Surface & Coatings Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Performance and microstructure characteristics in polyimide/nano-aluminum composites

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ARTICLE INFO

Article history:
Received 31 August 2016
Revised 16 January 2017
Accepted in revised form 24 January 2017
Available online xxxx

Keywords:
Polyimide
Aluminum particles
Composite
Dielectric
Mechanical properties

ABSTRACT

Polyimide (PI) composites with high dielectric permittivity have received a great deal of attention in the embedded capacitors and energy-storage devices due to its excellent thermal stability and good mechanical properties. In this study, nano-aluminum (Al) particles were introduced into PI to prepare promising PI/nano-Al composite. The results indicated that the dielectric constant of the composite films increased with the increase of nano-Al contents and the highest dielectric constant was 15.7 for a composite film incorporating 15 wt% nano-Al. The microstructures of PI/nano-Al composite have been investigated by scanning electron microscopy (SEM), translation electron microscopy(TEM), synchrotron radiation small angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (XRD). The effects of mixture doping concentration on volume resistivity and loss tangent are analyzed. The correlation effects of the Al nanoparticles on the different factors which influence the dielectric performance in PI matrix such as microstructure, resistivity, and interface of the composites were discussed in detail. This composite film would be possessing potential application in flexible energy-storage devices.

1. Introduction

Recently, polymeric based composites associated with high dielectric permittivity and low dielectric loss, and high volume resistivity have been in increasing demands owing to continuous development towards the miniaturization and multifunctionalities of apparatus used in high charge-storage capacitors [1,2] and microelectronic components, such as capacitors embedded in flexible printing circuit [3,4]. Adding high permittivity ceramic fillers or conductive fillers are the two common strategies to fabricate high permittivity polymer based composites [5,6]. The drawback of ceramic filler polymer based composites is the high concentration of fillers will lead to a dramatic decrease of mechanical properties [7–9]. Compared to ceramic fillers of polymer based composites, the disadvantage of conductive filler is consequently increased dielectric loss [10]. Polyimide (PI) as excellent insulating polymer at a high temperature have attracted wide interest as a basis enhancing PI properties and extending their applications, [11–15] which innovative materials have been employed for various contemporary applications such as insulation materials, frequency conversion motors, and proton conductive membranes. The dielectric, insulating and mechanical properties of pure PI films do not quite meet the requirements to be used as an insulating material in high charge-storage capacitors. In the same way, PI can be improved by introducing the high permittivity ceramic fillers or conductive fillers into its matrix. Especially, the addition of inert inorganic oxides such as $BaTiO_3$ [8], Calcium Copper Titanate (CCTO) [6], CNT [16] and others [17] in PI matrix has attracted considerable attention as hybrid materials due to enhanced their dielectric property enhancements and mechanical stability improvements. Metal and polyimide composites were researched for polyimide dielectric performance enhancement. For example, Dang et al., have obtained PI and Ag composite films with high dielectric constant and excellent thermal stability as good candidate for energy storage devices [18]. Wang et al., researched SiO_2 coated Ag and PI based composites, and obtained remarkably improved high thermal conductivity and dielectric performance [19]. Yang et al., discovered that by coating the surface of CCTO nanoparticles with Ag, the dielectric permittivity of PI/CCTO@Ag composites is significantly increased to 103 (100 Hz) at 3 vol% filler loading. The surface coating of nano-fillers is useful for enhancing dielectric performance [20]. To our best knowledge, a low cost metal Al nanoparticles (nano-Al) with nature oxide Al_2O_3 coating for nanofillers of polyimide matrix has not yet been reported.

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http://dx.doi.org/10.1016/j.surfcoat.2017.01.095
0257-8972/

In this paper, a low cost metal Al nanoparticles (nano-Al) with inartificial Al_2O_3 coating for nanofiller of polyimide matrix was synthesized by using in-situ polymerization, which the nano-Al was modified by employing surface chemical reaction. The distribution of nano-Al particles was observed by the scanning electron microscope (SEM) and transmission electron microscope (TEM). The dielectric, thermal and mechanical properties of the PI/nano-Al composites were investigated by dielectric tests, thermal gravimetric analysis (TGA), and tensile tests, respectively. The as-synthesized PI/nano-Al composites show high electric, superior electrical and mechanical properties. Meanwhile, PI composite with 15 wt% nano-Al loading has been exhibited higher dielectric constant (15.7) among the all of tested PI composites. The in-situ polymerization process is critical in dispersing the nano-Al particles into the PI matrix homogeneously to ensure the good electrical and mechanical properties of the PI/nano-Al films.

2. Experimental details

2.1. Fabrication of the PI/nano-Al composite samples

PI/nano-Al composites were prepared by using in-situ polymerization. The nano-Al surface modification was carried out by using the dry toluene reflux method and described in detail in reference [21]. First, modified nano-Al and *N*,*N*-dimethylacetamide (DMAC) were added into a three-opening round-bottomed flask and the flask was placed in an ultrasonic bath with continuous stir. The mechanical stirrer and ultrasonic wave were simultaneously utilized until a stable suspension was obtained. Then 4, 4′-oxy dianiline (ODA) was added into the flask and dissolved in the suspension. (The mixture of nano-Al particles and pyromellitic dianhydride in the flask exposed in ultrasonic bath for 2 h in DMAC solvent). Finally, the PMDA was divided into five portions and one portion was added into the suspension at one time to ensure the complete dissolution of the portion before adding another one, until all five portions were added. Then polyamic acid (PAA) suspension was stirred for 4 h at this viscosity until the suspension turns to yellow. The yellow PAA was cast onto a glass dish using a doctor blade. Composite films were obtained after forming, heat treatments and imidization. The resulted films are light yellow, transparent with thicknesses about 40 μm. The nano-Al doping concentrations in all composite films are 1, 3, 5, 10 and 15 wt%, respectively.

