

Encapsulation of Aluminum Flakes by Dispersion Polymerization of Styrene in a Nonaqueous System with Reactive Surfactants

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Received 12 January 2000; accepted 17 October 2000

ABSTRACT: Dispersion polymerization of styrene in ethanol was carried out to encapsulate aluminum flakes. The effects of three reactive surfactants, two anionic and one nonionic, were investigated. It was confirmed prior to encapsulation that these surfactants did not polymerize by themselves but did promote polymerization of styrene. The capsules obtained were characterized with respect to the morphology and mean size. The encapsulating efficiency of the polymer of the wall material, the wall thickness, and the molecular weight distribution were measured. The effects of the concentrations of styrene monomer and reactive surfactants on these characteristics were determined and discussed. Aluminum flakes were coagulated to form secondary particles and they were covered with fine polymer particles, which were precipitated in the continuous phase. To improve encapsulation, the auxiliary addition of nonionic surfactant was attempted. By controlling those concentrations, capsules covered with polymer layer were prepared. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 675–683, 2001

Key words: reactive surfactant; polymerization; encapsulation; styrene; aluminum

INTRODUCTION

Metallic coatings are frequently used as a finishing coat of structural materials, in particular automobile bodies, to give them luster and a shiny appearance. A commonly used metallic pigment mostly used is the aluminum flake, which has the advantages of light weight and low cost. On the other hand, aluminum easily reacts with oxygen to convert into the oxide, resulting in loss of the luster, and when in contact with water or acid, it generates hydrogen. Therefore, it is necessary to protect aluminum from being exposed to the at-

mosphere while the paint is fabricated, stored, and used for coating. One of methods to realize this protection is to encapsulate metallic particles with polymer walls.^{1–4} However, polymer readily separates from a metallic particle because of its low small affinity with it. A satisfactory solution of this problem has not been found to date.

The authors have reported preparation of particulate composites, which are made up of polymer and inorganic powder reactive to water, by suspension polymerization.^{5, 6} In this method, the inorganic powder has been dispersed in a liquid monomer that becomes a solid wall material by polymerization. Protection from water of continuous phase was actualized by using a high volume fraction of the monomer and by enhancing its viscosity through preliminary bulk polymeriza-

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Journal of Applied Polymer Science, Vol. 81, 675–683 (2001)
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Table I Raw Materials

	Grade or Trade Name	Manufacturer
Aluminum flake	1200 M	Toyo Aluminum K. K.
Styrene monomer	Primary (>99.0%)	Kanto Chemical Co., Inc.
Ethanol	Primary (>99.5%)	Kanto Chemical Co., Inc.
Anionic-1 ^a	Latemul S-180	Kao Corp.
Anionic-2 ^a	Aqualon HS-1025	Daiichi Kogyo Seiyaku Co., Ltd.
Nonionic-S ^a	Aqualon RN-20	Daiichi Kogyo Seiyaku Co., Ltd.
V-65 ^b	—	Wako Pure Chemical Industries Ltd.
Span20 ^c	—	Kanto Chemical Co., Inc.
Span80 ^d	—	Kanto Chemical Co., Inc.

^a Reactive surfactant.^b 2,2'-Azobis(2,4-dimethylvaleronitrile).^c Sorbitan monolaurate.^d Sorbitan monooleate.

tion. For the purpose just described, it is desirable to reduce the volume of the polymer as much as possible. If the amount of monomer was simply reduced in suspension polymerization, the inorganic powder dispersed in monomer would come into contact with water. Therefore, it is necessary to use a nonaqueous medium as the continuous phase. Ethanol was selected in this study.

Styrene is used as the principal wall material after the polymerization process. Ethanol is a good solvent for styrene monomer and a poor solvent for polystyrene; that is, the present system is classified as dispersion polymerization.

Encapsulation of inorganic powder suspended in an aqueous medium by dispersion polymerization has been reported.⁷⁻⁹ In this technique, surfactant molecules were adsorbed on the surface of inorganic particles, and then precipitation of oligomer into the adsorbing surfactant layer was promoted to form a capsule wall. Dispersion polymerization in alcohol has also been studied,¹⁰⁻¹³ but we cannot find reference to its application to encapsulation of metallic particles.

In the present study, some reactive surfactants with a vinylic double bond were used in expectation of copolymerization with styrene and achieving strong adhesion of the resultant polymer to aluminum flakes. The addition of common, nonionic surfactants as auxiliary surfactant was also attempted to improve the state of the wall material.

