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Synthesis and performance of sodium salt of MAA/St/SAS copolymer dispersant

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Abstract. A new type of dispersant for pesticide water dispersible granules (WDGs), sodium salt of methacrylic acid/styrene/sodium allylsulfonate copolymer (SMSA) was synthesized. 90 wt% atrazine WDG was prepared to evaluate the dispersion performances of SMSA. It is found that SMSA has high performance and strong resistance to hard water, and the suspensibility of 90 wt% atrazine WDG before and after hot storage could reach 93.14% and 92.22% in standard hard water, and 87.19% and 85.33% in three-fold standard hard water, respectively.

1. Introduction

Polycarboxylate dispersant is an important anionic polymer dispersant, which has many advantages, such as flexible molecular structure, environmentally friendly production process and good dispersion performance, etc. Thus, it has been widely used in plastic filling, coatings, pesticides, inks, ceramics, printing and dyeing, cement and other fields [1-4].

Atrazine is one of the most widely used herbicides [5], and is commonly used in 38 wt % and 40 wt % suspension concentrate, 50 wt% wettable powder and 90 wt% WDG. Among them, WDG has the advantages of easy disintegration, high suspensibility and environmental friendliness. In recent years, polycarboxylate dispersants have been widely used in the research and development of pesticide WDG. Terpolymer dispersant [6] was synthesized with acrylic acid, sodium styrene sulfonate and maleic anhydride, and was applied to 70% imidacloprid WDG. A new nano-composite dispersant, sodium salt of styrene-methacrylic acid copolymer/montmorillonite was designed and synthesized [7].

WDG generally undergo a long-term transportation and storage process, which may affect the performance of WDG. Hot storage stability test is usually used to study the storage stability of WDG. So far, the dispersant products used for preparing WDG have the problems of rapid decrease of suspensibility and poor resistance to hard water after hot storage. In this paper, sodium salt of methacrylic acid/styrene/sodium allylsulfonate copolymer (SMSA) was synthesized. The structure of SMSA dispersant was characterized, and applied to 90 wt% atrazine WDG. The dispersion properties of WDG before and after hot storage have been studied in water with different hardness.

2. Experimental

2.1. Materials

Sodium allylsulfonate (SAS) ($\geq 95\%$) was purchased from Shandong Shouguang Songchuan Industrial Auxiliaries Co., Ltd. (China), sodium alpha-olefin sulfonate (AOS) was purchased from Shanghai Chuxing Chemical limited company (China), Atrazine ($\geq 97\%$) was purchased from Shandong



Binnong Technology Co., Ltd. (China), GYD04 (sodium salt of copolymer of acrylic acid and maleic anhydride) was purchased from Beijing Guangyuan Yinong Company (China), 2700 (sodium polycarboxylate) was purchased from Huntsman Company (USA), styrene (St), methacrylic acid (MAA), isopropanol, $\text{Na}_2\text{S}_2\text{O}_8$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 , and NaOH were all analytical grade and purchased from Beijing Chemical Reagent Company (China).

2.2. Synthesis of SMSA

A series of SMSA dispersants were synthesized by solution free radical polymerization [8] with MAA/St molar ratio of 3.0:1.0 and different SAS/St molar ratio. The reaction was carried out at 80°C for 5 h. Then, the resultant was neutralized to pH 8.5 with 30% NaOH aqueous solutions. After the isopropanol was removed by distillation, the SMSA was obtained by drying the liquid product. The synthetic route of SMSS is shown in figure 1.

