

THE EFFECT OF SILICA MORPHOLOGY ON PROPERTIES OF PVA/SILICA NANO-COMPOSITES*

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Abstract Two kinds of poly(vinyl alcohol) (PVA)-silica composites were prepared with different methods. One composite was prepared by directly mixing PVA with 80 nm silica nano-particles which were made from tetraethoxysilane (TEOS). The another was obtained by the mixing PVA and hydrolyzed TEOS in the presence of acid-catalyst. The properties of the two PVA/silica hybrids were characterized by means of scanning electron microscopy (SEM), UV-Visible spectroscopy, solubility tests, limiting oxygen index (LOI) test, tensile test and dynamical mechanical analysis (DMA), respectively. The results indicate that PVA-TEOS composites (PT for short) display more transparency than PVA-silica nano-particles hybrids (PS for short). At the same time, The PT composites presented more excellent performance than PS in water resistance, fire resistance and mechanical properties. Moreover, the T_g of PT increased with increasing TEOS content, while that of PS decreased.

Keywords: Silica; Poly(vinyl alcohol); TEOS; Network; Nano-composite.

INTRODUCTION

Organic-inorganic hybrids are very important and widely used in various fields as they combine the desirable properties of the inorganic part (thermal stability, rigidity) with that of the organic part (flexibility, formability, toughness)^[1, 2, 3]. In recent decades, polymer-silica hybrids with enhanced thermal and mechanical properties^[1, 4, 5], better flexibility and a variety of tailored properties have attracted lots of interest for various applications such as adsorption^[6], pervaporation^[7, 8], nonlinear optical materials^[9], catalysis^[10], sensors^[11] and enzyme encapsulation^[12].

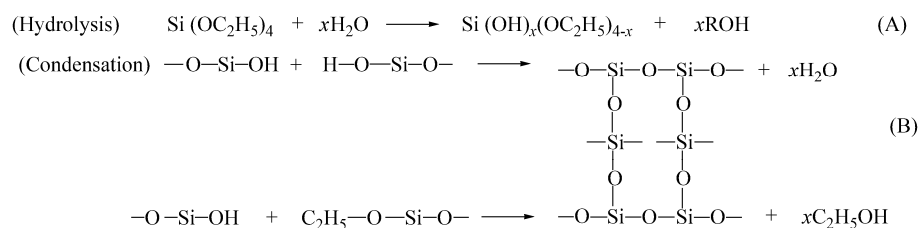
Sol-gel reactions have been extensively studied for over three decades as a method to prepare ceramic precursors and inorganic glasses at relatively low temperature. This technique has attracted more and more attention because of the convenience for preparing polymer composites. In the past three decades, the sol-gel process was used to create novel inorganic-organic composites materials^[5, 13, 14]. The sol-gel reactions could be presented in two steps^[8] (hydrolysis and condensation) as shown in Scheme 1. In the first step TEOS was hydrolyzed in the presence of a catalyst (A), and silanol groups were formed. Then these resulting silanol groups yielded siloxane bonds due to the dehydration reaction (B) with other silanol groups or ethoxy groups. In the presence of basic catalyst (ammonia), the silanol groups would mostly be condensed which got a three-dimensional network to obtain a silica particle^[15]. However in the presence of acid catalyst and in low temperature environment only a small number of silanol groups would be condensed and most silanol groups kept intact and then to form a linear polymeric silica rather than a spherical rigid particles.

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**Scheme 1** Hydrolysis and condensation reaction for TEOS

Nakane *et al.*^[16] and Uragami *et al.*^[8] have prepared the PVA-silica composites by sol-gel method. They mixed TEOS and PVA together to obtain the composites and discovered that the hybrids had increased T_g and enhanced density with a certain amount of TEOS but depressed properties in the presence of excess TEOS. The author considered that the loading TEOS acted as cross-linking component made the composite denser, while the excess TEOS would tend to form bigger silica sol particles to damage the properties of composites. But there wasn't a systematic research to compare the two states of silica in the same content in these composites. Thus, in this study, two poly(vinyl alcohol) (PVA)-silica composites were prepared with different structure of silica. One was prepared by mixing silica particle directly with PVA solution. The another one was obtained by mixing hydrolyzed TEOS with PVA solution. The relationship between the structure of the two PVA/silica hybrid membranes and their various different properties were discussed in detail.

