

Aqueous Polyacrylate/Poly(silicone-co-acrylate) Emulsion Coated Fertilizers for Slow Nutrient-Release Application

Yazhen Shen, Changwen Du, Jianmin Zhou

State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China

Correspondence to: C. Du (E-mail: chwdu@issas.ac.cn)

ABSTRACT: Waterborne polyacrylate/poly(silicone-co-acrylate) emulsions were synthesized to develop coated fertilizers. The effects of the *n*-butyl acrylate (BA)/methyl methacrylate (MMA) ratio, vinyltriethoxysilane, and synthesis method on the water resistance, glass-transition temperature, mechanical properties, and nutrient-release profiles were investigated. The results show that miniemulsion polymerization with a BA/MMA ratio of 55:45 was the most suitable for slow nutrient-release applications. Under these conditions, the preliminary solubility rate of the nutrient was about 3%, and the 30-day cumulative nutrient release was 15% at 25°C. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40369.

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INTRODUCTION

Controlled release fertilizers (CRFs) have been developed to improve plant nutrient use efficiency and to minimize nutrient losses and reduce the environmental threats and health problems often associated with poor fertilization management.^{1–5} Fertilizers coated with hydrophobic polymers are the major categories of CRFs as they have excellent nutrient-release profiles.^{5–8}

In recent years, the waterborne coating technique has been applied widely because it can remove the possible secondary pollution caused by volatile organic solvent-based coatings.^{9,10} Aqueous polyacrylate emulsions have the advantage of excellent film-forming characteristics, an appropriate viscosity, and a low price.^{11,12} However, hydroxyl and carboxylic groups in aqueous polyacrylates make aqueous polyacrylate polymers hydrophilic and swell dramatically in wet environments. The low tolerance of aqueous polyacrylates to water reduce the nutrient-release duration of CRFs. Our previous research, in which a crosslinker was used to modify the polyacrylate, showed that the preliminary solubility rate of the nutrient was 25%, and the cumulative nutrient release was 40% after 9 days at 40°C.¹³ The nutrient release was further slowed through additional measures in the study. First, the *n*-butyl acrylate (BA)/methyl methacrylate (MMA) ratios had an important effect on the physicochemical properties of the emulsion.^{14,15} Moreover, the hydrophilicity of aqueous polyacrylate was reduced by organic silicone because of the stronger water repellency.^{16–21} Poly(silicone-co-acrylate) emulsions were prepared by three methods: seeded polymerization, copolymerization, and miniemulsion

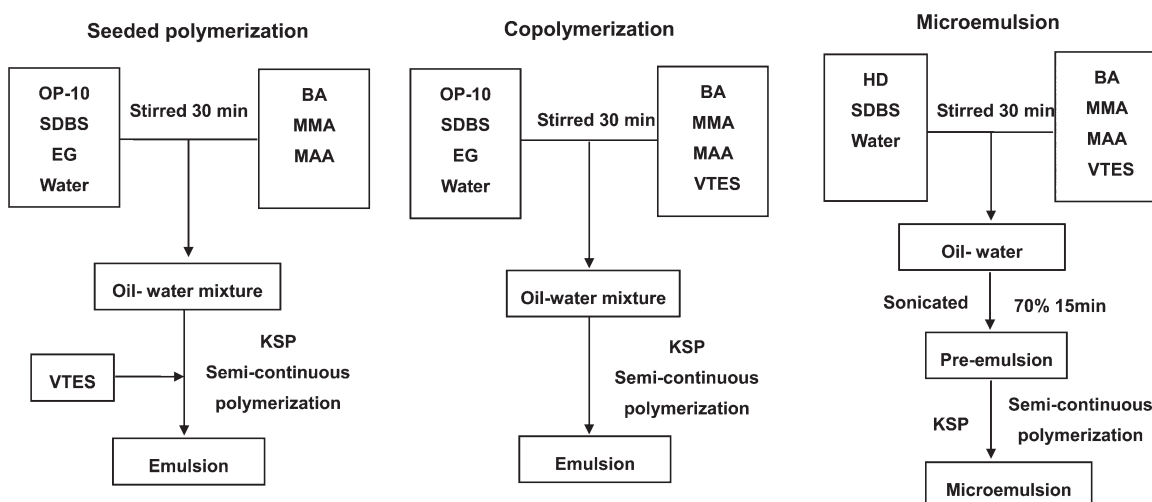
polymerization. In seeded polymerization and copolymerization, the principal locus of particle nucleation is in the monomer-swollen micelles. It is necessary for the monomer to diffuse from monomer droplets to the growing polymer particles, which causes highly premature crosslinking because of the easily hydrolysis and condensation of organic silicone.¹⁴ To suppress the hydrolysis and self-condensation of vinyltriethoxysilane (VTES), ethylene glycol (EG) was used to prepare poly(silicone-co-acrylate) by seeded polymerization and copolymerization. The miniemulsion is a relatively stable oil-in-water dispersion, which is typically obtained by the shearing of a system containing a monomer, water, a surfactant, and a costabilizer.²² Monomer droplets in a miniemulsion become the dominant site for particle nucleation, and this allows organic silicone to avoid contact with water and suppresses the organic silicone from undergoing hydrolysis and condensation.²³

