

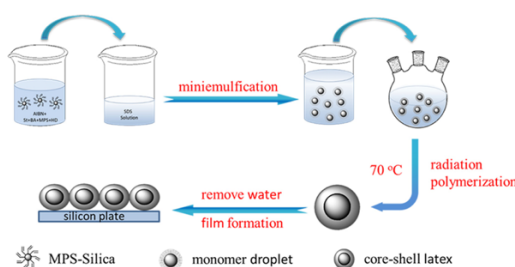
Research of the Synthesis and Film Performance of Silica/Poly(St-BA-MPS) Core-Shell Latexes Obtained by Miniemulsion co-Polymerization

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Abstract: Colloid silica nanoparticles were hydrophobic modified by γ -methacryloxypropyl trimethoxysilane (MPS) for the encapsulation into polymer. The alkoxy-silane-functionalized core-shell latexes were successfully synthesized *via* miniemulsion copolymerization of the butyl acrylate, styrene with MPS as the functional monomer in the presence of the modified silica. When these latexes dried at room-temperature, the post-cross-linking occurred due to the alkoxy-silane groups on the particle surface and lead to the formation of the films. The morphology of the nanocomposite latexes and the mechanical properties, thermal properties, fire-resistant, optical properties and micro-structure of the resulted films were characterized and discussed. Scanning electron microscope result showed most of the nanoparticles dispersed homogeneously in the polymer matrix when the content of MPS-silica was 10%. However, when the content of MPS-silica nanoparticles was beyond 10%, the aggregation of the nanoparticles became obvious. The tensile test showed that the stress at break increased a lot with the increase of silica content. The thermal and fire-resistant behaviors of the nanocomposite films were improved greatly by the incorporation of silica particles. The optical test showed that the hybrid film was comparable to the pure polymer film at around 84% transmittance.



Keywords: core-shell latex, silica, nanocomposite film, miniemulsion.

1. Introduction

In the past decades, it has been shown the presence of silica particles in polymer materials is beneficial to improve the properties of the final productions.¹⁻⁶ Silica nanoparticles are widely chosen for their excellent properties (rigidity, hardness, thermal stability, *etc.*), which is responsible for enhanced properties. Besides, the low cost of silica nanoparticles is very attractive for industrial applications compared with other nanoparticles such as carbon nanotube, graphene and *etc.* Therefore, polymer/silica nanocomposites are very attractive from industrial perspective such as coatings and adhesives.⁷⁻⁹

Among the techniques for polymer/silica nanocomposite particles synthesis, emulsion polymerization¹⁰⁻¹³ and miniemulsion polymerization¹⁴⁻¹⁹ are the most popular methods. The prepared nanocomposite latexes are main core-shell and raspberry-like structures. Wu *et al.* synthesized nanocomposite particles with different morphologies through miniemulsion polymerization by adjusting the silica size and surfactant concentration.¹⁴ Katharina Landfester reported a controllable method to synthesize silica nanocomposites with various morphologies particles.²⁰

Bourgeat-Lami and co-workers investigated the mechanism of silica encapsulated in droplets and latex particles by miniemulsion polymerization.¹⁶ However, these works are focused on theoretical research including the synthesis method and morphology control, and little attentions have been paid on the hybrid films properties of these latexes. Therefore, it is necessary to investigate the films performance to meet the demand for more industrial applications.

Recently, Liu and coworkers reported the film properties of raspberry-like polymer/silica nanocomposites *via* soap-free emulsion polymerization and the sol-gel process.²¹ They found that the film properties were improved by incorporating silica nanoparticles. The raspberry-like structure nanocomposites were also prepared by Ge and coworkers.²² They found that the mechanical and fire-retardant properties were improved with the addition of silica nanoparticles. In addition, Armes *et al.* synthesized film-forming colloidal nanocomposite particles by aqueous emulsion polymerization.²³⁻²⁵ The results showed that the transparence of the films decreased with increasing silica contents, while the fire-retardant property improved. Among these works, raspberry-like polymer/silica nanocomposite emulsions were the most used and many authors took advantage of this structure to improve the properties of the films. However, a significant problem associated with the raspberry-like nanocomposite particles is the free silica particles in the

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emulsion and it is hard to achieve high silica encapsulation efficiency, which is not conducive to the properties improvement of the prepared films. Therefore, some researchers prepared the film-forming polymer/silica nanoparticles with core-shell structure and investigated the film properties. Wu and coworkers successfully synthesized silica/poly(methyl methacrylate-co-butyl acrylate) (poly(MMA-BA)) core-shell structure latex.²⁶ The resulted film presented high transparency compared the pure polymer film. The mechanical and UV weathering resistant properties also improved significantly. Arai et al. prepared core-shell particles with silica as core and poly(MMA-BA) shell.²⁷ They found that the heat-resistance and transparency were excellent due to the reinforcement effect of the silica particles. In addition, the resulted acrylic resin showed an excellent toughness and stiffness balance.

