

An amphoteric poly(VAc-DBM-AM-DMAPS) emulsion focusing on the ecological sand-fixing in salty desert: Structure and properties

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ABSTRACT: In order to control the impacts of blown sand in salty desert, in this article, the amphoteric emulsion, for the first time, was applied as an ecological sand-fixing material. This study started from the synthesis of the poly{vinyl acetate-dibutyl maleate-acrylamide-co-3-[N-(2-methacryloyloylethyl)-N,N-dimethylammonio]-propane sulfonate} [P(VAc-DBM-AM-DMAPS)] copolymer emulsion. Then, the structures, composition, thermal property of the emulsion were characterized by ¹H-NMR, FTIR, and DSC, respectively. The basic properties of the emulsion and salt tolerance of the latex films were measured by using viscometer, dynamic light scattering, and laser Doppler electrophoresis also. And the sand-fixing properties of the emulsion were evaluated. Finally, the influence of the emulsion on the growth of soil microbe and plants were discussed for understanding its ecological effect. The experimental results showed that the emulsion has been successfully synthesized and could be as an ecological sand-fixing material. The related reason is that, first, the emulsion could significantly improve the compressive strength and water retaining; second, the emulsion had good thermal aging, freeze-thaw stabilities and salt tolerance to withstand the changes in temperature and NaCl concentration of salty desert; third, the influence of the emulsion on the growth of plants and microbe of sand also showed a dependable ecological effect.

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INTRODUCTION

In the arid and semi-arid ecosystems, water scarcity is becoming a world-wide problem of increasing severity. To overcome this shortage, lower quality-water, such as groundwater, is widely used. However, groundwater typically contains solutes of varying concentrations, and its utilization may noticeably affect soil characteristics, resulting in soil salinization. Therefore, with the increasing use of low quality water and conventional agriculture practice, soil salinization, nutrients poorness and desertization turn into the serious environmental and worldwide socio-economic problems.¹⁻⁴

So far, there are more than 100 countries in the world suffering from desertization in salt-affected soils.⁵⁻¹⁵ According to Tòth *et al.*, the total area of salt-affected soil was about one billion hectares, occurring mainly in the arid and semiarid regions of Asia, Africa, Australia, and South America.⁶ In China, there were over 99.13 million hectares of salt-affected soils suffering desertization.⁷ The degraded saline land usually caused many negative influences, such as desertization, damage to crops, and

loss of fertilizer, and so on.¹⁶ For the reason, the desertization of salt-affected soils was one of the most serious problems confronting sustainable agriculture in semi-arid and arid regions.

It is well known that the salinity limits the fertility of soil. In fact, accumulation of excess Na⁺ in soil causes numerous adverse phenomena on soil physical and chemical properties, including deficient essential elements for plants growth in nitrogen (N), phosphorus (P), and potassium (K).¹⁷ And excessive exchangeable sodium favors the decrease soil permeability, available water capacity and infiltration rate.¹⁸ In addition, in the arid zones, the intense evaporation tends to accumulate salts in the upper soil profile, especially when it is associated with an insufficient leaching or where soluble salts move upward in the soil profile from a water table instead of downward.¹⁹ These modifications further accelerate soil degradation due to salinization.

Three major constraints are well-described for desertization of salt-affected soils: (1) water deficit arising from the low water potential of the rooting medium, (2) ion toxicity associated

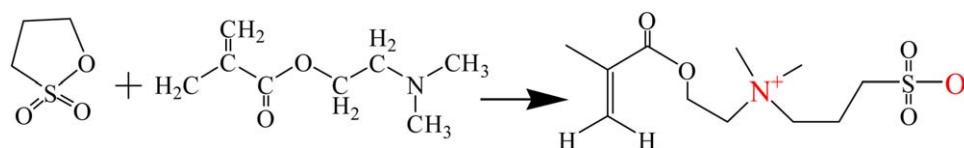


Figure 1. Schematic representation of DMAPS prepared. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with the excessive uptake of mainly Cl^- and Na^+ , (3) the sand-drift triggered resulting in the low seed germination and the growth of soil microbe by strong wind erosion. The problem of low soil water potentials maybe overcome by adjustment of plant internal osmotic potential, usually by an increase in salt content.²⁰ And saline soil reclamation was carried out by using halophytic vegetation such as *Suaeda maritima* Dum., *Sesuvium portulacastrum* L., *Clerodendron inerme* Gaertn., *Ipomoea pes-caprae* Sweet, *Heliotropium curassavicum* L. and one tree species *Excoecaria agallocha* L. and so on.^{21–24} However, the ratio of seed germination only by vegetation restoration was extremely low due to the adverse wind erosion in high salt-affected sandy land. Based on the above mentioned problems found in present research, the sand fixation under high salt stress was regarded as the key step for salty desert restoration.

The polymer materials, as the new sand-fixing materials to prevent sand wind erosion, have received much attention. They mainly included polyacrylamide, polyvinyl alcohol, vinyl acetate-ethylene copolymer emulsion, and polyurethane and so on.^{25–35} For example, the polyurethane (PU) designed by TORAY of Japan was used in Qinghai salt-affected sandy land of China. The experimental results showed that there was excellent sand-fixing capability at the beginning period of using PU; however, with the extension of time, PU began to pulverize and lost the sand-fixation performance very soon. Moreover, PU cost too high to be applied in large-scale. Therefore, the performance and cost became the main consideration for the materials applied in the sand-fixing of high salt-affected sandy land.

Usually, the emulsions, especially the emulsions made with vinyl acetate monomers, had a much lower cost and good adhesive.^{36–40} With its peculiar performance, the emulsions became the all-important choice for desertification and soil salinization control. One of the most important emulsions was the copolymer with vinyl acetate (VAc) and dibutyl maleate (DBM) in its backbone, which possessed certain required properties and obviously low cost to meet wide uses.^{41–43} Through analyzing and studying the salt-tolerant behavior of polymer materials, it was considered that amphoteric copolymers had the most appropriate salt-tolerant characteristics for future application,^{44–46} because they contained ammonium cations and sulfonic anions separated by alkyl groups and have been the focus of extensive study in academic and industrial laboratories because of their potential for salt tolerance. So, a novel kind of ecological sand-fixing polymer material was proposed for the use in salty desert. As a new sand-fixing material, P(VAc-DBM-AM-DMAPS) emulsion had the following primary advantages: (a) it could be diluted to different concentrations by water; (b) it was an environment-friendly product with no additional pollution; (c) the presence of emulsion could form an elastic and viscous crust in high salt-affected soil surface at natural condition; (d)

it was easy to produce and had a low cost; and (e) it could accelerate an growth in halophytic vegetation and microbe of sand.

