Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 195 (2018) 1–6

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Investigation of phase separated polyimide blend films containing boron nitride using FTIR imaging

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ARTICLE INFO

Article history:
Received 13 August 2017
Received in revised form 2 January 2018
Accepted 10 January 2018
Available online 10 January 2018

Keywords:
Polyimide
Boron nitride
Phase separation
FTIR imaging

ABSTRACT

Immiscible aromatic polyimide (PI) blend films and a PI blend film incorporated with thermally conductive boron nitride (BN) were prepared, and their phase separation behaviors were examined by optical microscopy and FTIR imaging. The 2,2′-bis(trifluoromethyl)benzidine (TFMB)-containing and 4,4′-thiodianiline (TDA)-containing aromatic PI blend films and a PI blend/BN composite film show two clearly separated regions; one region is the TFMB-rich phase, and the other region is the TDA-rich phase. The introduction of BN induces morphological changes in the immiscible aromatic PI blend film without altering the composition of either domain. In particular, the BN is selectively incorporated into the TDA-rich phase in this study.

1. Introduction

Polymer films with high thermal conductivities are important in the field of denser and more powerful electronic devices, electronic packaging, and semiconductor chips for heat dissipation [1–3]. Among the organic polymers, aromatic polyimides (PIs) have been used widely in the electronic devices, semiconductor devices, and printed circuitry board industries because of their high glass transition temperatures, dimensional stabilities and heat resistances, as well as their excellent mechanical, adhesion and dielectric properties [4–7]. To generate PI films that are thermally conductive, they are prepared as composite films with thermally conductive inorganic fillers, such as carbon nanotubes, graphene sheets, alumina (Al_2O_3), aluminum nitride (AlN), zinc oxide (ZnO) and boron nitride (BN), because PI films have low thermal conductivities [8–19]. Recently, several thermally conductive PI composite films, which are prepared using various thermally conductive inorganic fillers, have been reported [20–24].

In general, the heat transport mechanism of the thermally conductive inorganic fillers is explained by the flow of phonons or lattice vibration energy [8,25]. Therefore, the composite films form a thermally conductive path to decrease the heat generated by phonon scattering in the polymer matrix. Commonly, loadings of more than 30 vol% of the thermally conductive inorganic fillers are necessary to achieve the desired levels of thermal conductivity in the thermally conductive polymer composites [26]. Higher inorganic filler loadings deteriorate the properties and the mechanical behaviors of the composite films and make the preparation of composite films difficult. Recently, phase separated aromatic polyimide (PI) blend films with thermally conductive inorganic fillers were introduced to enhance thermal conductivity while avoiding the limitations of PI composite films [27–30]. In phase separated aromatic PI blend films, two PI phases were separately aligned along the out-of-plane direction, and the thermally conductive inorganic fillers were selectively located in one phase. The phase separated aromatic PI blend films can solve the disadvantages of polymer-thermally conductive inorganic fillers composite films. Moreover, controlling the thermally conductive inorganic fillers in the phase separated polymer blends is a good method for achieving high thermal conductivities in polymer films.

Polymer blending, which is the mixing of more than two polymers together to develop new materials, has attracted considerable scientific and industrial interest because it is an easy and cost-effective way to produce materials for various applications. The chemical and physical properties of the polymer blends can be controlled by the chemical composition, properties of the individual components, interfacial characteristics, molecular weight, type of backbones or side chains, and so on. However, most polymer blends show phase separation because of the large unfavorable enthalpy of mixing and absence of any specific interaction between the blended polymers [31,32]. In other words, immiscible polymer blends make multi-phase structures, which can be

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https://doi.org/10.1016/j.saa.2018.01.025
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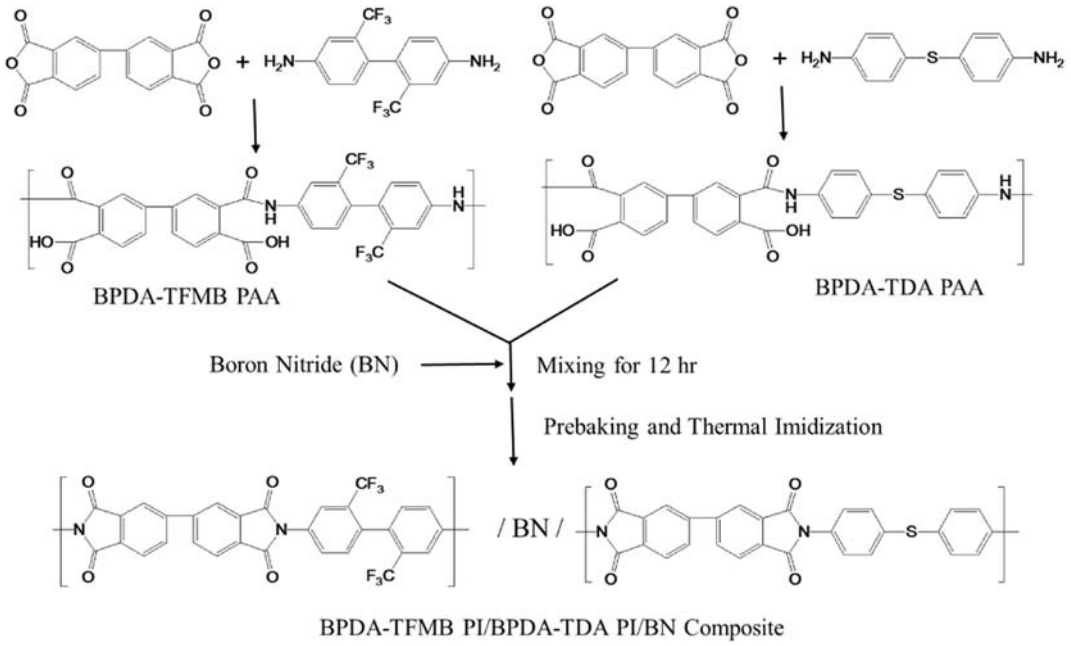

