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ORIGINAL CONTRIBUTION

Synthesis and surface properties of PDMS–acrylate emulsion with gemini surfactant as co-emulsifier

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Abstract Composite latex particles of acrylate and polydimethylsiloxane (PDMS) with high PDMS content was prepared by emulsion copolymerization and characterized by particle size analyzer, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR). With gemini surfactant as the co-emulsifier in the system, the PDMS content in the system reached 50%, which was far higher than the other reported values. Through the characterization of the particle size analyzer, the particle size augmented with the increase of the amount of PDMS, which could be said that the polysiloxane had participated into the reaction and had been introduced into the colloid particle. The results of FTIR indicated that almost all the monomer had been exhausted in the reaction because there was no C=C and D_4 characteristic peaks in the spectrum. Besides the surface properties also were measured by surface tension analysis, water absorption, and the static contact angle, it could be found that with the increase of polysiloxane content, the excellent properties acquired by PDMS were clearly revealed by the findings, such as the decrease of surface tension and water absorption, and the increase of static contact angle. All the measurements were consistent with the conclusion that the composite latex particles of polysiloxane and acrylate with high siloxane content had been prepared successfully.

Keywords PDMS · Acrylate · High content · Gemini surfactant

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Introduction

Polysiloxane and their composite materials have attracted much attention due to the excellent properties, such as water repellency, high flexibility, low glass transition temperature, low surface energy, biocompatibility, etc. [1–4]. However, organic siloxane have their own insuperable disadvantages; for instance, the high-cost, poor cohesiveness and film-forming property limit their further application in many fields. In contrast, acrylate and polyacrylate were widely applied for its low-cost, good cohesiveness, and excellent film-forming property. It is a common knowledge that the greater the difference between the combining polymers, the more likely synergistic properties will result from the combination [5]. Therefore, the coalescence of polysiloxane and polyacrylate would bring unimaginable effect in their composite materials. Many significant works, recently, basing on organic siloxane have been shown in the published papers by Park et al. [6], Medda et al. [7], and Bauer et al. [8], contributing to the technical synthesis of some performance-specified coatings.

The latices of siloxane-acrylate copolymer have been widely applied in many areas because of their non-toxic and non-contaminating characters [9, 10]. In recent years, interest has been shown in the combination of acrylate with siloxane to obtain stable polymer latices and other polymer materials with improved performance. It is well known that the more siloxane in the copolymer, the more excellent properties of siloxane would be embodied, so the question of how to improve the siloxane content of latices is becoming more and more important. Some efforts have been made to solve the problem. Chengyou Kan et al. [11], Weidong He et al. [12], and Zhangqing Yu et al. [13] have devoted themselves to introducing octamethyl cyclotetrasiloxane (D_4) and vinyl septamethyl cyclotetrasiloxane (VD_4)

into the reaction system to enhance the siloxane content in the copolymer. But, the large amount of Si–O–Si chains formed by D_4 ring-opening polymerization were hard to be emulsified, which could engender floating oil, and the reaction of the multi-vinyl group could produce tangles in the chains causing a rapid augmentation of molecular weight so as to generate coagulum. Therefore, the siloxane content in the copolymer was no more than 25% all the time.

A gemini surfactant is a molecule composed of two identical hydrophilic head groups and two hydrophobic tail groups (Fig. 1). It is very similar to two single-chain surfactants linked covalently by a spacer group. The spacer group can vary in length and chemical structure, be flexible or rigid, and be hydrophilic or hydrophobic [14]. Gemini surfactants have some excellent solution and interfacial properties. First, the critical micelle concentration values of gemini surfactants are one to two orders lower in magnitude than that of the corresponding single-chain surfactants [15]. Second, they are much more efficient than their corresponding monomeric surfactants in decreasing the surface tension of water [16]. For example, the C20 (surfactant concentration required for lowering the surface tension of water by 20 mN/m) for 12–2–12 gemini is 0.0083 wt%, whereas that for C12TAB is 0.25 wt% [14]. Finally, gemini surfactants with short spacers form large, threadlike aggregates, whereas the single-chain equivalent forms only small spherical micelles. For example, 12–2–12 gemini has been shown to form long worm-like micelles at a concentration as low as 1.5 wt%. As a result, aqueous solutions of these gemini surfactants have a very high viscosity at relatively low surfactant concentration and show shear-induced viscoelastic behavior at concentrations as low as 0.7 wt% [14].

