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Double phase separation in preparing polyimide/silica hybrid films by sol–gel method

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Abstract

In this paper, the phase separation process of the polyimide/silica hybrid films made from polyamic acid (PAA) and precursor (TEOS-A) hydrolyzed tetraethoxysilane under acidic condition in *N*-methyl-2-pyrrolidone (NMP) through sol–gel method was investigated by the scanning electron microscope (SEM). A double phase separation was discovered for the preparation of the hybrid films. With evaporation of the solvent NMP at lower than 100 °C, the component miscibility of TEOS-A and PAA decreases so that the first phase separation took place and a larger particle phase of TEOS-A precursor with size around 2.0 μm was formed. The second phase separation from the matrix phase appeared, as PAA was imidized at elevated temperature, which destroyed the interaction between carboxyl group of PAA and hydroxyl group of TEOS-A, and a nanoscale SiO_2 particle phase formed. The formation mechanism of the double phase separation was explained by the ''capture–release'' model. According to the model, the second phase separation can be controlled by synthesizing amic acid–imide copolymer with different contents of carboxyl group.

Keywords: Phase separation; Morphology; Polyimide/silica hybrid

1. Introduction

Polymer–inorganic hybrid materials, which offer enormous scientific and technological promise in areas ranging from microelectronics to nanobiotechnology, is an exciting area of research [1–4]. The sol–gel method provides an available route to prepare these hybrids [5]. Among the various possible polymer architectures, polyimides (PI) are particularly promising because of their outstanding characteristics, such as high mechanical strength and modulus, low thermal expansivity and dielectric constant. The influence of the interaction between PI and inorganic component on the morphology of hybrids is the primary problem for hybrids. Several methods [6–10] to control the morphology of hybrids are available by increasing the interaction between PI and inorganic component. In our recent work, we also prepared hybrid films with good miscibility derived from diamines containing different hydroxyl groups by sol–gel method [11,12].

The morphology of hybrid is affected by the phase separation process. Nandi et al. [13] postulated that the carboxylic groups of the polyamic acid act as coupling sites between the polymer and the metal oxide and that the water released during the imidization reaction of the polyamic acid (PAA), takes part in the hydrolysis and the polycondensation of the metal oxide precursors. The ''site-isolation'' concept was introduced to explain how the loss of mobility within the polyamic acid matrix, during imidization, prevents agglomeration of the evolving metal oxide particles. In common cases, the hybrid material thus prepared has a two-phase structure of silica particles with uniform diameter dispersed quite regularly within a polyimide matrix. Inoue [14] thought that the formation of a regular structure was interpreted in terms of process from the bicontinuous phase to the dispersed phase. Goizet

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and Joly [15,16] have reported that the morphology of two populations of SiO_2 particles, which are with different sizes, is different from other previous studies. In our experimental conditions, we also discovered the morphology of hybrids with two populations of SiO_2 particles from the double phase separation. The phenomenon could not be explained by Nandi's or Inoue's viewpoints. In order to understand the hybrid morphology thoroughly, the formation process and mechanism of the hybrid morphology need further study. The transitional morphology of the hybrids was investigated. The phenomenon of the double phase separation in preparing PI/SiO_2 hybrid films by sol–gel process using polyamic acid (PAA) and precursor (TEOS-A) hydrolyzed tetraethoxysilane under acidic condition in *N*-methyl-2-pyrrolidone (NMP) was observed. In this communication, the double phase separation of PI/SiO_2 hybrid films and the formation mechanism are discussed.

2. Experimental

3,4,3′,4′-Benzophenone dianhydride (BTDA, ACROSOGANICS) and 4,4′-oxydiphthalic anhydride (ODPA, ACROSOGANICS) were used after drying at 180 °C under vacuum for 5 h. 4,4′-Oxydianiline (ODA, Shanghai Research Institute of Synthetic Resins) and tetraethoxysilane (TEOS, Shanghai Chemical Reagent Co.) were used as received. 4,4′-Diamino-4″-hydroxyltriiphenylmethane (DHTM) and 3,5-diaminobenzoic-4′-biphenyl ester (DABBE) were synthesized in our laboratory [12,17]. *N*-Methyl-2-pyrrolidinone (NMP, Qunli Chemical Reagents Corp., Shanghai, China) was purified by vacuum-distillation over phosphorus pentoxide and stored over 4-Å molecular sieves.

