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Computer simulation of surface tension for complex emulsion system

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The computer simulation of surface tension for the complex emulsion systems of polytetrafluoroethylene (PTFE) modified polyacrylate were carried out in this paper. A mathematical model was founded using statistical method.The effects of the components and their proportions have been discussed in detail. The surface tension of 21 samples have been simulated, and the error value of the simulation is 0.2–5.0%. The study results show that the mathematics model can accurately simulate the effects of the experimental parameters mentioned above on the surface tension.

KEY WORDS: emulsion, surface tension, computer simulation, polyacrylate, polytetrafluoroethylene (PTFE)

1. Introduction

Emulsion is an important disperse system because of its widely use in the field of energy resources, chemical engineering, foodstuff, etc. At present, the method of single factor turns was used to optimize the experimental conditions of the emulsion polymerization, which makes the recipe selection of emulsion become very complicated. The simulation has become a parallel way with the theoretical method. It has been used in the field of emulsion polymerization in recent years [1–3]. Bogeng Li et al. [4] had studied the modeling and simulation of semi-continuous emulsion polymerization. The surface tension as an important property of emulsion affects straightly the physical chemistry property of

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emulsion film. Under the simple and limited experimental conditions, a set of calculation methods about surface tension [5] have already been set up and used to predict the thermal balance modality of emulsion system. It has been reported that the surface tension of simple system was simulated [6–8] using molecule dynamics and numerical value method. Those simulation works can not simulate surface tension accurately because of the shortage of physical chemistry parameters and the neglect of subtle processes.

In the PTFE modified polyacrylate system, the surface tension of emulsion is related to the theoretic surface tension of polymer and monomer, the ratio of monomer and surfactant, the volume of water and the amount of the PTFE powder, also related to the property of the other additives in the emulsion system. In this paper, a statistics method has been adopted to set up a mathematic model of surface tension for PTFE modified polyacrylate system. It does not pay attention to the calculation of subtle complex thermodynamic process and submicroscopic process, but with a view to the statistic of experimental data. This mathematics model indicates the effect of polymer and monomer property, the dosage of monomer and water on surface tension of emulsion. Through compare the experimental value with computer value, there are the same changeable tendency of the surface tension with the change of the dosage of monomer and PTFE. The mathematics model can be responsible extrapolated to describe the surface tension of coatings materials.

2. Experimental

2.1. Main reagents and instruments

n-Methyl methacrylate (MMA), *n*-styrene (St), *n*-butyl acrylate (BA) were distilled and stored at 15°C. Sodium dodecyl sulfate (SDS), dodecyl polyoxy ethylene (OP-10) and fluorine–carbon surfactant ($C_{10}F_{19}OC_6H_4SO_3Na$) (6201) were of reagent-grade used as the surfactants without further purification. Ammonium persulfate was of reagent-grade. Polytetrafluoethylene (PTFE) power (2 μm) made in Shanghai of China was used as functional reagent. The water used was distilled following deionization.

American 410 Water GPC (USA), surface tension apparatus.

2.2. Emulsion preparation [9]

A typical example was prepared by emulsion polymerization as follows. The pre- emulsified PTFE were added to a four-necked jacketed glass reactor (500 ml) fitted with a reflux condenser and a nitrogen gas inlet tube. The distilled water, SDS, OP-10 and $NaHCO_3$ were added to the reactor. The stirring speed was 500 rpm for the following experiments. When the temperature was ramped to

50–60°C, about 10% (wt%) of the mixed monomers and 20% of the initiator with concentration 0.5–1.0% (20–40 ml) were fed into the reactor. The temperature was kept between 60 and 70°C until the mixture in the reactor appearing blue fluorescence. The appropriate dropping rate was kept without much circulation between 70 and 80°C until the monomers and initiator were completely added. Then the temperature was increased and kept it between 80 and 85°C for 1 h. The latex was cooled to room temperature and filtered through glass wool to remove coagulum. Finally the pH was adjusted to 6–7 with thick ammonia.

