

Study on the Polymer Latex Agglomeration by Another Polymer Latex

LIUCHENG ZHANG,* YANQIU LIU, and ZHIQING LIU

Hebei Institute of Technology, Tianjin, People's Republic of China

SYNOPSIS

In this paper, the agglomeration of polymer latex that was caused by another latex was studied. The basic pattern and the factors affecting the agglomeration have been ascertained. Two agglomerating peaks appeared as the amount of added agglomeration latex increased. The agglomerating mechanism corresponding these two peaks has been proposed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Emulsion polymerization is an important technique in polymer production and multistage emulsion polymerization; particularly, the synthesis of latex interpenetration polymer networks (LIPN) has become one of the most active fields in emulsion polymerization application.¹ The properties of products produced by emulsion polymerization depend on the latex particle size and its distribution. For instance, the ABS resin synthesized by multistage emulsion polymerization has the best properties when the rubber latex particle diameter is between 0.3 and 0.7 μ .² However, it is difficult to obtain latex particles having a mean diameter of not less than 0.2 μ by the usual emulsion polymerization process, which generally gives latex particles in the size range 0.04–0.15 μ . Thus, for the particle application, an effective method is required to increase the initial latex particle size to the desired size. Generally speaking, there are two processes for producing large particles. These are

- (i) agglomeration of the latex particle during the course of polymerization, and
- (ii) agglomeration of the latex system having a small particle size by posttreatment.

In this paper, the term “agglomeration” means the process that changes stable latex having small particles into another stable latex having larger particles by using postpolymerization treatments including physical or/and chemical ones. The early agglomeration can be classified into two processes: one is carried out under the action of physical factors such as freezing and pressure gradient^{3,4}; the other is under the action of chemical agents such as inorganic salts^{5,6} or organic chemicals, e.g., benzene, methylbenzene, acetone, and hydrophilic polymers, such as polyurethanes, hydroxyethyl cellulose, and polyvinyl acetals. But those techniques have significant disadvantages, such as a high energy consumption, a rather low limit of the maximum size of the agglomerated latex particles, difficulties in controlling and reproducing the agglomerated latex particle diameters, and high quantities of coagulum. In recent years, it has been reported in the patent literature that one polymer, latex A (to be agglomerated latex), can be agglomerated by adding another polymer, latex B (called agglomerating latex), so that the latex particle size was increased. This method is economical, reliable, and effective and has been used in the production of impact resins.^{2,7–11} But the mechanism and the characteristics of this agglomerating process have not been reported in the literature; therefore, in this paper, the behavior and the mechanism of the agglomeration was studied using poly(*n*-butyl acrylate) as the agglomerated latex A and *n*-butyl acrylate–acrylic acid copolymer as the agglomerating latex B, based on the inter-

* To whom correspondence should be addressed.

action between hydrophilic free polymer and polymer latex.¹²⁻¹⁹

In a dilute solution of polymers, because of the volume restriction effect of the polymer chains, the chain segment density is smaller near the inert surface than that in the bulk solution¹⁵; this is called the depletion effect. The simplest pattern of this theory can be described as follows: Consider that there are two inert flat plates immersed in a polymer solution; suppose the segment density is uniform through the whole solution and the distance between the two flat plates is D and the diameter of solute macromolecule is d ; then, three domains that closely approach a parallel flat plate in a polymer solution can be identified: (1) when $D \geq 2d$, the chain segment densities between and outside the plates are the same, so there is no free-energy change accompanying this process; (2) when $d \leq D < 2d$, the segment density between the plates is everywhere less than the bulk value owing to the volume restrictive effect; (3) when $D < d$, there is no polymer left between the plates. As D decreases in this region, the free energy of the system falls because the solvent is excluded from between the plates and this process has a negative free energy of mixing (dilution) with the bulk solution outside the plates. Consider the approach of two surfaces in the domain $d \leq D < 2d$; suppose the polymer concentrations between and outside the plates are v_2 and v_2' (volume fraction), respectively; then, according to the Flory-Huggins theory, the free-energy change, ΔG_s , is given by²⁰

