Formation of Interconnected Globular Structure of Silica Phase in Polyimide–Silica Hybrid Films Prepared by the Sol–Gel Process

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Poly(amic acid) (PAA), a precursor of polyimide, derived from pyromellitic dianhydride and bis(4-aminophenyl) ether, was converted to a poly(amic acid) triethylamine salt (PAA–NEt_3) that was soluble in methanol, which is a common solvent used in the sol–gel processing of silica. Tetramethoxysilane was hydrolyzed and condensed in a methanol solution of PAA–NEt_3. Films were cast from the resulting mixtures, and the solvent was evaporated at 20 or 60 °C. Finally, the polyimide–silica hybrid films were obtained by heating the precursor films to 300 °C. The hybrid films containing up to 50 wt % silica were self-standing and transparent. The formation of an interconnected globular structure of silica with uniform diameter was confirmed by scanning electron microscopy (SEM). This is in contrast to hybrid films previously prepared by the sol–gel reaction of tetraethoxysilane in a *N,N*-dimethylacetamide (DMAc) solution of PAA that had dispersed silica particles with average diameters of approximately 5 μm. The diameters of the silica spheres were 0.2 and 0.08 μm when hybrid films prepared using methanol as the solvent were dried at 20 and 60 °C, respectively. According to the results of dynamic mechanical analysis (DMA), the storage modulus became larger, and the decrease of the modulus at the glass transition temperature (T_g) was reduced by increasing the silica content in the hybrid films. A single peak corresponding to the glass transition temperature of the polyimide was observed in the tan δ spectra. The intensity of the maximum peak was lower for the films prepared by the low-temperature drying method than the peaks exhibited by the films prepared with high-temperature drying. The hybrid films in the present study showed higher storage modulus values, a reduction in the decrease of the glass transition temperature, and lower tan δ maximum intensities as compared to the films previously prepared with DMAc that contained the same amount of silica.

Introduction

Preparation of new hybrid materials composed of inorganic metal oxides and organic polymers by using sol–gel processes has been addressed from the viewpoint of formation of molecular composite materials. A fascinating point of this technology is that metal alkoxides, which are starting materials of the sol–gel process, are organic compounds and are soluble in organic solvents. The sol–gel process consists of the hydrolysis of the metal alkoxide, followed by the polycondensation of the hydrolyzed products. Thus, theoretically, organic–inorganic hybrid materials can be prepared by using the sol–gel process in a solution of organic polymers. In fact, the hybrid materials of silica (silicon dioxide) and polymers have been prepared from tetraalkoxysilane and polymers such as poly(oxytetramethylene,[1–4] poly(oxyethylene),[5] sodium poly(4-styrenesulfonate),[6] perfluorosulfonic acid ionomer,[7,8] poly(ether ketone),[9] poly(dimethylsiloxane),[3,10,11] polysiloxane elastomers,[12–17] polyoxazoline,[18,19] and polyimides.[20]

In a previous paper, we reported the preparation of the polyimide–silica (PI–SiO_2) hybrid materials starting from tetraethoxysilane (TEOS) in the *N,N*-dimethylacetamide (DMAc) solution of poly(amic acid) (PAA, a precursor of polyimide), which was prepared from pyromellitic dianhydride and bis(4-aminophenyl) ether, followed by heating at 300 °C to convert the PAA into polyimide.[21] This process made hybrid films that were fairly tough even when they contained 70 wt % of inorganic silica. This silica was observed as individual particles with diameters