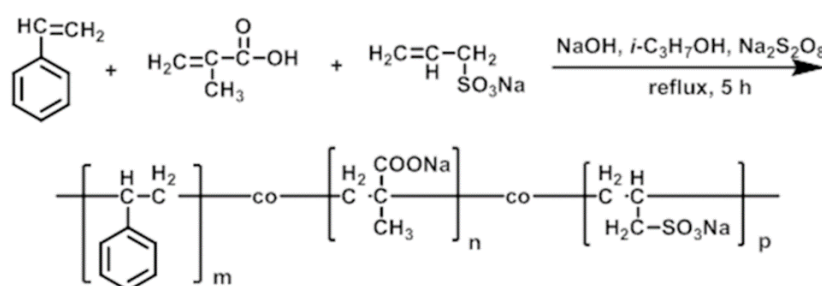


Figure 1. Synthetic route of SMSA.

2.3. FT-IR spectrum and ^1H NMR of SMSA

IR spectrum of SMSA was recorded on a VERTEX 80V spectrophotometer (Brucker, German) using KBr disc technique. ^1H NMR spectrum of SMSA was recorded on a Avance III HD 700 MHz NMR instrument (Brucker, German) using D_2O as the solvent.

2.4. Preparation and performance of 90 wt% atrazine WDGs

2.4.1. Preparation of 90 wt% atrazine WDGs. 93.0 g of atrazine, 5.0 g of dispersant, 2.0 g AOS were ground to a uniform powder by using an IKA A11 pulverizer (Germany), then deionized water was added, and granulated in a shear granulator (GL2-25, Zhangjiagang Create Mechanical Manufacturing Co., Ltd, China). The WDGs were obtained after drying. Samples prepared by SMSA dispersant, GYD04 dispersant and 2700 dispersant were denoted as S_{SMSA} , S_{GYD04} and S_{2700} , respectively.

2.4.2. Preparation of standard hard water. Standard hard water was prepared by adding 0.304 g of anhydrous CaCl_2 and 0.139 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to a beaker and dissolving with 1000 mL deionized water.

2.4.3. Determination of suspensibility. 1.0 g of 90 wt% atrazine WDG was put into a measuring cylinder with stopper, dissolved and diluted to 250 mL by water with different hardness, respectively. The cylinder was inverted 30 times in one minute. After the cylinder had been heated on a water bath for 30 minutes at 30°C , 225 mL of the supernatant fractions were removed, and the residue at the bottom was dried at 70°C and weighed. The suspensibility w (%) is calculated by equation (1).

$$w = \left(1 - \frac{m_2 - m_1}{m}\right) \times \frac{10}{9} \times 100\% \quad (1)$$

Where, m is the mass of initial sample; m_1 is the mass of the evaporating dish; m_2 is the sum of the mass of residue and evaporating dish.

2.4.4. Determination of disintegration. 0.50 g of WDG was quickly poured into 90 mL standard hard water in a 100 mL cylinder with stopper at 25°C, and it was rotated around the middle of the cylinder at a speed of 8 r/min. The rotation times that WDG completely disintegrate are called the disintegration of WDG.

2.4.5. Hot storage stability test. About 5.0 g WDGs were sealed in a 50 mL ampoules, and then placed in an oven at (54 ± 2) °C for 14 days.

2.4.6. Confocal laser scattering microscopy (CLSM) images. WDG samples were dispersed in standard hard water to obtain the atrazine WDG suspensions (1000 mg/L). CLSM (FV1000, Japan) were used for observing the morphology of atrazine particles in atrazine WDG suspensions.

3. Results and discussion

3.1. Structure of SMSA

As shown in figure 2, the peak located at 516 cm^{-1} is attributed to $-\text{SO}_3^{2-}$ vibration. The peaks appeared at 701 and 752 cm^{-1} assign to the bending vibration of $-\text{CH}$ on benzene ring. The peak at 1541 cm^{-1} corresponds to $-\text{COO}^-$ absorption. The peak at 1398 cm^{-1} is the bending vibration of $-\text{CH}$ in $-\text{CH}_3$, and the typical peak at $2895\text{--}2966\text{ cm}^{-1}$ is the stretching vibration of $-\text{CH}_3$ and $-\text{CH}_2$. There is no $-\text{CH}$ stretching vibration absorption peak of $\text{cis-CH}_2=\text{CH-}$ in the range of $665\text{--}730\text{ cm}^{-1}$, which indicates that the polymerization proceeded completely.