EXPERIMENTAL

Materials

Tetraethoxysilane (TEOS) was obtained from Kermel Chemical reagent plant (Tianjin, China) and used without further purification. Poly(vinyl alcohol) (PVA) was 88% hydrolyzed with an average polymerization degree of 1700 (SINOPEC Sichuan Vinylon Works). Hydrochloric acid (38%), ammonia (28%) was purchased from Shantou Xilong Chemical Co., Ltd and used as received.

Synthesis of Silica Nano-particles and TEOS Hydrolysis Solution

Tetraethoxysilane (4.2057 g), 48.74 g of ethanol, 4 g of deionized water and 1 g of ammonia were mixed together and then the reaction was maintained at 40 °C for 24 h with continuous agitation. The silica nano-particles aqueous solution was obtained after washing the above mixture five times with deionized water by centrifugation.

To prepare the TEOS hydrolysis solution, TEOS (5 g) and 10 g of ethanol were mixed together first. After that, hydrochloric acid (1 mol/L) was added slowly into the mixture to adjust the PH to 3. And then the mixture was maintained at 0 °C for 48 h in refrigerator to obtain the TEOS hydrolysis solution.

Preparation of PVA-Silica Nano-composites

The hybrid films of PVA-silica nano-composites were prepared by a direct solution mixing method. The solution mixing method included two steps. The first step was to obtain the "solution" containing filler (silica & TEOS) and the polymer solution. And the second step was to mix the "solution" with the polymer solution, followed by the controlled evaporation process to fabricate the hybrid films.

Step 1: The filler solution had been obtained above. The polymer solution was prepared as follows. PVA was washed several times with deionized water and dried before used to remove impurities. 2 g of washed granular PVA and 40 g of deionized water were added to a flask, and then stirred for 2 h at 85 °C until PVA was dissolved completely to form a polymer solution.

Step 2: The preparation of PVA-silica nano-composites (PS for short) and PVA-TEOS composites (PT for short) is shown as follows. The silica dispersion and TEOS hydrolysis solution from the above step were sonicated for 10 min before used. A certain amount of silica solution and hydrolyzed TEOS solution were added slowly to the PVA solution respectively at ambient temperature until homogeneous and transparent solutions

were obtained. The above PS and PT solutions were placed in vacuum oven at 40 °C to remove the bubbles. And then the mixtures were poured into a self-developed mold and placed in an oven at 60 °C for 12 h to obtain the PS and PT films. After that the films were kept at room temperature for 48 h to ensure the solvent was fully evaporated. The thickness of the obtained nano-composite films were about $100 \pm 10 \mu\text{m}$. The content of silica based on the polymer matrix was varied as 1%, 2%, 5%, 10%, 20% and 30%. PS30 mentioned below indicates a PVA-silica nano-composite with 30% silica content. The silicon content in hydrolyzed TEOS solution was consistent with that in silica solution. It means that the PT30 has the same silicon content as PS30.

Characterization of Samples

The thickness of the films was measured by a micrometer screw-gauge at 5 different positions of each film. The transmittance of the hybrid composite films was quantified with a UV-Visible spectrophotometer (UV 1600 Shimadzu) in the wavelength range from 300 to 800 nm at room temperature.

Morphology of the films and distribution of nano- SiO_2 particles was observed by scanning electron microscopy (SEM) using a JSM-5900LV instrument operated at an acceleration voltage of 5 kV. The films were fractured in liquid nitrogen.