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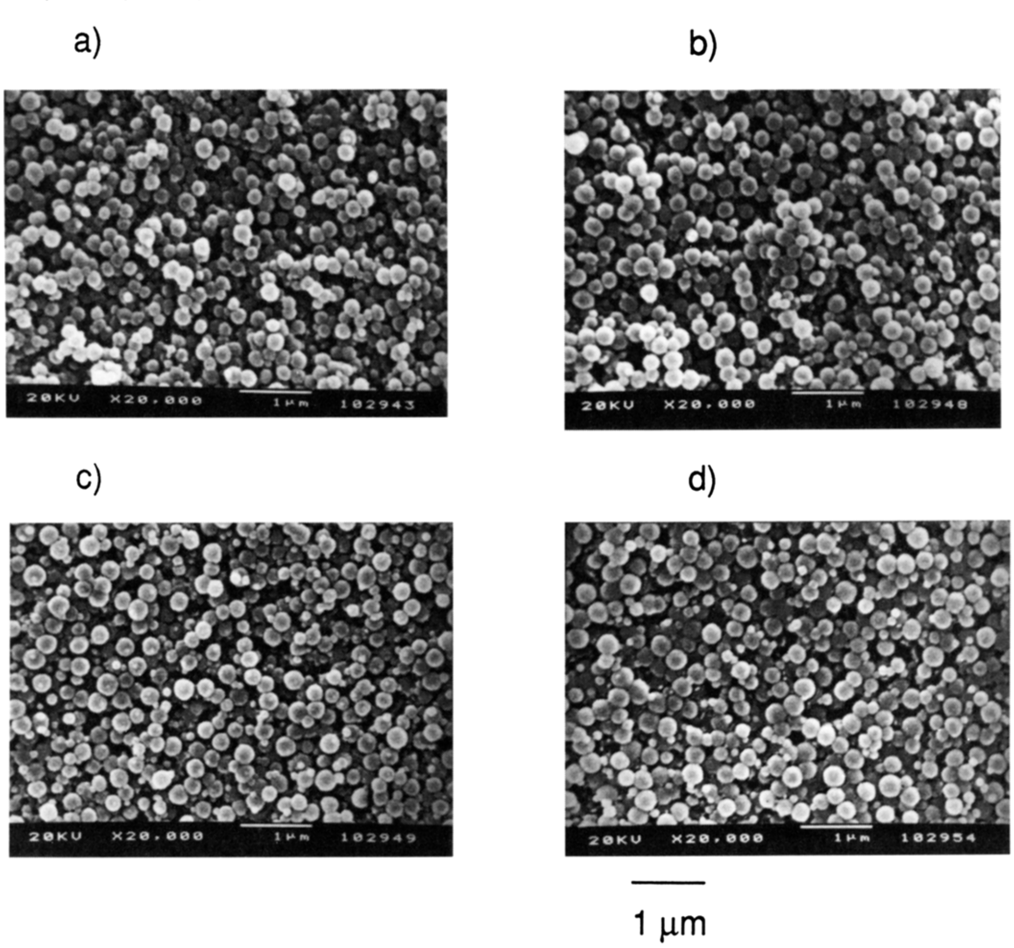

Figure 1. SEM photographs of polyimide-silica hybrid films cured at 800 °C. (a–d) Hybrid films containing 10, 20, 30, and 40 wt % of silica, respectively.

of 2–10 µm by means of a scanning electron microscope (SEM). Dynamic mechanical analysis indicated poor adhesion between the silica particle and the matrix polyimide. This fact was theorized as the cause of the unsatisfactory mechanical properties of the hybrid films.

The morphology of two-phase systems is known to have an effect on the mechanical and dynamic mechanical properties of polymer blends.[22] In subsequent experiments, we introduced ethoxysilyl groups as the diamine monomer into the polyimide matrix to connect the silica particles with the polyimide matrix.[23] Remarkable improvement was achieved in the mechanical properties of the films. Furthermore, the particle size of silica could be controlled by changing the quantity of ethoxysilyl group in the polyimide matrix.

In this paper, we report a new system of the preparation of PI–SiO_2 hybrid films by using methanol as the solvent. This process also controls the morphology of the silica phase by changing the solvent of the hybrid films. To avoid the problems encountered previously with preparing these films in methanol, a methanol soluble polyamic acid triethylamine salt was used instead of free polyamic acid.

Experimental Section

Scanning electron microscope photographs were obtained from both a JEOL-T220 and a Hitachi P-800 instrument. Dynamic mechanical analysis (DMA) was performed with a Toyoseiki Rheolograph Solid at 10 Hz using a heating rate of 3 °C/min.

Tetramethoxysilane (TMOS) was obtained from Shin-etsu Chemical Co. and was used without further purification. Pyromellitic dianhydride (PMDA, **1**) and bis(4-aminophenyl) ether (ODA, **2**) were purified by sublimation before use. DMAc was distilled over calcium hybride under reduced pressure. Methanol and triethylamine were used as received.

