMA, Flexural, Electrical	[9]
LLDPE	xGnPs	DMA, TMA, TGA	[13]
PP	xGnPs	DMA, TMA	[14]

MATERIALS AND METHODS

Materials

The graphene nanoplatelets used in this study, with the commercial name of xGnP-C-750, were purchased from XG Sciences, Inc. These graphene nanoplatelets are approximately 2nm thick with a less than 2µm average diameter and a typical surface area of 750m²/g, as reported by the manufacturer. Poly(vinyl alcohol) (PVA) was purchased from Nippon Gosei Singapore PTE LTD with the commercial name of Gohsenol PVA GH-22 (hydrolysis 86.5-89.0 mol%, viscosity 45-55 mPa.s).

Preparation of PVA/xGnP nanocomposite film

PVA pellets (0.5 g), as a benchmark for preparation of a series of nanocomposite films with xGnP loadings between 0.5 and 7 wt%, were added to 100 ml deionized water, followed by stirring at 95°C until the PVA pellets were dissolved completely. Certain amounts

of the xGnP were dispersed in 20 ml deionized water by sonication at room temperature for 60 min to produce a colloidal dispersion of xGnP. The dispersion obtained was then combined with the PVA aqueous solution by stirring at 95°C for 30 min. The resulting composite was casted into a flat-bottomed mold and dried in oven at 50°C.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) experiments were conducted using a TA Instrument TGA Q500 from room temperature to 700°C at linear heating rate 10°C min⁻¹ under a nitrogen flow. Approximately 5-8mg of cut samples was used to determine the decomposition temperatures.

Dynamic mechanical analysis

Dynamical mechanical analysis (DMA) experiments were conducted using a TA Instrument DMA Q800 in film tension mode at a fixed frequency of 1 Hz. The sample dimensions were 40 × 5 × 0.5 mm³. The sample was tested with a temperature ranging from room temperature to 100 °C at atmospheric pressure and a heating rate of 6 °C min⁻¹. Storage modulus (G') and loss tangent (tan δ) will be obtained. T_g will be taken as the peak temperature of tan δ curve.

Tensile test

The tensile tests to determine the tensile strength and modulus were carried out on a tensile testing dumbbell-shaped sample according to the ASTM D638 using an Instron 3365 at a crosshead speed of 10 mm min⁻¹. The tests were performed at standard laboratory atmosphere (23 °C ± 2 °C and 50 ± 5 percent relative humidity).

Characterization of dielectric properties

The dielectric properties of sample were measured by using Agilent 4291b RF impedance analyser. The sample was prepared in a plate shaped with dimension 2.5cm×2.5cm. In this measurement, HP16453A dielectric materials test fixture was used and calibrated before the measurement. The sample was placed between two electrodes, forming a capacitor setup.

RESULTS AND DISCUSSIONS

Mechanical properties

The results of tensile properties obtained from this research are shown in Figure-1. The numbers 0.5, 1.0, 3.0, 5.0, and 7.0 indicate the weight percent of the xGnP incorporated in the composite. As demonstrated in Figure-1, upon increasing the xGnP nanofiller loading, the mechanical behaviour of the nanocomposite exhibits an enhancing trend. The tensile strength of the composite containing 0.5 wt% xGnP is up to 41MPa, while that of the neat PVA sample is 32 MPa. As the xGnP content is further increased from 1.0 to 3.0 wt %, the tensile strength increase slightly from 42 to 44 MPa, without a pronounced



change. However, the tensile strength decreased when the loading is beyond 3 wt%.

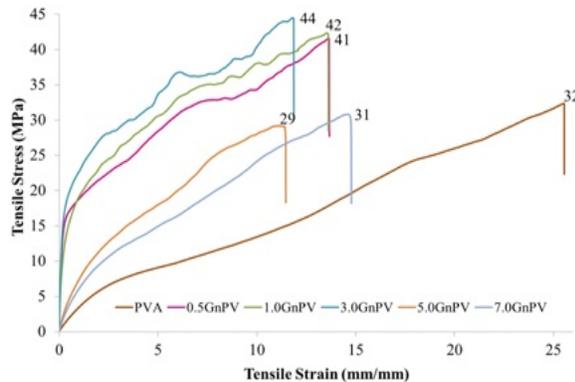


Figure-1. Stress vs. strain curve of PVA and PVA/xGnP nanocomposite films with various wt% of xGnPs.

