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Synthesis and Characterization of High-Dielectric-Constant Nanographite–Polyurethane Composite

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In the face of ever-growing demand for capacitors and energy storage devices, development of high-dielectric-constant materials is of paramount importance. Among various dielectric materials available, polymer dielectrics are preferred for their good processability. We report herein synthesis and characterization of nanographite–polyurethane composite with high dielectric constant. Nanographite showed good dispersibility in the polyurethane matrix. The thermosetting nature of polyurethane gives the composite the ability to withstand higher temperature without melting. The resultant composite was studied for its dielectric constant (ε) as a function of frequency. The composite exhibited logarithmic variation of ε from ~ 3000 at 100 Hz to ~ 225 at 60 kHz. The material also exhibited stable dissipation factor ($\tan\delta$) across the applied frequencies, suggesting its ability to resist current leakage.

INTRODUCTION

High-dielectric-constant materials are often required for use in various applications such as capacitors, energy storage devices, and pulsed power systems.[1,2] Polymer nanocomposites have garnered widespread attention among the materials research community owing to their processability and ability to be molded into various shapes with superior mechanical and thermal properties.[3] There are two widely applied routes to fabricate high-dielectric-constant materials, viz. the traditional approach based on addition of high-dielectric-constant ceramic filler to a polymer matrix[1,3–5] and another based on fabrication of a percolative system by incorporation of conductive fillers such as carbon black, carbon nanotubes, graphene, conductive fibers, or metal particles into a polymer matrix.[6–10] The latter route is preferred owing to its low filler content compared with ceramic–polymer composites.[11] Additionally, there are reports of all-polymeric[12–14] or macromolecular system-based[2] percolative materials with high dielectric constant. Percolative systems can be analyzed based on the theory of percolation, with the percolation threshold representing the critical volume fraction of conducting filler below which the conductivity of the composite decreases by several orders of magnitude.[15] It is observed that polymeric composites exhibit very high dielectric constant when the concentration of the conductive filler reaches the percolation threshold. This is attributed to Maxwell–Wagner interfacial polarization in heterogeneous composite systems.[16]

Carbon-based fillers are materials of choice for inclusion in such high-dielectric-constant percolative systems. It has been reported that composites formed from multiwalled carbon nanotubes and polyvinylidene fluoride exhibit dielectric constant (ε) of 300 with low percolation threshold of 1.61% (0.0161 volume fraction).[7] Meanwhile, the composite of graphene and polyvinylidene fluoride exhibited an ε value of 100 at the percolation threshold of 0.61%, whereas functionalization with polyvinyl alcohol resulted in ε of 225 at the percolation threshold of 2.24%.[11] Graphene encapsulated with polystyrene has also been reported to exhibit an ε value of 10.3 at the percolation threshold of 4.0%. Among carbon-based fillers, nanographite (NGP) has been reported to cause a remarkable improvement in ε at lower frequencies while retaining the ε value of ~ 300 in the high-frequency region. A composite formed from nanographite (NGP) and polystyrene showed ε of ~ 12 at low frequency at the percolation threshold of 1.1%.[17] When combined with polyvinyl chloride, NGP exhibited ε of 1000 at low frequency, which reduced to ~ 12 at high frequency at the percolation threshold of 0.4.[18] However, the polymers used in such composites are relatively unstable at high temperature owing to their thermoplastic nature. We report herein a polyurethane (PU)-based NGP composite as a high-dielectric-constant material. PU is a class of thermosetting polymer with high mechanical strength, making it highly efficient even for operation at relatively high temperature without loss of its material properties. Additionally, composites formed from carbon nanotubes and PU have been reported to exhibit electromagnetic wave absorption,[19] reflecting the ability of these materials to form a polarizable composite with NGP filler. Hence, the properties of this high-dielectric-constant material were explored in this work.

