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Thin Layer Copolymerization of Methyl methacrylate and Butyl acrylate in Concentrated Emulsion

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Summary

In this study, stable concentrated emulsions of methyl methacrylate and butyl acrylate (MMA-BA) were first prepared using sodium dodecyl sulfate/cetyl alcohol (SDS/CA) as composite surfactants and polyvinyl alcohol (PVA) as liquid film reinforcer. A novel polymerization method, thin layer copolymerization of the concentrated emulsion was subsequently carried out with benzoyl peroxide/N, N'-dimethyl phenylamine (BPO/DMA) as redox initiators at low temperature. The effects of the thickness and area of the thin layer, the outside temperature, as well as environment of the polymerization on the amount of volatilization of water and monomer in the system were investigated. It has been found that the liquid film reinforcers and the polymerization environment were responsible for the polymerization stability. In addition, the conversion-time relationships of the thin layer polymerization and the tube polymerization, as well as the effect of polymerization environment on the polymerization rate were also investigated. The size and distribution of particle diameter and morphology of latex particles were determined with transmission electron microscope (TEM).

Introduction

As a novel method, concentrated emulsion polymerization has stimulated extensive researches. In comparison with conventional polymerization, concentrated emulsion polymerization has not only a paste-like appearance, a special nucleation mechanism of the latex particle and a super high solid content, but also low energy consumption, high equipment efficiency and no waste releasing, which reduces environmental pollution and fulfils the requirements of green chemical technology.

In the middle of the 1980s, Ruckenstein and coworkers started pioneering research work in concentrated emulsion polymerization [1, 2], and their researches largely focused on minority monomers, such as styrene and styrene/acrylamide. Besides, the majority of polymerization reactions based on these systems were carried out with thermolysis initiators, for example, azo-compounds [3-5]. From the 1990s to present, some basic theoretical researches on concentrated emulsion polymerization were carried out [6-9].These researches show that stirring is not suitable during polymerization reaction, because of the paste-like appearance of the emulsion system. When the volume of reactor is larger, the heat generated by the polymerization reaction is hard to diffuse

[10], and the stability of concentrated emulsion system is reduced. Recently, redox initiator systems containing cumene hydroperoxide and ferrous sulfate/sodium metabisulfite; benzoyl peroxide/N, N'-dimethyl phenylamine were introduced into concentrated emulsion polymerization to make polymerization take place at low temperature, and the preliminary rules of concentrated emulsion polymerization in small tubes, using redox initiator system were deduced [11-13]. However, the heat generated by the reactions accelerated the polymerization reaction, a so-called self-heating phenomenon, leading to instability in concentrated emulsion polymerization.

To solve the heat conduction problem in concentrated emulsion polymerization, a special polymerization method, a thin layer polymerization using redox initiator system was developed, which could facilitate the heat conduction, ensuring a high polymerization rate and the stability of concentrated emulsion, as well as avoiding monomers losing. Therefore, polymer colloids, powdery resins and decomposable composites of super high content solid can be directly prepared.

The technique of thin layer polymerization is different from the tube polymerization, where concentrated emulsion was first centrifuged to expel air bubble and transferred into a special mold, and then the air in the mold was replaced with nitrogen. The mold was sealed and placed in an oven or a temperature-controlled water bath to carry out the polymerization. In this study, a redox initiator system based on BPO/DMA was used to initiate thin layer polymerization of methyl methacrylate and butyl acrylate in concentrated emulsion at low temperature. The effects of the liquid film reinforcers and the polymerization environment on polymerization stability were investigated. The factors affecting the amount of volatilization of water and monomer in the thin layer of concentrated emulsion system and the kinetics of the polymerization were discussed in detail. The size and distribution of particle diameter and morphology of latex particles obtained at different conditions were also analyzed.