Dianhydride was added to the NMP solution containing equimolar amount of diamine in ice bath. The solid content of the solution was 15 wt%. The mixture was stirred at room temperature for 12 h to get a viscous PAA solution. A precursor (TEOS-A) solution hydrolyzed tetraethoxysilane was made from a mixture of TEOS in NMP and deionized water (mole ratio of TEOS and $H_2O = 1:4$) with pH value 1.5 adjusted by oxalic acid stirring at 50 °C for 1.5 h, and then added into PAA solution of NMP under stirring. The mixture was stirred at room temperature for 2 h to get a transparent solution. The polyimide/silica films with thickness of about 30 μm and 30 wt% SiO_2 content were obtained from the solution which was coated on a glass substrate and subsequently cured at 60 °C for 6 h, at 80 °C for 2 h, at 140 °C for 2 h, at 220 °C for 2 h and at 300 °C for 1 h in vacuum.

Some amic acid–imide copolymers (PA-I) with different imidization degrees were prepared by controlling the amount of the dehydration agent which is a blend of acetic anhydride and pyridine in PAA solution. Theoretically, the imidization degree is controlled by changing the mole amount of acetic anhydride (0 mol%, 20 mol%, 40 mol%, 60 mol%). When the mole ratio of added acetic anhydride to carboxyl group is 1, the theoretical imidization degree is 100%. The precursor (TEOS-A) solutions were added, respectively, into the PA-I solutions. The resultant solutions were coated on the glass substrates and thermally treated with same curing processes as above to get the hybrid films with silica content of 8 wt%.

The morphology was investigated by scanning electron microscopy (SEM) using a LSM-5900LV (Japan) operating at 20 kV. Fourier transform infrared spectra (FTIR) of films were recorded on a Nicolet 560 FTIR spectra photometer.

3. Results and discussion

Fig. 1 shows the SEM photographs of the fractured cross sections of the PI (BTDA/ODA)/SiO_2 hybrid film with 30 wt% SiO_2 cured at different temperatures, which is correspondent to the phase separation process. Fig. 1(a) is the SEM photograph of the hybrid film cured at 60 °C for 3 h in vacuum, which shows the transitional morphology in the first phase separation process from a continuous phase to a dispersed phase corresponding to the typical spinodal phase separation mechanism. Fig. 1(b) and (c) shows the morphologies of hybrid film after subsequent cure. As shown in Fig. 1(b)–(d), with a gradual increase of temperature, the particle sizes are 2.8 μm, 2.0 μm and 1.8 μm, respectively, which suggest that the condensation degree of SiO_2 precursor increases. At the same time, it is observed that there are many small spherical particles (∼70 nm) in the polymer matrix after cured at 220 °C for 2 h in the magnification photograph of (d), while no such small spherical particles exist in the magnification of (c). Energy Dispersive Analysis System of X-ray has defined the composition of the smaller particles, composed of oxygen and silicon in a ratio of $O/Si = 2$. The results show that a secondary phase separation process from the matrix phase occurred in preparation of the PI/SiO_2 hybrid film. The phenomenon of double phase separation is also discovered in other systems as shown in Fig. 2.

The first phase separation occurred at a relatively lower temperature and the secondary phase separation occurred at a higher temperature. Two populations of SiO_2 particles are derived from double phase separation processes, influenced by three possible factors including the evaporation of solvent, the condensation of TEOS-A and imidization of PAA. In order to find out the major factor in the first phase separation, a dissolution experiment of the hybrid film cured at 60 °C for 6 h was performed in NMP. The result shows that both the PI matrix and spherical particles in the hybrid film are soluble in NMP. It indicates a lower condensation degree of TEOS-A, which agrees with the hydrolysis and condensation mechanism of TEOS under acidic condition [18]. Furthermore, because of the lower degrees of both PAA imidization and TEOS-A condensation, the first phase separation is induced by the solvent evaporation, which leads to a decrease of the component miscibility between PAA and TEOS-A.