Consequently, in this paper, $C_{12}H_{25}N^{+}(CH_3)_2–CH_2–CH_2–N^{+}(CH_3)_2C_{12}H_{25}\cdot 2Br^{-}$ was introduced into the system as one of the co-emulsifiers; with the gemini surfactant in the system, the emulsion with 50% content of polydimethylsiloxane (PDMS) was prepared, and the PDMS content was far higher than the other reported values. The emulsion prepared in the present study were characterised by particle-size analyzer, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR). Besides, the surface properties also were measured by surface tension analysis, water absorption, and the static contact angle. All the measurements were consistent with the conclusion that a copolymer of siloxane and acrylate with high siloxane content had been prepared successfully.

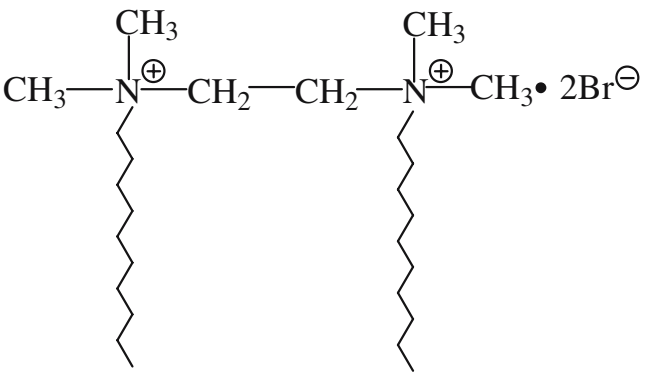

Fig. 1 Molecular scheme of gemini surfactants

Experimental section

Materials and methods

Butyl acrylate (BA), methyl methacrylate (MMA), acrylic acid, acrylamide, and acrylonitrile were supplied by Xilong Chemical (China); octamethyl tetracyclosiloxane (D_4), 3-(methacryloxypropyl)-trimethoxysilane (MPS), and hexamethyldisiloxane (HMDS) came from Yudeheng Couple Agent Factory (China); and all the monomers were purified by vacuum distillation before use. Dodecyl benzenesulfonic acid (DBSA) and span-20 were purchased from Xilong Chemical; $C_{12}H_{25}N^{+}(CH_3)_2–CH_2–CH_2–N^{+}(CH_3)_2C_{12}H_{25}\cdot 2Br^{-}$ was supplied by Chengdu Institute of Organic Chemistry, and Potassium persulphate was supported by Jinshan Chemical Factory (China); all of the surfactants and initiator were used as received.

Preparation of the latices

The latices were prepared in aqueous media by successive monomer addition under kinetically controlled conditions [17]. Potassium persulphate (0.2 g, dissolved with 10-ml water) was used as initiator and deionized water as solvent; a series of polymerizations was carried out under the same conditions. The monomers including BA (17.0 g, 0.13 mol), MMA (9.0 g, 0.09 mol), acrylonitrile (1.0 g, 0.019 mol), D_4 (25.0 g, 0.08 mol), HMDS (2.5 g, 0.015 mol), and MPS (2.5 g, 0.01 mol) were mixed together in a container and stirred with a magnetic stirrer for half an hour. Acrylic acid (0.5 g) and acrylamide (1.0 g) were dissolved with 10-ml water. Then, all the surfactants (DBSA, 1.5 g; Span-20, 1.0 g; gemini surfactant, 0.05 g), about 30% of the monomer, a third of the initiator solution, and 80-g deionized water were put into a 250-ml four-necked flask fitted with a mechanical stirrer, nitrogen inlet, and reflex condenser. The pH valued in the system was controlled to ~1 by the addition of HCL.

After removing air with nitrogen gas for 30 min, the polymerization was performed at 85 °C. After 30 min, the other monomer and the initiator (which were put into the dropping funnel at first) were added into the system over 120 min, and the temperature was maintained for another 6 h.

The latices prepared in the experiment with corresponding percentages of siloxane (w/w%) were labelled PDMS-15, PDMS-30, PDMS-40, and PDMS-50; when no PDMS was used, we named the particles PDMS-0.

Characterization of the morphology of the particles

The particles size distribution was determined in aqueous media by Malvern master sizer/E particle size analyzer (UK). From the data, the average diameter of the particles could be obtained.