3. Foundation of the mathematical model

The surface tension is an important property for the emulsion and coatings, because it is related to the water endurance (water-fast property) and appearance of latex film. The factors effecting surface tension in the mathematical model are the species of monomer, the volume fraction of the mixed monomer, and the dosage of water and PTFE. The statistical results of the experimental datum indicate that the surface tension is not linear changing with the change of the dosage of water and PTFE but one approximate asymptotic, as shown in figure 1. During the model set up, the reason was considered that a great deal of water were added into the system, which can make the surface tension, therefore, the volume of water becomes the main effect factor of the surface tension of emulsion. But PTFE was added into the emulsion making the surface tension decrease. So the formula 1 was produced in this study. The premise of setting up the formula 1 is hypothesis that there is no change of reaction temperature and time with adding monomer and PTFE in the system. In the formula 1, C_1 represents the effect of the monomer volume fraction on the emulsion tension, C_2 represents the ratio of PTFE and emulsion, γ_0 is fundamental surface tension which represents the effect of quality and component of the mix monomer in the system.

$$\gamma = \gamma_0 \times c_1 + \gamma_{H_2O} \times (1 - c_1) \times \beta + \gamma_{H_2O} \times (1 - c_1)^2 \times \alpha - \gamma_{PTFE} \times \frac{c_2}{c_2 \times \zeta + \lambda} \tag{1}$$

The formula 2 (the former section of formula 1) represents the property of pure polyacrylate emulsion. Twenty kinds of emulsion composed of different monomer and volume fraction of monomer were prepared and the surface tension γ were determined. The data were used in the formula 2 respectively, which composed a set of equations, wherein, γ_{H_2O}, γ_0 and C_1 of every equation are known. So We can get the solution of $\alpha$and β from a set of equations.

$$\gamma = \gamma_0 \times c_1 + \gamma_{H_2O} \times (1 - c_1) \times \beta + \gamma_{H_2O} \times (1 - c_1)^2 \times \quad \alpha \tag{2}$$

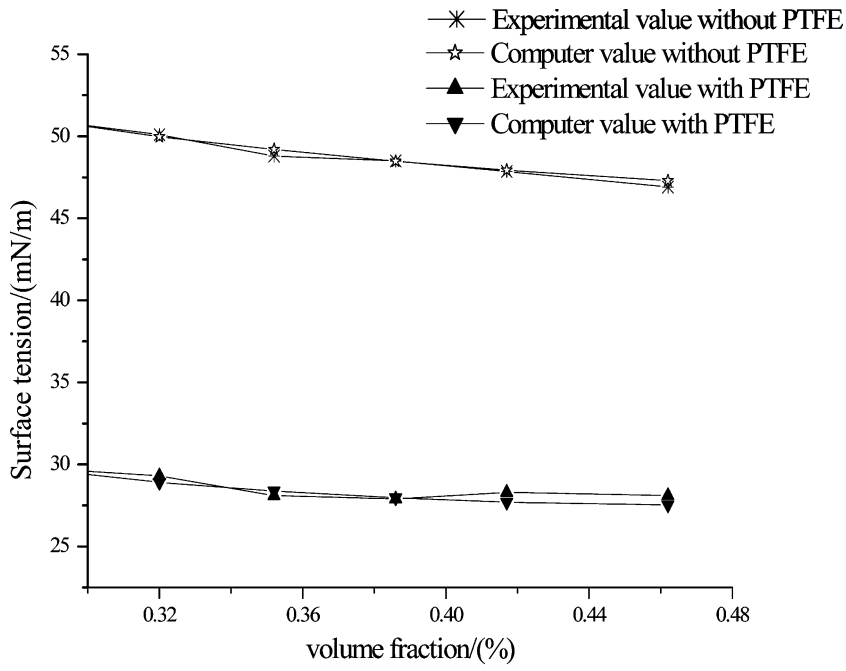

Figure 1. Effect of the monomers volume fraction on the surface tension.

