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Zhongliang Ma[a]; Xiangmei Wang[a]; Lihua Zhang[a]
[a] Chemical Industry and Ecology Institute, North University of China, Shanxisheng-Taiyuan, P.R. China

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The Effect of Weight Fraction of H-PDMS on the Latex Membrane and the Stability of Composite Emulsion of H-PDMS/Acrylate

ZHONGLIANG MA, XIANGMEI WANG* and LIHUA ZHANG

Chemical Industry and Ecology Institute, North University of China, Shanxisheng-Taiyuan 030051, P.R. China

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High hydrogen-containing polymethylsiloxane(H-PDMS)/polyacrylate composite emulsion was synthesized by a drop-adding method for monomer emulsion. The effects of weight fraction of H-PDMS on the stability of composite emulsion, water resistance and heat-aging resistance of the latex membrane have been investigated. The TEM demonstrated that latex particles are a core-shell structure. By analyzing the spectrums of FTIR and ^{1}H-NMR, it can be indicated that H-PDMS had reacted with acrylate monomer resulting chemical bond formation. The core-shell structure and chemical bond play an important role to restrain phase separation of composite emulsion and enhance the stability of the emulsion. By analyzing the surface tension, apparent viscosity and morphological structure, the results showed that the stable composite emulsion system can be obtained in which the average latex particle size was smaller than 90 nm when weight fraction of H-PDMS is below 16% (based on the weight of acrylate monomer), the stable emulsion system can be obtained in which the average latex particle size becomes larger than 90 nm when the weight fraction of H-PDMS is above 20% of the acrylate monomer. The DSC demonstrated that the T_g of pure polyacrylate is 49°C, and there is only one T_g (35°C) when the weight fraction of H-PDMS is 13%, but there are two T_g (15°C and 25°C) when the weight fraction of H-PDMS is 16%. In addition, the water resistance and heat-aging resistance of composite latex membrane enhanced gradually with the increase of amount of H-PDMS.

Keywords: high hydrogen-containing polymethylsiloxane, modification, polyacrylate emulsion, composite emulsion, stability

1. Introduction

Polyacrylates have many specific properties such as good film-forming, gloss, transparency, and mechanical properties, and their corresponding products have been widely used as coatings, paints, adhesives. However, the poor ultraviolet light resistance and lower (or higher) temperature resistance limit their application. In contrast, polydimethylsiloxanes (PDMS) have many excellent properties such as high flexibility and hydrophobicity, low surface tension and surface energy, low glass transition temperature (Tg), weather resistance, low solubility, low dielectric constant, UV light and excellent thermal stability, non-polluting. But, the disadvantages are their low tensile strength and relative high costs Thus, the combination of polyacrylates with PDMS, to overcome their defects while retaining their advantages, has been of importance and has been of interest the past few decades (1,2). Modification of polyacrylates latex by PDMS was an convenient and effective method, so there is much literature regarding the study. Among these works, two methods were popularly used: (a) organosilicon as a modification monomer was employed in copolymerization of acrylate, but acrylate and organosilicon was not entirely copolymerized, which caused the bad water-resistance and weatherability of the composite emulsion (3–5); (b) copolymerization of acrylate monomers with PDMS were performed (6–9).

The PDMS/polyacrylate coating agent obtained by the addition of high hydrogen-containing PDMS (10,11) has the advantage over the copolymer coating agent of acrylate and organosilicon in many respects, such as the water-resistance and weatherability. Whereas, the solubility parameter (δ_p) of PDMS is $15.6 \times 10^3 (\mathrm{J/m^3})^{1/2}$ and the solubility parameter of polyacrylate of a different structure is between $(18.0 \ll 21.0) \times 10^3\ (\mathrm{J/m^3})^{1/2}$, they belong to a representative incompatible system. In particular, the silicon-hydrogen bond causes the stability of composite emulsion to become even worse, so it's key to synthesize a stable composite emulsion of H-PDMS/polyacrylate.