Crosslinking chemistry provides another route to improve the properties of water-based emulsion polymers, such as mechanical properties, water repellency, solvent resistance and adhesion to inorganic substrates.²⁸ In these researches, the incorporation of alkoxy-silyl moieties into latex has been widely adopted to promote the crosslinking of the latex films. J. M. Ramos-Fernández *et al.* prepared BA, MMA, and MPS copolymer by miniemulsion method. When 10% MPS was added, the modulus of the film increased twofold respect of the reference sample.²⁹ Guo *et al.* prepared self-crosslinking poly(methyl methacrylate-co-butyl acrylate-co-styrene-co-vinyl triethoxysilane) latex film by seed emulsion polymerization. It was found that vinyltriethoxysilane improved the mechanical properties and water resistance at certain vinyltriethoxysilane contents.³⁰ Zhang *et al.* prepared MPS-functionalized poly(styrene-co-butyl acrylate) latex *via* miniemulsion copolymerization. The crosslinking improved the storage modulus and decrease the swelling ratio of the films.³¹

The poly(styrene-co-butyl acrylate) (poly(St-co-BA)) latex has been prepared and investigated in some papers. However, the influence of nano silica particles and crosslinking chemistry on the properties of poly(St-co-BA) latex film in the same preparation process has no reports. In the present paper, core-shell hybrid latexes with alkoxy-silane-functionalized poly(St-co-BA) as shell and silica as core were synthesized by miniemulsion polymerization method. The crosslinking can occur during the film formation process of the emulsion at room-temperature because of the existence of alkoxy-silane group on the shell, which can simplify the manufacturing process of the film formation and improve the stiffness, solvent resistance and adhesion to inorganic substrates of the film. The presence of nanosilica can not only enhance the mechanical property but also improve the thermal stability and fire-resistance of the films. So the combination of nano silica and crosslinking reaction is beneficial to prepare poly(St-co-BA) nanocomposites with much superior properties.

Table 1. Recipe for polymer/silica nanocomposites

| Designation | St-BA (g) | MPS (g) | MPS-SiO ₂ (g) | HD (g) | AIBN (g) | SDS (g) | H ₂ O (g) |
|-------------|-------------|---------|--------------------------|--------|----------|---------|----------------------|
| Poly(St-BA) | 16:24 | 0 | 0 | 1.44 | 0.84 | 1.2 | 160 |
| Si-0 | 15.2:22.8 | 2 | 0 | 1.44 | 0.84 | 1.2 | 160 |
| Si-1 | 13.68:20.52 | 1.8 | 4 | 1.3 | 0.756 | 1.08 | 160 |
| Si-2 | 12.16:18.24 | 1.6 | 8 | 1.152 | 0.672 | 0.96 | 160 |
| Si-3 | 10.64:15.96 | 1.4 | 12 | 1.008 | 0.588 | 0.84 | 160 |

2. Experimental

2.1. Materials

Silica aqueous dispersion was supplied by Shandong Better Company, China. MPS was purchased from Shanghai Meryer, China. The styrene (Jilin Chemistry Company) and butyl acrylate (Jilin Chemistry Company) were distilled before use. Hexadecane (HD) was purchased from Acros. Sodium dodecyl sulfate (SDS), anhydrous ethanol and acetone were supplied by Beijing Chemistry Reagents Company and used as received. Azobisisobutyronitrile (AIBN) was purchased from Shanghai Chemistry Reagent Company, China. Deionized water was used in all experiment processes.

2.2. Modification of silica nanoparticles

Colloidal silica particles were modified according to the procedure of previous work.⁴ All the reagents were added to a three-necked flask. After the pH of the dispersion was adjusted to 9.6, MPS was added to the dispersion and stirred mechanically. The stir process was continued for 24 h and then refluxed for 2 h. Finally, the mixture was centrifuged and washed five cycles to remove the unreacted MPS. The obtained MPS-silica nanoparticles were dried at 70 °C in a vacuum.

