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Synthesis and characterization of PDMS-Acrylate latexes with MPS-PDMS oligomer as macromonomer and Gemini Surfactant as co-emulsifier

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Summary

The copolymers of polysiloxane and acrylate with methacryloxypropyl trimethoxysilane (MPS) –polydimethylsiloxane (PDMS) oligomer as macromonomer and Gemini surfactant as co-emulsifier were prepared by emulsion copolymerization and characterized by ^{1}HNMR, Gel-permeation chromatography (GPC), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and FT-IR.
Firstly, the oligomers of MPS-PDMS with different Si-O-Si chain length (8, 12, 24 and 36) were synthesized by the hydrolysis of MPS and the ring-opening polymerization of octamethyl tetracyclosiloxane (D_4), the ^{1}HNMR and FT-IR spectra indicated that when the reaction time was prolonged to 2 h, more than 90% of -Si $(OCH_3)_3$ groups were hydrolyzed; Then, the emulsion polymerization was carried out with the oligomer as macromonomer and Gemini Surfactant as co-emulsifier. XPS investigation of the latexes showed that with the increase of Si-O-Si chain length, more and more polysiloxane occupied the outer layer of membrane, which agreed well with the conclusion of contact angle and AFM measurements. With Gemini surfactant as co-emulsifier in the system, the PDMS content in the system could reach 50%, which was far higher than the other reported value.

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 and biocompatibility etc [1-4]. However, polysiloxane 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’s a common knowledge that the greater the difference between the combining polymers, the more likely synergistic properties will result from the combination [5]. Many significant works, recently, basing on organic siloxane have been shown in the published papers by Park [6], Medda [7] and Bauer [8] et al, contributing to the technical synthesis of some performance-specified coatings.

The latexes of siloxane-acrylate copolymer have been widely applied in many areas because of their non-toxic and non-contaminating characters [9, 10]. 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 enhance the siloxane content of latexes is becoming more and more important. Commonly, the polymerization temperature of the acrylate is higher than 80°C, under such conditions, the Si $(OCH_3)_3$ groups are easy to hydrolyze, forming a network structure even to coagulum. This is the main reason why the siloxane content in the copolymer could not be enhanced in the copolymer. Some efforts have been done to solve the problem. Chengyou Kan [11], Weidong He [12] and Zhangqing Yu [13] have devoted themselves to introducing D_4 and vinyl septamethyl cyclotetrasiloxane (VD_4) into the reaction system to enhance the siloxane content. But, the large amount of Si-O-Si chains formed by D_4 ring-opening polymerisation 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. So 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 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 C_{20} (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 $C_{12}TAB$ is 0.25 wt% [14]. Finally, Gemini surfactants with short spacers form large, threadlike aggregates, while the single-chain equivalent forms only small spherical micelles. For example, 12-2-12 Gemini has been shown to form long wormlike micelles at a concentration as low as 1.5 wt%.

In this paper, the MPS-PDMS oligomers with different Si-O-Si chain length (8, 12, 24 and 36) were prepared aforehand as the macromonomer to react with acrylate. Because the oligomer do not contain Si $(OCH_3)_3$ groups, it will not hydrolyze in the course of reaction, so the siloxane content in the latexes would be enhanced.

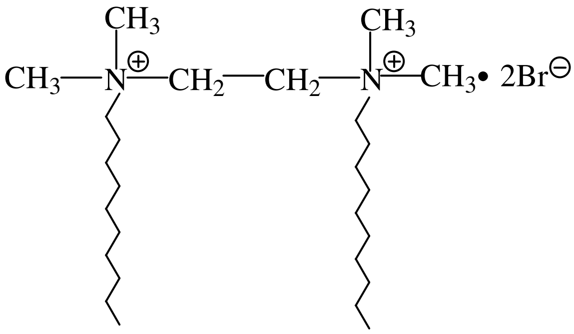


Fig. 1 Molecular scheme of Gemini surfactants

Consequently, $C_{12}H_{25}N^+(CH_3)_2$-CH_2-CH_2-$N^+(CH_3)_2C_{12}H_{25}\cdot 2Br^-$ was introduced into the system as one of the co-emulsifiers, the latexes with 50% content of siloxane was prepared, and the siloxane content was far higher than the other reported values. The latexes prepared in the present study were characterised by ^{1}HNMR, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and FT-IR. Besides, the surface property also was measured by 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.