$$\Delta G_s = (KT/V_1)\delta V\left(\frac{1}{2} - x_1\right) \times [f(1-f)](v_2 - v_2')^2 \quad (1)$$

where v_1 is the volume of a solvent molecule; x_1 , the Flory-Huggins interaction parameter; k and T , Boltzmann constant and absolute temperature, respectively; δV , a volume element initially containing polymer volume fraction v_2 ; and f , a constant that is greater than zero and less than 1. Thus, ΔG_s is positive provided that $(\frac{1}{2} - x_1) > 0$.

If the plates given above are replaced by two inert spheres, for instance, two latex particles, the basic pattern is the same. Typical potential energy curves for the close approach of two parallel plates (curve a) and of two spheres (curve b) in a polymer solution are shown in Figure 1. In summary, the free-energy change is positive for $d \leq D < 2d$; there is a free-energy maximum ΔG_{\max} at $D = d$; when $D < d$, the free-energy change is negative and there is a mini-

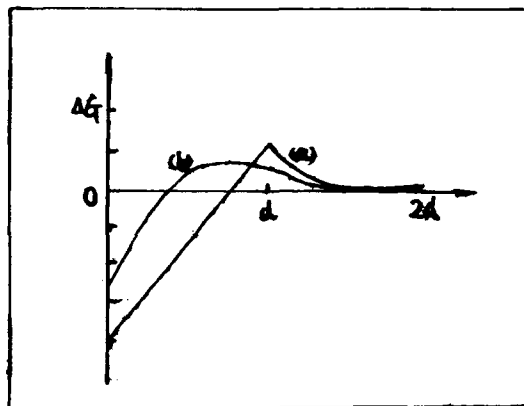


Figure 1 The distance dependence of the change in free energy resulting from the free polymer in the dispersion medium: (a) parallel flat plates; (b) spheres.

mum ΔG_{\min} near to $D = 0$. The agglomeration stems from this ΔG_{\min} .

From eq. (1), it can be seen that the free-energy change, ΔG_s , in magnitude is proportional to the square of the difference in the polymer concentration between the plates and that in the bulk phase. As the polymer concentration is increased, both ΔG_{\max} and $|\Delta G_{\min}|$ increased. At some critical concentration C , G_{\min} will be sufficiently negative to induce agglomeration and result in the increase of the latex particle size. It should be noticed that $|\Delta G_{\min}|$ increases more rapidly than does ΔG_{\max} because $(v_2 - v_2')^2 \approx v_2'^2$ for ΔG_{\min} and $(v_2 - v_2') < v_2'^2$ for ΔG_{\max} . As a result, ΔG_{\max} at C_1 is generally still too small to prevent the latex from agglomeration. A further addition of polymer would be expected to increase ΔG_{\max} , so that at some larger critical polymer concentration C_{11} , stability will be imparted, those are the contents of the mechanism of volume restriction for dilute solutions of hydrophilic polymers. When there are other interactions in the polymer solution, e.g., the absorption of polymer chains on the surface of the latex articles, the above-mentioned basic pattern does not change.^{14,7-19} Certainly, when those interactions in the polymer solution are very intensive, the volume restriction effect may become secondary.

The investigations also showed that the larger the molecular weight and dissymmetry of macromolecules, the smaller the value of C_1 for the agglomeration resulting from the volume restriction effect discussed above. Another important mechanism of agglomeration for the free polymer in the polymeric latex is the "bridging effect,"^{12,13} which considers that the free polymer chains in the latex can be ab-

sorbed by several latex particles. The agglomeration becomes intense with the increase of the polymer concentration and takes a maximum value at some polymer concentration.¹⁴ It has been shown by Asakura¹⁵ that under suitable conditions the free energy of the agglomerating system as a function of polymer concentration may have two minimum points: one is caused by the volume restriction effect and the other is caused by the bridging effect.

Based on the above viewpoints, this paper explores the agglomeration mechanism of the latex system used in our work.

