

Synthesis and characterization of polyacrylate composite with thiol-modified nanosilica as chain transfer agent

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ABSTRACT: Polyacrylate composites with thiol-modified nanosilica as chain transfer agent were prepared. The FTIR results indicated that the chemical bond has formed between polyacrylate and modified nanosilica. The change of molecular weight distribution proved that the thiol group on the nanosilica surface played the chain transfer agent role just as common thiol. A possible mechanism of modified nanosilica in the polymerization was proposed and the core-shell may be formed finally. In addition, the dispersion of nanosilica in the polyacrylate also improved as a result of the organic bridge structure between the nanosilica and polyacrylate. The thermal decomposition temperature increased as much as 10°C for polyacrylate with 10 wt % modified nanosilica composites compared to polyacrylate. The coatings hardness increased from 2 to 6 H and the abrasion resistance improved from 28 to 10 mg under the same conditions. Especially, the gloss change of coatings with different content of modified nanosilica indicated that the polyacrylate composites have obviously better aging resistance performance compared to polyacrylate. It may be ascribed to the property that nanosilica can absorb large UV light. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42756.

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INTRODUCTION

Polyacrylate has been widely used in the field of coating industry for its good film-forming, transparency, adhesion, and fast curing speed, etc.^{1–3} Especially, in recent years, polyacrylate with high solid content and low viscosity has been widely studied and adopted in many fields of automobile painting,⁴ steel corrosion,⁵ and equipment coatings² so as to meet the requirements of environment and resource protection. However, some drawbacks such as wide molecular weight distribution, poor solvent resistance, and poor mechanical properties, limit its application. One method is to control the polyacrylate chain length and molecular weight, which determine the final physical and mechanical properties of polymer.⁶ The other is developing organic-inorganic composite materials, which combine the advantages of organic polymers matrix and inorganic nanoparticles fillers.⁷

Thiols are well-known as efficient and ideal chain transfer agents for common polyacrylate synthesis such as methyl methacrylate (MMA) and styrene (St).⁸ The high efficiency of thiols in the control of the molecular weight distribution has been attributed to the weakness of the S—H bond and their ability to scavenge radicals by H-atom abstraction, which can decrease the polymer molecular weight, without a significant change in

the polymerization rate.^{9–11} Most of the works on the behavior of thiols focus on the small molecular thiols, such as thiophenols,¹² phenols,¹³ 2-mercaptoethanol,¹⁴ 2-benzoxazolethiol, and 2-benzothiazolethiol^{15,16} etc. Therefore, the unpleasant odor of small molecular thiols limits its application in polymerization and small molecular fragments will residue in the coating film. Studies on the macromolecular thiols and grafted thiols have received scarce attention.

The other important chain transfer agent reported is intercalated chain transfer agent,¹⁷ with which the polymer/nanoparticles was synthesized. The nanoparticles were usually used to prepare polymer composite so as to enhance the mechanical properties of polymer matrix. Especially, the polyacrylate/nanosilica hybrid materials have been widely used in many fields.^{18,19} The introduction of nanosilica in the polymer can improve the abrasion resistance, aging resistance, and climate resistance of the polyacrylate materials. However, the nanosilica has tendency to agglomeration or clustering due to the dominant intermolecular van der Waals interactions between the particles.²⁰ Thus, uniform dispersion of nanosilica in the polyacrylate matrix is of prime importance. In recent years, many reports focus on the nanosilica modification in order to turn their surface from hydrophilic to organophilic. A lot of methods has been used to

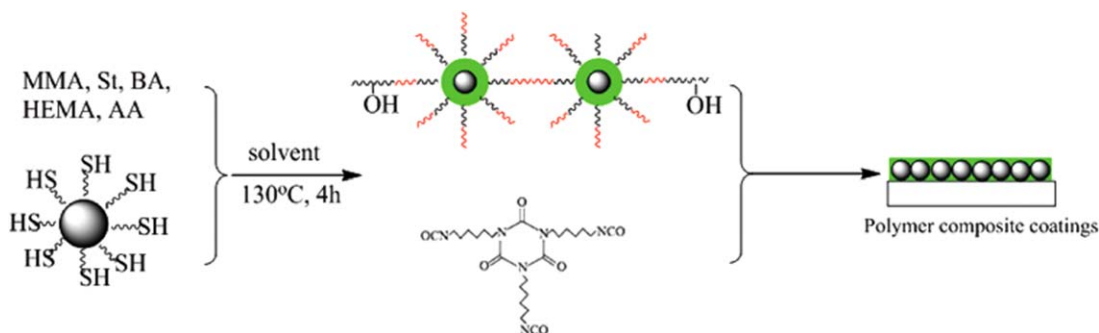


Figure 1. Schematic diagram of PA/SiO₂ hybrid coating. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modify nanosilica, for example, silane coupling agent, reactive agent, and hyperbranched polymer.^{21–23} The surface reactive agent on the nanosilica can not only improve the agglomeration of nanosilica in the polymer matrix, but also can provide active reactive functional group to participate the polymerization process. Therefore, the nanosilica modified by surface reactive agent have wide application in polymer/silica hybrid materials preparation.