In this work, the salt tolerance of the P(VAc-DBM-AM-DMAPS) latex films were investigated at different salinities. And the main purpose of this work was to evaluate the sand fixation ability of the emulsion in high salt-affected sandy land. The correlations between the structure of the emulsion and the sand fixation ability were analyzed by compressive strength test. Another batch experiments were carried out to determine the adaptability of the emulsion in salty desert. Additionally, the effects of the emulsion on the growth of plant and soil microbe were evaluated.

EXPERIMENTAL

Materials

Acrylamide (AM) was purchased from Kelong Chemical Reagent Corporation (Chengdu, China). Vinyl acetate(VAc) and dibutyl maleate(DBM) used in this work were provided by Sichuan Weinilun Industry Corp. (Chongqing, China) and used as received without further purification. $\text{K}_2\text{S}_2\text{O}_8$ was purchased from Sinopharm Chemical Reagent (Beijing, China). Nonionic surfactant, Pluronic L35 was supplied by Haian Petrochemical Corp. (Jiangsu, China), and was used as received. Amphoteric surfactant, 3-(*N,N*-dimethylmyristylammonio) propanesulfonate, was purchased from FLOWER'S SONG Chemical Reagent Corporation (Chengdu, China) and was used without further purification. Analytical pure 2-(Dimethylamino)ethyl methacrylate and Propane sultone were purchased from Aladdin Industrial Corporation. Deionized water was used in all preparations.

Procedure of Preparing Amphoteric Emulsion

Synthesis of Amphoteric Monomer. The amphoteric monomer DMAPS was synthesized as depicted in Figure 1. The reaction was carried out in a 250-mL four neck flask which was equipped with a thermometer, a dropping funnel, a mechanical stirrer and a reflux condenser. When *N,N*-dimethylaminoethyl methacrylate (17.27 g) and acetone (34.54 g) were added into the flask, and the reaction process was started with a stirring speed of 120 r/min at 30 °C. About 10 min later, a mixture of 1,3-propane sultone (12.2 g) and acetone (12.2 g) was added dropwise for 30 min. After the addition, the mixture was stirred for 4 h at the same temperature and then allowed to stand at room temperature for a week. Then the precipitated white crystals were collected by filtration, washed with dry mixture of acetone and diethyl ether several times, and dried under reduced pressure to obtain DMAPS. And the $^1\text{H-NMR}$ of DMAPS was shown in Figure 2.

Preparation of the P(VAc-DBM-AM-DMAPS) Emulsion. When the given emulsifier, buffer and distilled water were added into a four-neck glass reactor (250 mL) with stirrer, reflux condenser

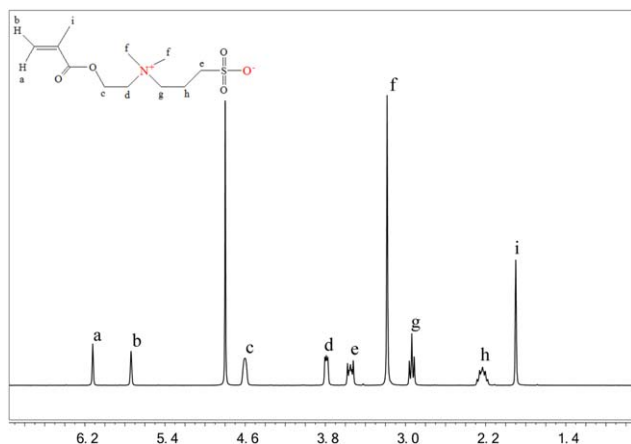


Figure 2. $^1\text{H-NMR}$ spectrum of DMAPS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tube, and three dropping funnels for monomers and initiator solution, the reaction process was started with a stirring speed of 120 r/min and 56 °C for 30 min to yield a completely dissolved reaction system, then the temperature was raised to 65 °C, 30 wt % of initiator solution (10 g in total) was quickly added to the flask. About 30 min later, 20% of mixed oil-soluble monomers (VAc and DBM) and 20% of water-soluble monomers (AM and DMAPS) were added dropwise in 15 min at a constant temperature of 76 °C for pre-emulsion.

When the circumfluence phenomenon disappeared, the remaining monomers mixture and initiator solution were added into four-neck flask, the total dropping time was lasted more than 4 h. Then the reaction was conducted in a raised temperature of 85 °C to completely exhaust the remaining monomers and initiator for the polymerization, which usually took one and half hour. The reactor was cooled to room temperature, followed by filtering to remove residual coagulum, then the P(VAc-DBM-AM-DMAPS) copolymer emulsion was obtained finally (Figure 3).

The Basic Properties of the P(VAc-DBM-AM-DMAPS) Emulsion

Generally, the basic parameters of the emulsions, which are related to the sand-fixing performance, are mainly the viscosity, size and size distribution of latex particle, as well as zeta potential values. They were measured by a LVDV-C viscometer (Brookfield, MA), dynamic light scattering and laser Doppler

electrophoresis using a ZetasizerR-HS (Malvern Instruments, UK), respectively.

The effects of the NaCl concentrations on the viscosity to the emulsion were also investigated.

The emulsion prepared was stored at room temperature (about 25 °C) for 6 months under the sealed condition for evaluating its storage stability. The mechanical stability was measured by centrifugation method, i.e., putting the prepared emulsion into a centrifugal machine for 20 min at 3000 rpm. The dilute stability and the stability against electrolytes were tested according to Ref. 47. The dilute stability was determined by diluting the emulsion to 3% solid content, then putting it into a 30 mL tube and keeping at room temperature for 3 days. The stability against electrolytes was determined by adding 16 mL emulsion to a 20 mL test tube and adding 4 mL NaCl or CaCl_2 solution (3% wt) and keeping the tube at room temperature for 2 days. All the stability properties of emulsion were simply evaluated by observing whether flocculation or precipitation appeared during the test.

FTIR Analysis

The apparatus used for measuring the FTIR spectra of the P(VAc-DBM-AM-DMAPS) membrane in the range of 500 – 4000 cm^{-1} , was a Nicolet 170SX Fourier transform infrared spectroscopy (FTIR, Japan). Each spectrum was collected at a resolution of 4 cm^{-1} . For the FTIR analysis, the dried P(VAc-DBM-AM-DMAPS) membrane was prepared for experimental purpose.

