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SILVER GARNISHED GRAPHENE/POLY VINYL ALCOHOL COMPOSITES AIMED AT AMPLIFIED DIELECTRIC BEHAVIOUR TOWARDS HIGH DIELECTRIC APPLICATIONS.

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ABSTRACT

The electrical conductivity and the specific surface area of conductive fillers in conductor-insulator composite films can acutely promote the dielectric pursuance of those films through altering their polarization density by interfacial polarization. On this grounds, the dielectric constants, conductivities and dielectric loss in polymer composite films of PVA incorporated Ag/graphene synthesized via solvent cast method are studied. X-ray diffraction patterns confirmed the formation of Ag/graphene/PVA with good compatibility. The decoration of Ag nanoparticles on the surface of graphene layers was demonstrated by the scanning electron microscope analysis. The dielectric constant of the prepared composites are complemented up to 11.89 at 1MHz and the magnified conductivity of the composites after the incorporation of Ag nanoparticles is 1.86×10^{-4} at 1MHz which is attributed to the movement of electrons across the barrier and insulating chains in the composites by Ag NPs loading. The composites also exhibited a minimum dielectric loss of 0.08 at 1MHz. The momentous gain in the dielectric constant and low losses obviously suggest that the prepared polymer nanocomposites could be apt for high dielectric applications.

Keywords: Conductivity / Dielectric loss / PVA / Graphene / Ag Nanocomposites

INTRODUCTION

The rapid development of electronic industries has received a great interest for high dielectric materials which is attributed to their capacity for storing large amount of electrical energy and credit worth for utilizing in the fields such as gate dielectrics, power industries, energy storage capacitors, electromechanical

transducers, microelectronics, and aerospace.¹⁻³ Polymer nanocomposites with high dielectric constants can be processed with excellent thermal and mechanical properties, flexibilities, low density and high breakdown strength.

A two-dimensional sp^2 hybridized carbon, graphene has been utilized in the polymer matrix to form composites due to its unique properties such

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as structural, thermal, mechanical and electrical properties. The delocalized π electrons located above and below the plane of graphene sheets enhance its electronic properties. Graphene has large surface area ($2630.00\text{m}^2\text{g}^{-1}$), high intrinsic mobility ($200000.00\text{cm}^2\text{v}^{-1}\text{s}^{-1}$), high Young's modulus ($\sim 1.00\text{T Pa}$), thermal conductivity ($\sim 5000.00\text{Wm}^{-1}\text{K}^{-1}$) and good electrical conductivity can be used in tailoring polymer composites with better conductivities.⁴⁻⁷

Metal nanoparticles, particularly silver nanoparticles are considered to be potential materials, having a wide range of applications in several fields such as printing, imaging, optical sensors, photonics, bioengineering, switching devices and conductive inks. The incorporation of silver nanoparticles could enhance the space charge polarization between the conducting fillers and polymer matrix is note worth factor for enhancing the dielectric permittivity and conductivities of the composites.⁸⁻¹⁰

The commercial water soluble polymer, polyvinyl alcohol with unique properties such as microporous structure, excellent thermal and mechanical properties, emulsifying, adhesives and its flexibility have made it a promising candidate for drug delivery, biotechnology applications, tissue engineering and in electronics.¹¹⁻¹² Nirmal maity¹³ clearly reports the improved values of the PANI functionalized graphene/PVDF composites which in turn the process involved several steps in dispersing the hybrid materials in the solvent to form the composites. Since PVA is water soluble polymer, it is easy to fabricate the composites compared with another polymer such as polyaniline and another synthesized polymer which in turn difficult to disperse in solvents. The better solubility and the easy processing based on PVA matrix give the enhancement observation in dielectric behavior.

In the present work, by combining all the advantages discussed above, we have designed a polymer based nanocomposites using Ag/graphene nanohybrids reinforced polyvinyl alcohol matrix by a simple solvent cast method. The unexplored electrical properties of this sort of composites encouraged us to design, synthesis, and study its electrical properties.

