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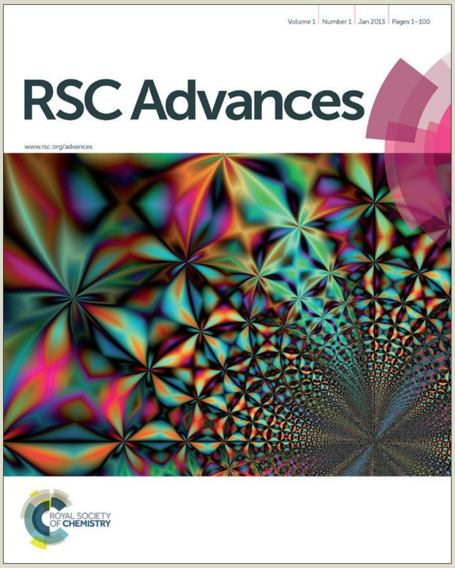

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Waterborne UV-curable Polyurethane Acrylate/Silica Nanocomposites for Thermochromic Coatings

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Abstract: Waterborne UV-curable polyurethane acrylate/silica (PUA/SiO_2) nanocomposites were prepared by sol-gel method. SiO_2 nanoparticles were modified by γ-Methacryloxypropyltrimethoxysilane (KH-570) and then introduced to the ends of the PUA main chains through radical polymerization. According to the transmission electron microscopy (TEM) results, the size of PUA/SiO_2 nanocomposite particles was approximately 70-100 nm. And it was easier to get uniform emulsion by sol-gel method than physically blending method. Surface tension and contact angle test both demonstrated the good wettability of the nanocomposites. Besides, curing kinetics process of PUA/SiO_2 films was analyzed by ATR-FTIR and gel content. It revealed that the modified SiO_2 could accelerate the curing speed of PUA coatings. Scanning electron microscope (SEM) and dynamic mechanical analysis (DMA) indicated that the nanosilica were well dispersed in the PUA matrix and the soft and hard segments of PUA/SiO_2 were well phase mixed. Furthermore, the nanocomposite films displayed enhanced rigidity, hardness, abrasion resistance and good weather resistance. Finally, waterborne UV-curable PUA/SiO_2 nanocomposites were applied to thermochromic coatings, showing excellent temperature sensitivity and reversibility.

Keywords: Waterborne polyurethane acrylate; UV-curable; Nanosilica; Thermochromic coating

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1. Introduction

Thermochromic coating as intelligent material has been studied and widely used in the fields of over-temperature alarm, temperature sensors, anti-counterfeiting mark, etc[1-2]. However, most solvent-based thermochromic coating is harmful to human health and living environment. Growing attentions in the environmentally friendly coating industry has led to the development of waterborne UV-curable coating that can be cured at ambient temperature by short exposures to UV light. The waterborne UV-curable thermochromic coating will be a new development direction of intelligent coating.

Among film formers of waterborne UV-curable coating [3,4], polyurethane acrylate (PUA) has received increasing concerns due to its excellent comprehensive performance, such as versatility, environmental friendliness, nice mechanical performance and toughness as well as good resistance to chemicals and solvents [5-9]. However, there are some limits in terms of weather resistance, hardness and abrasion resistance in their applications. In recent years, organic-inorganic hybrids have attracted considerable attention due to their enhanced coating properties, such as improved abrasion resistance, thermal stability, etc [10-14]. On the basis of the previous studies, the shortages of PUA can be improved by adding reinforcement such as inorganic oxides [15-17], clay [18-19] and fiberglass [20] to the polymer matrix, under proper conditions. Currently, the research about waterborne UV-curable PUA/SiO_2 hybrids becomes more and more popular. As the diisocyanate monomer is more sensitive to water, the hybrids are usually prepared by physically blending method [21] or sol-gel method [22-25] instead of in situ polymerization [26-27]. However, SiO_2 is easy to aggregate in PUA matrix by physically blending. When the sol-gel method is used, the precursor firstly is dissolved in the PUA dispersions, and then hydrolyzed under the catalytic action of the acid, alkali or some

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salt, forming nanoparticles uniformly dispersed in the polymer matrix. But during the UV curing process, these catalytic substances may influence the curing effect.

In this study, waterborne UV-curable PUA/SiO_2 nanocomposites incorporating nanosilica obtained from colloidal silica as reinforcement were prepared with a new form of sol-gel method. With this method, the nanosilica connected PUA chain with chemical bond by crosslinking reaction (gel process) between C=C bonds. These double bonds on nanosilica particles were achieved by the hydrolysis and condensation of γ-Methacryloxypropyltrimethoxysilane (KH-570). The morphology, curing kinetics process, dynamic mechanical properties, optical properties, hardness and abrasion resistance of the PUA/SiO_2 hybrid films as well as temperature sensitivity of the thermochromic coating were studied. To the best of our knowledge, it was the first time that PUA/SiO_2 nanocomposites were successfully applied to the thermochromic coatings and the coating showed good temperature sensitivity and reversibility.

2. Experimental

2.1. Materials

Polyethylene Glycol (PEG, Mn = 400) was distilled at 110 ℃, under -0.1 MPa for 4 h before use. 2,2-Dimethylol Propionic Acid (DMPA, Aladdin Reagents Co., LTD) was dried at 80 ℃ for 3 h in a vacuum oven. Acetone was dried over 4 Å molecular sieves before use. 2,4-Diisocyanatotoluene (TDI), N-methyl-2-pyrrolidone (NMP, as solvent), hydroxyethyl acrylate (HEA), triethylamine (TEA), dibutyltin dilaurate (DBTDL, as the catalyst), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methyl-propiophe (Photoinitiator 2959, TCI Shanghai), HgI_2, KI and $AgNO_3$ were used as received. Colloidal silica (solid content: 30%, particle size: 15 nm) and γ-Methacryloxypropyltrimethoxysilane (KH-570) were obtained from WD

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SILICONE CO., LTD. The reagents with no instructions were all from Sinopharm Chemcial Reagent Co., Ltd.