DSC Analysis of P(VAc-DBM-AM-DMAPS) Membrane

The thermal property of the copolymer was investigated by a DSC Q20 differential scanning calorimetry (DSC, USA) over a temperature range of –20 °C to 160 °C at a heating rate of 10 °C/min under nitrogen flow. The sample weight with 6 mg was used.

The Salt-Tolerance Properties of Latex Film

The emulsion was prepared into membranes at room temperature. All the prepared membranes were in a uniform size and thickness. And salts were dissolved in deionized water with concentration varied from 0.0 wt % to 5.0 wt %, and then, the membranes were soaked in the salt water for 72 h at room temperature. The water absorption of membranes at different

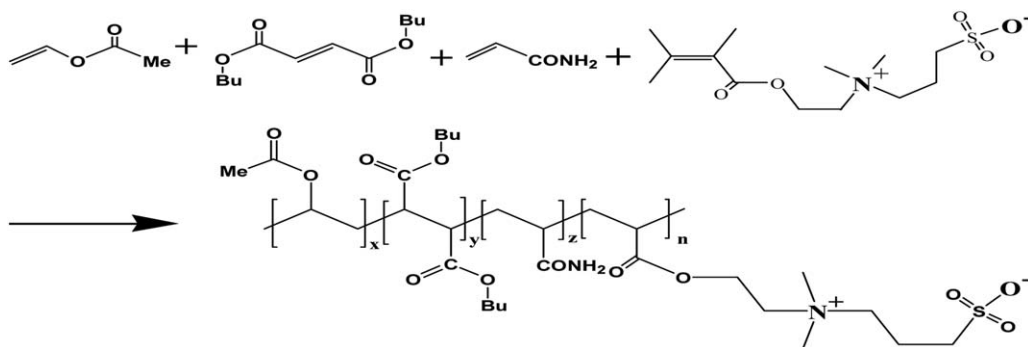


Figure 3. Synthesis of amphoteric P(VAc-DBM-AM-DMAPS) emulsion.

Table I. The Basic Property Parameters of P(VAc-DBM-AM-DMAPS) Emulsion

Emulsion	Particle size (nm)	Particle size distribution	Viscosity (mPa s)	Zeta potential (mV)
P(VAc-DBM-AM-DMAPS)	210.7	0.229	31.5	-1.69

salinities was determined by difference method and the results were then calculated.

Sand-Fixing Properties of the Emulsion

Preparation of Fixed Sand Specimen. The specimens were prepared with identical volume but different concentrations of P(VAc-DBM-AM-DMAPS) emulsion as follows: 10 g sand (from Qinghai Sandy Land) with 0.3 g salt and 1 g emulsion with concentrations of 2.0% were mixed homogeneously, then the mixture was transferred into a mold to make a sand column (2.2 cm in height and 2.0 cm in diameter) for the compressive strength test, and then stood at the room temperature for 4 h followed by a 24 h in stove at 60 °C for drying completely.

Compressive Strength of Fixed Sand Specimen. The compressive strength is a key parameter used to evaluate the effectiveness of sand fixation. Compressive strength is described as the hardness of specimen that is, in fact, attributed to the fixing power of materials. In this test, the completely dried sand column was put in an electronic tensile testing machine (WDW-5, Jinan Chuanbai Instrument, Chain), the value was recorded as the compressive strength (MPa).

Thermal Aging Ability of Fixed Sand Specimen. The specimen column was subjected to heat aging in an air circulation oven at 60 °C for a continual period of 10 days, regarding one day as a cycle. The compressive strength of each sample was measured after every cycle for evaluating the thermal aging stability of the sand-fixing material.

Freeze-Thaw Property of Fixed Sand Specimen. One cycle of freeze-thaw process involved a 22 h long freezing at -18 °C and 2 h for thawing at 25 °C. The specimen column should go through 10 such cycles, and then was subjected the compressive strength test for obtaining its freeze-thaw stability related to the used sand-fixing material.

Water-Retaining Property of Fixed Sand Specimen. The water-retaining ability was an important parameter for assessing the effectiveness of sand-fixing materials in high salt-affected dry sandy land. Therefore, the following experiment was designed to evaluate the water retaining capacity when the P(VAc-DBM-AM-DMAPS) emulsion with varied concentrations was applied in salt desert. Totally, 100 g sand mixed with 3 g salt was filled in a container with diameter 95 mm. When the crust surface was formed after spraying different concentrations of emulsion, the water was sprayed on sand surface in accordance with the amount of 1 L/m². The wet specimens were placed in oven at a constant temperature of 25 °C. Thereafter, the water content of each salt-affected sand specimen was determined at the same time interval of 1 h based on the weight loss:

$$\text{Water content} = \frac{[(\text{wet sand weight} - \text{dry sand weight}) / \text{water weight}] \times 100\%}{}$$

Ecological Effect of the Sand-Fixing Emulsion

Plants Growth. A simulation ecological sand-fixing experiment was designed in laboratory, i.e., the alfalfa (*Medicago sativa* Linn), a kind of halophytes, was sowed in the salt-affected sand soil, then the P(VAc-DBM-AM-DMAPS) emulsion was sprayed on the surface of the sand soil for sand fixation, hereafter the growth of halophytes was observed.

Microorganism Analysis. After 3 month later, the salt-affected sand soil was picked from 0 to 20 cm depth in each site with three replicates to examine the changes of microorganism. The numbers of microbe in the salt-affected sandy land were usually estimated by the plate count method.^{48,49}

RESULTS AND DISCUSSION

For practical purposes, the ecological sand-fixing materials should be stable, nontoxic, nonpolluting, and adaptable to the climatic and environmental conditions in the treated area. Meanwhile, these materials should be highly effective, long-acting, and inexpensive. According to these principles, we developed a novel P(VAc-DBM-AM-DMAPS) emulsion to apply in high salt-affected sandy land.

