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Fabrication, characterization and microwave properties of polyurethane nanocomposites reinforced with iron oxide and barium titanate nanoparticles

Z. Guo [a,*], S.-E. Lee [a], H. Kim [a], S. Park [a], H.T. Hahn [a], A.B. Karki [b], D.P. Young [b]

[a] Mechanical & Aerospace Engineering and Materials Science & Engineering Department, University of California-Los Angeles, Los Angeles, CA 90095, USA
[b] Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70803, USA

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Abstract

Polyurethane (PU) nanocomposites reinforced with magnetic iron oxide nanoparticles and/or dielectric barium titanate nanoparticles fabricated by the surface-initiated-polymerization approach were investigated. The polymer matrix incorporated with different nanoparticles shows different presenting status surrounding the nanoparticles, i.e., chemical bonding, physical entanglement and bulk polymer chain. The nanoparticles have a different effect on the thermal stability of the polymer nanocomposites. By embedding different functional nanoparticles, unique physical properties were observed, such as enlarged coercivity and larger dielectric constant (real permittivity). The synergistic effect of the binary nanoparticle reinforced PU nanocomposite was explored. The addition of the iron oxide nanoparticles does have some effect on the permittivity. However, little difference was observed in the magnetic properties and permeability after the introduction of the dielectric barium titanate nanoparticle into Fe_2O_3/PU nanocomposites. The permeability and permittivity of γ-Fe_2O_3 and $BaTiO_3$ nanoparticle reinforced PU nanocomposites were investigated with frequencies ranging from 10 MHz to 1 GHz. The predicted microwave properties from Bruggeman's equation were consistent with the measured data, except for the real permittivity of Fe_2O_3/$BaTiO_3$/PU. The volume average method (VAM) usually used for fiber-reinforced composites with reinforcements in the thickness direction was applied in this nanocomposite system. The predicted real permittivity by VAM was found to be in better agreement with the measured data than that predicted by Bruggeman's equation.

Keywords: Magnetic; Ferroelectric; Nanostructures; Microwave properties

1. Introduction

Polymer nanocomposites have been reported for their potential wide applications such as UV shielding [1–4], electromagnetic interface shielding [5,6], microwave absorption [7,8] and stimuli–responsive structural biomimicking smart control [9] because of their easy processability, low-cost manufacturing and good adhesion to substrates. For microwave absorption, the fillers could be chosen from either magnetic or dielectric materials [10]. Most of the polymer matrices are insensitive to electromagnetic wave radiation and only serve as hosting binders between the nanoparticles. The hosting polymer chains facilitate local stress transfer from the polymer matrix to the tougher nanoparticles and provide good adhesion between the composite and the substrate. The active component of absorption is the magnetic or dielectric fillers, which absorb the microwave owing to the interactive loss process of dielectric or magnetic dipoles of the fillers [11]. Thus, composites with higher filler loading have great potential to increase absorption ability. However, subsequent manufacturing puts a limitation on the availability of high-quality nanocomposites with high filler loadings.

* Corresponding author. Current address: Chemical Engineering Department, Lamar University, Beaumont, TX 77710, USA. Tel.: +1 4098807654.
E-mail address: zhanhu.guo@lamar.edu (Z. Guo).

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High particle loading can cause heavy cracks or even bubbles (voids), which will definitely decrease the mechanical properties [12–14]. Towards achieving nanocomposites with high particle loading and good mechanical performance, coupling agents have been widely used to improve particle dispersion and to enhance the interaction between the nanoparticles and the polymer matrix [2,15,16].

Recently, a facile surface-initiated-polymerization (SIP) method has been introduced to fabricate polyurethane (PU) nanocomposites reinforced with single-phase iron oxide nanoparticles [17] or silicon carbide nanoparticles [18]. Both have shown improved mechanical properties in the composites with a high particle loading, and the filling materials are observed to have a significant effect on the mechanical behavior of the polymer. The superparamagnetic iron oxide nanoparticles were observed to behave as ferrimagnetic with increased coercivity (coercive force) due to the weaker dipolar interparticle interaction induced by the non-magnetic polymer spacer. Ferroelectric ceramics such as barium titanate possess a high dielectric constant with a great potential for energy storage supercapacitor [19] and dielectric microwave absorber applications [20–22]. The addition of two different types of nanoparticles could enhance the overall performance of the polymer nanocomposites by introducing individual constituent nanoparticles with different properties. However, there are few papers reporting on these.