In this paper, the effects of weight fraction of high hydrogen-containing PDMS on the stability of

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*Address correspondence to: Xiangmei Wang, Chemical Industry and Ecology Institute, North University of China, Shanxisheng-Taiyuan 030051, P.R. of China. Tel: +86-0351-3922116; E-mail: wangxiangmei@nuc.edu.cn

H-PDMS/polyacrylate composite emulsion synthesized by drop-adding method, the Tg and the hydrophobicity and heat-aging resistance of H-PDMS/polyacrylate membrane were studied.

2. Experimental

2.1. *Materials*

Hydrogen-containing polydimethysiloxane (H-PDMS) (hydrogen amount is 1.52% per mole chain unit, $M_n = 21000$) was purchased from Xinghuo Chemistry Reagent Co., Ltd, Jiangxi, China. Normal butyl acrylate (n-BA) and methyl methacrylate (MMA) were distilled before experiments. Ammonium persulfate, octylphenol polyethenoxy ether (OP-10) and sodium dodecylsulfate (SDS) were of analytical grade. All other chemicals were of analytical grade and used as supplied.

2.2. *Synthesis of the composite emulsion of H-PDMS/acrylate*

The composite emulsion of H-PDMS and acrylate was prepared at 7°C, through a drop-adding method for monomer emulsion with the fixed recipe n-BA/MMA weight ratio (2:3), the composite emulsifier of OP-10/DBS is 5% (OP-10/DBS = 1/1, by weight), acrylic acid weight fraction (3%), ammonium persulfate weight fraction (0.5%) and H-PDMS weight fraction (16%), all of the above weight fractions are based on the acrylate weight. The solid content of the composite emulsion was about 45%. The conversion rate of monomer was determined through a quality analytic method after the polymerization.

2.3. *Characterization of the composite emulsion*

The apparent viscosity of composite emulsion was determined on the NDJ-G type Rotary Viscometer (Balance Device Group Co., Shanghai, China). The surface tension of composite emulsion was measured on a J-Z-200A type Automatic Boundary Tension Determinator (Precision Test Machine Co., Ltd Cheng De, China). The two measurement temperatures are 20°C.

The composite emulsion was dropped on the gold–filled copper web after the concentration of emulsion was diluted to 0.5%, naturally dried, and the latex was observed by H-600 type Transmission Electron Microscopic (Japan). The granulometry instrument of Malvern Zetasizer Nano ZS was used to measure the latex particle size distribution of composite emulsion.

The method determined for high or low temperatures resistance of the emulsion was carried out as follows: A certain amount of emulsion was put into a test tube with a lid and was placed in the constant temperature oven at 60°C or refrigeratory at −10°C for 4 h, then it was observed whether the composite emulsion appeared as lamination or gel, the phenomena of lamination or gel indicated that composite emulsion is unstable.

2.4. *Characterization of the polymer*

The composite emulsion was dried in vacuum at 60°C for 10 h and ethylene dichloride was used as a solvent to eliminate the large numbers of homopolymer. The remains were further purified in a soxhlet apparatus for 36 h by using normal heptane as solvent to eliminate the homopolymer remnants to obtain the copolymer of H-PDMS and acrylate. FTIR and ^{1}H-NMR spectroscopic analysis were performed using a Nicolet-20sx-B type Fourier Transform Infrared and Avance 400 type Nuclear Magnetic Resonance Spectrometer (Brukerg Co, Swiss) with chloroform deuterium as solvent.

T_g of the polymer was measured by Modulated DSC 2910 DSC (USA) on the conditions of heating rate 10°C/min after the composite emulsion was dried in vacuum at 60°C.

2.5. *Measurements of the water and heat-aging resistance of latex membrane*

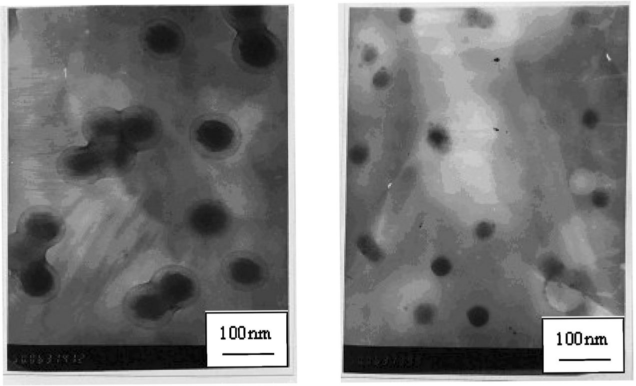
The composite emulsion was placed in a mold, then placed in oven (120°C) for some time to form a latex membrane; the glossiness maintenance of the membrane was measured by a vancometer.