The Basic Properties of the P(VAc-DBM-AM-DMAPS) Emulsions

Droplet Size, Polydispersity Index, Zeta Potential, and Viscosity. The basic properties of the emulsion, such as particle size, viscosity, and zeta potential, directly affect the efficiency of sand-fixation in practical application. Therefore, studies of the basic properties of the emulsion are of great importance and practice. The particle size of emulsion was a physical index of their dispersion homogeneity, presenting the internal effect of emulsions on their ability of sand-fixing. The data of the particle sizes and polydispersity index (PDI) of P(VAc-DBM-AM-DMAPS) emulsion has been determined and was listed in Table I. According to Table I, we could find that the particle sizes of the emulsion were smaller than 1 μm and thus, indicating that, they could easily seep into the pore space of aeolian sand and form a crust on sand surface layers. In addition, the average value of PDI was lower than 0.5, which was considered that the particles of the emulsion are monodisperse due to a successful polymerization process.⁵⁰

Usually, if the particles had a higher negative or positive zeta potential, they would make the dispersion stable because of the repellency of each other, therefore, for emulsions, it meant a good stability. Additionally, the zeta potential of emulsion would affect the growth of soil microbe in the around environment. Contrarily, the low zeta potential of colloid particles

Table II. Stabilities of P(VAc-DBM-AM-DMAPS) Emulsion

Emulsion	Properties			
	Storage stability	Mechanical stability	Dilution stability	Electrolyte stability
P(VAc-DBM-AM-DMAPS)	No precipitate	No precipitate	No floccule	No floccule

would result in aggregation because of the attractive forces between them,⁵¹ but it would not influence the growth of soil microbe. Hence, the zeta potential of emulsion was closely related to its ecological effect. Based on our research, the emulsion with negative Zeta potential or low positive Zeta potential would not visibly impede the growth of soil microbe.⁵² The measured zeta potential of the emulsion (Table I) told that there was no negative influence on the growth of soil microbe and P(VAc-DBM-AM-DMAPS) was suitable for ecological sand-fixing.

The concretion strength of sand-fixing emulsion increased with increasing viscosity, but the penetration rate and depth decreased with its increasing viscosity. As a result, the high viscous emulsion would be left at the sand surface to form a thin and hard consolidated layer, which was adverse to the penetration of H₂O molecule. However, the emulsion with low viscosity led to a faster penetration rate and deeper penetration depth, which may prevent the formation of a crust with sufficiently binding strength. So, the befitting viscosity of emulsions, and emulsion's dilution, are key factors for successful sand fixation. The analysis results indicated that the measured viscosity of the emulsion was suitable for sand-fixing.

Stability. For practical purposes, the ecological sand-fixing materials should be stable. First is the storage stability, it was conducted in 6 month later of keeping the prepared emulsion at room temperature. The emulsion presented very good storage stability because there was no flocculation, no layering effect found in the emulsion. Followed by the test of other stabilities of the emulsion, including the mechanical stability, and the stability against electrolyte, the observed results were listed in Table II also. Because there was no precipitate or floccule found in tests, we can say that the prepared P(VAc-DBM-AM-DMAPS) emulsion has the respected stabilities referred to sand fixation.

The Effect of Salt on the Viscosity of Emulsion. The evaluation of polymer emulsion on salt tolerance is very important and necessary, because the polymer emulsion will be used as the sand-fixing material in high salt-affected sandy land. It is well known that the polymer emulsion is sensitive to salt and many chemicals. And the viscosity played a considerable role in sand-fixing capability and salt tolerance of polymer.⁵³ So, the viscosity of emulsion was a key parameter for evaluating salt tolerance and sand-fixing properties. Figure 4 showed the viscosity of 30.0 wt % emulsions of P(VAc-DBM-AM) and P(VAc-DBM-AM-DMAPS) at various NaCl concentrations. For P(VAc-DBM-AM) emulsion, the viscosity values decreased with the increase in salt concentration. However, a contrasting salt effect was observed in the case of the P(VAc-DBM-AM-DMAPS) emulsion, the viscosity values increased considerably for the P(VAc-DBM-AM-DMAPS) emulsion by changing the solvent from

salt-free water to 1.0 wt % NaCl. On one hand, the addition of NaCl increased the solution ionic strength, weakened the electrostatic attraction between the charges in the polymer chains, and broke up intramolecular zwitterionic associations, leading to an extension of the polymer chain. Therefore, the viscosity was expected to increase with increasing concentration of the added NaCl. On the other hand, presence of NaCl made the aqueous system more hostile to the hydrophobes, which forced them to associate inter- or intramolecularly. While the viscosity values decreased in more than 1.0 wt % NaCl in compare to the viscosity in 1.0 wt % NaCl, they still remained higher than that in salt-free water, exactly the same result of adding more NaCl to a polyampholytic copolymer solution has been discovered by other workers. The decrease in viscosity may be attributed to the salt-out effect of NaCl: the solubility of the hydrophobic parts of the molecule decreased, the polymer chains were unable to manifest effective intermolecular associations and the viscosity decreased. These results indicated that the structure had important role on the effect of salt on the viscosity of emulsion. Additionally, the concretion strength of sand-fixing emulsion increased with increasing viscosity, and the increasing viscosity may further improve sand-fixing properties of the emulsion in salty desert. So, the P(VAc-DBM-AM-DMAPS) emulsion would be a prospective candidate for the sand-fixing material in high salt-affected sandy land areas.

FTIR Spectroscopy Analysis

The chemical structure of P(VAc-DBM-AM-DMAPS) copolymer was investigated by a Nicolet 170SX Fourier transform

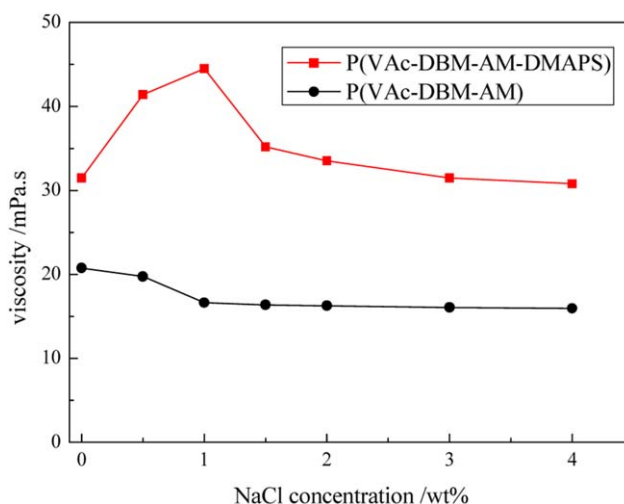


Figure 4. Variation of viscosity of the emulsion with NaCl concentration at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