The goal of this work was to study the chain transfer properties of thiol-modified nanosilica on the polyacrylate synthesis in organic media. Furthermore, the effect of modified nanosilica on the properties of polyacrylate composite coating was investigated.

EXPERIMENTAL

Materials

Nanosilica used in this study with mean size of 20–50 nm were purchased from Zhejiang Hongcheng Materials of China. MPTMS was purchased from Sigma Chemical and was used as a coupling agent. MMA (A.R.), St (A.R.), *n*-Butyl acrylate (A.R.), hydroxyethyl methacrylate (HEMA, A.R.), and acrylic acid (AA, 99.5%) were obtained from Tianjin Fuchen Chemical Reagent Factory, China. Xylene and butyl acetate were purchased locally. BPO used as initiator was obtained from Akzo-Nobel N.V. N3390 from Bayer was used as curing agent. All other chemicals, were analytical pure reagents (AR) and used as received without further treatment.

Preparation of Modified Nanosilica

The modified nanosilica was prepared according to our previous works.²¹ The highest grafting ratio of 16.8%, corresponding to thiol group content of 1.9 mmol/g, was obtained with 75 mL MPTMS to modify 10 g nanosilica. The thiol-modified nanosilica was dried and collected. The detailed preparation process and characterization are omitted in this work.

Preparation of Polyacrylate/Nanosilica Composite

The polyacrylate/nanosilica composite was synthesized with thiol-modified nanosilica as chain transfer agent. A typical synthesis procedure was as follows: a 500 mL, four-necked flask equipped with a mechanical stirrer, nitrogen purging system, thermometer, and a refluxing device was used as a reactor. First, 45 g xylene and 45 g butyl acetate were mixed and introduced into the flask, which was deoxygenated via 15 min nitrogen purge and then heated to 130°C and maintained half an hour.

Second, a different amount of thiol-modified nanosilica was added into the flask under strong mechanical stirring. Third, 45 g MMA, 42 g St, 63 g BA, 54 g HEMA, 6 g AA, and 6 g BPO were mixed into a clean beaker with vigorously magnetic stirring. Then the mixed monomers were dropped into the above solvent about 4–5 h under 130°C. Forth, after all the mixed monomers adding into the flask, the reaction maintained at 130°C for 2 h, 2 g BPO dissolved in mixed solvent of 5 g xylene and 5 g butyl acetone was added into the above flask, then the reaction end can be determined by the solid content reached 70% and the monomer conversions determined gravimetrically nearly to 100%. The synthesis scheme was given as shown in Figure 1.

Preparation of Thermosetting Coating with Prepared Polyacrylate Composite

The thermosetting coating was prepared by mixing two different components according to the NCO/OH mole ratio of 1.05 : 1. The component A is a mixture of polyacrylate composite, xylene, leveling agent, and defoaming agent with mass ratio of 50 : 10 : 0.1 : 0.1, and the component B is a mixture of curing agent N3390 and butyl acetone with mass ratio of 12 : 8. Then, the coatings was glued on the tinplate, the film was dried at the room temperature and the film properties were investigated.

Instrument and Characterization

FTIR spectra were recorded on a flouirier transform infrared spectrometer (Nicolet 360) with KBr pellets. The viscosities of coating were measured by a NDJ-79 rotation viscometer (Shanghai Scientific Instrument, China) at 25°C. Gel permeation chromatography (GPC) was used to determine the molecular weight after the grafted polyacrylate was cleaved from nanosilica with hydrofluoric acid.²⁴ The GPC is Waters1515, which used a refractive index (2410) detector with THF as the eluent. Samples were firstly treated by centrifugal separation and then prepared by dissolving 10 mg of polymer in 1 mL of THF and passing them through a 0.22 μm organic filter in order to remove any particulate contaminants. Analysis was performed at 35°C with a flow rate of 1 mL/min, and the poly (styrene) narrow standards were used. The thermal stability of the polyacrylate composites was measured by thermogravimetric analysis (TGA) using a Beijing Henven Scientific Instruments HCT-1 thermogravimetric analyzer. The samples were heated at a rate of 10°C/min from room temperature to 900°C under nitrogen. Transmission electron microscopy (TEM, Hitachi

