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Electrical and mechanical property study on three-component polyimide nanocomposite films with titanium dioxide and montmorillonite

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ABSTRACT

Polyimide (PI)-matrix composite films containing titanium dioxide (TiO_2) nanoparticles and layered montmorillonite (MMT) have been fabricated by employing in-situ polymerization and their microstructure has been investigated by synchrotron radiation small angle X-ray scattering, wide-angle X-ray diffraction and scanning electron microscopy. The effects of mixture doping concentration on volume resistivity, loss tangent, permittivity, and breakdown field strength are analyzed. The breakdown field strength of TiO_2 and MMT doped PI nanocomposite (PTM) shows a maximum value at the inorganic content of 5 wt.%, which is 10% higher than that of comparable two-component PI/TiO_2 nanocomposite films. Meanwhile, the tri-layered PTM/PI/PTM nanocomposite film, prepared by in-situ polymerization, exhibits improved electrical properties than that of the monolayer PTM film.

1. Introduction

Recently, polymer nanocomposites have attracted wide interest as a method of enhancing polymer properties and extending their applications [1,2]. These innovative materials have been employed for various contemporary applications such as insulation materials, [3] frequency conversion motors [4], nonlinear optical devices [5], fuel cells [6], and proton conductive membranes [7]. Due to the rapid development of electrical engineering and electronic technology, polyimide (PI) with excellent insulating characteristics at a high temperature has received more and more attention in electrical and electronic fields [8–11]. The electrical and mechanical properties of pure PI films do not quite meet the requirements to be used as an insulating material in the frequency conversion motor. However, they can be improved by introducing the inorganic oxide nanoparticles into the PI matrix. Especially, the addition of inert inorganic oxides such as TiO_2, montmodlonite (MMT), SiO_2 and others in polymer matrix has attracted considerable attention as hybrid materials due to their improved mechanical stabilities and enhanced dielectric properties. Zha et al. [12,13] and Tsai et al. [14] reported that PI/TiO_2 nanohybrid materials possess exceptional characteristics due to the interesting properties of each component. H. L. Tiay et al. [15] reported that the improved morphology of the PI/MMT nanocomposites resulted in their enhanced mechanical and thermal properties. PI/silica hybrid films prepared via a sol–gel process exhibited good mechanical properties, too [16].

Among inorganic nanoparticles, TiO_2 is one of the most promising materials in research and application fields because of its versatile functions. Thanks to the favorable properties of TiO_2, considerable attention has been devoted to the manufacture of well-dispersed TiO_2 in polymer matrix used as the photo-catalytic activity, high refracting index and low costs [17]. The MMT is a clay mineral consisting of stacked silicate sheets with 1 nm in thickness and larger than 200 nm in length. These sheets have a high aspect ratio (more than 100) and a disk-like morphology. MMT has a high swelling capacity, which is essential for efficient intercalation of polymers, and it is composed of stacked silicate sheets that provide high electrical and tensile properties, as do the polymeric hybrid materials. According to the previous reports [18–21], two kinds of nanoparticles were added into the polymer matrix to take advantages of the excellent properties of TiO_2 and MMT with high volume resistivity and dielectric strength, and the desirable results would be expected.

In this paper, two inorganic nanoparticles (nano-TiO_2 and MMT) modified by employing surface chemical reaction were introduced into the PI matrix by using in-situ polymerization. The as-synthesized PI/TiO_2 + MMT nanocomposite (PTM) films show superior electrical and mechanical properties. Meanwhile, tri-layer sandwiched PTM composites have been designed and exhibited the best electrical and mechanical properties among the three kinds of composites tested (PI/TiO_2, mono-layer PTM and tri-layer structured PTM). The in-situ

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polymerization process is critical in dispersing the two kinds of nanoparticles into the PI matrix homogeneously to ensure the good electrical and mechanical properties of the three-component PTM nanocomposite films.

2. Experimental details

2.1. Fabrication of the samples

PTM hybrid films were prepared by using in-situ polymerization, as shown in Fig. 1. First, modified nano-TiO_2, MMT and N, N-dimethylacetamide (DMAC) were added into a three-opening round-bottomed flask with a stirrer and the flask was placed in an ultrasonic bath. 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-TiO_2 and MMT particles and pyromellitic dianhydride (PMDA) 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 is stirred for 4 h at this viscosity until the suspension turns to yellow. Hybrid films were obtained after forming, heat treatments and imidization. The films are light yellow, transparent with thicknesses about 30 μm. The nano-TiO_2 and MMT doping concentrations in the three kinds of composite films are 5, 10, 15 and 20 wt.%.

