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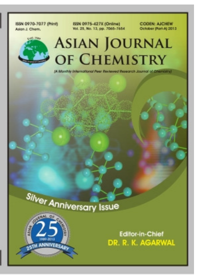

Synthesis and Properties of Novel Silicone-Acrylate Self-Emulsifying Emulsion

YUANYUAN QU[1] and HAOFEI HUANG[2,*]

[1]Department of Chemical Engineering, Zibo Vocational Institute, Zibo 25500, Shandong Province, P.R. China
[2]Chemical Engineering and Technology Specialty, Shandong University of Technology, Zibo 25500, Shandong Province, P.R. China

*Corresponding author: Tel: +86 533 2781630; E-mail: 1982hhf@163.com

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In this pater, a novel silicone-acrylate self-emulsifying emulsion was synthesized by emulsifier-free emulsion polymerization. Its structure was characterized by FT-IR, DSC and TEM. Owing to emulsifier-free polymerization applied and nano-sized emulsion particle, the performance of the film was excellent and met the commercial standards of film-forming polymer for antifouling coating. This emulsion may provide a new idea and method for the development of environmentally friendly marine antifouling coatings.

Key Words: Silicone-acrylate emulsion, Emulsifier-free polymerization, Nano-sized particle, Antifouling coating.

INTRODUCTION

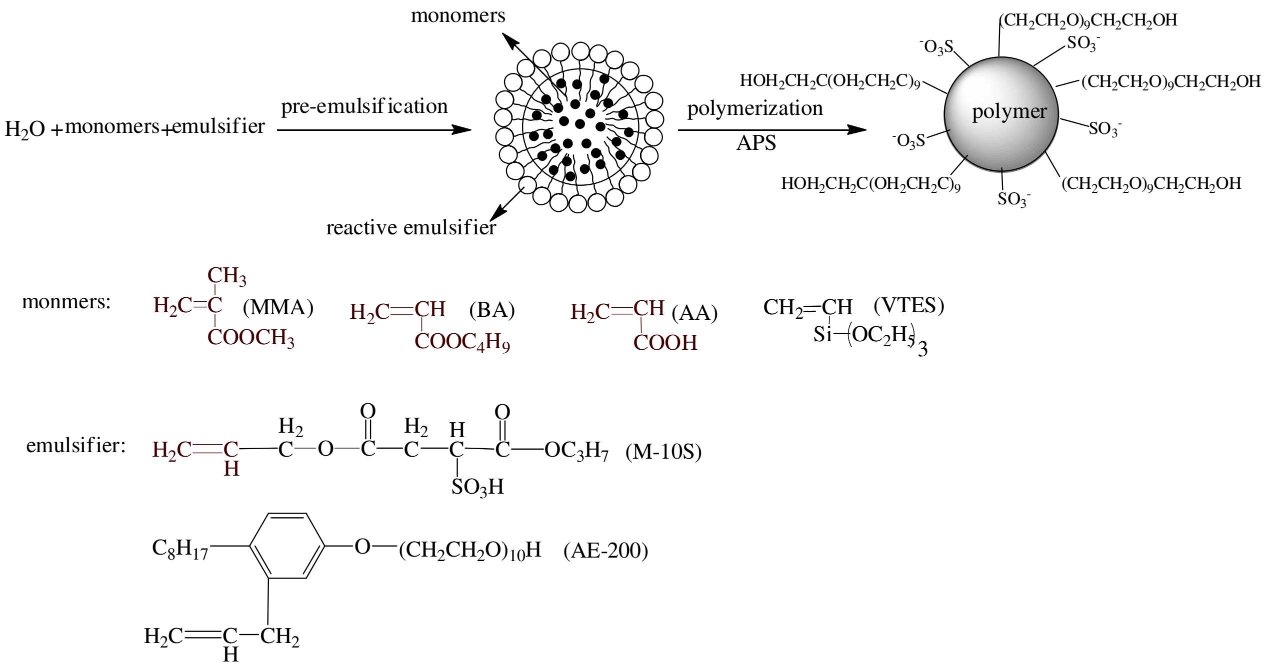
Acrylic resins have played an important role as film-forming polymer for coating industry because this class of resins exhibit excellent film forming ability and adhesion property[1]. With the development of silanes used as crosslinkers in polymers, silicone-acrylate resins were also synthesized and effectively improved the weatherability, water and stain resistance of traditional acrylic resins[2]. Now, such resins have been progressively used in the antifouling coatings[3,4]. However, silicone-acrylate resins used in commercial antifouling coatings usually employ large scale of xylene, toluene and other volatile organic compounds (VOCs)[5,6]. With the increasing regulatory environmental pressure to reduce volatile organic compounds, development of waterborne antifouling coatings using polymer emulsions has become necessary to antifouling industry.

