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Synthesis and cryogenic properties of polyimide–silica hybrid films by sol–gel process

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Abstract

Polyimide–silica hybrid films were prepared from tetraethoxysilane (TEOS) and polyamic acid (PAA) via sol–gel process in the solution of *N*,*N*-dimethylacetamide (DMAc). The cryogenic mechanical and electrical properties of polyimide–silica hybrid films were studied taking into account the effects of silica content. The results indicated that the cryogenic modulus increased with the increase of silica content while the tensile strength and failure strain had a maximum value at proper silica contents. Moreover, the tensile strength and modulus of the hybrid films at cryogenic temperature (77 K) were obviously higher than those at room temperature, while the failure strain of the hybrid films was much lower at cryogenic temperature (77 K) than that at room temperature. The mean electrical breakdown strength of the hybrid films was shown to range from 151 to 225 kV/mm at cryogenic temperature (77 K).
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Keywords: Polyimide; Hybrid film; Cryogenic properties

1. Introduction

Polyimide films have been widely used in many applications because of their excellent heat resistance, stability and electrical insulating properties. Some applications, however, require further property enhancements and the desired improvements can be obtained through incorporation of inorganic micro- and nano-fillers such as silica nanoparticles. In recent years much attention has been paid to preparation of homogeneous organ–inorganic hybrid materials via the sol–gel process [1–3]. This procedure has also been utilized for the preparation of polyimide–silica hybrid materials [4–6]. So far remarkable progress has been made in synthesis of polyimide/silica composites, and it has been displayed that the mechanical and thermal properties of PI films at room temperature can be effectively enhanced by incorporation of silica particles [7–13].

On the other hand, with the rapid developments in spacecraft and superconductive cable technologies, study on cryogenic properties of PI hybrid films is of great significance [14–16]. The requirements for polyimide films in these special applications are extremely severe, and PI hybrid films with improved cryogenic mechanical and electrical breakdown properties are desired. Cryogenic mechanical behaviors of materials are generally very different from those at room temperature. The results for the mechanical properties obtained from room temperature cannot simply be transferred to the cryogenic case. Thus, it is important and necessary to study the mechanical properties at cryogenic temperature of PI/silica hybrid films for cryogenic engineering applications. So far, few studies have been carried out on the cryogenic properties of PI and hybrid films [14–17]. To our best knowledge, up to now, no literature has been reported on the cryogenic properties of PI/silica hybrid films.

In the present study, PI/silica hybrid films were synthesized via the sol–gel process, and the cryogenic mechanical and electrical properties of the hybrid films were studied. The effects of silica content on the tensile

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strength, tensile modulus, failure strain and cryogenic electrical breakdown strength of the hybrid films were discussed in detail.

2. Experimental

2.1. Materials

Pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) were chemical reagent grade and purchased from Tianjin Chemicals Co. (Tianjin, China) and further purification was done by sublimation before use. *N*,*N*-Dimethylacetamide (DMAc, analytical reagent grade) was purchased from Beijing Reagent Co. (Beijing, China) and dried over molecular sieves before use. Tetraethoxysilane (TEOS) was obtained from Tianjin Chemicals Co. (Tianjin, China) and used without further purification. Common reagents, such as hydrochloric acid and ethanol were used without further purification.

2.2. Preparation of poly(amide acid) and neat polyimide film

Poly(amic acid) was prepared from PMDA and ODA with molar ratio of 1:1 as follows: In a typical example, to a 150 ml flask were added 6.5439 g (30 mmol) PMDA, 6.0071 g (30 mmol) ODA and 70 g DMAc. The system was equipped with nitrogen inlet and mechanical stirrer. The total concentration of the reaction solution was 12 wt%. The mixture was stirred at room temperature under nitrogen for about 5 h to allow the viscosity to increase. The neat polyimide film (as reference) was prepared by casting the solution onto a glass plate. After the film had been dried at room temperature for 1 h, the film was heated at 80, 120, 150 °C for 1 h each, and at 250, 300 °C for 0.5 h each, to obtain yellow colored transparent films.

2.3. Preparation of polyimide–silica hybrid films by sol–gel process

In a flask, the different contents of TEOS were first added to a small quantity of DMAc, and a sol was obtained by slow dropping into proper water and hydrochloric acid under stirring. The sol was added to 30.00 g of 12 wt% polyamic acid solution and stirred for 6 h until the solution became homogeneous and viscous. The rest steps for preparing the PI/silica hybrid films are the same as the pure PI film, and yellow but transparent films were obtained.