Measurement of XPS and FTIR

The XPS measurement was made on a Kratos Analytical AXISHISi spectrometer with a monochoromatized AL Ka X-ray source (1,486.6 eV photons) at a constant dwell time of 100 ms. A concentric hemispherical analyzer (CHA) was performed in the constant analyzer transmission mode to measure the binding energies of emitted photoelectrons. The binding energy scale was calibrated by the Au $4f_{7/2}$ peak at 83.9 eV, as well as by the Cu $2p_{3/2}$ peak at 76.5 and 932.5 eV. In addition, FTIR spectra were recorded using a Nicolet MX-1E FTIR spectrometer, and KBr plates were used in preparing the samples.

Surface tension and water absorption

The surface tension of the latices with different siloxane content was measured using a JZHY-180 tensiometer. The measurement accuracy was verified by frequently measuring the surface tension of twice-deionized water (72–73 mN/m), and the reported values of the surface tension were the average three measurements at room temperature (25 °C).

For measuring the water absorption and contact angle, some membranes were formed from the lattices. The latices were spread on a cleaned glass plate and allowed to dry and form membranes at room temperature, and then the membranes were placed into a vacuum oven (DZF-6050, Shanghai, China) for 24 h at 60 °C to remove any remaining water. Afterward, the membranes were immersed into deionized water at 25 °C for 24 h. The mass of each sample was carefully recorded, and the water absorption was calculated as a percentage of the initial and final weight using the following formula:

$$\%\text{Water absorption} = [(\text{final weight} - \text{initial weight})/\text{initial weight}] \times 100$$

Measurement of static contact angle

To measure the hydrophobicity of polymer surfaces, the contact angle analysis was taken. A drop of water was formed on the testing surface by applying force on a syringe equipped with a repeatable dispenser and a needle. The contact angle of the water droplet on polymer films was measured using the goniometric method (ERMAG-1, Japan) [18]. The reported values were the average values of three measurements performed on different parts of the sample surface.

Results and discussion

Particles size distribution

For testifying that the monomer of siloxane had participated into the reaction, the dosage of all emulsifiers and monomer except for organic siloxane were kept for no change. If organic siloxane participated into the reaction, the particle size would increase with the increased siloxane content (form 0 to 50%). The particle size distribution of PDMS-0 and PDMS-50 measured by particle size analyzer were shown in Fig. 2. In this case, the average particle size of the PDMS-0 and the subsequent siloxaned particle size determined by light scattering were 101 and 138 nm, respectively. From Fig. 2, it can be found that the average diameter evidently increased after the addition of organic siloxane. Furthermore, there was no new nucleation formed with the increase of the PDMS amount. As a result, it could be assumed that polysiloxane had been introduced into the micelles and grafted with the acrylic particles.

Figure 3 exhibited the augment of the particle size from PDMS-0 to PDMS-50, which were agreed well with the addition amount of organic siloxane. The influence of the holding stage on particle size was also taken into account; when the time lasted for 4 h in the holding stage, the average diameter and the particle size distribution were similar to that of 6 h, which could be interpreted that almost all the monomers of organic siloxane had been successfully grafted with the acrylic particles.

Comparative experiment and FTIR spectra

In the present study, HMDS was used to terminate the process of ring-opening polymerization, and thus, the chain

