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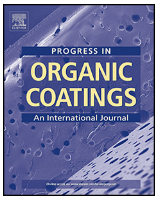

Nonionic surfactant-stabilized raspberry-like polymer/silica nanoparticles latex with film formability

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ABSTRACT

Raspberry-like P(St-BA)/SiO_2 nanoparticle latexes were prepared via miniemulsion polymerization of styrene (St) and butyl acrylate (BA) in the presence of 20 nm glycerol-modified SiO_2 sol as a Pickering emulsifier and octaphenyl polyoxyethylene (CA-897) as a nonionic surfactant, using 2,2-azobis (isobutyronitrile) (AIBN) as an initiator. 2-(Methacryloyl) ethyltrimethylammonium chloride (MTC) was introduced to act as an auxiliary monomer to enhance the attraction of SiO_2 sol onto latex nanoparticles (NPs) via increasing their electrostatic interaction with negative-charged SiO_2 sol. The average particle sizes of the latex particles can be well controlled from 200 to 360 nm by variation of the SiO_2 sol content as well as soft monomer BA component. The latex NPs displayed a good colloidal stability with excellent resistance to both strong acidic and basic environment. Furthermore, the nanosized latexes exhibited good film formability. The influence of reaction parameters, e.g., the initial silica amount and soft monomer BA content was systematically investigated on the film performances, such as hardness, abrasive resistance, water absorption, gloss. The results indicated that the increase of SiO_2 sol content can contribute to the increase of the film hardness and water absorption ability, while increasing BA component is beneficial to the improvement of the film gloss.

1. Introduction

Facing the increasing health problems caused by industrial pollution, more and more attention has being paid to the development of eco-friendly materials [1]. Concerning the coatings industry of a huge market, unlike the solvent based coatings (SBC), water-borne coatings (WBC) may offer a most practical and effective solution to the anti-pollution age, since the latter is involved in a lower content of volatile organic compounds (VOC) [2]. Generally, WBC film should be hydrophobic and robust to resist water sorption and internal/external stresses, and at the same time WBC pre-coatings which normally assume as water-borne suspensions should present some hydrophilicity to maintain their sufficient colloidal stability [2–4]. However, compared to traditional SBC, the motivation by the decreased cost and environmental safety of WBC is generally at the expense of their protective barrier properties, such as film formability, mechanical properties (hardness), gloss, scratch and/or water resistance, etc [5].

Due to their unique structure and special properties, polymer/inorganic nanocomposites have gained considerable academic and industrial interest over recent decades in the development of functional materials for a wide range of applications from optics, catalysis, microelectronics, medicine, coating, cosmetics, biology, etc [6–9]. Concerning the contradictory requirements of WBC applications, it is very important to develop new technologies to fabricate polymer–inorganic nanocomposite latexes which can not only stabilize as WBC pre-coating dispersions but also have good film processability [10–14]. Among these, miniemulsion polymerization has attracted increasing interest as a technique for synthesizing polymer-inorganic nanocomposite latex with well-controlled size and structure [15–17]. As a component of coating materials,

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silica nanoparticles (SiO_2 NPs) are one of the most popular candidates, due to their monodispersed nanosize, surface and interface effects, thermal stability and high modulus [3,18–20]. Although there are many studies on fabrication of SiO_2 NPs/polymer colloidal particles, few works have been performed on the film performances of these hybrid colloidal particles [21]. Recently, Wu et al. [21] reported a successful synthesis of silica/poly(methyl methacrylate-butyl acrylate) (SiO_2/P(MMA–BA) core–shell nanocomposite colloids via emulsion polymerization, which has an ability to form a nanocomposite film with good transparency. The incorporation of soft BA composition can be used to improve the film formability as well as its toughness. Using a kind of glycerol-modified SiO_2 NPs (12 nm in diameter), Armes' group developed an organic surfactant-free emulsion polymerization method to prepare poly(styrene-*co*-*n*-butyl acrylate)/silica nanocomposite particles (P(St-BA)/SiO_2), which are able to form a transparent film with improved fire retardency [22,23]. However, the single employment of SiO_2 NPs as an inorganic surfactant tends to induce a flocculation, instead of formation of individual nanoparticles, especially for the system with increased BA content [23]. Furthermore, there are no systematic study on the P(St-BA)/SiO_2 latex film in their reports, such as hardness, scratch resistance, gloss, etc [22,23].

In the past five years, our group has been performing a systematic research on development of PSt/SiO_2 nanocomposite particles through a miniemulsion polymerization method [24–26]. Our research results indicate that the application of a cationic initiator, together with a cationic auxiliary monomer, is beneficial to the formation of well-dispersed PSt/SiO_2 NPs. The experimental data also showed that a cationic surfactant, instead of an anionic one, can attract more SiO_2 NPs to form stable PSt/SiO_2 NPs latexes through the stronger electrostatic interactions between them. From the perspective of green chemistry, a nonionic polyethylene glycol surfactant is less toxic than the cationic-charged surfactant [27]. Our most recent study indicated that an amphiphilic copolymer, poly(ethylene glycol)–poly(lactic acid) (PEG–PLA), was able to act as a biocompatible surfactant to stabilize inorganic silicate nanoparticles through the interactions between the hydrophobic PLA and silicate surface [28].