In this paper, the SIP method is used to fabricate PU nanocomposites reinforced with two different nanoparticles, i.e., magnetic γ-Fe_2O_3 and ferrielectric barium titanate. The thermal stability of the nanocomposite was qualitatively characterized by thermogravimetric analysis (TGA), and the chemical interaction between nanoparticles and polymer was characterized by derivative thermogravimetry (DTG). The magnetic properties of the nanocomposites filled with different γ-Fe_2O_3 particle loadings and two different nanoparticles were investigated. The effect of high dielectric constant ceramic barium titanate nanoparticles and magnetic γ-Fe_2O_3 nanoparticles on the microwave properties (permittivity and permeability) of the PU nanocomposites was explored. The microwave properties were further analyzed by Bruggeman's equation and the volume average method (VAM). The feasibility of the VAM in microwave property prediction is discussed compared with the experimental measurement.

2. Experimental

2.1. Materials

The fillers used for composite fabrication are barium titanate powder ($BaTiO_3$, 50 nm, NanOxide™ HPB 1000, TPL, Inc., NM) and iron oxide (γ-Fe_2O_3, 23 nm, Nanophase Technologies Corporation) nanoparticles. The polymer matrix used was a commercial, clear PU coating (CAAPCOAT FP-002–55X, manufactured by the CAAP Co., Inc.). It contains two-part urethane monomers, i.e., 80 wt.% diisocyanate and 20 wt.% diol. The liquid resin has a density of 0.83 g cm^{-3}. The PU catalyst (a liquid containing ~20–65 wt.% aliphatic amine, 1–50 wt.% parachlorobenzotrifluoride and 10–35 wt.% methyl propyl ketone) and accelerator (PU STD-102, containing 1 wt.% organotitanate and 99 wt.% acetone) were provided by CAAP Co., Inc. All the chemicals were used as-received without further treatment.

2.2. Nanocomposite fabrication

The PU composites reinforced with magnetic (iron oxide) and/or ferroelectric (barium titanate) nanoparticles were fabricated by the recently developed SIP method [17,18]. SIP was observed to yield nanocomposites with a high particle loading up to 65 wt.% for iron oxide [17] and 35 wt.% for silicon carbide [18] in a PU matrix while still maintaining structural integrity. This method uses physicochemically adsorbed moisture and hydroxyl groups on the nanoparticles as a linking site between the nanoparticles and the polymer chains. The composite fabrication process is briefly described as follows. The nanoparticles were added into the catalyst–accelerator (CA) tetrahydrofuran (THF) solution and sonicated for ~1 h. The sonication energy enhances the reactivity of the surface and promotes the adsorption of CA onto the nanoparticle surface while evaporating the physically adsorbed moisture. The monomers were then introduced into the above solution dropwise within half an hour, and the polymerization was continued in the same conditions. The final solution was poured into a mold, and the solvent was evaporated naturally in ambient conditions.

2.3. Characterization

Particle structural characterization was performed by scanning electron microscopy (SEM; JEOL field emission scanning electron microscope, JSM-6700F).

The physicochemical attachment of the CA mixture onto the nanoparticle surface was verified by TGA (Perkin-Elmer). The sample was prepared by dispersing the nanoparticles into THF, adding the CA, stirring for half an hour, and washing the precipitated nanoparticles with excess THF to remove the extra CA. TGA was carried out from 25 to 600 °C with an argon flow rate of 50 cm^3 min^{-1} at a heating rate of 10 °C min^{-1}. Fourier transform infrared (FT-IR) spectrometry was used to characterize the CA on the nanoparticle surface further. Its spectra were recorded in a FT-IR spectrometer (Jasco, FT-IR 420) in transmission mode under dried nitrogen flow at 10 cm^3 min^{-1}. The FT-IR nanoparticle samples were prepared by mixing with powdered KBr, grinding and compressing into a pellet.

The thermal stability of the nanocomposites and the particle percentage in the nanocomposites were characterized and determined by TGA, following the same procedures as above. Particle dispersion in PU was