In this study, waterborne polyacrylate and poly(silicone-co-acrylate) emulsions were synthesized, and the effects of the BA/MMA ratio and polymerization technique on the properties of the coating and nutrient-release profiles of CRFs were investigated. A suitable emulsion could be used to coat fertilizer and further slow the nutrient release of CRFs.

EXPERIMENTAL

Materials

The commercial granular compound fertilizers (NPK, 15-12-15) that we used were provided by Fulilong Guangdong Fertilizer Co., Ltd. MMA (Analytical pure), BA (Chemical pure),



Scheme 1. Procedures for the synthesis of poly(silicone-co-acrylate) emulsions by seeded polymerization, copolymerization, and miniemulsion polymerization.

methacrylic acid (MAA; Chemical pure), and EG (Analytical pure) were obtained from Nanjing Chemical Regent Co., Ltd. Sodium dodecylbenzenesulfonate (SDBS; Analytical pure) was obtained from Chengdu Kelong Chemical Reagent Co., Ltd. Nonyl phenyl polyoxyethylene ether-10 (OP-10; Laboratory pure) was received from Hebei Xingtai Kewang Auxiliary Agent Co., Ltd. Potassium persulfate (KPS; Chemical pure) and hexadecane (HD; Chemical pure) were supplied by Sinopharm Chemical Reagent Co., Ltd. VTES (Laboratory pure) was received from XFLP Silicones Co., Ltd. All of the reagents were used as received. Deionized water was used to prepare all of the solutions and emulsions.

Synthesis of the Polyacrylate and Poly(silicone-co-acrylate) Emulsions

Polyacrylate emulsions with different BA/MMA ratios were synthesized by semicontinuous polymerization. The emulsions polymerization was carried out in a 1000-mL, three-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel. The aqueous phase was prepared by the dissolution of 8.24 g of OP-10 and 4.12 g of SDBS in 248 g of water. The organic phase was prepared by the mixture of the desired amount of BA and MMA with 3.5 g of MAA. The total amount of BA and MMA was 200 g. Both phases were vigorously stirred for 30 min, and the temperature was raised to 80°C until the end of polymerization. A concentration of 25 wt % of the oil-water mixture in the flask was used as the initial charge. The rest of the mixture and the initiator solution (52 mL, 0.01 g/mL, KPS) were fed alternately in four doses over 3 h, and then, the polymerization was conducted under an air atmosphere for an additional 3 h.