Herein, in this study, we developed an elegant approach to fabricate a kind of raspberry-like P(St-BA)/SiO_2 nanoparticles with film formability through miniemulsion polymerization of styrene (St) and butyl acrylate (BA) monomers in the presence of glycerol-modified SiO_2 NPs (20 nm) as a Pickering emulsifier as well as octaphenyl polyoxyethylene (CA-897) as a nonionic surfactant, using 2,2-azobis (isobutyronitrile) (AIBN) as an initiator. In order to enhance the electrostatic interactions between the polymeric matrix and SiO_2 NPs, a cationic 2-(methacryloyl)ethyltrimethylammonium chloride (MTC) was used as auxiliary monomer to promote the formation of raspberry-like NPs. BA monomer was incorporated into the hybrid NPs latexes to increase the film formability as well as film flexibility. The effect of SiO_2 NPs content and soft BA monomer component on the size and colloidal stability of P(St-BA)/SiO_2 NPs latexes was systematically investigated. The P(St-BA)/SiO_2 film were studied concerning their hardness, abrasive resistance, water absorption, gloss. It was found that the functionalized SiO_2 NPs could play a role in adjustment of physical properties of the latex films, including hardness, abrasive resistance, water absorption, while the increase of BA content can be used to improve the film gloss.

2. Experimental

2.1. Materials

Styrene (St, purity≥99%) was bought from Sinopharm Reagent Co., Ltd., China. Butyl acrylate (BA) was obtained from Tianjin Bodi Chemical Reagent Company, China. Methacryloyloxyethyl trimethyl ammonium chloride (MTC, 76.7% aqueous solution) was purchased from Yancheng Chemical Reagent Co., Ltd., China. Octaphenyl polyoxyethylene (CA-897, 40 oxyethylene units, 50% aqueous solution) was bought from Rhone-Poulenc Company, France. A glycerol-modified silica sol (Bindzil CC30, 20 nm in diameter, solid content 30 wt%) was obtained from Eka Chemicals Co., Ltd. Hexadecane (HD) was purchased from Alfa Aesar, USA. 2, 2-Azobis (isobutyronitrile) (AIBN) was purchased from Shanghai Gaoqiao Petrochemical Company, China, and purified by recrystallization.

Table 1
Recipes of the typical miniemulsion polymerizations at 70 °C.

Run	St (g)	BA (g)	SiO_2 (g)	BA/(BA + St) (g/g)	SiO_2/(BA + St) (g/g)
1	2.1	2.9	0	0.58	0
2	2.1	2.9	1.75	0.58	0.35
3	2.1	2.9	3.5	0.58	0.70
4	2.1	2.9	7	0.58	1.40
5	1.45	3.55	7	0.71	1.40
6	1.25	3.75	7	0.75	1.40
7	1	4	7	0.80	1.40

Fixed chemical amount: CA-897: 0.20 g, MTC: 0.15 g, HD: 0.23 g, AIBN: 0.15 g, H_2O:38 g. The total weight of St and BA monomers fixed at 5.0 g.

2.2. Preparation of P (St -BA)/SiO_2 latex nanoparticles and latex film

The P(St-BA)/SiO_2 nanoparticles were prepared via miniemulsion polymerization according to the feed ratios shown in Table 1. In a typical synthetic experiment, 0.15 g of AIBN was dissolved in 0.23 g of hexadecane with a mixture (5 g in total) of St and BA monomers under ultrasonication. The mixture was then dropped into the 38 g aqueous solution of MTC (0.15 g) and CA-897 (0.20 g) under magnetic stirring for 30 min, followed by ultrasonication (Ningbo Xingzhi JY92-II DN) in an ice bath to form a miniemulsion system. The resulting miniemulsion was purged with nitrogen for 10 min and then slowly heated to 70 °C, followed by the addition of silica sol. The polymerization was carried out at 70 °C for 8 h under nitrogen atmosphere to obtain P(St-BA)/SiO_2 NPs latexes.

To prepare the latex films, P(St-BA)/SiO_2 NPs latexes were casted onto on a clear glass plate, followed by natural evaporation under room temperature to get uniform P(St-BA)/SiO_2 latex film. For the sake of comparison, pure P(St-BA) film was prepared by the same process. The samples were numbered from 1 to 7, according to the feed chemical composition.

2.3. Testing and characterization

2.3.1. Characterization of P(St-BA)/SiO_2 NPs latexes

2.3.1.1. Analysis of hydrodynamic sizes for P(St-BA)/SiO_2 NPs latexes. The hydrodynamic sizes of the NPs latexes were measured at 25 °C by a Zetasizer (Malvern Nano S, UK). The measurement for each sample was repeated thrice.