EXPERIMENTAL

1. Materials

n-Butyl acrylate (*n*-BA): chemically pure, distilled under vacuum and stored at -10°C . Methyl methacrylate (MMA): chemically pure, distilled under vacuum and stored at -10°C . Ethylene glycol dimethacrylate (EGDM): distilled under vacuum and stored at -10°C . Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) and sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$): all chemically pure. Acrylic acid (AA): chemically pure, distilled under vacuum. Sodium dodecyl benzene sulfonate (SDBS): $> 97\%$ pure.

2. Preparation of Latex (B)

Distilled water, 80 mL, 0.35 g of SDBS, 0.1 g of $\text{K}_2\text{S}_2\text{O}_8$, and a specified amount of *n*-BA (see Table I) was charged into a 500 mL four-neck flask and heated to 70°C under nitrogen. The polymerization was carried out over 2 h; then, in the second stage,

Table I Amount of *n*-BA in the First Stage Polymerization and the Composition and Amount of Monomer Mixtures in the Second-stage Polymerization

No.	<i>n</i> -BA (g) in First Stage	<i>n</i> -BA (g) (in Second Stage)	AA (g) (in First Stage)	AA (g) (in Second Stage)
1	10	21.2	0	0
2	10	20.0	0	1.2
3	10	18.8	0	2.4
4	10	15.0	0	4.0
5	10	20.0	0	6.0
6	10	13.2	0	8.0

the monomer mixture (*n*-BA + AA) and 0.1 g of $\text{K}_2\text{S}_2\text{O}_8$ was dropped in 30 min, followed by maintaining it for 3 h at 70°C .

3. Preparation of Latex (A)

Distilled water, 250 mL, 1.0 g of SDBS, 87.5 g of *n*-BA, 3.5 g of EGDM, 0.4 g of $\text{K}_2\text{S}_2\text{O}_8$, and 1.0 g of sodium tetraborate was charged into a 1000 mL four-neck flask and heated to 75°C under nitrogen; the polymerization was carried out over 3 h at 75°C .

4. Agglomerating Process

A definite quantity of the agglomerating latex (B) was added to a fixed quantity of latex A under agitation at room temperature (25°C) for 30 min; then sample is removed for examination. The sodium tetraborate was used to adjust the pH value of the latex.

5. Measurement of Viscosity and Surface Tension

A rotational viscosimeter and an Engler viscosimeter were employed to measure the polymer latex viscosity. The surface tension was measured by the bubble pressure method at $25 \pm 0.1^{\circ}\text{C}$.

6. Measurement of Particle Diameter

The latex particle diameter was measured by UV-3000 ultraviolet spectroscopy and distribution of particle diameter was measured by an H-600 transmission electron microscopy and an IBAST/II image analyzer.

RESULTS AND DISCUSSION

1. Latex Particle Diameter and Its Distribution

Varied amounts of latex B were charged into the same quantity of latex A and the mixture was subjected to agitation for 30 min. Samples were removed and the agglomerated latex particle diameter was measured. Let *R* stand for the percentage weight of the solid component of latex B and latex A. The average latex particle diameter of the aggregated latex particles as function of *R* is shown in Figure 2. The figure indicates that the average particle diameter has two maximum values (two peaks) with increasing *R*. The first peak is at $R = 1\text{--}2\%$, which