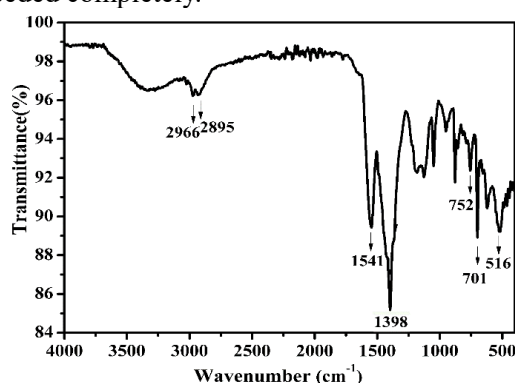
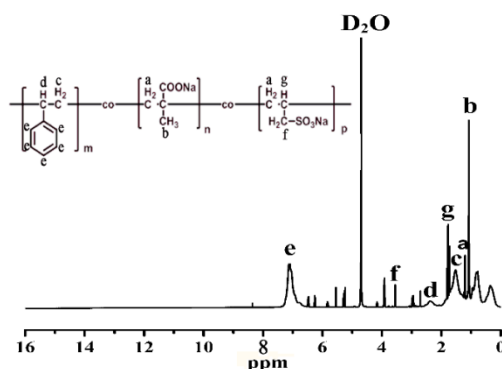


Figure 2. FT-IR spectrum of SMSA.

As shown in figure 3, a resonance at δ 4.70 ppm attributes to D_2O solvent. The chemical shift of H on benzene ring (labeled e) is at 7.30–6.62 ppm. The resonance centered at δ 2.38 is the chemical shift of $-\text{CH}$ banded to benzene ring (labeled d). The peak at 1.51–1.20 ppm is the chemical shift of $-\text{CH}_2-$ in the main chain (labeled a, c), while the peak centered at δ 1.11 ppm is identified as the $-\text{CH}_3$ in the side chain (labeled b). The peak centered at δ 1.85 ppm is the chemical shift of $-\text{CH-}$ in the main chain (labeled g), and the resonance centered at δ 3.41 ppm is the chemical shift (labeled f) of $-\text{CH}_2-$ in the side chain. All the results of FT-IR and ^1H NMR indicate that the structure of the SMSA is consistent with that of the designed dispersant.

Figure 3. ^1H -NMR spectrum of SMSA.

3.2. Influence of SAS/St mole ratio on dispersion performance of SMSA

Based on the previous research, we selected SAS monomer to copolymerize with styrene and methacrylic acid, and investigated the influence of SAS/St mole ratio on the dispersion performance of SMSA. As demonstrated in figure 4, with the increase of SAS/St molar ratio, the suspensibility of WDG in standard hard water and three-fold standard hard water both firstly increases and then decreases. When the SAS/St molar ratio is 0.25, the highest suspensibility is 93.14% and 87.19% in standard hard water and three-fold standard hard water, respectively, showing strong resistance to hard water. However, when the SAS/St molar ratio is more than 0.25, the suspensibility decreases gradually. The excessive SSS will greatly increase the hydrophilicity of SMSA dispersant, which will enhance the interaction between atrazine WDG particles, and leads to the agglomeration between the original drug particles, and reduce the suspensibility.

Besides, it can be seen from figure 4 that the disintegration times of atrazine WDG in standard hard water and three-fold standard hard water both decrease firstly and then increase with the increase of SAS/St molar ratio. When the molar ratio of SAS/St is 0.25, atrazine WDG has the best disintegration performance. The proportion of hydrophilic/hydrophobic groups in the molecular structure of polycarboxylate dispersant will affect the disintegration performance and pore size distribution of WDG [9]. When the amount of SAS monomer is too much, more strong hydrophilic $-\text{SO}_3^{2-}$ groups will make WDG with denser structure during processing, which is not conducive to the formation of larger pores and the disintegration of WDG particles.

