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Novel high-temperature-resistant single-polymer composites based on self-reinforced phthalonitrile end-capped polyarylene ether nitrile

Lifen Tong, Penglun Zheng, Hailong Tang, 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

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ABSTRACT

A series of phthalonitrile end-capped polyarylene ether nitrile (PEN-Ph) with different structures has been synthesized by adjusting the molar ratio of biphenyl (BP) to hydroquinone (HQ). Furthermore, based on the PEN-Ph, self-toughened and self-reinforced single-polymer composites were successfully prepared. The relationship between structure, morphology, and properties of the PEN-Ph system was also investigated in detail. From the polarizing micrographs, it is concluded that the sample-1# (molar ratio of BP to HQ is 10:93) possesses larger size spherocrystal. Moreover, the T_g decreases from 206.1 to 178.2 with the increasing HQ content. The mechanical measurement demonstrates that the sample-2# (molar ratio of BP to HQ is 20:83) shows the best tensile strength. Most importantly, the polarizing micrographs which illustrated the morphologies of PEN-Ph as a function of temperature, provide the direct evidence for the PEN-Ph crystals solidification by crosslinking reaction. Hence, taking the thermal and mechanical properties in consideration, the sample-2# will be a good candidate for the high-temperature-resistant single-polymer composites.

1. Introduction

Presently, single polymer composites have emerged as a new novel composites world-wide, in which the fillers and matrix are belonging to the same polymer or to the same type of polymers, resulting in the excellent performance such as ideal recyclability, light weight, and superior interfaces, etc. [1–3] Much progress has been made in the design and preparation of the single polymers composites which used the semi-crystalline thermoplastics polymers, such as polyethylene, polyester, isotactic polypropylene, etc., and they all present excellent performance [2,4–6].

Polyarylene ether nitriles (PEN), as a new class of special engineering plastic materials, have sparked an extraordinary increase in worldwide attention from the scientific community and accompanying commercial interest due to its unique properties (high thermal stability, superior mechanical properties as well as good workability) [7–10]. By introducing phthalonitrile to the end of PEN chain, it endow PEN with better flexibility, leading to better crystallinity of the polymer. Moreover, the phthalonitrile end-capped polyarylene ether nitrile (PEN-Ph) shows more excellent thermal and mechanical properties compared with the conventional PEN, and possesses the self-toughened and reinforced characteristics [8,11].

The relationship between structure, morphology and properties of polymers in the composites offer an effective pathway to obtain novel and desired properties via structure manipulation. In present work, a series of PEN-Ph with different structures had been synthesized by adjusting the molar ratio of biphenyl to hydroquinone. Furthermore, a series of novel self-toughened and reinforced single-polymer composites based on PEN-Ph were successfully prepared, and the relationship between their structures and properties had also been studied in detail. Compared with previous reported methods for preparing single-polymer composites [1,6], the casting film method employed in this work is simpler to obtain single-polymer composites. Most importantly, the PEN-Ph crystals can be embedded in the PEN-Ph matrix through the crosslinking reaction [12], resulting the PEN-Ph crystals cannot be damaged in high temperature condition. Thus, PEN-Ph thick films will be a good candidate for high-temperature-resistant single-polymer composites.

2. Experimental section

2.1. Materials

N-Methyl-2-Pyrrolidone (NMP) was supplied by Tianjin BODI chemicals, Tianjin, China. 4-Nitrophthalonitrile (99%) was

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

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Table 1
Structure and thermal properties of the PEN-Ph system.

Samples	0#	1#	2#	3#	4#
Molar ratio of reactants					
BP	100	93	83	73	63
HQ	0	10	20	30	40
DCBN	100	100	100	100	100
Thermal properties					
T_g (°C)	206.1	196.4	191.8	186.5	178.2
T_m (°C)	351.7	322.4	291.3	293.3	–[a]
ΔCp (W/g)	0.01792	0.02433	0.04556	0.06989	0.11450

[a] The detail parameter cannot be measured due to its amorphous structure.

purchased from Alpha chemicals (Dezhou) Co. Ltd., Dezhou, China. Biphenyl (BP), hydroquinone (HQ), 2, 6-dichlorobenzonitrile (DCBN), potassium carbonate (K_2CO_3) and toluene were commercially available and used without further purification.

2.2. Synthesis of PEN-Ph and preparation of the single-polymer composites

According to the previous report [11], PEN-Ph with different structures has been synthesized by adjusting the molar ratio of the BP to HQ, and the detailed synthesis raw material proportion was listed in Table 1. The single-polymer composites based on PEN-Ph were prepared by casting method, with the procedure of raising the temperature slowly from 80 °C to 200 °C during 5 h. Finally, the PEN-Ph thick films with different structures were obtained after thermostatically processing at 280 °C for 4 h.