The poly(silicone-co-acrylate) emulsions were prepared with three methods: seeded polymerization, copolymerization, and miniemulsion polymerization (Scheme 1). VTES was prone to hydrolysis and polycondensation with itself. To suppress the hydrolysis and self-condensation of VTES, EG was used when during the preparation of the poly(silicone-co-acrylate) by seeded polymerization and copolymerization. However, EG was

absent during the preparation of the poly(silicone-co-acrylate) by miniemulsion, for VTES was protected from the aqueous phase by a waterproof oil droplet, and the hydrolysis reactions were dramatically reduced in the miniemulsion. The same polymerization parts as used in the polyacrylate emulsion are not discussed, and the different parts were as follows. For the seeded polymerization, 31 g of EG was added to the water phase at the beginning, and 5 g of VTES (2.5 wt % of the total acrylate monomer mass) was injected to the flask after the completion of the oil-water mixture addition;^{17,24} For copolymerization, 31 g of EG was added to the water phase, and the oil phase was prepared by the mixture of 5 g of VTES with the acrylate monomer from the very beginning; For the miniemulsion polymerization,^{25–27} 8.24 g of HD displaced OP-10 and was used as a costabilizer; meanwhile, the oil phase was prepared by the mixture of 5 g of VTES with the acrylate monomers. Both phases were mixed and stirred vigorously for 30 min to get the pre-emulsions. The pre-emulsion was then sonicated for 15 min at 70% output with ultrasound (KQ-500, Kun Shan Ultrasonic Instruments Co., Ltd.). The resultant miniemulsion was transferred into a 1000-mL, three-necked flask, and the polymerization was performed just as the with polyacrylate emulsion mentioned previously. Eight emulsions were synthesized, and the solid content of all of the emulsions was about 40%. The details of emulsions are indicated in Table I. Only one ratio of BA to MMA (55:45) was considered when we synthesized the poly(silicone-co-acrylate) by copolymerization and miniemulsion polymerization. This was because the BA/MMA ratio of 55:45 was the most suitable ratio for the coatings from the nutrient-release profiles of S1, S2, and S3.

Preparation and Characterization of the Isolated Films

The use of isolated films has been reported as an alternative, convenient way of predicting coating properties and as a good way to screen different coatings.²⁸ Isolated films were obtained by the casting method, where a polymeric emulsion was cast onto a nonstick substrate, and water was evaporated completely in an oven at 80°C for 8 h. The swelling degree was determined

Table I. Recipes for the Synthesis of the Emulsions and the Properties for the Isolated Films

Sample code	BA/MMA ratio	Polymerization technique	T_g (°C) ^a	T_g (°C) ^b	Elongation at break (%)	Tensile stress at break (MPa)	Stiffness (Shore A) ^c
S1	55:45	Semicontinuous	5.10	-1.33	361.8 bc	1.97 e	60 d
S2	50:50	Semicontinuous	11.09	5.82	362.3 bc	4.72 c	60 d
S3	45:55	Semicontinuous	19.58	13.36	281.5 d	8.50 a	75 c
S4	55:45	Seeded polymerization	4.02	-4.42	862.7 a	1.97 e	45 f
S5	50:50	Seeded polymerization	9.22	2.36	804.0 a	3.49 d	80 b
S6	45:55	Seeded polymerization	13.73	9.53	383.1 b	6.25 b	85 a
S7	55:45	Copolymerization	5.62	-4.42	407.7 b	2.50 e	50 e
S8	55:45	Miniemulsion polymerization	5.75	-4.42	311.5 cd	3.78 d	60 d

^a T_g of the films as measured by DSC.

^b T_g of the films as calculated according to the Fox equation.

^cSamples with the same letter were not significantly different at $p \leq 0.05$ level.

by the following procedure: the weighed film (W_{f1}) was immersed into deionized water and remained sinking at 25°C. After this, the swollen films were removed periodically from the water, and the surface was wiped off with a piece of filter paper to determine the weight (W_{f2}). The swelling degree was defined as follows:²⁹

$$(W_{f2} - W_{f1}) / W_{f1} \times 100$$

The lower swelling degree indicated better water-resistance properties in the isolated films.

About 10 mg of isolated film was weighed, and differential scanning calorimetry (DSC, Perkin-Elmer Pyris1) was performed at a heating rate of 20°C/min. The thermal behavior of the samples was examined under a nitrogen atmosphere between -100 and 150°C. The glass-transition temperature (T_g) was taken at the onset of the corresponding heat-capacity jump. As a rule, two successive scans were made for every sample. All of the calculations were performed with the second heating cycle data.