2.3. Preparation of the polymer/silica nanocomposite latexes

The nanocomposite latexes were synthesized in miniemulsion polymerization according to the previous work and the recipe as shown in Table 1.^{4,16,32} Compared with the previous work, MPS was added and poly(St-BA-MPS) copolymer was prepared, which was named as Si-0. According to the different core-shell ratios, the nanocomposite latexes designated as Si-1, Si-2, and Si-3, respectively. The MPS was covalently attached onto the silica particles by hydrolysis and condensation reactions. The MPS-silica particles carried the vinyl group, which copolymerized with St, BA and MPS during the following miniemulsion polymerization process and formed the core-shell structure of poly(St-BA-MPS)/MPS-silica nanocomposite. Besides, the pure copolymer of poly(St-BA) was also prepared. The preparation of poly(St-BA-MPS) was as follows. The mixture of St, BA, MPS, hexadecane and AIBN were combined with a continuous phase consisting of water and SDS. The two-phase system was stirred 1 h for pre-emulsification and homogenized by ultrasonication for 10 min under cooling with an ice-water bath. The polymerization was continued for 5 h at 70 °C in a 3-neck 500 mL round bottom glass reaction flask with a Teflon stirring paddle and a Friedrichs condenser under N₂ air.

2.4. Films preparation

A dry film could be obtained when a certain amount of prepared emulsion was poured into a silicon plate of well-controlled depth and dried at room temperature for a week.

2.5. Measurements

2.5.1. Fourier transform infrared spectroscopy (FTIR) tests

FTIR spectra of the untreated silica and MPS functionalized silica particles were recorded by Nicolet AVATAR-360 spectrometer. All the samples were dried in a vacuum before tests. Besides, attenuated total reflectance-FITR spectroscopy was also used to investigate the crosslinking reaction of the nanocomposite films.

2.5.2. Thermogravimetric analysis (TGA) tests

The amount of MPS grafted on the silica surface and the film thermal property were conducted on TGA Perkin Elmer Pyris 1 instrument with the temperature ramp rate of 10 °C/min from 40 to 600 °C under N₂ environment.

2.5.3. Conversion tests

The polymerization conversion was calculated gravimetrically.

2.5.4. Morphological observation

Transmission electron microscope (TEM) was conducted on a JEOL JEM-1011 electron microscope at an acceleration voltage of 100 kV. The samples were prepared by diluting the dispersion in water. One droplet of the diluted samples was placed on a 230-mesh carbon-coated copper grid and left dry at room temperature. The dispersion and morphologies of the silica particles in the polymer matrix were carried out with a SUPRA 40 (ZEISS) scanning electron microscope (SEM) at an acceleration voltage of 10 kV. All samples were coated with a thin gold layer before the SEM analysis.

2.5.5. Gel content tests

Films were obtained by pouring a certain amount of emulsion onto a silicon plate and dried at room temperature for a week, afterwards the films were annealed at 70 °C in a vacuum. The dried latexes particles were prepared by freezing-dried the emulsion under a vacuum for 48 h. The gel content of the film and latex particles were calculated as follow: 1 g of either the films or the dried latex were extracted with toluene at room temperature for 24 h. The gel content was calculated as the mass ratio between the remaining amount of solid and the initial amount of the film. The remaining and initial amounts were all except the silica content.

2.5.6. Tensile tests

The mechanical properties of the films were measured with a tensile machine (Instron-3365) at a stretching speed of 200 mm/min at 23 °C according to ASTM D638. Five samples were measured for each datum point and then took the average.

2.5.7. Burning experiment

The burning behavior of the nanocomposite films was pictured as photographs to get fire-resistant property.

2.5.8. Optical transparency test

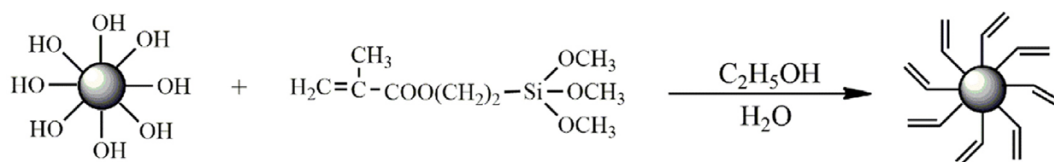
The transparency was measured using a haze meter WGT-S system (Shanghai Precision and Scientific Instrument Co. Ltd, China). At least five different positions for each sample were tested and then took the average.

