A Process for Preparing Polyethylene Wax Microspheres and Optimization of Their Dissolution Precipitation by Response Surface Methodology

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ABSTRACT: Polyethylene wax (PEW) microspheres were prepared by the dissolution precipitation method using a PEW byproduct as the starting material. The influence of surfactant type on the morphology and melting point of the product was investigated. The effects of each factor, including the concentration of anionic surfactants, cooling rate, and stirring rate, on the particle sizes were studied using a three-level, three-factor Box–Behnken design. The experimental parameters were optimized using response surface methodology. The melting point was found to increase when the blend surfactant was employed. The optimal conditions were an anionic surfactant concentration, cooling rate, and stirring rate of 1.0–3.5%, 1.00 °C/s and 1000 rpm, respectively. Under these conditions, the mean particle size was 15 μm, and the highest yield was 94.25%. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1476–1483, 2013

INTRODUCTION

Polyethylene wax (PEW), an important chemical product, has been widely used in throughout the chemical industry including fields such as plastics, asphalt, rubber, electric cable, and coatings. High quality micronized wax also has been used for personal cosmetics and personal care products.[1] All of these products are prepared using high-quality PEW, but numerous PEW products are produced as byproducts during polyethylene (PE) production and are characterized by a broad molecular-weight distribution, a low melting temperature, and a high degree of branching. This byproduct is of low industrial value. Therefore, a green economic process for preparing PEW microspheres with this byproduct as a starting material should be developed, which will not only expand the application of the PEW byproduct, but also improves efficiency in the PE industry.

Polymeric particles were not successfully prepared until 1955.[2] Since then, techniques for preparing polymeric particles have been extensively studied, but only few have been successful. These techniques can be classified into two major categories: physical methods such as mechanical crushing, spray drying, and refrigeration ball milling[3] and chemical methods such as successive seeded emulsion polymerization,[4] emulsifier-free polymerization,[5,6] dispersion polymerization[7,8] the two-step swelling technique,[9,10] and chemical reactions in aerosols.[11,12]

High energy consumption and complicated operations are required in the former, and the shape of the particles is usually lumpy or striped. The latter requires multiple ingredients such as a monomer, an initiator, an inhibitor, and an emulsifier. The time required for preparing 20 μm particles may take one day to several weeks depending on the method being used.

Dissolution precipitation is an emerging method for making micronized polymers, and there have been no reports regarding the preparation of PEW microspheres using PEW byproducts from the PE production process. The process of preparing PEW micro-spheres is affected by various factors, such as the concentration of surfactants, the cooling rate, and the stirring rate. When many factors and interactions affect the desired response, the response surface method (RSM) is an effective tool for finding their optimal values. RSM is a statistical method that uses quantitative data in an experimental design to solve multivariable equations and optimize processes or products. This article reported the experimental results.

EXPERIMENTAL

Materials and Apparatus

The starting materials used in this article are PEW with a melting range of 68.4–78.9°C. Sodium dodecyl sulfate, sodium stearate, Span 80, Tween 20, and PE glycol were used as

Table I. Materials and Experimental Apparatus

Materials	Specification	Manufacturer
PEW	Tech	C.N.P.C
Sodium dodecyl sulfate	CP	T.T.R.C
Sodium stearate	CP	Sinopharm Chemical Reagent Co., Ltd
Span 80	CP	T.T.R.C
Tween 20	CP	T.T.R.C
Polyethylene glycol	CP	T.T.R.C
Xylene	CP	Beijing Chemical Works
n-heptane	CP	Beijing Chemical Works
Ethanol	CP	Beijing Chemical Works
SEM	JSM-5600LV	Japan
Automated Melting Point System	X-6	Bejing Tianchengwode Biotech Co.,Ltd

anionic/nonionic surfactants. Xylene and *n*-heptane were used as organic solvents. Ethanol was used as a precipitant. Other parameters and apparatuses are listed in Table I.

The PEW used in this article was a byproduct provided by China National Petroleum Corporation (C.N.P.C., China) without further purification or fractionation. Therefore, the molecular-weight (as well as the chain-length) distributions were most likely broad.