Weight loss of each sample was determined by a gravimetric method. The test piece was dried before and weighed (W_a), then it was impregnated in water at 25 °C for 24 h. After that, dried off the sample and weighed it again (W_b). The weight loss of the films ($W\%$) was determined by the equation:

$$W\% = \frac{W_a - W_b}{W_a} \times 100\%$$

The limiting oxygen index (LOI) of each sample was determined by a test method for flammability of rigid cellular plastics. The samples were set in dimensions of 5 cm $\times$ 15 cm $\times$ 0.1 cm. Adjust the oxygen content and record the oxygen index when the sample blazed to a designed scale in 2 min rightly.

An Instron universal testing machine was used to evaluate the tensile properties under a crosshead speed of 5 mm/min. At least five samples were characterized for each measurement and the reported stress-strain curves represented an average result.

Dynamic mechanical analysis (DMA) measurements were carried out on a TA Company Q800. The temperature was varied from 0 to 100 °C with the rate of 2 K/min. The frequency was 1 Hz and the amplitude of the variations was fixed to 10 μm .

RESULT AND DISCUSSION

The morphology of silica filler was characterized by SEM. Figure 1 shows the SEM micrograph of silica nanoparticles (NPs). Silica NPs having a diameter of $80 \pm 10 \text{ nm}$ and with a good size distribution have been prepared, and they are well dispersed in solvent without large aggregations. But no particles are found in the TEOS hydrolysis solution in the same magnification. It is indicated that the TEOS hydrolysis solution didn't have the big sphere rigid particles. The silica is prepared by Sol-gel method and the process of reaction is showed in Scheme 1. In step A, TEOS is hydrolyzed in the presence of a catalyst, and silanol groups are formed. In step B, these resulting silanol groups can yield siloxane bonds due to the dehydration reaction. In the presence of basic catalyst (ammonia), the silanol groups will mostly be condensed which get a three-dimensional network to obtain a silica particle^[15]. However in the presence of acid catalyst and in low temperature environment, only a small number of silanol groups can be condensed and most silanol groups are kept intact. Then linear polymeric silica is obtained, as a result, there is no big particle found under the SEM.

Since the size of silica particles is about 80 nm, while the linear polymeric silica from TEOS in the acid catalyst is invisible under the SEM, the transparency of these hybrid films must be different. To quantify the optical transparency of the PS and PT composite films, UV-Visible spectroscopic studies were performed. Figure 2 shows the percentage transmittance of the hybrid films against wavelength as observed through UV-Visible spectroscopy. From the figure, it is evident that the transmittance decreases with increasing the

amount of silica as well as TEOS. However, the reduction of transmittance in PS is larger than that in PT. The embedded figure shows the percentage transmittance at 500 nm for various films. The PT hybrid films are nearly completely transparent. The transmittance of PT hybrid films (PT5 90.85%, PT20 86.16%, PT30 85.95%) are very close to that of PVA (91.07%). While the PS hybrid films have large reduction compared with PVA, and the transmittance of PS30 is only 58.34%. It is well known that the nano particles with size greater than 100 nm can diffract light, which reduces the transmittance of composites^[17]. Although the size of silica particle is about 80 nm, the agglomeration of silica in the composite is inevitable with large loading of silica. So the PS hybrid films display a low light transmittance with high loading of silica NPs. On the contrary, PT hybrids scarcely diffract light and exhibit a high light transmittance. The results are in according with the Fig.1. In addition, the transmittance results show that the PT composites have a smaller size of filler and better dispersion.