2.3.1.2. Morphological observation of P(St-BA)/SiO_2 NPs latexes. The morphologies of the NPs latexes were investigated by a Transmission Electron Microscope (TEM, FEI tecnai G20, FEI Corp., USA). To prepare the TEM samples, the NPs latexes were centrifuged to remove the by-products to get the purified NPs precipitates, which was then redispersed in water under ultrasonication. The NPs suspensions were dropped onto a carbon-coated copper grid to be air-dried.

2.3.1.3. Colloidal stability of P(St-BA)/SiO_2 NPs latexes and the pH effect on their stability. To study the colloidal stability, the hybrid

NPs latexes put into the aqueous solutions of 0.1–1.0 M of NaCl or $CaCl_2$ [29]. At an interval period, the solution was observed visually to check if flocculation happens. To investigate the effect of pH values on their stability, an aqueous solution of 30 wt% NaOH or 30 wt% HCl was slowly dropped into the 5 mL P(St-BA)/SiO_2 NPs latexes to adjust the pH of the system to check if the emulsion latexes aggregate.

2.3.2. Performance testing of composite latex film

2.3.2.1. Morphological observation of composite latex film. The morphology and structure of the as-prepared products was observed using scanning electron microscopy (JEOL, JSM-7100F, Japan).To prepare the SEM samples, the latexes were casted onto on small clear glass wafers, followed by natural evaporation under room temperature to get uniform P(St-BA)/SiO_2 latex film.

2.3.2.2. Water absorption. Water absorption was characterized by soaking the latex films in water at 25 °C and the films were weighed at a specific period. Water uptake rate (W_u) is defined according to following equation:

$$W_u = \frac{(W_e - W_0)}{W_0} \tag{1}$$

where W_0 is the original weight of the films before soaking, and W_e is their corresponding weight at equilibrium soaking time.

2.3.2.3. Hardness testing. Pendulum hardness of the latex film was measured according to Method B of the Chinese-standard GB/T 1730-90 through the paint films-pendulum damping test. Samples were uniformly coated with coating applicator onto glass plates, thickness of film about 50 μm. The pendulum hardness X was determined according to the Eq. (2) using a paint film pendulous hardness meter (QBY-II film pendulum hardness tester, Tianjin Weida Testing Machine Factory, China).

$$X = \frac{t}{t_0} \tag{2}$$

where t and t_0 were the times of oscillation for oscillating bar from 6° to 3° on the paint film and glass plate, respectively.

2.3.2.4. Abrasive resistance. To test abrasion resistance, the latex films were measured by a QMN paint film abrasion tester (Tianjin Weida Testing Machine Factory, China). The latex films which formed on a round iron sheet panel were checked by the scratch tester. The panels were placed in an abrasion machine, which uses two grinding wheels that moves back and forward at a constant rate and force over the substrate. The abrasion resistance is measured by the weight loss of the latex films after the two grinding wheels have been performed 100 circles.

2.3.2.5. Gloss. For gloss testing, the latex films were applied to a glass panel. The specular film gloss was measured by the Chinese-standard GB9754-88 on gloss tester (KGZ-1B specular gloss meter, Shanghai Jieying Electronic Technology Co., Ltd., China). The latex films were was tested by the method of GB9754-88, and the test angle was set as 60°. Each sample was repeated for five times to give the average gloss value. The higher gloss value means a better gloss.

3. Results and discussion

3.1. Preparation and characterization of the P(St-BA)/SiO_2 NPs latexes

3.1.1. Morphology of the P(St-BA)/SiO_2 NPs latexes

A series of P(St-BA)/SiO_2 NPs latexes were synthesized by a miniemulsion polymerization technique using CA-897 as a nonionic surfactant. The effect of initial silica amounts and St/BA ratio on the size of the particles and the resulting film properties were summarized in Table 1. Since SiO_2 NPs are negatively charged and CA-897 has a neutral surface, a cationic MTC monomer bearing quaternary ammonium group was selected as an auxiliary monomer to promote the formation of the P(St-BA)/SiO_2 NPs.

The morphology and size distribution of the P(St-BA)/SiO_2 NPs were characterized by transmission electron microscopy (TEM) imaging. As shown in Fig. 1, in the presence of the nonionic surfactant of CA-897, all the P(St-BA)/SiO_2 NPs assumed as a reasonably monodispersed spherical structure. However, control experiment in the absence of MTC presented a bare surface, suggesting that nanosilica could not be absorbed on the NPs surfaces probably because both nanosilica and P(St-BA) NPs are negatively charged and repel each other (Fig. 1A). The introduction of MTC resulted in a formation of P(St-BA)/SiO_2 NPs with a distinct raspberry-like morphology (Fig. 1B). This change can be explained that the incorporation of positively charged MTC (3 wt% of total St and BA monomers) is enough to promote the deposition of nanosilica on the NPs latexes via increasing the electrostatic interactions