Preparation

The PEW microspheres were prepared through a multi-stage dissolution precipitation method that was performed in a 500-mL, four-necked, round-bottom flask equipped with a paddle stirrer, a thermometer, a nitrogen gas inlet, a reflux condenser, and inlet tubes for the feed of materials. PEW (10.0 g) and 100.0 mL of solvent (xylene and *n*-heptane in a mass ratio of 2 : 22.5[13]) were fed into the flask, and the solution was heated to 85°C under a nitrogen atmosphere at an agitation rate of 50 rpm agitation. The temperature was maintained for ∼ 30 min until the PEW completely dissolved. After feeding the surfactant blends into the flask, the solution was heated to 90°C with a high agitation rate and held at that temperature for 6–8 h; the solution was then rapidly cooled by placing the flask into an ice bath to precipitate the polymer. The precipitate was washed with ethanol at a low temperature several times, and the solvent was completely removed by vacuum distillation.

Characterization

The morphology of the particles was observed by scanning electron microscopy (SEM, JEOL JSM-5600LV). The specimens were prepared by drying the samples on the specimen holder and covering the surface of the samples with a layer of gold powder.

The melting point was measured on a micro melting-point apparatus (X-6). The samples were heated at a setting of 100 V, and the heating rate was held constant until the samples melted

completely. The average melting-point value was obtained after repeating this measurement three times.

The yield of PEW microsphere powder was calculated using eq. (1), in which y, W_p, and W_f represent the yield of PEW microspheres, the mass of finished products, and the mass of starting materials, respectively.

$$y = \frac{W_p}{W_f} \times 100\% \qquad (1)$$

Experimental Design and Statistical Analysis

Different surfactants were used to find the optimum surfactant blends. Subsequently, the effects of three variables, the concentration of surfactant, the cooling rate, and the stirring rate on particle size were studied to determine the optimum combination of conditions, using a central-composite experimental design for the RSM.

The concentration of the nonionic surfactant was not taken into account because it mainly acts as a defoamer and stabilizes the dispersion. In addition, there was no change when the anionic surfactant concentration increased during a series of single-factor experiments before optimization by RSM.

The model proposed for the response Y (particle size) was given below:

$$Y = b_0 + b_1A + b_2B + b_3C + b_4A^2 + b_5B^2 + b_6C^2 + b_7AB + b_8AC + b_9BC$$

where b_0 is an offset term; b_1, b_2, and b_3 are related to the linear effect terms; b_4, b_5, and b_6 are related to the quadratic effect terms; and b_7, b_8, and b_9 are associated with the interaction effects.

The variables and their ranges were as follows.

A is the concentration of anionic surfactant (0.5–7.0 wt %), B is the cooling rate (0.01–1.00°C), and C is the stirring rate (300–1100 rpm). The adequacy of the polynomial model was expressed by the multiple coefficient of determination, R^2. The significance of each coefficient was determined using the F and P values. To deduce the optimum conditions, a graphical technique was used in which one variable was fixed at a predetermined optimum condition. The optimum condition was verified by monitoring the results, and the results were compared with the model predictions.

RESULTS AND DISCUSSIONS

The Effect of Surfactants on the Morphologies and Melting Points of Products

The effect of surfactants on the melting points of samples is given in Table II. The melting point increased when surfactant blends were employed. The highest melting point, 82.4°C, appeared in Sample 3 (Table II, entry 3). A preferable nucleating area was obtained at a higher agitation rate.[14] In this region, the polymer chains could maintain a pediocratic thermodynamic motion, and a broader nucleating area was provided. When the surfactant blend consisted of sodium dodecyl sulfate and PE glycol, the electronic shell covered the surfaces of the

Table II. Melting Points of Samples with Different Surfactants

Entry	Anionic surfactant	Nonionic surfactant	PEW/anionic/nonionic (wt/wt/wt)	$T_{o.\,m}$ (°C)	T_m (°C)
0	–	–	100.0/0/0	68.4	78.9
1	Sodium dodecyl sulfate	Span 80	98.5/1.0/0.5	80.3	85.7
2	Sodium dodecyl sulfate	Tween 20	98.5/1.0/0.5	80.1	84.7
3	Sodium dodecyl sulfate	Polyethylene glycol	98.5/1.0/0.5	82.4	86.1
4	Sodium stearate	Span 80	98.5/1.0/0.5	79.5	84.1
5	Sodium stearate	Tween 20	98.5/1.0/0.5	81.1	85.1
6	Sodium stearate	Polyethylene glycol	98.5/1.0/0.5	79.4	84.5

$T_{o.m}$: onset temperature of melting; T_m: melting temperature.

droplets, and the electrostatic repulsion appeared to limit the frequency of collisions between polymer chains. At the same time, PE glycol chains also covered the surfaces of the droplets and not only controlled the shape of products but also limited the foaming caused by sodium dodecyl sulfate. Therefore, the best nucleating area was provided when the surfactant blend was employed, and the nuclei were closest together.