Experimental

Materials

Methyl methacrylate and Butyl acrylate (MMA and BA, analytic grade, The Sixth Factory of Tianjin Chemical Reagents, China) were distilled under reduced pressure, dried and then stored in a refrigerator. Sodium dodecyl sulfate (SDS, chemical grade) was purchased from Japan. Cetyl alcohol (CA, chemical grade, The Chemical Factory of Guangdong Xilong, China), Benzoyl peroxide (BPO, The Chemical Factory of Hubei University, Wuhan, China) was recrystallized and dried under reduced pressure. N, N'-dimethyl phenylamine (DMA, analytic grade, The Chemical Factory of Hubei University, Wuhan, China), Hydroxypropyl cellulose (HPC), Poly (N-vinylpyrrolidone) (PVP, M_n=40000) were purchased from Shanghai Chemical Reagent Factory. Hydroquinone (analytic grade, Shanghai Chemical Reagent Factory, China) and Polyvinyl alcohol (PVA-1788, analytic grade, Sichuan Nylon Factory, China) were used as received.

Preparation and polymerization of concentrated emulsions

Table 1 showed a typical recipe used in the preparation of MMA/BA concentrated emulsion. A known volume of an aqueous solution of SDS, CA and PVA was added into a three-neck flask of 250ml capacity at room temperature, equipped with a mechanical stirrer, a funnel, and a nitrogen inlet. Monomer mixtures of MMA and BA containing BPO as oxidant were dropped into the flask under stirring at a suitable rate to avoid phase separation. The whole process was under the protection of nitrogen. After the entire dropping process, solution of reducer DMA was injected into the system. Vigorous stirring stopped after 5 minutes.

Test-tube polymerization

Each prepared gel-like concentrated emulsion was transferred to a preweighed 10mL centrifugal test tube and centrifuged at a moderate rate to expel air bubble. Then the air in the tube was replaced with nitrogen and the tube was sealed with a rubber septum. The test tube was placed in a temperature-controlled water bath to carry out polymerization.

Thin-layer polymerization

Each prepared gel-like concentrated emulsion was transferred to a preweighed 10mL centrifugal test tube and centrifuged at a moderate rate to expel air bubble. Then the concentrated emulsion was transferred to a special mold to form a thin layer, and the air in the mold was replaced with nitrogen. The mold was placed in a temperature-controlled water bath or oven to carry out polymerization.

Table 1 A typical recipe used in the preparation of the MMA/BA concentrated emulsion

Component	Amount(Wt/g)
Dispersed phase: MMA/BA (1/1)	50.00
Continuous phase: H_2O	10.00
surfactant: SDS/CA (2/1)	1.50
Initiator: BPO	0.45
Reducer: DMA	0.09
reinforcers of liquid film: PVA	0.10

The volume fraction of dispersed phase (Φ) was 83.3%

Measurement and characterization

The stability of concentrated emulsion

Each concentrated emulsion (free of initiators) was transferred into a preweighted 10-mL centrifugal tube using a spatula. After mild centrifugation, the tube was placed in a 30°C temperature-controlled water bath for 24 h. The stability was measured in terms of the weight fraction (α) of the bulk phases separated from the concentrated emulsion. The larger the value of α, the less stability of the concentrated emulsion was. And α was calculated according to the following equation:

$$\alpha=\varphi_1/\varphi_0\times100\% \qquad (\mathbf{1})$$

Where φ_1 represent the weigh of the bulk phases separated from the concentrated emulsion, φ_0 represented the total weigh of the monomer.

The test of volatility of water and monomer in the thin layer concentrated emulsion system

After mild centrifugation, each concentrated emulsion (free of initiator) was transferred into a pre-weighted mold. The amount of volatilization of water and monomer in the system was measured gravimetrically by changing the thickness or area of thin layer or outside temperature. And then the percentage of volatilization was obtained at a certain time (20min). The percentage Q (%) of volatilization of water and monomer in the system was calculated according to the following equation:

$$Q(\%) = W / W_0 \times 100\% \qquad (2)$$

Where W ($W = W_0 - W_n$) represents the amount of volatilization of water and monomer in the system; W_0 and W_n represents the initial and final weight of concentrated emulsion respectively.