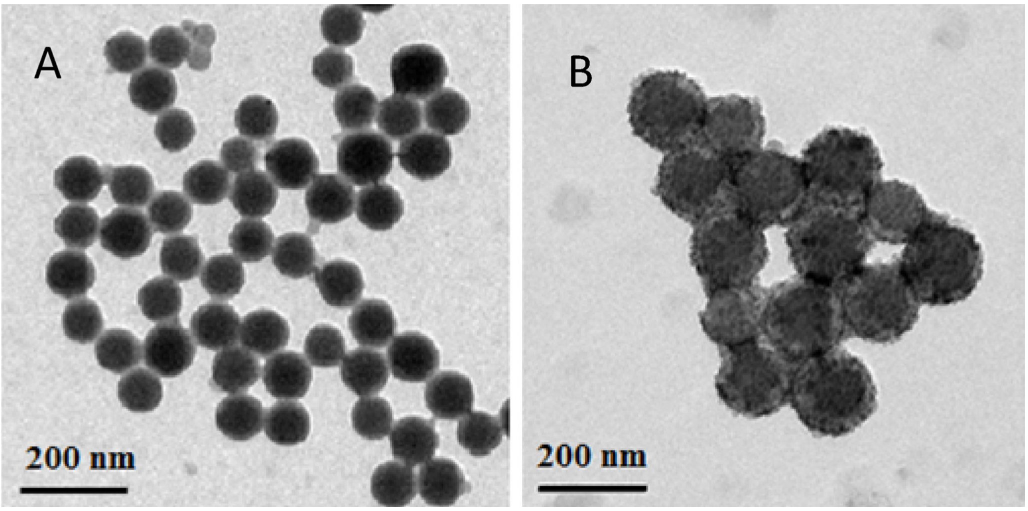

Fig. 1. TEM images of P(St-BA)/SiO_2 NPs latexes in the absence or presence of cationic MTC monomer.

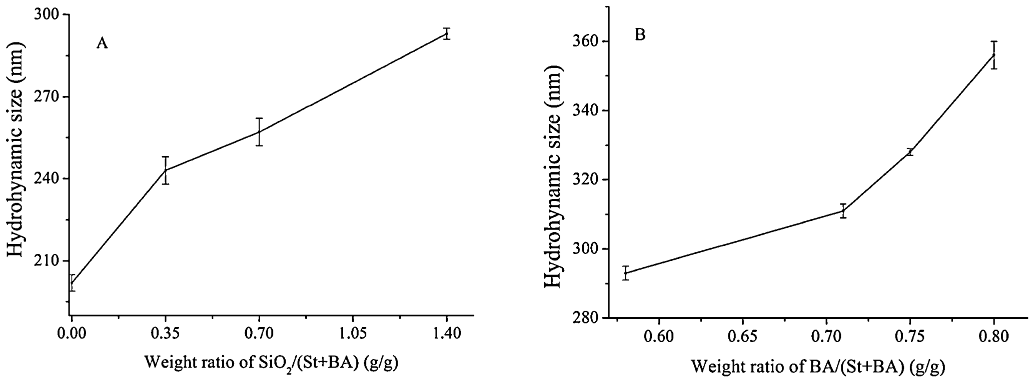

Fig. 2. Dependence of the hydrohynamic sizes on the weight ratio of nanosilica (A) and BA (B).

between them. These results are in agreement with our previous report on PSt/SiO_2 NPs system where a negative-charged surfactant was used as a surfactant [24]. The above study also suggests that, in case of both negative-charged surfactant and neutral one, a cationic monomer could play a key role on the formation of raspberry-like PSt-based/SiO_2 NPs latexes.

3.1.2. Size adjustment of the P(St-BA)/SiO_2 NPs latexes

In order to optimize the properties and functions of nanostructured materials/devices, it is desirable to control the size of their nanoparticulate components [30]. The effect of nanosilica amount on the particle size of NPs latexes was firstly investigated. As shown in Fig. 2A, increasing initial silica weight ratio from 0 to 1.40 resulted in the increase of hydrodynamic sizes of the NPs latexes from 202 ± 3 to 293 ± 2 nm. This behavior can be explained that higher nanosilica concentration increased their possibility to be adsorbed on the polymeric latexes, thus resulting in a formation of P(St-BA)/SiO_2 NPs latexes with a larger size.

Fig. 2B illustrates the variation of the particle size of the P(St-BA)/SiO_2 NPs latexes as a function of BA content. It was found that the average diameters rapidly increased from 293 ± 2 to 356 ± 4 nm when the BA weight ratio based on the total monomers increased from 0.58 to 0.80. One possible reason is that the BA component owns carbonyl group, which is beneficial to the formation of hydrogen bonding with the hydroxyl groups on nanosilica. Therefore, the higher BA content led to a larger amount of SiO_2 particles to be adsorbed on the latexes, resulting in an increase in particle size. Another reason may be that an increase of BA content in the latexes will increase their softness, which can be more expansible in aqueous solution and thus assumed a bigger hydrodynamic size.