The tensile properties of the isolated films were measured with a universal testing machine (CMT 5254, Shenzhen SANS Testing Machine Co., Ltd., China) according to the procedures outlined in ASTM D 638-03. A dumbbell-shaped die wide (type A2) was cut from the isolated film. The initial gauge length was 10 mm, and the measuring speed was 200 mm/min. The elongation at break and tensile stress at break were measured on the basis of three independent drawing experiments performed under the same conditions. Hardness tests (Shore A) were conducted on a hardness tester (XL-A, Jiangdu MingZhu Testing Machine Co., Ltd., China), with reference to ASTM D 2240-03 at $23 \pm 2^\circ\text{C}$ and a relative humidity of 50%.³⁰ All of the hardness data were the average values of three runs.

Preparation of the Coated Fertilizers

The fertilizer granules were coated in a Wurster fluidized bed equipped with a bottom-spray pneumatic nozzle (LDP-3, Changzhou Jiafa Granulation Drying Equipment Co., Ltd.). The process parameters were as follows: product temperature = 45–50°C, spray rate = 2.5 g/min, and atomization pressure = 0.1 MPa. The amount of coating emulsion was 75 g per 300 g of orig-

inal fertilizer granules 2–3 mm in diameter. The average coating thickness was about 100 μm . In all cases, the coated granules were tray-dried in an oven at 80°C for 8 h before further evaluation.

Fourier Transform Infrared Photoacoustic spectroscopy (FTIR-PAS) Characterization and Detection Release Profiles of the CRFs

An FTIR spectrometer (Nicolet 380) equipped with a photoacoustic accessory (model 300, MTEC) was used for the determination of the spectra of the CRFs coated with S1, S3, and S4. The spectra were recorded in the wave-number range 500–4000 cm^{-1} , and the mirror velocity was set to 0.63 cm/s ; 32 successive scans were conducted with a resolution of 4 cm^{-1} .

Five grams of coated fertilizer was immersed in 100 mL of deionized water at 25°C. A 100-mL solution was removed periodically (to determine the amount of nutrient release) and was replaced by deionized water (100 mL) with three replicates; The relative nutrient content was evaluated by solution conductivity³¹ with an electrical conductivity apparatus (DDS-320, China). On the 30th day of release, the coated fertilizers were ground to determine the content of residual nutrient. The release profiles were estimated as the cumulative release percentages versus time.

RESULTS AND DISCUSSION

Effect of the BA/MMA Ratios on the Swelling Degree of the Isolated Films

The swelling degrees of the isolated films are important evidence of water-resistance performance, and a lower of swelling degree indicates a stronger water-resistance performance. As shown in Figure 1, the increase in MMA caused stronger water-resistance performance in both the polyacrylate [Figure 1(a)] and poly(silicone-co-acrylate) films [Figure 1(b)]. The polymer chains were arranged closely, and the free space between the polymer chains decreased with increasing MMA. This improved the water resistance of the film.

Effect of the Synthesis Methods on the Swelling Degree of the Isolated Films

The swelling degrees of the poly(silicone-co-acrylate) emulsions prepared in different ways are shown in Figure 2. In the case of