EXPERIMENTAL

Materials

Raw materials used are listed in Table I. Aluminum flakes were washed with ethanol before en-

capsulation because they were supplied suspended in an oil. Styrene monomer was washed with 100 mol m⁻³ sodium hydroxide to remove inhibitor. Absolute ethanol was used as a continuous phase medium and 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65) was used as an initiator.

Three reactive surfactants were used: two anionic surfactants, trade names of Latemul S-180 and Aqualon HS-1025; and one nonionic surfactant, Aqualon RN-20. In this paper, the surfactants are referred to as Anionic-1, Anionic-2, and Nonionic-S, respectively. The structural formulae¹⁴ of each principal ingredient are shown in Figure 1. Data of chain length and hydrophile-lipophile balance (HLB) values are not published. The hydrophilic groups are a sulfonate group for Anionic-1 and Anionic-2 and a polyoxyethylene chain for Anionic-2 and Nonionic-S.

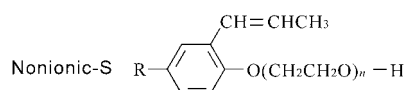
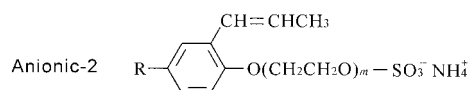
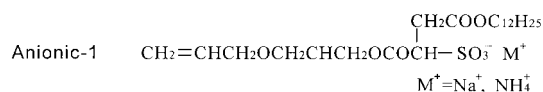


Figure 1 Structural formulae of reactive surfactants: Anionic-1, Latemul S-180; Anionic-2, Aqualon HS-1025; and Nonionic-S, Aqualon RN-20.

Table II Encapsulation Conditions

Temperature	333 K
Duration	24 h
Stirring speed	3.3 s ⁻¹
Reactive surfactant concentration, C_r	0–1.0 wt %
Initiator concentration	10 mol m ⁻³ – continuous phase
Styrene monomer concentration, C_m	0–400 mol m ⁻³ – continuous phase
Auxiliary surfactant concentration, C_a	0–0.5 wt %

The auxiliary surfactants used were two non-ionic surfactants, sorbitan monolaurate (Span20) and sorbitan monooleate (Span80), which have a polyoxyethylene chain as a hydrophilic group.

Materials except aluminum and styrene were used as received from the manufacturers.

Observation of Polymerization State

Styrene at a concentration of C_m , the reactive surfactant at a concentration of C_r , and the initiator at 10 mol m⁻³ were dissolved in ethanol to prepare a continuous phase. This solution was put in a test tube and then heated at 333 K for 6 h in a water bath to polymerize. After cooling, the production state of the polymer was observed with the naked eye and classified as one of three grades: no change, opaque, or precipitation. In the case of using Anionic-1, polymerization duration was varied from 6 to 24 h. The polymer produced was filtered, dried, and weighed to evaluate the conversion, x .

Encapsulation

0.50 grams of aluminum flakes were mixed with 400 cm³ of the continuous phase. This suspension was stirred at room temperature for 18 h to make the surfactant adsorb onto the surface of the aluminum flakes. After styrene and V-65 were also added, the suspension was stirred for 1 h. Encapsulation was carried out at 333 K for 24 h with stirring. Experimental conditions are listed in Table II.

A separation flask, with an inner diameter of 85 mm and capacity of 500 cm³, was used as the encapsulation tank. To inhibit the air entrapment from the free surface of the dispersion, four baffles made of aluminum were installed. A disk turbine-type impeller with six blades, set at a

third of the liquid depth from the bottom, was used as the stirrer.

Characterization

The morphology of the capsules prepared was observed with an optical microscope. The mean size, d_p , was measured with a particle-size analyzer (Shimadzu Corp., SA-CP3) by the centrifugal settling-light transmission method. Part of the capsule was fired within a porcelain crucible at 1073 K for 3 h in an air stream to make metallic aluminum convert to aluminum oxide and polymer combust. The weight of aluminum in the capsule was calculated from the weight of aluminum oxide produced, and then it was reduced to the weight of the polymer in the wall material, W_{pc} . The total weight of the polymer produced, W_p , was found by subtracting the initial weight of aluminum flakes from the weight of the entire products. The encapsulating efficiency of the polymer precipitated, F , was defined as the ratio of W_{pc} to W_p . The mean thickness of the capsule wall, T , was estimated by dividing the volume of the wall material by the capsule surface area, which had been calculated from d_p . Part of the capsule was dissolved in tetrahydrofuran, and the supernatant was used to measure the molecular weight distribution of the polymer in the wall material by liquid chromatography.

