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Dual responses of magnetite-graphene hybrid in polyurethane under magnetic and electric stimuli

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ABSTRACT

Dual responsive material composed of magnetite nanoparticle (MNP) and graphene nanosheet (GP) as a hybrid filler and polyurethane (PU) as an electrostrictive matrix was fabricated. The hybrid filler was synthesized by the in-situ growth of MNP on the GP surface. The obtained hybrid particles behaved simultaneously as a superparamagnetic and conducting material. The hybrid-composites possessed electronic polarization and high response towards electric field, as they showed excellent recoverability and fast response during the temporal test under electric field. The highest storage modulus sensitivity was obtained from the 0.5%v/v MNP-GP/PU at the value of 3.97 under the applied electric field of 2 kV/mm. In the deflection experiment, the 0.5%v/v MNP-GP/PU composite exhibited the largest bending distance of 13.65 mm under the electric field of 500 V/mm. On the other hand, the 3.0%v/v MNP-GP/PU yielded the maximum bending of 15.35 mm under the magnetic field of 1650 G.

1. Introduction

Stimuli-responsive substances have recently been of interest in various applications such as actuator and sensor. Electro- and magneto- active elastomers are elastomeric matrices which have the ability to react simultaneously to both external electric and magnetic stimuli and yield physical or mechanical responses [1,2]. When an external stimulus is applied to the material, its volume and internal stress are modified due to the interactions between the stimulus, the structures, and ingredients within the specimen. Specifically, this phenomenon generates mechanical feedbacks; for examples, stress, strain, and bending [3–6]. The typical requirements of an appropriate stimuli-responsive matrix are flexibility and recoverability to fulfill functionality. Electroactive polymers (EAPs) have gained attentions in actuator applications due to their flexibility, mechanical strength, energy consumption, large actuation stroke, and electromechanical coupling [7,8]. Polyurethane (PU) is an emerging polymer in the EAPs class which has a shape varying capability [9,10]. Deka et al. reported that the hyperbranched polyurethane showed a capability to recovery its shape by 93% within 30 s after the release of stress at 60 °C [11]. Moreover, PU exhibited a better strain response (8.3%) and a lower Young's modulus (32 MPa) when compared with other dielectric polymers as shown by Racherla (2011) [12]. The basic functionality of many actively moving polymers can be achieved by designing and implementing the sensitive and active junctions on the structure to behave as a multifunctional smart material system (MSMS) [13].

Recently, magnetic nanoparticles have received considerable attention due to their low toxicity, low cost, and with alterable magnetic and electric properties [14]. They have been widely used as a carrier in transdermal drug delivery [15], a separator in microfluid [16], a microstructure in actuator device [17], and a thin film in supercapacitor [18]. One of the most well-known magnetic particles is magnetite (Fe_3O_4), it has been classified as a superparamagnetic material with high saturation magnetization value [19]. Not only of its magnetic properties, magnetite also exhibits good electrical conductivity, compared with the other iron oxides, which is achieved by electron hopping inside the cubic spinel structure between ferric ions and ferrous ions [20]. For example, the adding of 1.0%v/v magnetite nanoparticles into the matrix possessed 67% storage modulus sensitivity increasing under applied electric field of 2 kV/mm when compared with pristine matrix [21]. However, the electronic conductivity of pure magnetite is still not sufficiently high for electrically induced mechanical response applications.

The unique features of graphene such as optical, electrical, and mechanical properties have been of interest by many works recently. Graphene is a one-atom-thick two dimensional carbon system providing the electrical conductivity more than 10^3 S/m [22]. Zhang et al. have demonstrated an enhancement in electrical

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conductivity of polyethylene terephthalate (PET) in the presence of graphene nanosheet in which the conductivity was raised up to 2.11 S/m from 10^{-14} S/m for the PET with 3.0%v/v of graphene embedded [23]. Thus, the combination of magnetite and graphene can be expected create a new functional hybrid material having the advantages of each constituent.

In this work, the hybrid filler material, consisting of synthesized magnetite nanoparticle (MNP) and graphene nanosheet (GP), was fabricated and dispersed into a PU matrix to create a hybrid nanocomposite with a multifunctional capability. This work describes the magnetic and electrical actuation responses of the nanocomposite in terms of the storage modulus sensitivity and bending behavior. The hybrid nanocomposite results are compared with the PU composites with individual pristine MNP and pristine GP.

2. Materials and methods

2.1. Materials

Magnetite nanoparticle was synthesized by using ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, Sigma–Aldrich), ferric chloride anhydrous ($FeCl_3$, Ajax Finechem), and ammonium hydroxide (NH_4OH, Merck) as the precursors. Graphene nanosheet (platelet thickness 6–8 nm; platelet size 15 μm; carbon content >99.5%) was purchased from XG® Sciences and used without further purification. Polyurethane (PU) from Behn Meyer Chemicals (T) Co., Ltd. was used as the matrix to fabricate the multifunctional composite films. Polydimethylsiloxane (PDMS, Sigma–Aldrich) with the viscosity of 100 cSt was used as a medium in the bending experiment.