The contact angle of distilled water and surface of cotton textile coated with the composite emulsion was determined by a JC2000 Contact Angle Determinator after the composite emulsion was brushed on the cotton textiles by the same process. Each measurement was finished within 30s after the droplet of water touched the surface of the cotton textiles, six repeated measurements were conducted for the same sample, the average value of six measurement results were used for the Results and Discussion.

3. Results and discussion

3.1. *The morphology and structure of the latex particle*

The morphology of the latex particles prepared in the experiment (H-PDMS content is 16% wt) was shown by the micrographs in Figure 1. The thin, unstained sections and the dark domains in the latex particles can be clearly differentiated from the TEM. As can be seen in Figure 1, the structure of latex particle is a core–shell morphology. This was due to the fact that H-PDMS and polyacrylate were incompatible, which led to phase separation in microstructure. In macrostructure, the phase separation was restrained by the chemical bond (the existence of chemical bond can be confirmed by the FTIR and ^{1}H-NMR) formed between H-PDMS and polyacrylate and the tangle of the



(a) 3% emulgent by monomer weight (b) 5% emulgent by monomer weight

Fig. 1. TEM photos relating to the effect of emulgent's amount on particle size of composite latex.

long molecular chains to each other. Therefore, the stable composite emulsion of H-PDMS and polyacrylate can be prepared by controlling the polymerization conditions.

The chemical bond formed by the polymerization of H-PDMS and polyacrylate was confirmed by FTIR spectrogram (Fig. 2) and ^{1}H-NMR spectrogram (Fig. 3).

In Figure 2, there were an evident absorption peak of Si—H group at 2165 cm^{-1}, a strong and wide stretching vibration absorption peak of Si-O-Si group at between 1100 cm^{-1} and 1108 cm^{-1}, a strong flexural vibration absorption peak of the Si-CH$_3$ group at 1261 cm^{-1}. The FTIR spectra of copolymer of H-PDMS and acrylate indicated that there was an characteristic peak of -Si- group by comparing FTIR spectra of the acrylate homopolymer (comparing b with c in Fig. 2), the characteristic peak of the -Si- group wasn't from the H-PDMS homopolymer because the copolymers have been purified to remove the homopolymer completely before the FTIR spectra were made. By comparing FTIR spectra of the copolymer and H-PDMS (a and c in Fig. 2), the absorption peak of the -Si-group from copolymer at about 2165 cm^{-1}, 1100 cm^{-1} to 1108 cm^{-1} and 1261 cm^{-1} were greatly weak, which can be explained by the content of H-PDMS being lower in the copolymer, especially the characteristic peak of the Si—H group. The Si—H bond from H-PDMS had reacted with the C=C bond from acrylate monomers by the silicon-hydrogen addition reaction to form a chemical bond. This is why the characteristic peak of the Si—H group was very weak.

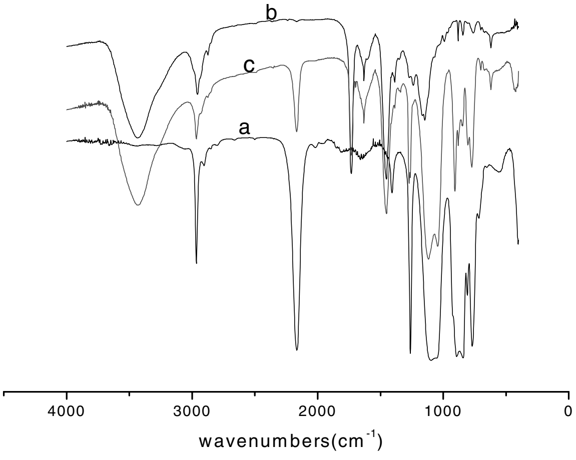


Fig. 2. FTIR spectrum of (a) H-PDMS, (b) pure acrylate polymer and (c) silicone-acrylate copolymer.