The SEM photographs of the samples are shown in Figure 1. Compared with other samples, Sample 3 showed a superior morphology in that the polymer precipitated as spheres. Better results were observed when the surfactant had a structure similar to that of the starting materials.[15] Because the PEW is a low-molecular-weight hydrocarbon polymer, sodium dodecyl sulfate was the preferred choice because it has a structure more similar to that of PEW than sodium stearate. In addition, PE glycol also had a structural effect when compared to Span 80 and Tween 20. The surface activity was more efficient with a longer lipophilic group for the same hydrophilic group, as was

reported previously.[16] However, the stability of the solution deteriorated and a little foam appeared with the addition of sodium dodecyl sulfate at a high agitation rate, and PE glycol acts as a defoamer in the solution.[17]

A surfactant blend, comprised of an anionic surfactant and a nonionic surfactant, has been reported to stabilize dispersions and has usually been used for preparing polymer microspheres, and the solubility of nonionic surfactants decreased in the oil phase but increased in the water phase on heating the solution. Therefore, if the nonionic surfactant was fed into the solution, a phase transition would occur when the temperature increased and exceeded a certain point resulting in the significant deterioration of the solution stability.[18] Use of sodium dodecyl sulfate to stabilize the solution through electrostatic repulsion caused control of the phase-transition temperature to be dependent on PE glycol. Consequently, superior solution stability could be obtained when the surfactant blend consisted of both an anionic surfactant and a nonionic surfactant.
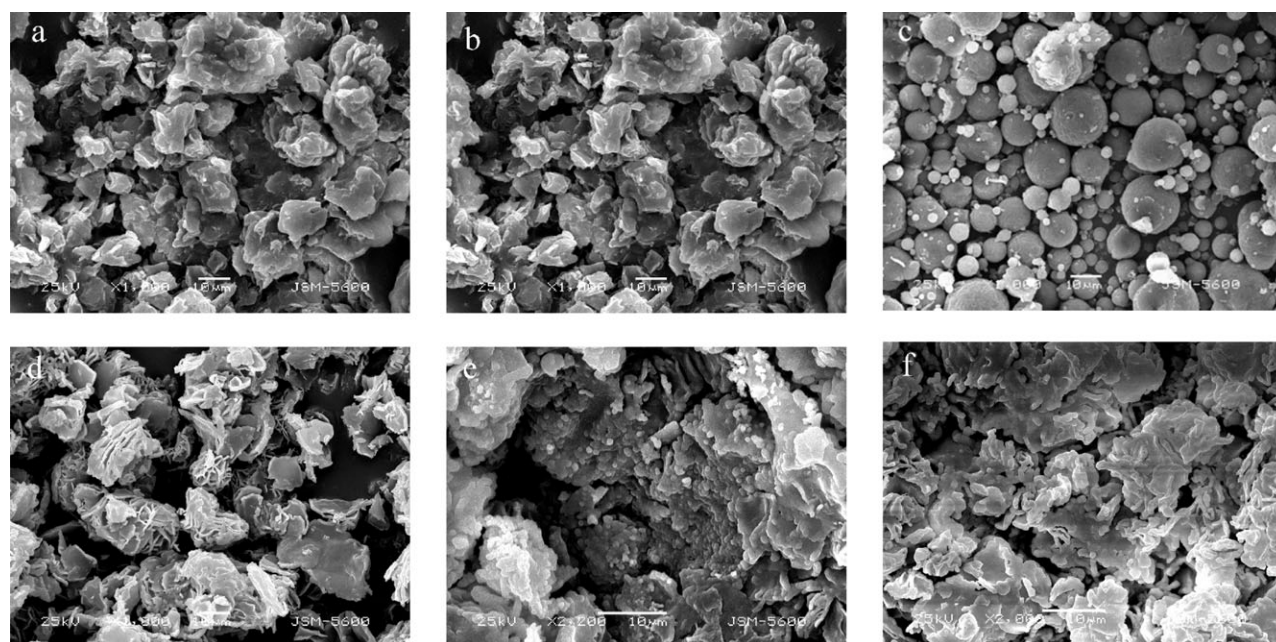

Figure 1. SEM photographs of samples using different surfactants. (a–f) Shows entries 1–6 in Table II.