3.1.3. Colloidal stability of the P(St-BA)/SiO_2 NPs latexes

The development of nanoparticles with good colloidal stability is very important for their applications in a wide range of industrial fields, including coatings, cosmetics, pharmaceutical, agrochemicals and food processing [4]. The stability of the P(St-BA)/SiO_2 NPs latexes was investigated against the solutions of NaCl or $CaCl_2$ at different concentrations from 0.1 to 1.0 M, respectively. The results indicated that all the NPs latexes were stable for 10 days at room temperature under the electrolytic solution treatment, indicating their good stability against electrolytes. Furthermore, under strong acidic and basic conditions (pH from 1.0 to 14.0), the latexes still maintained their stability, indicating their good ability to resist acid environment. The good colloidal stability of the latex may be attributed to the employment of nonionic surfactant PEG-based CA-897 which has been recognized as a good stabilizer for biomedical applications [31], and to the introduction of the hydrophilic cationic MTC as an auxiliary monomer. Interestingly, the increase of nanosilica content did not affect the colloidal stability of the latexes, probably caused by the homogeneous dispersion of SiO_2 NPs on the latex NPs (seen from Fig. 1B).

3.2. Performances of the P(St-BA)/SiO_2 NPs latex film

The above results indicate that P(St-BA)/SiO_2 NPs latexes had a monodispersed raspberry-like morphology where the SiO_2 NPs can be homogeneously dispersed in the polymer matrix at the nanoscale level via enhanced electrostatic and/or other kind of interactions [21]. It is believed that the synergistic integration of the SiO_2 NPs with polymer phase will facilitate their film formability by preventing the severe aggregation of inorganic NPs in polymeric matrix and improving the inorganic/organic interface and the comprehensive film properties. To check this hypothesis, the latex films were prepared by casting of P(St-BA)/SiO_2 NPs latexes onto a clear glass plate, followed by normal air dry under room temperature. Pure P(St-BA) NPs latex film was prepared by the same process as a control. The film performances were evaluated concerning their surface morphology, hardness, abrasive resistance, water absorption, gloss.

Fig. 3 demonstrates the SEM images of the latex films. As shown in Fig. 3A, the composite latex film in the absence of SiO_2 appeared a homogeneous dispersion system but wrinkled, it was possibly because the interaction between the polymer microspheres and water molecule occurred with the evaporation of water in the drying process. Moreover, compared with the pure polymer latex film and the nanocomposite latex film (Fig. 3B), the nano-silica particles closely accumulated in an uniform way. SEM images demonstrated that the raspberry-like structure of the composite microspheres and good film-forming properties of the latex film.

3.2.1. Hardness and abrasive resistance

The mechanical properties of the coating materials are important factors for their applications as coating materials [20]. The hardness of the latex films was firstly investigated as a function of nanosilica content. From Fig. 4A, we can see that the increase of SiO_2 weight ratio from 0 to 1.40 greatly increased the hardness of the latex films from 0.010 to 0.053. As a kind of inorganic NPs, nanosilica owns high modulus, so their homogeneous dispersion in the polymer matrix as well as the good interface between them are helpful to exert their optimal nanosize effect, resulting in an effective improvement of the film hardness. On the other hand, the film formability and toughness are also very important factors. Considering the brittleness of SiO_2 materials and polystyrene, butyl acrylate as soft component was introduced. Since polybutyl acrylate has a glass transition temperature below room temperature [32], the hardness of the latex film decreased from 0.053 to

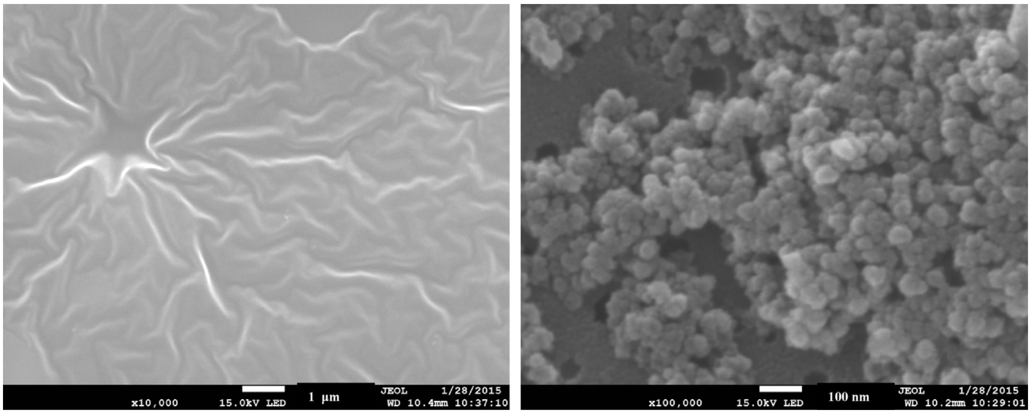

Fig. 3. SEM images of P(St-BA)/SiO_2 NPs latex films in the absence (Run1) or presence (Run 3) of SiO_2 NPs.