However, it is not clear which factor plays a major role in the formation of the small spherical particles when curing at high temperature. Generally, a majority of the imidization reaction of PAA takes place above 200 °C with disappearance of most carboxyl groups [19]. According to the fact the small SiO_2 particles appear in the process of imidization simultaneously, a "capture–release" model (Scheme 1) based on

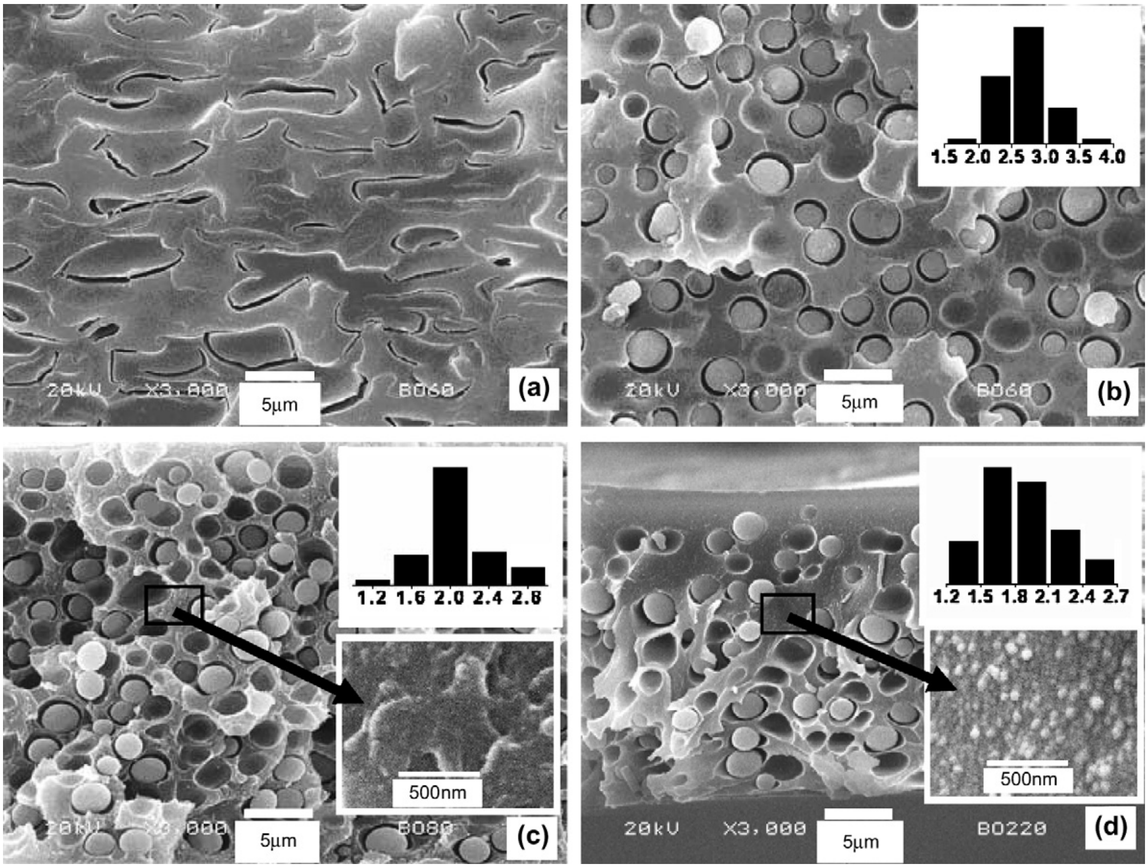


Fig. 1. SEM photographs of hybrid film cured at different conditions. (a) Cured at 60 °C for 3 h; (b) cured at 60 °C for 6 h; (c) cured after (b) and 80 °C for 2 h; (d) cured after (c), and 140 °C for 2 h, 220 °C for 2 h.

the hydrogen bonding between carboxyl group of PAA and hydrogen group of TEOS-A is put forward and further verified by the experiments as follows. The characteristic absorption band of Si–OH [20] near 958.46 cm^{-1} was observed in the FTIR spectra (Fig. 3(a)) of the hybrid sample cured at 60 °C, in which a soluble PI was directly used. When the hybrid film was prepared by PAA and cured at 60 °C, a band at near 966.18 cm^{-1} in the spectra (Fig. 3(b)) can be observed. However, when the hybrid film was cured at 300 °C, this band changed the position from 966.18 cm^{-1} to 958.46 cm^{-1} (Fig. 3(c)). It may be considered that the electron density of Si–OH decreases because of the hydrogen bonding between carboxyl group of PAA and hydroxyl group of TEOS-A, which makes the wavenumber of the absorption band in Fig. 3(b) to increase. The result is consistent with the ‘‘capture–release’’ model in Scheme 1.