The chemical shift ratio of hydrogen in the CH$_3$ group and Si—H group of H-PDMS was 3.637 on the ^{1}H-NMR spectrogram, while the chemical shift ratio of hydrogen in CH$_3$ group and Si—H group of copolymer of H-PDMS and acrylate was 4.348 on the ^{1}H-NMR spectrogram. The change of chemical shift ratio suggested that the content of hydrogen in the Si—H group of copolymer decreased, which illustrated that the Si—H group of H-PDMS reacted with the carbon-carbon double bond from acrylate monomers by a silicon-hydrogen additive reaction to form a chemical bond.

3.2. *The effect of weight fraction of H-PDMS on stability of the composite emulsion*

The experimental results of the effect of different weight fraction of H-PDMS on the stability of composite emulsion were shown in Table 1. As shown, the surface tension of distilled water was 72.7 mN/m, and the surface tension of polyacrylate emulsion was 37.5 mN/m. The surface tension of composite emulsion decreased rapidly with H-PDMS content, the surface tension of composite emulsion remained at about 30 Nm/m when H-PDMS content varied from 10%–16% wt, the surface tension and apparent viscosity of the composite emulsion increased when the H-PDMS content reached 20% wt. This suggested that H-PDMS played a role similar to the emulsifier when the H-PDMS content was lower and the composite emulsion system appeared as phase separation owing to the fact that H-PDMS and polyacrylate were an incompatible system when the H-PDMS content was higher. Thus, the H-PDMS content is key to the stability of the system.

In addition, the latex particle size of composite emulsion increased with the weight fraction of H-PDMS, the average particle size of composite emulsion with 16% wt H-PDMS was 90 nm and the particle size distribution was narrow, the average value of particle size of composite emulsion with 20% wt H-PDMS was 300 nm and the particle size distribution wasn't homogeneous, which resulted in the composite emulsion being unstable.

3.3. *The effect of weight fraction of H-PDMS on T_g of latex membrane*

The DSC of polymer of acrylate monomers and H-PDMS with different weight fraction is shown in Figure 4, the results show that the T$_g$ of pure polyacrylate was 49°C, the

Table 1. Effect of PHMS amount on the properties of compounded latex

PHMS amount × 100	*0*	*10*	*13*	*16*	*20*
Percent conversion for polymerization × 100	96.35	90.59	91.24	92.41	93.52
Apparent viscosity of emulsion (20°C) /mPa·s	15.0	13.5	21.0	25.0	25.0
Interfacial tension /mN·m^{-1}	37.5	30.0	30.3	30.9	32.9
Mean particle diameter of latex /nm	40	–	–	90	300 (uniform)
High-temperature stability	White emulsion	White emulsion	White emulsion	White emulsion	White emulsion
Low-temperature stability	Frozen	Frozen	Separating layer	White emulsion	Floating oil