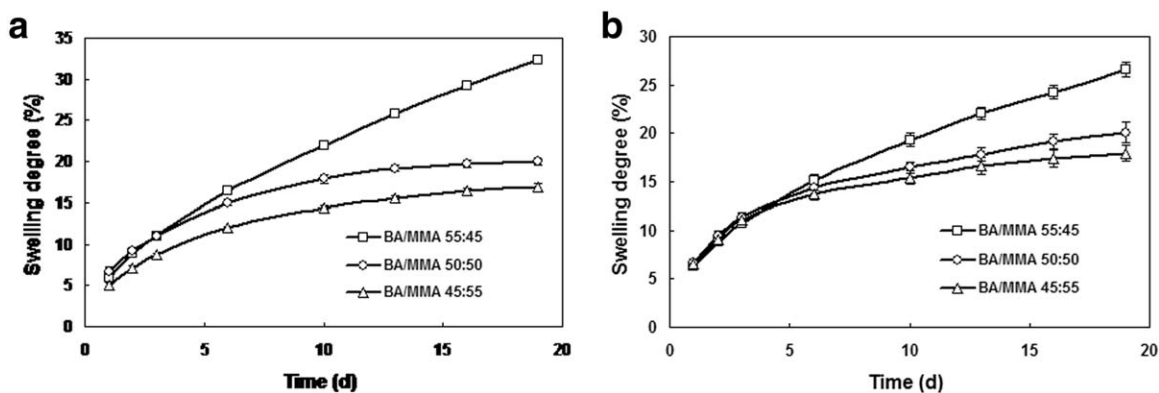


Figure 1. Effect of the BA/MMA ratios on the swelling degrees of isolated films obtained by (a) polyacrylate and (b) poly(silicone-*co*-acrylate) emulsions prepared by seeded polymerization.

the BA/MMA ratio of 55:45, the poly(silicone-*co*-acrylate) emulsions prepared by miniemulsion polymerization suggested the lowest swelling degree, whereas those prepared with the other methods revealed similar swelling degrees. That is because the hydrophilic EG was absent in the preparation of the poly(silicone-*co*-acrylate) by miniemulsion.

Glass-Transition Temperatures of the Isolated Films

The glass-transition temperature, which was closely related to the film-formation states of the CRF coating, could be used as an indirect indicator to select the coatings of CRFs. As shown in Table I, the measured T_g 's increased with increasing MMA and decreased with increasing of BA, regardless of the polyacrylate and poly(silicone-*co*-acrylate) emulsions. The effects of VTES on the glass-transition temperature was associated with the synthesis technique. When the poly(silicone-*co*-acrylate) emulsion was prepared by seeded polymerization, the T_g 's were lower than those of the corresponding polyacrylate isolated films with the same BA/MMA ratios. When the poly(silicone-*co*-acrylate) emulsions were prepared by copolymerization and miniemulsion, the T_g 's were higher. If the ethoxy group of VTES did not hydrolyze, the glass-transition temperature would have been lower because the T_g of poly(VTES) was -90°C .³² In addition, the glass-transition temperature increased with the

crosslinks in the copolymer films. These two opposite aspects could, therefore, affect the final glass-transition temperature.³³ VTES was added to the flask after the completion of the oil-water mixture in seeded polymerization, whereas it was injected into the flask at the beginning of the copolymerization and miniemulsion. The addition of VTES in the later period of the polymerization reaction prevented the prolonged contact between the alkoxy silane and water thus, alleviated the hydrolysis processes. Normally, the T_g values of coatings suitable for CRFs were $5\text{--}15^\circ\text{C}$.³⁴ Thus, neither S3 or S4 were suitable for CRF coatings. The T_g 's were predicted according to the Fox equation (Table I). The measured T_g 's were all higher than the predicted one because the Fox equation assumes that all of the monomers are randomly copolymerized and ignores the influence of segment distribution on the T_g 's of the copolymer. In the copolymerization system of poly(MMA-*co*-BA), the obvious difference in the reactivity ratio between MMA (1.88) and BA (0.43) caused more block copolymerization.¹⁴

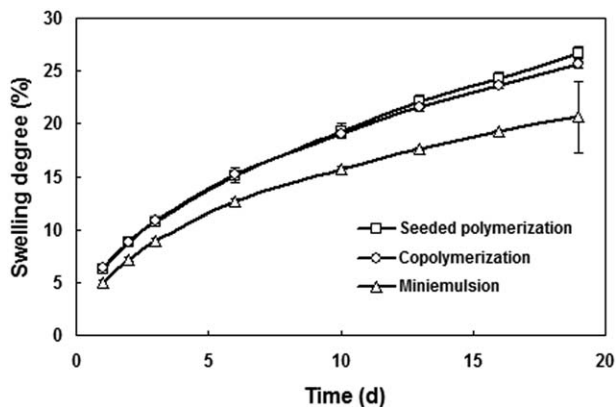


Figure 2. Effect of the synthesis methods on the swelling degrees of the isolated films.