EXPERIMENTAL PROCEDURES

Synthesis of Nanographite

NGP was synthesized from natural flaked graphite (Sigma Aldrich) using a microwave exfoliation method.[20] In a typical procedure, natural flaked graphite was suspended in a mixture of concentrated sulfuric acid and nitric acid (4:1, v/v) at room temperature and stirred continuously for 16 h. The material thus obtained is called graphite intercalated compound (GIC). GIC was neutralized with water then vacuum filtered followed by drying at 100°C to remove the remaining moisture. GIC was then expanded by exposure to instant thermal shock in a microwave oven at 800 W for 20 s to obtain exfoliated graphite (EG). EG was immersed in 70% aq. solution of methanol, followed by sonication in an ultrasonic bath for 8 h to yield NGP.

Synthesis of Nanographite–Polyurethane Composite

All chemicals were procured from Alfa Aesar. Synthesis of PU followed reported literature[21] with addition of NGP before emulsification to obtain NGP–PU composite by in situ polymerization. Polypropylene glycol (MW = 2000) ethylenediamine anhydrous (EDA), triethylamine (TEA), dibutyltin dilaurate, and dimethylolpropionic acid (DMPA) were dried at 120°C in vacuum for 24 h. Polyether with terminal isocyanate (OCN–R–NCO) was prepared by reacting slight excess of isophorone diisocyanate (IPDI) with polypropylene glycol. As-obtained polyether (20.0 g) was heated to 120°C for 4 h then brought to 80°C, at which temperature eight drops of catalyst dibutyltin dilaurate and 6.2 g IPDI were added. The mixture was allowed to react for 2 h, after which 1.09 g DMPA [dissolved in minimum amount of *N*,*N*-dimethylformamide (DMF)] was added and the reaction was continued. After 4 h, the required amount of NGP (0–8 wt.%) was added. This reaction was allowed to proceed further for 10 h. The mixture was brought to room temperature and neutralized using TEA. A homogenous dispersion was formed by adding distilled water and EDA, which acts as a chain extender. The film that formed immediately on a glass slide from that dispersion was allowed to dry at ambient temperature for over a week.

Characterization

NGP was characterized by x-ray diffraction (XRD) analysis using a Rigaku Mini Flex x-ray diffractometer with Cu K_α radiation (λ = 0.154 nm) operated at 40 kV and 40 mA in the 2θ range of 20°–80°. Scanning electron microscopy (SEM) of the composite was carried out using a JEOL JSM 6380 I. The Fourier-transform infrared (FTIR) spectrum of the NGP–PU composite was obtained using a Bruker FTIR spectrometer with Eco-ATR accessory. Conductivity measurements were carried out using a Keithley 2400 source meter. Dielectric measurements on the composite sample were performed by forming a parallel-plate capacitor with composite film sandwiched between two Cu electrodes using impedance analysis at variable frequency using a CH604E electrochemical workstation (CH Instruments, USA).

RESULTS AND DISCUSSION

The XRD pattern of NGP is shown in Fig. 1a, showing characteristic (002) peak at 26.5° and (004) peak at 54.5°, which correspond to the graphitic crystal lattice. The peak at 11.5° may be ascribed to graphitic oxide formed as a byproduct of acid intercalation. The overall peak broadening as compared with the XRD pattern of graphite (Fig. 1a, inset) suggests loss of the highly ordered crystalline staking of sp^2-hybridized carbons in NGP. This loss of crystallinity and introduction of oxide functionality results in the improved dispersibility of the NGP in the polymer matrix, while the retained graphitic crystallinity makes the filler conductive, as required to form a percolative dielectric system. The polyurethanes exhibit two peaks corresponding to 2θ values of 11° and 19° with very low intensity.[22] Therefore, the presence of NGP, which exhibits peaks in the same region, greatly masks the peaks of polyurethanes in the XRD spectrum. However, intercalation of NGP with polyurethane segments can be visualized from the apparent broadening and occurrence of an additional hump at 22.5°. Figure 1b presents scanning electron micrographs of NGP–PU composite, obtained from the unpolished surface of the composite (inset) and the fractured cross-section of the film. The surface of the composite was observed to be smooth with the presence of a small amount of granular protrusions due to agglomerated filler. The morphology of the fractured surface was layered, which is attributed to the homogenous dispersion of NGP in the PU matrix.