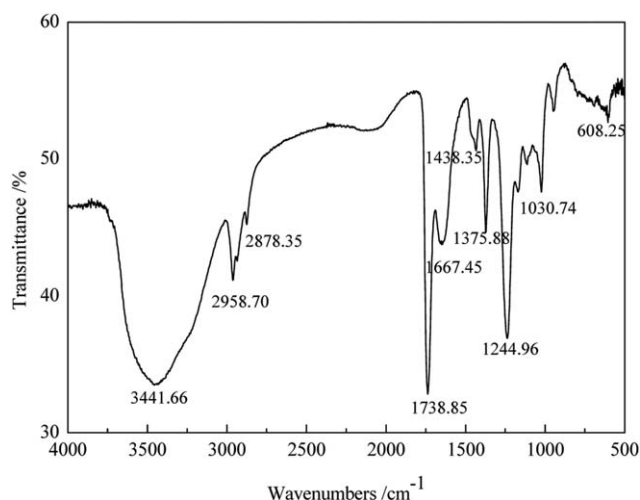


Figure 5. FTIR spectra of P(VAc-DBM-AM-DMAPS) copolymer emulsion.

infrared spectroscopy (FTIR, Japan) over the spectral ranges of 500 – 4000 cm^{-1} . Figure 5 showed the FTIR spectra of P(VAc-DBM-AM-DMAPS) copolymer. The relatively broad and strong band around 3441.66 cm^{-1} was assigned to the stretching vibration of the hydroxyl groups ($-\text{OH}$) of the water molecules. The stretching absorption peak of carbonyl group ($\text{C}=\text{O}$) appeared at about 1738.85 cm^{-1} , and adsorption peaks at 1030.74 cm^{-1} and 1244.96 cm^{-1} belonged to the symmetric and asymmetric stretching vibration of $-\text{SO}_3^-$ group, respectively; The sharp peak at 2958.70 cm^{-1} responded to the stretching vibration of alkyl $\text{C}-\text{H}$ bond of the methyl and methylene, and the peak at 608.25 cm^{-1} came from the stretching vibration peak of $-\text{C}-\text{S}-$ bond. The $\text{C}=\text{C}$ stretching vibration absorption for the monomers disappeared in the FTIR spectra of P(VAc-DBM-AM-DMAPS) copolymers. These results showed that copolymerization has taken place among vinyl acetate, dibutyl maleate, and acrylamide, as well 3-[*N*-(2-methacroyloylethyl)-*N,N*-dimethylammonio]-propane sulfonate as expected and the functional groups remained unaffected during polymerization.

Thermal Property Analysis

It was well-known that the thermal property of polymer material was very important. The high salt-affected sandy land regions usually presents a great temperature difference between day and night, for allowing the copolymer emulsion to meet the requirement of sand-fixing at varying temperature, it is necessary to design and determine the glass transition temperature (T_g) by adjusting the ratio of the main monomers.

The T_g could be obtained directly from the onset of the corresponding heat capacity jump of DSC curve. The DSC curve of the copolymer was shown in Figure 6, it could be seen that there was only one T_g value of 9.8 °C in the DSC curve, telling that the emulsion was a kind of random copolymer and the consistency among the chain segment was fairly good.⁵⁴ Based on our previous research,³² the result indicated that P(VAc-DBM-AM-DMAPS) emulsion can meet the requirement of sand-fixing under the varying temperature of salty desert.

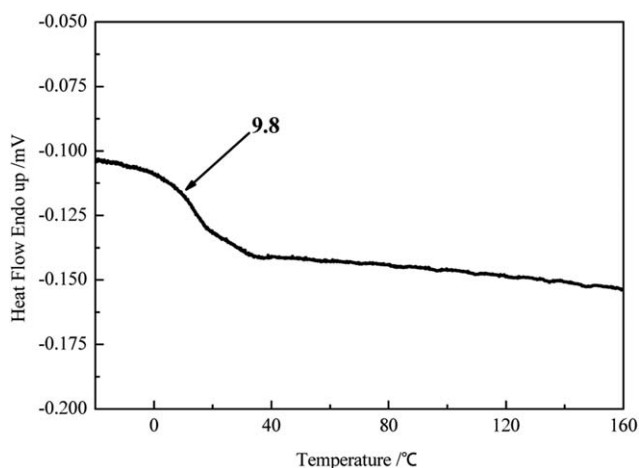


Figure 6. DSC curve of P(VAc-DBM-AM-DMAPS) copolymer emulsion.

The Salt Tolerance of P(VAc-DBM-AM-DMAPS) Latex Film

It was well-known that, as evaporation proceeded slowly under natural condition, the latex film was formed from P(VAc-DBM-AM-DMAPS) emulsion, and the intense evaporation tended to accumulate salts in the upper soil profile and increase salt concentration, which would directly affect the sand-fixing properties of the emulsion. In order to make sure whether the latex film could meet the requirement of sand-fixing under the varying NaCl concentration, the water absorption at different NaCl concentration has been determined to evaluate sand-fixing capability of P(VAc-DBM-AM-DMAPS) emulsion in salty desert. The influence of NaCl concentration on water absorption of the latex film was evaluated by changing the ionic strength of NaCl solution as shown in Figure 7. It was found that there was a sharp decrease of the water absorption when NaCl concentration varied from 0.0 wt % to 1.0 wt %, and then the water absorption decreased gradually when NaCl concentration raised from 1.0 wt % to 5.0 wt %. This phenomenon was also found in a previous report.⁵⁵ The reason for the phenomenon may attribute to the swelling of the amphoteric group of DMAPS under high concentration of ions in the permeability process as

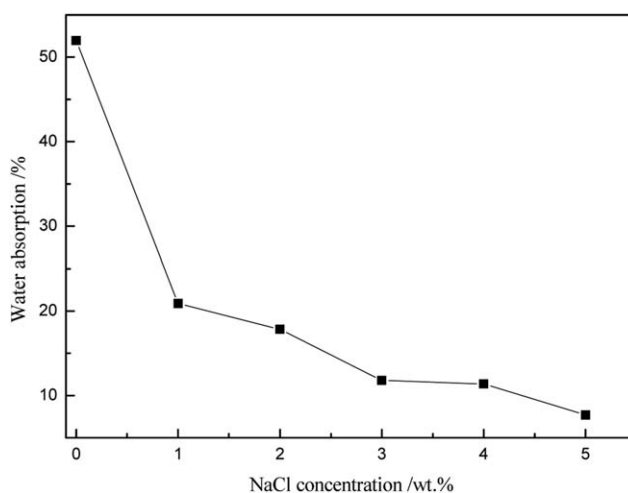


Figure 7. Variation of the water absorption of latex film with increasing NaCl concentration.