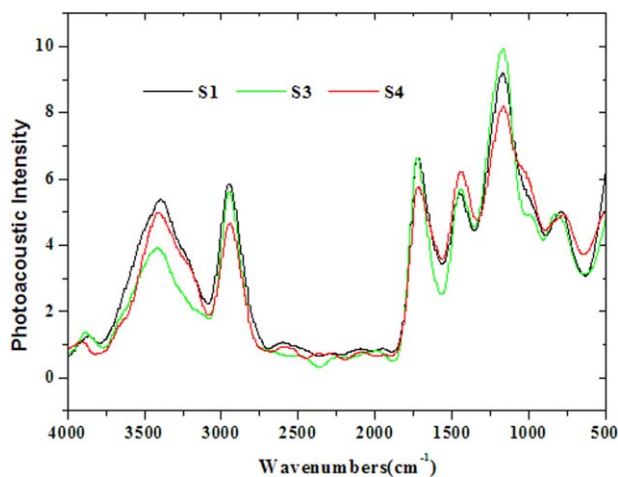


Figure 3. FTIR-PAS spectra of CRFs coated with S1, S3, and S4. S1 and S3 denote polyacrylate emulsions with BA/MMA ratios of 55:45 and 45:55, respectively. S4 represents the poly(silicone-*co*-acrylate) emulsion prepared by seeded polymerization with a BA/MMA ratio of 55:45. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

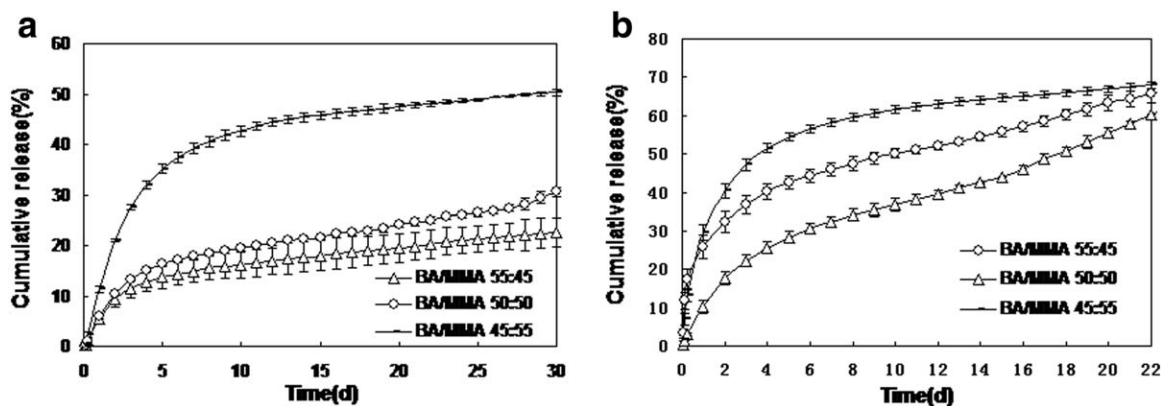


Figure 4. Effect of the BA/MMA ratios on the nutrient-release profiles of CRFs coated with (a) polyacrylate and (b) poly(silicone-co-acrylate) emulsions prepared by seeded polymerization.

Mechanical Properties of the Isolated Films

It is necessary to develop CRF coatings that combine the flexibility, strength, and stiffness. The elongation at break is a measure of the film flexibility, whereas the tensile stress is a measure of the film's strength. The stiffness is characterized by shore A hardness. Table I demonstrates the mechanical properties of the isolated films. An increase in the MMA content led to a strain-hardening coating with a low flexibility, regardless of the polyacrylate and poly(silicone-co-acrylate) emulsions. Compared with S1, the poly(silicone-co-acrylate) emulsion prepared by seeded polymerization (S4) showed a higher flexibility and lower stiffness. The strain-softening coating could be explained by the lower T_g of the poly(silicone-co-acrylate) film prepared by seeded polymerization. The tensile strength of the film formed from miniemulsion polymerization presented a higher value compared with the film formed from seeded polymerization and copolymerization. EG, in addition to suppressing the hydrolysis and self-condensation of VTES, also had a plasticizing function. It decreased the intermolecular interactions; therefore, the strength was lowered.³⁵ EG was absent in the preparation of the poly(silicone-co-acrylate) by miniemulsion, whereas it was present when in the preparation of poly(silicone-co-acrylate) by seeded polymerization and copolymerization.