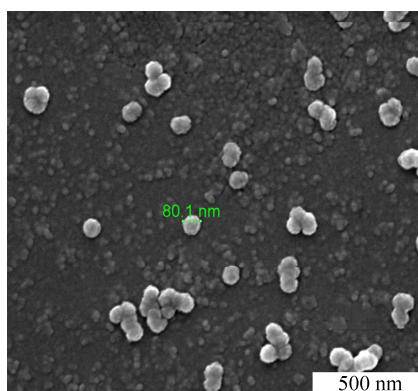


Fig. 1 SEM image of silica particles prepared by TEOS

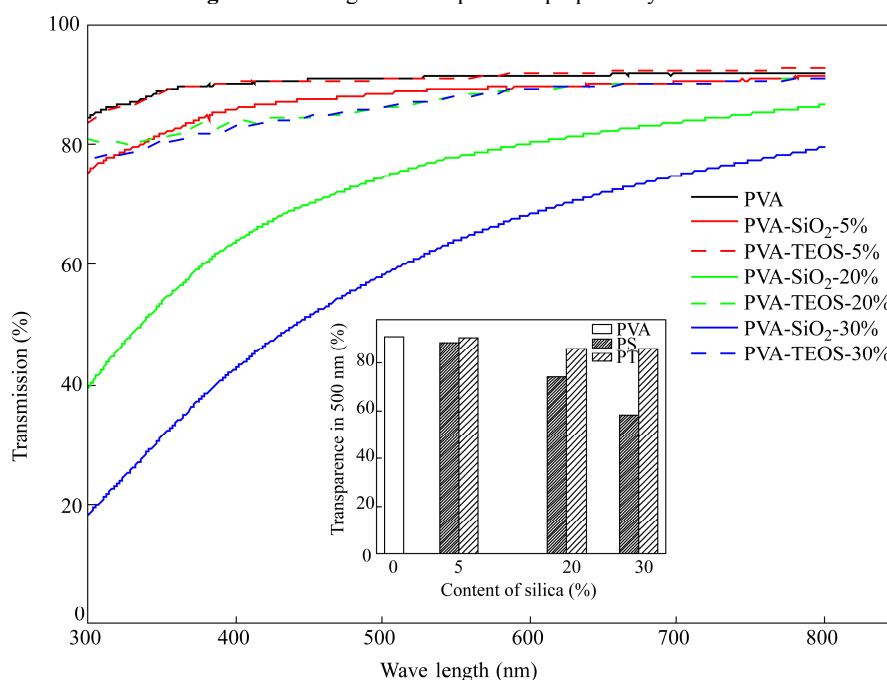


Fig. 2 UV-Visible spectroscopic results of pure PVA and PVA composite films with various amounts of silica and TEOS (The embedded figure shows the percentage transmittance at 500 nm for various films.)

The morphology of these composites was characterized by SEM. Figure 3 shows the morphology of various hybrid films after brittle failure. The morphology of PVA is smooth, while the PS and PT hybrids are out of

flatness. From the SEM of PS composites, the surface of PS composites has many convex hulls. The convex hulls are supposed to be the silica particles with PVA coated outside. It is evident that the silica dispersion in the matrix is homogenous from the figure. From the figure of PT composites, the surface of PT composites has much wrinkles rather than humps. Since the PVA has many —OH groups which can bond with silanol groups in the surface of hydrolysis TEOS. They may crosslink to form a network and the wrinkle of the surface is a receivable evidence that PT hybrid films have strong interfacial interactions between the PVA chains and TEOS. But the PS composites do not have any wrinkles from the figure. We predict that the interface of silica particles and PVA has weaker interactions compared to PT composites.