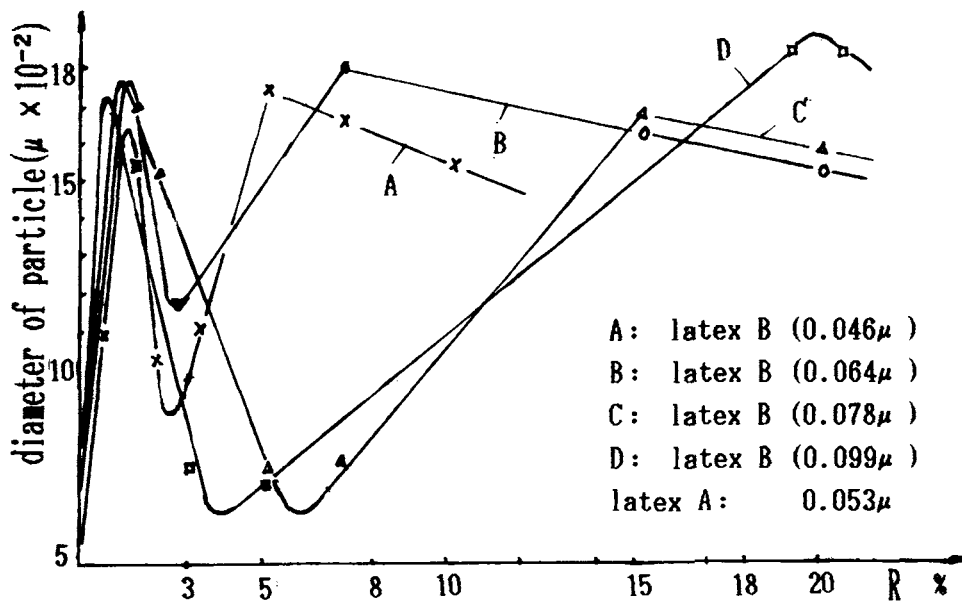


Figure 2 Dependence of the average diameter of the aggregated particles on *R*.

is consistent with Ref. 2. The second peak is in the range of higher *R*, which has not been reported earlier. The position of the peaks depends on the particle diameter of latexes A and B. For the same latex A, *R* corresponding to the first peak decreases as the particle diameter of latex (B) increases; on the contrary, the *R* corresponding to the second peak increases as the particle diameter of latex (B) increases (see Fig. 2). Thus, the two peaks approach each other as the particle diameter of latex B decreases.

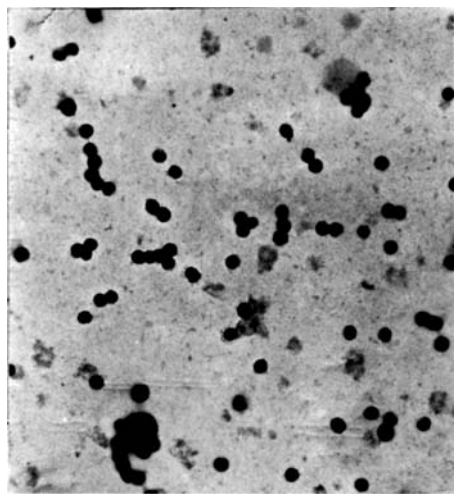


Figure 3 TEM of the agglomerated latex particles at the first peak.

The distribution width of particle diameter defined by Hansion²¹ follows:

Distribution width index D_w^-/D_n^-

$$= [\sum NiDi^4 / \sum NiDi^3] / (\sum NiDi / \sum Ni)$$

where D_n and D_w stand for number-average diameter and weight-average diameter, respectively, and N_i and D_i stand for the number and diameter of the particle i , respectively.

Figure 2 shows that the particle diameter distribution is narrower at the first peak ($R = 1.5\%$) than at the second peak after agglomeration. The distribution width is 1.0689 at the first peak and 1.1998 at the second peak (Figs. 3-6).

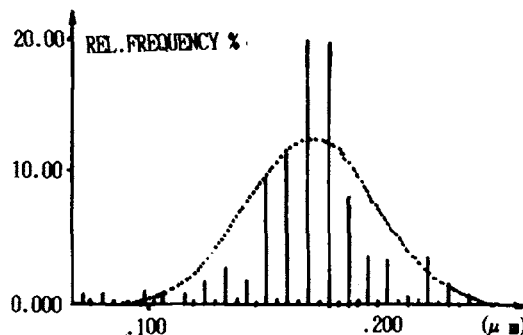


Figure 4 Particle diameter distribution at the first peak ($R = 1.5\%$).