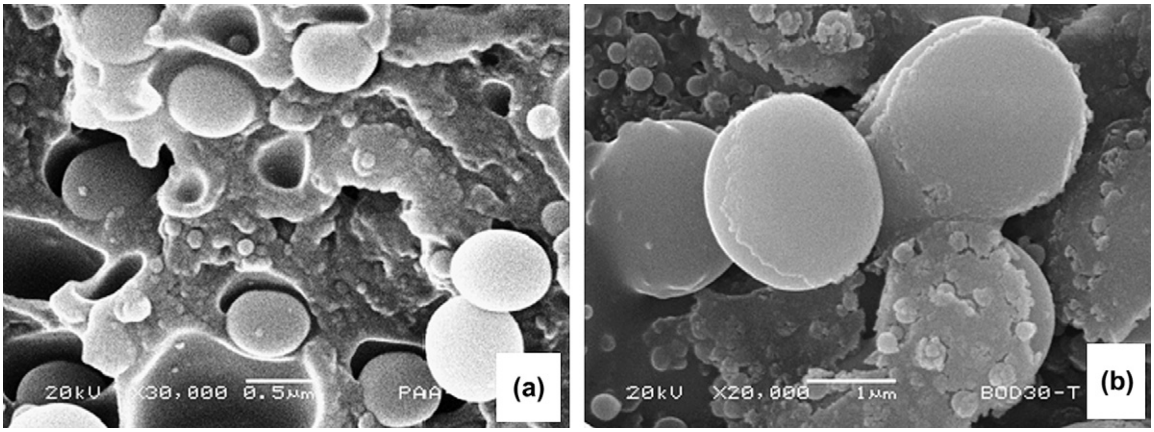
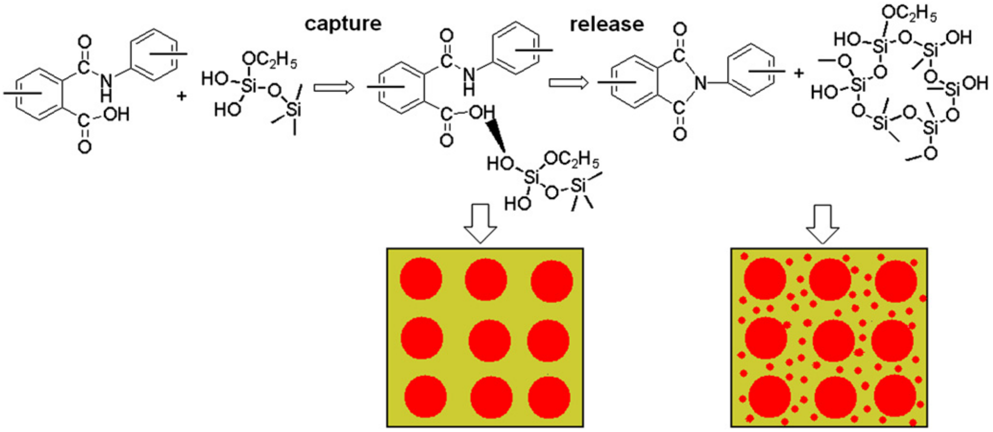


Fig. 2. SEM photographs of hybrid films. (a) PI (ODPA/ODA/DABBE [17])/SiO_2 hybrid films with 22 wt% silica contents cured at 300 °C; (b) PI (BTDA/ODA/DHTM [12])/SiO_2 hybrid films with 30 wt% silica contents cured at 800 °C.



Scheme 1. Schematic representation of double phase separations of PI/SiO_2 hybrid.