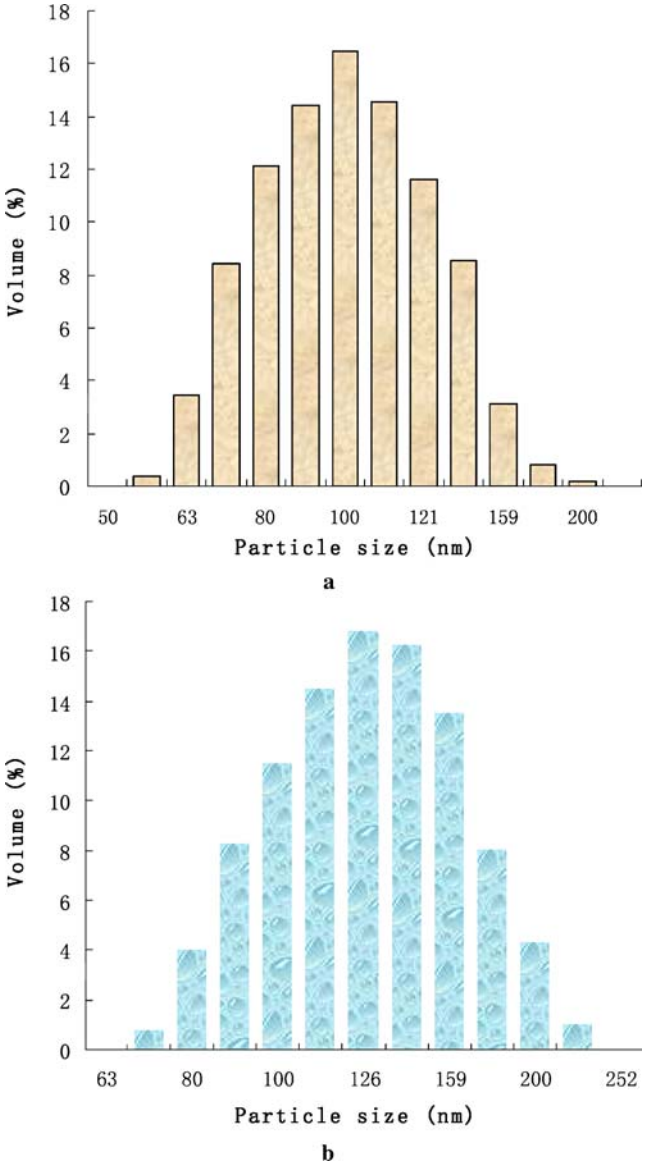

Fig. 2 The particles size distribution of PDMS-0 (**a**) and PDMS-50 (**b**)

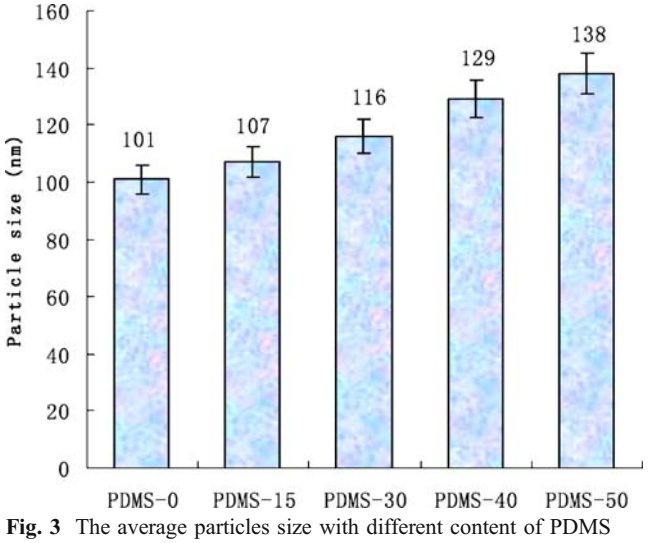

Fig. 3 The average particles size with different content of PDMS

of Si–O–Si would be short enough to be emulsified sufficiently. When no HMDS was added into the system, even if the amount of total emulsifiers reached 10%, the stable emulsion still could not be obtained. In addition, the emulsion, without adding the gemini surfactant, also were prepared tentatively; the outcome displayed that the content of PDMS could reach only 30% at the most. Once the content of PDMS was higher than 30%, there would appear a floating oil phenomenon. Via the double effect of HDMS and gemini surfactant, the stable emulsion with 50% content of polysiloxane was prepared without the floating oil and coagulum. Because of the special structure of the gemini surfactant, the tails could not tightly be arranged like the conventional surfactant. Besides, the polarity of the ionic polar was stronger than that of conventional surfactant, so there would form worm-shaped, more or less, micelles that could tone the emulsion effect. The mixture of conventional/gemini surfactants would exhibit the synergism in the surface tension reduction efficiency and mixed micelles formation [15]. At the end of the reaction, the conversion of the monomer reached 95% (determined gravimetrically in an independent experiment), which was consistent with the view that nearly all monomer had participated in the reaction.

The results of the FTIR analysis of PDMS-50 are shown in Fig. 4. The strong bands at 1,730.1 cm^{-1} attributed to the C=O stretching of acrylate. There were no peaks corresponding to C=C and C–H stretching at 1,640 and 3,102 cm^{-1}, which suggested that almost all the monomer had participated in the reaction, and there was no C=C bonds left in the system. At the positions of 800.6 and 1,259.4 cm^{-1}, there were two strong peaks that could be ascribed to the group of Me_2SiO (D) in the structure of PDMS. The characteristic peaks of Si–O–Si were also shown at 1,026.9 and 1,090.5 cm^{-1} in the spectrum. Besides, at the area of 1,090 to 1075 cm^{-1}, there were no clear peaks; that is to say that almost all of D_4 had participated in the polymerization and no monomer was left. In addition, there were no peaks concerning $(CH_3)_3Si–O–Si\ (CH_3)_3$ at the region of 1,080 to 1,040 cm^{-1}. All the data could prove that nearly all organic siloxane had participated in the polymerization and no monomer left.