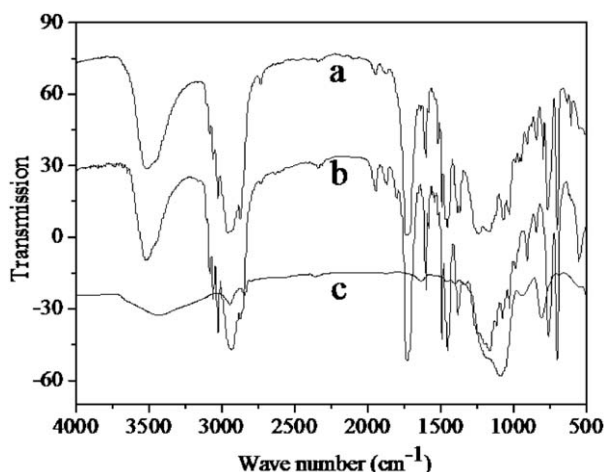


Figure 2. FTIR spectra of (a) polyacrylate composite, (b) polyacrylate, and (c) thiol-modified nanosilica.

JEM-2100UHR, Japan) was used to study the dispersion and core-shell structure of the composite.

The gloss of polyacrylate composites coating film was measured using a reflectometer (model micro-TRI-gloss, BYK Gardner, Silver Spring, MD) equipped with a shield having a circular 19 mm-diameter aperture. Three instrumental measurements at the geometry of 60° were carried out for each sample but at different positions of the film. The pencil hardness of films was determined according to the testing method of ASTM D3363. The abrasion resistance was tested in accordance with ASTM D4060 by subjecting the cured film at room temperature to a YL-3315 Taber Abrader (Youtu Instrument, China) using a wheel under 500 g loads and 300 cycles abrasion. The transmittance of films was characterized by a UV-vis spectrophotometer (type UV-160A, wavelength range 200–800 nm). The thickness of films is 120 μm .

RESULTS AND DISCUSSION

Preparation and Characterization of Polyacrylate Composites

The goal of the work is to regulate the polyacrylate structure and control its molecular weight distribution by using thiol-modified nanosilica as chain transfer agent. Therefore, FTIR is an effective method to determine whether the modified nanosilica participate in the polymerization. Figure 2 displays the differences among the structures of modified nanosilica, polyacrylate, and polyacrylate composite. In FTIR spectra of modified nanosilica, the absorption peak 2570 cm^{-1} is extending vibration of S—H, the absorption peak at 2626 and 2855 cm^{-1} is related to symmetric and asymmetric stretching of $-\text{CH}_2$. The weak absorption peak at 1100 cm^{-1} belongs to extending vibration of Si—O—Si. In comparison of FTIR spectrums of modified nanosilica and polyacrylate/nanosilica, the absorption peak of Si—O—Si appears in polyacrylate/nanosilica, which explains that nanosilica is copolymerized with acrylate monomers completely. While the absorption peak at 2570 cm^{-1} , corresponding to thiol groups, was covered by the strong absorption peak of nanosilica and the difference is not clear before and after modification.

Table I. Molecular Weights of the Synthesized Polyacrylate with Different Amount of Thiol-Modified Nanosilica

Polyacrylate	Thiol-modified nanosilica (wt %)	M_n	PDI
PA-I	0	8730	2.34
PA-II	2.5	7520	2.25
PA-III	5.0	5100	2.17
PA-IV	7.5	4130	2.10
PA-V	10.0	2540	1.92

The molecular weights of the prepared polyacrylate/nanosilica composite are listed in Table I. It can be observed that the polydispersity index (PDI) of polymer composite was less than the polyacrylate without nanosilica, while the number average molecular weight (M_n) of the polyacrylate changed with the amount of thiol-modified nanosilica. As the additive amount increased from 0 to 10%, the M_n of the polyacrylate decreased from 8730 to 2540 accordingly. The relatively narrow molecular weight distribution (PDI) of the polyacrylate decreased also suggest that the acrylic polymerization proceeded in a controlled manner. The GPC results indicated that the thiol group grafted onto the nanosilica surface played an important role of chain transfer agent in the polymerization.

