Polymer Testing 66 (2018) 164–171

Contents lists available at ScienceDirect

Polymer Testing

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

Material Properties

Secondary dispersion of $BaTiO_3$ for the enhanced mechanical properties of the Poly (arylene ether nitrile)-based composite laminates

Yue Yuan, Mingzhen Xu*, Hai Pan, Dengxun Ren, Kui Li, Xiaobo Liu**

Research Branch of Advanced Functional Materials, School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu, 611731, PR China

ARTICLE INFO

Keywords:
Polyarylene ether nitrile
Composite laminates
Barium titanate
Dielectric properties
Mechanical properties
Thermal properties

ABSTRACT

Secondary dispersion of the nano barium titanate ($BaTiO_3$) was performed to obtain the fiber-reinforced polyarylene ether nitrile-based (PEN) composite laminates with improved mechanical properties. $BaTiO_3$/PEN composite films were prepared via casting with ultrasonic dispersion, and then the glass fiber-reinforced (GF) composite laminates were obtained by the hot-melting method, which were favored to realize the secondary dispersion of the $BaTiO_3$ nanoparticles. The fracture surface of the $BaTiO_3$/PEN films and $BaTiO_3$/PEN/GF composite laminates investigated by SEM showed that the $BaTiO_3$ dispersed homogenously both in the PEN matrix and the gaps between the fibers. The mechanical and thermo-mechanical properties of the laminates were characterized and results indicated that the nano-$BaTiO_3$ particles and fibers show enhanced synergistic effects. That is, with increasing the $BaTiO_3$ content, the flexural strength and modulus of the composite laminates increased correspondingly, as well as the glass transition temperatures. Additionally, with the introduction of nano-$BaTiO_3$ particles, the dielectric constants (> 5.5 at 1 kHz) of the composite laminates were improved obviously and the low dielectric loss (~ 0.02 at 1 kHz) was maintained. The temperatures at weight loss 5% ($T_{5\%}$) of all the composite laminates with various content of $BaTiO_3$ were over 490 °C both in N_2 and air atomosphere. Good dielectric properties and outstanding thermo-mechanical properties would enable the PEN-based fiber-reinforced composite laminates as the candidates in the material fields of structure-functional integrations.

1. Introduction

With the rapid development of modern science and technology, increasing requirements have been pursued for the high-performance composites. Due to their superior strength/stiffness-to-weight, fatigue damage resistance, outstanding corrosion resistance, glass fiber-reinforced plastic (GFRP) composites have been widely used in the fields of buildings, sport goods and automotive industries [3,20]. Among them, the thermosetting resin-based laminates and thermoplastic resin-based laminates play equal parts in the application of composites in the beginning. However, with the improvement of the production efficiency, traditional thermosetting resin-based composites have been at the relative disadvantage position due to their long-time curing processes which would significantly reduce the production efficiency, increasing the requirements of the equipment and the production cost [13]. Compared with that of thermosetting resins, the process of thermoplastic resins was efficient and low-cost. Moreover, the recyclable characteristics of thermoplastic resin especially for the resin-based composite laminates have attracted increasing interests under the promise of environmental protection [14–16]. Recently, glass fiber-reinforced thermoplastic composite laminates, are widely studied and used in aerospace, electronics, sports, military industry and other fields of functional materials [2,21], due to their easy processing, recyclability and good chemical resistance with the high specific stiffness and strength of fibers, as well as their controllable thermo-mechanical properties.

Polyarylene ether nitrile (PEN) is a kind of high-performance thermoplastic polymer, possessing high heat resistance, flame resistance, radiation resistance, outstanding mechanical strength and creep resistance [12,19]. In comparison with that of the other thermoplastic resins, such as thermoplastic polyimide (TPI), and poly ether ether ketone (PEEK), PEN still presents significant advantages, including low processing temperature (~280 °C) and short molding period (0.5 ~ 1h). In our previous work, PEN-based fiber-reinforced composites were prepared and results indicated that the composites exhibit satisfactory mechanical properties [22], which were better than that of PEEK and TPI composites due to the presence of the polar nitrile groups [6,9–11].