3. Results and discussion

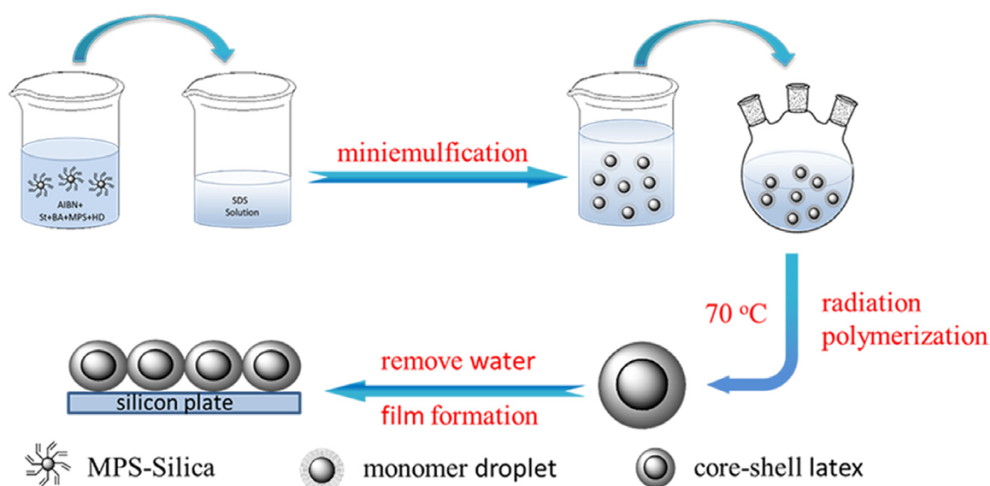
3.1. Characterization of nanocomposite emulsions

In order to graft the polymer chains to the silica nanoparticles surface, hydrophilic silica nanoparticles were modified with MPS according to the procedure of previous work.⁴ The illustration of the preparation process is shown in Scheme 1. The characterization of the modified silica nanoparticles were also had been described before, the result indicated that about 2.5 wt% modification agent grafted to the silica surface successfully. The alkyloxy groups of MPS react to silanols through hydrolysis reaction. The silanols attach to the silica surface by condensed with the hydroxyl groups exist on the nano-silica surface. Furthermore, silica carry vinyl groups result in a hydrophobicity of the particles surface. Therefore, the MPS-silica could be dispersed in the monomer uniformly, in addition, it is beneficial to copolymerize with monomer and encapsulate with polymer shell. The preparation of hybrid particles and the film formation process is shown in Scheme 2. Figure 1 shows the diameters and morphologies of the core-shell structure nanocomposite latexes. It can be obviously observed that the MPS-silica nanoparticles were coated by a dark shell about 30 nm, and the average diameter of the hybrid particles are about 120 nm compared with the diameter of colloidal silica 85 nm, which indicating the successful grafting of poly(St-BA-MPS) copolymer on the MPS-silica nanoparticles surface.

Figure 2 shows the conversion-time curves of poly(St-BA) and the silica nanocomposites emulsion. The result shows that the polymerization conversion and rate are not strongly influenced by the silica content. All the reactions behave high polymerization rate. After 1 h, the conversion is more than 70% for these latexes. The final conversion is beyond 90% for poly(St-BA) and Si-0 latexes. Even for the silica hybrid latexes, the conversion is still higher than 85%.



Scheme 1. Grafting reaction of MPS onto the silica particles.



Scheme 2. Miniemulsion polymerization of St, BA, and MPS on the MPS-Silica particles and film formation process.