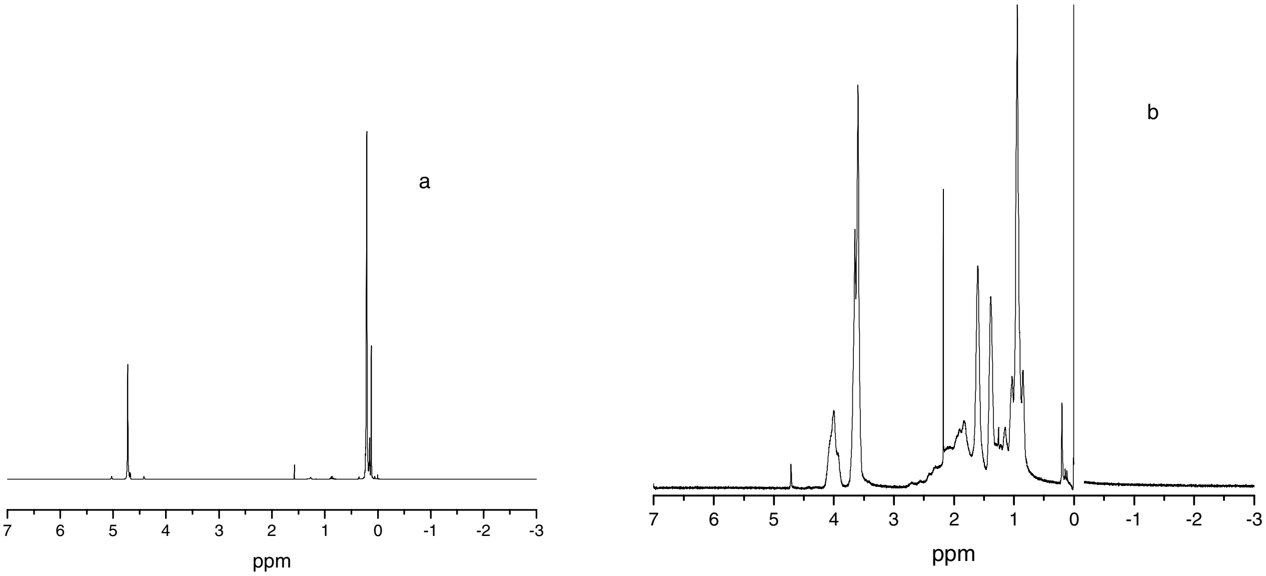


Fig. 3. ^{1}H-NMR spectrum of (a) H-PDMS, (b) silicone-acrylate copolymer.

T$_g$ of latex membrane containing 13% wt H-PDMS was 35°C. The reason for the decrease of the T$_g$ with increasing H-PDMS weight fraction is the copolymerization of H-PDMS and acrylate monomer. The T$_g$ of latex membrane containing 16% wt H-PDMS was two values (15°C and 25°C), this was due to the fact that PDMS and polyacrylate were typically in a compatible system which results in the formation of self-microscopic fields of PDMS with an increase of its weight fraction and results in the microscopic phase separation to appear as two different T$_g$ corresponding respective homopolymers. However, the macroscopic phase separation was difficult due to the chemical bond which formed between H-PDMS and polyacrylate.

3.4. *The effect of weight fraction of H-PDMS on hydrophobicity of latex membrane*

The experimental results of the contact angle between distilled water and the surface of cotton textile coated with the latex of H-PDMS and polyacrylate are shown in Figure 5. As can be seen, the contact angle increased with the H-PDMS content. The average contact angle of pure polyacrylate was 42.3°, the average contact angles were 110° and 118° when the H-PDMS contents were 13% wt and 16% wt, respectively. This suggested that PDMS had higher hydrophobicity than pure polyarcylate, which could improve the water resistance of the latex membrane.

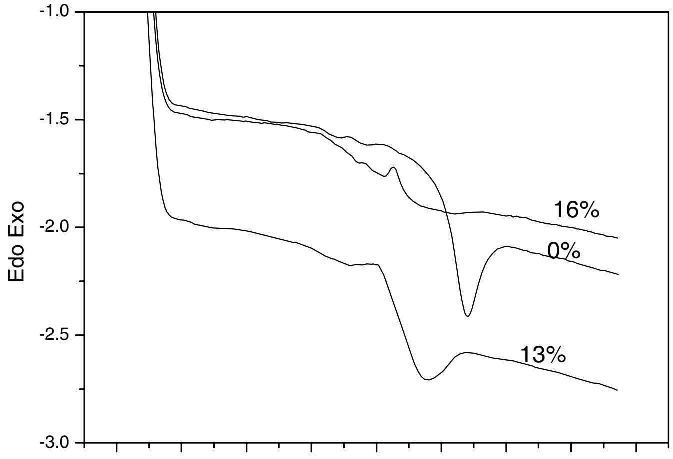
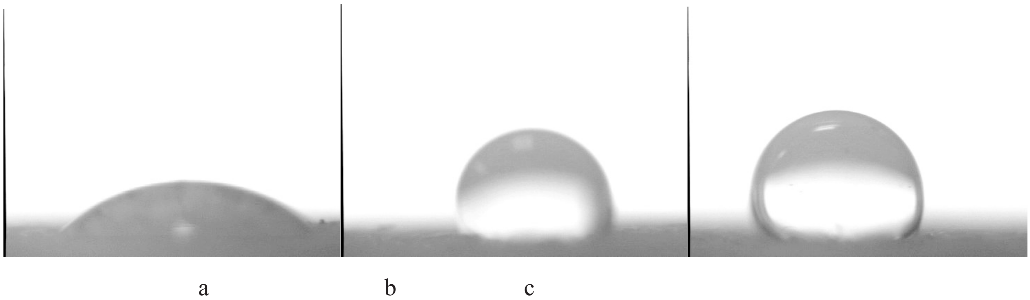