To further substantiate the results as above, some hybrid films were prepared by amic acid–imide copolymer (PA-I) with different imidization degrees. Characterization of the imidization degree of the copolyimides is shown in Fig. 4. The FTIR result expresses that the factual imidization degrees [21] of the PA-Is are 0%, 27.7%, 45.5% and 55.4%, respectively. Fig. 5 is the SEM photographs of hybrid films with 8 wt% SiO_2. According to the SEM results, there are two populations of SiO_2 particles in the system when PAA was used in hybrid solution. Decreasing carboxyl group content, morphology of hybrid films changes: the size of bigger SiO_2 particles increases from 300 nm to 1 μm; however, the number of SiO_2 nano-particles in the hybrid decreases and almost disappears when the imidization degree is 55.4%. The result proves the model (Scheme 1).

4. Conclusions

In this paper, we report the double phase separation in the preparation of PI/SiO_2 hybrid films from PAA and precursor TEOS-A by the sol–gel method. The formation mechanism of two populations of SiO_2 particles in hybrid films was explained by the ‘‘capture–release’’ model. Firstly, the hydrogen bonding between the carboxyl group in PAA and the hydroxyl group in TEOS-A was formed in a homogeneous solution. When the solvent NMP evaporated, the component miscibility between TEOS-A and PAA decreased, and the first phase separation took place. Then the secondary phase separation occurred with the imidization of PAA which destroyed the hydrogen bonding at elevated temperature. The precursors TEOS-A were released from polymer chains in the matrix

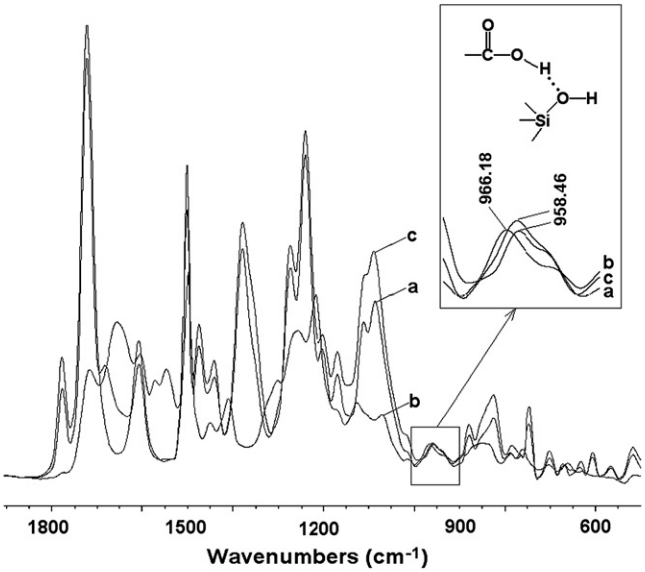


Fig. 3. FTIR spectra of the PI (ODPA/ODA/DABBE)/SiO_2 hybrid (11 wt% silica content). (a) Cured at 60 °C for 6 h from soluble PI; (b) cured at 60 °C for 6 h from PAA; (c) cured at 300 °C for 2 h from PAA.

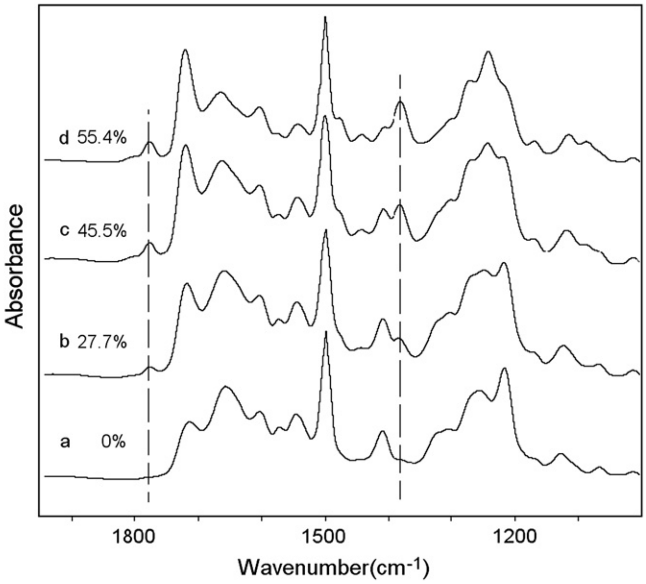


Fig. 4. FTIR spectra of the PA-I (ODPA/ODA) cured at 60 °C for 6 h. (a) 0% imidization degree; (b) 27.7% imidization degree; (c) 45.5% imidization degree; (d) 55.4% imidization degree.