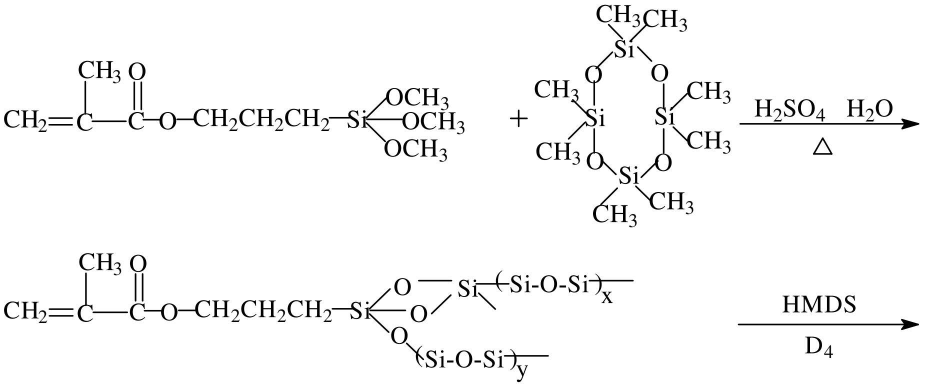
Experimental section

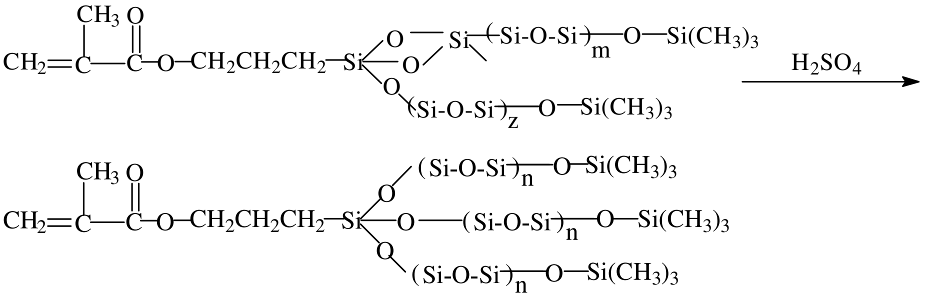
Materials

Butyl acrylate (BA), methyl methacrylate(MMA), acrylic acid and acrylamide 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 monomer 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 Daochun Chemical and Potassium persulphate was supported by Jinshan Chemical Factory (China), all the surfactants and initiator were used as received.

Synthesis of the MPS-PDMS oligomer

Firstly, D_4 (10g), H_2SO_4 (1ml), MPS (0.83-3.75g) and a quantity of water were added into a 100 ml four-necked flask fitted with a mechanical stirrer, nitrogen inlet and reflex condenser, the temperature was performed at 80°C, then the mixture of D_4 (12.7g) and HMDS (0.85-3.83g) was introduced into the system within 15 minutes, the reaction was maintained for 2 hours. After this, the oligomer was taken out from the flask and dissolved in 50ml toluene solution, then 15ml H_2SO_4 (30%) was added into the system to readjust the Si-O-Si long chain for getting a more even preformed polymer, at last, H_2SO_4 was washed by deionized water from the system, the oligomer was separated from toluene solution through vacuum distillation. The schematic formation of oligomer was listed below:





(Average value, n=8, 12, 24, 36)

Fig. 2 Schematic formation of MPS-PDMS oligomer

Preparation of the PDMS-Acrylate latexes

The latexes were prepared in aqueous media by successive monomer addition under kinetically controlled conditions [17]. Potassium persulphate (0.2g, dissolved with 10ml water) was used as initiator, a series of polymerizations was carried out under the same conditions. The monomer including BA (17.0g), MMA (9.0 g) and the oligomer (27.5g) were mixed together in a container and stirred with a magnetic stirrer for half an hour. Acrylic acid (0.5g) and acrylamide (1.0g) were dissolved with 10 ml water. Then, all the surfactants (DBSA 1.5g, Span-20 1.0g, Gemini Surfactant 0.05g), about 30% of the monomer, a third of initiator and 80g deionized water were put into a 250 ml four-necked flask fitted with a mechanical stirrer, nitrogen inlet and reflex condenser. After removing air with nitrogen gas for 30 min, the polymerization was performed at 85°C. After 30 minutes, 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 latexes prepared in the experiment with corresponding Si-O-Si chain length were labelled PDMS-8, PDMS -12, PDMS-24 and PDMS -36, when no siloxane was used, we named the particles PDMS -0.