RESULTS AND DISCUSSION

Polymerization State

The polymerization state observed in a test tube is summarized in Figure 2. No product was obtained by heating a reactive surfactant solution without styrene ($C_m = 0$). This result indicates that the reactive surfactants do not polymerize by themselves.

Styrene solution without reactive surfactant ($C_r = 0$) became opaque, indicating slight polymerization. The natural logarithm of chain length, Z , of polystyrene oligomer precipitated from the ethanol–styrene system at 333 K is expressed by the following equation.¹³

$$\ln Z = 24.433 - 1.693(\phi_m \delta_m^2 + \phi_s \delta_s^2)^{1/2} \quad (1)$$

where δ is the Hildebrand solubility parameter in units of (cal^{1/2} cm^{-3/2}), ϕ is volume fraction, and subscripts m and s designate monomer and sol-

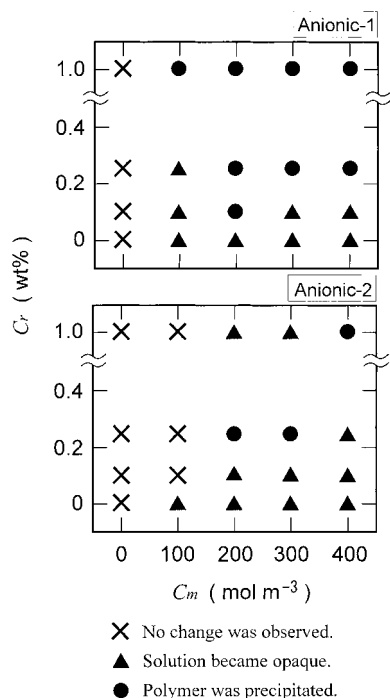


Figure 2 Effect of the reactive surfactant and styrene concentrations on the polymerization.

vent, respectively. At a styrene concentration of $C_m = 100 \text{ mol m}^{-3}$, a chain length of $Z = 19$ is obtained with a volume fraction of $\phi_m = 0.01$, and solubility parameters of $\delta_m = 9.3$ and $\delta_s = 12.7$ for styrene and ethanol.¹⁵ In the same way, $Z = 24$ is obtained at $C_m = 400 \text{ mol m}^{-3}$. That is, oligomer is precipitated as the propagation reaction proceeds slightly. The polymerization is immediately slowed down, and a large quantity of precipitates could not be produced.

When both reactive surfactant and styrene were used, the polymerization was considerably promoted. In particular, at a reactive surfactant concentration of $C_r = 0.25 \text{ wt } \%$, the quantity of polymer precipitated was the largest. It somewhat decreased at $C_r = 1.0 \text{ wt } \%$.

The change in the conversion, x , of styrene with polymerization duration, t , is shown in Figure 3. As seen in this figure, that the addition of reactive surfactant accelerates the polymerization of styrene. The conversion was 12% at $t = 24 \text{ h}$ without reactive surfactant. By using Anionic-1 of 0.25 wt %, the conversion increased to 25% at $t = 24 \text{ h}$. The reactive surfactant may copolymerize with styrene or adsorb onto the polymer chains to stabilize them in the continuous phase so that the polymerization could continue.

Morphology

The optical micrographs of the capsules produced by using each reactive surfactant at $C_r = 0.25 \text{ wt } \%$ are shown in Figure 4. In each case, aluminum flakes have coagulated to form secondary particles. The polymer products were fine particulate in shape, and they adhered to the surface of aluminum particles. With Anionic-1, a few polymer particles of $<1 \mu\text{m}$ in diameter sparsely adhere to aluminum particles. With Anionic-2 or Nonionic-S, a large number of polymer particles were produced and they covered the aluminum particles. When the styrene concentration was raised to $C_m = 300 \text{ mol m}^{-3}$, polymer particles $>5 \mu\text{m}$ were produced. The coverage seems, however, to be still incomplete in each case.

The effects of concentrations of reactive surfactant and styrene, C_r and C_m , respectively, on the morphology of the capsules were judged from the optical micrographs. These results are summarized in Figure 5. Encapsulation did not occur without either reactive surfactant or styrene. This result may be due to a shortage of the polymer produced.

