Materials Letters 128 (2014) 267–270

Contents lists available at ScienceDirect

Materials Letters

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

Novel phthalonitrile-terminated polyarylene ether nitrile with high glass transition temperature and enhanced thermal stability

Lifen Tong, Kun Jia*, Xiaobo Liu*

Research Branch of Advanced Functional Materials, Institute of Microelectronic & Solid State Electronic, High-Temperature Resistant Polymers and Composites Key Laboratory of Sichuan Province, University of Electronic Science and Technology of China, Chengdu 610054, PR China

ARTICLE INFO

Article history:
Received 7 March 2014
Accepted 19 April 2014
Available online 1 May 2014

Keywords:
Crosslinking
Dielectrics
Polymers
Thermal properties

ABSTRACT

A series of polyarylene ether nitrile terminated with phthalonitrile (PEN-*t*-Ph) with different molecular weights have been prepared by adjusting the stoichiometric ratio of reaction. This novel PEN-*t*-Ph integrated the advantages of thermoplastic PEN resin and thermosetting phthalonitrile-based resin due to the crosslinking reaction of phthalonitrile (Ph) on the end of PEN-*t*-Ph chain. Therefore, PEN-*t*-Ph polymer can be fabricated using thermoplastic processing while being used in thermosetting fields. Thermal studies exhibited that the glass-transition temperatures of the various PEN-*t*-Ph crosslinked films were all above 209 °C, and were independent of the molecular weights of PEN-*t*-Ph. Besides, all the PEN-*t*-Ph crosslinked films possessed excellent thermostability with the 5 wt% weight loss temperatures all exceeding 518 °C. Dielectric measurement showed that the PEN-*t*-Ph with number-average molecular weight of 34,128 g mol^{-1} presented the highest dielectric constant and lowest dielectric loss, paving the way for its application in electronic materials.

1. Introduction

Resin matrix composites have become one of the indispensable components in aerospace field due to their increasing application. However, the traditional thermosetting resin possesses poor toughness because of the network structure after curing [1–3]. This largely limits the damage tolerance of composite materials.

During the past decades, a large amount of engineering polymers have been developed as matrices in advanced materials for structural applications in aerospace industry and commercial production. As a high-performance engineering polymer, polyarylene ether nitrile (PEN) has attracted considerable attention due to its unique properties such as high thermal stability, outstanding chemical inertia, and excellent radiation resistance [4–7]. Moreover, the nitrile groups of strong polarity would promote adhesion of the polymer to many substrates [8]. However, the PEN products are processed at high temperature but used at low temperature [9], which hinders the practical application of the PEN resin.

In this paper, we synthesized a novel polyarylene ether nitrile terminated with phthalonitrile (PEN-*t*-Ph). The phthalocyanine rings can be formed via crosslinking of phthalonitrile group on the end of PEN-*t*-Ph chain, leading to a high thermal stability [10,11]; thus the PEN-*t*-Ph polymer, combining the advantages of thermoplastic PEN resin and thermosetting Ph-based resin, can be fabricated as thermoplastic and used as a thermoset. Besides, the molecular weights of PEN-*t*-Ph were adjusted by changing the stoichiometric ratio of biphenol with respect to other reactants, and its influence on the thermal, mechanical, and electrical properties of polyarylene ether nitrile terminated with phthalonitrile was investigated in detail.

2. Experimental

Materials: *N*-methyl-2-pyrrolidone (NMP) was supplied by Tianjin BODI chemicals, Tianjin, China. 4-nitrophthalonitrile (99%) was purchased from Alpha chemicals (Dezhou) Co. Ltd., Dezhou, China. Biphenol (BP), hydroquinone (HQ), 2, 6-dichlorobenzonitrile (DCBN), potassium carbonate (K_2CO_3) and toluene were commercially available and used without further purification.