2.3. Characterizations

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. The micro-morphologies of the PEN-Ph were characterized by scanning electron microscope (SEM) (JSM 6290LV). For optical microscopy observation, a MP41 optical microscope was used in this study. All optical micrographs presented in this paper were taken under crossed polarizer. 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.

3. Results and discussion section

3.1. Morphological properties

In order to investigate the relationship between the structure and morphology of polymers, the morphological properties were measured by polarizing microscope and SEM. Fig. 1a–d shows the polarizing microscope images of the PEN-Ph with different structures. It can be seen that the size of PEN-Ph crystals in sample-1# (Fig. 1b) was the biggest, and there existed Maltese cross phenomenon, indicating that most crystals are spherocrystals. In addition, there is no crystals in the sample-4# (Fig. 1d), so there is nothing in the polarizing microscope of sample-4#. Furthermore, SEM was applied to further study the morphology of the PEN-Ph crystals. Fig. 1e shows the fracture morphology of sample-1#. It can be seen that the PEN-Ph crystals were spherical. This result was well consistent with the polarizing microscope analysis.

3.2. Crystals embedded in PEN-ph matrix

Fig. 2 shows the polarizing micrographs which illustrate the morphologies of PEN-Ph (sample-1#) as a function of temperature to certify the phenomenon that the PEN-Ph crystals can be embedded in PEN-Ph matrix through the crosslinking reaction among the phthalonitrile at the end of the PEN-Ph main chains. It can be seen that when the temperature is above 200 °C, the PEN-Ph crystals almost did not change. Even the temperature reached 480 °C, the PEN-Ph crystals did not disappear, providing the direct evidence for the PEN-Ph crystals solidification by crosslinking reaction.

3.3. Thermal and mechanical property

Fig. 3a shows the DSC curves of the various PEN-Ph single-polymer composites, and the detailed date were listed in Table 1. It

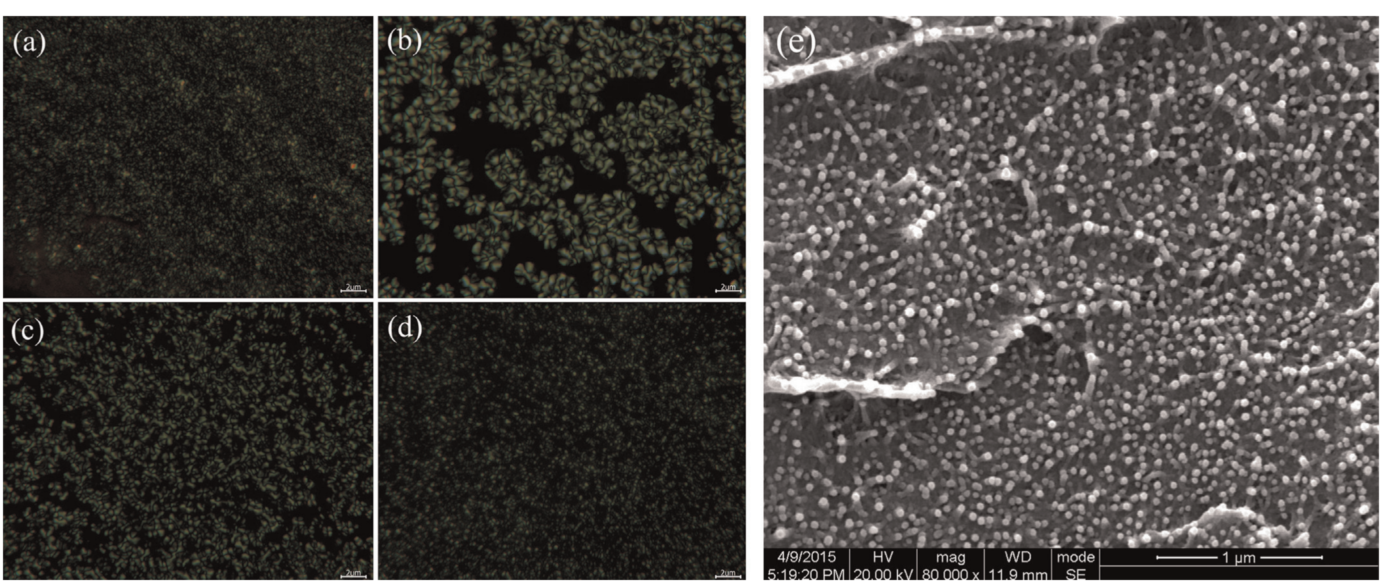

Fig. 1. (a–d) Polarizing micrographs illustrate the morphologies of PEN-Ph with different structures with scale bar of 2 μm, (a) sample-1#, (b) sample-2#, (c) sample-3#, (d) sample-4#; and (e) the fracture morphology of sample-1# thick film.