To identify the role of modified nanosilica on the thermal properties of polyacrylate, TGA of neat polyacrylate film and the corresponding polyacrylate/nanosilica films are shown in Figure 3 and Table II.

According to the TGA curves, the weight loss within the temperature regions of 0 – 200°C is associated with physisorption water and residual solvent in the polyacrylate film,²⁵ while the weight loss from 200°C is the polyacrylate decomposition process. The temperature corresponding to 5 wt % loss is defined as the thermal degradation temperature (T_d), T_d of the formed composites are found to increase with increasing modified nanosilica in the polyacrylate. The highest T_d for various

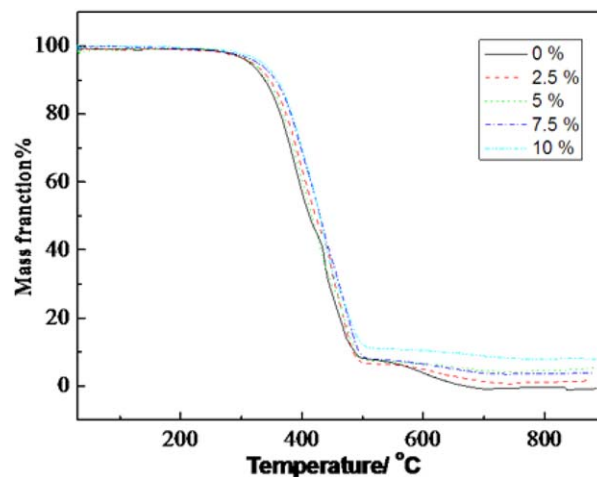


Figure 3. TGA curves of polyacrylate with different amount of thiol-modified nanosilica. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. The Weight Loss Data of Polyacrylate with Different Amount of Thiol-Modified Nanosilica

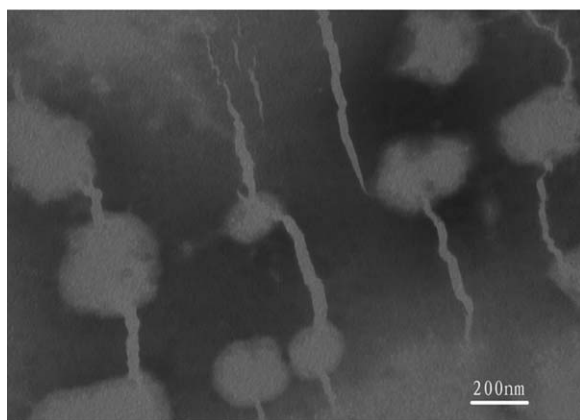
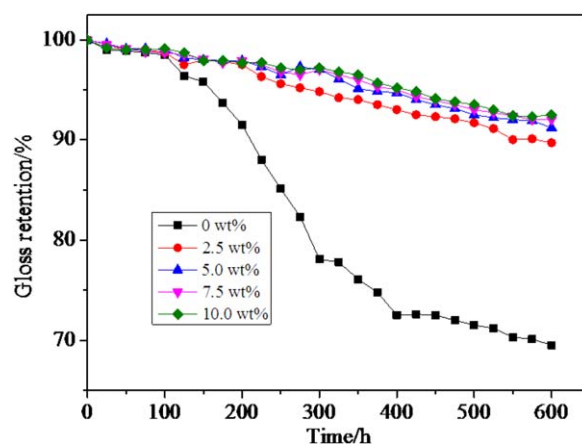
Nanosilica (wt %)	Weight residue (%)	T_5 (°C)	T_{10} (°C)	T_{50} (°C)
0%	0.09	320.6	342.4	414.0
2.5%	2.01	326.4	350.6	422.6
5%	5.61	325.4	346.2	424.4
7.5%	6.77	327.6	356.0	427.5
10%	8.80	331.4	357.0	423.7

samples is up to 331.4°C, that is, that of 10 wt % nanosilica addition. The char yields of various composites, as expected, increased with increasing modified nanosilica content. At 800°C, the residual values are close to the nanosilica content. The TGA data of T_5 and T_{10} for 5% modified nanosilica is anomaly and not in trend. It may be resulted from the higher crosslink density of portion polyacrylate. The residue after the TGA analysis at 800°C is more than 5% also indicated that the polymer with higher crosslink density. Obviously, the modified nanosilica particles within the hybrid matrix have made the polyacrylate more stable against thermal decomposition, and this effect is stronger for samples with higher silica contents.