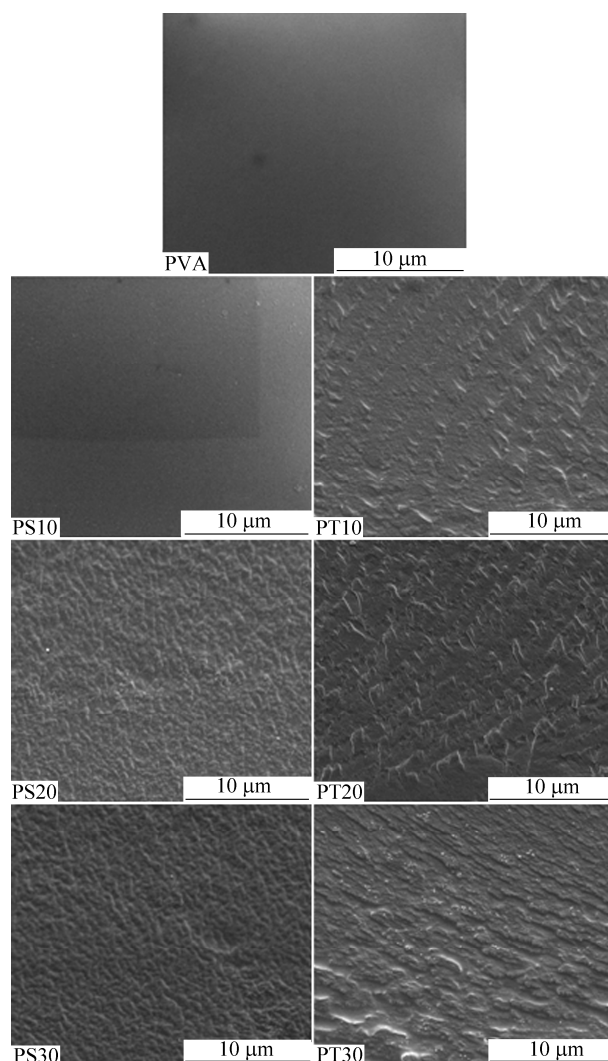


Fig. 3 The morphology of pure PVA membrane, PS10, PS20, PS30, PT10, PT20 and PT30 respectively

Since PVA has terminal —OH groups, which are easily available for bonding with silanol groups in the silica surface. The bonding can result in two types of interfacial interactions (covalent bonding and hydrogen bonding). If the hydrogen bonding is the majority of interaction, the PVA-silica hybrid film would dissolve or swell in water, whereas if covalent bonds are formed the PVA-silica composites would be rendered insoluble when exposed to water^[18]. Table 1 shows the weight loss of various composites after exposure to water for 24 h. Hybrid films all display a significant decrease in solubility with the increase in TEOS or silica content. The weight loss of PT10, PT20 and PT30 are negligibly small (5.7%, 3.8% and 1.1% by weight, respectively) while

the weight loss of PS10, PS20 and PS30 are much greater (93.6%, 77% and 42% respectively) by contrast. It may due to the formation of more hydrogen bonds between silica and PVA in the PS composites and more covalent bonds between hydrolyzed TEOS and PVA in the PT composites. The PT hybrid films are almost insoluble in water, which may be attributed to strong interfacial interactions and structure of crosslink network.

Table 1. The weight loss of various composites after exposure to water for 24 h

Content of silica (%)	Weight loss (%)	
	PS	PT
PVA	100	
1	100	100
2	100	16.68
5	100	8.2
10	93.6	5.7
20	77	3.8
30	42	1.1

The limiting oxygen index (LOI) of various composites was characterized by a test method for flammability of rigid cellular plastic. From the Fig. 4, the LOI all increase with the increment of TEOS and silica NPs. It indicates that the composites can hinder the break of molecular chain with the addition of silica as well as TEOS. But the increment of LOI in PT hybrids is much greater than that of PS hybrids which indicates that the PT composites have better fire resistance than PS composites. This may result from the covalent bonding between hydrolyzed TEOS and PVA forming a crosslink network which can strengthen the PVA chain more efficiently. Since the silica itself is nonflammable, so the LOI of PS hybrid films also increases with the increment of the silica NPs content. But the poor improvement of PS can be attributed to the weak interfacial interactions between the silica NPs and PVA chains comparing to those of PT.

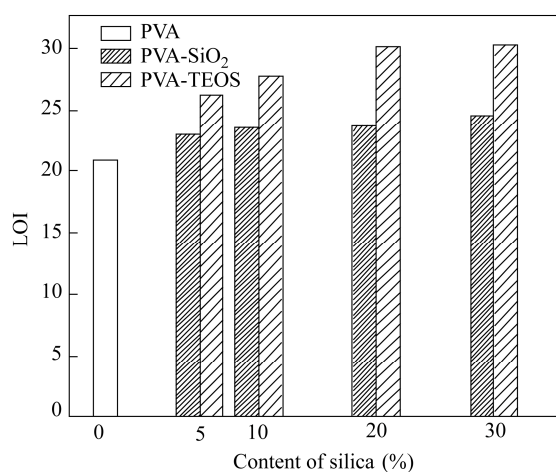


Fig. 4 The limiting oxygen index versus silica content in PS composites and TEOS content in PT composites respectively

