

Polyacrylate/silica hybrids prepared by emulsifier-free emulsion polymerization and the sol–gel process

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Abstract Polyacrylate/silica hybrids were prepared by emulsifier-free emulsion polymerization and the sol–gel process. The influence on the properties of polyacrylate/silica hybrids of the synthetic conditions, such as the dosage of polyvinyl alcohol, the ratio of the monomers, the dosage of tetraethoxysilane and the dosage of γ -methacryloxypropyltrimethoxysilane, was investigated. The hybrid material was characterized by Fourier transform infrared, differential scanning calorimeter, thermal gravimetric analyzer and dynamic light scattering. The results indicated that there were chemical bonds between SiO_2 and polyacrylate, that the thermal stability and the average diameter of polyacrylate emulsion particle increased with the incorporation of SiO_2 , and that the glass transition temperature (T_g) of polyacrylate/ SiO_2 was 8 °C higher compared with that of pure polyacrylate.

Keywords Hybrids · Emulsifier-free emulsion · Sol–gel · Mechanical properties · Water resistance

Introduction

Organic–inorganic hybrid materials have been extensively investigated in recent years [1–6]. Organic polymers, as characterized by good flexibility, ductility and processability, have long been applied in various industries. In contrast, inorganic materials possess some properties that are not achievable by polymers, such as high rigidity, mechanical strength, and thermal stability. How to combine the advantages

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of these two classes of materials to yield a composite with superior properties that meet the industrial standards is nowadays highly demanded.

Polyacrylate/SiO₂ particles are usually produced by emulsion polymerization or microemulsion polymerization. However, the residual emulsifier in latexes would have negative effects on the purification and the properties of the products and induce the environmental pollution. To avoid the drawbacks resulted from emulsifier, the investigations on developing emulsifier-free latexes have been made by some researchers [7–10]. Compared with the conventional emulsion polymerization, the emulsifier-free emulsion polymerization endows latexes with more advantages [7]: no emulsifier migration during film formation, excellent shear stability and monodisperse particle size distribution. Consequently, emulsifier-free emulsion polymerization is a very promising method for the preparation environmentally friendly polyacrylate emulsion with excellent properties. The sol–gel process is an effective way to prepare polymer/silica organic–inorganic hybrids, in which a nanometer size silica component is dispersed in a polymer matrix. In polymer/silica hybrid films, it is expected that the silica component will work as the hard segment in the soft polymer matrix to bring about the excellent performances of the coating. Silane coupling agents are commonly used to achieve miscibility of the polymer and silica [11].

In this paper, we focus on the preparation of polyacrylate/silica hybrids by emulsifier-free emulsion polymerization in which tetraethoxysilane (TEOS) and polyvinyl alcohol (PVA) are used as a silica component precursor and polymeric colloid stabilizer respectively, and on the investigation of the influence on the properties of polyacrylate/silica hybrid materials of the synthetic conditions such as the dosage of PVA, the ratio of the monomers, the dosage of TEOS and the dosage of γ -methacryloxypropyltrimethoxysilane (MPTMS).

Experimental

Materials

Polyvinyl alcohol 1799 (PVA 1799), styrene (St), *n*-butyl acrylate (BA), potassium persulfate (KPS), MPTMS, methacrylic acid (MAA), TEOS, and NH₃·H₂O were all analytically pure without further purification.

Preparation of hybrids

The deionized water and PVA (10 wt % in water) were charged into a four-necked reaction vessel equipped with a reflux condenser, a mechanical stirrer and a digital thermometer. After they were stirred at 350 rpm for 30 min, all the monomers (St–BA–MAA–MPTMS) and all the TEOS were added into the vessel. Then the aqueous solution of KPS was dropped into the vessel at 80 °C within 1 h. After the addition, the polymerization was kept at 85 °C for 2 h. Finally, the pH was adjusted to 7–8 with NH₃·H₂O. Table 1 presents a typical recipe of the emulsion polymerization system:

Table 1 Typical recipe used in emulsion polymerization

Materials	PVA (10 wt%)	St	BA	MAA	MPTMS	TEOS	KPS
Weight/g	15	5	10	1	0.8	2	0.05

Measurements of physical mechanical properties of hybrid films

Preparation of hybrid films

The films were made by solvent evaporation method. The hybrids emulsion was cast onto the level polytetrafluoroethylene (PTFE) templates, the water inside was removed at room temperature for 48 h and at 50 °C for another 12 h, and finally the films were kept in a desiccator to avoid moisture.