Synthesis of PEN-t-Ph: Polyarylene ether nitrile terminated with phthalonitrile was synthesized via nucleophilic aromatic substitution polymerization according to the previous report [12]. Depending on the excess content of BP, the synthesized PEN-*t*-Ph products possess different molecular weights. Specifically, excess amount (1.0%, 2.0%, 3.0%, and 5.0%) of BP is used in the synthesis, and the corresponding PEN-*t*-Ph are denoted as a, b, c, and d, respectively.

* Corresponding authors. Tel./fax: +86 28 83207326.
E-mail addresses: jiakun.uestc1985@gmail.com (K. Jia), liuxb@uestc.edu.cn (X. Liu).

http://dx.doi.org/10.1016/j.matlet.2014.04.132
0167-577X/

Preparation of PEN-t-Ph films: The PEN-*t*-Ph films were prepared by a solution casting method. Firstly, the purified PEN-*t*-Ph was added into a three-necked flask and dissolved in NMP solvent at 200 °C for 30 min with stirring to prepare the PEN-*t*-Ph solution. Then the PEN-*t*-Ph solution was cast on a clean glass plate, and dried in an oven to evaporate the solvent following the procedure of 80 °C, 100 °C, 120 °C, 140 °C, 160 °C, 180 °C and 200 °C for 1 h. Lastly, the film was cured at higher temperature of 320 °C for 4 h to obtain the PEN-*t*-Ph crosslinking film.

Characterizations: Gel permeation chromatography (GPC) analysis was conducted with a PL-GPC220 system using polystyrene as standard and THF as the eluent. Differential scanning calorimetry (DSC) was performed on TA Instruments DSC-Q100 at a heating rate of 10 °C/min and a nitrogen flow rate of 50 mL/min from 80 °C to 350 °C. Thermogravimetric analysis (TGA) was used to determine the thermal decomposition of the copolymers by using TA Instruments TGA-Q50 with a heating rate of 20 °C/min from 80 °C to 800 °C in nitrogen. Mechanical tests were performed on a SANS CMT6104 series desktop electromechanical universal testing machine (Shenzhen, China) at a strain speed of 5 mm/min at room temperature. Dielectric measurements were performed using a dielectric analyzer (DEA 2970, TA Instruments).

3. Results and discussion

Gel permeation chromatography analysis: Table 1 shows the molecular weight of the PEN-*t*-Ph measured by GPC. It is clear that the number-average molecular weight (Mn) and the weight-average molecular weight (Mw) of PEN-*t*-Ph decreases with increasing BP content, while a larger polydispersity index is obtained in the case of higher BP content.

Thermal properties: Thermally induced phase transition behaviors of the various PEN-*t*-Ph films were investigated by DSC under nitrogen atmosphere. Fig. 1(A) depicts the DSC curves of the various PEN-*t*-Ph crosslinked films. It can be seen that the glass transition temperatures of samples **a–d** are in the range of 210–214 °C and independent of varying molecular weight of PEN-*t*-Ph. This result should be attributed to the crosslinking reaction among the phthalonitriles on the end of the PEN-*t*-Ph chain to form the phthalocyanine ring whose structure is extremely stable. Another reason is that glass transition asymptotically reaches a limiting value as molecular weight increases for the macromolecular polymer; due to this the macromolecular chains' extremities increase the free volume resulting in the decrease of glass transition temperature. Fig. 1(B) shows the TGA curves of the various PEN-*t*-Ph crosslinked films. With the molecular weight of polymer increasing, the initial decomposition temperature and char yield both increases. Basically, the various PEN-*t*-Ph crosslinked films all possess excellent thermostability with the temperatures corresponding to the weight loss of 5 wt%, all exceeding 518 °C. These results should also be attributed to the crosslinking reaction among the phthalonitriles on the end of the PEN-*t*-Ph chain. With the molecular weight decreasing, the crosslinking reaction becomes more intense, preventing the possible degradation of PEN-*t*-Ph.

Table 1
Analysis results of gel permeation chromatography.