Figures 5 and 6 show the stress-strain curves of some of the samples. PVA shows a typical curve having a yield point. The elongation at break drops dramatically by the addition of silica in PVA, and PS20 even exhibits a brittle fracture. While the elongation at break of PT composites is slightly lower compared to PVA, PT30 can maintain 96% of elongation. The entire Young's modulus of the composites increases with the increment of silica as well as hydrolyzed TEOS. Although the improvement is similar, from the results above, the strengthening mechanism is not the same. Silica spherical particle is a rigid part in the PS composites and can bond with PVA by the hydrogen bond. The loading stress on materials will transfer to silica particles and result in an increment of Young's modulus. But the silica particles tend to aggregate with increasing their content

making the elongation at break small. In the PT composites linear polymeric silica is formed. The linear polymeric silica will take part in the crosslink network with $-\text{OH}$ groups of PVA. Because of the strong interfacial interactions and network, the PT composites are enhanced. Since the network has some elasticity, the PT films have greater elongation at break compared to PS hybrids. From the figure, the PT composites have obvious strain hardening performance. It also proves that the network in PT composites makes contribution to the strengthening mechanism.

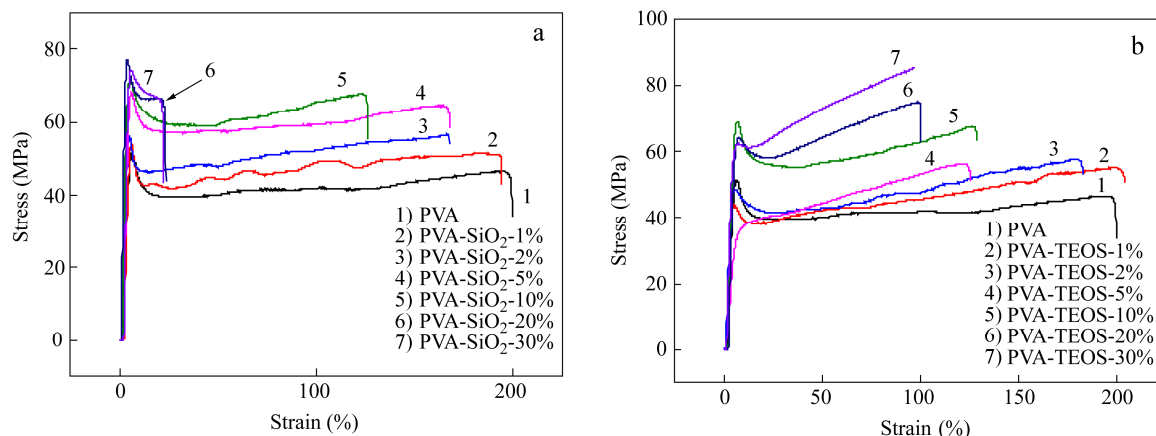


Fig. 5 The stress-strain curves of PS composites with various contents of silica (a) and PT composites with various contents of hydrolyzed TEOS (b)

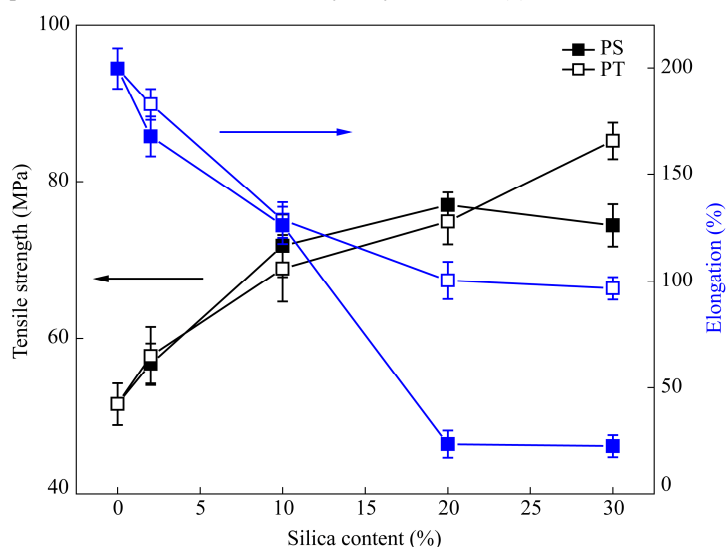


Fig. 6 The Young's modulus and elongation of PS and PT composites with various content of silica