Preparation of a Methanol Solution of Poly(amic acid) Triethylamine Salt. First, PAA (**3**) was prepared from 4.00 g (20 mmol) of **2** and 4.36 g (20 mmol) of **1** in 80 mL of DMAc as described in the literature.[27] To the solution of PAA in DMAc was added 6.06 (60 mmol) of triethylamine, and the mixture was stirred for 4 h at room temperature. The homogeneous solution obtained was slowly added into 1.5 L of THF, and the precipitate was collected by filtration. PAA–NEt_3 (**4**) thus obtained was dried under reduced pressure and then dissolved in methanol at a concentration of 9.2 wt % for further use in the sol–gel procedure.

Typical Procedure for PI–SiO_2 Hybrid Films. In a sealed flask, 1.80 mL of TMOS and 1.00 mL of water were added to 13.5 g of the 9.2 wt % solution of **4** as prepared above. The mixture soon became homogeneous, and was kept for 24 h in a sealed flask. Films were prepared by casting the solution onto glass plates. After drying at 20 or 60 °C, the films were heated at 100 °C for 1 h, at 200 °C for 1 h, and finally at 300 °C for 1 h to obtain the PI–SiO_2 hybrid film.

In the thermogravimetric analysis, the obtained hybrid film was stable until 500 °C.

Results and Discussion

The PI–SiO_2 hybrid films were prepared as shown in Scheme 1. The poly(amic acid) (PAA) obtained from pyromellitic dianhydride and bis(4-aminophenyl) ether

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Scheme 1

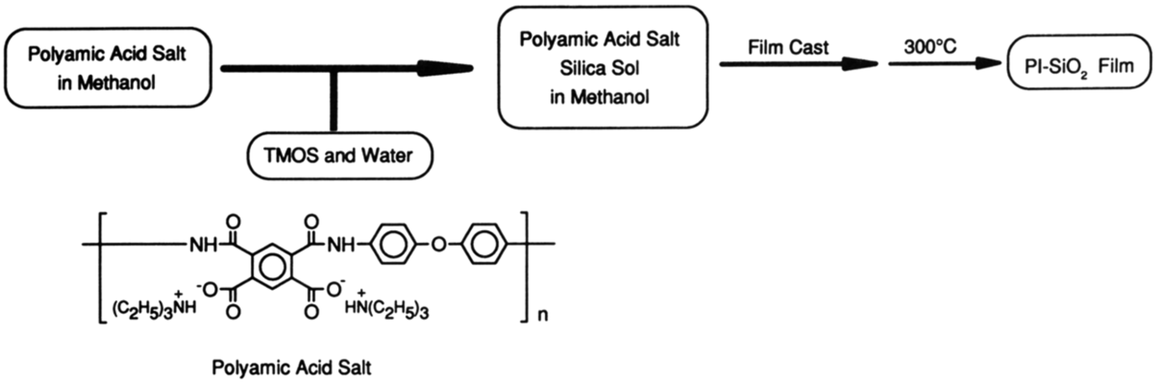

Table 1. Preparation of Polyimide–Silica Hybrid Films

poly(amic acid)-triethylamine salt[a] (g)	H_2O (mL)	TMOS (mL)	silica content[b] (wt %)
13.5	1.0		
13.5	1.0	0.20	10
13.5	1.0	0.50	20
13.5	1.0	0.77	30
13.5	1.0	1.20	40
13.5	1.0	1.80	50

[a] Poly(amic acid)triethylamine salt was dissolved in methanol at a concentration of 9.2 wt %. [b] Silica content was calculated under the assumption that the sol–gel reaction proceeded completely.

in DMAc was mixed with triethylamine, which was an amount equimolar to the carboxylic function. The resulting mixture was poured into tetrahydrofuran (THF) to isolate the poly(amic acid) triethylamine salt (PAA–NEt_3). Tetramethoxysilane (TMOS) was reacted with water in the methanolic solution of PAA–NEt_3 at room temperature. This reaction was carried out in a sealed apparatus to prevent the evaporation of methanol. Initially a clear homogeneous solution was obtained with the solution becoming slightly opaque at about 4 h. After the reaction mixture was allowed to stand for 24 h, a film of the PAA–NEt_3–SiO_2 mixture was prepared by casting the solution onto a glass plate. The film was dried at 60 °C, and then the free-standing film was cured at 300 °C to convert the PAA–NEt_3 into polyimide.