Sampling

The films were sampled to dumbbell form with 80 mm pan and 5 mm middle breadth, and then the temperature and the relative humidity of the samples were kept at 20 ± 2 °C and 60–70% for 4 h.

Measurement of tensile strength

The thickness of the films in the midline was measured via YQ981 Leather Thickness Measure Instrument made by Middle Mountain Sword Tool Factory. All data were averaged for at least three points. Tensile strength was measured by GFU55 Function Materials Examination Machine made by Taiwan High Iron Science and Technology Stock Company with extending speed 300 mm/min.

Measurement of elongation at break

Elongation at break was measured during the measure of tensile strength. When the specimen was extended, the distance between the two standard lines was recorded.

$$X = (L_1 - L)/L \times 100\%$$

X is the elongation at break (%), L_1 is the distance between the midline of specimen at break (mm) and L is the distance between the midline of former samples (mm).

Measurement of water absorption

The water resistance of the films was characterized by water absorption measurements. Film specimens (weight W_0 , dimensions $3 \times 3 \times 0.1$ mm) were immersed in water at room temperature for 24 h to attain swelling equilibrium. The weights (W_1) of the films were measured again after removing the excess surface water with a filter paper. The water absorption (WS) of the films was calculated with the following expression [3]:

$$WS = [(W_1 - W_0)/W_0] \times 100$$

Characterization

Fourier transform infrared (FT-IR) analysis

FT-IR analysis of the polyacrylate and polyacrylate/silica films after the solvent (anhydrous ethanol) purification was performed by VETOR-2 FT-IR (Bruker Company in German).

Thermal analysis (DSC)

The thermal properties were measured under a nitrogen atmosphere with a differential scanning calorimeter DSC-204 (made by Germany Netzsch). About 10 mg of the samples was scanned over the temperature range from -50 to 150 °C at a heating rate of 10 °C min^{-1} , quenched to -50 °C immediately after the furnace reached 150 °C, and scanned again from -50 to 150 °C at a heating rate of 10 °C min^{-1} . The reported result was taken from the second heating run of the experiments in order to avoid experimental artifacts arising from the previous thermal history and incomplete chemical reactions.

Thermal decomposition

Thermal gravimetric analyzer (TGA) Hi-Res TGA 2950 (made by TA instruments Ltd., USA) was used to measure the thermal decomposition temperature (T_d) of the hybrid films. The samples (8–12 mg) were heated from room temperature to 600 °C at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere.

Dynamic light scattering (DLS)

Polymer particle size was measured by a dynamic light scattering (DLS) (made by Brookhaven Instruments Co.). The sample was diluted to the required concentration with distilled water before the measurement.

Results and discussion

Effect of PVA dosage

Effect of PVA dosage on the mechanical properties of hybrid films

Figure 1 demonstrates the mechanical properties of hybrids with various dosage of PVA. When PVA is less than 6 wt% of the total amount of the monomers, the tensile strength and elongation at break progressively increases as the dosage of PVA increases, because PVA is used as polymeric colloid stabilizer during the emulsifier-free emulsion polymerization, that is, the decrease of PVA will increase the interfacial tension and result in colloidal instability. When PVA exceeds 6 wt%,

Fig. 1 Mechanical properties with different dosage of PVA

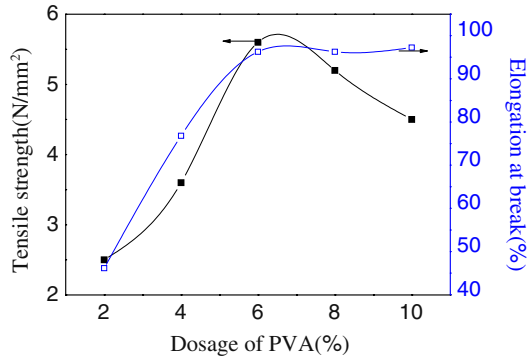
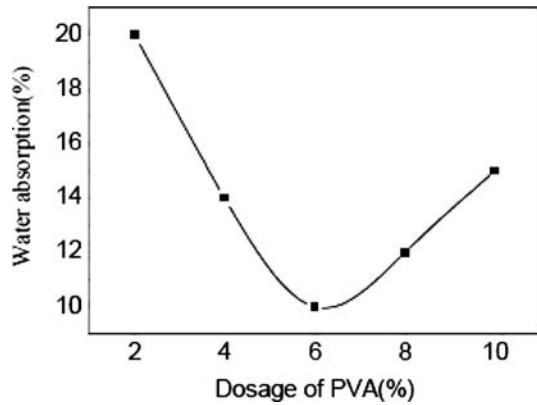