Samples	Mn	Mw	Mw/Mn
a	75,423	119,394	1.583
b	44,009	78,560	1.789
c	34,128	65,579	1.921
d	9352	22,457	2.401

Mechanical properties: Mechanical properties such as tensile strength and elastic modulus of the various PEN-*t*-Ph films are shown in Fig. 2. As we can see, all the PEN-*t*-Ph crosslinked films show excellent mechanical properties, with tensile strengths exceeding 90 MPa and elastic modulus over 1700 MPa. Moreover, as molecular weight decreases, the tensile strength firstly increases to the maximum value followed by a decrease. And sample **b** possesses most superior mechanical properties with tensile strength of 110 MPa and elastic modulus of 2492 MPa. All in all, the various PEN-*t*-Ph films possess high thermal stability as well as high mechanical strength, which will have a good prospect in composites application.

Electrical properties: The dielectric properties of the various PEN-*t*-Ph crosslinked films were measured as a function of frequency. As shown in Fig. 3(A), the dielectric constants of all the PEN-*t*-Ph crosslinked films show a slight decrease with increasing frequency from 100 Hz to 200 kHz. Besides, the dielectric constant first increases and then decreases with the molecular weight decreasing. Sample **a** shows the lowest dielectric constant of 3.6 and sample **c** has the highest dielectric constant of 4.4 at the frequency of 1 kHz. The low degree of crosslinking of samples **a**, **b**,

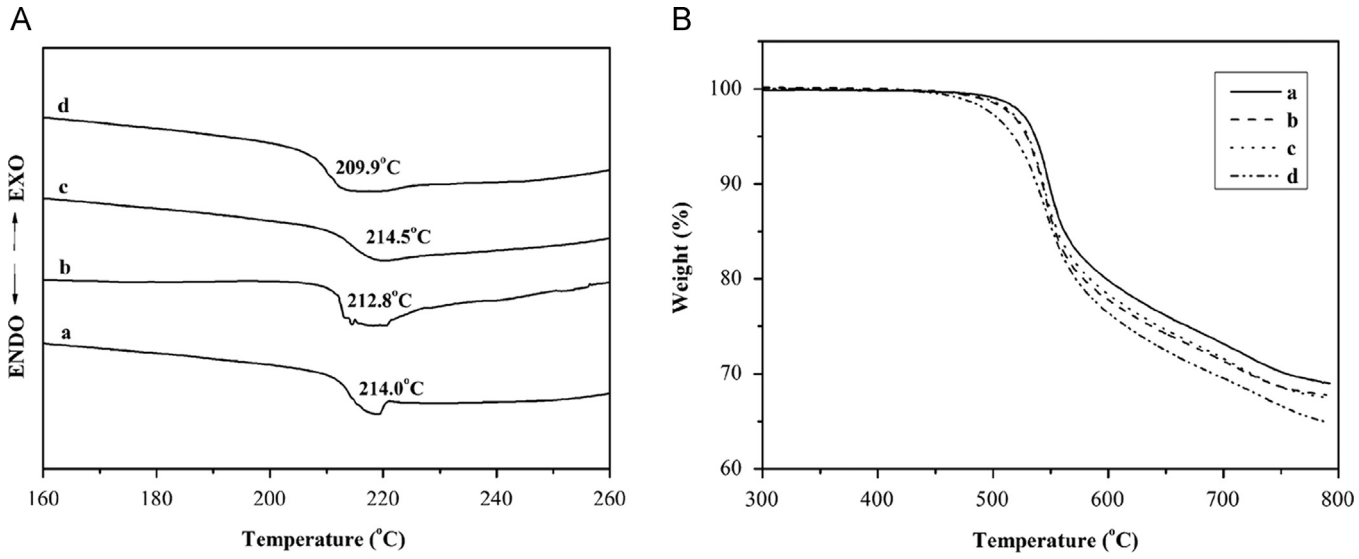

Fig. 1. (A) DSC curves of various PEN-*t*-Ph crosslinked films; (B) TGA curves of various PEN-*t*-Ph crosslinked films.