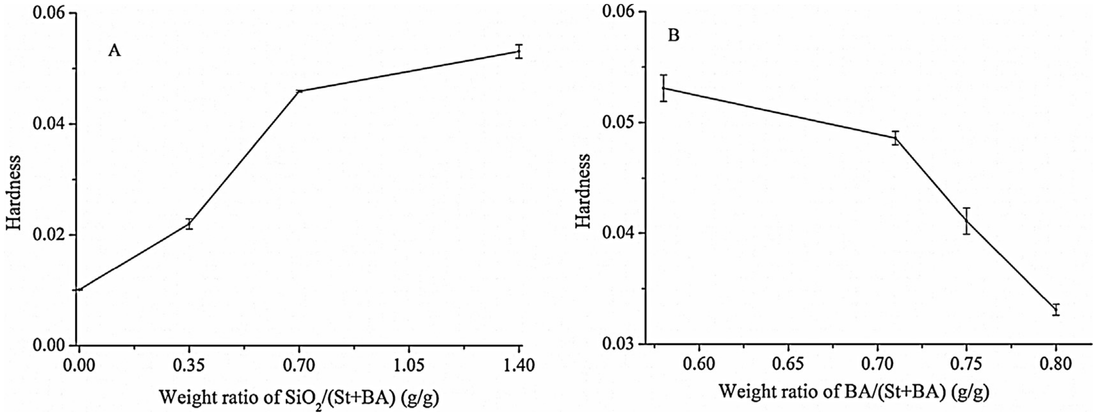

Fig. 4. Dependence of the film hardness on the weight ratio of nanosilica (A) and BA (B).

0.033 with the increase of BA weight ratio from 0.58 to 0.80. From these results, it can be seen that a good balance may be found for obtaining a kind of coating films with required mechanical properties via adjusting the content of SiO_2 and/or BA component, dependent on their specific applications.

In the coatings industry, abrasive resistance of materials refers to the resistance of coatings for friction mechanical action. It reflected that the hardness, adhesion and cohesion combined effect of the coating [33]. To evaluate the abrasive resistance, experiments were performed by grinding the samples by two wheels on a paint film abrasion tester. After grinding 100 circles, the weight loss of all the latex films was less than 1 wt% (data not shown), indicating their good abrasive resistance.

3.2.2. *Water absorption*

As mentioned above, for water-borne coating application, the pre-coating latexes should present some hydrophilicity to maintain their sufficient colloidal stability [2], which on the other hand may increase the water uptake ability of the WBC film. The water absorption behaviors of the latex films were investigated as a function of the nanosilica and BA content.

As shown in Fig. 5A, the water absorption rate greatly increased from 20 ± 1.4 to 139 ± 2.8% when the SiO_2 weight ratio based on the total amount of St and BA increased from 0 to 1.40. Since the glycerol-modified SiO_2 NPs have a large amount of hydroxyl groups on their surface, they should present more hydrophilicity than the St and BA components. The research from our group and others' indicated even SiO_2 NPs can act as "Pickering emulsifier" to prepare nanocomposite NPs [24–26]. Therefore, increasing SiO_2 NPs component greatly increased the hydrophilicity of the latex materials, thus resulting in a rapid increase of their water adsorption capacity. However, the water absorption ability can be balanced by incorporating hydrophobic BA component into the latex films. From Fig. 5B, we can see that the increase of BA weight ratio from 0.58 to 0.80 induced the decrease of the water absorption rate of the latex film from 139 ± 2.8 to 74 ± 0.8%. Again, similar to hardness behavior, the water absorption ability of the latex films can be well balanced by adjusting the relative ratio of nanosilica and BA component. It has to be noted that, for biomedical applications, a moderate hydrophilic surface is more desirable for cell attachment and growth [34]. In this sense, the current nanocomposite films with adjustable hydrophilicity may be very useful to decorate biomaterial surface to extend their biological applications.

3.2.3. *Gloss*

Gloss is the ability of a surface to reflect light to the specular angle, which is one of most important indicator for decorative coatings specially used for aesthetic purposes [35]. The gloss value of the latex films was evaluated concerning the different content of nanosilica and BA. It can be seen from Fig. 6 that the increase of the SiO_2 weight ratio decreased the film gloss, while the increase of BA weight ratio is beneficial to the gloss improvement of the films. This is because that higher amount of nanosilica may induce a bigger fluctuation during film formation, thus resulting in a higher roughness and a lower gloss value. However, the higher content of soft BA component may enhance the interfacial interactions of nanosilica with polymeric matrix, so a smoother surface was favored. On the other hand, the increase of BA content can enhance the flexibility of the latexes, which is beneficial to the film formability. Therefore, the latex film with better transparency and gloss was obtained.