A comparison of the FTIR spectra of samples PDMS-0, PDMS-15, PDMS-50, and PDMS-100 was shown in Fig. 5. It could be seen that with the increase of the amount of PDMS, the corresponding absorption peaks were strengthened. Additionally, there was no extensive adsorption peak of Si–OH in the spectra, indicating that all Si–OH hydrolyzed from $Si–OCH_3$ practically had initiated the ring-opening polymerization.

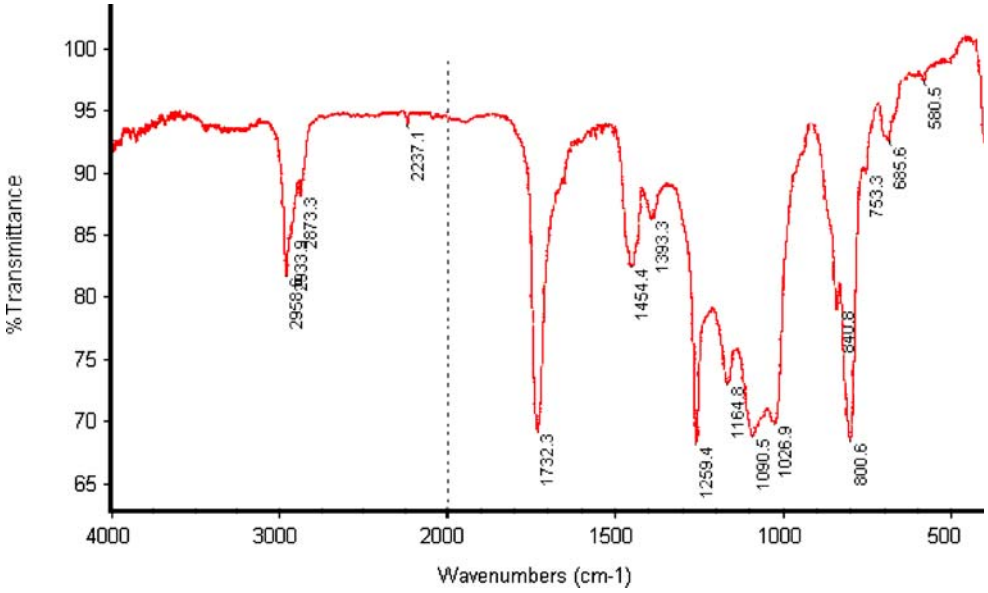

Fig. 4 The FTIR spectrum of PDMS-50

X-ray XPS

The surface properties of polymers are very important for understanding their physical, chemical, and optical properties. Although the investigation can be carried out by the normal analytic techniques, such as NMR and FTIR, it cannot deeply probe the structure and bonding state of polymers in the subsurface level, even the extreme layer [19, 20]. It is a common knowledge that the positions of the main peak of chemical elements are seldom overlapped in elemental analysis, so the main peak may be reckoned as the fingerprint region for a given elements. In this case, almost every element in the sample can be measured, and the atomic ratio can also be obtained from elemental analysis. The technology of XPS had been widely used to study the composition of elements containing the Si element and the atomic ratio of C/Si in these reports [21–23]. Clearly, if PDMS had been successfully grafted with acrylate particles, there would present the characteristic peaks of the Si element, and the atomic ratio of C/Si in the given sample would be agreed well with that of C/Si calculated by the monomer. To confirm this idea, the elements on the surface of the particles were measured by XPS.

The characteristic peaks of Si 2s and Si 2p in Fig. 6 manifested that the presence of Si element on the surface of the particles was evident; that is to say that the monomer of PDMS had been successfully grafted with acrylate in the micelles. In addition, Fig. 6a and b also indicated that the obvious peak of about 402 eV might be ascribed to the presence of N in the gemini surfactant.

