



Materials and Product Engineering

# Application of waterborne acrylic emulsions in coated controlled release fertilizer using reacted layer technology<sup>☆</sup>

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## ABSTRACT

Waterborne acrylic emulsions modified with organic siloxanes and aziridine crosslinker were synthesized and applied as coating of controlled release fertilizer. The free films were characterized and the nutrient release profiles of the coated fertilizers were determined. The results show that methyl silicone oil and methylsilanolate sodium could not improve water resistance performance and glass transition temperature  $T_g$  of coatings, while the firmness is enhanced. Aziridine crosslinker improves the water resistance performance, firmness and  $T_g$ . Incorporation of methyl silicone oil and aziridine crosslinker gives an excellent aqueous acrylic emulsion for coated controlled release fertilizer, with the 30-day cumulative nutrient release reduced to 16% and an estimated nutrient release duration over 190 days. Therefore, this waterborne coating is promising to meet the requirements for controlled release of nutrient and environmental protection.

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## 1. Introduction

Controlled release fertilizers (CRFs) are preferred alternatives to soluble fertilizers. Due to proper nutrient release throughout the growing season, crops can uptake more nutrient, increasing nutrient use efficiency and benefiting environmental protection [1–3]. With their excellent controlled release effect, the polymer coated fertilizers are the most promising controlled release fertilizers [4].

Polymer coated fertilizers can be prepared by coating conventional fertilizer particles with various polymer materials, such as polyolefins [5], polyvinyl chloride [6–8], polysulfone [7], and polyacrylamide [9,10]. These polymers are usually dissolved in specific organic solvent to obtain polymer solutions. The solution is sprayed on the surface of fertilizer granules and the solvent is removed through evaporation [10–13]. This coating process demands costly volatile organic solvent and may lead to secondary pollution [14,15]. Recently, waterborne coating technique has been used widely because of strict pollution regulation. Waterborne polyacrylate is considered as environmentally friendly materials. Polyacrylate is biodegradable because it contains susceptible ester bonds, does not influence the soil structure and soil microorganism community activity, and benefits soil fertility. In addition, the aqueous acrylic emulsions have excellent film-forming characteristics and appropriate

viscosity, but its application in coated controlled release fertilizers is limited by the hydrophilicity of waterborne polymer [16]. Siloxanes and aziridine crosslinker have been used to improve the water resistance performance of polymers by modifying the acrylic emulsion [17–22]. The crosslinking reaction of aziridine is very weak at room temperature and will be rapidly accelerated with the increase of temperature [23–27], which provides a way for the crosslinking process concomitantly with film-forming (reacted layer technology) in the fertilizer coating using Wurster fluidized bed [28,29].

In our previous research, waterborne acrylic emulsion was used as the coating of controlled release fertilizers, but the release duration was too short for some crops with long growth periods [30]. In this study, waterborne acrylic emulsion modified with organic siloxanes and aziridine crosslinker are synthesized to increase the nutrient release duration. The free films are characterized and the nutrient release profiles of the coated fertilizers are determined.

## 2. Experimental

## 2.1. Materials

The commercial granular NPK compound fertilizer (NPK 15-12-15) with 2–3 mm in diameter (Fulilong Guangdong Fertilizer Co. Ltd.) was used to prepare the coated fertilizers. Methyl methacrylate, butyl acrylate, and ethylene glycol (EG) were purchased from Nanjing Chemical Regent Co., Ltd.; methacrylic acid was from Shanghai Ling Feng Chemical Reagent Co., Ltd.; sodium dodecyl benzene sulfonate was from Chengdu Kelong Chemical Reagent Co., Ltd.; alkyl phenol polyethoxy (OP-10) was from Hebei Xingtai Kewang Auxiliary Agent Co., Ltd.; and

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potassium persulfate was from Sinopharm Chemical Reagent Co., Ltd. Methyl silicone oil (MSO) was from Boyang Industrial Co., Ltd. and methylsilanolate sodium (MSS) was from Beijing Ruichen Chemical Auxiliary Agent Co., Ltd. The chemical structures of MSO and MSS are demonstrated in Fig. 1. Crosslinker (SaC-100) was from Shanghai UN Chemical Co., Ltd. and the cross-linking reaction formula is shown in Fig. 2.

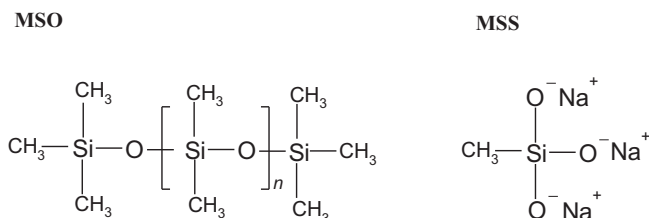


Fig. 1. The chemical structures of methyl silicone oil and methylsilanolate sodium.