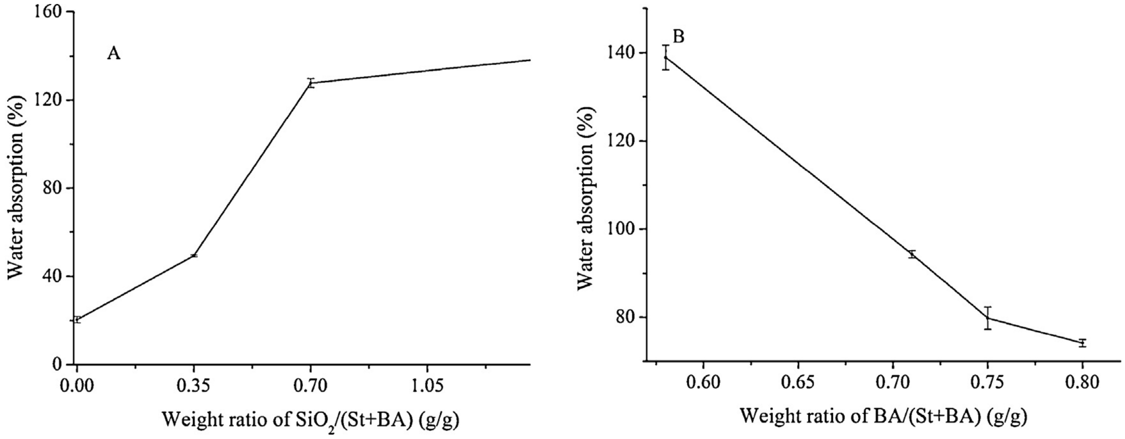

Fig. 5. Dependence of the water absorption of the films on the weight ratio of nanosilica (A) and BA (B).

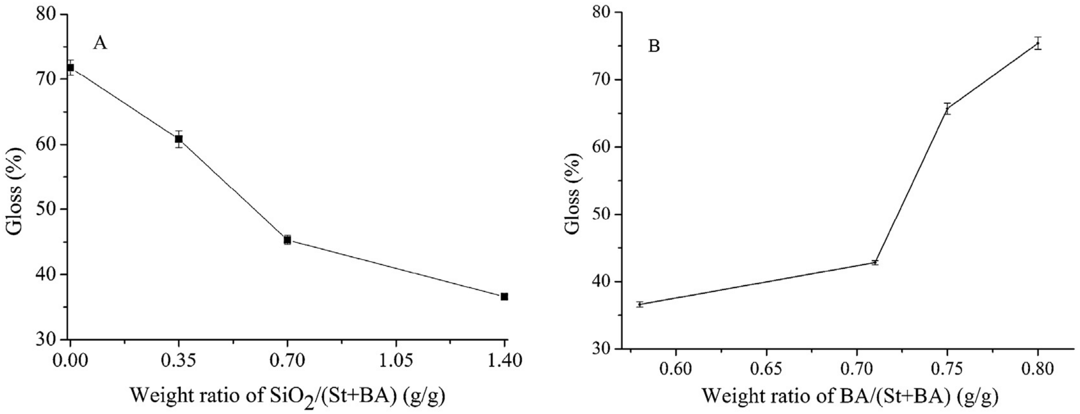

Fig. 6. Dependence of the gloss value of the films on the weight ratio of nanosilica (A) and BA (B).

4. Conclusions

In summary, a series of raspberry-like P(St-BA)/SiO_2 nanoparticle latexes by copolymerization of styrene (St) and butyl acrylate (BA) initiated by 2,2-azobis (isobutyronitrile) (AIBN), in the presence of 20 nm glycerol-modified SiO_2 sol (as a Pickering emulsifier) and octaphenyl polyoxyethylene (CA-897, as a non-ionic surfactant). The results indicated that the introduction of an auxiliary monomer, 2-(methacryloyl)ethyltrimethylammonium chloride (MTC), is very important for the formation of the raspberry-like P(St-BA)/SiO_2 nanoparticle latexes through increasing their electrostatic interaction with negative-charged SiO_2 sol. The size of the raspberry-like latex nanoparticles can be controlled by changing the content of SiO_2 sol as well as soft BA monomer. All the latex nanoparticles had good colloidal stability and film formability. The film performances, such as hardness, water absorption ability, gloss, can be well controlled by adjustment of the relative composition ratio of SiO_2 sol to BA component.