Kinetics of thin layer polymerization

During the polymerization process, 0.5g sample was withdraw from the mold at regular intervals and transferred to a pre-weighed glass container containing hydroquinone. The products were dried at about 100°C for 12 h, and then the weight of the MMA/BA copolymer (W_1) was obtained. Polymerization conversion (C%) was calculated according to the following equation.

$$C\% = W_1 / W_0 \times 100\% \qquad (3)$$

Where W_0 denotes the monomer mass used for polymerization.

The size and morphology of the latex particles

The copolymer particles were dispersed in deionized water and then coated onto a copper grid. After being dried at room temperature, the samples were examined with TEM (JEM-100SX, JEOL, Tokyo, Japan). The size and polydispersity of the particles were also measured by PCS (photo correlation spectrum) on an Autosizer Loc-FC963 apparatus (Malvern Instruments, Worcester, UK). Polydispersity was represented with a “Poly” value.

Results and discussion

Effect of the reinforcers of liquid film and environment on polymerization stability

The stability of the concentrated emulsions refers to the resistance to the formation of two separate phases. Concentrated emulsions should remain stable not only at room temperature but also at the reaction temperature. The stability of the concentrated emulsions is closely related to the subsequent polymerization reaction.

Table 2 indicated the effect of the reinforcers of the liquid film and the polymerization environment on the amount of bulk phase separated after polymerization. As expected, the extent of the effect on the stability of polymerization was different for the three kinds of reinforcers of the liquid film. The result was arranged as following order: PVA <PVP<HPC < none. The hydrophilicity of PVA was stronger than that of PVP and HPC, which was due to the higher content of hydroxy group in PVA. Moreover, the stronger liquid film formed among liquid cells increased the polymerization stability of the concentrated emulsions because of the association originated from hydrogen bonds. Table 2 also showed that different polymerization environments could affect the polymerization stability of the concentrated emulsions. The heat conduction efficiency in the water bath was higher than that in oven because it was easier for the water medium to remove the reaction heat inside the polymerization system, which resulted in the lower partial temperature in the water bath than in the oven. As a result, the amount of monomer loss decreased and the polymerization stability became higher.

Table 2 Effect of the reinforcers of liquid film and polymerization environment on polymerization stability (φ= 0.83, 30°C, 5h)

reinforcer	α (%)	others	environment	α (%)	others
PVA	1.06	[E]= 0.55mol.l^{-1}	oven	2.56	[E]= 0.55mol.l^{-1}
PVP	1.36	[SDS]/ [CA]=2:1 mol			[SDS]/[CA]=2:1 mol
HPC	1.76	[I]=0.296mol.l^{-1}	water bath	1.21	[I]= 0.296mol.l^{-1}
No	2.56	[BPO]/[DMA]= 1:0.4 mol			[BPO]/[DMA]= 1:0.4 mol

The amount of volatilization of water and monomer in the thin layer polymerization system

The effects of thickness and area of the thin layer, outside temperature, polymerization environment, etc on the amount of volatilization of water and monomer in the thin layer polymerization of concentrated emulsion were shown in table 3 and 4.

Table 3 The effect of the thickness of the thin layer on the amount of volatilization of water and monomer in the system (%)

t(min)	Thickness/ cm			
	0.25	0.40	0.70	1.00
20	0.240	0.120	0.096	0.034
40	0.230	0.136	0.096	0.028
60	0.230	0.119	0.092	0.031
80	0.240	0.120	0.094	0.033
100	0.240	0.120	0.094	0.022
120	0.270	0.116	0.091	0.027
140	0.260	0.135	0.101	0.025
the average	0.250	0.120	0.094	0.031
$m_0 \times 10^4$	4.9	2.3	1.8	0.6

(SDS)/(CA)= 2:1 mol, [E]= 0.55mol.l^{-1}, water= 10ml, t= 10°C, PVA= 0.1g, S= 25.52cm^2