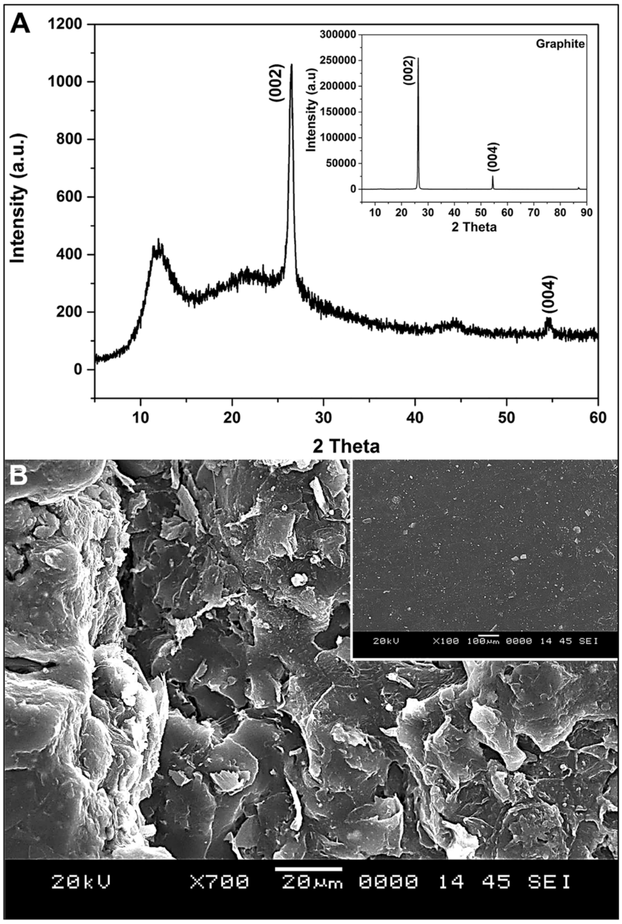

Fig. 1. (a) X-ray diffraction pattern of NGP–PU composite and graphite (inset). (b) Scanning electron micrograph of fractured NGP–PU composite and NGP-PU composite surface (inset).

The FTIR spectrum of the NGP–PU composite is shown in Fig. 2. The IR spectrum of NGP–PU film was recorded from 4000 cm^{-1} to 600 cm^{-1}. Characteristic bands at 3389 cm^{-1} and 1695 cm^{-1} correspond to hydroxyl and carbonyl groups. The bands observed between 2966 cm^{-1} and 2869 cm^{-1} are due to symmetric and asymmetric stretching of C–H bond with the carbonyl group. The peaks observed between 1651 cm^{-1} and 1457 cm^{-1} are typical of stretching and bending of C=O and N–H bonds. Other peaks at lower wavenumber are due to asymmetric stretching and bending of C–C bonds in different electronic environments of bonded heteroatoms such as O and N. The absence of peaks in the region from 2500 cm^{-1} to 2000 cm^{-1} indicates the complete polymerization and absence of any isocyanates group held by the prepolymers.[22] The fairly high transmission observed for the composite is attributed to the presence in the polymer matrix of NGP, which has no IR signature of its own.

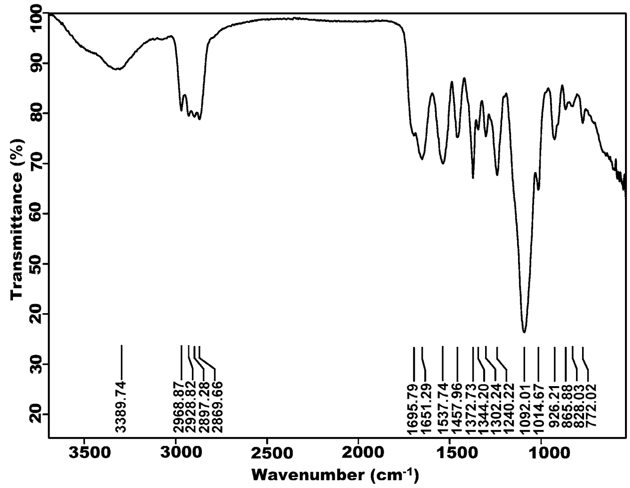

Fig. 2. FTIR spectrum of NGP–PU composite.