Table III. Significance of Regression Equation Coefficients for Particle Sizes

Variables	Regression coefficients	Standard error	Computed F value	Significance level (P value)
b_0	25.60	2.04	16.57	0.0006
Linear				
b_1	−1.13	1.61	0.49	0.5077
b_2	−15.00	1.61	86.63	<0.0001
b_3	−6.38	1.61	15.65	0.0055
Quadratic				
b_4	2.00	2.28	0.77	0.4093
b_5	0.25	2.28	0.012	0.9157
b_6	2.50	2.28	1.2	0.3090
Interaction				
b_7	10.32	2.22	21.6	0.0023
b_8	8.58	2.22	14.9	0.0062
b_9	4.33	2.22	3.79	0.0926
R	0.9773			
R^2	0.9552			

Results of RSM

The regression equation representing the relationship between particle size and the test variables derived from RSM are as follows:

$$Y = 25.60 - 1.13A - 15.00B - 6.38C + 2.00AB + 0.25AC - 2.50BC + 10.32A^2 + 8.58B^2 + 4.33C^2$$

where Y is a coded fitting equation. A P value less than 0.05 indicates that a variable was significant. A P value less than 0.001 indicates that a variable was highly significant and had a greater influence than other variables. Variables are significant if their absolute F value became larger and their P value became smaller. Significance of regression equation coefficients for particle sizes were listed in Table III. The most significant variable was found to be the linear cooling rate (B), followed by concentration of anionic surfactant (A^2). According to the F and P values, the terms b_1, b_4, b_5, b_6, and b_9 did not show statistical significance.

The multiple coefficient of correlation ($R = 0.9773$, Table III) and the total determination coefficient ($R^2 = 0.9552$, Table III) indicated high agreement between the experimental and predicted particle sizes. The 3D surface plots were drawn to illustrate the main and interactive effects of the independent variables on the dependent variable. The response surface is shown in Figure 2. One of the variables was kept at the optimum level while the remaining two variables were changed within their experimental ranges.

The effects of the addition of an anionic surfactant and the cooling rate on particle sizes are shown in Figure 2(a). The cooling rate had a linear effect on particle sizes, whereas the addition of an anionic surfactant had a quadratic effect.

The influences of the addition of an anionic surfactant and the stirring rate on particle sizes are presented in Figure 2(b). The particle size decreased with increased stirring rate, but the curve became flat when the stirring rate reached 800 rpm. The
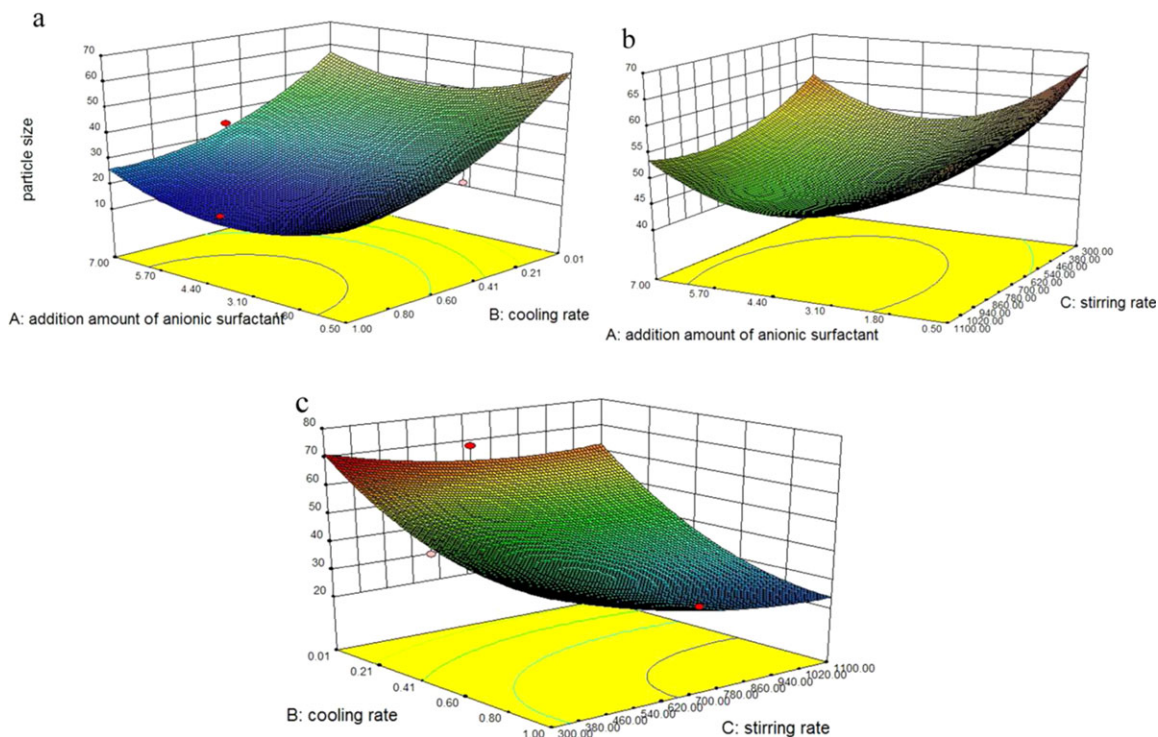