Measurements

^{1}HNMR spectra of the oligomer were measured by a BRUKER AM 500 spectrometer using DUAL-5 mm probe for ^{1}HNMR. The samples were dissolved in $CDCl_3$ (10–15 wt/vol %) at 25°C. The AFM analysis was carried out by MMAFMLN2068EX (vecco instruments, USA). GPC analysis of the molecular weight distribution of these oligomers was performed on a Waters system comprised of a U6K injector, a 510 HPLC pump, and a R401 refractive index detector. The eluting solvent was THF at a flow rate of 0.8mL/min. The retention time were calibrated against known monodipersed polystyrene whose *M*w/*M*n ratio are less than 1.10.

XPS measurement was made on a KRATOS Analytical AXISHISi spectrometer with a monchoromatized AL Ka X-ray source (1486.6 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 Cu $2p_{3/2}$ peak at 76.5 and 932.5 eV. In addition, FT-IR spectra were recorded using a NICOLET MX-1E FT-IR spectrometer and KBr plates were used in preparing the samples.

For measuring the contact angle, some membranes were formed from the latexes.The latexes 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 hours at 60°C to remove any remaining water. The contact angle of 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

It is well known that H_2SO_4 could break the Si-O-Si long chain in toluene solution, so, in this paper, H_2SO_4 was used to destroy and rearrange the Si-O-Si structure (including the Si-O-Si short chain formed in the intramolecule of MPS), the catalyst and balance were conducted under the condition of concentrated sulphuric acid in order that the silane could be combined in an amount equal to the reactive mole ratio. HNMR is the most useful for the measurement of hydrogen chemical environment because of its high sensitivity to hydrogen bond strength, while the area of apex also evidently reflects the abundance of hydrogen in different chemical shift [18-20]. The ^{1}HNMR of oligomer was shown in Figure.3, it could be seen that all the relevant peaks of MPS could be found in the figure, the peaks at 0 ppm and 6 ppm result from the group of CH_3 in the long chain of Si-O-Si and the vinyl group (CH_2=C) in the molecule of MPS. According to the H atom numbers of MPS, before hydrolysis, there should be a strong peak at 3.7ppm caused by the group of Si $(OCH_3)_3$ (peak area~4.5), with the process of hydrolysis, the area of peak would lessen, after 2h, there was only a weak peak at 3.7ppm (peak area~0.442), that is to say more than 90% of Si $(OCH_3)_3$ groups have been hydrolyzed in the reaction (calculated from the peak area in the figure).

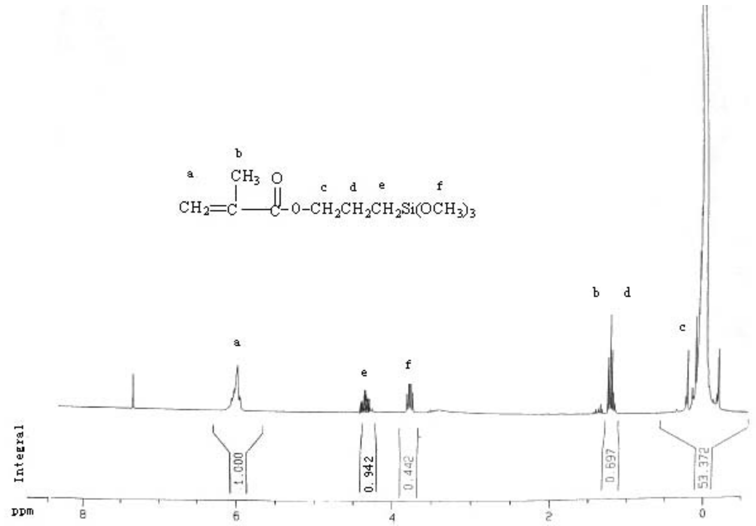


Fig. 3 ^{1}HNMR of MPS-PDMS oligomer

In addition, the molecular weight distribution of oligomers was determined by GPC, it cold be found all the measured values were less than the theoretical values, but not exceeding 8%, the deviation might be aroused by operate miss. So, it could be said the oligomers were synthesized successfully.