Complete coverage of the surface of an aluminum particle was not accomplished by using Anionic-1 at any concentration. When Anionic-2 at $C_r \leq 0.5 \text{ wt } \%$ or Nonionic-S at $C_r \leq 0.25 \text{ wt } \%$ was used, capsules entirely covered with fine polymer particles were prepared. The coverage deteriorated at higher reactive surfactant concentration. Compared with the result in Figure 2, that satisfactory capsules were not always prepared even

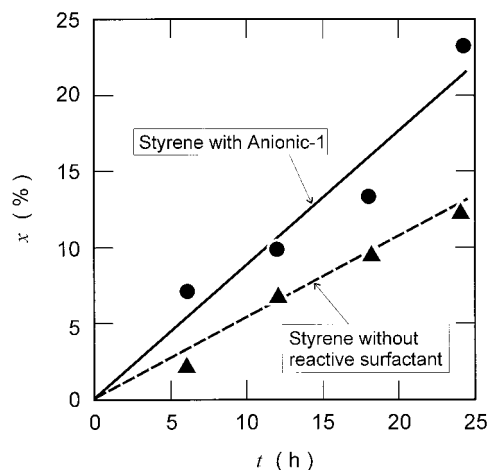


Figure 3 Change in the conversion of styrene with the polymerization duration. Anionic-1 as reactive surfactant was used at 0.25 wt %.

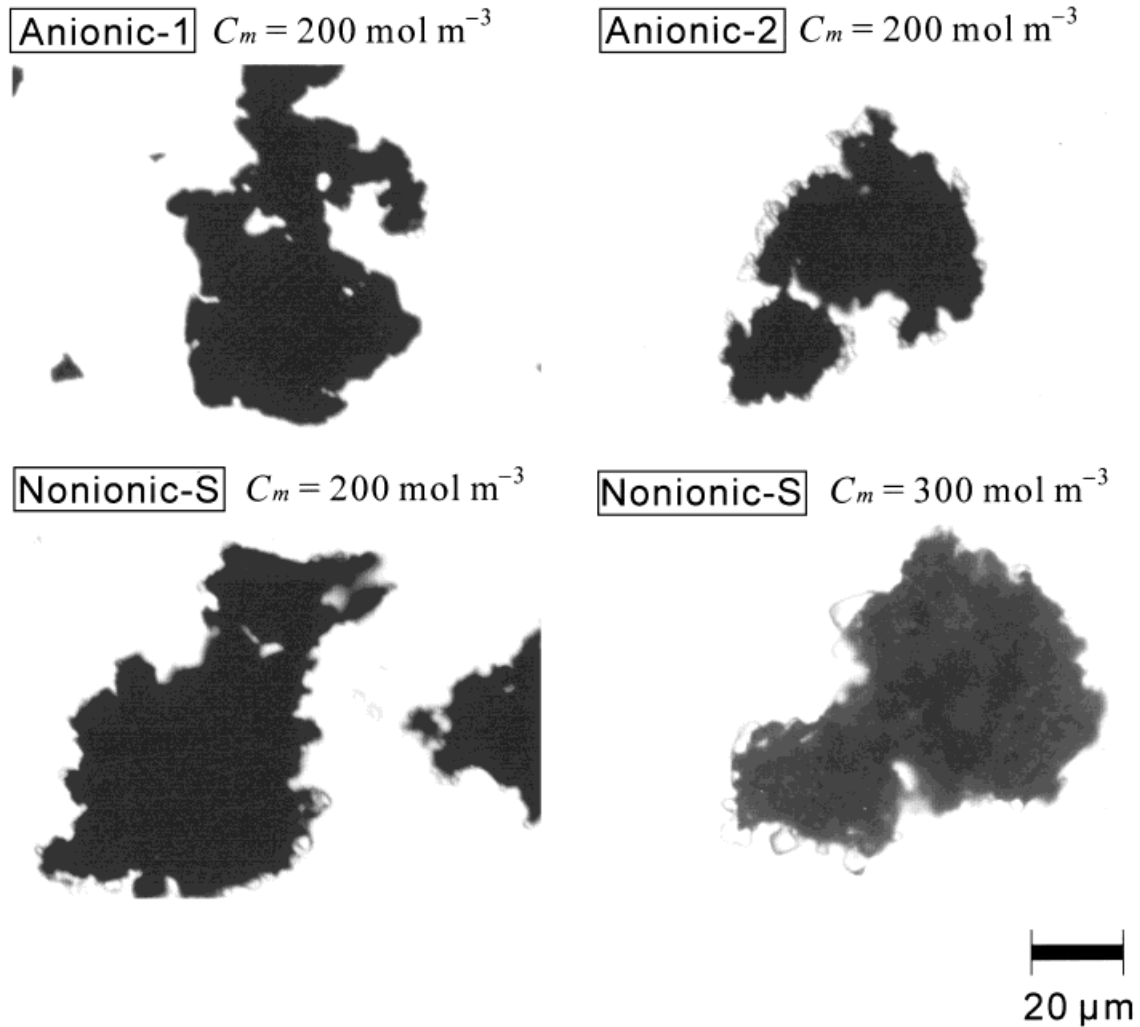


Figure 4 Optical micrographs of the capsules obtained with reactive surfactant concentration $C_r = 0.25$ wt%.