Figure 2. 3D graphics surface optimization of preparing precipitation technique of PEW microspheres. (a) The concentration of anionic surfactant and the cooling rate, (b) the concentration of anionic surfactant and the stirring time, (c) the cooling rate and the stirring rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
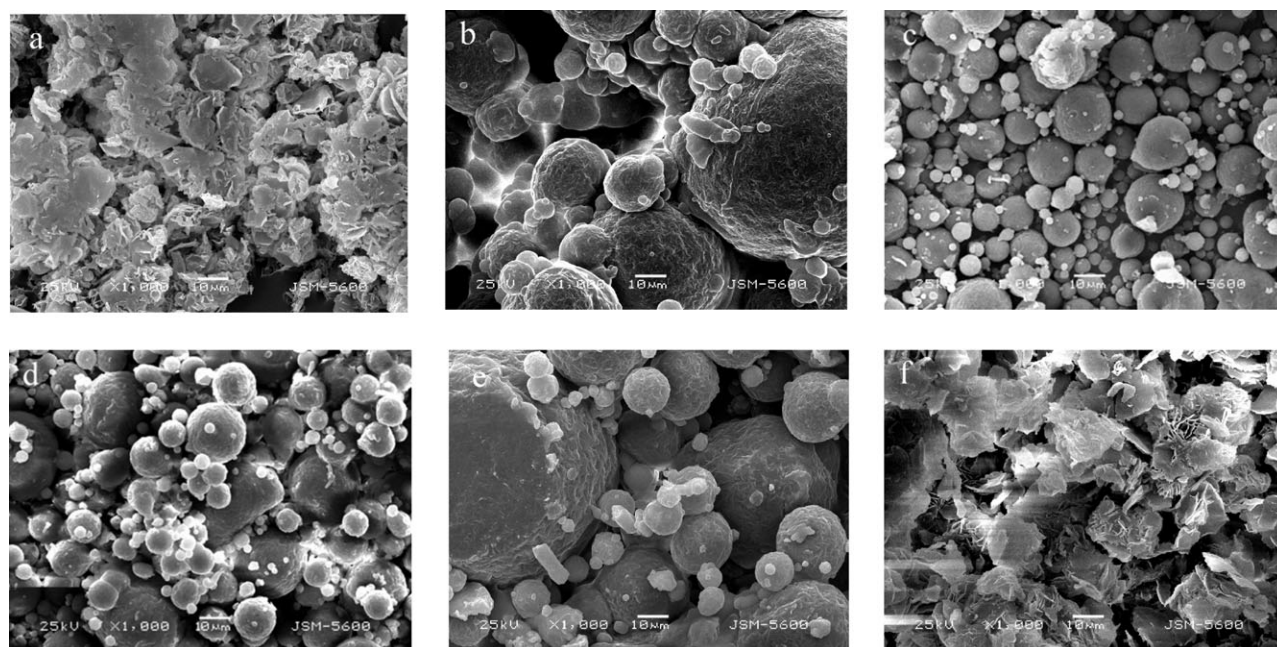
Figure 3. SEM photographs of samples using different concentration of surfactants. (a–f) The concentration of anionic surfactant of 0.5, 0.8, 1.0, 3.0, 5.0, and 7.0 wt %, respectively.

influences of the cooling rate and the stirring rate are shown in Figure 2(c). These results showed that the response surface had a minimum point. The minimum particle size was 14.7944 μm when the addition of anionic surfactant was 3.57 wt %, the cooling rate was 1.00 °C/s, and the stirring rate was 1099.99 rpm.