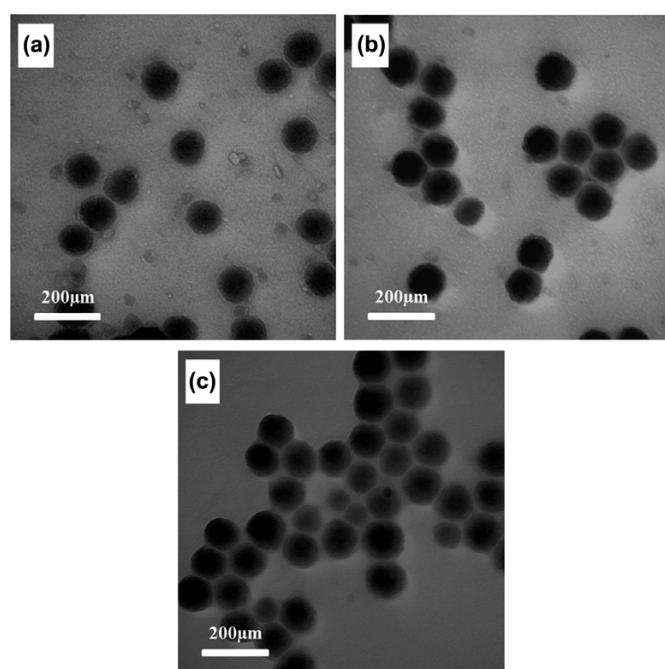


Figure 1. TEM images of the silica hybrid particles (a) Si-1, (b) Si-2, and (c) Si-3.

3.2. Cross-linking reactions of the films

Reactive alkoxy silane monomers such as MPS have been used in some researches to promote the crosslinking reaction of latex films. Premature crosslinking or post-crosslinking can take place for the latexes depending on the structure of the alkoxy silane monomers, pH and polymerization method. Premature crosslinking is due to the premature hydrolysis and condensation of the alkoxy silane moieties during the polymerization process, while the post-crosslinking takes place during the film formation process. The researches indicated that miniemulsion polymerization could suppress the premature crosslinking and promote the post-crosslinking effectively due to its polymerization mechanism.²⁸⁻³⁴ In a miniemulsion polymerization system, nucleation occurs primarily within the monomer droplets which are stabilized against coalescence and diffusional degradation.

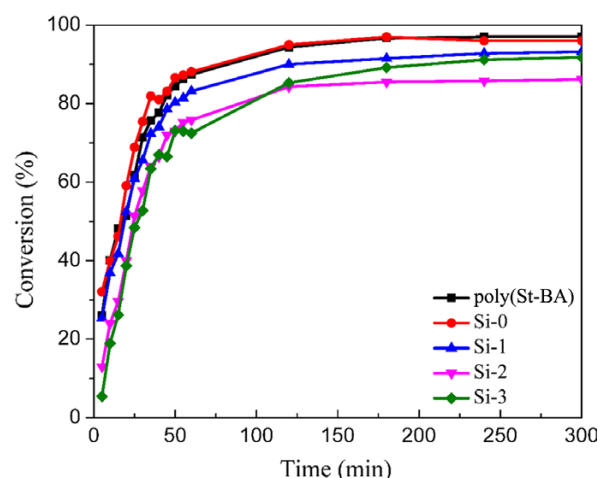


Figure 2. Conversion-time curves of poly(St-BA) and the silica nanocomposites.

It is hard for monomer to diffuse from monomer droplets to growing polymer particles and the alkoxy silane monomers are protected from the aqueous phase by the waterproof oil droplets. Thus the hydrolysis and condensation reactions are inhibited during the polymerization process. Therefore, the crosslinking reactions mainly occur during the film formation process by the post-crosslinking mechanism for the miniemulsion polymerization.

Gel content can indicate the degree of crosslinking of the materials. Figure 3 shows the gel content of the freeze-dried latex particles and the films. It can be found that the gel content of Si-0 is about 25% for the freeze-dried latex particles. Besides, the gel content decreases with the increase of silica nanoparticles content which is lower than 20%. As for the films, the introduction of MPS increases the gel content significantly compared with the poly(St-BA) film. It also can be found that the gel content of all the films with MPS is about 85%, which is much higher than the gel content of the freeze-dried latex particles. Therefore, it can be concluded that the crosslinking reactions mainly occur during the film formation process by the post-crosslinking reaction mechanism in the present research. FTIR was also used to confirm the occurrence of crosslinking

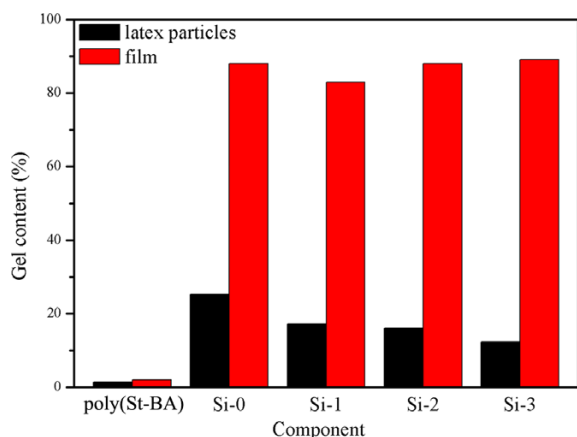


Figure 3. Gel content for different films.