However, with the development of high-tech industry, the strict

* Corresponding author.
** Corresponding author.
E-mail addresses: mzxu628@uestc.edu.cn (M. Xu), liuxb@uestc.edu.cn (X. Liu).

https://doi.org/10.1016/j.polymertesting.2018.01.014
Received 16 January 2018; Received in revised form 19 January 2018; Accepted 19 January 2018
Available online 03 February 2018

requirements have been proposed for the multicomponent composites, because of the traditional fiber-reinforced composites could not meet the application requirements yet. Thus, the typical nanoparticle-reinforced multicomponent composites have been developed rapidly, due to their controllable structures and properties [1,4,5]. Nevertheless, the aggregation of the nanoparticles in the matrices has been the main factors that limit the improvements of the mechanical and other properties [4,7].

In this work, a secondary dispersion technology were used to prepared the improved fiber-reinforced PEN composite laminates with $BaTiO_3$ nanoparticles dispersed homogeneously in the matrix. The $BaTiO_3$ was dispersed in the PEN solution with ultrasonic and the composite films were obtained via film casting method. Then, the composite films were melted on the glass fabrics (GF) with hot-melting method, during which the $BaTiO_3$ nanoparticles would realize the second dispersion along with the flowing of PEN chains. The dispersion of $BaTiO_3$ nanoparticles in the composites was monitored by SEM and the improved properties of the $BaTiO_3$/PEN/GF composite laminates were characterized and discussed in detail.

2. Experimental section

2.1. Materials

N-methylpyrrolidone (NMP, purity 99%) were purchased from Tianjin Bodi Chemical Holding CO., Ltd., Tianjin China. $BaTiO_3$ (average diameter: < 100 nm) was purchased from Aladdin industrial Co., Shanghai, China. The model of the GF fabric is EW170-100 provided by Shenyang Gaote glass fiber Co., Shenyang, China. Polyarylene ether nitrile (PEN) was synthesized in our lab and the structures were presented in Scheme 1 (a) [17,18].

2.2. Preparation of the $BaTiO_3$/PEN composite films

The $BaTiO_3$/PEN composite films were obtained by film casting method combined with ultrasonic dispersion technology, as shown in Scheme 1 (b). Firstly, a certain amount of $BaTiO_3$ and NMP solvent was gradually added to a three-necked bottle to form a suspension with the help of ultrasonic waves and mechanical stir for 1h. Then, a certain amount of PEN was added to the suspension and dissolved at elevating the temperature. The mixture was maintained for 2h with mechanical stirring at 140 °C to make sure that nano-$BaTiO_3$ particles were well dispersed in PEN solution. Thereafter, the $BaTiO_3$/PEN solution was drop-casted onto a clean and horizontal glass plate and dried at 80 °C, 100 °C, 120 °C for 1h and 160 °C, 200 °C for 2h. Subsequently, the films were naturally cooled to room temperature, and the $BaTiO_3$/PEN composite films were obtained. The mass fraction of the nano-$BaTiO_3$ particles in the PEN matrix was fixed at 5 wt%, 10 wt%, 15 wt%, 20 wt % and 30 wt %, respectively (that is: 10 wt% means PEN and $BaTiO_3$ were 9g and 1g, respectively). Pristine PEN film was prepared using a similar method for comparison purpose.

2.3. Preparation of the $BaTiO_3$/PEN/GF composite laminates

The $BaTiO_3$/PEN composite laminates were prepared as follow (Scheme 1 (c)): The PEN solution containing the corresponding proportion of nano-$BaTiO_3$ particles was obtained, as the method mentioned above. Then GF fabric (10 × 10 cm^2) was brush-coated with the solution onto a horizontal glass plate and dried at room temperature for 5h, in an oven at 80 °C, 100 °C, 120 °C for 1h then 160 °C, 200 °C for 2h, respectively. Five layers of GF prepreg fabrics and six layers of composite films (10 × 10 cm^2) were stacked on top of each other to ensure uniformity, then putting them in a stainless steel mold and hot-pressing under a pressure of 20 MPa at 280 °C for 1h. The composite laminates were naturally cooled down to room temperature in the mold. The mass ratio was designed to give a prepreg of 50 wt% polymer matrix and 50 wt% GF by weight. Various $BaTiO_3$ contents (0 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 30 wt%, by the weight of PEN) of composite laminates were obtained.