The effect of the thickness of the thin layer on the amount of volatilization of water and monomer in the system (table3)

At 10 ºC, the effect of different thickness of the thin layer on the amount of volatilization of water and monomer in the system per 20 min was presented in table 3, while the area of lamella remained constant. From table 3, it could be found that at the same thickness of the thin layer, the total amount of volatilization of water and monomer in the concentrated emulsion system was constant per unit time. Since outside condition was constant (1kp, 10 ºC), the total amount of volatilization of water and monomer only depends on the area of the layer. It was also found that, with the increase of the thin layer thickness, the percentage of volatilization of water and monomer decreased per unit time. The reason is that the volatilization ratio of concentrated emulsion is a constant number, and the total amount of volatilization of water and monomer is constant at the same area of the thin layer and outside condition (1kp, 10 ºC). Therefore, when the area of the thin layer and outside condition (1kp, 10 ºC) remained constant, the total weight of concentrated emulsion increased with the increase of the thin layer thickness. But the total amount of volatilization of water and monomer didn't change, which led to the decreasing percentage of volatilization of water and monomer in the unit weight of concentrated emulsion per unit time. The volatilization of water and monomer $m_0 \times 10^{-4}$(g.cm^{-2}.min^{-1}) in per unit time and area was calculated.

The effects of the outside temperature and the environment on the volatilization rate of monomer and water in the system

The effect of the outside temperature on the volatilization rate of water and monomer was presented in table 4, which showed that the volatilization rate of water and monomer increased rapidly with the increasing temperature. Obviously, outside temperature has dominant effect on volatilization rate of water and monomer, i.e., the stability of concentrated emulsion decreased with the increasing temperature, since molecular mobility is getting higher with increasing temperature, which results in easier transfer of monomer phase through cell film. Therefore, temperature has remarkable effect on stability of the concentrated emulsion. Table 4 showed that, at three different temperatures, the volatilization rate of water and monomer in water bath was lower than that in air, because heat-conduction in water bath was easy at any temperature.

Table 4 Effect of the outside temperature and the environment on the volatilization rate of monomer and water ($\times 10^{-5}$g.cm^{-2}min^{-1})

Polym. Envi.	10 ºC	20 ºC	30 ºC
in air	1.85	3.62	5.52
in water bath	1.83	3.58	5.46

[SDS]/[CA]= 2:1*mol*, [E]= 0.55mol.l^{-1}, S= 25.52cm^2, *h*= 0.65cm, PVA= 0.1g Polym. Envi.: Polymerization Environment

The polymerization rate of the thin layer polymerization

The comparison of the polymerization rate between the thin layer polymerization and the tube polymerization

The conversion-time curves of the thin layer and tube polymerization at 30 ºC in water bath were plotted in figure 1. In the tube, when the polymerization time was only five hours and twenty minutes, conversion reached 90%. From figure 1, it could be seen that the polymerization rate of the tube polymerization is faster than that the thin layer polymerization. The reason is that monomer loss in thin layer polymerization is larger, which leads to lower monomer concentration. In addition, the larger area of heat dispersion, the lower of self-heating temperature was [11].

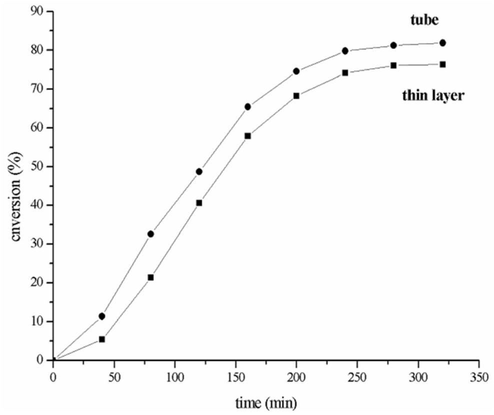

Fig.1 The conversion-time curves of the thin layer and tube polymerizations (water= 10ml, [SDS]/[HD]= 2:1 mol, [E]= 0.55mol.l^{-1},PVA= 0.1g, [I]= 0.198mol.l^{-1}, φ= 0.83, 30℃)