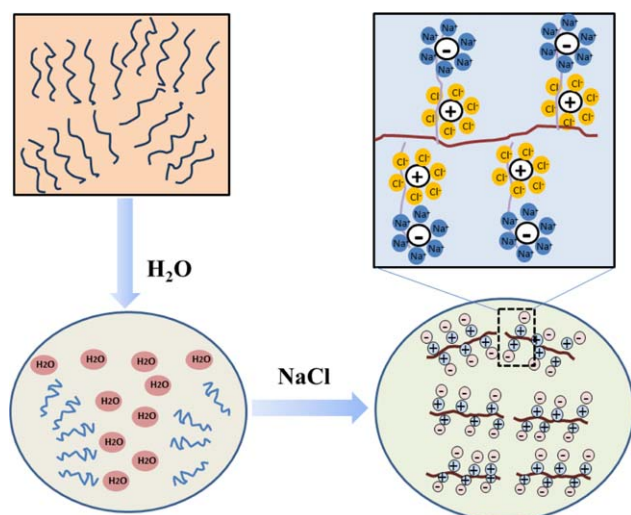


Figure 8. Schematic illustrations of the pores shrink in the water environment and swell in the salt solution environment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shown in the schematic diagram in Figure 8. When the external solution was pure water, the amphoteric group of DMAPS formed a hydration layer via electrostatic and the swelling of the amphoteric group of DMAPS was not strong enough.⁵⁶ With the increase in NaCl concentration, the presence of Na⁺/Cl⁻ might break the intra-chain and intra-group association of P(VAc-DBM-AM-DMAPS) and give rise to chain expansion,⁵⁷ resulting in the decrease of water absorption,⁵⁸ which increased the cohesion of the latex film and improved sand-fixing capability of the emulsion.

Sand-Fixing Performance of the Emulsion

Compressive Strength. The compressive strength was defined as the hardness of crust formed by sand and emulsion, which can be used to evaluate the bonding force or cohesion between the sand particles after fixation with emulsion. And, the sand used in this study was taken from the mobile dune of Qinghai sandy land, where the sand soil generally contains salt as high as about 3% because of the saline lake nearby. The sand was mixed by emulsion with different concentration, from 2.0, 3.0, 4.0, 6.0, 8.0, to 10.0% according to the procedure described in section 2.5.1. The reason is that the wind erosion usually is different in different natural environment of salty deserts, so, in practical application, we need different concentration of sand-fixing materials to provide the desired mechanical strength to resist bigger outside force without cracks. The compressive strength of each fixed sand specimen was shown in Figure 9. When this NaCl contained sand was mixed with emulsion to form the homogeneous mixture, a part of emulsion filled up the voids of sand, and other part stayed on the surface of the sand particles. The long-chain macromolecules of polymer enwrapped the particles surface and induced physical binding between the polymer and the sand particle through complex electrostatic interactions, resulting in bonds and interlink. Therefore, the compressive strength of fixed sand specimen was obtained.

Furthermore, it could be seen that the compressive strength increased gradually with the increase of emulsions concentra-

tion, it was attributed to the density of the bond between the mixed sand samples particles, the emulsions could infiltrate into the sand and contact the sand particle fully, causing strong interaction, and therefore the compressive strength increased with the increase of emulsion concentration. Also, the specimens fixed by P(VAc-DBM-AM-DMAPS) emulsion with same concentrations rendered the compressive strengths as 0.38, 0.41, 0.44, 0.6, 0.67, and 0.92 MPa, respectively. It indicated that even low concentration of P(VAc-DBM-AM-DMAPS) could provide the desired mechanical strength to resist bigger outside force without cracks.

Figure 9, at the same time, showed the compressive strength of P(VAc-DBM-AM) emulsion fixed sand specimen, it was clearly telling the far less compressive strength than that caused by P(VAc-DBM-AM-DMAPS) fixation. The differences of the compressive strength by different emulsions treatments could be certainly attributable to the different structure of the two emulsions. For the amphoteric group of P(VAc-DBM-AM-DMAPS) emulsion, the presence of salt might weak the electrostatic attraction between the charges in the polymer chains, break up the intramolecular zwitterionic associations and give rise to chain expansion, leading to an extension of the polymer chain, and as a result, the viscosity was expected to increase, which improved sand-fixing capability of the emulsion. As a whole, all the results suggested that P(VAc-DBM-AM-DMAPS) emulsion would be a prospective candidate of sand-fixing material in high salt-affected sandy land areas.

SEM Analysis. In order to understand the effect of emulsion on the sand fixation performance, detailed surface microstructure analysis of sand modified by P(VAc-DBM-AM-DMAPS) emulsion was carried out by scanning electron microscopy (SEM). The SEM images clearly showed the influence of emulsion on the sand fixation property. As shown in Figure 10, for untreated sample, the transition zone around sand particles was more open and isolated from each other, more gaps left [Figure 10(a)]; therefore, it was very easy to lead to dust weather with the wind due to the loose adhesion.

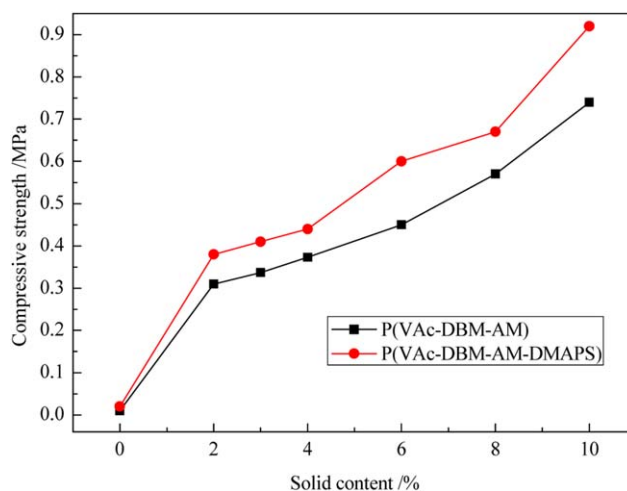


Figure 9. Comparison of the compressive strength of emulsions with different structure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