2.2. Synthesis of hybrid material

The hybrid material was synthesized via the *in-situ* growth of MNP onto the GP surface. The MNP was prepared by the chemical co-precipitation method of $FeCl_2{\cdot}4H_2O$ and $FeCl_3$ with a fixed mole ratio of $FeCl_2{\cdot}4H_2O$ and $FeCl_3$ of 2:1, in the presence of GP in the three-neck-round bottom flask at 0 °C [24]. The hybrid material was obtained by fixing the mole ratio of $FeCl_3$ to GP at 2:1. In the first step, GP was dispersed in 50 mL distillated water and sonicated for 30 min. Both $FeCl_2{\cdot}4H_2O$ and $FeCl_3$ were dissolved in 50 mL distillated water and then poured into the GP solution with vigorous stirring under nitrogen gas atmosphere for 60 min. NH_4OH as a precipitating agent was added into the mixture and continuously stirred for 30 min. The resultant product called hybrid material (MNP-GP) was filtrated and washed with distilled water before dried in a vacuum oven at 80 °C for 1 day.

2.3. Preparation of hybrid nanocomposite

A Brabender internal mixer (Bremen, Plastograph) was used to blend the hybrid material and PU at various hybrid material concentrations of 0.01, 0.1, 0.5, 1.0, and 3.0%v/v and also to produce PU composite films with 1.0%v/v of pristine MNP and 1.0%v/v of pristine GP. The processing was carried out at 220 °C for 5 min. To shape the specimens to be 1 mm thick, the compression molding machine (Wabash, Model 9354) was operated at a pressure of 15 tons and a temperature of 225 °C for 10 min.

2.4. Characterizations and testing

2.4.1. Characterizations of hybrid material

Chemical structures of MNP, GP, and the hybrid material were characterized by a FT-IR spectrometer (Thermo Nicolet, Nexus 670) in a wavenumber range of 4000–400 cm^{-1}. The absorbance intensity was collected by using a 32 scans and a deuterated triglycine sulfate as a detector.

Crystal structures of MNP, GP, and the hybrid material were classified by a wide angle X-ray diffractometer (XRD, Bruker AXS, D8 Advance) with 40 kV/30 mA of CuK-alpha radiation source. The diffraction was carried out in the 2θ range of 10°–80° with a scan speed of 1 °/min.

Electrical conductivity of hybrid material was determined by a conductivity meter (Keithley, Model 8009) connected to a power source (Keithley, Model 6517A). Voltage (V) was directly applied to the specimen and the resultant current (I) was continuously monitored. The electrical conductivity was calculated via the following equation:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{I}{K \times V \times t} \quad (1)$$

where σ is the electrical conductivity (S/cm), ρ is the specific resistivity (Ω.cm), R_s is the resistance (Ω), t is the specimen thickness (cm), and K is the geometric correction factor (2.14×10^{-2}) for the test fixture, it was calibrated by using the standard silicon wafer with the specific resistance of 107.373 Ω under the linear Ohmic regime.

Magnetic properties namely magnetization and coercivity were evaluated by a vibrating sample magnetometer (VSM, LakeShore, Model 7404). External magnetic field of ±10,000 G was operated with 80 points/loop and a scan speed of 10 s/point.

2.4.2. Electromechanical and bending measurements

The electromechanical performance was evaluated by a melt rheometer (Rheometric Scientific, ARES) in the oscillatory shear mode connected to a DC voltage supply (Instek, GFG 8216A). The strain sweep was first tested to determine the linear viscoelastic regime and the suitable strain was chosen for measuring storage modulus (G′). The frequency sweep and temporal response were carried out at the appropriate strain (0.02%) as the function of electric field strength (0–2 kV/mm) at a fixed temperature of 300 K.

The dielectrophoresis force (F_d) and magnetophoresis force (F_m) were evaluated by monitoring the deflection response under applied electric field (0–500 V/mm) and magnetic field (0–1650 G), respectively. The specimen was fixed at one end and the other free end was subjected to the fields and the bending characteristics were determined. The bending distance of the specimens was measured by using a Scion Image program (Beta 4.0.3). F_d, in a silicone oil (viscosity of 100 cSt) chamber, was calculated from the static force balance, using the following equation (Eq. (2)), consisting of the elastic term, the gravity term, and the buoyancy term [25]:

$$F_d \approx F_e + mg(\tan\theta) - \rho v g(\tan\theta) \quad (2)$$

where F_e is the elastic force calculated from non-linear deflection theory, m is the mass of the specimen, g is the gravity (9.8 m/s^2), θ is the deflection angle, ρ is the density of the fluid (Silicon oil = 0.97 g/cm^3), and v is the volume of the displaced of fluid.

For the magnetic response, the F_m in air was estimated through the classical beam theory, according to Farshad [26], as shown in Eq. (3):

$$F_m = 2Ei\Delta/L^3 \quad (3)$$

where E is the elastic modulus, i is the cross sectional second moment, Δ is the deflection, and L is the length of the specimen. The applied magnetic field was calculated via the gap distance between the specimen free end and the magnet tip with the initial gap of