under conditions where a large quantity of the polymer was produced. Adhesion of the fine polymer particles onto the surface of aluminum particles may be obstructed at too high concentration because the polymer precipitated is also stabilized by excess surfactant molecules.

When styrene concentration was as high as $C_m = 400 \text{ mol m}^{-3}$, the coverage was very small. In this condition, the number of polymer particles precipitated in the continuous phase and their chain length is larger. Therefore, they coalesced more frequently, resulting in the larger size. It is difficult for large polymer particles to adhere to and closely cover aluminum particles.

The effect of the styrene concentration, C_m , on the mean size, d_p , of the capsules prepared at $C_r = 0.25$ wt % Anionic-2 is shown in Figure 6. The

value of d_p was significantly increased with the increase in C_m . However, the system became agglomerated at $C_m = 400 \text{ mol m}^{-3}$.

The effect of the reactive surfactant concentration, C_r , on the mean size, d_p , of the capsules prepared at $C_m = 200 \text{ mol m}^{-3}$ is shown in Figure 7. The results show that d_p was not dependent on C_r , which indicates that secondary aluminum particles were formed in the earliest stage of the polymerization process and did not coalesce or break in the later stage. This result also suggests that the adsorption of the reactive surfactant onto the aluminum particles has saturated at $C_r \leq 0.25$ wt % Anionic-1 and $C_r \leq 0.1$ wt % Anionic-2 or Nonionic-S.

The effects of the reactive surfactant concentration, C_r , on the encapsulating efficiency, F , of

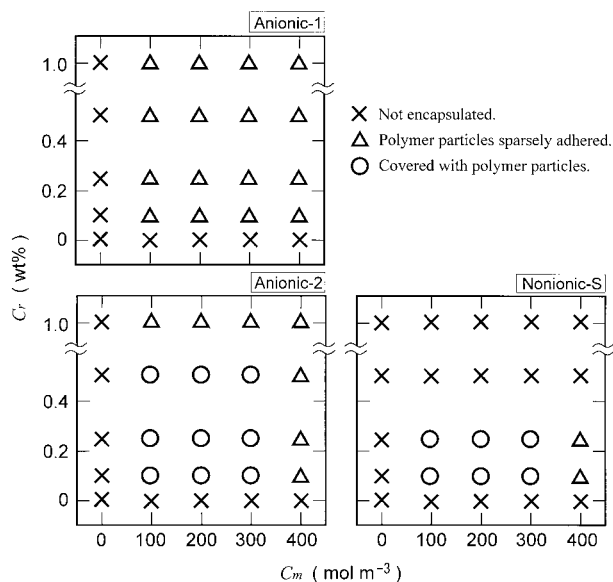


Figure 5 Change in the morphology of the capsules with the reactive surfactant and styrene concentrations.

the polymer precipitated when Anionic-2 or Nonionic-S was used are shown in Figure 8. F was no more than ~40%, and dependence of C_r on it was not recognized. This result means that the quantity of reactive surfactant adsorbed onto aluminum particles was small and the amount of styrene absorbed into the adsorbing layer of surfactant was also small. To improve the encapsulating efficiency, some device for promoting the adsorption of reactive surfactant is necessary. The difference

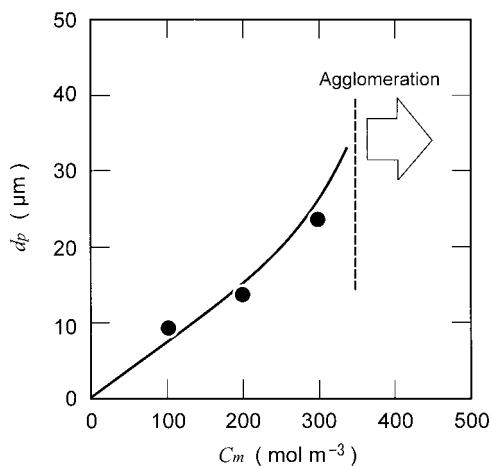


Figure 6 Effect of the styrene concentration on the mean size of the capsules obtained with Anionic-2 at 0.25 wt %.