Verification of Results
To examine whether the equation obtained using RSM fit the relationship between particle size and experimental variables well, a confirmatory experiment was carried out with the concentration of anionic surfactant adjusted to 3.5 wt % at a stirring rate of 1100 rpm. The particle size obtained from the process was 15 μm, corresponding to an error of 1.37% when comparing to the particle size predicted from RSM. This result showed that the method to prepare PEW microspheres using RSM was accurate and reliable.

Effect of Concentration of the Surfactant on the Morphology. Figure 2 shows that a quadratic dependence of particle size on the concentration of anionic surfactant was found and that the actual optimum concentration was 1.0–3.5 wt %. Some representative test results are shown in Figure 3 and verified the experimental results above. Serious flocculation was observed when the anionic surfactant concentration was 0.5 and 7.0 wt %, producing material that looked like lumps or rods. A possible reason for this phenomenon could be connected to collisions in the solution. Polymer chains are known to exist in solution as droplets that are formed when PEW is dissolved in the organic solvent under high agitation; the droplets collide with each other frequently, and the collision can be partially prevented by the electronic shell formed from sodium dodecyl sulfate covering the surface of the droplets. Therefore,

flocculation can be controlled in this manner when the droplets collide with each other.[19] The electronic shell was not strong enough to prevent collisions between chains in solution when sodium dodecyl sulfate concentration was low (0.5 wt %). This phenomenon resulted in the polymer chains flocculating upon collision and forming another phase. When the concentration of sodium dodecyl sulfate increases (1.0–3.0 wt %), the electronic shell was strong enough to decrease the collision frequency, and flocculation was prevented. Furthermore, the stability of the solution was improved when PE glycol was added.

However, a greater surface area of the polymer chains was covered by anionic surfactant as the concentration was increased; this phenomenon caused excessive charges that appeared to promote the collision frequency, resulting in low solution stability and a broad size distribution. Sodium dodecyl sulfate is known to act as a foaming agent, so the defoaming function of PE glycol would be overwhelmed by the addition of sodium dodecyl sulfate. The polymer did not form spheres when the concentration of sodium dodecyl sulfate was too high (7.0 wt %), and serious flocculation occurred. Li, S. Y.[20] had shown that the polymer products were spheres within a certain concentration range under the critical micelle concentration (cmc)

Effect of the Cooling Rate on the Morphology of Products. The effect of cooling rate on particle size is shown in Figure 4. It can be observed that the cooling rate had a linear relationship with the particle size; the particle size decreased as the cooling rate increased. Representative SEM photographs of samples made with different cooling rates are shown in Figure 4. When the cooling rate was 1.00 °C/s, the nucleation occurred promptly. Conversely, when the PEW precipitated more slowly, the particles were non-spherical and tended to fuse together.
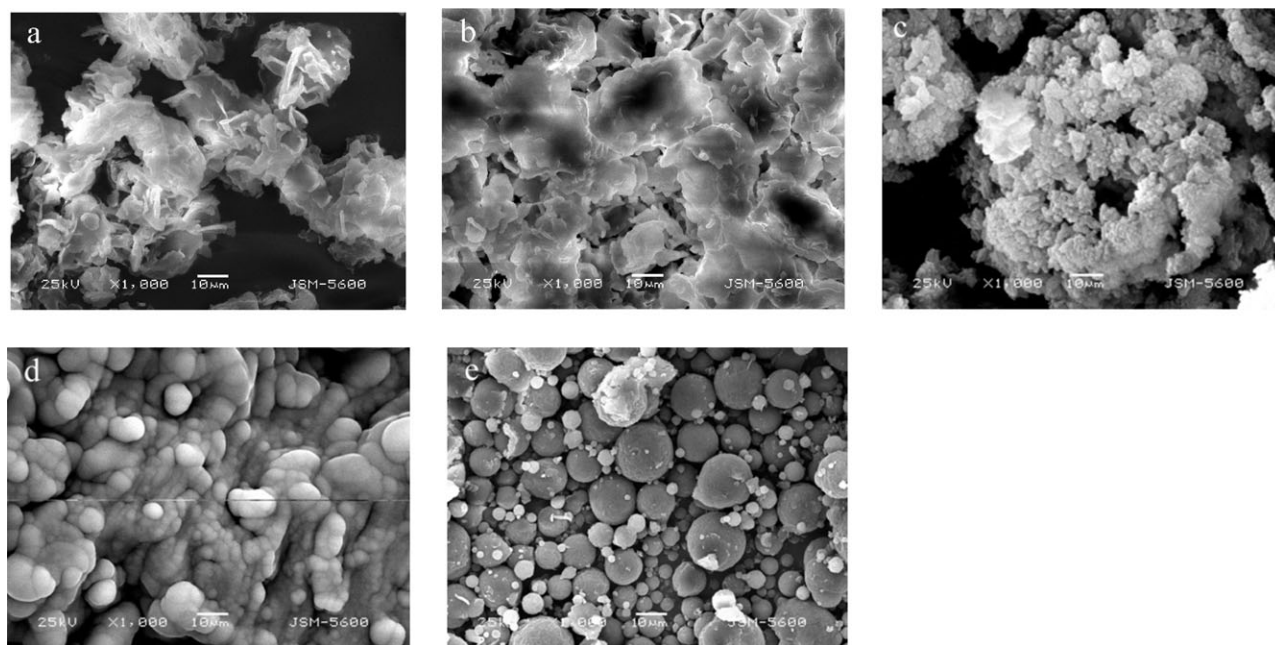
Figure 4. SEM photographs of samples using different cooling rates. (a) Cooling rate of 0.05 °C/s. (b) Cooling rate of 0.10 °C/s. (c) Cooling rate of 0.30 °C/s. (d) Cooling rate of 0.60 °C/s. (e) Cooling rate of 1.00 °C/s.