2.4. Characterization

The fracture surface micromorphology of the films, composite laminates and pure $BaTiO_3$ were observed with scanning electron microscope (SEM, JEOL, JSM-5900 LV). The dispersion was observed by polarizing optical micrograph using an optical microscope (MP41). Mechanical properties of the films and the flexural tests of the composite laminates were measured by utilizing a SANS CMT6104 Series Desktop Electromechanical Universal Testing Machine. The films were cut into stripes (120 × 10 mm^2) for measurement and five parallel measurements were carried out for each sample (stretching speed 5 mm/min). Flexural tests (three-point bending mode) were held according to the GB/T9341-2008 standard test method with a crosshead displacement speed of 10 mm/min and the test fixture was mounted in a 10 kN capacity. The samples (dimension: 80 × 15 × 12 mm^3) were tested with a support span/sample thickness ratio of 15:1, and gained as average value for every three samples. Differential scanning calorimetry (DSC) analysis of the composite films was carried out on a TA Instrument DSC Q100 under nitrogen. Dynamic mechanical analysis (DMA) was conducted on Instrument DMA Q800 V7.5. Test Conditions: The sample size was 20×10×1 mm^3, three-point bending mode, the heating rate was 5 °C/min, temperature range was 35–260 °C, under nitrogen. Dielectric properties of the $BaTiO_3$/PEN/GF composite laminates were tested by a TH 2819A precision LCR meter (Tong hui Electronic Co., Ltd.) at room temperature. The composite laminates were cut into small pieces of samples and both sides were coated with a thin layer of conductive silver paste to form a plate capacitor (10 × 10 mm^2). The dielectric properties experiments were carried out at different frequencies ranging from 200Hz to 200 kHz under TA Instruments DEA 2970. The composite laminates were cut into a rectangle (30 × 70 mm^2), and the dielectric properties experiments were carried out at high frequencies ranging from 1 GHz to 18 GHz by Aglient E8363A microwave network analyzer. Thermogravimetric analysis (TGA) was conducted on a TA instrument Q50 series analyzer system under nitrogen or air atmosphere at a heating rate of 20 °C/min from 50 to 700 °C. Before testing, the films need to be treated in an oven at 220 °C for 2h to remove the residual solvent.

3. Results and discussion

3.1. The properties of $BaTiO_3$/PEN composite films

Nano-$BaTiO_3$ particles were dispersed into the PEN solution to obtain the composite films. Fig. 1 (a) and (b) showed the surface morphology and the dispersion of $BaTiO_3$ in the solution, respectively. It can be seen in Fig. 1 (a) that nano-$BaTiO_3$ particles present a uniform sphere with an average size of about 50 nm. Fig. 1 (b) showed the polarizing microscope image (POM) of the dispersion of nano-$BaTiO_3$ in PEN solution after ultrasonication treated for 1h. It can be seen that no aggregation of $BaTiO_3$ particles were observed, indicating the homogenous dispersion, which is important for improving the mechanical property of composite films.

SEM was also employed to investigate the fracture surface morphology of pristine PEN and $BaTiO_3$/PEN composite films. Fig. 2 (a) (b) and (c) presented the fracture surface of pristine PEN film, and $BaTiO_3$/PEN composite films with 5 wt% and 30 wt%, respectively. The fracture surface of pristine PEN film (Fig. 2 (a)) shows a typical ductile fracture, which is rough and no obvious cracks can be observed. The ductile fracture would result in improved mechanical properties, came down to a high value of elongation at break. Fig. 2 (b) shows the fracture surface of the composite film with 5 wt% nano-particles, and the particles are homogenously dispersed in the PEN matrix; no cracks and voids were