Table 1 summarizes the preparation methods of the PI–SiO_2 hybrid films. The silica content in the table denotes the values calculated using the assumption that the sol–gel reaction proceeded completely. It was remarkable that all films were transparent and uniform, whereas the hybrid films prepared previously by using free PAA and TEOS in DMAc were transparent only in case of the films of less than 10 wt % silica content.[21] The present hybrid films having silica contents up to 50 wt % were obtained as self-standing films, while those of over 50 wt % silica content were too brittle to be self-standing.

As mentioned in the previous article,[21] the expected quantity of silica can be obtained with complete thermal decomposition of polyimide when the hybrid films were heated at 800 °C in air. It is interesting to note that in the present case, a self-standing white film of silica could be obtained from the hybrid film having silica content of 40 wt %. The SEM photograph (Figure 1) of the cured silica film showed the fine uniform globules with a diameter of 0.2 μm, whose size was independent of the silica content in the hybrid films. This behavior differs from the behavior observed in the hybrid films prepared previously with a DMAc solution of PAA,[21] where the silica particle size increased with increasing silica content. Furthermore, the silica particles in the new system were interconnected. The connected-globule structure implied that the interconnected spherical domains were dispersed regularly in the polyimide matrix. In the present case, however, it is difficult to rule out the possibility that formation of the globule structure was caused by exposing the films to 800 °C to decompose the polyimide matrix. Next, the matrix polyimide in the hybrid films was removed by hydrolysis with hydrazine hydrate. As shown in Figure 2, the same interconnected globular structure was observed with the same size silica globules. This fact suggested that the

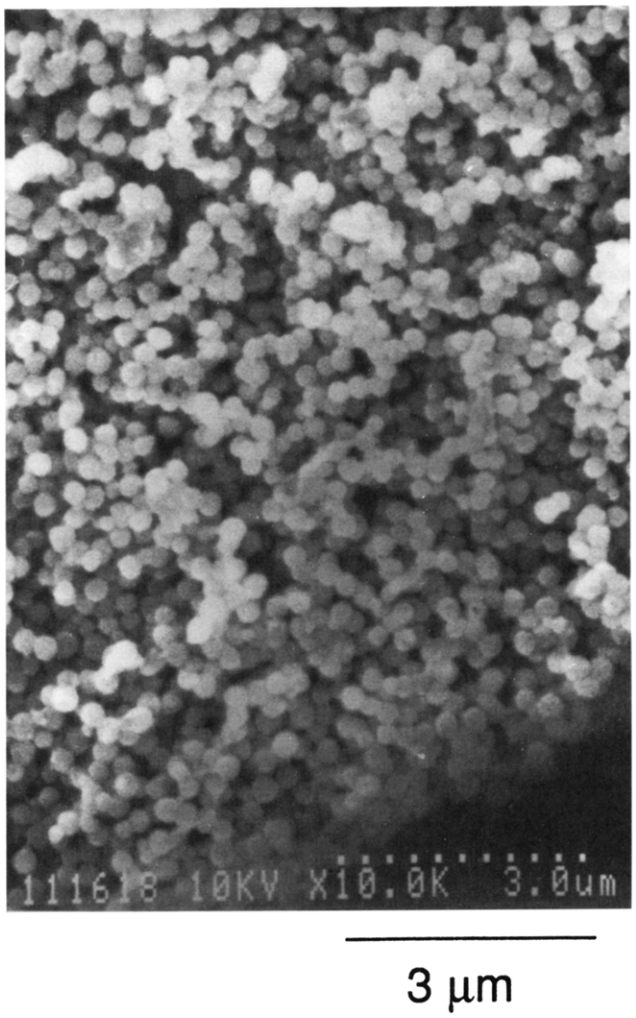

Figure 2. SEM photograph of scanning electron microscope of polyimide–silica hybrid film (silica content 40 wt %) treated with hydrazine hydrate.