Fig. 2 Water absorption of hybrids with different dosage of PVA



the tensile strength will decrease because the overabundant PVA will overshadow the strength properties of hybrids.

Effect of PVA dosage on the water resistance of hybrid films

As shown in Fig. 2, the water absorption is the lowest when the dosage of PVA is 6 wt%, but the water absorption will increase when a large amount of PVA (more than 6 wt%) is used, because there are a lot of $-OH$ groups on the PVA molecular.

Effect of the BA/St ratio

Effect of the BA/St ratio on the mechanical properties of hybrid films

Figure 3 demonstrates the variation of the properties of polyacrylate/silica hybrids with different BA/St molar ratios. Obviously, the BA/St ratio has obviously impact on the mechanical properties of polyacrylate/silica hybrid materials. The incorporation of the hard monomer (St) enhances the rigidity and strength of the hybrid

Fig. 3 Mechanical properties with different ratios of BA/St

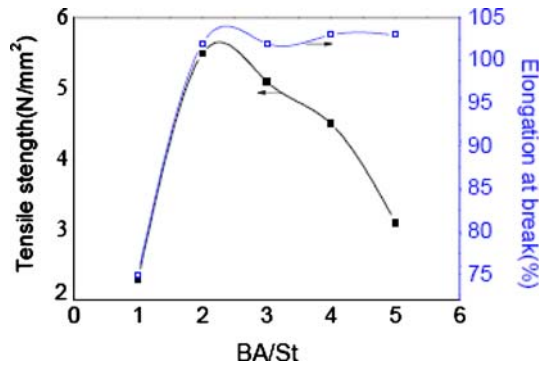
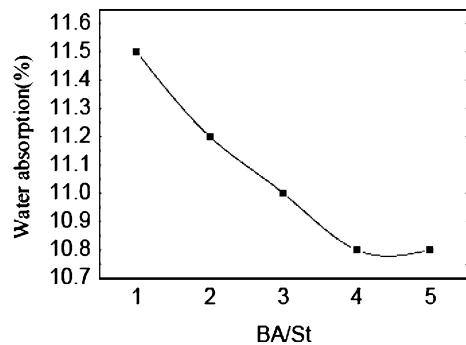


Fig. 4 Water absorption of hybrids with different ratios of BA/St



materials. However, the flexibility of the hybrid materials is improved and the strength decreases with the incorporation of the soft monomer (BA).

Effect of the BA/St ratio on the water resistance of hybrid films

Figure 4 indicates that the influence of BA/St ratio on the water resistance of hybrid films is not evident. The films will become sticky with increase of BA/St ratio. On the contrary, the film will become stiff and even break into pieces with decrease of BA/St ratio.

Effect of MPTMS dosage

Effect of MPTMS dosage on the mechanical properties of the hybrid films

The influence of the different MPTMS dosage on the properties of the hybrid films is shown in Fig. 5.

MPTMS added was expected to increase the miscibility of the polymer and SiO₂. When the dosage of MPTMS is increased, the overabundant bridge bond forms between the inorganic and the organic materials will result in increase of the brittleness and the particle size and decrease of the physical mechanical properties of the hybrids.