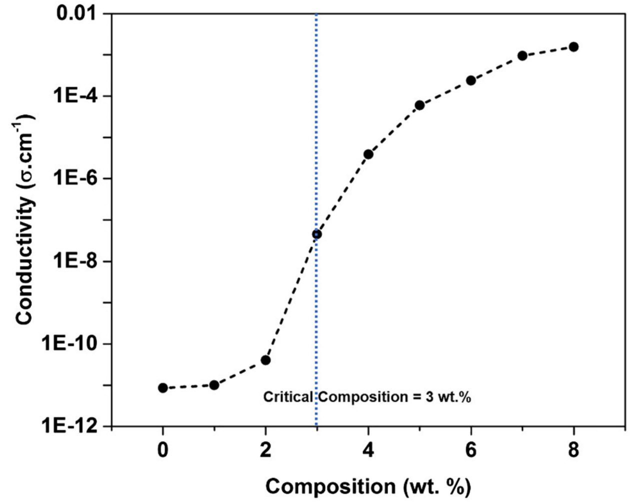

Fig. 3. Variation in conductivity of NGP–PU composites with different filler contents.

The conductivity of NGP–PU composites with different contents of NGP was measured to determine the percolation threshold (φ_c) of NGP in PU (Fig. 3). The results showed that the conductivity of the composite film increased suddenly near 3 wt.% and stabilized after 5 wt.%. Therefore, the φ_c value obtained from this graph corresponds to the 3 wt.% NGP composition. This film was further used to study the dielectric properties of the NGP–PU composite.

The dielectric constant of the film was determined at various frequencies to evaluate the dielectric behavior of the NGP–PU composite under the effect of an alternating current field. The dielectric constant of the material was calculated using Eq. 1.

$$\varepsilon = \frac{l}{2\pi f \cdot \varepsilon_0 Z A} \tag{1}$$

where l is the thickness of the film, A is the area of the film, and Z is the impedance measured at frequency f.

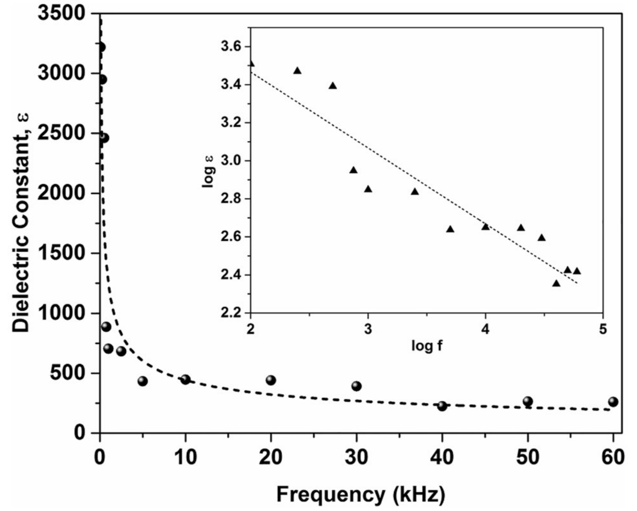

Fig. 4. Variation of dielectric constant (ε) as function of frequency (*f*) (inset: log ε versus log *f* at percolation threshold) for NGP–PU composite.

Dielectric measurements were carried out on the NGP–PU composite in the frequency range from 100 Hz to 60 kHz (Fig. 4). Great enhancement in ε was obtained at lower frequencies, while retaining suitably high ε at the higher frequencies. At 100 Hz, the value of the dielectric constant was ~ 3000, whereas at 60 kHz it was found to be ~ 225, representing a significant improvement over pure PU ($\sim$ 08). Great enhancement in ε around the percolation threshold is generally observed,[17] which is why this composite with filler content equal to φ_c exhibited such a high value of ε. Additionally, such high values of ε, in the vicinity of φ_c, can be attributed to Maxwell–Wagner interfacial polarization in heterogeneous composite systems.[16] Because of the interfacial polarization, large local fields are generated within the composite, which results in the high value of ε for the critical composition of NGP. The reason behind the exceptionally large ε at low frequencies is probably due to the fact that the polarization of the dipoles can follow the change in the applied electric field, which is possible only at lower frequencies. Additionally, ε is dependent on the applied frequency, which is predicted by percolation theory as per Eq. 2.[23]

$$\varepsilon(f, \varphi_c) = f^{-v} \qquad (2)$$

A log–log plot of Eq. 1 is shown as an inset of Fig. 4. The value of v, as estimated from the slope of the line, was found to be 0.3. This agrees with reported values for such systems.[17,23]