Figure 4 shows the TEM image of polymer composite, from which we can see that the composite particle size was about 200 nm, and the particles well dispersed in solution indicating that the polymers had been successfully coated on the surface of nanosilica particles and a core-shell structure had formed. The cracks connecting the particles may result from the ungrafted polyurethane chain during the curing process.

The Influences of Modified Nanosilica on the Preproperties of Coating Film

The polymer composites film formation and its properties are affected not only by the nature of the polymers, but also by the adding method of inorganic particles.²⁶ In the work, the polyacrylate was synthesized onto the nanosilica surface and the nanoparticles participate the copolymerization, therefore, the uniform polymer composite will be formed and the properties will be more effectively improved. The coatings prepared by

**Figure 4.** TEM image of polyacrylate composite.**Figure 5.** Effect of different amount of modified nanosilica on the gloss change value after 600 h UV exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polyacrylate/nanosilica can be used varnish to protect steel, wood, and other. The gloss change, transparency, and mechanical properties of coating films is important, therefore, the influences of modified nanosilica on the above properties were mainly investigated.

Gloss

Change in gloss values of the coatings film as a function of surface degradation is one of the way to understand the ability to resist the test environment.²⁷ Figure 5 shows the gloss change before and after 600 h exposure of the coating films to UV light with different times. From the starting time, the gloss values for the neat polyacrylate coatings film and polyacrylate/modified nanosilica coating films before exposure to the UV light are more or less same. This is attributed to the inherent property of polyacrylate matrix, while the well-dispersed nanosize particles in films and the particles are so small that the surface roughness is very small. So, the gloss of neat polymer and polymer composites have not obvious different, and the polymer composites can also be used as surface varnish.^{28,29}

After the films exposed to 600 h UV radiations, the gloss value of the coatings without modified nanosilica reduced drastically. The coating with modified nanosilica also show less reduction in gloss values compared to the neat polyacrylate, but the value change decreased with the increase of adding amount of modified nanosilica. It indicated that the addition of modified nanosilica improved the stability and anti aging of polyacrylate. This can be attributed to the nanosilica's reflection and absorption of UV light.

Transparency

The transparency of the polymer composite films is important to varnish coatings. Figure 6 shows the graph of the transparency of coatings film with 120 μm thickness on the surface of paper. From the graph, it can be seen that that the transparency of the coating system is not affected due to addition of modified nanosilica, supporting the fact that nanosilica do not affect the clarity of the coatings. There are two possible reasons for the above phenomena. First, according to optical principles, when the particles size was smaller than one half of the

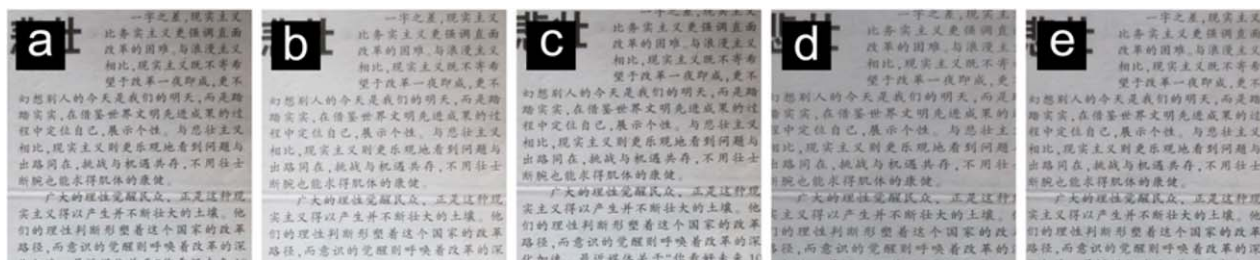


Figure 6. The graph of the transparency of coatings film containing different amount of modified nanosilica with 120 μm thickness on the surface of paper. (a) 0 wt %, (b) 2.5 wt %, (c) 5 wt %, (d) 7.5 wt %, and (e) 10 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