Figure 7 shows the temperature dependence of $\tan\delta$ of the composites and pure PVA. The T_g of PVA decreases by adding silica, and the peak becomes broader. With interesting, the PT hybrids films have an increment in T_g to the contrary. The decrease in T_g upon incorporation of silica in polymer composites has been documented previously^[19, 20]. Preghenella^[19] have reported reduction in T_g with increasing content of fumed silica in epoxy nano-composites. Sun and coworkers^[20] also noticed a reduction in T_g of the silica-filled composites because of the presence of residual moisture and organic materials in the silica surface. On the contrary, owing to the strong interfacial interactions between TEOS and PVA chains as well as the network structure of silica, the PT hybrids have an increment in T_g .

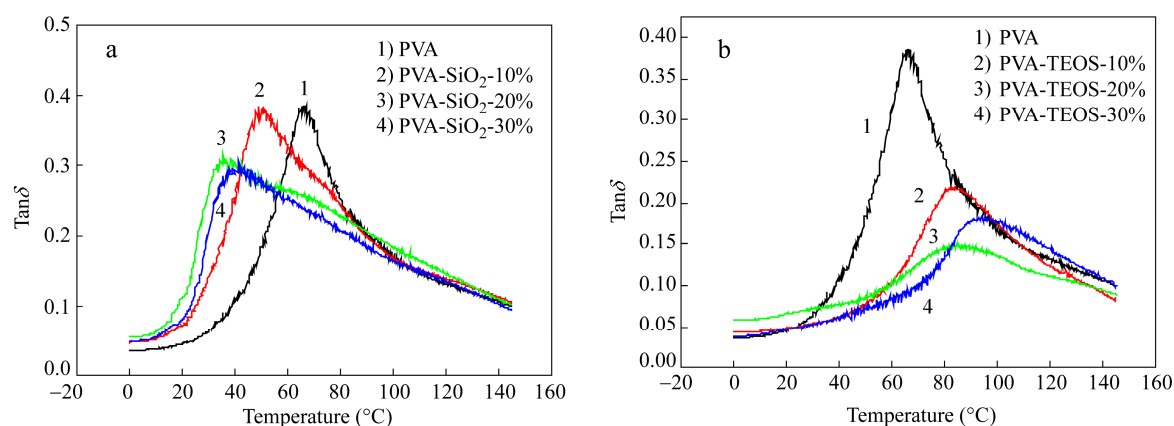


Fig. 7 The temperature dependence of $\tan\delta$ of PS composites (a) and PT composites (b)

CONCLUSIONS

In this article, two kinds of poly(vinyl alcohol) (PVA)-silica composites were prepared with different methods. The properties of the two PVA/silica hybrids were characterized by means of scanning electron microscopy (SEM), UV-Visible spectroscopy, solubility tests, limiting oxygen index (LOI) test, tensile test and dynamical mechanical analysis (DMA), respectively. The results indicate that the silica has a size of 80 nm, while the TEOS is invisible under SEM which causes that the PT composites are more transparent than PS composites. The PT composites have better water and fire resistance compared to PS composites. It may due to the network and strong interfacial interactions in the PT hybrids. The mechanical properties of these two composites reveal that the PT composites have greater elongation at break. With interesting, the T_g of composites increases with the increment of hydrolyzed TEOS content and decreases by adding silica. This may due to the network in PT composites and the residual moisture or organic materials in PS composites. Although the two hybrids are all prepared with silica, they display almost opposite performances with different structure of silica. This can propose guidance for future preparation of nano-composites.

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