

ABSTRACT

In recent years, much research efforts have been devoted to the preparation of polymer composites that show high dielectric constant, low dielectric loss, and excellent flexibility because of their potential application in energy storage devices such as embedded capacitors. In order to enhance the energy storage property of embedded capacitors, some critical properties of dielectric materials such as high dielectric constant, low dielectric loss and good flexibility are eagerly desired. However, the traditional dielectric materials such as organic polymers and inorganic ceramics fail to meet the rigorous requirements of advanced capacitors. Since most of the polymers for dielectric applications have low dielectric constant (<10), the developments of polymer composites with high dielectric constant have attracted ever-increasing attention and have gained remarkable progress.

Graphene oxide (GO) is a carbon-based single atom thick layered material. GO contains various oxygen bearing functional groups such as hydroxyl, carbonyl and epoxy groups on the surface along with the carboxylic groups at the edges. These functional groups make GO highly hydrophilic and therefore easy to disperse in water. The carboxylic and hydroxyl groups of GO gets ionized in water and stable GO colloid is formed due to electrostatic repulsion of negatively charged GO. Because of its diverse functionalities and stable aqueous suspension, GO has been frequently used as a filler for the preparation of polymer composites offering superior thermal, mechanical, electrical and gas barrier properties to the base polymer. However, the properties of GO-based polymer composites strongly depend on the degree of mixing between the two phases, orientation and interfacial interaction between them. The desired properties can be achieved depending on the method of preparation employed. Hence, knowing this rationale, GO was chosen as the primary filler in this work.

The main objective of the present study is to combine the advantage of GO, metal oxide nanoparticles and polymer matrix to obtain composite materials with prominently enhanced dielectric properties for energy storage applications. For this reason, GO was first synthesized from natural graphite powder using modified Hummers method. The synthesized GO powder was incorporated into various polymer matrices such as Hydroxypropyl methylcellulose (HPMC), Polyvinyl alcohol (PVA), water soluble Polypyrrole (WPPy), Polyvinylidene fluoride (PVDF), Poly (4-styrenesulfonic acid) (PSSA) and Polyethylene glycol (PEG) to prepare polymer composites using colloidal processing technique. In addition, various fillers such as Zinc Oxide (ZnO), Titanium dioxide (TiO₂) and Vanadium pentoxide (V₂O₅) were used in combination with GO to form hybrid fillers and incorporated into these polymer matrices to form multiphase polymer composites. The physicochemical properties of these polymer composites were investigated using various analytical techniques such as Fourier transform Infrared Spectroscopy (FTIR), Raman spectroscopy, UV-vis spectroscopy (UV), X-ray diffraction (XRD), Thermogravimetric analysis (TGA), Polarized optical microscopy (POM) and Scanning electron microscopy (SEM). The dielectric properties of all the composites were investigated using an impedance analyzer as a function of frequency and temperature to ascertain their feasibility for energy storage applications.

PNCs comprising of HPMC and PVA as a polymer matrix with a unique combination of GO and ZnO nanoparticles as fillers have been prepared. The structural, thermal, morphological, mechanical, optical and dielectric properties of these nanocomposites were investigated in detail. The FTIR and XRD analysis indicate that GO was completely exfoliated within HPMC/PVA blend matrix leading to the formation of exfoliated nanocomposites. The SEM results revealed the uniform dispersion of GO and ZnO nanoparticles throughout the polymer matrix, indicating the strong interfacial interaction between polymer matrices and nano-fillers. The nanocomposites showed high dielectric constant and low dielectric loss. The increase in dielectric constant of HPMC/PVA/GO/ZnO

nanocomposites is due to increase interfacial polarization between GO/ZnO nano-fillers and the polymer matrix. A high dielectric constant of about 103.51 (50 Hz, 150°C) and low dielectric loss of about 3.14 (50 Hz, 150°C) was obtained for nanocomposites with 2.5 wt % GO and 25 wt % ZnO loadings.

A series of WPPY/PVA/GO composites with different GO loadings (0-3 wt %) were prepared successfully. The synthesized GO shows good compatibility between WPPy and PVA matrix due to the presence of a highly hydrophilic oxygen-containing functional groups of GO. The morphological studies substantiate the homogeneous dispersion of GO into the polymer matrix. The dielectric property investigations revealed that the different wt % of GO loading into polymer matrix plays a significant role in determining the frequency dependence of dielectric composites. The dielectric constant increases as a function of frequency from 27.93 (50 Hz, 150°C) for WPPy/PVA (50/50) blend to 155.18 (50 Hz, 150°C) for composites with 3 wt % GO loading. The dielectric loss increases from 2.01 (50 Hz, 150°C) for WPPy/PVA (50/50) blend to 4.71 (50 Hz, 150°C) for composites with 3 wt % GO loading. Thus, it can be concluded that the improvement in the properties of WPPY/PVA/GO composites can be ascribed to the good dispersion of GO into the polymer matrix and strong interfacial adhesion between them.