On the other hand, from formula 1, we can get an equations group of the surface tension composed of 10 kinds of different amount of PTFE powder modified polyacrylate. And using the statistics analyzing method – least-square and iterative technique, the coefficient ζ and λ are obtained. In the formula 1, α, β, ζ, λ are correlated parameters, wherein $\alpha = 0.7239$, $\beta = 0.1542$, $\lambda = -1.0582$, $\zeta = 0.004685$.

4. Results and discussions

4.1. Selection for expressing way of γ_0

The group contribution methods and parachor methods have been used to estimate the surface tension of the simple system. In 1920s, Macleod [10] and Sugden [11] put forward the group contribution method and used it to estimate the parachor, and ulteriorly estimate surface tension. Because the high precision parameter was needed, its application was confined [12]. The surface tension of mix system, γ_0 can also be expressed similarly using the quartic rate of parachor (P) and molar volume (v) of atoms and structure in copolymer [13], $\gamma_0 = \left(\frac{P}{v}\right)^4$, wherein parachor P and molar volume V represent the total contribution of atoms and structure to the surface tension, viz.,

Table 1
Select of expression for γ_0.

Ratio of monomers A/B/C[a]	Parachor method γ_0 (mN/m)	Ratio of monomers A/B/C	Volume relationship Method γ_0 (mN/m)
18:10:5	45.3826	22:11:0	41.31
9:15:9	45.3836	21:11:1	50.94
18:5:10	45.3816	18:10:5	56.35
		20:10:3	54.41

[a]A −− butyl acrylate, B−−methyl methacrylate, C −− styrene.

$$p = \sum_{i=1}^{n} p_i \quad v = \sum_{i=1}^{n} v_i \tag{3}$$

In the formulas (3), it seems that the parachor method can reflect neither the effect of monomer nor monomer volume on the surface tension, because the value of P/V is almost a constant in any system.

Formula 1 shows that γ_0 is the fundamental parameter of the surface tension of emulsion, which reflects the effect of monomer. The surface tension of monomer is given in a chemical handbook, but it could not be used for the complicated emulsion systems. Experimental results show that γ_0 was related to the ter-roots of monomer volume fraction, so we put forward a method, volume relationship method, which the monomer volume involved in the calculating of γ_0, as shown in formula 4. Table 1 indicates that the calculation value of γ_0 using the volume relationship method is related to the ratio of monomers, while it is almost same using the parachor method.

$$\gamma_0 = \sum_{i=1}^{n} \gamma_i \left(\frac{\mathrm{V}_i}{\mathrm{V}_{\mathrm{total}}} \right)^{\frac{1}{3}} \tag{4}$$

4.2. *Effects of the volume fraction and amount of the monomers on surface tension*

The surface tension of emulsion mainly depends on the species and amount of monomers, dosage of water and the way of polymerization. Under the same synthetic method and experimental conditions, the effects of dosage of water and mixed monomers on the surface tension can be indicated by the changing the fraction volume of mixing monomers/emulsion (C_1) in this system. Pure polyacrylate and 6% PTFE modified polyacrylate emulsions were prepared with the different volume fraction of comonomers (a 18:10:5 BA:MMA:St ratio), 0.27, 0.29, 0.32, 0.35, 0.40, and the effect of C_1 in formula 1 was studied by comparing

Table 2
Effect of volume fraction on the surface tension.

Ratio monomers, A:B:C:D[a]	Experimental value, γ (mN/m)	Compute value, γ (mN/m)	Error (%)
22:11:0:70	46.1	45.17	2.0
21:11:1:70	48.1	48.25	0.3
20:10:3:70	49.0	49.36	0.7
18:10:5:70	52.5	52.47	−0.05

[a]A – butyl acrylate, B – perspex, C – styene, D – water.

surface tension of experimention with simulation. Figure 1 shows the surface tension of pure polyacrylate emulsion and 6% PTFE modified polyacrylate emulsion both decreases slight with the increasing of the monomer volume fraction. Nevertheless, the surface tension of pure polyacrylate emulsion is much higher than that of 6% PTFE modified. Meanwhile, Figure 1 shows that there is a same change tendency of the simulation value and experimental results. However, when surface tension was extrapolated to the utmost condition, $C_1 = 1$ (only monomer) and $C_1 = 0$ (no monomer), the simulation value is not apparently consisted with the experimental value. In fact, too large or small C_1 has already been beyond the range for the emulsion system. The reason is that the mathematics model (formula 1) is suitable for the condition of $C_1 = 0.23 - 0.4$.