## 2.2. Synthesis of acrylic emulsions and preparation of free films

The emulsions were prepared by semicontinuous emulsion polymerization, carried out in a 1000 ml three-necked flask equipped with a reflux condenser, a stirrer, and a dropping funnel. The aqueous phase was prepared by dissolving 8.24 g OP-10, 4.12 g sodium dodecyl benzene sulfonate, and 31 g EG in 248 g deionized water. The organic phase was prepared by mixing 110 g butyl acrylate, 90 g methyl methacrylate and 3.5 g methacrylic acid. Both phases were vigorously stirred for 30 min and the temperature was raised to 80 °C until the end of polymerization. 25% (by mass) of the oil-water mixture in the flask was used as the initial charge. The rest mixture and the initiator solution (52 ml, 0.013 g·ml<sup>-1</sup> K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) were fed alternately in 4 doses over 3 h. Siloxane (MSO or MSS) was then injected to the flask, and the polymerization was conducted under air atmosphere for another 3 h. One acrylic emulsion (A) and two silicone-acrylic emulsions (B and C) were obtained. 0.75% (mass) of aziridine crosslinker was dissolved in deionized water, and then slowly added to acrylic emulsion at room temperature with continuous stirring for 15 min. Emulsions A, B and C were modified with crosslinking to emulsions A<sup>a</sup>, B<sup>a</sup> and C<sup>a</sup> correspondingly, as shown in Table 1. The solid content of all emulsions was 40%. The free films were obtained by casting the prepared emulsion (2.0 g) onto a 9 cm<sup>2</sup> leveled plastic cap and dried in an oven at 60 °C for 24 h. The free films were removed from the plastic caps for further use.

## 2.3. Characterization of the free films

The swelling degree is defined as  $(w_2 - w_1) / w_1 \times 100\%$  [26]. The free films with the same thickness were immersed in 100 ml deionized

**Table 1**  
Compositions of emulsions,  $T_g$  of free films and nutrient release durations of CRFs

Emulsion code	Siloxane	Siloxane content/g	EG/g	Crosslinker/g	$T_g$ /°C	Duration/d
A	/	0	0	0	10.4	23
B	MSO	5	31	0	5.50	29
C	MSS	5	31	0	8.93	33
A <sup>a</sup>	/	0	0	1.5	12.54	87
B <sup>a</sup>	MSO	5	31	1.5	12.79	191
C <sup>a</sup>	MSS	5	31	1.5	15.37	90

water at 25 °C for 72 h. The mass of films before ( $w_1$ ) and after ( $w_2$ ) immersion were recorded in triplicate.

For the glass transition temperature ( $T_g$ ), 8–10 mg of free films was weighed and differential scanning calorimetry (DSC, Perkin-Elmer Pyris 1, USA) was used at a heating rate of 20 °C·min<sup>-1</sup>. The thermal behavior was examined under the nitrogen atmosphere between -50 °C and 150 °C.  $T_g$  was taken at the onset of the corresponding heat capacity jump. As a rule, two successive scans were made for every sample. All calculations were performed on the second heating cycle.

The surface morphology of free films was examined by optical microscope at a magnification of 1000× (Olympus, S83084).

A FTIR (Nicolet 380, USA) equipped with photoacoustic accessory (Model 300, MTEC, USA) was used for the spectra of free films, with a wave number range of 500–4000 cm<sup>-1</sup> and mirror velocity of 0.32 cm·s<sup>-1</sup>. 32 successive scans were recorded with a resolution of 4 cm<sup>-1</sup>.

## 2.4. Preparation and release characteristics of 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: fluidized bed temperature, 45–50 °C; spray rate of coating emulsions, 2.5 g·min<sup>-1</sup>; atomization pressure, 0.1 MPa. The amount of coating emulsions was 125 g per 500 g original fertilizer granules. The average coating thickness was about 100 μm. In all the cases, the coated pellets were tray-dried in an oven at 45 °C for 24 h.

Ten-gram coated fertilizers were immersed in 100 ml of deionized water at 25 °C. 100 ml was analyzed and replaced by 100 ml fresh deionized water, three replicates. The released nutrient content was evaluated by the solution conductivity [31], measured with an electrical conductivity apparatus (DDS-320, China). On the 30th day of study, the coated fertilizers were ground to determine the content of residual nutrient. The release characteristics were estimated as the cumulative release percentage versus time. The nutrient release duration of CRFs is denoted by the time for release of 80% of the total nutrient content. The durations of A and B were found from the cumulative release curve, and those of other CRFs are calculated as follows:  $(80 - Y_{30}) / V_{10-20} + 30$ , where  $Y_{30}$  stands for the fraction released at the 30th day, and  $V_{10-20}$  is the average daily release rates from the 10th to the 20th day.

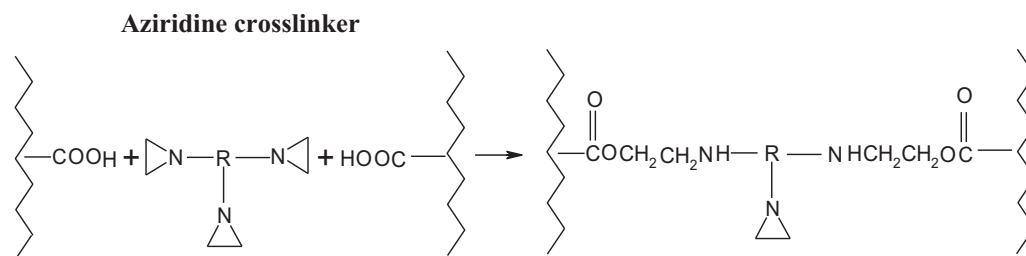


Fig. 2. Mechanism of cross-linking reaction.

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