Particle Size as it Relates to the Minimum Film Formation Temperature of Latices

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SYNOPSIS

The relationship between the particle sizes and minimum film formation temperature (MFT) of polymer colloids was studied. Early workers had developed theoretical models predicting small particle colloids should coalesce easier and have lower MFTs than those of large colloids. Early published work examining this question reported that MFT was independent of particle size. In 1990, Eckersley and Rudin, using monodisperse acrylic latexes ranging from 148–1234 nm, reported finding that MFT was a function of particle size as predicted.

We synthesized a series of monodisperse acrylic copolymer latexes ranging from 63–458 nm and measured MFTs of these latexes and blends of them. We have also found particle size does affect MFT with small particle polymer colloids having lower MFTs than larger ones. Our results differ somewhat in that the MFTs of our latexes are below the glass transition temperatures (T_g) of the polymers while Eckersley et al. report MFTs above T_g.

INTRODUCTION

The film formation process of emulsion copolymers is obviously of great importance. This paper shows the relationship between the particle size of an emulsion copolymer system and the minimum temperature at which a continuous film will form from the latex. The minimum film formation temperature (MFT) is a tool commonly used in the coating industry. In emulsion systems, a continuous film forms when the polymer particles become coalesced.

To understand film formation, it is essential to have an understanding of particle coalescence. An early attempt to devise a mechanism for latex film formation was developed by Dillon, Matheson, and Bradford in 1951.[1] They postulated that polymer latex particle surface forces such as surface tension drive particles to coalesce. They applied the model developed by Frenkel[2] in 1945 to describe the coalescence of spheres by viscous flow. This model is represented by eq. (1).

$$\Theta^2 = 3\gamma t/2\pi r\eta, \tag{1}$$
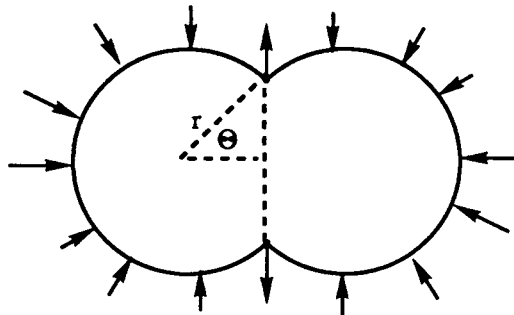
where γ = surface tension, t = time, r = particle radius, and η = viscosity of the polymer comprising the latex particles.

From eq. (1), it is obvious that as coalescence proceeds the half-angle of coalescence, Θ, increases with increasing surface tension and time and decreases with increasing particle size and particle viscosity. Above the T_g the particle viscosity, η, of linear polymers is a function of molecular weight and temperature. Since γ and t do not vary from particle to particle in any given emulsion, the particle radius, r, is the key variable. Therefore, one can expect particle size to have an effect on film formation.

Dillon et al.[1] and Brown[3] disagreed whether surface tension or capillary forces provided the main

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Table I   Monomers Used in Emulsion Polymerizations

Monomer	Abbreviation	Inhibitor Level	Source
Methyl methacrylate	(MMA)	60 ppm HQ	Rohm and Haas
Ethyl acrylate	(EA)	200 ppm MeHQ	Union Carbide
Methacrylic acid	(MMA)	200 ppm MeHQ	Rohm and Haas

HQ, hydroquinone; MeHQ, monomethyl ether of hydroquinone.

driving force for particle coalescence. Though different in mechanisms, their proposed models both suggest that small particles should more readily coalesce than large ones.

Eckersley et al.[4] reviewed the theoretical models of film formation and concluded that models based solely on a capillary driving force are inadequate to describe the film formation phenomenon because films are more highly coalesced than predicted. They proposed a model where interfacial tension forces act with the capillary force to cause film coalescence.

Brodnyan and Konen[5] appear to be the only other published workers who have examined the particle size to MFT relationship experimentally. They concluded that MFT appeared to be independent of particle size. They saw some differences, but because of the magnitude of the random error in their MFT measurements they could not obtain any significant relationship of MFT and particle size. The emulsion polymers they used in their study had very fine particle sizes but very broad distributions. We felt the breadth of their particle size distributions may have masked the expected relationships and so we chose to conduct our study with monodisperse latexes.