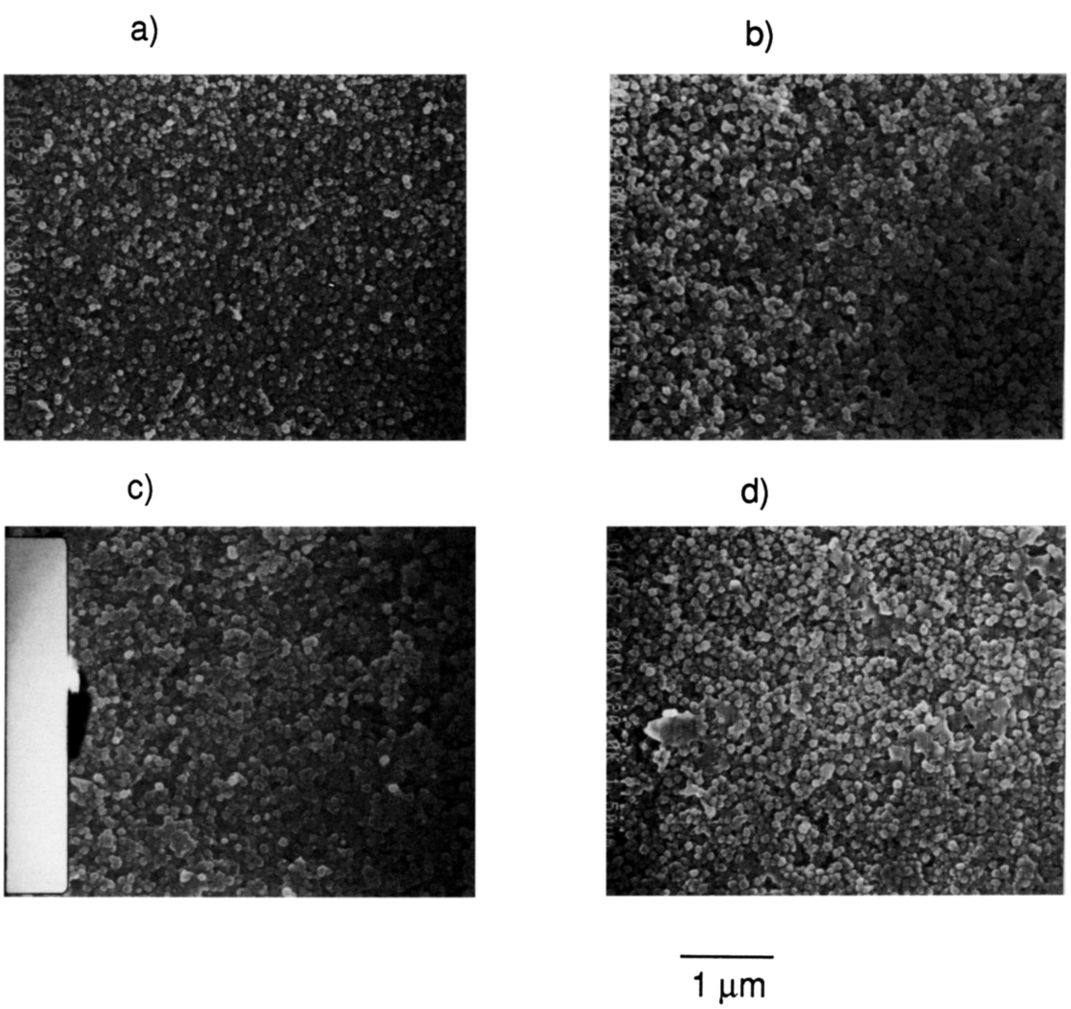

Figure 3. SEM photographs of scanning electron microscope of polyimide–silica hybrid films prepared by low-temperature drying process. (a–d) Hybrid films containing 10, 20, 30, and 40 wt % of silica, respectively.

hybrid films morphology was retained even after oxidation at 800 °C. Another such interconnected globular structure was reported in the epoxy resin and poly(ether sulfone) system, where the formation of the morphology was explained as a reaction-induced phase separation.[24] Since the silica existed in an expanded state in the methanol solution of PAA-NEt$_3$, the sol–gel reaction induced phase separation by spinodal decomposition to form a cocontinuous structure.

When the films of PAA-NEt$_3$ containing silica were dried at 20 °C instead of 60 °C and then treated as described above to convert to the PI–SiO$_2$ hybrid films, the size of the globules was only 0.07 μm as shown in Figure 3. The interconnected globular structure was also observed in films made with a drying temperature of 20 °C. According to the theory described by Inoue,[24] the metastable cocontinuous structure of the silica phase turned into the connected globular structure because of an increase of interfacial instability with the evaporation of the solvent. In this case, the formation of globules occurred with self-similar growth, and fine uniform particles were observed in the SEM photographs. The reason why the hybrid films possessed larger globules at 60 °C compared with the case of 20 °C can be explained by increased molecular mobility of the silica. Thus, it was possible to control the size of silica globules by altering the drying temperature.