The De Genne's reptation theory describes polymer chains as moving in a snake-like fashion in the bulk state.[21] Hou and Lloyd[22] have shown that greater space allows the polymer chains to move more easily in solution; therefore, poymer chains should move freely in solution. Although polymer chains moved freely in the solution, at very low temperatures, the collision frequency was low. When the cooling rate decreased, and the time for precipitation became longer, the polymer chains collided with each other more often. When the temperature of the solution was lowered slowly, the number of interaction between the polymer chains and solvent molecules was decreased, and the polymer chains flocculated upon collision and formed a second phase. This phenomenon is known as phase separation and has been effectively described by thermodynamic theories.[23]

Effect of the Stirring Rate on the Mean Particle Size and Yield of Products. The influence of the stirring rate on particle size is shown in Figure 2, and the stirring rate showed a linear relationship with particle sizes, similar to the cooling rate. The effect on the yield is shown in Figure 5. The yield increased with an increased stirring rate, but the yield changed little once the stirring rate exceeded 1000 rpm.

A possible reason for this phenomenon could be connected to the dissolution of the polymer in solution. A very small droplet could have formed using the surfactant blend when the polymer was dissolved in solution with high agitation, which improved mass transfer and heat transfer. Thus, smaller and more numerous droplets could have formed with increased agitation.[23] The collision frequency would also be higher with an increased agitation rate, resulting in the flocculation of polymer chains and lower yields. Therefore, the agitation rate of 1000 rpm was optimal in this study, producing the highest yield of 94.25%.

Comparison Between the Products and Micronized Wax Used in Cosmetic Industry

Figure 6 compares the SEM photographs of different brands of PEW used in the cosmetic industry prepared by Nanjing Tianshi Experimental Powder Co., Ltd with the products prepared by dissolution precipitation in this article; some main appropriates are given in Table IV. The shapes of the PEW, as shown in Figure 6(a–c), were not spherical, which indicates a lower handling efficiency and fluidity during the cosmetics production process.

In contrast, the PEW microspheres prepared in this article showed the preferred spherical-shape distribution compared with the other products (Figure 6); therefore, this method can improve not only the handling and the fluidity of cosmetics but
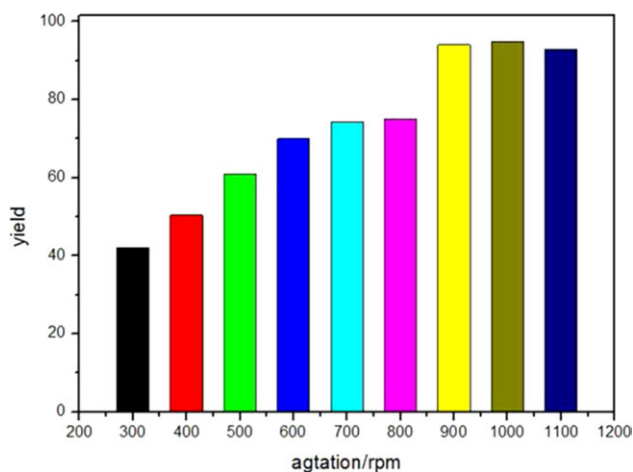