EXPERIMENTAL

Materials

Polymerization-grade monomers were used without further purification as shown in Table I.

The only emulsifier used was sodium lauryl sulfate. This was a dental grade from Onyx Chemical Corporation and was used as received. Reagent grade ammonium persulfate (APS) from Mallinckrodt Inc. was used as the initiator in all experiments. Water was deionized by passage through a mixed bed ion exchange column.

PREPARATION OF EMULSION POLYMERS

In Situ Seed Emulsion (R1)

The emulsion polymerization procedure used for the in situ seeded emulsion, R1, was as follows: 4.0 g

sodium lauryl sulfate (.5 wt % based on total monomer weight) was added to 1065 g deionized water in a stirred, 3-L, 4-neck glass reactor. The reactor was then heated to 80°C under a nitrogen atmosphere. Immediately after the addition of 80.0 g monomer solution (10% of the total), 2.0 g APS dissolved in 120 g deionized water (.25 wt % based on monomers) was added. The total monomer solution contained 400 g MMA (50 wt %), 376 g EA (47 wt %), and 24 g MAA (3 wt %). A 10-min reaction period followed, during which in situ seed particles formed. The remaining 90% of the monomer solution was metered into the reactor over 60 min concurrent with a separate metering of 308 g deionized water. The reaction was held at 80°C for 60 min after the completion of the monomer and water additions. The polymer was filtered through four layers of cheesecloth. The observed nonvolatile of the final polymer was 34.5% (35.0 theoretical), indicating 98.6% conversion.

Seeded Emulsion Polymerization

The general procedure for the seeded emulsion polymerizations was a batch procedure (Table II). The seed polymer and all but 100 g deionized water were added to a stirred, 1-L glass reactor. The reactor was heated to 80°C under a nitrogen atmosphere. A monomer solution of 50 wt % MMA, 47 wt % EA, and 3 wt % MAA was then added. The initiator was dissolved in the withheld water (.25 wt % APS based

Table II   Seeded Emulsion Polymerizations

Seeded Latex	R7	R5	R48
g MMA	100	100	100
g EA	94	94	94
g MAA	6	6	6
g APS	0.5	0.5	0.5
g R1 seed latex	58	29	—
g R5 seed latex	—	—	161
g Deionized water	622	612	599
% Theoretical nonvolatile	25.0	25.0	25.0
% Observed nonvolatile	25.1	24.8	24.9
% Conversion	100	99.2	99.6

Table III   Seed Polymers and Monomer : Seed Polymer Ratios

Ref. No.	Seed Polymer	Monomer : Seed Ratio
R7	R1	10 : 1
R5	R1	20 : 1
R48	R5	5 : 1

on the total monomer weight) and was then added to the reactor. Diluting the initiator helps to minimize the electrolyte effect, which can cause coagulation of the seed polymer. The reaction was held at 80°C for 1 h, cooled, and filtered through cheesecloth.

Different sizes of seed particles and different ratios of monomer to seed were used to achieve the desired particle sizes (Table III).

Emulsion Characterization

Particle size measurements were determined by transmission electron microscopy (TEM).

Molecular Weights

Molecular weights were obtained via gel permeation chromatography (GPC). This was done to make sure there were no large differences in molecular weights that could have an effect on the MFT. Mo-

lecular weights were all quite high and in the range where T_g is not influenced by molecular weight.

T_g

T_gs were obtained using a Perkin–Elmer DSC-7. Conditions were:

Pan: closed pan
Temp. range: 263–343°K
Heating rate: 20°/min
Runs: 4–6 runs/sample
Sample prep: latex air dried 48 h at 30°C; each pan heated to 413°K for 2 min prior to loading
T_g value: onset value in °C

MFT

Minimum film formation temperatures were determined using an aluminum bar with sample channels milled into the surface. The sample channels are 17.1 in long, 1 in wide, and .06 in deep. Under one end of the bar is a heat source and under the other end of the bar is a cooling device. An equilibrium temperature gradient is established over the entire length of the bar. The MFTs were run on samples diluted to 15.0% nonvolatile. Three milliliters of sample were spread evenly over the entire length of the channel. The bar was then covered with a plastic lid equipped with a nitrogen inlet. A gentle flow of nitrogen was passed over the bar to minimize and