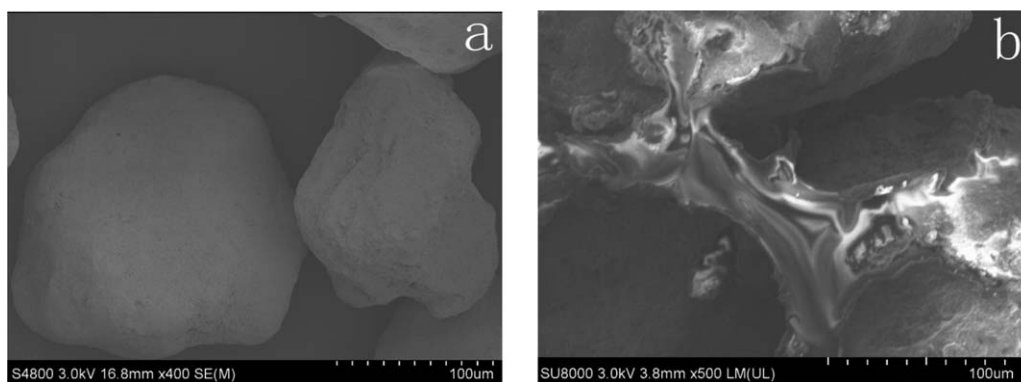


Figure 10. The surface morphology images of sand containing 3% NaCl of unfixed and fixed with P(VAc-DBM-AM-DMAPS) emulsion: (a) unfixed; (b) fixed with 2.0% emulsion concentration.

However, the sands containing 3% NaCl sprayed with 2.0% concentrations P(VAc-DBM-AM-DMAPS) emulsion showed a dense contact in the sand-sand particle transition zone, and the neighboring sand particles tended to overlap or connect. The long-chain macromolecules of polymer enwrapped the particles surface to create bonds and interlink and then formed elastic and viscous crust on sand surface or between sand particles [Figure 10(b)]. The presence of crust on loose sand surface would enhance the bonding force or cohesion between the sand particles and increase sand stability.

Thermal Aging Ability of the Emulsion. In the natural environment, the chemical components of the sand-fixing emulsions may be greatly changed because of solar radiation, temperature, oxidation, wind erosion, leaching by rainwater, and other factors. With the passage of time, such environmental factors could shorten the life-span of sand-fixing emulsions, especially in desert regions with such harsh environmental conditions. In order to consider the effects of temperature on the sand fixation capacity of the emulsion, the sand containing 3% NaCl treated with the emulsion concentration of 2.0% were subjected to continuous thermal aging tests. Dependence of compressive

strength on the cycle of thermal aging test was shown in Figure 11. The results showed that there were no obvious changes in the compressive strength with the increase of thermal aging cycle during the 10 cycles, indicating the P(VAc-DBM-AM-DMAPS) emulsion had a good thermal aging resistance.

Freeze-Thaw Property of the Emulsion. For the same reason, the resistance of the emulsion to freezing was also determined for knowing its suitability when used in low-temperature environment of salty desert. The specimens containing 3.0% NaCl treated with the emulsions concentration of 2.0% were subjected to compressive strength test for evaluating the freeze-thaw stability of the sand-fixing emulsions. Figure 12 showed the result after the cycle of freeze-thaw test. The results showed that there were no distinct changes in the compressive strength with the increase of freeze-thaw aging cycle during the 10 cycles, which suggested that P(VAc-DBM-AM-DMAPS) emulsion had good freeze-thaw stability.

Both the experimental results about thermal aging ability and freeze-thaw property of the emulsion told that, the P(VAc-DBM-AM-DMAPS) emulsion could adapt a great temperature

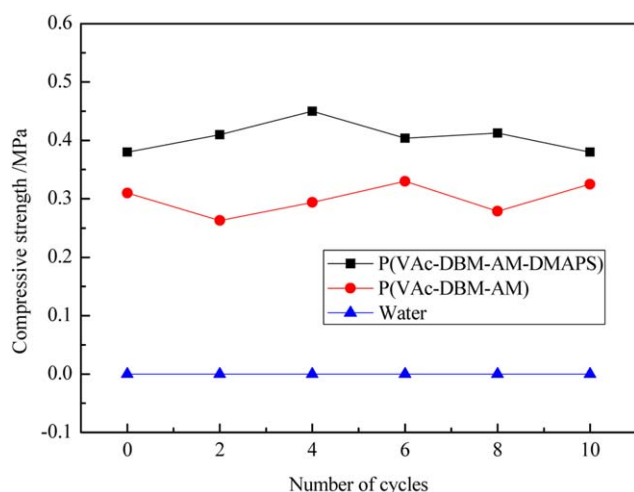


Figure 11. The compressive strength change of sand-fixing specimens with thermal cycle frequency. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

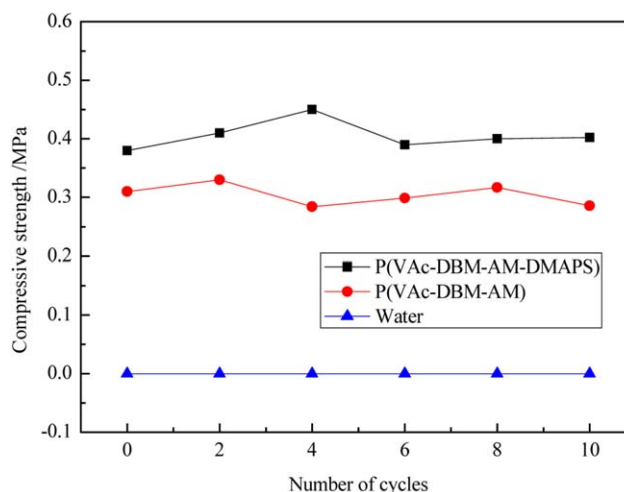


Figure 12. The compressive strength change of sand-fixing specimens with freeze-thaw cycle frequency. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

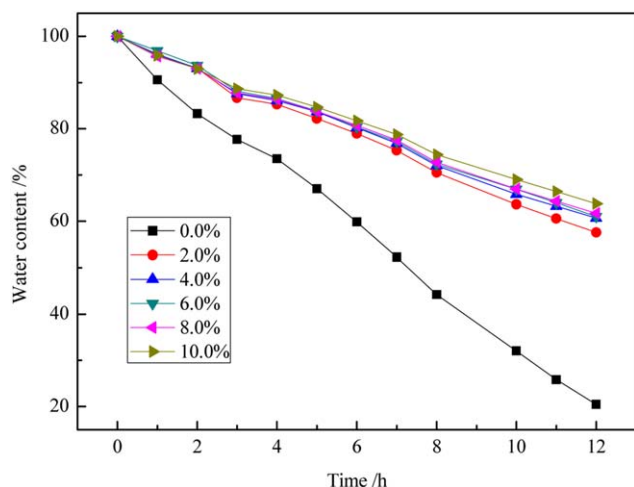


Figure 13. The emulsion concentration vs. the water content of sand at different drying time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

difference between day and night in high salt-affected sandy lands, and could be used for the sand fixation in salty desert.