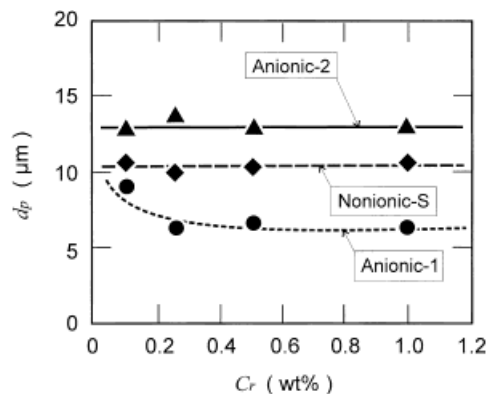


Figure 7 Effect of the reactive surfactant concentration on the mean capsule size.

between Anionic-2 and Nonionic-S for F was insignificant.

Usually, the surface of a metallic particle is hydrolyzed by moisture in the atmosphere to get intensive hydrophilicity. Therefore, a surfactant molecule orients its hydrophilic group toward the surface of a metallic particle in ethanol. Regarding encapsulation, the actions of Anionic-2 and Nonionic-S were almost the same and better than that of Anionic-1. These results suggest in the present system that a polyoxyethylene chain acts as a hydrophilic group more effectively than a more polar sulfonate group. In the following description, results obtained using Anionic-2 and Nonionic-S will be discussed.

Effect of Addition of Auxiliary Surfactant

To improve the encapsulating efficiency, it is necessary to make the styrene monomer or polysty-

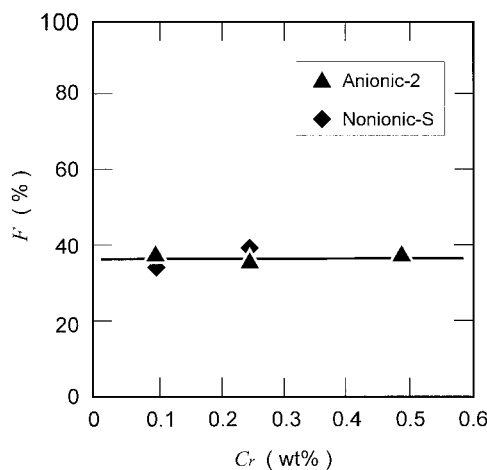


Figure 8 Effect of the reactive surfactant concentration on the encapsulating efficiency of the polymer precipitated.

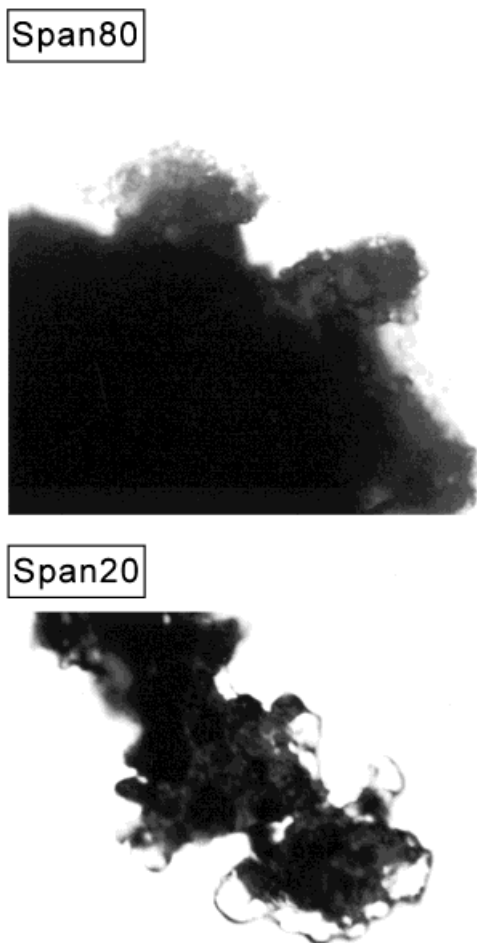


Figure 9 Optical micrographs of the capsules obtained with Nonionic-S at 0.25 wt %, 0.5 wt % auxiliary surfactant, and 200 mol m^{-3} of styrene.

rene oligomer absorb into the adsorbing layer of the reactive surfactant on the surface of aluminum particles and polymerize in that place. For this reason, the addition of Span80 or Span20 as auxiliary surfactant was attempted to thicken the adsorbing layer of the surfactant.