There existed strong interfacial interactions between xGnP and PVA matrix has attribute to the good dispersion state of xGnP within the matrix. This result the efficient load transfer between nanofiller and PVA matrix took place during the tensile test. However, when the xGnP loading was over 3 wt%, the agglomerates which act as stress concentration points or defects are formed within the polymer matrix, leading to the decrease of strength. It is assumed that adding xGnP beyond the mechanical percolation of the nanocomposite, the phenomenon of graphite nanoplatelet re-agglomerate will occurs due to their van der Waals force [10]. As a result, this reduced the efficiency of the mechanical improvement.

Dynamic mechanical properties

The effect of the interfacial interactions on the bulk properties of the nanocomposites was further investigated by studying the thermomechanical properties of the composites. The storage modulus and T_g as a function of xGnP content were shown in Figure-2 and Figure-3, respectively. In the legend, the numbers (0.5, 1.0, 3.0, 5.0, and 7.0) indicate the weight percent of the xGnP incorporated in the composite. The temperature-dependence plots of the storage modulus of PVA and its xGnP nanocomposites, as measured from 25 to 100°C, are shown in Figure-2. As shown in and Figure-2, the glassy-state storage modulus (at 30 °C) of PVA/xGnP nanocomposites at 0.5, 1, 3wt % xGnP loading increases about 230%, 200% and 180% beyond that of pure PVA sample, respectively. While the storage modulus of 5.0GnP and 7.0GnP increased slightly by 12%, and 50% beyond the pure PVA, respectively.

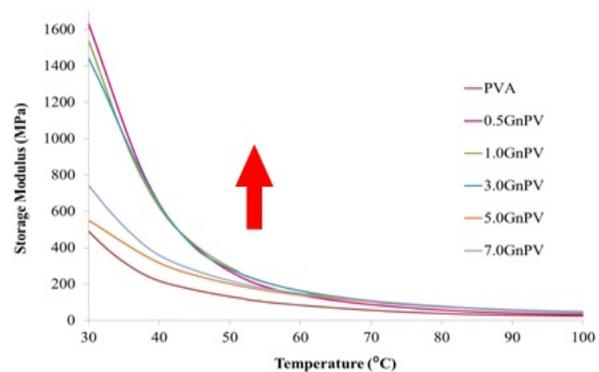


Figure-2. Storage Modulus of PVA and PVA/xGnP nanocomposite films with various wt% of xGnPs.

T_g is mainly associated with the large segmental motion of polymer chains in amorphous or semi-crystalline polymers. The presence of hard regions such as nanofillers could restrict the mobility of polymer chains around or absorbed on the surface of xGnP, leading to the formation of a stiffened interphase. These phenomena might be due to mechanical interlocking or chemical interactions. In this study, the interaction of the xGnP nanofillers with the host PVA significantly increases its T_g (identified by location of the tan delta peak, Figure-3 by as much as 14.1°C. The highest value of T_g is an indication of good dispersion of the nanoparticles and a correspondingly large amount of interfacial area with altered polymer chain mobility throughout the composites. Furthermore, the sharp increase in T_g of 0.5GnP is related to the better accessibility of the xGnP surface by the polymer chains at very low nanofiller content. The decreasing T_g values with increasing loading (5GnP and 7GnP) are an indication that xGnP may tend to phase separate (partially agglomerate), suggesting a lower dispersion ability. It can be clearly observed that the trend in dynamic mechanical properties (T_g) is in excellent agreement with that in the tensile characteristic. The comparison suggests existence of strong correlation between the tensile properties and the immobilized fraction of the polymer chains in the amorphous region.

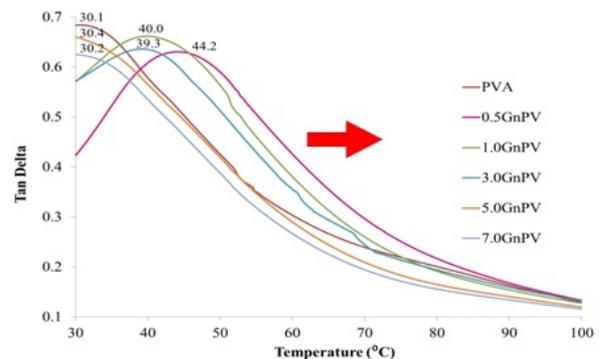


Figure-3. Tan Delta of PVA and PVA/xGnP nanocomposite films with various wt% of xGnPs.