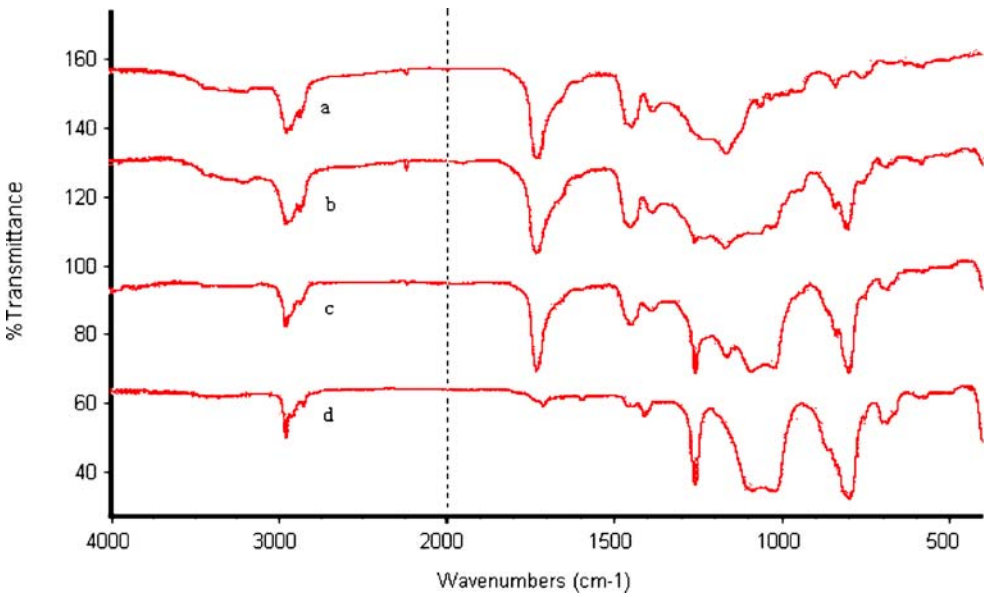

Fig. 5 The comparison of FTIR spectra of PDMS-0, 15, 50, and 100 (**a**, **b**, **c,** and **d**, respectively)

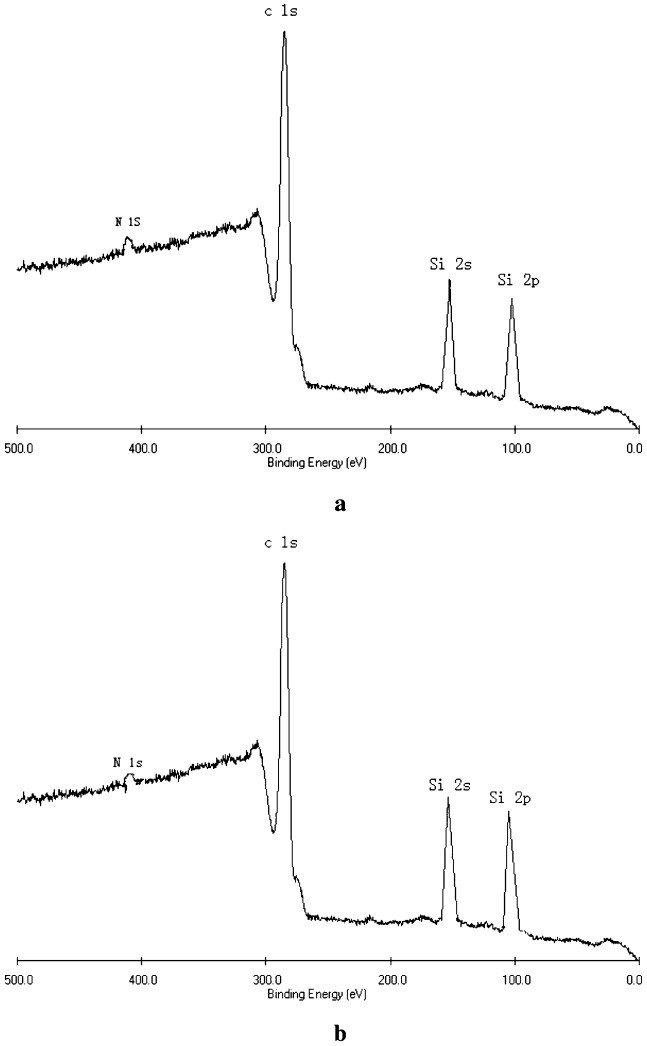

Fig. 6 XPS characterization of PDMS-30 (**a**) and PDMS-50 (**b**)

From Table 1, it could be surveyed that the atomic ratio of C/Si (4.5) in PDMS-30 and (3.2) in PDMS-50 were smaller than that of C/Si calculated from the monomer.