2.2. Preparation of waterborne UV-curable PUA/SiO$_2$ nanocomposites

Synthesis of waterborne UV-curable PUA was carried out in a three-step process and network structure of PUA/SiO$_2$ hybrid was formed by sol-gel method (shown in Fig. 1). PEG (9.84 g), DBTDL (1 drop) and TDI (9.42 g) were introduced into a four-neck flask fitted with mechanical stirrer, thermometer and reflux condenser. Specially, TDI was added dropwise at a constant flowrate to avoid imploding and agglomeration. The prepolymerization of polyurethane was kept at 60 ℃ under a nitrogen atmosphere for 2 h. Next, DMPA (1.65 g) dissolved in NMP (5 g) was added and reacted at 75 ℃ for 1.5 h. Subsequently, HEA (2.85 g) was added into the flask. The mixture was heated to 80 ℃ for 1.5 h, and then waterborne UV-curable PUA was acquired. At the moment, the NCO content that was tested by the standard dibutylamine back-titration method was close to zero. After cooling to room temperature, TEA (1.5 g) was rapidly added to neutralize the carboxyl of the PUA chain. Distilled water (30 ml) was added dropwise at a constant flowrate under high speed of mechanical stirring to make PUA prepolymers fully emulsified. And 30 min later, stable PUA emulsion with the solid content of 36.6% was obtained. Afterwards, PUA/SiO$_2$ nanocomposites was formulated by addition of colloidal silica and KH-570 to PUA emulsion successively at the mass ratio of 10:3. The sol-gel process started at this stage and the system showed a semi-crosslinked (semi-IPN gel) state.

Then, PUA/SiO$_2$ emulsion was mixed with 2 wt% photoinitiator 2959 and casted onto Teflon mould or a glass plate at room temperature and followed by drying the coating at 105 ℃ for 0.5 h. Finally, the coating was irradiated using full-automatic UV solidifying

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machine at room temperature, which was demoulded for properties measurement.

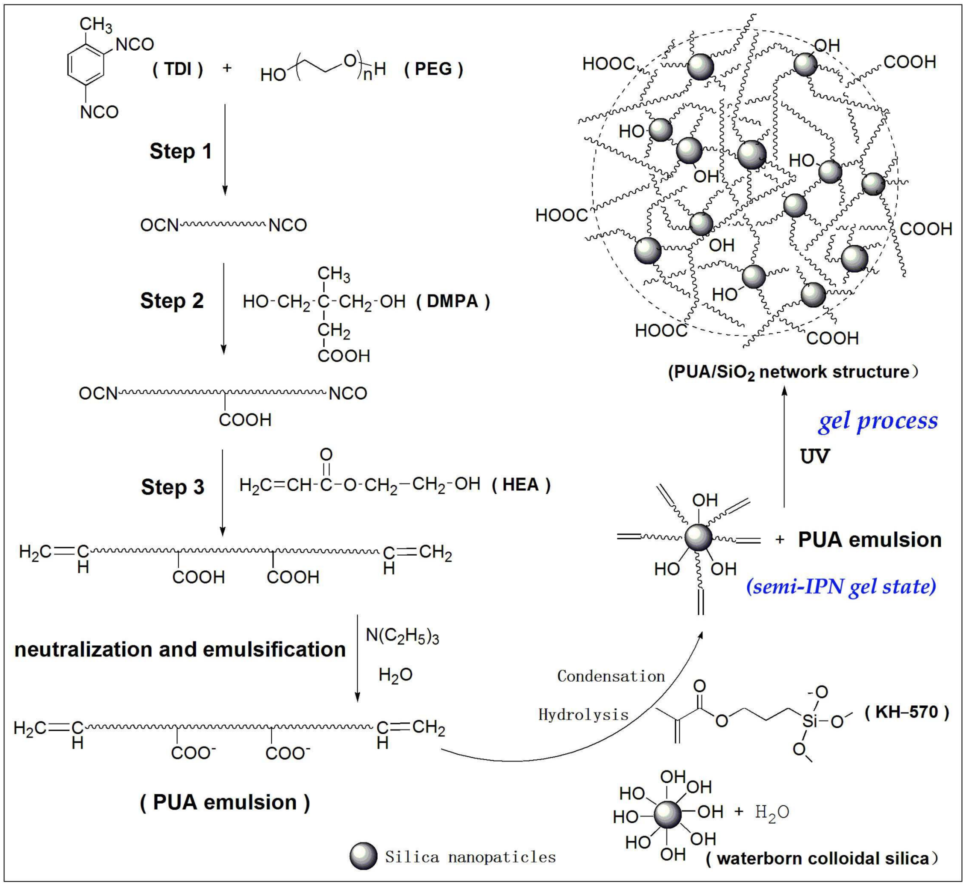

Fig. 1 Synthesis scheme to prepare PUA and PUA/SiO$_2$ nanocomposite.