Figure 5. Change of yield using different agitation rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
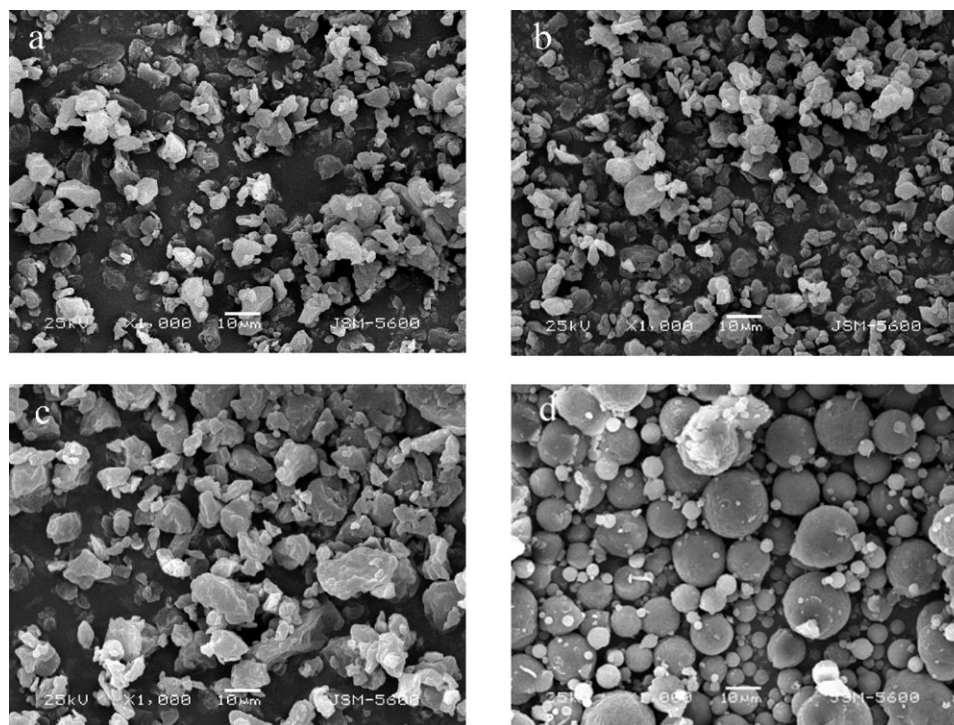
Figure 6. Comparison between the products and micronized waxes used in cosmetic industry. (a) Brand of PEW-0221. (b) Brand of PEW-0251. (c) Brand of PEW-0252. (d) The products in this paper.

also the softness, hardness, and wear resistance of synthetic fibers. Furthermore, these microspheres can also be used as lubricants and color concentrate dispersants to improve the facility of production, surface brightness, lubricity, and thermal stability of thermoplastics.

CONCLUSION

The present results demonstrated that the dissolution precipitation method can be used to prepare PEW microspheres. The conclusions are as follows:

1. PEW micro-spheres were successfully prepared by the dissolution precipitation method with PEW byproducts as the starting materials. The key feature in the preparation of the polymer particles was the use of a surfactant blend consisting of sodium dodecyl sulfate and PE glycol.

Table IV. Main Parameters of PEW Prepared by Nanjing Tianshi Experimental Powder Co., Ltd

Entry	Brand	Product types	Appearance	Melting points (°C)	Particle sizes (µm)
1	PEW-0221	PEW	Ultrafine powders	106	9
2	PEW-0251	PEW	Ultrafine powders	116	11
3	PEW-0252	PEW	Ultrafine powders	95	15

Moreover, the melting point of the polymer particles increased with use of the surfactant blend.

2. The particle sizes were optimized using statistical software. After determining the composition of the surfactant blend, three independent variables, including the concentration of anionic surfactant, the cooling rate, and the stirring rate, were investigated to obtain the optimal conditions. The RSM results indicated that the variables with the largest effect were the cooling rate and the concentration of anionic surfactant, with optimal values of 1.00 °C/s and 1.0–3.5 wt %, respectively. The stirring rate was optimized at 1000 rpm. Under these conditions, the mean particle size was 15 µm.

3. The yield of products increased when the stirring rate increased, whereas the yield hardly changed when the stirring rate was too high. Under these conditions, the highest yield was 94.25%.

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