It is well known that the polysiloxane have the phenomenon of surface segregation. The surface segregation of copolymers or their blends is derived by the components with low-surface tension, such as Si-containing or F-containing copolymers [24]. Just because of the surface enrichment property, the atomic ratio of C/Si (4.5) in PDMS-30 and (3.2) in PDMS-50 were lower than that calculated from the monomer. In addition, the atomic ratio of C/Si decreased with the amount of PDMS used in the system, which could be regarded as a proof that the added polysiloxane had reacted with the acrylic particles.

Table 1 The atomic ratio of C/Si in different samples

Sample	Element	CPS	Sensitivity	Atomic ratio (C/Si)
PDMS-15	C	2,071.3	0.25	6.7
	Si	3,58.6	0.29	
PDMS-30	C	2,398.8	0.25	4.5
	Si	622.5	0.29	
PDMS-40	C	2,417.1	0.25	3.6
	Si	876.2	0.29	
PDMS-50	C	2,690.0	0.25	3.2
	Si	978.5	0.29	

Surface tension

Polysiloxane and their composite materials have been widely used as one of the components in copolymers to achieve low surface tension [25, 26]. It has been reported that the surface tension of PDMS of various molecular weights could reach 16~21 mN/m at room temperature [27], which is lower than the critical-wetting surface tension of most low-energy substrates, excluding fluorocarbons [28]. This behaviour could be attributed to the Si–O–Si structure of the copolymer, which also accounts for the tendency of the polymer to accumulate at the interfaces between phases.

In our present work, the surface tensions of samples from PDMS-0 to DPMS-50 were determined, and these data were listed in Fig. 7. From Fig. 7, the surface tension decreased with the increasing PDMS content. PDMS-50 showed a surface tension value of 23.5 mN/m, which was reduced by 37.0% compared with PDMS-0 (37. 3 mN/m). Therefore, it could be said that the introduction of PDMS could decrease the surface tension greatly, which agreed well with other reports [27].

Water absorption

Water absorption is a common problem in acrylate-based composites, especially in interfacial regions. In contrast to epoxy resins, organic siloxane is a hydrophobic material. Modification of acrylate ester with polysiloxane should

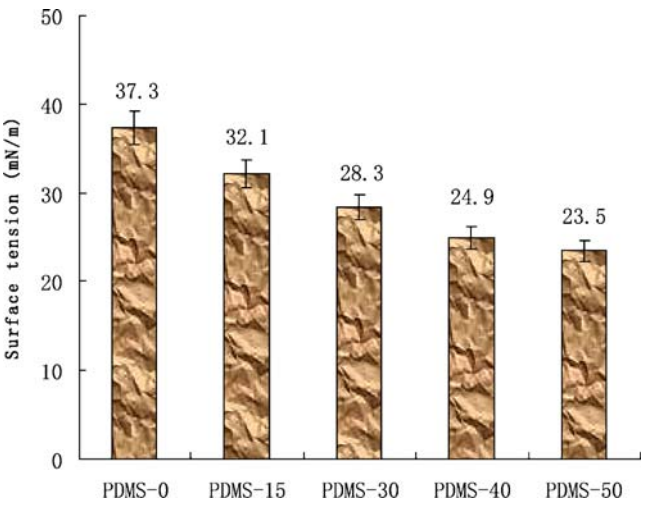

Fig. 7 The surface tension of different samples

improve physical properties because of the decrease in water diffusion [29]. The mass of each sample was carefully recorded, and the water absorption was calculated as the described above formula.

From Fig. 8, it could be seen that the water absorption decrease with increasing PDMS. PDMS-50 showed a water absorption value of 4.21%, which was reduced by 50.1% compared with PDMS-0 (8.52%). Therefore, it could be said the introduction of PDMS could decrease the water absorption greatly, which agreed well with other literatures [29].

Surface hydrophobicity

Polysiloxane have been widely used in textile finishing for imparting desirable properties such as softness, crease resistance, and particularly, water repellency [30, 31]. Due to the hydrophobicity and low surface energy of polysiloxane, if the polysiloxane had been grafted with acrylic particles, the particles should have higher water contact angle and create a hydrophobic surface, while the water contact angle can commonly be used as a criterion for the evaluation of hydrophobicity of a solid surface [32]. It is well known that the wetting behavior of a solid surface is important for various commercial applications and depends strongly on both the surface energy and roughness [33, 34]. For PDMS–acrylate particles prepared in this study, if the PDMS grafted with acrylate completely, the particles should, in principle, have higher water contact angle than the particles not containing PDMS due to the hydrophobicity of PDMS.