2.2. Measurements

The cross-section SEM images were obtained by a JEOL field-emission scanning electron microscope under operating voltage of 15 kV, model JSM-6700F. The small angle X-ray scattering (SAXS) tests were carried out at Shanghai Synchrotron Radiation Facility, by using a wavelength of 0.124 nm, a sample to detector distance of 5 m, and an exposure time of 10 s. The 2D scattering patterns were collected on a CCD camera, and the intensity vs. scattering angle is obtained by integrating the data from the 2D scattering patterns. TEM-HRTEM was carried out on TEM (JEOL JEM-2010). X-ray diffraction (XRD) measurements were performed at a Rigaku D/max-rB X-ray diffractometer with Cu K_α ($\lambda = 0.15418$ nm) incident radiation. The diffraction patterns were collected at room temperature in the 2θ ranges of 10 to 60°. The dielectric constant of hybrid PI films was tested using an impedance analyzer (Aglient 4294A) with 16451B Dielectric Test Fixture in the frequency range of 1–10^7 Hz. The DC volume resistivity measurements are performed using a Keithley electrometer with 8009 resistivity measurement kit at a voltage of 500 V.

3. Results and discussion

The morphology of nano-Al filler was tested TEM. As seen in Fig. 2a, the spherical nano-Al size is about 10 nm. The nano-Al has the passivated oxide layer (a kind of insulating layer) around its core surface shown in Fig. 1b. The dispersion of the nano-Al within the polyimide matrix was further investigated and the SEM micrographs of the fractured section of the composites prepared by in situ polymerization were shown in Fig. 1c–f.it can be seen that a homogeneous dispersion of the nanoparticles in the PI matrix are separated in low doping (3% doping) sample, and the nano-Al particle sizes of the composite are smaller than 100 nm. Meanwhile a few agglomerations with polyimide containing nano-Al particles are observed as indicated in the SEM image (see Fig. 1b) at higher doping (10% doping) sample. With loading increase of Al nanoparticles, the microstructure change is observed to occur up to 10 wt%, which a number of micro-size layer-like clusters with polyimide molecules coating nano-Al particles begin to appear from place to place and their magnitudes are found to further increase. (see Fig. 1e, f) The formation of large size particle clusters in polymer matrix is determined by the kinetics of composite preparation. The attractive van der Waals forces between nanoparticles are relatively weak because of the long particle-to-particle distance at low nanoparticle loading, which may be the main reason why the nanoscale dispersion is obtained for the composites with nanoparticle loading 3 wt%. With further increasing the Al nanoparticle loading, the particle-to-particle distance decreases obviously and the more attractive van der Waals forces begin to create agglomeration of the particles from place to place. More interesting, the Al nanoparticles still uniformly dispersed in micro-size clusters, which these cluster formed many layers with parallel orientation at leading of 10% nano-Al. This is beneficial for increasing the overall performances of PI/nano-Al composites.

For further confirmation of dispersion of nano-Al, the microstructures of PI/nano-Al composites with content 3 wt% were characterized using TEM technique in Fig. 2 a, b. It can be observed that the nano-Al particles (black spots) are homogeneously dispersed in the polyimide matrix with the particle size in nano-scale, and the particles size is about 10 nm. The FFT pattern of HRTEM revealed the crystalline nature of nano-Al and the (111) plane of aluminium were observed (inset of Fig. 2b). Meanwhile, the EDX pattern obtained from TEM (Fig. 2a) indicated the existence of abundant aluminium and slight oxygen. The homogeneous dispersion of Al particles is attributed to the coaction of mechanical stirring and ultrasonic wave which is an effective way to produce the stable suspension. XRD patterns for the PI/nano-Al with 3 and 10 wt% doping, and pure PI film were given in Fig. 2c. In the XRD patterns of PI/nano-Al composite with the presence of Al particles, the strong diffraction peak of Al is at $2\theta = 38.5$ and 44.7° (PDF:040787). A wide peak in the range of 18.2° in the PI/nano-Al spectrum clearly demonstrates the existence of the amorphous structure of polyimide, which in another way indicates the effectiveness of our synthesizing polyimide method. In the pure film XRD spectrum, on the other hand, the position of the wide peak is shifted to the left slightly in Fig. 2c, this indicates that the crystalline of PI matrix was enhanced. The thermogravimetric analysis (TGA) was examined to evaluate the thermal stability of the PI/nano-Al composites with different Al content. Results are shown in Fig. 2d. It can be found that the thermal stability of the PI/nano-Al with 3% Al content have the highest value in decomposition temperature, about 551.1 °C, among three of the composite films tested when 5 wt% mass lose is reached. This superior in thermal stability of PI/nano-Al with 3% Al content also indicates a rather good compatibility between the inorganic particles and the organic matrix with addition of Al.

As a useful method for testing microstructure of polymer based composite materials, small angle X-ray scattering (SAXS) technology has been used to characterize composite polymers in our previously research [22]. A two-dimensional (2D) SAXS pattern of the PI/nano-Al composite is shown in the Fig. 3a. The PI/nano-Al composites with various inorganic doping concentration have quite similar SAXS patterns, which are all isotropous 2D patterns of scattering intensity with scattering angle. This indicates that ordered microstructure is not presences in PI/nano-Al composites. SAXS data can be analyzed to get the particle size distribution (PSD), unordered fractal structure and interface information for PI composites. The method [23] used to estimate PSD with

Please cite this article as: X. Liu, et al., Surf. Coat. Technol. (2017), http://dx.doi.org/10.1016/j.surfcoat.2017.01.095