The effect of polymerization environment on the polymerization rate

Figure 2 plotted the conversion against time under different environment. Both polymerization rate and conversion of the thin layer polymerization in water bath was higher than that in the oven, while temperature remained constant. Since the efficiency of heat conduction in water bath was higher than that in the oven, and the accumulation of heat in the thin layer polymerization could be diffused by water, avoiding much more monomer loss and reducing the formation of bulk oligomers. In addition, monomer concentration was higher, which led to the increased polymerization rate, Therefore, the polymerization environment has remarkable effect on polymerization rate of concentrated emulsion.

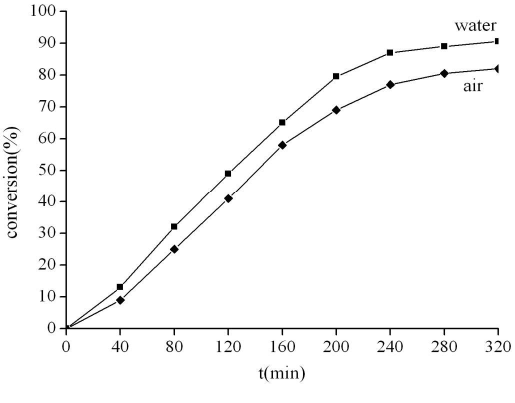

Fig.2 The effect of polymerization environment on the polymerization rate (water= 10ml, [SDS]/ [HD] = 2:1mol, [E] = 0.55mol.l^{-1}, PVA 0.1g, [I] = 0.296mol.l^{-1}, φ= 0.83, 30 ℃)

TEM images of the colloid particles of thin layer polymerization

Figure 3 presented the changes of the latex particle sizes and its distribution under different polymerization environments. According to the results of a previous paper [13], about 100 colloid particle sizes were measured, and the average size and standard deviation was calculated by PCS. It could be seen from figure 3 that, in the oven, the average size of the polymer colloid particles D_0 was 104.5nm and standard deviation d_0 was 14.6%; in the water bath, D_w was 92.4nm and standard deviation d_w was 8.9%. The results showed the average size and the distribution of colloid particle sizes were changed distinctly with polymerization environment. In contrast to polymerization in the oven, the average size and distribution of polymer particle sizes were both reduced in water bath. The reason might be that colloid particles grew in monomer cells, and the strength of liquid cell membranes was larger. Generally, monomers couldn't transfer easily at low temperature. However, the stability of system decreased at high temperature, where liquid cells coalesced easily [6]. Because the efficiency of heat conduction was higher in the water bath, the internal heat diffused easily during polymerization. In addition, the temperature generated by self-heating was low. Thus the concentrated emulsion was stable in the water bath.

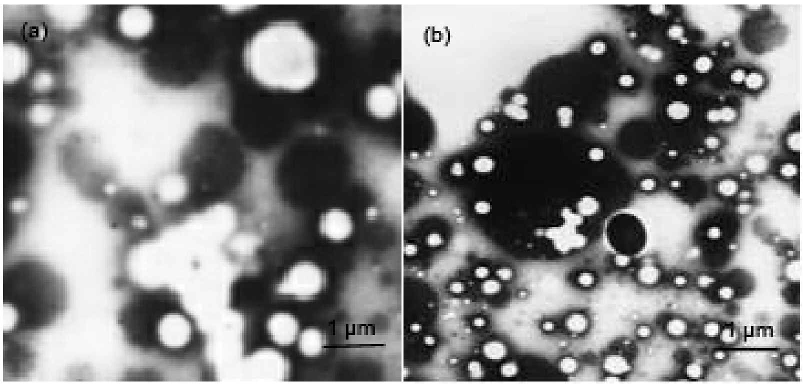

Fig. 3 TEM images at the different polymerization environment (×20,000): (a) oven, (b) water bath

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