Thermal stability properties

The thermal stability of the composite materials was assessed by thermogravimetric analysis (TGA) in inert atmosphere. Figure-4 showed that the onset temperature for neat PVA degradation was about 300 °C, which was attributed to main-chain pyrolysis. At about 450 °C, the total amount of polymer was seemed to be pyrolyzed. The TG curve of the PVA/xGnP nanocomposite samples had shown a similar decomposition profile as neat PVA matrix. Interestingly, at temperature range from 350 to 480 °C, which is the degradation stage of the polymer, the TG curve of PVA/xGnP nanocomposites has mildly shifted to a higher temperature range with respect to the neat polymer matrix. This indicate that xGnP were uniformly exfoliated into PVA matrix, and the finer dispersed xGnP could act as “efficient heat sinks,” which consumed more heat than the matrix and did not allow the accumulation of heat within the latter, and thereby prevented oxidation at those stages of degradation.

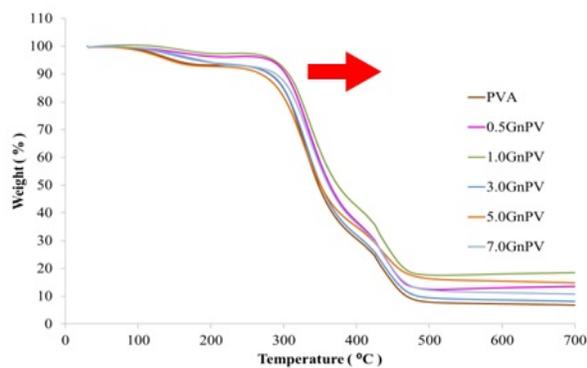


Figure-4. TG curve of PVA and PVA/xGnP nanocomposite films with various wt% of xGnPs.

Dielectric properties

The nanocomposites show a high dielectric constant upon the addition of xGnP fillers, as a result of interfacial polarization, as illustrated in Figure-5. As shown, the dielectric permittivity (ϵ') of the nanocomposites having filler content of less than 3wt% exhibit weak frequency dependence. However, when the filler content was increased to 3wt% and above, the ϵ' of the nanocomposites exhibits strong frequency dependence and decreased sharply between the frequencies ranges from $10^6 - 10^7$ Hz. This phenomenon may be attributed to interfacial polarization. Interfacial polarization is also referred to as the Maxwell–Wagner–Sillars (MWS) effect or polarization, a phenomenon that appears in heterogeneous media consisting of phases with different dielectric permittivity and conductivity, and which is attributed to the accumulation of charges at interfaces. This MWS effect can be characterized by the frequency dependence of dielectric constant in the low frequency range. When the xGnP filler content was low, the dielectric constant is almost independent of frequency because no plentiful accumulation of interfacial charges

inside the nanocomposites. This is due to the nanosheets were isolated; that is, they were placed so far apart that there was no interaction between them. As soon as percolation threshold was achieved (at 3wt%), the xGnP begin to approach each other and form “quasi-cluster” which means that they were not completely in contact to each other. This means that there were many xGnPs separated by very thin dielectric PVA layers. Thus, a lot of charges were blocked at the interfaces between the filler and polymer matrix, owing to the MWS effect, which makes a remarkable contribution to the increment of the dielectric permittivity in the low-frequency range. However, when the frequency was over 10^8 Hz, the dielectric permittivity of composites was dominated by the micro capacitance-structure model (frequency-independent), so that it was maintained at stable value.

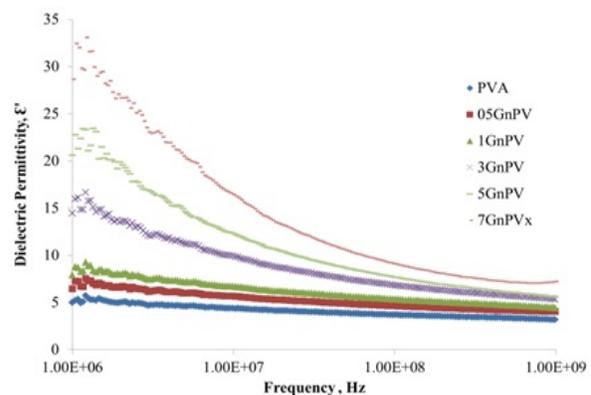


Figure-5. Dependence of dielectric constants on frequency for PVA and PVA/xGnP nanocomposite films.

CONCLUSIONS

It has been demonstrated that xGnP can effectively improve the thermal stability, physical, dynamic mechanical and dielectric properties of PVA/xGnP nanocomposites. These results can be further optimized by enhancing the adhesion at the PVA-xGnP interface, and by improving the dispersion and orientation of the platelets by selecting appropriate processing methods such as electrospinning. Overall, exfoliated graphite nanoplatelets have demonstrated an exciting new ability to simultaneously improve multiple physical, thermal and mechanical properties of polymer composites making xGnP a multifunctional nano-reinforcement.

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