Fig. 1. Preparation of polyimide composite films.

optimized with respect to the needs of the industrial application. Consequently, the characteristics and morphologies of the phase separated films generated from immiscible polymer blends can be tuned by the components, compositions, and chemical structures of the blended polymers.

In this study, phase separated aromatic PI blend films, one consisting of 2,2′-bis(trifluoromethyl)benzidine (TFMB) and one containing 4,4′-thiodianiline (TDA) moieties, were prepared, and the thermal conductivity of the thermally conductive PI blend film and PI blend composite films were measured. In addition, phase separation behaviors of the blend film and the thermally conductive PI blend film containing BN were investigated by FTIR (Fourier-transform infrared) imaging to investigate the behavior of incorporated thermally conductive BN. Several studies have used optical microscopy (OM), atomic force microscopy (AFM), scanning electron microscopy (SEM) and FTIR spectroscopy to examine the phase separation behaviors of thermally conductive PI blend films as well as PI blend films with thermally conductive inorganic fillers [15,16,18,19,29]. FTIR spectroscopy is a very sensitive technique that can be used to identify specific functional groups. However, FTIR imaging provides both the spectral information and spatial information, which enables the direct examination of the chemical distribution of polymer blends [33,34]. To investigate the phase separation behavior of the thermally conductive PI blend film and PI blend composite film, we first employed FTIR imaging. By knowing the infrared signature of the TFMB, TDA and BN units, the behavior of BN incorporated in the PI blend composite film can be investigated using FTIR imaging.

2. Experimental Section

2.1. Materials

3,3′,4,4′-Biphenyltetracarboxylic anhydride (BPDA) was supplied by Chriskev Company and purified by recrystallization from acetic anhydride. 4,4′-Thiodianiline (TDA) and 2,2′-bis(trifluoromethyl)benzidine (TFMB) were purchased from Aldrich and Chriskev, respectively, and purified by vacuum drying at 100 °C. *N*,*N*-Dimethylacetamide (DMAc) was obtained from Aldrich and distilled over calcium hydride under reduced pressure. Amorphous BN was acquired from Nanostructures & Amorphous Materials and used as received.

2.2. Preparation of Poly(amic acid) Solutions

Two poly(amic acid) (PAA) solutions, BPDA-TFMB and BPDA-TDA, were prepared from polycondensation reactions by adding equimolar

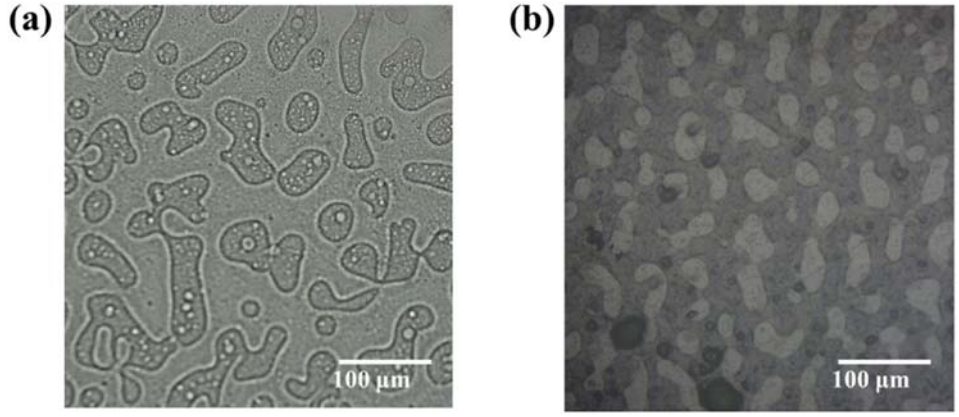

Fig. 2. Optical image of (a) BPDA-TDA/BPDA-TFMB (50:50% (w/w)) PI blend film and (b) the BPDA-TDA/BPDA-TFMB (50:50% (w/w)) PI blend film containing 15 wt% BN.