2.4. Measurement and characterization

The tensile properties of PI and PI/silica hybrid films at room and cryogenic (77 K) temperature were measured by an Instron 1122 universal tensile tester at the loading rate of 2 mm/min. The dimensions of film specimens were 10 mm × 120 mm. The thickness of films was 25–39 μm, and the specimens were cut from free films. The gauge length was 50 mm. More than six samples were tested for each composition. The electrical breakdown strength of the hybrid films was measured with a 1 kV/s loading rate of voltage, and the area of the copper electrode used was ~3.14 cm^2. Scanning electron microscope (SEM) photographs of the fracture surfaces of films at cryogenic temperature were taken with a SHIMADZU SS-550 SEM.

3. Results and discussion

3.1. Process for sol–gel reaction and preparation of polyimide–silica hybrids

The sol–gel process is based on the homogeneous hydrolysis and condensation of metallic alkoxides to form a 3-dimensional inorganic network. Sol–gel process was a good method for the preparation of polyimide/silica hybrid composites, which could reduce or avoid aggregation of the silica particles in the polyimide matrix [18]. Moreover, it was reported [19] that the uniform spherical particles with a perfectly smooth surface and a uniform diameter of 100 ± 10 nm were obtained under certain concentration and hydrolysis time. Generally, the sol–gel reaction of PI/silica requires water to hydrolyze TEOS [5,20–22]. However, the existence of water might induce the hydrolysis of polyamic acid, reducing the molecular weight of the polyamic acid. Therefore, an acid-catalysis system containing a very low content of water in the sol–gel reaction was employed in our present work to avoid the possible hydrolysis degradation of polyamic acid during reaction.

In the present research, the sol–gel reaction was carried out in a solution of polyamic acid in DMAc because of the polyimide is not soluble in organic solvents. Thus, PI–silica hybrid film was prepared as follows: Polyamic acid was prepared first from PMDA and ODA in DMAc, and TEOS reacted first with water and acidic catalyst and changed into sol. The sol was added into the polyamic acid solution of DMAc, and the resulting homogeneous mixture after stirred for 6 h was cast onto a glass plate to prepare the polyamic acid–silica hybrid film, and finally the PI–silica hybrid film was obtained by heating the precursor film from 80 to 300 °C. The reactive scheme of the sol–gel process has been proposed as follows [20,21].

3.1.1. Metathesis

$$\mathrm{RCOOH + SiOEt \leftrightarrow SiOOCR + EtOH} \quad (1)$$

$$\mathrm{RCOOH + SiOH \leftrightarrow SiOOCR + H_2O} \quad (1A)$$

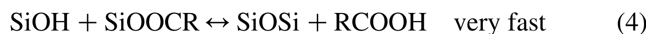
3.1.2. Esterification

$$\mathrm{EtOH + RCOOH \leftrightarrow EtOOCR + H_2O} \quad (2)$$

3.1.3. Hydrolysis

$$\mathrm{SiOEt} + \mathrm{H_2O} \leftrightarrow \mathrm{SiOH} + \mathrm{EtOH} \quad (3)$$

3.1.4. Condensation



$$\mathrm{SiOH} + \mathrm{SiOOCR} \leftrightarrow \mathrm{SiOSi} + \mathrm{RCOOH} \quad \text{very fast} \quad (4)$$

$$2\mathrm{SiOH} \leftrightarrow \mathrm{SiOSi} + \mathrm{H_2O} \quad \text{slow} \quad (5)$$

$$\mathrm{SiOH} + \mathrm{SiOEt} \leftrightarrow \mathrm{SiOSi} + \mathrm{RCOOH} \quad \text{slow} \quad (6)$$

$$\mathrm{SiOOCH} + \mathrm{SiOEt} \leftrightarrow \mathrm{SiOSi} + \mathrm{EtOOCR} \quad \text{very slow} \quad (7)$$