2.3. Preparation of thermochromic coating

The thermochromic coating was prepared by mixing PUA/SiO$_2$ binders, photoinitiator 2959, HgI$_2$, KI, AgNO$_3$ and deionized water. The synthesis reaction equations [28] of thermochromic pigments are as follows:

$$\begin{aligned} &HgI_2 + 2KI \longrightarrow K_2HgI_4 \text{(colourless)} \\ &K_2HgI_4 + 2AgNO_3 \longrightarrow Ag_2HgI_4 \text{(yellow)} \end{aligned} \tag{2.1}$$

2.4. Characterizations

Fourier transform infrared spectroscopy (FTIR) spectrometer was used to characterize the chemical structure of PUA and PUA/SiO$_2$. Samples for infrared analysis were prepared by drying emulsion on KBr wafer and analyzed from 4000 cm^{-1} to 400 cm^{-1}. For cured coatings, an affix of attenuated total reflectance (ATR) was necessary. The morphology of PUA/SiO$_2$

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nanocomposite emulsion particles was examined by transmission electron microscopy (TEM). The testing was performed on a JEM-2100 (HR) operating at 200 KV. Wettability of PUA/SiO_2 dispersion was tested by surface tension meter and contact angle meter.

The surface morphology of the hybrid films was investigated with a field emission scanning electron microscope (Quanta200, FEI Corp., Holland). Dynamic mechanical analysis (DMA) of the PUA/SiO_2 films were carried out using the dynamic mechanical analyzer (Diamond DMA, PerkinElmer Instruments, Shanghai) under a dry nitrogen atmosphere, at a heating rate of 3℃/min from -80 to 150℃ and a frequency of 1 Hz. Curing kinetics process was studied by ATR-FTIR and gel content test [29]. The gel content was calculated by the following formula:

$$Gel = \frac{m_1}{m_0} \times 100\% \tag{2.2}$$

where "m_0" is the mass of the cured coating and "m_1" is the mass of the cured coating after extracting for 48 h in the soxhlet extractor with acetone.

Optical properties were characterized by UV-visible spectra in the 325-1000 nm. Pencil hardness of the coating was measured according to GB/T 6739-2006 by a QHQ hardness tester. A paint film scriber was used to test the adhesion to the substrate. Abrasion resistance was studied through rotating abrasive rubber wheel method and calculated as the loss in mass after 500 abrasion cycles with a loading of 500 g. The temperature sensitivity of the thermochromic coating was detected by observing the color changes of the coating in the warm water (T=40 ℃) and room temperature water (T=20 ℃).

3. Results and discussions

3.1. Infrared Analysis

The FTIR spectra of PUA and PUA/SiO_2 nanocomposites were shown in Fig. 2. From

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the spectrum (a) of PUA emulsion, there was no absorption peak at 2273 cm^{-1}, suggesting that all -NCO were consumed. The peaks at 3440 cm^{-1} and 1723 cm^{-1} were respectively ascribed to the stretching vibration peaks of N-H and C=O. The characteristic peaks of CH_3, CH_2, C=C, N-H, and C-O could be found at 2947cm^{-1}, 2871cm^{-1}, 1635 cm^{-1}, 1531cm^{-1} and 1224cm^{-1}, respectively. But the characteristic absorption of C=C at 1635 cm^{-1} disappeared from the spectrum (b) of PUA cured film. Therefore, it revealed that PUA prepolymers had been synthesized and C=C completely participated in radical polymerization after being exposed to UV irradiation. From the spectrum (c) of the cured hybrid film with 4 wt% SiO_2, the peaks at 1105 cm^{-1} and 810 cm^{-1} which were the characteristic absorption of asymmetric and symmetric stretching vibration of Si-O-Si became stronger. Moreover, a new peak appeared at 471 cm^{-1} which was attributed to the blending vibration absorption of Si-O-Si. It indicated that SiO_2 could be introduced into PUA to form a network structure with the help of KH-570 as desired through this method.

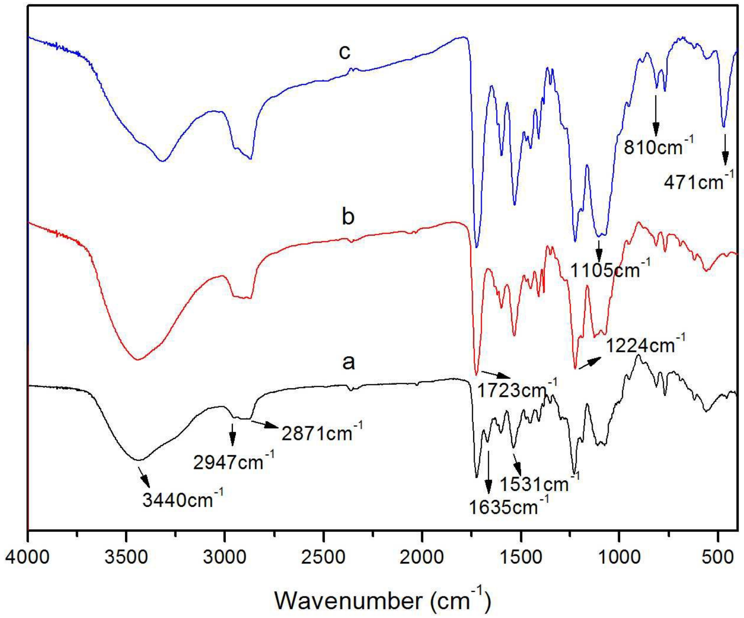

Fig. 2. FTIR spectra of PUA and hybrid film: (a) PUA emulsion, (b) PUA cured film, (c) PUA/SiO_2 cured film with 4 wt% SiO_2.