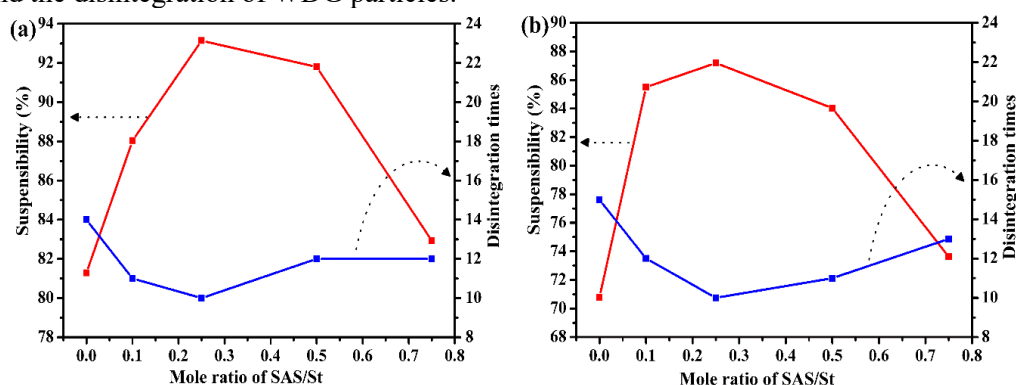


Figure 4. Influence of SAS/St mole ratio on suspensibility and disintegration performance of WDG; (a) standard hard water; (b) three-fold standard hard water.

3.3. Influence of hot storage on WDG performance

3.3.1. Influence of hot storage on the suspensibility of WDG. As demonstrated in figure 5 a, the initial suspensibility of S_{GYD04} , S_{2700} and S_{SMSA} in standard hard water are 91.61%, 92.09% and 93.14%,

respectively. After hot storage for 14 days, the suspensibility of S_{2700} and S_{SMSA} in standard hard water are 91.32% and 92.22% respectively, showing good hot storage stability. However, the suspensibility of S_{GYD04} decreases to 39.71% after hot storage. This is partly due to the agglomeration occurs between the atrazine particles during the hot storage process, which will increase the particle size of S_{GYD04} . According to Stokes law [10], the larger the particle size is, the faster the sedimentation rate is, and the more unstable the suspension system become, which will lead to the decrease of the suspensibility of S_{GYD04} . As shown in figure 5 b, the suspensibility of S_{GYD04} in three-fold standard hard water is significantly lower than that in standard hard water; the suspensibility of S_{2700} and S_{SMSA} after hot storage is 76.88% and 85.33% in three-fold standard hard water, indicating that SMSA dispersant has excellent hot storage stability and strong resistance to hard water.

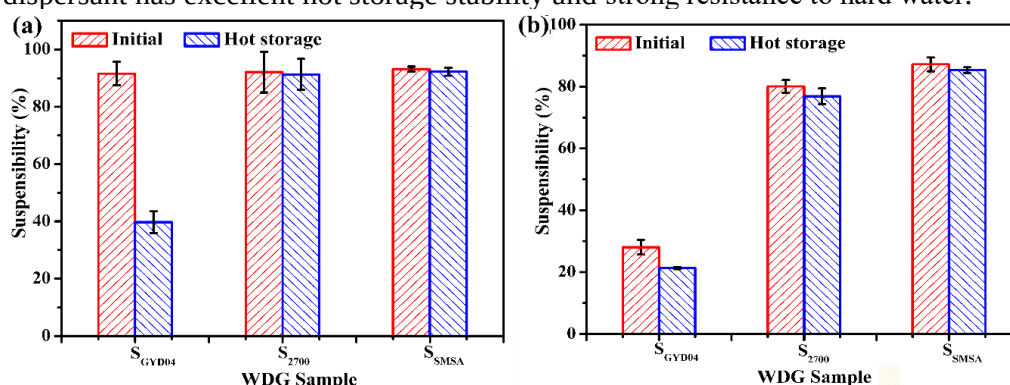


Figure 5. Influence of hot storage on WDG suspensibility: (a) standard hard water; (b) three-fold standard hard water.

