Materials Science and Engineering C 61 (2016) 312–323

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Magneto-electro-responsive material based on magnetite nanoparticles/polyurethane composites

Karat Petcharoen, Anuvat Sirivat *

Conductive and Electroactive Polymers Research Unit, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand

ARTICLE INFO

Article history:
Received 12 September 2015
Received in revised form 28 November 2015
Accepted 10 December 2015
Available online 12 December 2015

Keywords:
Smart material
Polyurethane
Magnetite nanoparticles
Magneto-electro-responsive material
Flexible actuator

ABSTRACT

Multi-functional materials in actuator applications have been developed toward reversibility and sensitivity under various actuating fields. In this work, magneto-electro-responsive materials consisting of a polyurethane (PU) matrix and its composites embedded with magnetite nanoparticles (MNP) as a dispersed phase were fabricated to tailor the electromechanical properties and bending performance under electric, magnetic, and electromagnetic fields. Due to the superior characteristics of MNP over other magnetic materials, the composites fabricated with electronic polarization were highly responsive under electric field. The highest storage modulus sensitivity belonged to the 1.0% v/v MNP/PU composite which possessed the value of 3.46 at the electric field 2 kV mm^{-1}. Moreover, all of the PU composites behaved as an electrostrictive material in which the stress depended quadratically on the electric field. It was demonstrated that the PU composites also possessed very good recoverability, fast response (<15 s) and large bending angle relative to that of pristine PU under applied electric field. Interestingly, the steady state storage modulus response was attained within the first electrical actuation cycle and the PU composite was a fully reversible material. In addition, it was shown that superparamagnetism was a common characteristic of all fabricated composites under magnetic field. The 3.0%*v*/*v* MNP/PU composite provided the largest bending distance up to 23.60 mm, and 14.10 mm under the magnetic field of 5000 G, and the electromagnetic field of 320 G, respectively. In summary, the MNP/PU composite material is a potential candidate to be used as a smart material under the influences of electric and/or magnetic fields over other existing dielectric materials.

1. Introduction

Smart materials are being developed for engineering applications such as small actuators, robots, micro valves, artificial muscles, and sensor systems. Many studies have utilized certain functional polymers that are able to react with a particular stimulus, such as thermal, light, chemical, electrical, and/or magnetic actuation; they are called the stimuli-responsive polymer [1–6]. A smart material system is supposed to have multiple functions through the additions of appropriate components to attain specific properties, also known as multifunctional smart material systems (MSMS) [7].

An electroactive polymer (EAP) is one of the electro-responsive materials that can deform under external electric field [8]. The most widely used EAP is polyurethane (PU) due to its flexibility, mechanical performance, speed of response, ease of processing, and capability of recovering upon temperature and external electric field stimuli [9-11]. In addition, PU has also received considerable attention in various human uses such as biosensors, skin bioengineering, tissue engineering, and implantable artificial pancreas due to its biocompatibility and durability [12–15]. The combination of filler within PU matrix creates a unique property and enables some attractive performances. Sahoo et al. (2005) prepared polypyrrole filled with PU as a shape memory composite and they found that the composite containing 20 wt.% of polypyrrole showed good electrical conductivity (10^{-2} S cm^{-1}) and had the best shape memory performance at applied electric field of 20 V mm^{-1} compared with neat PU [16]. Meng et al. (2008) reported that at multi-walled carbon nanotube content below 2 wt.% embedded in PU, the composited attained good shape recoverability at 100% strain and at 70 °C [17]. Therefore, adding appropriate filler is a promising method to promote specific functional behaviors of a EAP matrix.

A simple way to effectively improve both electrical and magnetic properties is the incorporation of magnetic particles [18–20]. The magnetite particles (Fe_3O_4) have attracted much interest as a material for drug targeting [21], ultra-filtration membranes [22], and sensor systems [23] due to their good biocompatibility, low toxicity, high saturation magnetization, and easy preparation. Therefore, magnetite can be used to provide the desired electrical and magnetic properties that are superior to other fillers.

From the point of view, the aim of the smart material lies in tailoring-design responsive materials with appropriated characteristics such as response time, storage modulus sensitivity, recoverability.

* Corresponding author.
E-mail address: anuvat.s@chula.ac.th (A. Sirivat).

http://dx.doi.org/10.1016/j.msec.2015.12.014
0928-4931/

Herein, we fabricated a new type of electro-responsive and magneto-responsive material based on polyurethane as the matrix and magnetite as the nano-sized filler in order to evaluate the response of the material under electrical and magnetic stimuli.

2. Materials and methods

2.1. Materials

Poly(ester-urethane) (PU); Behnmeyer LPR®4525, consisted of butanediol as the chain extender, diphenylmethane diisocyanate as the hard segment, and adipate ester as the soft segment, was used as the EAP matrix. For the synthesis of magnetite nanoparticles (MNP), ferric chloride anhydrous (Ajax Finechem, AR grade) and ferrous chloride tetrahydrate (Sigma–Aldrich, AR grade) were used as the precursors. Ammonium hydroxide (Merck, AR grade) acted as the precipitating agent and ethanol (Lab-Scan, AR grade) was used to remove the excess synthesizing agents.

2.2. Fabrication of MNP/PU composites

The MNP were synthesized via the chemical co-precipitation method at 0 °C in order to obtain an average particle size of 10 nm as shown in Fig. 1, following the procedure from the previous work [24]. 1.5 g of $FeCl_2 \cdot 4H_2O$ and 3.0 g of $FeCl_3$ were dissolved in 100 ml of deionized water under nitrogen atmosphere with vigorous stirring at 0 °C. Then, NH_4OH 10 ml was slowly dropped into the yellow solution in order to precipitate the black MNP and continuously stirred for 30 min. The product was filtrated and thoroughly washed with deionized water and ethanol. Finally, the MNP was dried in vacuum oven at 80 °C for 24 h.