Many important factors influencing the kinetics of hydrolysis and condensation reaction in the sol–gel process include temperature, pH value, nature of the solvent and the type of alkoxide precursors. Hydrolysis precedes the condensation reaction, but may not go to completion prior to the onset of condensation. The relative rate of the hydrolysis to condensation reactions determines the final structure of the hybrid material. According to the literature [4], an acid-catalysis sol–gel reaction provides relatively fast hydrolysis and a slow condensation reaction. In the present research work, polyamic acid (PAA) was prepared first from PMDA and ODA in DMAc. TEOS reacted first with water and acidic catalyst and changed into sol. In this step, the hydrolysis and condensation reaction would start. The sol was added to the PAA solution, the reaction would go on to form silica particles. When the heterogeneous polyamic acid solution with TEOS became homogeneous after stirred for 6 h, the hydrolysis and condensation reaction can be considered complete in principle. Thereafter, the homogeneous mixture was cast onto a glass plate, and then was heated from 80 to 300 °C to prepare the PI–silica hybrid film by thermal imidization. In this process, the formation of silica spherical particles was completed before the imidization of polyamic acid into polyimide, and maintained unchanged form when the hybrid film was heated from 80 to 300 °C due to their heat-resistant, and the solvent lost by volatilization. Generally, the product of hydrolyzing reaction of TEOS by sol–gel process is inorganic silica gel network. Additionally, the small pore sizes associated with the silica gel may lead to a greater level of efficiency of entraining PI chains in the pores of the inorganic silica network. Moreover, the slow condensation reaction implies slow formation of the silica network, therefore, providing a favorable environment for polyimide chains being able to penetrate into the silica networks. Consequently, this would lead to improvement in their mechanical properties.

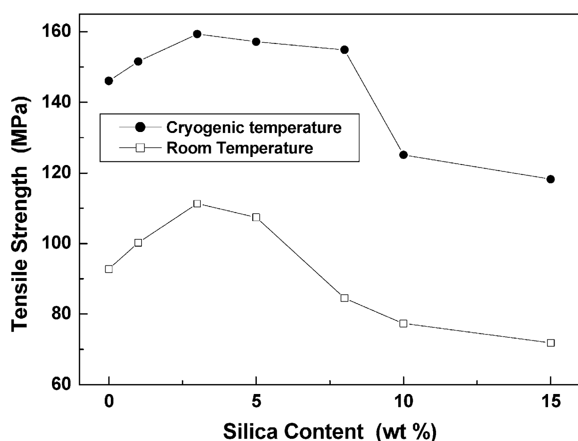


Fig. 1. Tensile strength of PI/silica hybrid films at cryogenic and room temperatures.

3.2. Mechanical properties of PI/silica hybrid films at cryogenic temperature and room temperatures

Fig. 1 shows the tensile strength of polyimide–silica hybrid films with the silica contents of 0, 1, 3, 5, 8, 10, 15 wt% at cryogenic and room temperatures. It was reported that the addition of silica particles to polyimide results in the decrease in the strength [5,22,23]. In our study, the tensile strength of hybrid films with relatively low silica content exhibited a higher level than that of the original neat polyimide film at both room and cryogenic temperatures. The increase in the tensile strength of the PI/silica hybrid composites could be caused by the strong interfacial interaction between silica and PI matrix (e.g. the formation of hydrogen bonding improved the compatibility of PI and silica [24]) and the good dispersion of silica particles in the matrix in our study to be shown later. The maximum of the tensile strength appeared at the silica content of 3 wt%. When the silica content was further increased, the tensile strength was decreased. This was likely because silica aggregations for the relatively high silica content cases would form in the matrix and these silica aggregations would lead to stress concentrations at the silica/PI interfaces.

As illustrated also in Fig. 1, the tensile strength of the hybrid films at cryogenic temperature (77 K) was obviously higher than that at room temperature. On the one hand, the molecules of polyimide matrix were tightly arranged at cryogenic temperature, resulting in that the tensile strength of the hybrid films at cryogenic temperature was higher than that at room temperature. Since no coupling agent was used in this study, there is no chemical reaction between silica and PI besides hydrogen bond and van der Waals bond. On the other hand, the silica/polyimide interface adhesion has been greatly improved at low temperature due to the compressive stress at the interface caused by the different thermal expansion behaviors between silica nanoparticles and polyimide matrix and tight clamping of the silica particles by PI molecular at cryogenic temperature, also leading to a higher hybrid composite strength. It was observed that the tensile strength increased with the increase of the silica content when the silica content was less than 3 wt%, and the maximum value of the tensile strength appeared at the 3 wt% silica content. This was attributed to good dispersion of nano-sized silica particles (about

40–60 nm in diameters observed from the SEM) at low silica contents in the PI matrix leading to efficient stress-transfer. When the silica content was higher than 3 wt%, the tensile strength decreased at cryogenic temperature with increasing the silica content. This was because the size of silica particle increased with the increase of silica content and was hundreds of nanometers or sub-micrometers as observed from the SEM photographs at high silica contents while large particles would easily prick up the stress concentration in the PI/silica hybrid composites. Moreover, the PI matrix became more brittle at cryogenic temperature, easily bringing about formation of cracks and then the decrease in the composite strength.