As the dielectric properties of a polymer composite are a function of the permittivity and conductivity of the polymer and the relative concentrations of the conducting and insulating phases, the dissipation factor (tan δ) plays an important role in understanding the dielectric loss of the material at different applied frequencies of the input current. The complex dielectric constant is defined by Eq. 3.

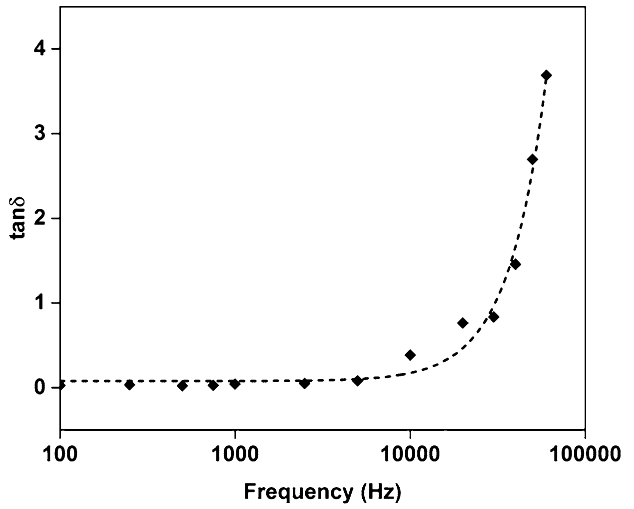

Fig. 5. Variation in dissipation factor with frequency of applied AC field.

$$\varepsilon = \varepsilon' - j\varepsilon'' \qquad (3)$$

The real part ε' is usually called the relative permittivity or dielectric constant, while the imaginary part ε'' is generally referred to as the loss factor. The dissipation factor tan δ is expressed as the ratio of ε' to ε'' as per Eq. 4.

$$\tan\delta = \frac{\varepsilon'}{\varepsilon''} \qquad (4)$$

where angle δ is the loss angle.

The variation of tan δ with respect to frequency is shown in Fig. 5. As observed, the composite exhibited a steady tan δ up to $\sim$ 10 kHz. On approaching frequencies above 10 kHz, the dissipation factor increased, which results in the dielectric loss of the system. This is an expected trend, as at high frequencies, the dielectric property of the material reduces due to heat loss caused by fast inversion of the polarization as the polarity of the applied AC field changes. This is in agreement with the reduction of ε as the AC frequency is increased. However, the increase in tan δ is low in magnitude. This factor contributes to the retention of the ε value of $\sim$ 225 for the NGP–PU composite in the high-frequency region.

Therefore, the NGP–PU composite with 3 wt.% NGP showed good dielectric properties with high ε and low tan δ variation across the applied frequency range of the AC field. Furthermore, desired enhancement in the dielectric constant of PU was obtained without any chemical modification but on the basis of percolation theory. However, as one moves towards higher wt.% of NGP in the PU matrix, the conductivity of the system increases, which renders the material unsuitable for use in dielectric applications. It is well understood that conductive filler in an insulating material exhibits the highest dielectric property just below the percolation threshold.[17] Therefore, 3 wt.% NGP content in the NGP–PU was found to be most suitable in this work.

CONCLUSION

Nanographite (NGP)–polyurethane (PU) composites with different NGP contents were fabricated. The composite exhibited good dielectric properties based on percolation theory. The percolation threshold of the NGP–PU composite corresponded to 3 wt.% NGP content. The NGP–PU composite showed exceptional dielectric constant of $\sim$ 3000 at low frequency and $\sim$ 225 under high-frequency AC field, representing a significant improvement over the dielectric constant of polyurethane. The composite also exhibited relatively low dielectric loss with increasing frequency. These properties of the NGP–PU composites make them suitable for use in various applications where material with high dielectric constant is required.

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