FT-IR analysis result of MPS-PDMS oligomer was shown in Fig. 4. The peaks corresponding to $CH_2=C$ and C-H stretching at 1640.3cm^{-1} and 3100.2 cm^{-1}suggested the existence of C=C in the polymer. At the positions of 796.5 cm^{-1} and 1258.3 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 showed at 1,026.7 cm^{-1} and 1,090.9 cm^{-1} in the spectrum. Besides, at the area of 1,090 cm^{-1} to 1,075 cm^{-1}, there were no clear peaks, that is to say that almost all of D_4 had participated into the polymerization and no monomer was left. In addition, there were only weak peaks at the point of 2,846.9 cm^{-1} and 1,190.8cm^{-1}, which could account for that nearly all group of $Si-O-CH_3$ had been hydrolyzed, tally with the conclusion of ^{1}HNMR, there were no peaks concerning $(CH_3)_3Si-O-Si\ (CH_3)_3$ at the region of 1,080 cm^{-1} to 1,040 cm^{-1}. All the data could prove that nearly all organic siloxane had participated in polymerization and no monomer left.

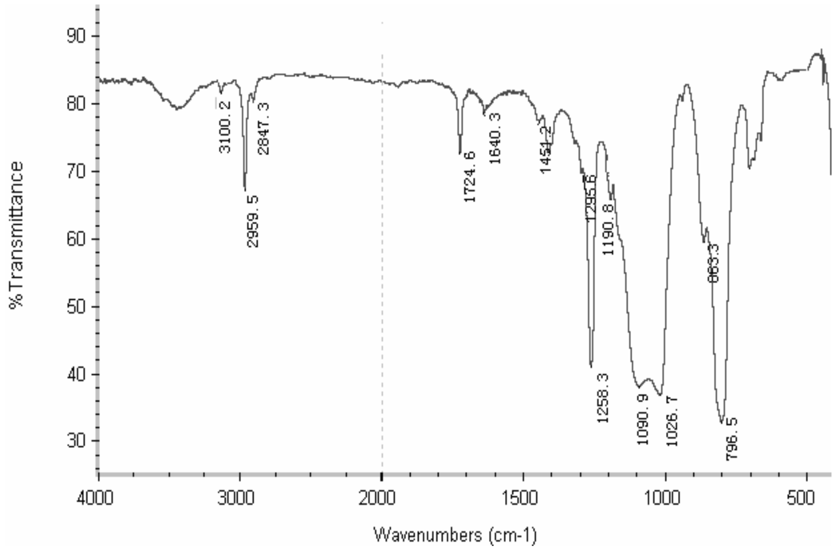


Fig. 4 FT-IR spectra of MPS-PDMS oligomer

In addition, the latexes without adding Gemini surfactant also was studied tentatively, the outcome displayed that the content of PDMS only could reach 20% at the most. Once the content of PDMS was higher than 20%, there would appear floating oil in the latexes. With the introduction of Gemini Surfactant in the system, the polysiloxane content in the latexes could reach 50%. Because of the special structure of Gemini Surfactant, the tails could not tightly arranged like conventional surfactant, besides, the polarity of the ionic polar was stronger than that of conventional surfactant, it would form micelles with worm shape which could greatly tone the emulsifying efficiency, so the dosage was far lower than that of the conventional surfactant. The mixture of conventional/Gemini Surfactants would exhibit the synergism in declining surface tension and the formation of mixed micelles [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 FT-IR outcome of PDMS-Acrylate latexes (PDMS-12) was shown in Fig. 5. The strong bands at 1728.2 cm^{-1} attributed to the C=O stretching of acrylate. There were no peaks corresponding to C=C and C-H stretching at 1640 cm^{-1} and 3102 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. The characteristic peaks of PDMS were similar with that of MPS-PDMS oligomer. The group of Si-O-CH_3 could not be observed in the spectrum because of the hydrolysis in the course of reaction.