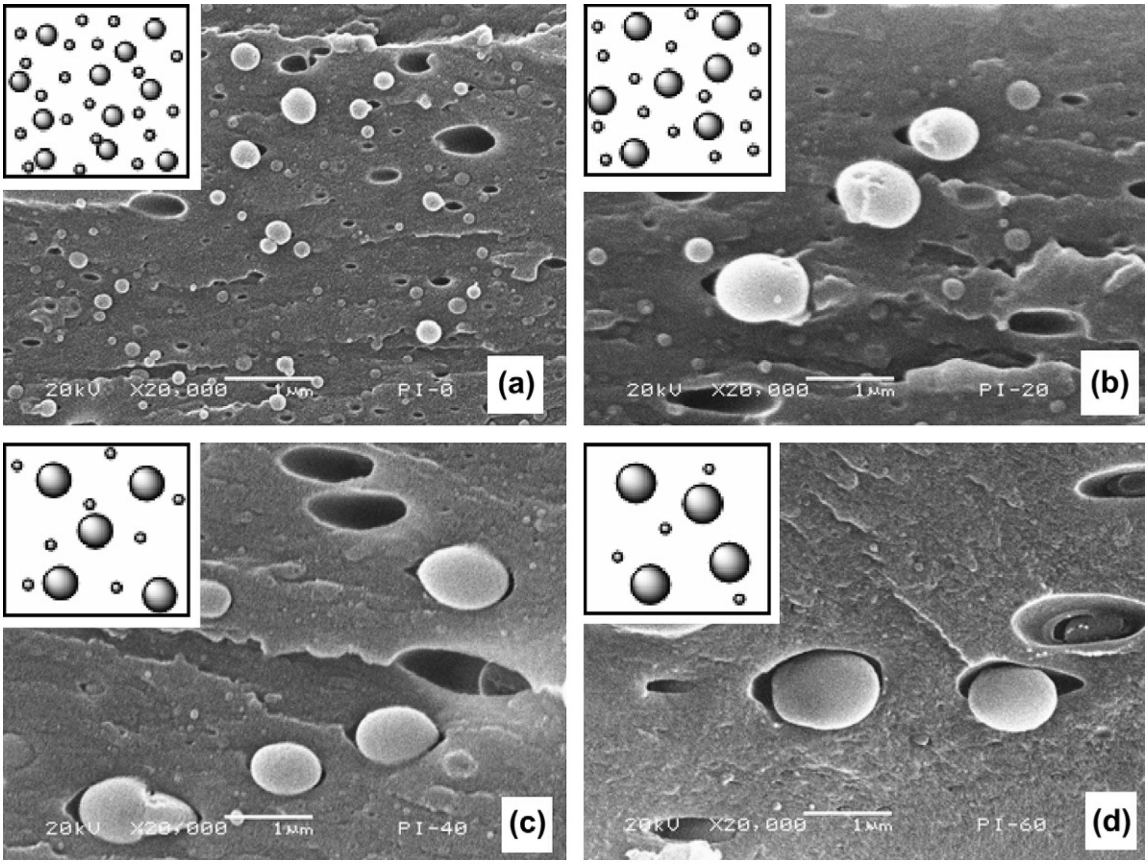


Fig. 5. SEM photographs of the PI(ODPA/ODA)/SiO_2 hybrids, cured at 300 °C (a) PAA; (b) PA-I, 27.7% imidization degree; (c) PA-I, 45.5% imidization degree; (d) PA-I, 55.4% imidization degree.

phase and condensed together to form the nano-SiO_2 particles. Our results support the overall objective to understand the phase separation of PI/SiO_2 hybrid films prepared with a sol–gel method. Moreover, the phase separation derived from the imidization reaction can be controlled with different carboxyl group contents in polymer.

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