2.2. Measurements

The Fourier-transform infrared (FTIR) spectra of composite films were recorded on IRPrestige-21 analyses. FTIR spectra of the nano-TiO_2 before and after treatment with the coupling agent were recorded on a BRUKER EQUINOX55 FTIR spectrophotometer. The cross section SEM images were obtained by a JEOL field-emission scanning electron microscope under operating voltage of 15 kV, model JSM-6700 F. 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. All of the samples were characterized by powder X-ray diffraction (p-XRD) using a Philips X' pert Pro diffractometer (Cu Kα radiation, secondary graphite monochromator, 2°2θ per min).

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. The electrical strength was performed according to IEC243. The samples were placed between two standard electrodes in the silicon oil and voltage increased at a rate of 1 kV/s until breakdown occurs.

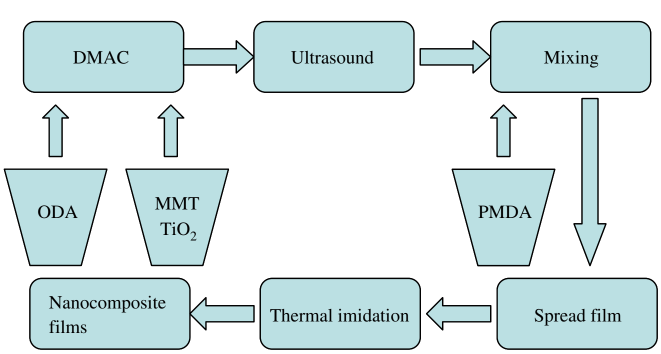

Fig. 1. Schematic representation of preparation process of PTM hybrid films.

3. Results and discussion

3.1. The microstructure of nanocomposite films

Typical SEM images of fractured sections of monolayer and trilaminar PTM films with 5 wt.% content are shown in Fig. 2, which indicates that the nanoparticles are surrounded by PI matrix. Moreover, the SEM image of a monolayer PTM film (as shown in Fig. 2a) reveals a homogeneous dispersion of nanoparticles in the PI matrix and all of the particles are separated and the nano-TiO_2 particle sizes of the hybrid containing 5% nano-TiO_2 are about 30–100 nm. Meanwhile agglomeration of polyimide containing clay particles is observed as indicated by the gray sheet in the SEM image. Fig. 2b shows a SEM of a fractured cross-section of the tri-layer PTM film (Fig. 7). The tri-layered PTM/PI/PTM structure is clearly seen in the image and the difference between the middle pure PI layer and two outside PTM layers is visible. We can simply label the layers from left to right as layers I, II and III, respectively. All three layers have the thickness about 10 μm and no obvious stripping between the layers.

The chemical structures of the PI/TiO_2, monolayer and tri-layer PTM films with 5 wt.% doping were characterized using FTIR technique, as

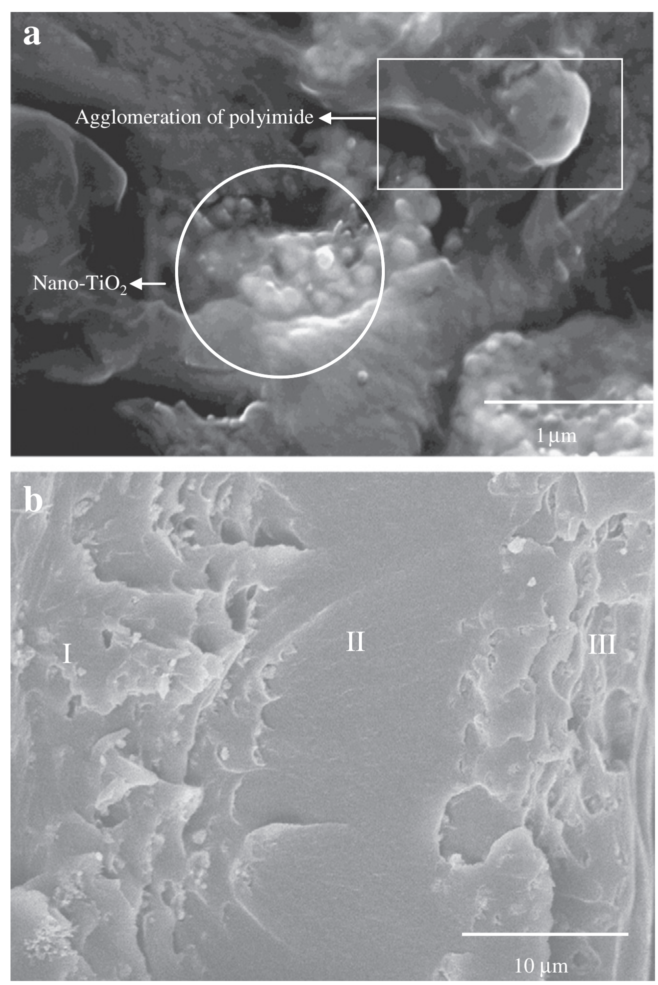

Fig. 2. SEM images of the cross-section of PTM hybrid films with content 5 wt.%: (a) high-magnification cross-section image of PTM film and (b) low magnification cross section image of a sandwiched PTM film.