4.3. *Effect of monomer components on surface tension of emulsion*

Formula 4 shows that γ_0 is related to ratios and amounts of the monomers. The simulation and experimental results of emulsion composed with different ratios of monomer (without PTEF) are given in table 2. The simulation error is less than 5% comparing with the experimental value.

4.4. *Effects of the amount of PTFE on emulsion tension*

Fluorine-containing polymers used in coatings have aroused much attention in recent years because of its attractive properties of hot-stability, hydrophobic and oleophobic ability and low surface energy. PTFE powder is emulsified by fluorine-carbon surfactant (6201) firstly. Through semi-starvation dripping method, acrylate monomers are added continuously to helical long carbon chain conformation of PTFE and the polymerization of acrylate monomer took place in it. A test of Gel Permeate Chromatography (GPC) indicates that the average molecular weight of PTFE modified polyacrylate emulsion become smaller and the distribution of molecular weight is more narrow with the increasing of amount of PTFE added, Table 3 showed the characteristic data of different film

Table 3
The characteristic data of different films.

	M_n^a	M_w^a	Polydispersity	R_t
Film of acrylate emulsion (a)	114,375	1,213,936	10.613605	7.323
Film of acryl ate emulsion modified				
By fluoropolymer (1)[b]	82,459	697,074	8.453595	7.508
By fluoropolymer (2)[b]	51,332	300,848	5.86880	7.799

[a] M_n is numerical average molecular weight and the M_w is weight average molecular weight.
[b](1), (2) represent 3 and 5 g fluoropolymer powder, respectively.

with GPC. The change of the molecular weight and size distribution will lead to change of the surface tension. The narrower the molecular weight distribution is, the more stable the emulsion is.

The change of the molecular weight and size distribution will lead to change of the surface tension. According to the experimental method, 3, 6, 9, 12 and 15% PTFE powder and the suitable dosage of acrylate are synthesized and determine on the surface tension of the emulsion, respectively. It can be explained as follows. Using semi-starvation dripping method, acrylate monomers are added continuously to helical long carbon chain conformation of PTFE. The polymerization of acrylate monomer took place in the spiral long carbon chains of PTFE, which can be much affected by spiral hindrance.

According to the experimental method, the emulsion of 3, 6, 9, 12 and 15% PTFE powder and the suitable dosage acrylate were synthesized respectively and the surface tension of the emulsion were determined. At the same time, we can predict the surface tension by formula 1. The results show in figure 2.

Figure 2 shows that the surface tension of emulsion will greatly decrease with PTFE added. There is the same trend between the predictive values and the experimental results determined with surface tension analysis instrument. Both experimental and simulation results have a very good coincidence with each other. When more than 6% fluoropolymer powder was added, the results of calculation appear slightly deviation. The reason is the gel appeared in the process of polymerization, which caused the loss of the drop fluoropolymer. Actually the dosage range of PTFE can be extended ulteriorly, if the operation of whole polymerization process is more carefully.

4.5. Relation between simulated and determined results

Twenty one kinds of different proportions of monomer and amount of PTFE emulsions were prepared and the surface tension was determined and simulated by formula 1. Figure 3 shows the relation between the experimental value and simulation value.