The optical micrographs of the capsules obtained at $C_r = 0.25 \text{ wt } \%$ Nonionic-S, $C_a = 0.5 \text{ wt } \%$ auxiliary surfactant, and $C_m = 200 \text{ mol m}^{-3}$ of styrene are shown in Figure 9. In the case of adding Span80, fine polymer particles of $\sim 1 \mu\text{m}$ in diameter form layers of $> 5 \mu\text{m}$ in thickness and cover a secondary aluminum particle. This result indicates that the adhesion of the fine polymer particles precipitated in the continuous phase onto the aluminum particles was accelerated by the use of auxiliary surfactant. In the case of adding Span20, a bulky polymer layer of $\sim 5 \mu\text{m}$ thickness covering the aluminum particles is

formed. A particulate boundary, observed in the case of Span80, is not recognizable, suggesting that monomer molecules and/or oligomers were absorbed into the polymer particle layer covering an aluminum particle and then further polymerized. Thus, the addition of auxiliary surfactant is shown to be effective. Linkage between part of the capsules was observed with either surfactant.

The effect of the auxiliary surfactant concentration, C_a , on the encapsulating efficiency, F , is shown in Figure 10. The addition of Span80 caused F to slightly increase to 50% with Anionic-2 or Nonionic-S. This increase was not dependent on C_a . By adding Span20, F was remarkably improved. At $C_a = 0.25 \text{ wt } \%$, $F = 56\%$ with Anionic-2, and $F = 80\%$ with Nonionic-S. Furthermore, F reached 85% with either surfactant at $C_a = 0.5 \text{ wt } \%$. This result suggests that Span20 significantly promotes the absorption of styrene as expected and, very likely, promotes the adsorption of reactive surfactant.

The effect of the auxiliary surfactant concentration, C_a , on the mean size, d_p , of the capsules obtained at $C_r = 0.25 \text{ wt } \%$ of Nonionic-S and $C_m = 200 \text{ mol m}^{-3}$ of styrene are shown in Figure 11. The value of d_p increased with the increase in C_a ; for example, d_p was $21 \mu\text{m}$ with Span80 and $27 \mu\text{m}$ with Span20 at $C_a = 0.5 \text{ wt } \%$. This result reflects the adhesion between capsules caused by the polymer layer acting as glue.

The effect of the auxiliary surfactant concentration, C_a , on the mean wall thickness, T , of the capsules obtained at $C_r = 0.25 \text{ wt } \%$ of Nonionic-S and $C_m = 200 \text{ mol m}^{-3}$ of styrene. In the case of

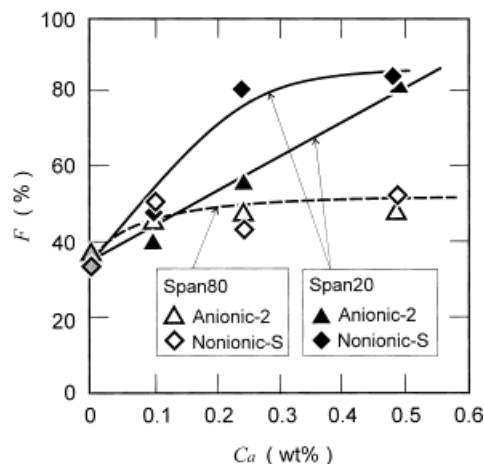


Figure 10 Effect of the auxiliary surfactant concentration on the encapsulating efficiency of the polymer precipitated.

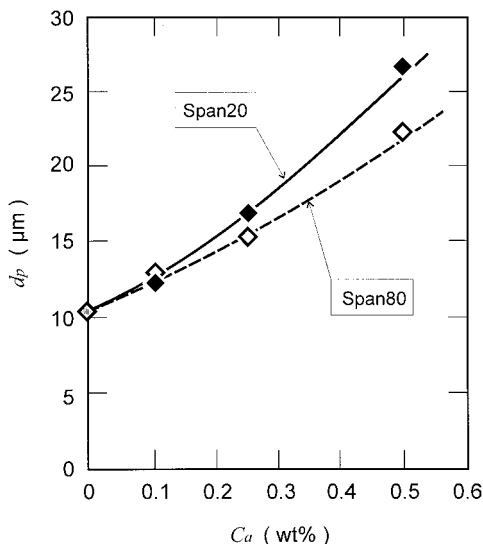


Figure 11 Effect of the auxiliary surfactant concentration on the mean size of the capsules obtained with Nonionic-S at 0.25 wt % and 200 mol m⁻³ of styrene.

adding Span20, T increased linearly with the increase in C_a because of the increase in d_p , as already mentioned, and the consequent decrease in the specific surface area. In the case of adding Span80, on the other hand, T increased very slightly. This result means that adsorption of Span80 has almost reached saturation even at $C_a = 0.1$ wt %, and more addition was not effective.