Acknowledgements

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References

[1] A. Aittomaki, P. Martikainen, M. Laaksonen, E. Lahelma, O. Rahkonen, Soc. Sci. Med. 75 (2012) 1303–1310.
[2] N.A. Swartz, K.A. Wood, T.L. Clare, Prog. Org. Coat. 75 (2012) 215–223.
[3] C.A. Heck, J.H.Z. dos Santos, C.R. Wolf, Int. J. Adhes. Adhes. 58 (2015) 13–20.
[4] F. Gambinossi, S.E. Mylon, J.K. Ferri, Adv. Colloid Interface Sci. (2014), http://dx.doi.org/10.1016/j.cis.2014.07.015
[5] M.S. Gebhard, Macromol. Symp. 187 (2002) 771–780.
[6] S. Kango, S. Kalia, A. Celli, J. Njuguna, Y. Habibi, R. Kumar, Prog. Polym. Sci. 38 (2013) 1232–1261.
[7] N. Misra, V. Kumar, J. Bahadur, S. Bhattacharya, S. Mazumder, L. Varshney, Prog. Org. Coat. 77 (2014) 1443–1451.
[8] A.M. Diez-Pascual, M. Naffakh, C. Marco, G. Ellis, M.A. Gomez-Fatou, Prog. Mater. Sci. 57 (2012) 1106–1190.
[9] Y. Lvov, E. Abdullayev, Prog. Polym. Sci. 38 (2013) 1690–1719.
[10] X. Zhao, S. Zhou, M. Chen, L. Wu, G. Gu, J. Appl. Polym. Sci. 119 (2011) 3615–3622.
[11] D.Z. Xu, M.Z. Wang, X.W. Ge, M.H.W. Lam, X.P. Ge, J. Mater. Chem. 22 (2012) 5784–5791.
[12] A.P. Romio, N. Bernardy, E.L. Senna, P.H.H. Araujo, C. Sayer, Mat. Sci. Eng., C—Bio. S. 29 (2009) 514–518.
[13] L. Bombalski, K. Min, H.C. Dong, C.B. Tang, K. Matyjaszewski, Macromolecules 40 (2007) 7429–7432.
[14] A. Samakande, R.D. Sanderson, P.C. Hartmann, J. Polym. Sci. Pol. Chem. 46 (2008) 7114–7126.
[15] N. Bechthold, F. Tiarks, M. Willert, K. Landfester, M. Antonietti, Macromol. Symp. 151 (2000) 549–555.
[16] F. Tiarks, K. Landfester, M. Antonietti, Langmuir 17 (2001) 5775–5780.
[17] K. Landfester, V. Mailander, Expert Opin. Drug Delivery 10 (2013) 593–609.
[18] M.H. Kim, H.K. Na, Y.K. Kim, S.R. Ryoo, H.S. Cho, K.E. Lee, H. Jeon, R. Ryoo, D.H. Min, ACS Nano 5 (2011) 3568–3576.
[19] D. Douroumis, I. Onyesom, M. Maniruzzaman, J. Mitchell, Crit. Rev. Biotechnol. 33 (2013) 229–245.
[20] K.D. Bouzakis, S. Hadjiyiannis, G. Skordaris, I. Mirisidis, N. Michailidis, K. Efstathiou, E. Pavlidou, G. Erkens, R. Cremer, S. Rambadt, I. Wirth, Surf. Coat. Technol. 177 (2004) 657–664.

[21] Y. Wu, D. Hu, Y.H. Su, Y.L. Hsiao, B. You, L.M. Wu, Prog. Org. Coat. 77 (2014) 1015–1022.
[22] A. Schmid, J. Tonnar, S.P. Armes, Adv. Mater. 20 (2008) 3331–3336.
[23] A. Schmid, P. Scherl, S.P. Armes, C.A.P. Leite, F. Galembeck, Macromolecules 42 (2009) 3721–3728.
[24] Y.H. Zhang, H. Chen, X.W. Shu, Q.C. Zou, M. Chen, Colloids Surf., A: Physicochem. Eng. Aspects 350 (2009) 26–32.
[25] Y.H. Zhang, Z.X. Chen, Z.F. Dong, M.G. Zhao, S.Y. Ning, P.X. He, Int. J. Polym. Mater. Polym. 62 (2013) 397–401.
[26] Y.H. Zhang, Q.C. Zou, X.W. Shu, Q.Q. Tang, M. Chen, L.M. Wu, J. Colloid Interface Sci. 336 (2009) 544–550.
[27] M. Goncalves, D. Maciel, D. Capelo, S.L. Xiao, W.J. Sun, X.Y. Shi, J. Rodrigues, H. Tomás, Y.L. Li, Biomacromolecules 15 (2014) 492–499.
[28] D. Maciel, Y. Wu, J. Rodrigues, X. Shi, Y. Yuan, C. Liu, H. Tomás, Y. Li, ACS Appl. Mater. Interfaces 6 (2014) 16687–16695.
[29] M.Y. Zhu, W.H. Qiao, H.Z. Liu, Y.L. Sun, J. Appl. Polym. Sci. 107 (2008) 624–628.
[30] B. Kowalczyk, I. Lagzi, B.A. Grzybowski, Curr. Opin. Colloid Interface Sci. 16 (2011) 135–148.
[31] H. Liao, H. Liu, Y. Li, M. Zhang, H. Tomás, M. Shen, X. Shi, J. Appl. Polym. Sci. 131 (2014) 40358.
[32] M. Fernandez-Garcia, J.L. de la Fuente, M. Fernandez-Sanz, E.L. Madruga, Macromol. Rapid Commun. 22 (2001) 1046–1052.
[33] F. Findik, Mater. Des. 57 (2014) 218–244.
[34] J.H. Lee, G. Khang, J.W. Lee, H.B. Lee, J. Colloid Interface Sci. 205 (1998) 323–330.
[35] V. Kumar, Y.K. Bhardwaj, N.K. Goel, S. Francis, K.A. Dubey, C.V. Chaudhari, K.S.S. Sarma, S. Sabharwal, Surf. Coat. Technol. 202 (2008) 5202–5209.