Fig. 2 displayed the Young's tensile modulus as a function of silica content at cryogenic and room temperatures. The Young's modulus of the hybrid films monotonically increased with increasing silica content at both cryogenic and room temperatures. This was because the Young's modulus of silica particle was much higher than that of PI matrix. Moreover, the modulus at cryogenic temperature was higher than that at room temperature. This was mainly due to the fact that the matrix and particle moduli at cryogenic temperature were higher than those at room temperature.

In Fig. 3, the failure strain (elongation at break) of hybrid films was shown as a function of silica content, and it exhibited a higher level than that of the original neat polyimide film with the silica content of up to 5 wt% at room temperature. The maximum of the failure strain also appeared at the 3 wt% silica content. This was because that the proper amount of interfaces between the silica and PI could effectively reduce the formation of the shear zone so as to could stop the development of the shear zone to cracks, and then leading to the increase in strength and ductility at room temperature. With the increase of silica content, the failure strain exhibited a decreasing tendency at cryogenic temperature. Moreover, it could be seen that the tensile failure strain at cryogenic temperature was much lower than that at room temperature. This was because the failure of the hybrid films were controlled mainly by the matrix, and the matrix fractures in a brittle manner at cryogenic temperature while in a relatively ductile mode at room temperature. As a result, the failure strain at cryogenic temperature was lower than that at room temperature.

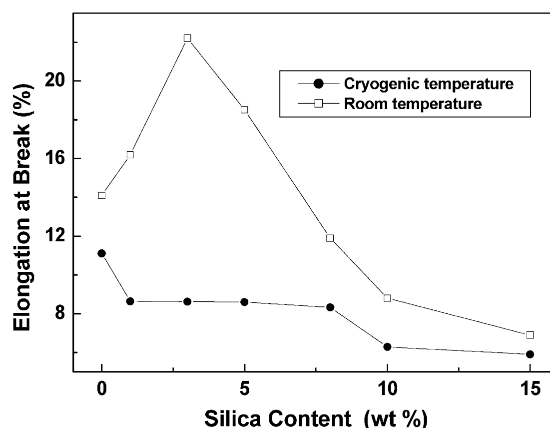


Fig. 3. Elongation at break of PI/silica hybrid films at cryogenic and room temperatures.

Moreover, it could be observed from the results when the silica content was relatively low (1–5 wt%), the failure strain of the films was more than 8%, showing usable ductility at 77 K. This indicated that the polyimide molecules could undergo deformation even if their segmental motions were frozen out at cryogenic temperatures. This observation was similar to that for other engineering plastics [25–27].

Furthermore, the results (Figs. 2 and 3) showed that the strength and ductility of PI/silica hybrid films could be simultaneously enhanced by the introduction of silica particles when the silica content was lower than 5 wt% at room temperature, while only the strength of the PI/silica hybrid films could be improved at cryogenic temperature. The improved effects might result from the interaction and

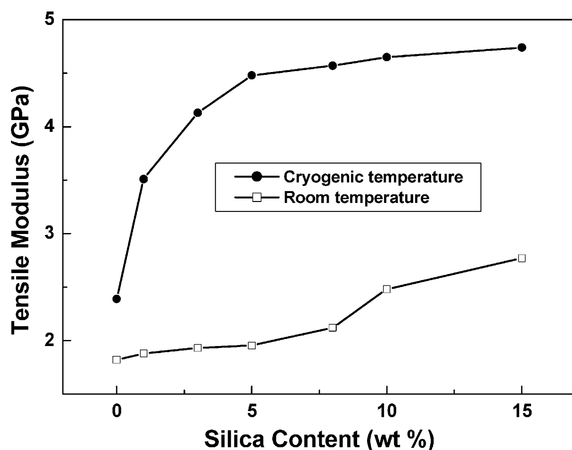


Fig. 2. Tensile modulus of PI/silica hybrid films at cryogenic and room temperatures.