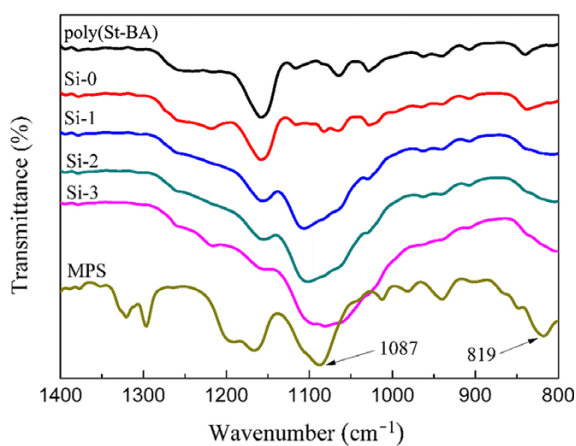


Figure 4. FTIR spectra of different films.

reactions. Figure 4 shows the FTIR spectra of the pure MPS and the films with different composition. It can be clearly observed the typical bands of MPS at 819 cm^{-1} and 1084 cm^{-1} in the spectra of MPS. However, the bands at 819 cm^{-1} and 1084 cm^{-1} disappear for the case of the nanocomposite films contrast with the MPS, which further indicates that the occurrence of the crosslinking reaction.

3.3. Dispersed phase morphology

The dispersion of silica nanoparticles in the polymer matrix was confirmed by SEM. Figure 5 shows the SEM morphology of the nanocomposite films with different silica content. It can be found that the surface of pure film (Si-0) is very flat. As for the nanocomposite films, when the content of MPS-silica nanoparticles is 10% (Figure 5(b)), most of the nanoparticles disperse homogeneously in the polymer matrix at the nanoscale level and only a slight aggregation take place. However, when the content of MPS-silica nanoparticles is beyond 10% (Figure 5(c) and (d)), the aggregation of the nanoparticles becomes obvious which will affect the mechanical properties of the latex films as discussed in the following part.

3.4. Mechanical properties of the films

Silica modified poly(St-BA) nanocomposites have been reported by

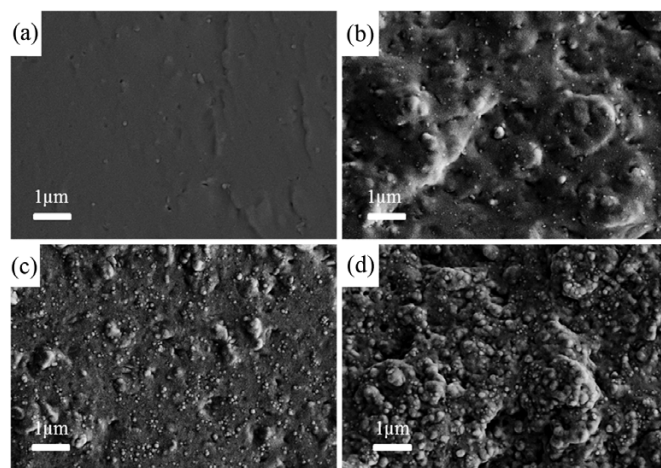


Figure 5. SEM cross section images of different films (a) Si-0, (b) Si-1, (c) Si-2, and (d) Si-3.

some researches. Zhang and Yang prepared poly(St-BA)/silica nanocomposites with the emulsion polymerization method.³⁵ When the silica content was 8%, the tensile strength and modulus were 1.09 MPa and 61 kPa separately. Zhang *et al.* prepared poly(styrene-butyl acrylate-acrylic acid)/SiO₂ composite by the soapless emulsion polymerization method. The addition of SiO₂ improved the hardness and adhesion force greatly.³⁶ R. Hashemi-Nasab and S. M. Mirabedini prepared poly(St-BA)/silica composite by the in situ emulsion polymerization method. The latex films with 30% silica showed much higher storage modulus (224 MPa at 0 °C and 0.265 MPa at 60 °C) and abrasion resistance ability.³⁷