3.3.2. Influence of hot storage on the disintegration performance of WDG. WDGs will disintegrate rapidly and disperse in water to form stable suspensions for the spray process. Therefore, disintegration is another important index for evaluating the performance of WDGs. As shown in table 1, the initial disintegration times of S_{GYD04} , S_{2700} and S_{SMSA} are 13, 19 and 10 respectively. The disintegration properties of three WDG samples show different changes after hot storage. Compared with the initial state, the disintegration times of S_{SMSA} and S_{2700} increase slightly after hot storage, and there are no non-disintegrating particles. The disintegration times of S_{2700} are significantly higher than that of S_{SMSA} . S_{GYD04} has some non-disintegrating particles after hot storage. Water wetting the surface and diffusing to the inner space of WDGs have been identified as necessary steps in any disintegration process [9]. It is suggested that the excellent disintegration of SMSA is attributed to the $-SO_3^{2-}$ groups, which will enhance the wettability and improve the disintegration performance of the WDG [11, 12]. Besides, the interaction between the $-SO_3^{2-}$ groups in SMSA molecule and $-NH_2$ groups in atrazine molecule is stronger, which is beneficial to the uniform adsorption of SMSA molecules on the surface of atrazine particles, prevent the agglomeration between WDG particles.

Table 1. Disintegration performance of WDG samples.

Samples	Disintegration times	
	Initial	Hot storage for 14 days
S_{GYD04}	13	●
S_{2700}	19	24
S_{SMSA}	10	13

● There are some small non-disintegrating particles

3.4. CLSM analysis of WDG suspensions

S_{GYD04} , S_{2700} and S_{SMSA} were dispersed in standard hard water respectively, and their morphologies were in situ studied by CLSM. From figure 6 b, it can be seen that there is a serious agglomeration between atrazine particles of S_{GYD04} sample after hot storage. For S_{SMSA} and S_{2700} (figure 6 c-f), almost no agglomeration of WDG particles occurred, but the atrazine grain size of S_{SMSA} is smaller than that

of S₂₇₀₀. Therefore, the growth of atrazine grain size is dependent on the structure of dispersants. The interaction between -SO₃²⁻ groups in SMSA molecule and -NH- groups in atrazine molecule is stronger, which is conducive to the uniform adsorption of SMSA molecule on the surface of atrazine particles and effectively inhibits the agglomeration between WDG particles and the growth of atrazine grain.