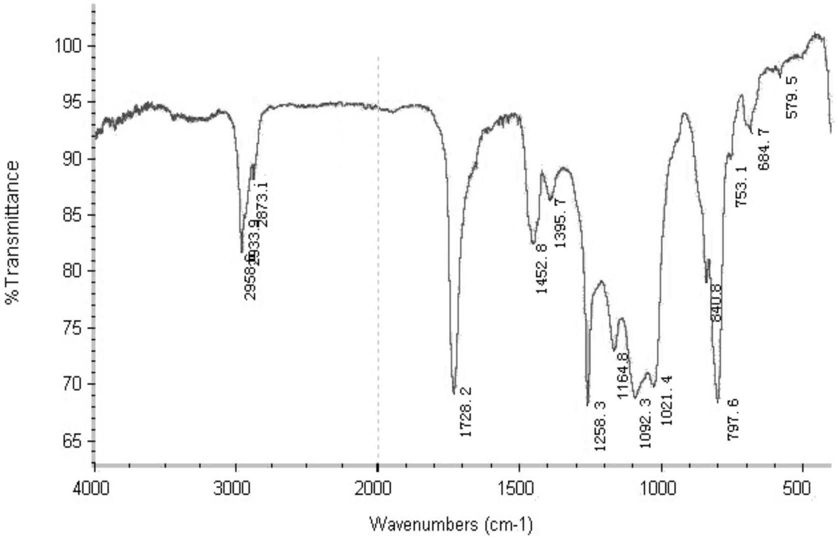


Fig. 5 FT-IR spectra of PDMS-Acrylate latexes

The surface properties of polymer 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 FT-IR, it cannot deeply probe the structure and bonding state of polymers in subsurface level, even the extreme layer [21, 22]. The technology of XPS had been widely used to study the elements composition of elements containing Si element and the atomic ratio of C/Si [23-25]. Clearly, if PDMS had been successfully grafted with acrylate particles, there would present the characteristic peaks of Si element, and the atomic ratio of C/Si in the given sample would be agreed well with the C/Si ratio 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 oligomers of MPS-PDMS had been successfully grafted with acrylate in the micelles, and the obvious peak about 402eV might be ascribed to the presence of N in the Gemini surfactant.

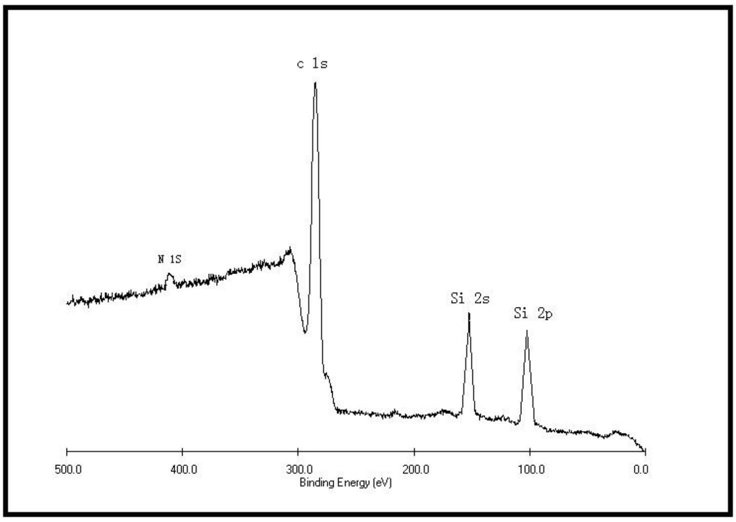


Fig. 6 XPS characterization of PDMS-Acrylate latexes

From Table 1, it could be surveyed that the atomic ratio of C/Si in different samples were lower than the C/Si ratio calculated by the monomer. It is well known that polysiloxane have the phenomenon of surface segregation, the surface segregation of copolymers or their blends is derived by the components with low surface tension [26]. Just because of the surface enrichment property, the atomic ratios of C/Si in all samples were lower than that calculated by the monomer (6-7). In addition, the atomic ratio of C/Si decreased with the increase of chain length in the system, that is to say, the more long chain length of Si-O-Si, the more obvious of surface segregation would be observed. In the sample of PDMS-36, the atomic ratio of C/Si is 2.8, which very closed to the C/Si ratio of PDMS (2.0), it could be said that almost all the outer layer of PDMS-36 was covered by PDMS.