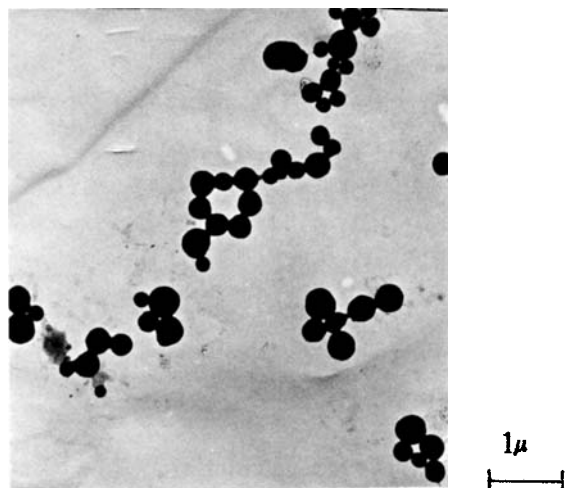


Figure 5 TEM of the agglomerated latex particles at the second peak.

2. Influence of pH Value and Polymer Hydrophilicity on the Agglomeration

It has been shown by our experimental results that the latex particle diameter after agglomeration increases with increasing pH, when maintaining all other conditions unchanged. The influence of pH on the agglomerated latex particle diameter is shown in Figure 7.

The polymer hydrophilicity can be expressed in terms of water absorption of polymers: The larger the water-absorption value of the polymer, the stronger the polymer hydrophilicity. For the same agglomerating latex B, the weaker is the hydrophilicity of the polymer in latex A, the larger should be the agglomerated latex particle diameter. For instance, the water-absorption values of PMMA and P(*n*-BA) are 0.1574 and 0.0105 (relative unit), respectively; under the same conditions, the agglom-

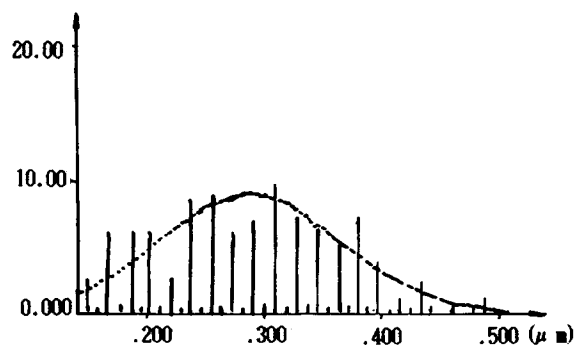


Figure 6 Particle diameter distribution at the second peak ($R = 15\%$).

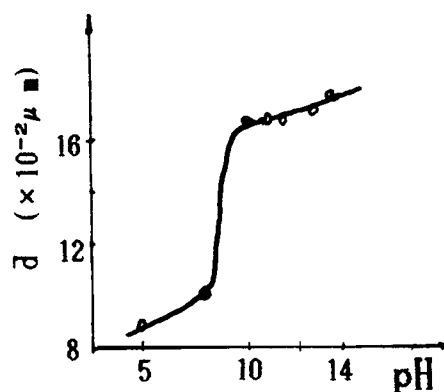


Figure 7 The influence of pH value on the agglomerated particle diameter. Particle diameter: 0.053 (latex A); 0.064 (latex B); $R = 1.5\%$.

erated latex particle diameters are 0.046 and 0.177, respectively.

3. Influence of Inorganic Salt on Agglomeration

By adding a small amount of inorganic salt into the agglomerating system, the agglomeration speed is enhanced. For instance, the agglomeration would reach its equilibrium in 20 min if a small amount of NaCl is added; otherwise, the agglomeration equilibrium state is not reached within 24 h in the absence of salt. However, excessive salt is not desirable because it causes macrocoagulation.