In traditional emulsion polymerization, however, the residual emulsifiers have negative effects on the adhesion, water and impact resistance of emulsions and can even cause environmental pollution[7]. To effectively avoid those shortcomings, emulsions prepared by the polymerization using reactive emulsifier (emulsifier-free polymerization) were developed and possessed good performance[8]. However, silicone-acrylate emulsions prepared with such promising method have been rarely reported and applied in the commercial antifouling coatings. Thus, research on novel and high-performanced silicone-acrylate emulsions should be important and valuable to the future development of environmentally friendly antifouling coatings.

In this paper, a novel silicone-acrylate emulsion was synthesized by emulsifier-free polymerization using 4-propyl-1-(1-propenyl) sulfosuccinate (M-10S) as reactive emulsifier. It was characterized by fourier transform infrared, differential scanning calorimeter and transmission electron microscopy. The properties of the emulsion, such as particle size, water resistance, adhesion, *etc*., were also investigated. We hoped that the performance of this novel emulsion might be accord with the requirements of the antifouling coating.

The process of synthesis was shown in **Scheme-I**. At room temperature, 100 g deionized water, 1.6 g M-10S and 0.15 g ammonium persulfate (APS) were subsequently added into a glass vessel equipped with a N_2 inlet, a mechanical stirrer and a reflux condenser. After the mixture solution was heated to 80 ºC, 24.5 g methyl methacrylate (MMA), 25 g butyl acrylate (BA), 0.5 g acrylic acid (AA) and 4 g vinyl triethoxy silane (VTES) were added dropwise within 3 h. Then the emulsion polymerization was carried out at 90 ºC for 1 h. Finally, the mixture was cooled to room temperature and the pH was adjusted to 7-8 by addition of ammonia. The monomer conversion was 97 %, gel rate was 0.5 %. The film was prepared as follows: the emulsion was dipped to tin panels (0.28 mm thickness, 50 mm × 120 mm). These panels were dried at 20 ºC for 3 days.

FT-IR spectrum of silicone-acrylate recorded on an EQUINOX55 Fourier transform infrared spectrometer was shown in Fig. 1. The characteristic vibration absorption of =C-H and C=C band at 3030 and 1670 cm^{-1} disappeared, indicating that the monomers took part in the emulsion polymerization. The absorption band at 2958 cm^{-1} were assigned to -C-H deformation vibration of methylene and methyl of methyl methacrylate, butyl acrylate, acrylic acid, vinyl triethoxy silane. The absorption