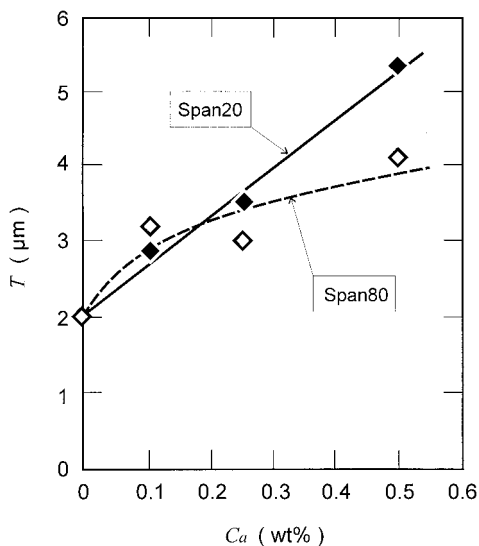


Figure 12 Effect of the auxiliary surfactant concentration on the mean wall thickness of the capsules obtained with Nonionic-S at 0.25 wt % and 200 mol m⁻³ of styrene.

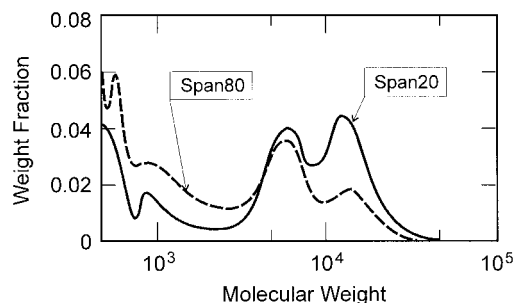


Figure 13 The molecular weight distribution of the polymer of the wall material with auxiliary surfactant at 0.5 wt %, Nonionic-S at 0.25 wt %, and 200 mol m⁻³ of styrene.

The HLB values of Span20 and Span80 are 8.6 and 4.3, respectively.¹⁶ Span80 is more lipophilic than Span20 and, therefore, more stable in the nonaqueous continuous phase. Accordingly, it can be thought that Span20 adsorbs more effectively onto the highly hydrophilic surface of aluminum particles, resulting in the larger encapsulating efficiency of the polymer precipitated.

The molecular weight distribution of the wall material prepared at $C_a = 0.5$ wt % of auxiliary surfactant, $C_r = 0.25$ wt % of Nonionic-S, and $C_m = 200$ mol m⁻³ of styrene is shown in Figure 13. When Span80 was added, it had a greatest peak at molecular weight <1000 and next at ~6000. This result indicates that most of the polymerization products were oligomers. The weight-average molecular weight was ~4500. When Span20 was added, the weight fraction decreased at molecular weight <4000 and, in contrast, increased at ~15,000 as well as ~60,000. The weight-average molecular weight was as high as 9500. Part of the higher molecular weight may be evidence of polymerization of a piece within a surfactant layer adsorbed on the aluminum particles and not only in the continuous phase.

CONCLUSION

This research confirmed that reactive surfactant promotes dispersion polymerization of styrene in ethanol. By using reactive surfactant with a polyoxyethylene chain, secondary aluminum particles could be covered with fine particulate polystyrene. Furthermore, by adding nonionic surfactant as auxiliary surfactant, the aluminum particles were encapsulated with the polymer layer. The most satisfactory encapsulation was carried

out when Nonionic-S was used as the reactive surfactant and Span20 was used as the auxiliary surfactant at concentrations $C_r = 0.25$ wt % and $C_a = 0.5$ wt %, respectively.

NOTATION

C_a : Auxiliary surfactant concentration
 C_m : Styrene monomer concentration
 C_r : Reactive surfactant concentration
 d_p : Mean capsule size
 F : Encapsulating efficiency of the polymer precipitated
 t : Polymerization duration
 T : Mean thickness of capsule wall
 W_p : Total weight of the polymer precipitated
 W_{pc} : Weight of capsule wall
 x : Conversion of polymerization
 Z : Chain length of polystyrene
 δ_m : Solubility parameter of monomer
 δ_s : Solubility parameter of solvent
 ϕ_m : Volume fraction of monomer
 ϕ_s : Volume fraction of solvent

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