Table IV   Summary of Properties of Emulsion Copolymers

Emulsion Number	Particle Diameter (nm)	Particle Polydispersity	Mn Mw Mz	T_g (°C)	MFT (°C)
R1	63	1.16	300,000 945,000 1,635,000	37	26
R7	147	1.04	590,000 1,040,000 1,475,000	40	30
R5	305	1.03	372,000 920,000 1,450,000	37	34
R48	458	1.01	438,000 895,000 1,335,000	39	36

Blends Results		
75% R1 + 25% R48	27	
65% R1 + 35% R48	29	
50% R1 + 50% R48	32	
35% R1 + 65% R48	33	
25% R1 + 75% R48	34	

average any effects of humidity. Once the entire sample had dried, the MFT was measured using an Omega 450 AET thermocouple with a surface probe. All MFT measurements were replicated four times and reproduced within ± 0.5°C. The MFT is that readily discernible point in a well-coalesced and continuous film below which there is appreciable change in film integrity as observed by cracking, cohesional, and adhesional failure.

Blends

In addition to examining the MFT of individual monodisperse particles, the large particle size emulsions were blended with small particle size ones and the MFTs measured.

DISCUSSION

The copolymerization procedures used were quite successful in producing the desired monodisperse copolymers emulsion. Our broadest distribution was the very fine particle size *in situ* seed R1. While the polydispersity in this case was larger (1.16) than one would desire for particle size standards, it was quite small for emulsions of such fine particle size and certainly adequate for our comparative needs and for use as a seed emulsion polymer for other latexes. The seeded latexes all were quite monodisperse with polydispersities less than 1.05. This and other data are summarized in Table IV.

Polymer glass transition temperatures were ob-

tained on air-dried samples of the latexes. This data was obtained so that if any unexpected heterogeneity arose during synthesis we would not mistakenly attribute it to the MFT/particle size effect.

T_g variations were small (38.5 ± 1.5°C) and not considered significant. We expected that the MFTs of latexes would be slightly above the T_g of the polymers if there were no additional forces acting to cause particles to coalesce. If there were additional significant forces, then the MFTs could be below the T_g. We found that all MFTs were below the T_g and approached the T_g as the particle size increased, indicating the surface and capillary forces were significant.[6] The MFT data for the monodisperse polymers is shown in Figure 1.

Our finding that the MFTs were less than the T_g is in contrast to the results obtained by Eckersley[4] and Rudin, who reported working with a polymer with a T_g of 5.8°C and an MFT range from 11.5–16.4°C. Our polymer T_g was 38.5°C and our MFTs ranged from 26–36°C (as much as 12.5°C less than T_g). We speculate this difference could be attributed to the fact that our polymers were linear (i.e., soluble in the solvent used for GPC molecular weight measurement) and Eckersley et al. report their polymer to be too crosslinked to be measured by GPC. We would expect crosslinked particles to be much more resistant to coalescence and hence have higher MFTs.

The blends of the 458- and 63-nm latexes demonstrated that as little as 25 wt % of the smaller particles was sufficient to reduce the MFT by 2°C.
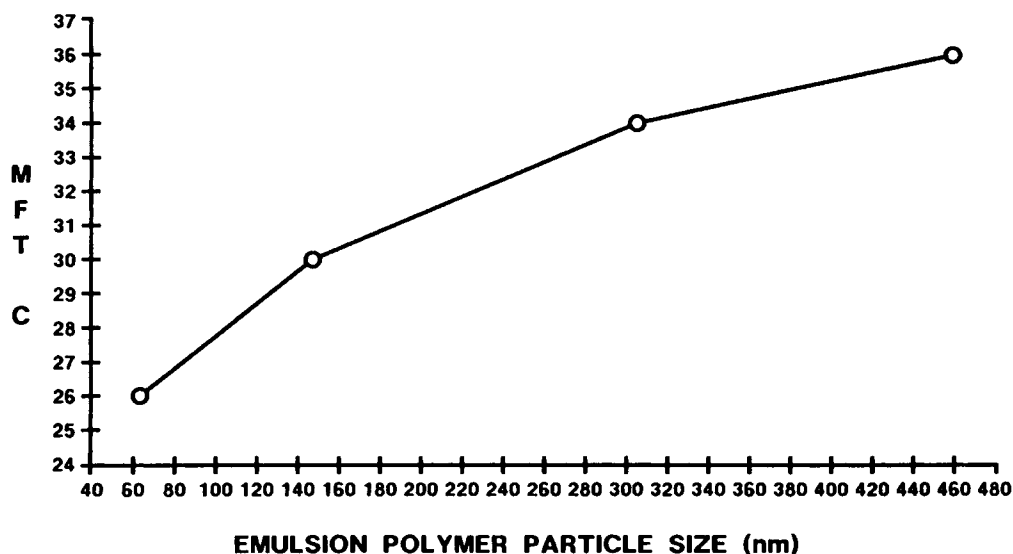