Fig. 5 Mechanical properties of hybrids with different dosage of MPTMS

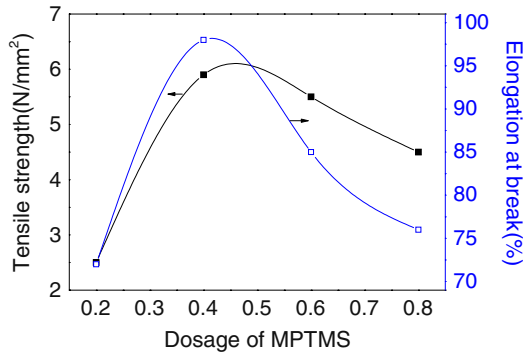
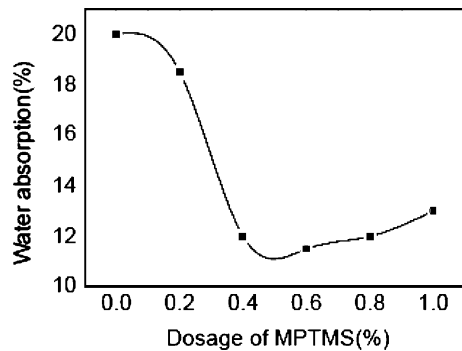


Fig. 6 Water absorption of hybrids with different dosage of MPTMS



Effect of MPTMS dosage on the water resistance of the hybrid films

It is thought that MPTMS acts as both a silane coupling agent and a crosslinking agent. As shown in Fig. 6, the films from the emulsions containing little or no MPTMS show poor water resistance. These results indicate that Si–O–Si bond formation via the hydrolysis and condensation of the Si(OR)₃ groups on TEOS and MPTMS plays an important role in the water resistance. The Si–O–Si bonds between the acrylic polymer component and the silica component will increase the miscibility, prevent the phase separation due to the formation of large silica particles, and lead to highly water-resistant films. The Si(OR)₃ groups remained in the hybrid emulsion will hydrolyze and self-crosslink during film formation. Nevertheless, there will be a lot of ropy matter in the emulsion if MPTMS dosage is too large.

Effect of TEOS dosage

Effect of TEOS dosage on the mechanical properties of the hybrid films

Figure 7 shows the effects of the TEOS dosage on the mechanical properties of hybrids films. With the increase of TEOS, the tensile strength increases while the

Fig. 7 Mechanical properties of hybrids with different dosage of TEOS

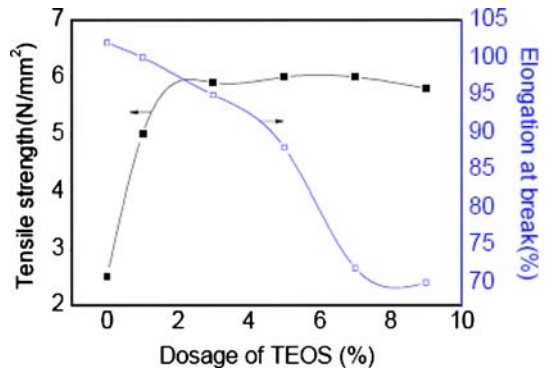
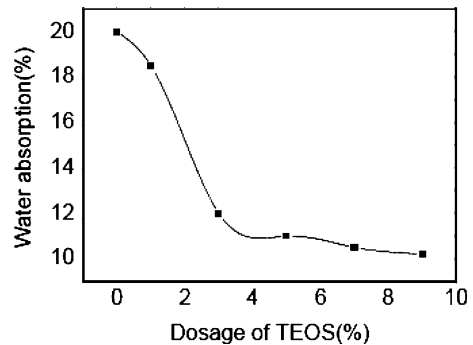


Fig. 8 Water absorption of hybrids with different dosage of TEOS



elongation at break decreases. So the Si–O–Si bonds formed contribute to the improvement of the stiffness of polyacrylate/SiO₂ hybrids.

Effect of TEOS dosage on the water resistance of hybrid films

In Fig. 8, the water resistance sharply increases with the increase of the dosage of TEOS when the dosage is less than 4 wt%, and slowly increases when the dosage is more than 4 wt%. The improvement of the water resistance is due to the three-dimensional crosslinking network in the acrylic polymer chains containing the silica component. The hydrolysis and condensation of the Si(OR)₃ groups on MPTMS and TEOS forms Si–O–Si bonds between the polyacrylate and the silica component.