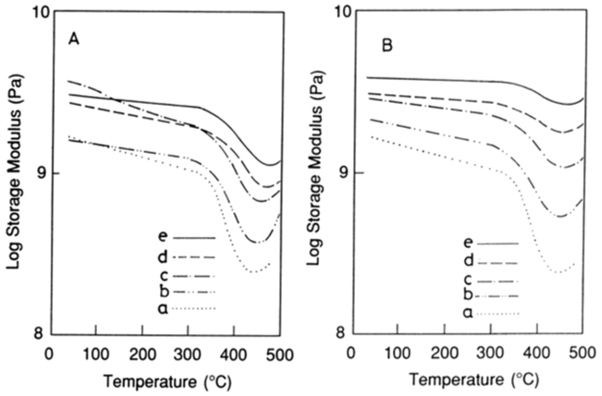

Figure 4. Dynamic mechanical analysis (storage modulus) of polyimide–silica hybrid films. (A) Solvent evaporated at 60 °C (high-temperature drying method). (B) Solvent evaporated at 20 °C (low-temperature drying method). In both spectra (A) and (B), (a–e) hybrid films containing 0, 10, 20, 30, and 40 wt % of silica, respectively.

Figure 4 shows the curves of the storage modulus measured by DMA for the films prepared with different drying temperatures. A glassy plateau region below 350 °C was followed by a transition region of decreasing storage modulus. As the silica content in the hybrid films increased, the values of the storage modulus became larger, and the decrease in the loss modulus at the glass transition temperature (T_g) was reduced. In the tan δ spectra (Figure 5), a single peak corresponding to T_g of the polyimide was

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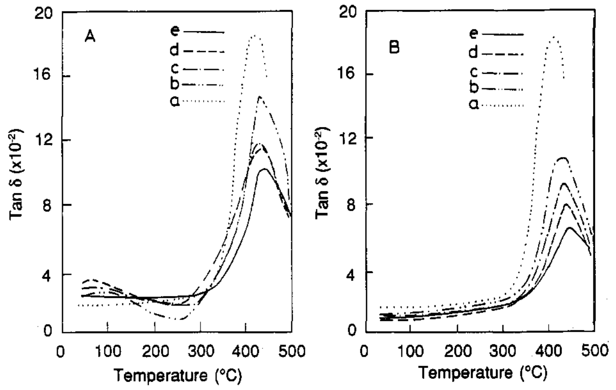

Figure 5. Dynamic mechanical analysis (tan δ) of polyimide–silica hybrid films. (A) Solvent evaporated at 60 °C (high-temperature drying method). (B) Solvent evaporated at 20 °C (low-temperature drying method). In both spectra (A) and (B), (a–e) hybrid films containing 0, 10, 20, 30, and 40 wt % of silica, respectively.

observed. The intensities of the maximum peaks decreased with increasing silica content in the films. The hybrid films in the present study, when compared to films made with a DMAc solution[21] of equal silica content, showed higher values for the storage modulus, a smaller decrease in glass transition temperature, and lower intensities of the tan δ maximum. The hybrid films prepared by the low-temperature drying method possessed higher storage modulus, and lower intensities of the maximum peak in the tan δ spectra than films prepared with elevated drying temperatures. The DMA results indicate that mobility of the polyimide molecule in the hybrid films made with the methanol solutions was more restricted because of expansion of the silica phase[25,26] than the polyimide in the films made by using DMAc.

In conclusion, the morphology of the PI–SiO_2 hybrid films was controlled by solvent selection. In the present study, the PI–SiO_2 hybrid materials were prepared by the sol–gel reaction of TMOS in the methanol solution of PAA–NEt_3. It was found that the silica phase in the films had a unique interconnected globular structure with particles of uniform diameter. The size of the silica globules was controlled by the drying temperature of the cast films. The effects of the interconnected globular structure on the physical behavior of the films were clearly observed in the dynamic mechanical analysis.

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