The composites between MNP filler and PU matrix, with various MNP concentrations of 0.01, 0.1, 0.5, 1.0, and 3.0% v/v, were fabricated using a Brabender internal mixer (Bremen, Plastograph) at 220 °C for 5 min. Then, a compression molding machine (Wabash, Model 9354) was used to obtain 1 mm thick composites at 225 °C for 10 min, under a pressure of 15 tons.

2.3. Characterization and testing

A scanning electron microscope (Hitachi, S4800) was used to examine the morphological structure of the synthesized MNP. The SEM images were obtained by using the acceleration voltage of 10 kV with a magnification in the range 100 kX.

A Wide angle X-ray diffractometer (Bruker AXS, D8 Advance) was used to study the crystalline structure of the magnetite, polyurethane and the composite. The CuK-alpha radiation source was operated at 40 kV/30 mA. Divergence slit and scattering slit 0.5 deg. together with 0.3 mm of receiving slit were used. It was operated with a scan speed of 1 deg./min and a scan step of 0.02 deg.

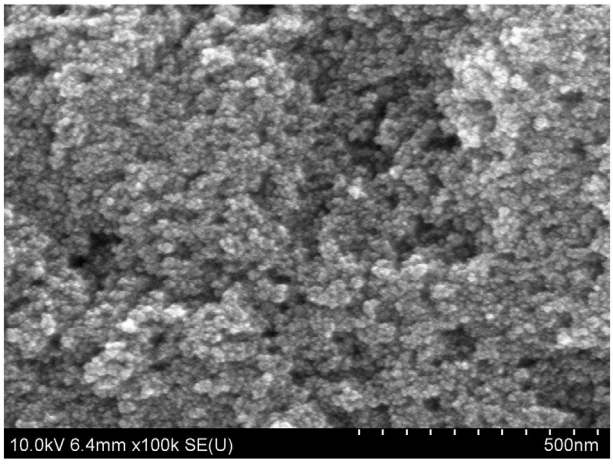

Fig. 1. SEM image of synthesized MNP.

A vibrating sample magnetometer (LakeShore, model 7404) was used to inspect the magnetization of the composites. It was operated under magnetic field strength of ±10,000 G with 80 points/loop and a scan speed 10 s/point.

A custom-built two-point probe was connected to a conductivity meter (Keithley, Model 8009) and a power source (Keithley, Model 6517A) for supplying the voltage and monitoring the resultant current. Electrical conductivity was calculated by using applied voltage (V) and the actual current (I), as in the following equation:

$$\sigma = \frac{I}{KVt} \tag{1}$$

where σ is the specific conductivity ($S\ cm^{-1}$), K is the geometric correction factor (2.14×10^{-2}), and t is the thickness of each specimen (cm).

An LCR meter (HP, model 4284A) was used to determine the dielectric constant, which was carried out by applying AC voltage of 10 V at 300 K. The sample films were coated with a silver paint before measurement.

A rheometer (Rheometric Scientific, ARES) was used to study the rheological behavior and the viscoelastic properties of samples. The thin film specimen was placed between parallel plates fixture with a diameter of 25 mm. A DC power supply (Instek, GFG8216A) was connected to the rheometer to deliver the electric field across the specimen. The oscillatory shear strain was applied and the dynamic storage modulus (G') was measured under the effect of electric field strength at the temperature of 27 °C. First, a strain sweep test was run to measure G' as a function of strain to determine the linear viscoelastic regime of the sample and a suitable strain within the linear regime was chosen. Then, the temporal sweep test was run to measure G' as a function of time, and the frequency sweep test was run to measure G' as a function of frequency at various electric field strengths (0–2 $kV\ mm^{-1}$). The G' is directly related to the rigidity or stiffness of specimen due to the polarization under electric field.

The dielectrophoresis force (F_d), magnetophoresis force (F_m), and electro-magneto-phoresis force (F_{EM}) were evaluated by monitoring the deflection responses under applied electric field (0–500 $V\ mm^{-1}$), magnetic field (0–5000 G), and electromagnetic field (0–320 G), respectively. The deflection apparatus was custom-built. The specimen was fixed at the top end and the other free end was subjected to the fields and the bending characteristics were determined. Each force (F_d, F_m, F_{EM}) is a distributed force acting throughout the specimen; it can be replaced by a single equivalent force at the position which produces the same moment. The bending angle and distance of the specimens were taken by using a Scion Image program (Beta 4.0.3). F_d was calculated from the horizontal static force balance, using the following equation (Eq. 2), consisting of the resisting elastic term, the gravity term, and the buoyancy term [25]:

$$F_d \approx F_e + mg(\tan\theta) - \rho Vg(\tan\theta) \tag{2}$$

where F_e is the elastic force, 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 fluid. The elastic force of the films was calculated through the non-linear deflection theory which was obtained from the standard curve between $(F_e l_0^2)/(EI)$ and d/l_0; where F_e is the elastic force, l_0 is the initial length of specimens, I is the second area moment, d is the deflection distance in the horizontal axis, and E is the Young's modulus which is equal to $2G'(1 + \nu)$; where G' is the shear storage modulus taken to be $G'(\omega = 1\ rad\ s^{-1})$ at various electric field strengths, and ν is the Poisson's ratio (0.5 for an incompressible sample).