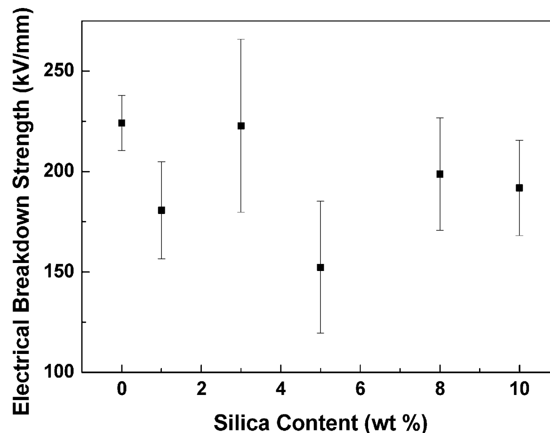


Fig. 4. Electrical breakdown strength of PI/silica hybrid films at cryogenic temperature.

the interpenetrating characteristic between PI molecules and silica, which led to the formation of the 'physical crosslink points' (here the physical crosslink points is an interpenetrating structure between silica and polyimide in which there exist silica points). As the silica content increased further, the particle aggregations appeared and their size as well as number increased, leading to the reduction in both the tensile strength and failure strain.

3.3. Electrical breakdown strength of PI/silica hybrid films at cryogenic temperature (77 K)

The electrical breakdown strength is an important parameter for selecting appropriate electrical insulation materials to avoid short circuit, especially under operation at cryogenic temperature. The electrical breakdown strength is generally dependent on temperature, specimen thickness