Scheme-I

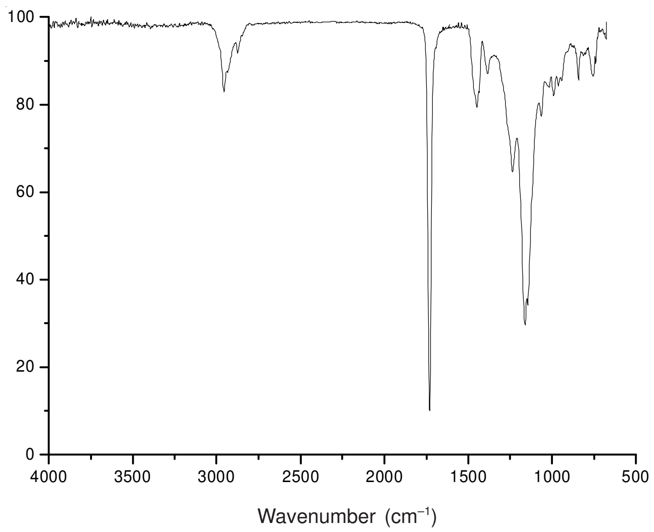


Fig. 1. FT-IR spectrum of silicone-acrylate

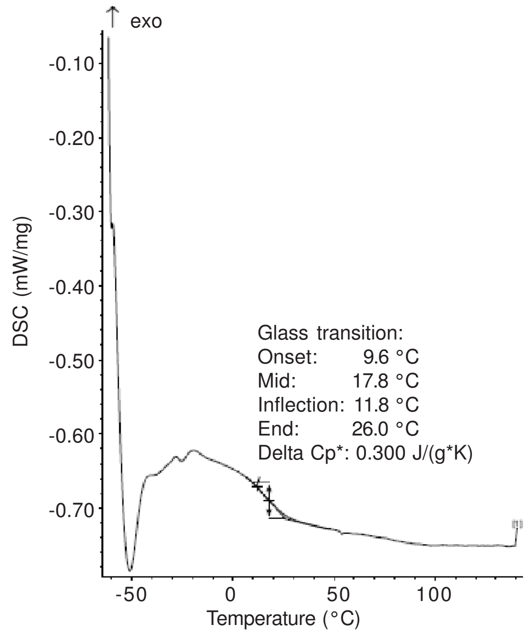


Fig. 2. DSC curve of the emulsion film

band at 1380 and 1458 cm^{-1} were due to deformation vibration of $-CH_3$ and $-CH_2$ of methyl methacrylate, butyl acrylate, acrylic acid, vinyl triethoxy silane. The absorption band at 1739 and 1169 cm^{-1} were attributed to the ester bonds of methyl methacrylate and butyl acrylate. And the absorptions of -Si-O- of vinyl triethoxy silane and $-SO_3$ of M-10S appeared at 1059 and 980 cm^{-1}, respectively. The glass transition temperature (Tg) of silicone-acrylate was analyzed by DSC (Perkin-Elmer DSC 7). As seen in Fig. 2, silicone-acrylate had only one glass-transition temperature (11.8 °C). The results of the FT-IR and DSC can be concluded that methyl methacrylate, butyl acrylate, acrylic acid, vinyl triethoxy silane and M-10S did not self-polymerize and they had all effectively participated in emulsion copolymerization.

The particle size and polydispersity index (PdI) of the synthesized emulsion were determined using nano-particle size analyzer (ZETASIZER nano series Nano-ZS90). The average particle size was 68.1 nm and the PdI value was just 0.072. The particle size and morphology were also characterized by TEM (Tecnai G220S-Twin) and the photo was shown in Fig. 3. It could be seen that the particles were uniform spheres and the size was also *ca.* 68 nm. These results confirmed that the synthesized emulsion was nano-sized emulsion and monodisperse. It is well known that the nano-sized emulsion is very important to obtain high quality films and smaller particle size and monodisperse particles provide much more improved properties including faster dry time and higher penetrability[9,10]. Thus, the polymerized nano-sized emulsion can be expected to be suitable for preparation of antifouling coatings and exhibit excellent performance.

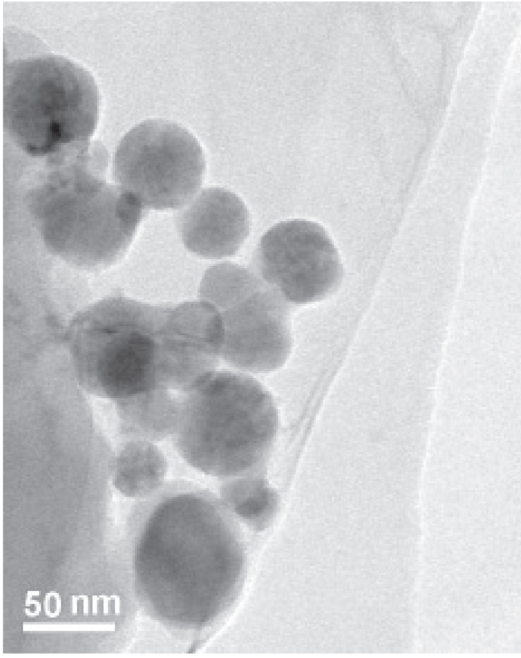


Fig. 3. TEM of the synthesized emulsion

The water absorption of the film was measured gravimetrically. The adhesion, dry time and impact resistance were tested, respectively according to ISO 2409:1992, ISO 6272-2-2006 and GB/T 1728-1979. All the results were summarized in Table-1. The water absorption of the film was just 1.6 %, which was as low as the resins using volatile organic compounds[11]. The excellent water resistance was due to the covalent bond formed between the active emulsifier and the other monomers during the polymerization and such bond prevented the migration of the emulsifier. 1 grade adhesion of the film was mainly attributed to the nano-sized emulsion particle which increased the capillary pressure and the total particle surface area when the emulsion film formed. The dry time and impact resistance could also met commercial standards.

TABLE-1
FILM PROPERTIES OF THE SYNTHESIZED EMULSION

Film properties	
Water absorption	1.6 %
Adhesion (level)	1 grade
Dry time	Surface drying in 28 h, film drying in 80 h
Impact resistance	50 kg cm

Conclusion

A novel silicone-acrylate self-emulsifying emulsion was successfully synthesized *via* emulsifier-free emulsion polymerization. The excellent performance of the emulsion revealed that this novel emulsion could be used as a potential raw material for environmentally friendly marine antifouling coating.

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