Novel three phase PNCs comprising of PVDF as a polymer matrix and TiO₂ nanoparticles and GO as hybrid fillers were successfully developed. The FTIR and XRD results infer strong interfacial interactions and good compatibility between the hybrid fillers and the PVDF matrix. The microscopic observations corroborate homogeneous dispersion and distribution of hybrid fillers within the PVDF matrix. The PVDF/TiO₂/GO nanocomposite films exhibited greater thermal stability than PVDF/TiO₂ (90/10) nanocomposite. The PVDF/TiO₂/GO nanocomposite containing 7 wt % TiO₂ and 3 wt % GO demonstrate good thermal stability up to 400°C. Furthermore, the dielectric properties of PVDF/TiO₂/GO nanocomposite films were significantly improved as compared to PVDF/TiO₂ nanocomposite film. It was observed that the dielectric constant and frequency

are inversely proportional to each other due to interfacial polarization effect. The dielectric constant increases from 18.57 (50 Hz, 150°C) for PVDF/TiO₂ (90/10) nanocomposite film to 165.16 (50 Hz, 150°C) for PVDF/TiO₂/GO nanocomposite film containing 7 wt % TiO₂ and 3 wt % GO loading. The dielectric loss also increases from 1.71(50 Hz, 150°C) for PVDF/TiO₂ (90/10) nanocomposite film to 3.68 (50 Hz, 150°C) for PVDF/TiO₂/GO nanocomposite film containing 7 wt % TiO₂ and 3 wt % GO loading. These intriguing properties of PVDF/TiO₂/GO nanocomposites could shed some light on the incorporation of different types of hybrid fillers in a suitable polymer matrix for the development of novel three-phase nanocomposites as intelligent materials for energy storage applications.

GO reinforced novel polymer composites comprising of PSSA and PVA blend matrix have been developed. The FTIR and Raman spectroscopy analysis indicate the strong interfacial interaction between GO and PSSA/PVA blend matrix. The XRD and SEM analysis confirm that GO was fully exfoliated into individual graphene sheets and dispersed homogeneously within the polymer matrix. In addition, the effective reinforcement of GO in the PSSA/PVA blend matrix has resulted in the enhancement of dielectric constant. The dielectric constant has increased from 82.67 (50 Hz, 150°C) for PSSA/PVA (50/50) blend to 297.91 (50 Hz, 150°C) for PSSA/PVA/GO composites with 3 wt % GO loading. The dielectric loss has increased from 1.56 (50 KHz, 140°C) for PSSA/PVA (50/50) blend to 2.64 (50 KHz, 140°C) for PSSA/PVA/GO composites with 3 wt % GO loading. The improved dielectric performance of PSSA/PVA/GO composites is attributed mainly to the homogeneous dispersion of GO in the polymer matrix and the strong interaction between PSSA, PVA, and GO.

Flexible dielectric composites comprising of PVA, PEG and GO with high dielectric constant and low dielectric loss have been developed. The spectroscopic investigations confirm the presence of GO in the composites. The morphological investigations of PVA/PEG/GO composites films demonstrate the homogeneous distribution of GO within the polymer matrix without any

discernible agglomerations. The thermal stability of composites has improved which could be due to strong hydrogen bonding interaction between functional groups of GO and polymer chains indicating good compatibility between PVA, PEG and GO. The homogeneous dispersion of GO into PVA/PEG blend matrix and the strong interfacial interaction through hydrogen bonding between functional groups of GO and the polymeric chain has resulted in the enhancement of dielectric properties of composites. The dielectric constant for PVA and PVA/PEG (50/50) blend film was found to be 10.71 (50 Hz, 150°C) and 31.22 (50 Hz, 150°C) respectively. The dielectric constant for PVA/PEG/GO composite with 3 wt % GO was found to be 644.39 (50 Hz, 150°C) which is 60 times greater than the dielectric constant of PVA and 20 times greater than that of PVA/PEG (50/50) blend film. The PVA/PEG/GO composites not only show the high dielectric constant but also show low dielectric loss which is highly attractive for practical applications.

Ultra-high-k composite films comprising of PVA as a polymer matrix and V_2O_5 and GO as hybrid fillers have been developed successfully. FTIR studies indicate the strong chemical interaction between V_2O_5 , GO and the polymer matrix. SEM results confirm that GO was homogeneously dispersed within the polymer matrix. The dielectric measurements show that PVA/ V_2O_5 /GO composites exhibit ultra-high dielectric constant and low dielectric loss. The dielectric constant increases from 189.40 (50 Hz, 40°C) for PVA/ V_2O_5 (95/05) composites to 5610.76 (50 Hz, 50°C) for PVA/ V_2O_5 /GO composites with 2.5 wt % GO loading and the dielectric loss increases from 3.76 (50 Hz, 80°C) for PVA/ V_2O_5 (95/05) composites to 9.77 (50 Hz, 150°C) for PVA/ V_2O_5 /GO composites with 2.5 wt % GO loading. The colossal increment in the dielectric constant of the composite can be attributed to Maxwell-Wagner Sillar (MWS) polarization effect and to the homogeneous dispersion of GO and V_2O_5 into the polymer matrix. These flexible PVA/ V_2O_5 /GO composites with such intriguing features are promising materials for energy storage applications.