Fig. 4. DSC curves of silicone-acrylate latex membrane with different PHMS content.



a—0% PHMS (mean contact angle = 42.3°)
b—13% H-PDMS (mean contact angle = 110°)
c—16% H-PDMS (mean contact angle = 118°)

Fig. 5. Effect of PHMS content on the contact angle of water with a cotton fabric coating surface.

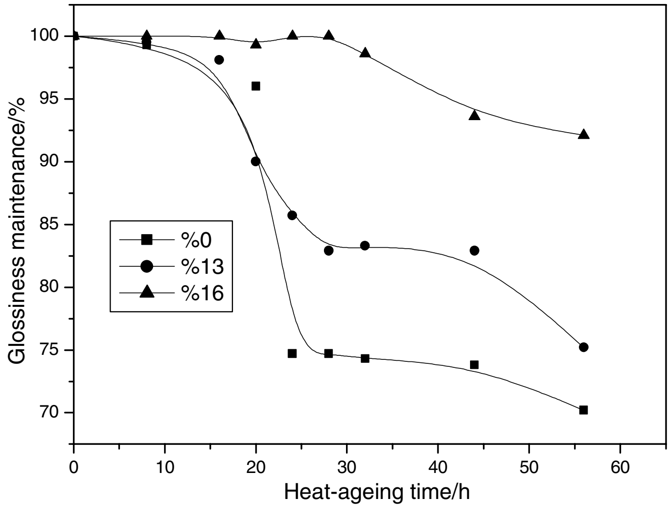


Fig. 6. Glossiness maintenance change with heat–ageing time for latex membrane of different PHMS content.

3.5. *The effect of weight fraction of H-PDMS content on heat–aging resistance of latex membrane*

Figure 6 is the gloss maintenance change with heat–aging time for the latex membrane with a different H-PDMS content.

The higher heat-durability of H-PDMS results in the phenomenon of higher glossiness maintenance of the latex membrane than pure polyacrylate latex membrane when they were heated at the same time, and this is more evident when heat-aging time are longer (Fig. 6). These improvements will make the fabric finished with the latex possess preferable performance.

4. Conclusions

Compared with acrylate emulsion, when the amount of H-PDMS is below 10% by weight (based mass of acrylate monomer), the surface tension of composite emulsion showed a decreasing trend and the apparent viscosity showed an increasing trend. This can be explained that a certain amount of H-PDMS in the composite emulsion plays a role similar to emulsifiers. When the content of H-PDMS varied from 10% to 16% by weight, the surface tension of composite emulsion kept about 30 mN/m, the apparent viscosity showed an increasing trend and the average latex particle size of composite emulsion is 90 nm. When the dosage of H-PDMS reached above 20%, the apparent viscosity and average latex particle size of composite emulsion increased, and the composite emulsion became unstable.

Both the core-shell structure of latex and the formation of the chemical bond between H-PDMS and acrylate monomer have an advantage in enhancing the stability of composite emulsion.

The T_g of latex membrane containing 13% H-PDMS was 35°C, which is lower than that of pure polyacrylate, and when the dosage of H-PDMS is 16% wt, the T_g of latex membrane appeared as two values (15°C and 25°C), which can be explained by the micro-phase separation behavior.

The hydrophobicty and heat-aging resistance of the latex membrane could be improved by increasing the amount of high hydrogen-containing polymethylsiloxane.

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