Effect of MPTMS/TEOS ratio

Effect of the MPTMS/TEOS ratio on the mechanical properties of hybrid films

Figure 9 demonstrates the properties of polyacrylate/silica hybrids obtained with different MPTMS/TEOS molar ratios. The incorporation of the silane coupling agent increases the miscibility, and prevent the phase separation due to the formation of large silica particles. The polyacrylate is reinforced by silica. However,

Fig. 9 Mechanical properties with different ratios of MPTMS/TEOS

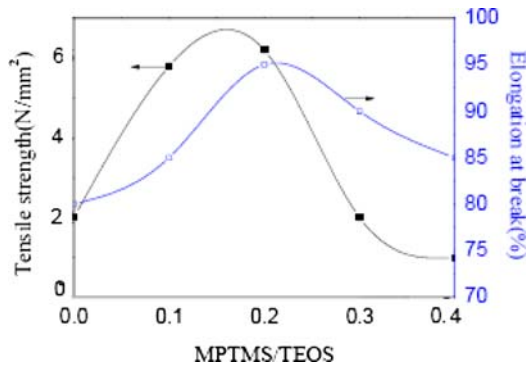
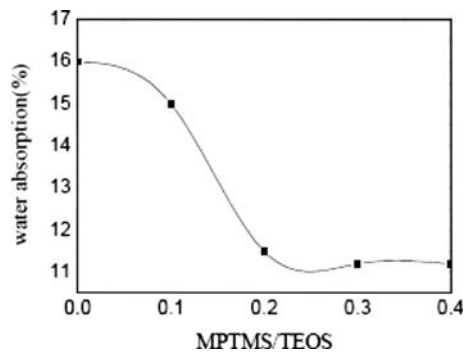


Fig. 10 Water absorption of hybrids with different ratios of MPTMS/TEOS



the emulsion becomes coagulated when MPTMS/TEOS molar ratio is more than 0.3.

Effect of the MPTMS/TEOS ratio on the water resistance of hybrid films

Figure 10 indicates the influence of MPTMS/TEOS molar ratio on the water resistance of hybrid films. The water resistance of the films increases with the increase of MPTMS/TEOS ratio when the ratio of MPTMS/TEOS is less than 0.28. This is because the polar –OH groups on the silanol surface will decrease the water resistance as TEOS hydrolyzes to be silanol. The condensation of some of the Si–OH groups on the surface of the silanol with the Si–OH of partially hydrolyzed MPTMS can increase the hydrophobicity. In other words, the formed Si–O–Si bonds help to increase the hydrophobicity.

FT-IR analysis

The chemical structure of polyacrylate and polyacrylate/SiO₂ films was studied by FT-IR and the results are shown in Fig. 11. Compared with the polyacrylate, the polyacrylate/SiO₂ samples exhibit a new peak at about 1,058 cm⁻¹, the formation of which is attributed to Si–O–Si asymmetric stretching vibration. The appearance of this new peak proves that the hydrolysis and condensation reactions of Si(OR)₃

Fig. 11 FT-IR spectra of polyacrylate and polyacrylate/SiO₂

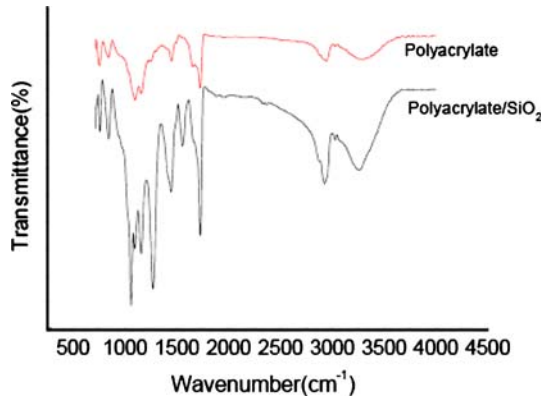
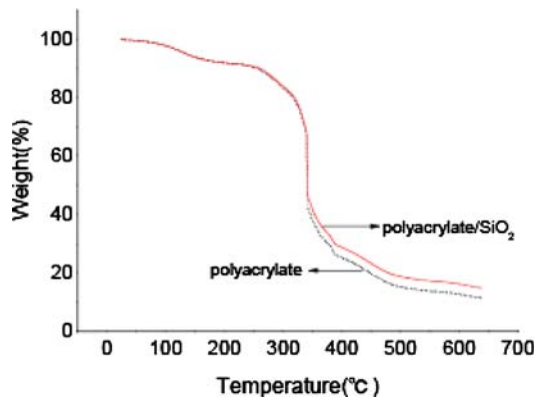


Fig. 12 TGA thermograms of polyacrylate and polyacrylate/SiO₂



groups occur and that the crosslinking silica network structure is formed in the polyacrylate/SiO₂ films. The complete disappearance of the band at 2,842 cm⁻¹ in the polyacrylate/SiO₂ shows the complete hydrolysis and condensation of Si(OR)₃ groups during the formation of hybrid films. The broad peak at around 3,254 cm⁻¹ is ascribed to -OH stretching vibration due to the presence of -COOH groups.