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

Sample	Element	CPS	Sensitivity	Atomic ratio (C/Si)
PDMS-8	C	2082.6	0.25	3.7
	Si	652.9	0.29	
PDMS-12	C	2377.5	0.25	3.5
	Si	787.9	0.29	
PDMS-24	C	2434.1	0.25	3.1
	Si	910.9	0.29	
PDMS-36	C	2685.9	0.25	2.8
	Si	1112.7	0.29	

Polysiloxane have been widely used in textile finishing for imparting desirable properties such as softness, crease resistance and particularly water repellency

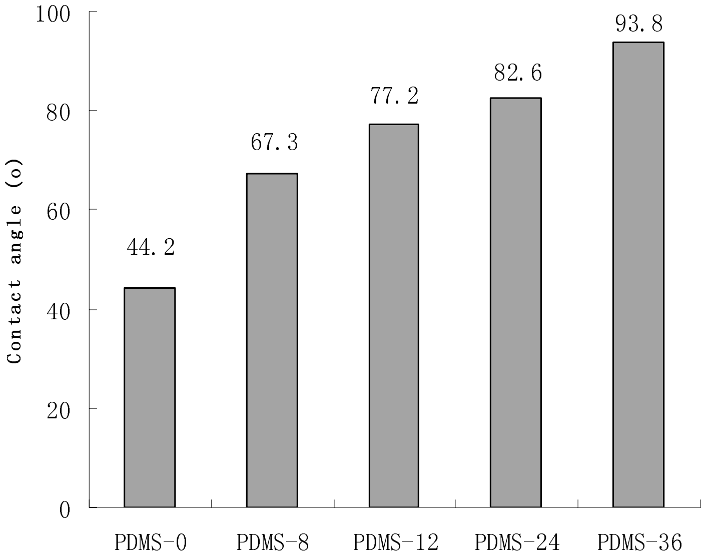


Fig. 7 The surface contact angle (water)

[27, 28]. 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 [29-31].

Although the polysiloxane content in all sample were 50%, the contact angle changed a lot from 67.3° (PDMS-8) to 93.8° (PDMS-36). From Fig. 7, it could be observed that the contact angle of water evidently increased with the increase of the Si-O-Si chain length, which revealed that the effect of water repellency became more obvious. Which is to say, the more long Si-O-Si chain length, the more surface hydrophobicity would be embodied.

AFM has become an advanced microscopic method for examining polymer materials such as engineering plastics, paint and coating, rubber, packing, fiber and a wide