Figure 1 Minimum film formation temperatures (MFT) versus particle size of monodisperse emulsion polymers
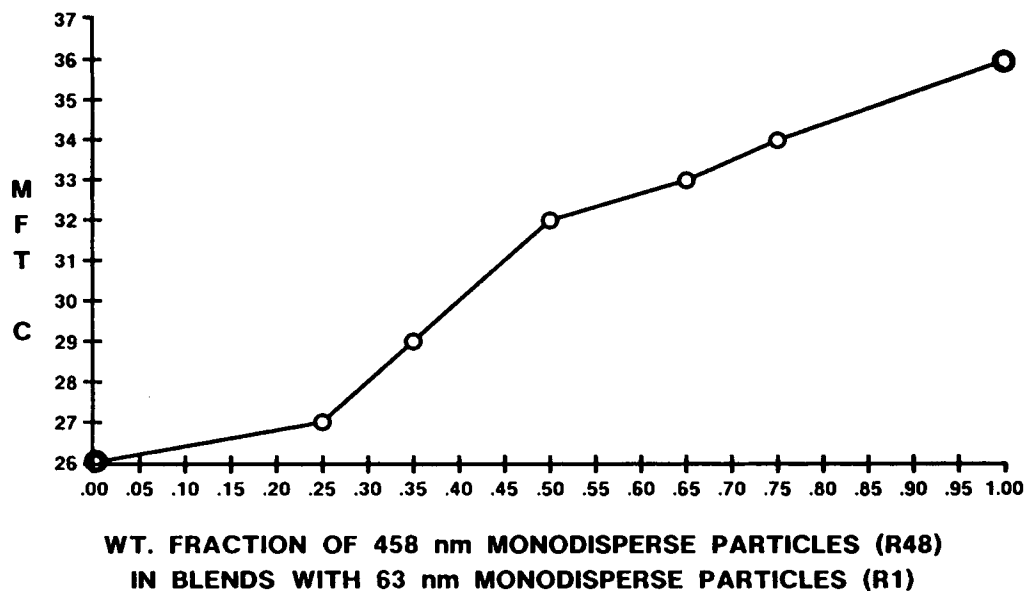
Figure 2 Minimum film formation temperatures (MFT) of blends of small (R1) and large (R48) monodisperse polymer particles

It seems that small particles function as a coalescent for the large particles. When more than 50 wt % of small particles is used, the efficiency of film formation is even more enhanced. At the highest concentrations of small particles, one could think of the large particles as hindering small-particle film formation. The blends MFTs are shown in Figure 2.

CONCLUSION

Our work with monodisperse latexes showed that particle size does affect the MFT value of latexes. A seven-fold decrease in particle size can lower the MFT as much as 10°C. This work differs from another report[4] also showing MFT to be a function of particle size in that our MFTs are below the polymer T_g whereas their work shows MFTs above T_g.

Blending the smallest particle size monodisperse latex with the largest one also reduced MFTs. This confirmed our suspicion that earlier work failed to demonstrate this effect because the particle size distributions were too broad and the smaller particles within the distribution masked the effect.

The knowledge gained should be useful in designing latexes for film applications. For example, films of higher T_g polymers might be obtained with equal or less coalescent added by designing a sufficient population of smaller particles into the latexes.

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