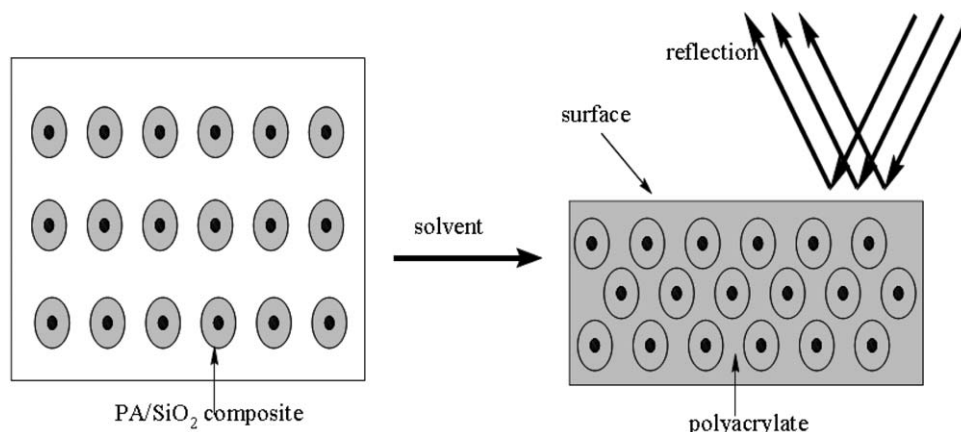


Figure 7. Effect of core-shell structure polyacrylate composite on the gloss of coatings.

wavelength of light, the light can pass around the films, and so no scattering and reflecting occurs in the visible light range leading to transparent coating films.³⁰ Second, the modified nanosilica was used as chain transfer agent, which result in the uniform dispersion of nanosilica in polyacrylate and the core-shell structure may be formed. The core-shell structure without rough surface and the absorption of nanosilica to the light is very weak as shown in Figure 7.

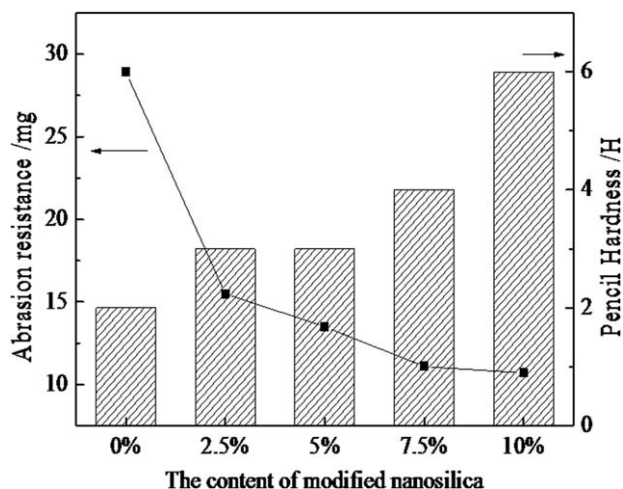


Figure 8. Effect of thiol-modified nanosilica on the abrasion resistance and pencil hardness of coating.

Hardness and Abrasion Resistance

Figure 8 shows the effect of addition of thiol-modified nanosilica on the abrasion resistance and hardness of the coating. It can be seen from the curves that, the neat coating show maximum weight loss as compared with the coating with thiol-modified nanosilica as chain transfer agent. As the concentration of modified nanosilica increases, the abrasion resistance of the coating improved from 28 to 10 mg under the above same conditions, indicating the improvement in the abrasion resistance of the coating. In addition, the pencil hardness shows continuous improvement with increasing thiol-modified nanosilica content. The pencil hardness has the most improvement to four higher grades till 10 wt % modified nanosilica content.

The improvement of abrasion resistance and pencil hardness of coating may be attributed to two possible reasons. First is the strong surface interaction between the modified nanosilica and polymer matrix, which improves the mechanical property of the coating system providing the substrate for the polymer forming. The core-shell structure will be formed during the polymer preparation process. The uniform dispersion of nanoparticles will reduce the agglomeration, which will decrease the surface roughness when nanoparticles adding the polymer, the mechanical properties will be improved to the greatest content.³¹ Second is the polyacrylate molecular weight, the polyacrylate with lower molecular weight corresponding to the higher modified nanosilica addition is more easily to form high density crosslink film for their more functional groups per molecule.

CONCLUSIONS

A polyacrylate was synthesized with the thiol-modified nanosilica as chain transfer agent. It was found that the addition of thiol-modified nanosilica can effectively regulate the molecular weight and the molecular weight dispersion of polyacrylate. The PDI of polyacrylate can reduce from 2.34 to 1.92 corresponding to 10 wt % modified nanosilica addition. Effect of modified nanosilica on the thermal property indicated that the thiol-modified nanosilica can improve the thermal decomposition temperature. The coating was prepared by synthesized polyacrylate and the transparency, gloss value change, abrasion resistance and pencil hardness of films were investigated, it was found that the above properties was improved with the increasing nanosilica addition. It can be attributed to the uniform dispersion of modified nanosilica into the polyacrylate matrix.

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