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3.2. Morphology Analysis

The morphology of PUA and PUA/SiO_2 nanocomposite was observed by TEM (shown in Fig. 3). The micrograph showed that the PUA particles were well dispersed and the average particle size was approximately 50 nm (Fig. 3a). When colloidal silica and KH-570 were introduced into the PUA matrix, SiO_2 particles modified by KH-570 dispersed uniformly on the surface of PUA and the composite nanoparticle sizes became larger (Fig. 3c and d). When the SiO_2 content rose from 4 to 6 wt%, the average size of the composite particles increased from 70 to 100 nm, since the increasing of KH-570 led to more hydrophobic structure and higher cross-linking density in the macromolecular chains. When only colloidal silica was added into the PUA matrix by physically blending method, SiO_2 nanoparticles with hydroxyl groups enclosed the polymer and showed the tendency to aggregate together (Fig. 3b). The results implied that it was easier to get uniform composite emulsion by sol-gel method than physically blending method, which would be of great importance in practical application.

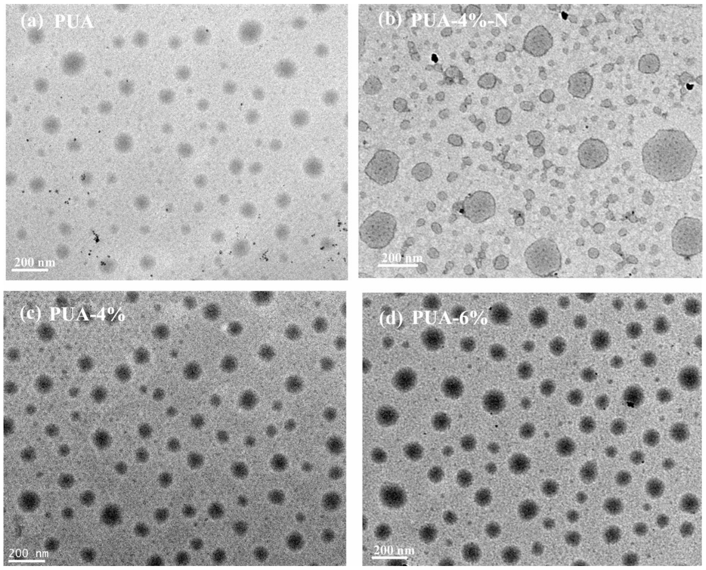

Fig. 3. TEM micrographs of PUA and PUA/SiO_2 hybrids particles: (a) pure PUA, (b) PUA with 4 wt% unmodified SiO_2, (c) PUA with 4 wt% modified SiO_2 and (d) PUA with 6 wt% modified SiO_2.

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SEM (shown in Fig. 4) was used to evaluate the dispersion of SiO_2 nanoparticles in PUA matrix. A smooth PUA film was observed in Fig. 4(a). In the cases of 2, 4 wt% SiO_2 content, the SiO_2 nanoparticles were well dispersed in the matrix, implying strong interaction between PUA and SiO_2 nanoparticles (Fig. 4(b) and (c)). But for the hybrid films with 6 wt% SiO_2 content, the field appears agglomerate phenomena (Fig. 4(d)), which arises from the aggregation among free SiO_2 particles.

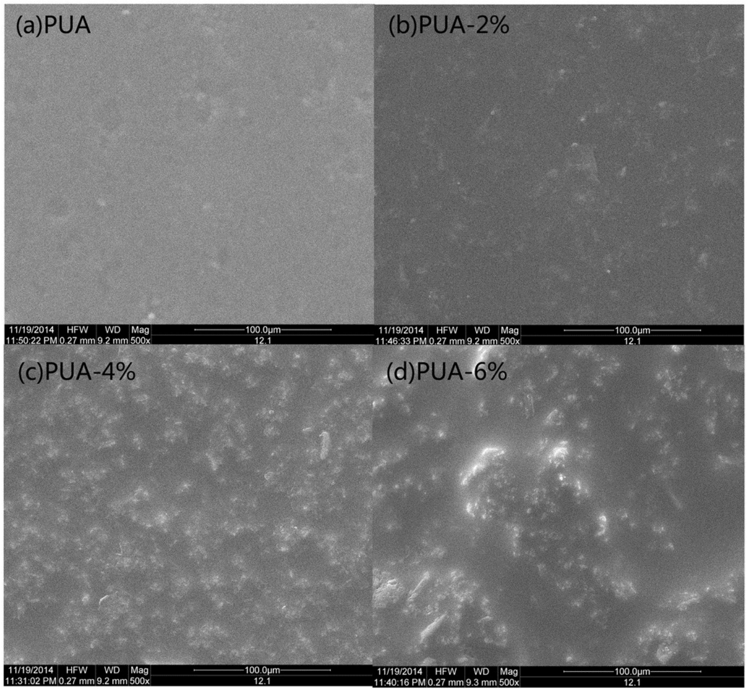

Fig. 4. SEM diagrams of the hybrid films: (a) pure PUA, (b) PUA with 2 wt% modified SiO_2, (c) PUA with 4 wt% modified SiO_2 and (d) PUA with 6 wt% modified SiO_2.

3.3. Wettability of PUA/SiO_2 composites

The wettability of polymer is usually measured by surface tension (σ) or contact angle (θ). The smaller σ or θ is, and the better wettability of the polymer has. The surface tension curve and contact angle images of PUA/SiO_2 nanocomposites were shown in Fig. 5. It described that σ decreased first, then basically flat and finally rose with the increasing of SiO_2 content. The nanocomposites with 2, 4 wt% SiO_2 content had better wettability than pure PUA. The contact angle showed the same change rule and confirmed the phenomenon. The

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reason for this phenomenon might be that σ was related to the volume and quantity of polar group in polymer chain [6]. The addition of SiO_2 led to more polar group which made σ smaller. But when the SiO_2 content reached 6 wt%, σ increased due to SiO_2 coagulation (as shown in SEM).