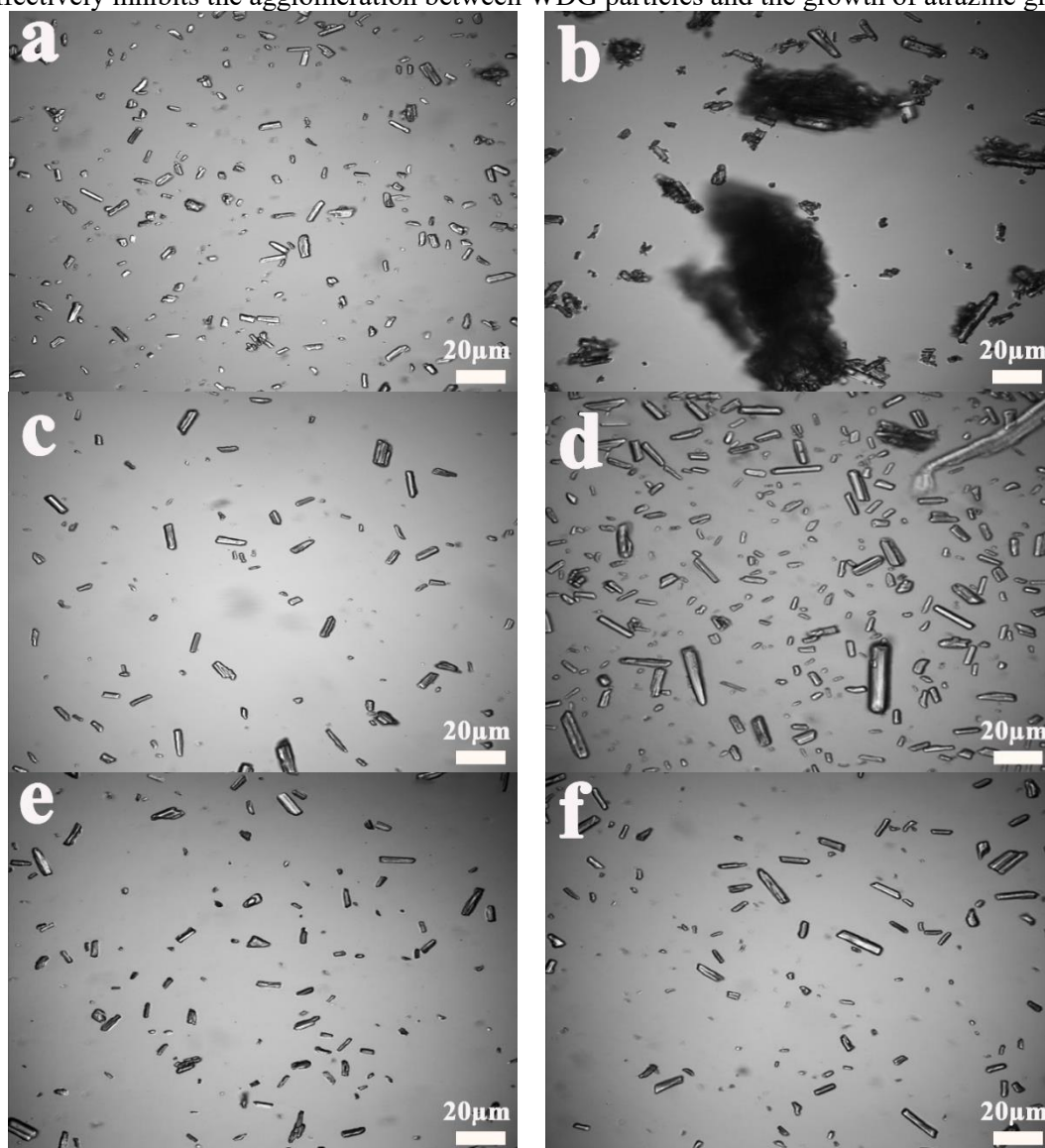


Figure 6. CLSM plots of WDGs in standard hard water: (a) S_{GYD04}, (c) S₂₇₀₀, (e) S_{SMSA}, initial; (b) S_{GYD04}, (d) S₂₇₀₀, (f) S_{SMSA}, after hot storage for 14 days.

4. Conclusion

The SMSA was designed and synthesized by solution-free radical polymerization, and was employed as the dispersant of 90 wt% atrazine WDG. It is found that SMSA has high performance and strong resistance to hard water, and the suspensibility of 90 wt% atrazine WDG before and after hot storage could reach 93.14% and 92.22% in standard hard water, and 87.19% and 85.33% in three-fold standard hard water, respectively.

The stronger interaction between -SO₃²⁻ groups in SMSA molecule and -NH- groups in atrazine molecule is conducive to the uniform adsorption of SMSA molecule on the surface of atrazine particles and effectively inhibits the agglomeration between WDG particles and the growth of atrazine grain. SMSA is a very promising dispersant for pesticide WDG.

Acknowledgments

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