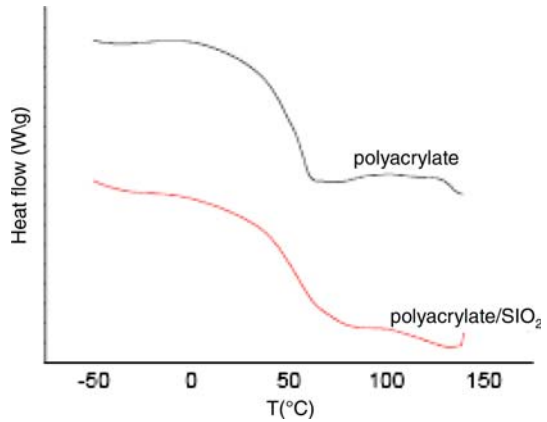
TGA analysis

Thermal decomposition behavior of polyacrylate and polyacrylate/SiO₂ films was investigated by TGA. The thermograms of polyacrylate and polyacrylate/SiO₂ are shown in Fig. 12. Both of the samples remained fairly stable because the weight loss was less than 7.82% even when the temperature was raised up to about 213.05 °C. The *T*_d of polyacrylate/SiO₂ was increased by the incorporation of SiO₂.

DSC analysis

The glass transition temperature (*T*_g) of polyacrylate and polyacrylate/SiO₂ films was determined by DSC. As shown in Fig. 13, the *T*_g of hybrids is 8 °C higher than

Fig. 13 DSC thermograms of polyacrylate and polyacrylate/SiO₂

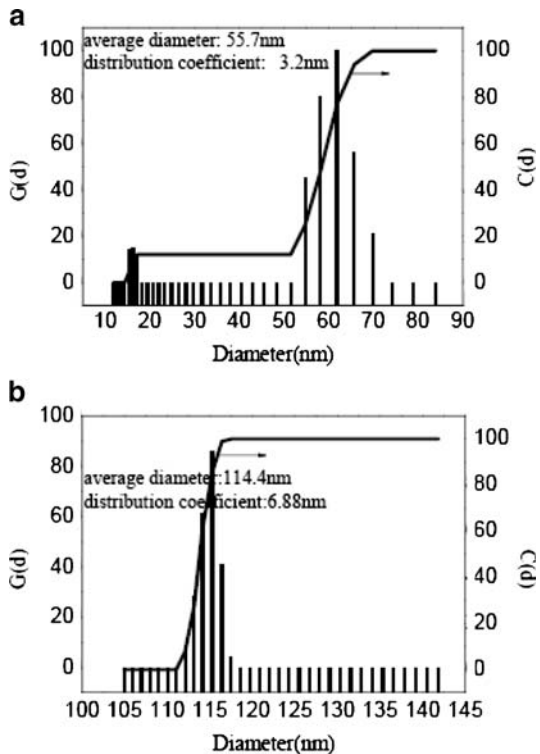


that of the polyacrylate because the movement of the polyacrylate is restrained by the interaction between the nano-silica and polymer molecule.

DLS analysis

As shown in Fig. 14, the average diameter of polyacrylate/SiO₂ is larger than that of polyacrylate, and the distribution coefficient becomes broad, which is because of the

Fig. 14 **a** The particle size distribution of the polyacrylate emulsion. **b** The particle size distribution of the polyacrylate/SiO₂ emulsion



unexpected crosslinking reaction before film formation and the likely aggregation of nano-silica.

Conclusions

A new kind of polyacrylate/SiO₂ hybrid materials was successfully synthesized via emulsifier-free polymerization method and sol–gel process. DLS analysis shows that the particle size of polyacrylate/SiO₂ was a little larger than that of polyacrylate. Compared with the polyacrylate films, the polyacrylate/SiO₂ films exhibited better thermal stability, better stiff properties and higher water resistance due to the existence of crosslinking silica network. Based on its excellent properties, the hybrid materials can be used as surface strengthening agent and sizing agent for papermaking.

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