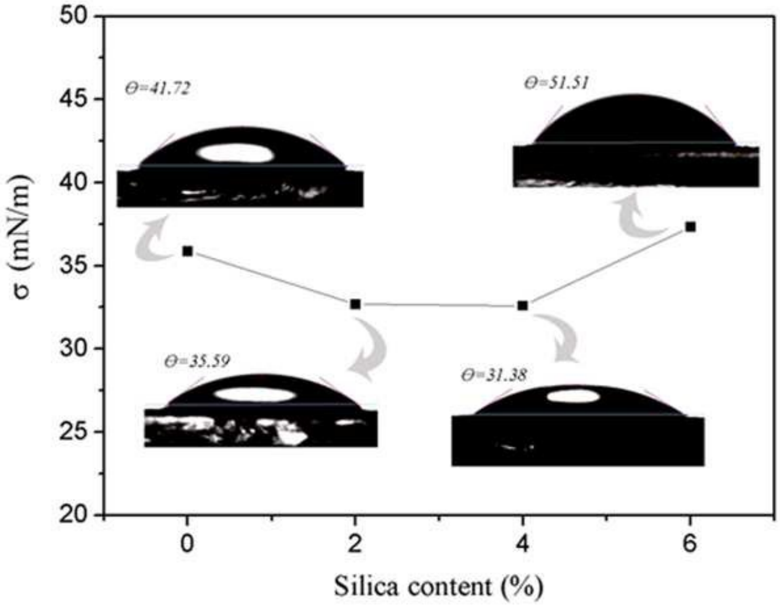

Fig. 5. Surface tension (σ) curve and contact angle (*θ*) images of PUA/SiO_2 nanocomposites with different SiO_2 content.

3.4. Curing kinetics process analysis

The curing kinetics process was analyzed by ATR-FTIR (Fig. 6(a)) of PUA film and gel content (Fig. 6(b)) of hybrid coatings at different curing time. The film thickness was 1 mm. As shown in Fig. 6(a), the absorption area of C=C bonds decreased with the extension of curing time. Also, the gel content of all the cured coatings rose rapidly first, and then slowly approached to a constant value with the extension of curing time (Fig. 6(b)). They both proved that C=C bonds participated in radical polymerization by UV radiation constantly until they were almost used up. In addition, the curing speed and gel content of the hybrid films increased with the increasing of SiO_2 content. The maximum gel content could reach 98%. When the SiO_2 content was added to 6 wt%, the curing speed slightly declined and its final

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gel content was close to that of the hybrid film with 4 wt% SiO_2. This phenomenon might be explained that with the rising of SiO_2 content, more amount of C=C bonds led to faster curing speed and bigger cross-linking density, resulting in the increase of gel content. When the SiO_2 content reached 6 wt%, excessive free silica had a shielding effect for UV light, which might slow down the curing speed in some degree. Thus we might make a conclusion that moderate modified nanosilica could improve the curing speed.

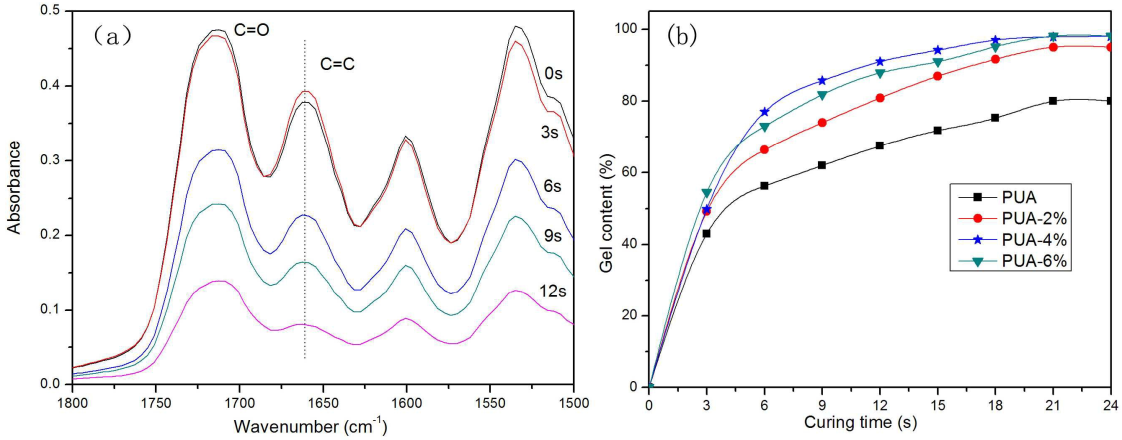

Fig. 6. The ATR-FTIR (a) of PUA film and gel content (b) of hybrid coatings at different curing time.

3.5. Dynamic mechanical analysis

It could be observed that the storage modulus (E′) of the PUA/SiO_2 nanocomposites films was higher than that of the pure PUA fim in Fig. 7. And, the storage modulus rose as the amount of SiO_2 increased. The reason might be that the incorporation of modified SiO_2 nanoparticles led to the rising of cross-link density, which strengthened the rigidity of the hybrid coatings.