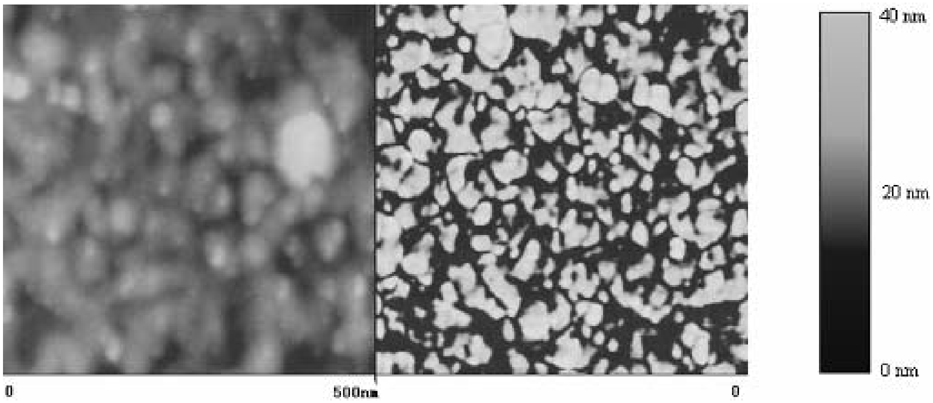


Fig. 8 AFM image of PDMS-12

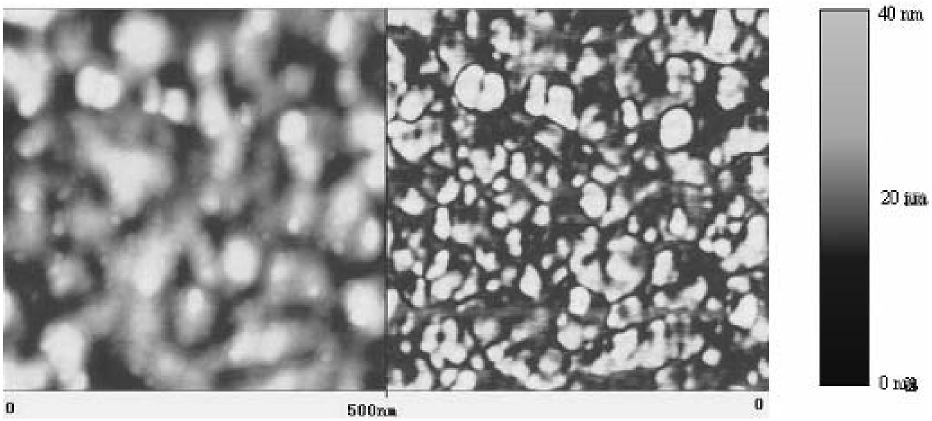
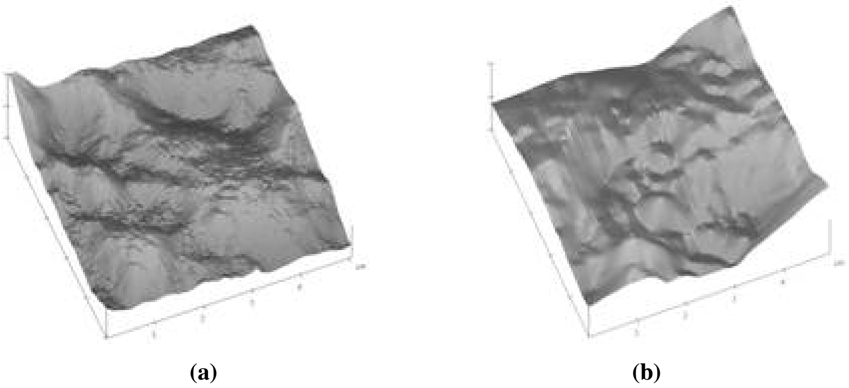


Fig. 9 AFM image of PDMS-36

range of consumer goods. More recently, the spectrum of AFM applications to polymers has been broadened substantially from relatively simple visualizations of morphology to more advanced examinations of polymer structure and properties on a nanometer scale due to the discovery of new AFM capabilities [32-34].

Fig. 8 and 9 showed the AFM images of PDMS-Poylacrylate polymer membrane (PDMS-12 and PDMS-36). The left area of these figures exhibited the roughness of the membranes, the brighter phase was the phase with higher position and the darker phase was the phase with lower position; the right area exhibited the modulus of the membranes, the brighter phase was the phase with higher modulus and the darker phase was the phase with lower modulus.

Because of the property of surface enrichment, the longer chain length of polysiloxane, the obvious surface enrichment would be occurred. It could be seen that the brighter area of roughness phase in Fig. 9 was larger than that of Fig. 8, agreed well with the above conclusion. Besides, polysiloxane with lower modulus compared with polyacrylate, from these figures, it could be seen that the dark area of modulus phase in Fig. 9 was larger than that of Fig. 8, according with the phenomenon of surface enrichment.



(a) **(b)**

Fig. 10 AFM topography mapping images of PDMS-12 (a) and PDMS-36 (b)

Roughness profiles of PDMS-12 and PDMS-36 were shown in Fig. 10 (a) and (b), respectively, the average roughness was described as the distance between the deepest and highest point on the given surface (5 µm×5µm). The analysis showed that the average roughness of PDMS-36 (Ra=39.76nm) was higher than that of PDMS-12 (Ra=29.63nm), but the variation in roughness was not distinct (no more than 40nm). This indicated that the film surfaces were comparatively smooth but with the increase of chain length, the roughness of the surface became more obvious, the outcome agreed well with the conclusion of contact angle.

Conclusions

It has been shown that the copolymer of acrylate and organic siloxane with different Si-O-Si chain length have been prepared by emulsion polymerisation. Because the oligomers were aforehand prepared, almost all the groups of Si $(OCH_3)_3$ have been hydrolyzed, which benefit to the synthesis of latexes. By the introduction of Gemini surfactant, the siloxane content in the copolymer could reach 50%, which is greater than the values reported in other literatures.

^{1}HNMR spectra indicated that when the reaction time was prolonged to 2 h, more than 90% of -Si $(OCH_3)_3$ groups were hydrolyzed, FT-IR also proved that the conclusion. XPS investigation of membranes with different chain length showed that with the increase of Si-O-Si chain length, the C/Si ratio in these samples decreased, that is to say the excellent properties of polysiloxane would be more fully embodied which accorded with the results of contact angle and AFM measurements. All the outcomes from the characterization testified that the siloxane-acrylate copolymer with 50% siloxane was successfully prepared in the experiment.

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