FTIR-PAS Characterization of the CRFs

The FTIR-PAS spectra of CRFs coated with S1, S3, and S4 are displayed in Figure 3. The wide absorption at $3250\text{--}3550\text{ cm}^{-1}$ (O—H stretching vibration) suggested lower intensity in S3 than in S1; this resulted from the higher monomer reactivity ratios of MMA compared to that of BA. We noted the absence of C=C bonds at 1645 cm^{-1} in S4; this showed that the vinyl groups in VTES did join the reaction and were consumed during the emulsion polymerization. In addition, the spectra of S4 in the range $990\text{--}1136\text{ cm}^{-1}$ were broader compared to S1 and S3 because of Si—O—Si and Si—O—C asymmetric stretching. Coupled with the high content of EG in the poly(silicone-co-acrylate) emulsions, all of the previous results provided evidence for the copolymerization of VTES onto the polyacrylate chain.³⁶

Nutrient Cumulative Release Profiles

The nutrient-release profile was essential for evaluating whether the coatings were suitable for CRFs. The final nutrient-release profiles of the CRFs were directly related to the physicochemical properties of the coating, that is, the water-resistance performance, glass-transition temperature, and mechanical properties. The effect of the BA/MMA ratio on the nutrient-release behavior of the CRFs is displayed in Figure 4. For the polyacrylate

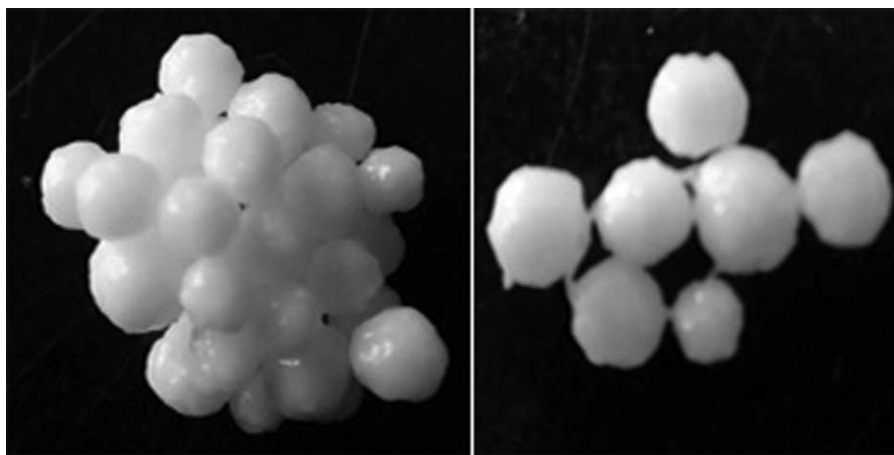


Figure 5. Optical pictures of the sticky coating of CRFs. The CRFs were coated with poly(silicone-co-acrylate) emulsions prepared by seeded polymerization with a BA/MMA ratio of 55:45 (S4).

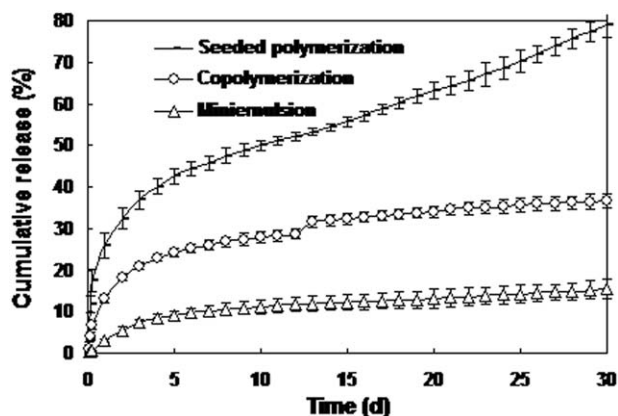


Figure 6. Effect of the synthesis methods on the nutrient-release profiles of CRFs.