From Fig. 9, it could be observed that the contact angle of water evidently increased with the increase of the content of PDMS, which revealed that the effect of water repellency became more obvious with the increase of PDMS amount. The results might be ascribed to the enrichment of PDMS on the surface of the particles, which agreed well with the fact that polysiloxane exhibited higher water contact angle in other literatures [35–37].

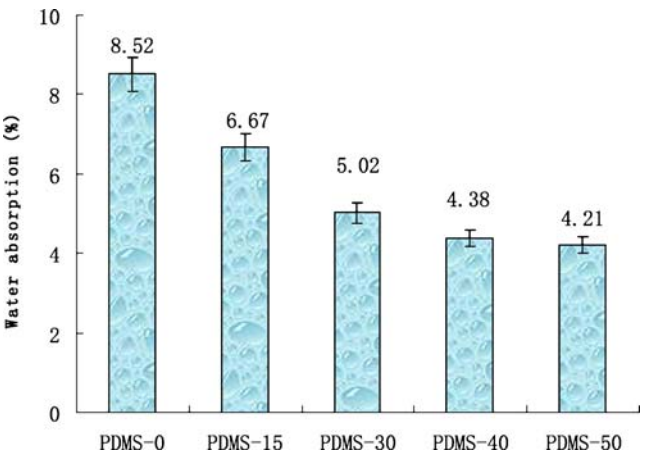

Fig. 8 The water absorption of different samples

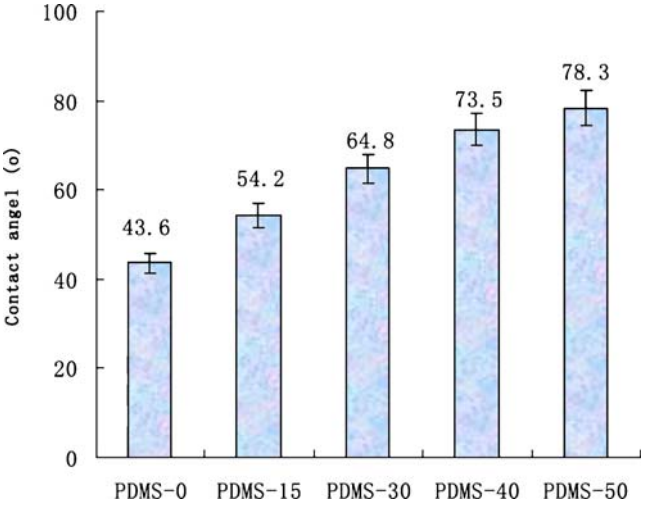

Fig. 9 The surface contact angle (water)

Conclusion

It has been shown that the copolymer of acrylate and organic siloxane with high siloxane content were prepared by emulsion polymerization. By introducing the gemini surfactant and HDMS, on one hand, the chains of Si–O–Si became shorter because of the introduction of HDMS, resulting in the easy emulsification of the Si–O–Si chain compared with the long chain. On the other hand, the effect of emulsification was strengthened due to the importation of the gemini surfactant. Under these conditions, the acrylate–siloxane copolymers were prepared, and the siloxane content could reach 50%, which is greater than the values reported in other literatures.

The emulsion prepared in the present study was characterized by a particle size analyzer, X-ray XPS, and FTIR. The results showed that the particle size augmented with the increase of PDMS amount, which could be considered that the attestation of the PDMS monomer had been introduced into the micelles and grafted with the acrylic particles. The FTIR spectra showed that practically all the monomer had participated in the copolymerization because there were no C=C and D_4 characteristic peaks in the spectrum, and with the increase of PDMS, the characteristic peaks of the PDMS were strengthened. The conclusion from the XPS measurement could also prove the above viewpoint.

The surface properties were also measured by surface tension analysis, water absorption, and the static contact angle. All the results from the characterization testified that, with the increase of PDMS amount, the excellent properties of polysiloxane were more evidently embodied. Therefore,

the siloxane–acrylate copolymer with 50% siloxane was successfully prepared in the experiment.

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