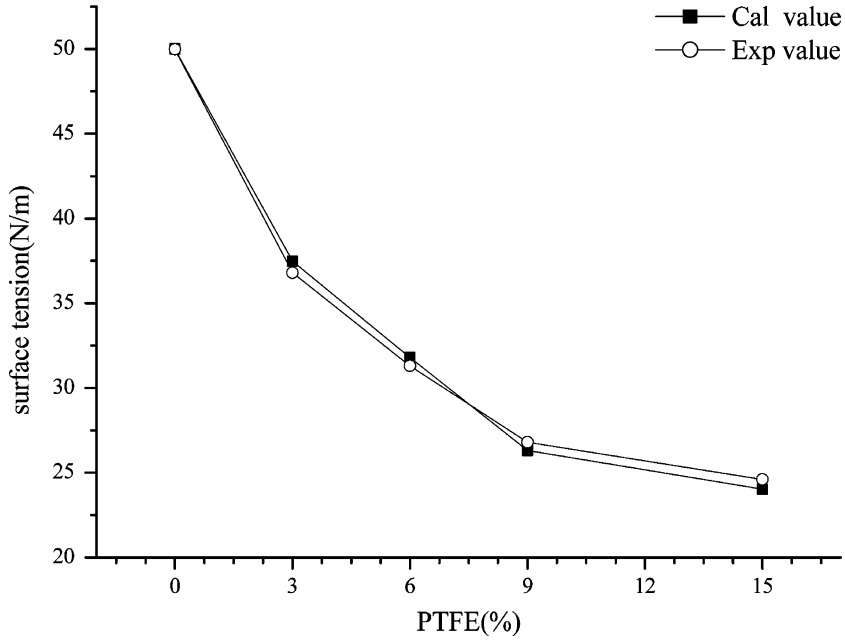

Figure 2. Effect of amount of PTFE on the surface tension.

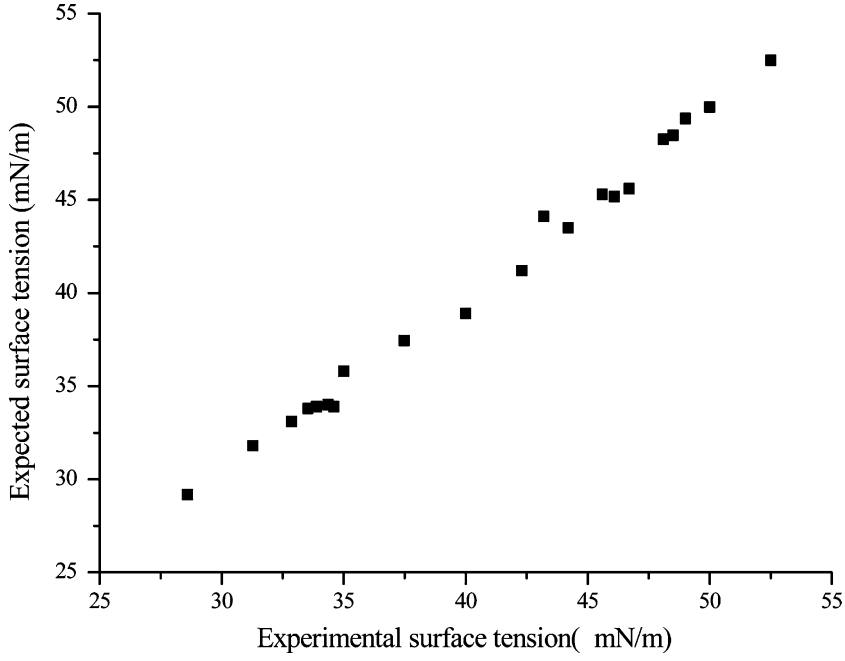

Figure 3. Relationship of surface tension between simulated and determined.

The results of both the determined and simulated value get well-coincidence with each other although they have a little destabilization phenomenon. When the amount of PTFE added was less than 3% in the emulsion system, both the simulation value and experimental value decreased, but it sharply decreased in between 3 and 10%. When PTFE was added more than 10%, the situation changed slowly.

5. Conclusion

A mathematical model to simulate the surface tension of emulsion was developed using statistics method in this paper. It does not pay attention to the calculation of subtle complex thermodynamic process and submicroscopic process, but with a view to the statistic of experimental data. The effects of the monomer, water and fluoropolymer, etc. on the surface tension were studied in the PTFE modified polyacrylate emulsion system. As a practical method, the surface tension predicted by the mathematics model presented in this paper can be used to predict other important property of emulsion film.

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