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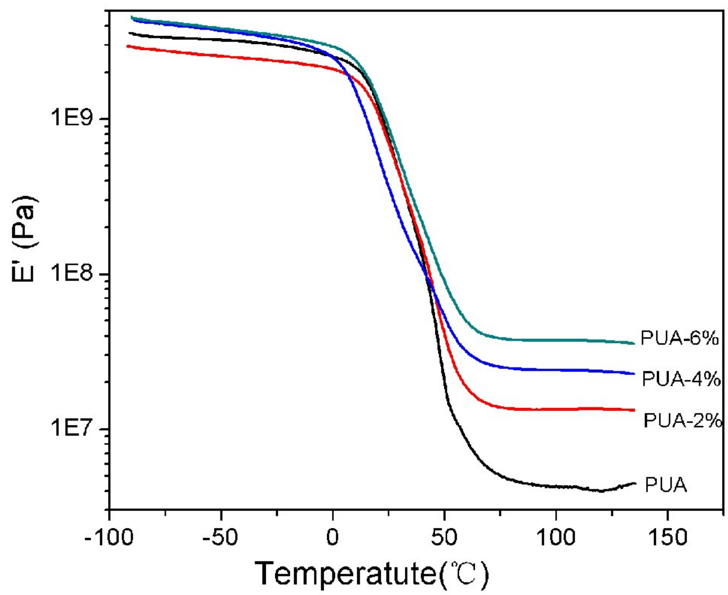

Fig. 7. Storage modulus E′ in dependence on temperature for the PUA/SiO_2 nanocomposites films.

Fig. 8 depicted the tanδ curve for the PUA and PUA/SiO_2 nanocomposites films. The nanocomposites films with 2 wt% and 4 wt% SiO_2 showed a single tanδ peak as pure PUA, which implied that soft segments and hard segments of the nanocomposite were well phase mixed. This was probably due to the excellent interaction between the hard and soft segments of PUA and SiO_2. For the nanocomposite film with 6 wt% SiO_2, two damping peak appeared. The two peaks could be ascribed to the glass transition temperature (Tg) of the soft and hard segments of PUA and free SiO_2 particles (as shown in SEM). Furthermore, the tanδ of PUA/SiO_2 nanocomposite films was shifted to a slightly higher temperature. This was because the existence of SiO_2 confined the mobility of PUA chains. And, the peak value of tanδ was found to decrease with an increased amount of SiO_2, which was due to the interfacial interaction between the PUA and SiO_2 nanoparticles. In conclusion, PUA and SiO_2 were well phase mixed and the incorporation of SiO_2 increased the Tg and the rigidity of PUA.

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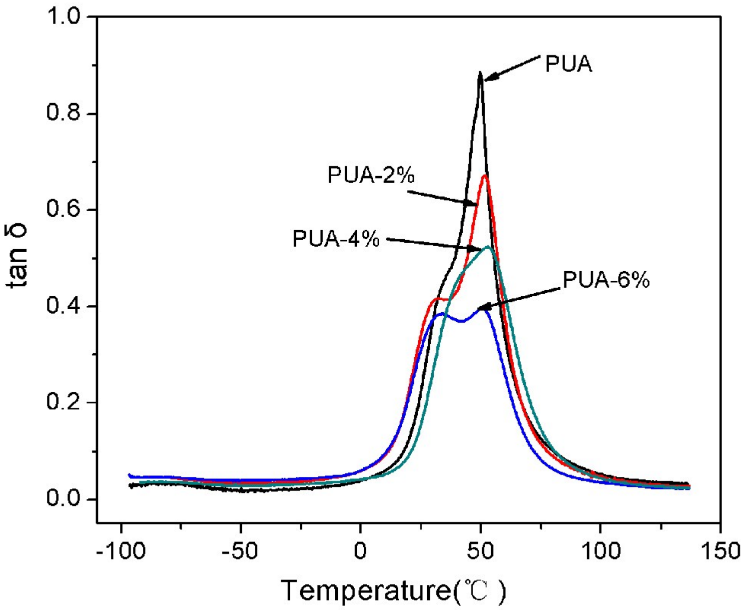

Fig. 8. Isochronal temperature dependence of tanδ for the PUA/SiO_2 nanocomposites films.

3.6. Optical properties

Fig. 9 illustrates that the transmittance of cured films (thickness: 300 μm) decreased with the increasing of SiO_2. Especially in the UV light region (below 400 nm), the transmittance dropped to 15%. This was because the surface roughness of films increased with the rising of SiO_2 content, which led to higher light scattering and lower transmittance. In addition, SiO_2 nanoparticles had strong UV absorption and showed good UV shielding effect. Therefore, SiO_2 could improve the weather resistance of PUA film, which might provide theoretical basis for the application of PUA/SiO_2 hybrid films in the field of painting or ink.

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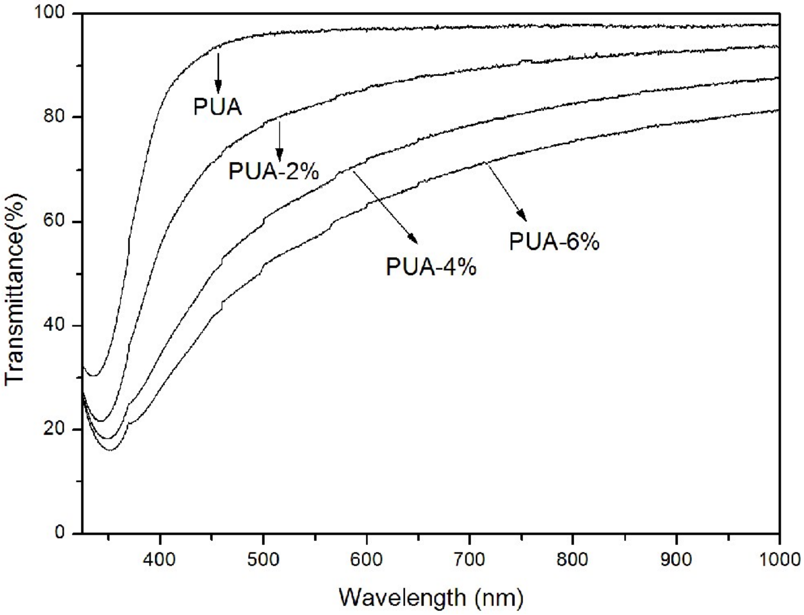

Fig. 9. UV-vis spectra of PUA and PUA/SiO$_2$ films with the thickness of 300 μm.