EXPERIMENTAL PROCEDURES

Synthesis of Graphene

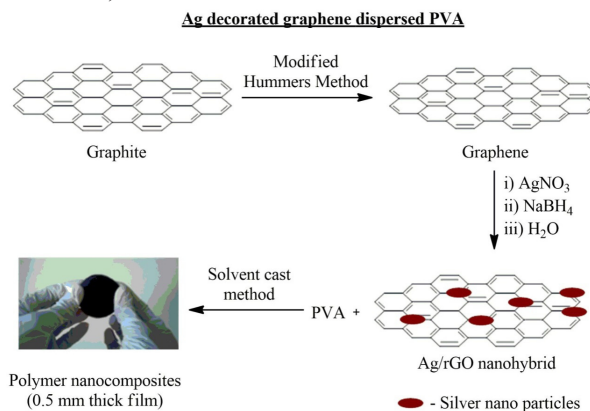
Graphene was synthesized using modified Hummers method¹³, (Scheme 1).

Preparation of Ag/graphenenanohybrids

The graphene powder was mixed with $5.0 \times 10^{-3}\text{mol dm}^{-3}$ AgNO_3 and stirred well at RT. The reducing agent NaBH_4 was slowly added to the above suspension and stirring was continued vigorously for 5 h and then it was washed several times with DD H_2O and centrifuged. The wet powder was dried for 10 h at 60°C to obtain Ag incorporated graphene hybrids, (Scheme 1).

Preparation of Polymer Nanocomposites

Ag/graphene nanohybrids were mixed well in ethanol and sonicated well for 2 h and the solution was added to PVA/water solution. Then the mixed solution was sonicated well for 3 h and stirred well for 3 h at 50°C to obtain ahomogeneous solution and it was cast into films at 60°C for 8 h. A 0.5mm film was obtained, (Scheme 1).



Scheme 1. Preparation of polymer nanocomposites

CHARACTERIZATION

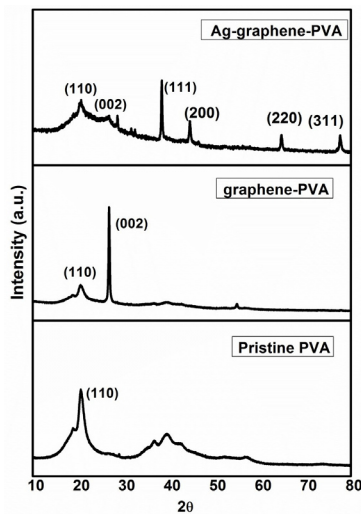
X-Ray diffraction (XRD) patterns were taken on Cuka radiation XRD-RIGAKU MINIFLEX II-C XRD system. Raman spectra were recorded on a confocal micro-Raman microscope (Renishaw Via Reflex) with Arp ion laser source of 0.6 mW power and 514.5nm. The dielectric constant, conductivity and dielectric loss were measured using BDS novocontrol-concept 80 instruments at 100 Hz-1MHz at room temperature.

RESULTS AND DISCUSSION

X-Ray Diffraction Studies

The X-ray diffractions patterns for pristine PVA, graphene reinforced PVA and AgNPs decorated graphene/PVA composites are depicted in figure 1. A peak appearing at $2\theta = 19.57^\circ$ (JCPDS File No: 38-1638) and the stacked peaks appearing at $2\theta = 21.30^\circ$ (JCPDS File No: 75-2078) correspond to (110) and (002) reflections, account for the presence of pristine PVA and graphene/PVA respectively. The peak at $2\theta = 42.32^\circ$ (JCPDS File: 89-3722) corresponding to (200) reflection entrenched the presence of Ag nanoparticles in the composites.¹⁴⁻¹⁵

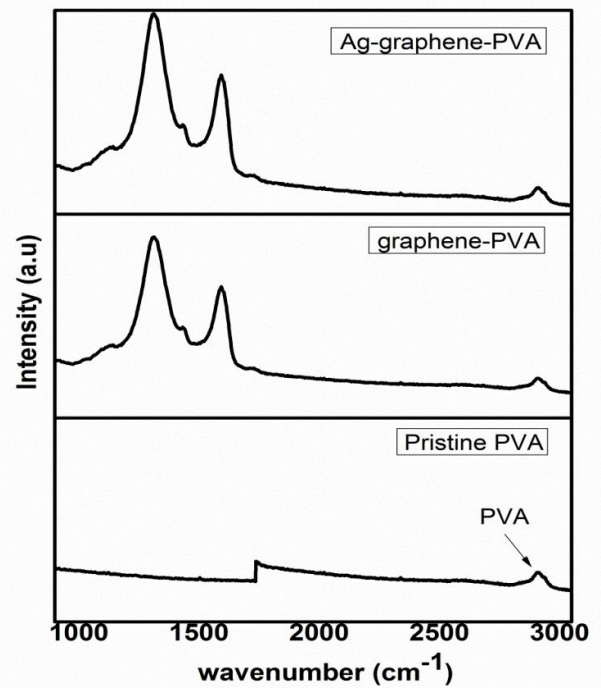
Figure 1.
X-ray diffraction patterns for PVA, graphene/PVA, Ag/graphene/PVA nanocomposites