Water-Retaining Property of the Emulsion. In order to increase available water capacity and promote the growth of halophytic vegetation, the water content of each sand specimen treated with different concentrations of P(VAc-DBM-AM-DMAPS) emulsion was determined to evaluate the water-retaining ability in high salt-affected sand. The fixed by P(VAc-DBM-AM-DMAPS) and untreated specimens were prepared with different drying time. The relation curves of water content and drying time of untreated and treated specimens were presented in Figure 13. It could be seen that the water content of treated specimens was much higher than that of untreated specimens during the test period. It implied that the P(VAc-DBM-AM-DMAPS) emulsion could increase available water capacity visibly and reduce salinity stresses of salt contained sand. In arid and salt-affected sandy land, Pujol *et al.*^{59,60} observed that reduced soil salinity, associated with increased water availability, was the primary factor affecting the seed germination. It was to say, the use of the sand-fixing material may promote germination and growth of halophytic vegetation.

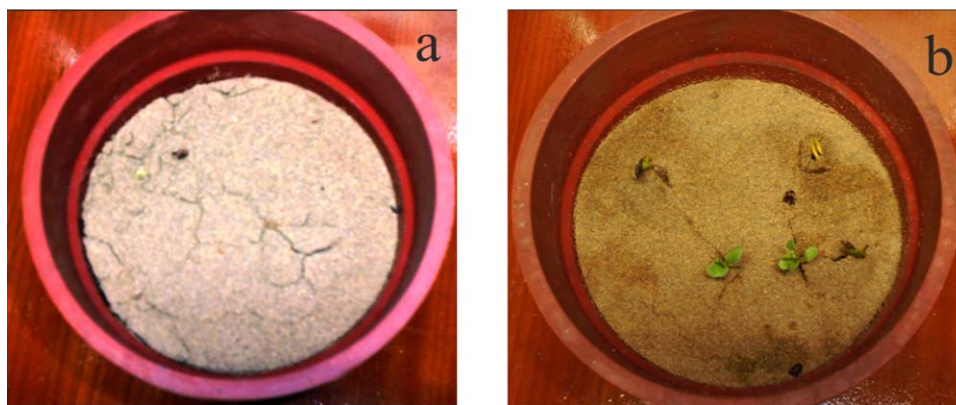


Figure 14. Parallel images of germination of alfalfa: (a) untreated; (b) treated with 3.0% emulsion concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Number of Microbe in P(VAc-DBM-AM-DMAPS) Emulsion Fixed Sand after 3 Months

Sample	Bacteria (/g)	Actinomycetes (/g)
Control	1.2×10^5	2.96×10^6
P(VAc-DBM-AM-DMAPS)	2.63×10^5	2.99×10^6

Furthermore, the water-retaining ability of the specimens treated by emulsion was increased with the increase of the emulsion concentration at the same time. The reason was that the compactness of the thicker crust formed on the sand surface could further improve water anti-evaporation capability. This may be important for germination and growth in halophytes and reproduction of sand microbe in the arid and high salt-affected environment, which would be planned in our future investigation.

Ecological Effect of the Emulsions

Changes of Sand Vegetation Situation Caused by the Emulsion. In order to study the influence of the emulsion on the germination and growth of plant seeds, the alfalfa (*Medicago sativa* Linn.) was sowed in salt contained sand. After sowed 15 days later, the germination and growth results of alfalfa were shown in Figure 14. We could see that, the alfalfa seed could germinate and grow well from the P(VAc-DBM-AM-DMAPS) emulsion fixed sand layer, the emulsion had no negative impact on the germination and growth of plant seeds. This was because the emulsion could construct a bridge between the shifting sand and linked the sand together to form a sand-fixing layer with good resistance to wind erosion, which could provide a suitable and stable environment for growth of plants.

Changes of Sand Micro-Ecology Caused by the Emulsion. Microorganisms play a considerable role in high salt-affected sand fertility and plant nutrition, and they can speed up the transformation of sand to the soil, and are the most active composition in the land ecological system. So the microbial ecosystem of sand is a primary parameter used to evaluate the effectiveness of high salt-affected sandy land's recovery. Table III showed result that the content of microbial biomass of high salt-affected sand soil was well-developed during the

experimental period. As shown in the Table III, because of desert regions with such harsh environmental conditions, the quantity of actinomycetes was significantly more than that of bacteria, and the observed increase the quantity of the actinomycetes and bacteria by P(VAc-DBM-AM-DMAPS) emulsion were on average far more than that of control. This rapidly increase caused by P(VAc-DBM-AM-DMAPS) emulsion could be assigned to the improved water-retaining ability, which promoted the germination and growth of halophytes that could provide a suitable and stable environment for the growth of sand microbe. Increasing in the number of bacteria could produce a lot of extracellular metabolites to make the sand surface stable, and to improve the resistance to wind erosion performance of sandy land. Increased number of actinomycetes also could decompose plant residues to increase organic matter content of sand land, and then promote the growth of plants.

CONCLUSION

Owing to such an extensive desertified saline soil in the world, we have successfully prepared the P(VAc-DBM-AM-DMAPS) emulsion used as an ecological sand-fixing material for the sand fixing in salty desert. And it was found that addition of a low content of the emulsion could obtain desired sand-fixing properties, such as outstanding sand-fixing ability, thermal aging resistance and freeze-thaw stabilities to withstand the temperature changes in salty desert. Besides, the water-retaining experiment showed that the sand treated with the emulsion showed good water-retaining and anti-evaporation properties. Moreover, its excellent salt tolerance made it the good choice for the sand fixing in high salt-affected sandy land. And the growth of plant and soil microbe proved its ecological effect. All these results indicated that P(VAc-DBM-AM-DMAPS) emulsion would be a prospective candidate for the ecological sand-fixing material and could be used for ecological restoration of high salt-affected sandy land.

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