Figure 6 and Table 2 show the stress-strain curves and the mechanical properties for the different films in the present research. The tensile result shows that the poly(St-BA) film exhibit low stress at break and high elongation at break. From comparison, it can be found that the stress at break of Si-0 can reach about 5 MPa, while the elongation at break decreased a lot. The change of the tensile properties is due to the crosslinking reaction which induces the improvement of stress at break but leads to the decrease of elongation at break inevitably. Compared with Si-0, the nanocomposite films show much higher stress at break and elongation at break, which indicate that

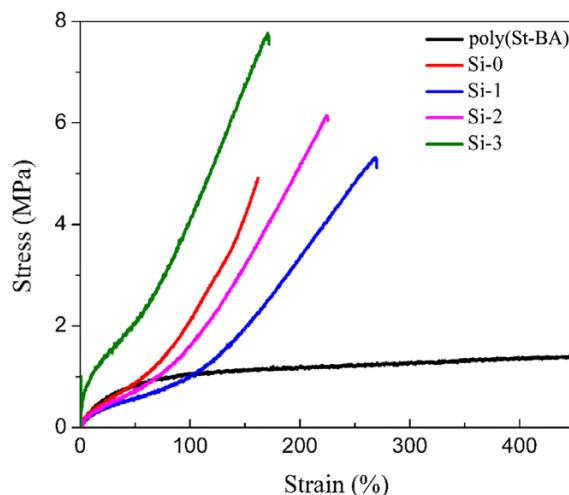


Figure 6. Stress-strain curves.

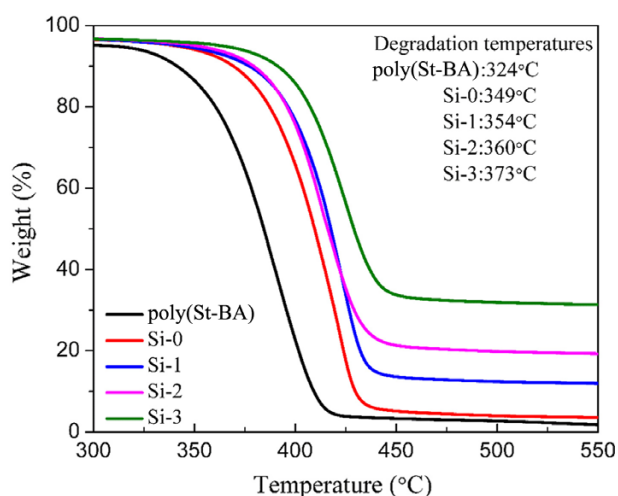
Table 2. Mechanical properties of the polymer/silica nanocomposite films

| Designation | Elastic modulus (MPa) | Stress at break (MPa) | Elongation at break (%) |
|-------------|-----------------------|-----------------------|-------------------------|
| Poly(St-BA) | 2.0±0.09 | 2.6±0.08 | 1092±41 |
| Si-0 | 6.3±0.07 | 4.9±0.09 | 162±19 |
| Si-1 | 2.9±0.05 | 5.3±0.16 | 276±26 |
| Si-2 | 4.1±0.05 | 6.1±0.12 | 225±25 |
| Si-3 | 5.4±0.07 | 7.8±0.08 | 173±9 |

the addition of silica nanoparticles further promotes the improvement of stress at break. The presence of MPS-silica particles as the core is the major factor for the improvement of tensile property. In addition, the stress at break increased from 5.3 MPa to 7.8 MPa with the increase of silica content for Si-1, Si-2, and Si-3 film, and there is little reduction in elongation at break. On the other hand, the Si-0 shows much higher elastic modulus than the nanocomposite films (see Table 2). The lower elastic modulus for the nanocomposite films can be explained as follows. First, higher content of nanoparticles leads to the aggregation of the particles which induces physical defect in the nanocomposite films and decreases the effective interfacial interaction. Second, the increase of the nanoparticles inhibits inter-particle polymer diffusion and reduces the mechanical properties. Similar results have also been found in other researches.³⁴

3.5. Thermal property of the films

Generally, the incorporation of silica nanoparticles into the polymer matrix can improve the thermal stability of the prepared materials. The TGA curves of the prepared latex films were shown in Figure 7. It can be seen that the thermal stability of poly(St-BA)/SiO₂ film was improved by the addition of MPS and nanosilica particles. The higher thermal stability of Si-0 than poly(St-BA) is due to the crosslinking reaction of MPS. With the addition of nanosilica particles, the thermal stability of nanocomposite films further increase. The beginning of degradation temperatures of Si-3 is higher than poly(St-BA) about 50 °C, which is beneficial to the industrial applications. On the other hand, the residual solid weights are about 2.6, 3.7, 12.3, 19.9,

**Figure 7.** TGA curves for the nanocomposite films with different composition.

and 31.7 wt%, respectively, which are consistent with our recipe given in Table 1.