RAMAN

The Raman spectra for pristine PVA, graphene/PVA, and AgNPs/graphene/PVA composites are illustrated in figure 2. The band appearing at 2902 cm^{-1} proved the presence of the pristine PVA.¹⁶ The bands appearing at 1308 cm^{-1} (D band for graphene) and 1585 cm^{-1} (G band for PVA) confirmed the presence of the graphene reinforced in PVA. The presence of Ag nanoparticles decorated in graphene is confirmed from the wavenumber shifts from 1308 cm^{-1} to 1304 cm^{-1} at D band and from 1585 cm^{-1} to 1580 cm^{-1} at G band respectively. The reason for this shift is attributed to the chemical interaction and charge transfer between AgNPs and graphene.¹⁷

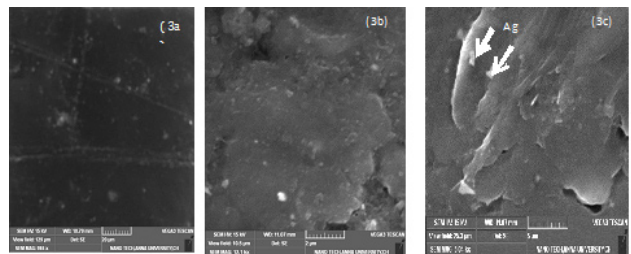
Figure 2.
Raman spectrum for Pristine PVA, graphene/PVA, Ag/graphene/PVA nanocomposites



SEM

The SEM image of pristine PVA, graphene/PVA, and Ag/graphene/PVA composites are shown in figure 3a, 3b, and 3c respectively. Figure 3a exhibited the cylindrical structure of pristine PVA and 3b revealed the graphene which is incorporated in PVA polymer and it also showed the rigid structure in the polymer matrix. Figure 3c clearly exhibited the adorning of Ag nanoparticles on the surface of the graphene.

Figure 3.
Scanning Electron Microscope image of Pristine PVA (3a), graphene/PVA (3b), Ag/graphene/PVA nanocomposites (3c).

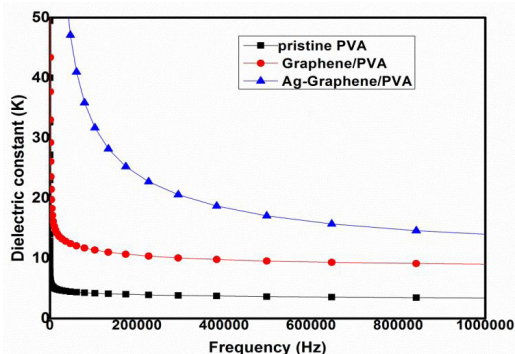


DIELECTRIC CONSTANT

The dielectric constants of pristine PVA, graphene reinforced PVA and AgNPs decorated graphene in PVA composites at 1MHz respectively were studied (Figure

4). As the conducting nature of the polymer matrix increases, the composites displayed the intensification of dielectric constant. For pristine PVA, the dielectric constant is found to be 3.44. After reinforcing graphene, there found the enhancement in the dielectric constant and the value is found to be 8.04.18 The reason is attributed to the interfacial polarization phenomenon due to the presence of graphene in PVA matrix. After decorating with AgNPs in graphene, the dielectric constant of the composites is raised up to 11.69, and the reason is attributed to the entrapment of free charges at the interface of conducting and insulating phase of the composites.¹⁹