3.7. Surface properties

Table I Influence of SiO$_2$ content on surface properties of PUA/SiO$_2$ films.

Sample	Pencil hardness	Abrasion resistance (500 g, 500 r)	Adhesion (Grade)
PUA	HB	0.04	0
PUA-2%	2H	0.03	0
PUA-4%	3H	0.02	0
PUA-6%	4H	0.01	1

Table I listed the surface properties of PUA and PUA/SiO$_2$ films, such as pencil hardness, abrasion resistance and adhesion. With the increasing of SiO$_2$ content, the pencil hardness rose from HB of pure PUA films to 4H of PUA/SiO$_2$ films with 6 wt% SiO$_2$, the abrasion resistance became better and the adhesion slightly reduced from 0 to 1 grade. That might be because with the increasing of SiO$_2$ content, both inorganic component and cross-linking density increased to gain the hardness and abrasion resistance. However, when SiO$_2$ was excessive, the volume shrinkage of cured films reduced, which led to the adhesion slightly reduced [24].

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3.8. Properties of the thermochromic coatings

3.8.1 Temperature sensitivity

When the thermochromic coating was put in warm water at temperature of 40 ℃, it rapidly turned from yellow to orange, then it restored yellow immediately when cooled to room temperature (shown in Fig. 10). The phenomenon could be explained like this. At room temperature Ag_2HgI_4 (pigment) showed yellow with quartet sphalerite structure. However, when the temperature increased to 40 ℃, Ag_2HgI_4 showed orange with cubic crystal. Therefore, the thermochromic coating changed from yellow to orange when heated to 40 ℃ and vice versa. It demonstrated that the thermochromic coating based on PUA/SiO_2 nanocomposites had good temperature sensitivity and reversibility.

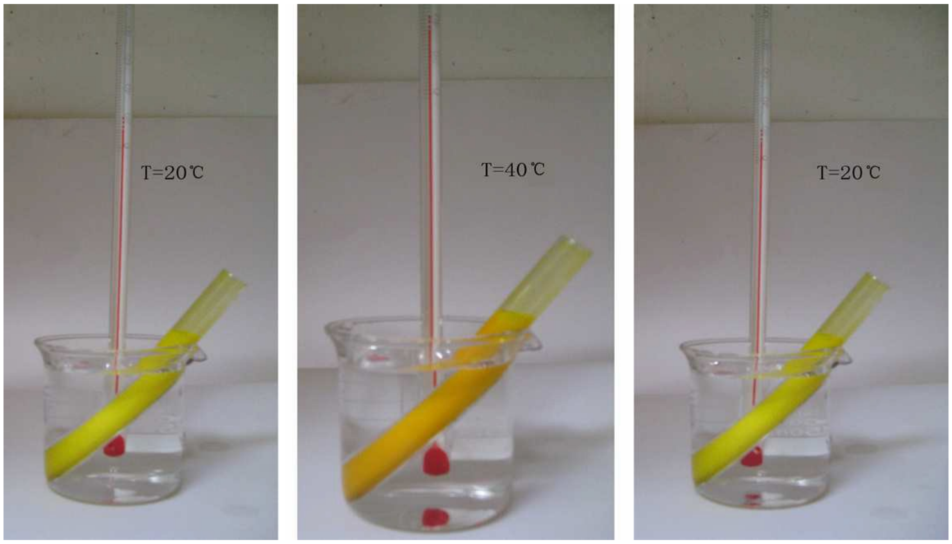

Fig. 10. Thermochromic effect of the waterborne UV-curable thermochromic coating.

3.8.2 The effect of SiO_2 content on temperature sensitivity

Fig. 11 showed the thermochromic effect of the waterborne UV-curable thermochromic coatings with 0, 2, 4, 6 wt% SiO_2 content. When all the thermochromic coatings were heated to 40 ℃, they rapidly turned from yellow to orange, then restored yellow immediately when cooled to room temperature (T=20 ℃). It demonstrated that the addition of SiO_2 had no effect on the temperature sensitivity of the waterborne UV-curable thermochromic coatings.

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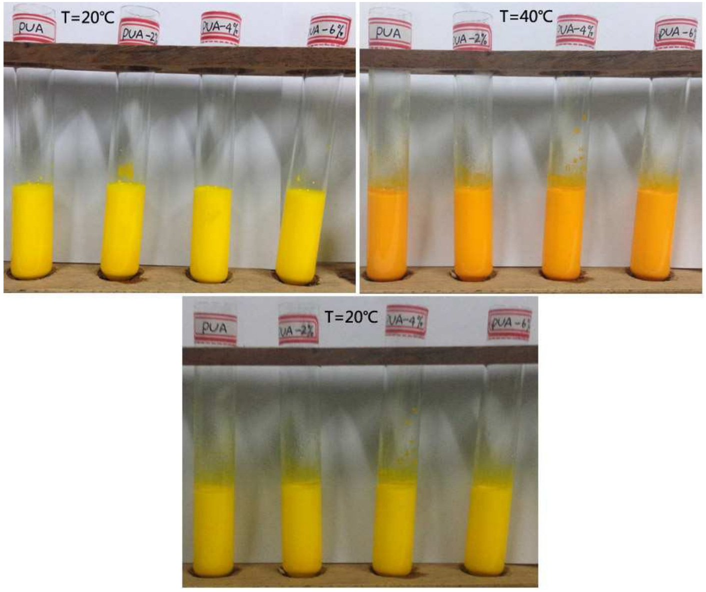

Fig. 11. Thermochromic effect of the waterborne UV-curable thermochromic coatings with different SiO_2 content.