3.6. Fire-resistant properties of the films

The incorporation of nano-silica particles into polymer matrix has been considered as a dominant method for preparing fire-resistant nanocomposite materials. In order to investigate the fire-resistant property of the prepared films, a simple test was applied. Figure 8 shows the digital images of the burning properties of polymer/Si-3 film and poly(St-BA) film recorded at different time intervals after ignition. Compared with poly(St-BA) film, the burning process of Si-3 film is much slower and without dripping. In addition, there are some remained solid content for Si-3, which are not dripped due to the crosslinking reaction and silica nanoparticles. This is very different from that of poly(St-BA) film, which drips badly and without remained after the test. The test result indicates that the addition of silica particles into polymer matrix improves the fire-resistant property of the films effectively.

3.7. Optical properties of the films

Figure 9 shows the optical clarity of these nanocomposite films and pure film. The value of the transparency of each sample is showed under the photos. It can be found that all the prepared films are highly transparent more than 83%. The transparency

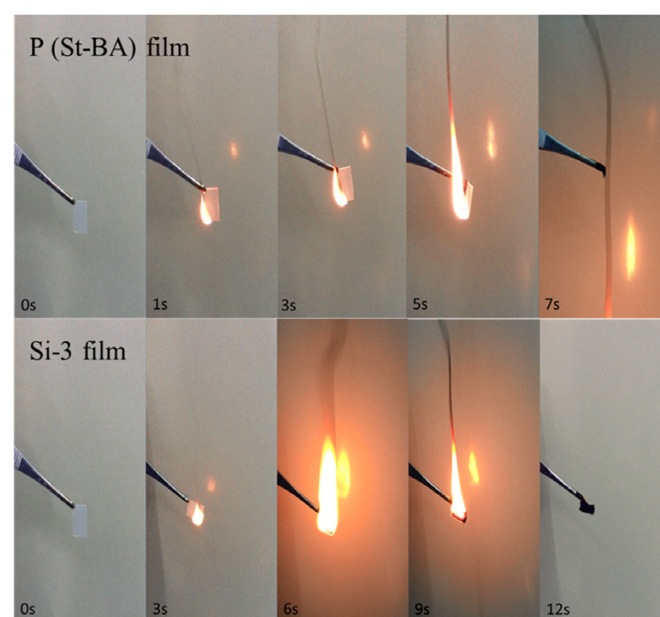
**Figure 8.** Digital images of the burning property of poly(St-BA) and Si-3 film recorded at different time intervals.



Figure 9. Transparency of (a) pure poly(St-BA) film and (b) polymer/SiO₂ nanocomposite films with the different SiO₂ contents (b) Si-0, (c) Si-1, (d) Si-2, (e) Si-3.

of the nanocomposite films is rarely reduced compared with that of the copolymer latex film. The reason for this phenomenon is due to good dispersion of silica nanoparticles in the polymer matrix and no obvious aggregation takes place. Since any significant aggregation or clustering would inevitably lead to substantial scatter of the light and decrease the transparency of the films.

4. Conclusions

In this study, nano-silica particles were hydrophobized by introducing the alkyl chains of MPS to the particle surface. FTIR and TGA results indicated that MPS had been successfully grafted on the silica surface. TEM images showed latexes have a homogenous structure with one MPS-silica as core and poly(St-BA-MPS) copolymer as shell. The compatibility and interaction between the MPS-silica and monomer leads to the formation of core-shell structure nanocomposite latexes. Besides, MPS-silica particles were homogeneously dispersed in the film and no obvious aggregation can be observed, which is conducive to the improvement in fire-resistant, thermal and mechanical properties of the as-prepared nanocomposite films compared with the film without MPS-silica particles. Moreover, the transparency of the nanocomposite film was rarely reduced compared with the pure poly(St-BA) film. On the other hand, FTIR test and other experimental results confirmed the occurrence of crosslink reaction, which is conducive to the improvement of the film performance. Thus, the as-prepared nanocomposite films show potential industrial applications in transparent coatings, adhesives, flame-retardant materials and so on.

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