Figure 4.
A plot of dielectric constants for Ag/graphene/PVA nanocomposites

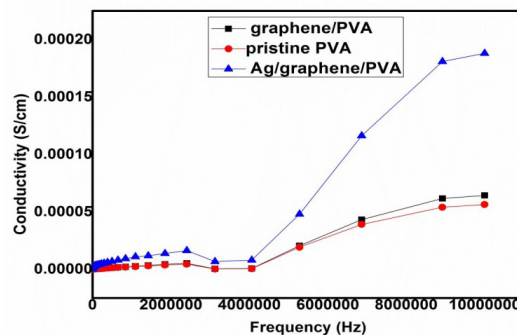


CONDUCTIVITIES

The conductivities of pristine PVA, graphene/PVA, and AgNPs/graphene/PVA composites at 1MHz respectively are depicted in figure 5. The conductivity of pristine PVA is found to be 5.2×10^{-5} cm. On reinforcing graphene, the conductivity of PVA matrix is boosted to 6.39×10^{-5} cm which is ascribed to the conducting path developed in the graphene/PVA composites.²⁰ The interfacial interaction formed at the boundary between rGO and PVA in the composites improved the conductivity. Upon incorporation of AgNPs in graphene, the formation of electrons tunneling between Ag-environment in graphene/PVA composites increased the conductivity to 1.86×10^{-4} cm.²¹⁻²² Rama K.Layeket al²³ reports that the conductivity if graphene/chitosan bio-nanocomposites are found to be 0.13 Sm^{-1} at 1.6 wt %, sulfonated graphene. The enhancement is due to the $-\text{SO}_3\text{H}$ group present in the graphene sheets. But our composites shows the better

conductivity after the incorporation of Ag nanoparticles to $1.86 \times 10^{-4} \text{ S/cm}$ at 1MHz which attributes the conducting nature of metals present in the composites and the better dispersion of Ag/graphene nanohybrids in the polymer matrix.

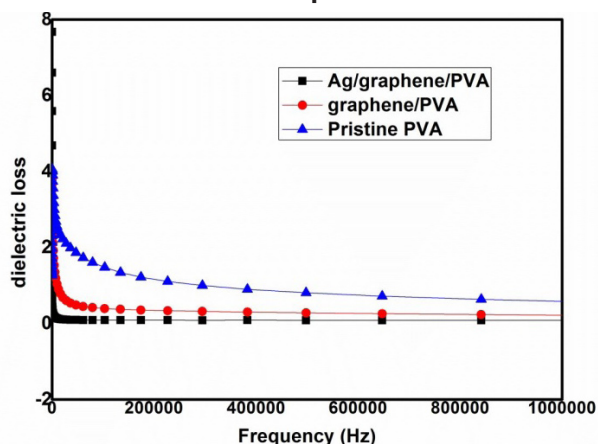
Figure 5.
A plot of electrical conductivity for Ag/graphene/PVA nanocomposites



DIELECTRIC LOSS

The dielectric loss of pristine PVA, graphene/PVA, and AgNPs/graphene/PVA composites at 1MHz respectively are depicted in figure 6. For pristine PVA, the dielectric loss is found to be 0.57. After reinforcing graphene in PVA, the dielectric loss reduced to 0.21 which is accounted for the interfacial polarization concept in the composites. After the incorporation of AgNPs in graphene, the dielectric loss of the composites is found to be 0.88 which is attributed to the space charge migration, direct current (DC) conduction and the movement of molecular dipoles (dipole loss).²⁴⁻²⁶

Figure 6.
A plot of dielectric loss tangent for Ag/graphene/PVA nanocomposites



CONCLUSION

In summary, we have successfully designed, synthesized and studied the electrical properties of a novel polymer-based nanocomposites using Ag/graphene nanohybrids reinforced polyvinyl alcohol matrix. The composite was easily synthesized using simple solvent cast method. The XRD studies evidently disclosed the presence of Ag/graphene in PVA matrix with good compatibility. The scanning electron microscopic analysis demonstrated the loading of Ag nanoparticles on the graphene layers in the composites. The effective dispersion of Ag/graphene nanohybrids in PVA matrix amplified the dielectric behavior of the polymer nanocomposites. The dielectric constant is increased up to 11.89 at 1MHz after the loading of Ag nanoparticles also the conductivity swelled to 1.86×10^{-4} at 1MHz which is certainly attributed to the charge transfer complex between the graphene and PVA by AgNPs loading. The dielectric loss of the composites is lowered to 0.08 at 1MHz. The potential electrical behavior of the processed conducting composites opens up the opportunity for futuristic studies towards its applications in many flexible electronic and electrostatic energy storage devices.

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