4. Conclusions

The above results indicated waterborne UV-curable PUA/SiO_2 nanocomposites were prepared and applied to thermochromic coatings. TEM image implied that it was easier to get uniform emulsion by sol-gel method than physically blending method. The size of PUA/SiO_2 nanocomposite particles was approximately 70-100 nm, and increased slightly with the incorporation of modified SiO_2. SEM examinations of hybrid films showed that the nanosilica were well dispersed in the matrix. Surface tension and contact angle test both demonstrated the good wettability of the PUA/SiO_2 nanocomposite, which was conductive to the dispersion of it in thermochromic coatings. DMA indicated that PUA and SiO_2 were well phase mixed and the incorporation of SiO_2 increased the rigidity and Tg of PUA. Meanwhile, the nanocomposite films displayed enhanced hardness, abrasion resistance and good weather resistance. It was particularly necessary to point out that moderate modified SiO_2 could promote the curing speed of PUA coatings. Consequently, the resulting thermochromic coating showed good temperature sensitivity and reversibility. As we know, thermochromic coating as temperature sensitive material, which can be used as a sensor with the function of

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anti-counterfeiting or reminding, is usually printed on the surface of an object by inkjet printing or other ways. The study laid a good foundation for the research of enviromental temperature sensors.

Acknowledgments

This work was partially supported by the program of seventh batch of "3551 Optics Valley talent plan" of Wuhan East Lake High-tech Development Zone, Combination Project of Guangdong Province and the Ministry of Education (2011B090400397), Independent research project of the Fundamental Research Funds for the Central Universities (2042014gf037).

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Waterborne UV-curable Polyurethane Acrylate/Silica Nanocomposites for Thermochromic Coatings

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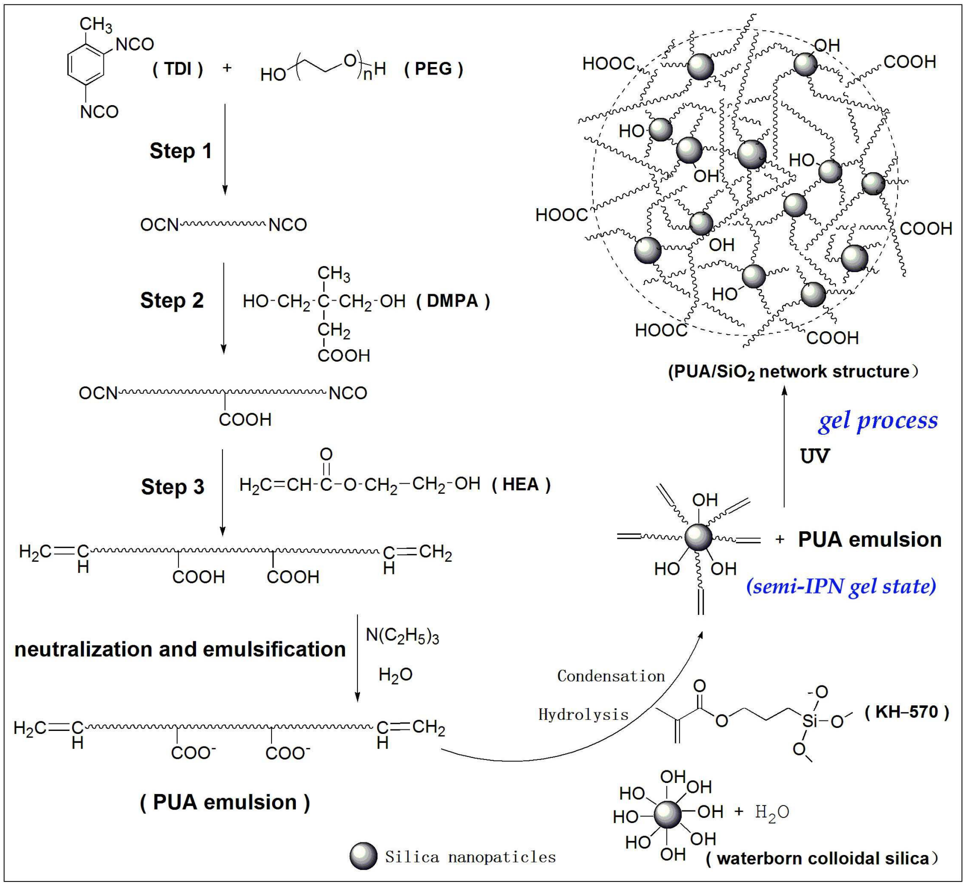
SiO_2 nanoparticles were modified by γ-Methacryloxypropyltrimethoxysilane (KH-570) and then introduced to the ends of the polyurethane acrylate main chains through radical polymerization, which might be the reason for high rigidity, hardness, resistance to abrasion and good weather resistance of PUA/SiO_2 nanocomposite coatings.



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