4. Agglomeration Mechanism

At least for the agglomerating system used in this paper, the agglomeration can be explained based on the agglomeration mechanism caused by the free macromolecules in the polymer latex. Apart from the experimental results mentioned above, there are at least two reasons to suggest the proposed mechanism: (1) The latex particles of the agglomerating latex B contain polyacrylic acid or copolyacrylic acid chains on their outer layers, which consist of highly hydrophilic carboxy groups. According to the theory of polymer solution, it is reasonable to believe that the polyacrylic acid or the copolymer (*n*-BA/AA) chains stretch into the water phase as shown in Figure 8. (2) The diameter of the particles of the agglomerating latex B (0.05–0.09 μ) and of the macromolecule (e.g., hydroxyethyl cellulose) (0.07–0.22 μ) are in the same order of magnitude. So, to regard this kind of latex particle as a macromolecule is rea-

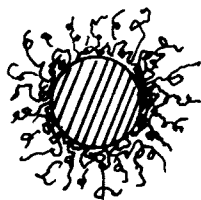


Figure 8 The morphology of latex B particles in water.

sonable. In fact, by increasing the value of the pH of the agglomerating system, the agglomeration becomes even more effective (see Fig. 7); this stems from increasing the degree of dissociation of carboxy groups and enhancing the chain extension.

We propose that the first agglomerating peak is caused by the "volume restriction effect." In fact, the position of the first agglomerating peak shifts forward with increasing particle diameter of the latex B, as shown in Figure 2. This is similar to agglomeration of the polymer latex by free macromolecules, i.e., the value of C decreases with increasing macromolecules. After the first peak, the agglomerated latex particle diameter decreases with further addition of latex B. This stems from that the activation energy of the agglomeration is too large to cause agglomeration.

The agglomeration model is described as follows: When the particles of latexes A and B approach each other due to Brownian motion, the segment between the two particles will be squeezed out owing to the volume restriction effect; this results in a depletion region between the two particles. A further approach occurs spontaneously because of the "osmotic effect" and, finally, the two particles adhere together. At the same time, a part of the polyacrylic acid and copolyacrylic acid chains shift to the surfaces of the particles of latex A, on which the agglomerations also occur between particles of latex A or between particles of latexes B and A; as a result, a small amount of latex B can cause a big increase in the

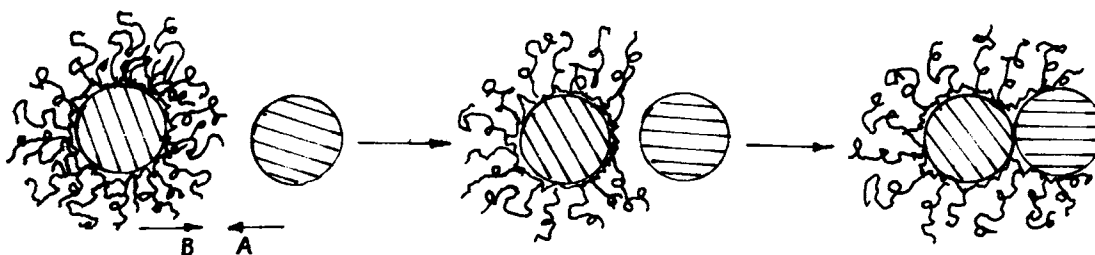


Figure 9 Sketch of the agglomerating process at the first peak.

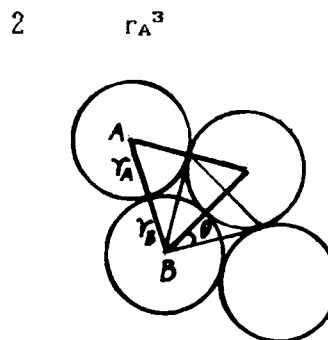


Figure 10 The calculation of coordination number n .

particle diameter after agglomeration. The process is shown in Figure 9. Of course, there is a small segment buried that lost its agglomerating effect in the agglomerating process.

For the second agglomerating peak, the determining factor for the agglomerating process is the bridging effect. For the system studied in this paper, the bridging mechanism indicates that the bridging agglomeration will demand a matched effect between particles of latexes B and A; nearly a particle of latex B should agglomerate with a fixed number of particles of latex A. We can consider that the first step is the close packing of particles of latex A which come near the surfaces of the latex B particles through the bridging of the polyacrylic acid chains, and the second step is the adjustment and rearrangement of the segments of polyacrylic acid or copolyacrylic acid chain, coherence of the latex particles, and formation new agglomerated latex particles.