emulsions [Figure 4(a)], an increase in the BA content resulted in a decrease in the nutrient-release rate. The nutrient-release profile of S1 was similar to that of S2, whereas the nutrient release rate of S3 was sharply accelerated. The water-resistance performance of S3 was improved; this was of benefit to the nutrient slow release. However, T_g (19.58°C) was much higher than that of coatings suitable for CRFs ($5\text{--}15^\circ\text{C}$). Additionally, the stiffness of S3 was greatly increased, and the flexibility was significantly decreased; this led to brittle coating. So, CRFs coated with S3 were more vulnerable to releasing nutrients through a fail mechanism.⁴ For poly(silicone-co-acrylate) emulsions prepared by seeded polymerization [Figure 4(b)], the nutrient release was the slowest for the BA/MMA ratio of 50:50 (S5), whereas the nutrient release of ratio at 55:45 (S4) was intermediate and that of the ratio at 45:55 (S6) was the fastest. The effects of the BA/MMA ratio on the nutrient-release profile were not in accordance with polyacrylate emulsions. In comparison with S5, T_g of S4 dropped from 5.1 to 4.02°C , and the hardness decreased from 60 to 45. All of these caused sticky coatings; thus, twin-coated granules were formed, and the coating integrity was damaged when they separated from each other (as shown in Figure 5).

The effect of the synthesis methods on the nutrient-release profiles of CRFs is demonstrated in Figure 6. In the case of the BA/MMA ratio of 55:45, the CRFs coated with the poly(silicone-co-acrylate) emulsion prepared by miniemulsion polymerization exhibited the slowest nutrient release. CRFs just delivered about 15% of the total nutrient in the 30 days of testing, whereas the CRFs coated with poly(silicone-co-acrylate) emulsions prepared by copolymerization and seeded polymerization released 36 and 78% of the total nutrient, respectively. Seeded polymerization (S4) resulted in a lower glass-transition temperature and a strain-softening effect. A lower glass-transition temperature and strain-softening effect led to a sticky coating (as shown in Figure 5), and this accelerated the nutrient release. In comparison with copolymerization (S7), miniemulsion polymerization (S8) resulted in a stronger water-resistance performance, a higher glass-transition temperature, and a strain-hardening effect. This suggested a slower nutrient release in the CRFs. Moreover, the high water-resistance performance was beneficial for slowing the

nutrient release of the CRFs. Nevertheless, we observed that the nutrient-release rate was not directly related to the water-resistance performance, and the mechanical properties of the coating had a greater influence on the nutrient release in this study.

CONCLUSIONS

To slow the nutrient release of the CRFs coated with aqueous polyacrylate emulsion, the effects of the BA/MMA ratio, VTES, and the synthesis technique on the coating properties and the nutrient-release behavior were investigated. The water-resistance performance, T_g , strength, and stiffness increased with increasing MMA content. VTES improved the water-resistance performance of the coating, but the effects on the glass-transition temperature, mechanical properties, and nutrient-release behavior varied with different synthesis techniques. When the BA/MMA ratio was 55:45, the poly(silicone-co-acrylate) prepared by seeded polymerization (S4) resulted in a low glass-transition temperature and a strain-softening coating. This accelerated the nutrient release. The poly(silicone-co-acrylate) prepared by copolymerization (S7) led to a higher glass-transition temperature and a lower stiffness, whereas the miniemulsion polymerization (S8) gave a higher glass-transition temperature and a strain-hardening effect and slowed the nutrient release. The preliminary solubility rate of the nutrient was about 3%, and the cumulative nutrient release did not exceed 15% within 30 days at 25°C . The nutrient-release rate was greatly decreased compared to that of the CRFs prepared in our previous study (where the preliminary solubility rate was 25%, and the cumulative nutrient release was 40% in the 9 days at 40°C).¹³ In summary, the waterborne poly(silicone-co-acrylate) emulsion synthesized by miniemulsion at a BA/MMA ratio of 55:45 could be used well in CRFs coatings.

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