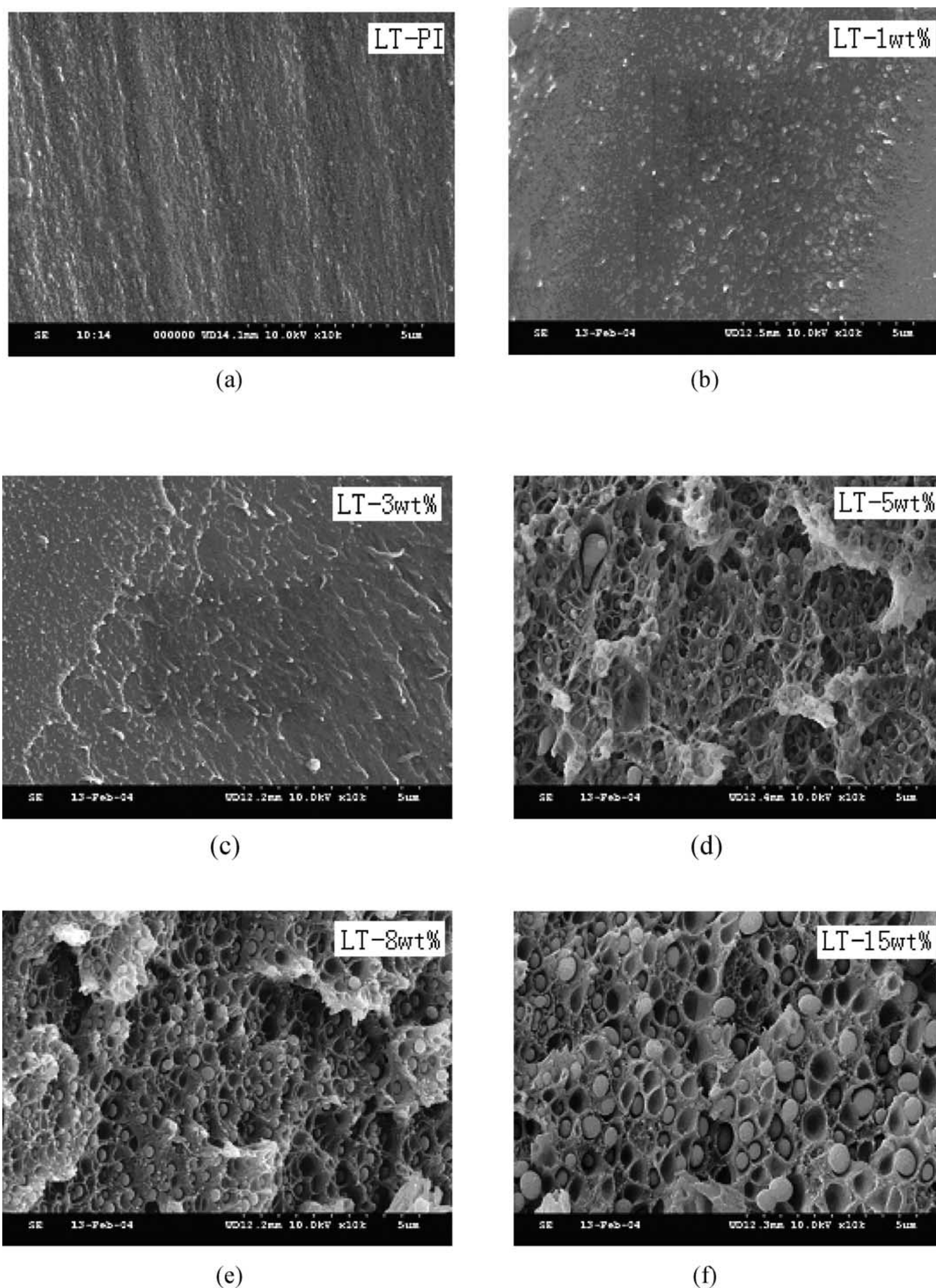


Fig. 5. SEM photographs of the fracture surfaces at cryogenic temperature (77 K) of the pure PI film (a) and the PI/silica hybrid film with 1 wt% silica (b), 3 wt% silica (c), 5 wt% silica (d), 8 wt% silica (e) and 15 wt% silica (f).

and humidity. Fig. 4 displayed the electrical breakdown strength versus silica content at cryogenic temperature (77 K). The electrical breakdown strength of hybrid films exhibited ruleless. It could be observed that the electrical breakdown strength of PI/silica hybrid films was ranged from 151 to 225 kV/mm at cryogenic temperature (77 K). This mainly depended on the characteristic of the sol–gel process. In general, the hydrolysis process of TEOS into SiO_2 was incomplete absolutely. Moreover, there are a few floating charges from carboxyl groups on the surface of silica particles formed in the sol–gel process, and could result in the decrease or fluctuation of the electrical breakdown strength at cryogenic temperature.

3.4. Morphology of fracture surfaces

In order to investigate the fracture surfaces of polyimide/silica hybrid films at cryogenic temperature, the morphology of the PI–silica hybrid films was studied using scanning electron microscopy (SEM). Fig. 5 showed the morphologies of the fracture surfaces of the samples (with the silica content of 0, 1, 3, 5, 8, 15 wt%) at cryogenic temperature. The unfilled samples exhibited characteristically smooth surfaces representative of failure in a homogenous material. It could also be observed that, the size in diameters of silica particles increased with the increase of silica content in the hybrid films from about 40–60 nm (as observed from the SEM of 1–3 wt% hybrid films) to sub-micrometers (as observed from the SEM of 5–15 wt% hybrid films). There was better compatibility between smaller silica nanoparticles and PI in the hybrid films with lower silica contents such as 1 and 3 wt%, and the strength of hybrid films can be improved. Moreover, the poor interface compatibility between silica particles and PI as well as the discontinuity of PI matrix appeared more seriously with the increase of silica content. Furthermore, bigger silica particles would more easily lead to easier crack propagation in the PI matrix. It followed that increasing silica concentration would bring about increased reduction in strength and ductility at cryogenic temperature for the high silica content cases.

4. Conclusions

PI/silica hybrid films with various silica contents were synthesized by sol–gel process. The silica content significantly influenced the tensile properties of PI/silica hybrid film at cryogenic and room temperatures. Results revealed that the tensile strength and ductility of PI/silica hybrid films could be simultaneously enhanced by the introduction of silica at room temperature and only the strength of the PI/silica hybrid films could be improved at cryogenic temperature when the silica content was less than 5 wt%. The tensile modulus of hybrid films monotonically increased with the increase of silica content. The tensile strength and modulus of the hybrid films at cryogenic temperature (77 K) were obviously higher than those at room temperature, while the failure strain at cryogenic temperature (77 K) was much lower than that at room temperature. It was observed that there was an optimal amount (3 wt%) of silica particles in the hybrid films, corresponding to the maximum tensile strength at both cryogenic and room temperatures. SEM photographs indicated that the size of silica particles increased with further increasing silica content, leading to the reduction in the strength and ductility.

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