Suppose r_A and r_B stand for the radii of latexes A and B, respectively; the coordination number n can then be calculated from Figure 10:

$$n = 2 / (1 - \cos \theta) \quad (2)$$

where $\theta = \arcsin[r_A / (r_A + r_B)]$.

Table II The Positions of the Second Agglomerating Peak^a

	Particle Diameter of Latex (B) (μ)			
	0.046	0.064	0.078	0.099
R_{11} (calculated value) (%)	5.080	9.550	13.63	20.45
R_{11} (experimental value) (%)	5.0	7.0	15.0	20.0

^a The particle diameter of latex A is 0.053.

The R in the second agglomerating peak can be given by eq. (3):

$$R = \left(\frac{1 - \cos}{2} \right) \left(\frac{100r_B^3}{r_A^3} \right) \quad (3)$$

The experimental and calculated values of R are shown in Table II. Table II indicates that the experimental results approximately accord with the theoretical results.

The experiments also indicate that the viscosity of system in this paper rapidly increases near the second peak (see Fig. 11) and then decreases. At the same time, the surface tension rapidly decreases (see Fig. 12). These phenomena stem from the formation of the network structure by the bridging effect. The further increasing of R will lead to the destruction of the network structure, so the viscosity is decreased.

As mentioned above, with the increasing of the latex B particle diameter, the position of the first peak shifts forward, and the second peak, backward.

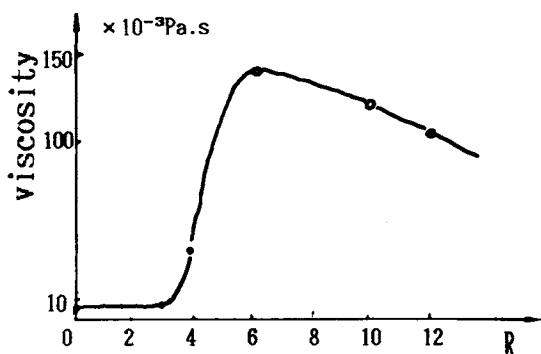


Figure 11 The viscosity of the system as a function of R , the particle diameters of latexes A and B are 0.053 and 0.065 μ , respectively; the position of second agglomerating peak is $R = 7.0\%$.

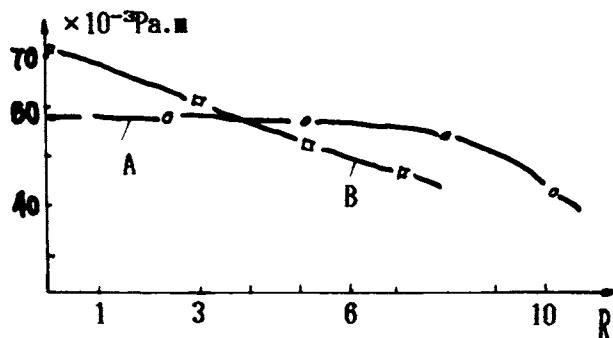


Figure 12 Dependence of the surface tension on the value of R . (A) System of latexes A and B; R = percentage weight ratio of the solid component of latex B with latex A. (B) System of latex B and water; R = percentage weight ratio of solid component of latex B and weight of water.

The dependent pattern of viscosity and surface tension on the value of R in the region adjacent to the second peak is different from that in the region adjacent to the first peak. Therefore, the agglomerating mechanism in the two peaks is also distinct. But it is astonishing that the average particle diameters corresponding to two agglomerating peaks are almost the same.

CONCLUSIONS

1. For the agglomerating system used in this paper, there are two agglomerating peaks, corresponding to that the particle diameters are almost the same and that the two peaks approach each other with the decrease of the latex B particle diameter.
2. It can be drawn out qualitatively that the main action for the first agglomerating peak is the volume restriction effect of the chain segments and the main factor determining the agglomerating process is the bridging effect for the second agglomerating peak.

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