

Effects of Core-Shell Latex Morphology on Film Forming Behavior

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Synopsis

A series of core-and-shell latex particles were made from methyl methacrylate/butyl acrylate copolymers. All latexes were almost monodisperse in particle size. The polymer hardness was varied by changing the methyl methacrylate/butyl acrylate ratio between the limits of 40/60 and 60/40 parts by weight. The minimum film temperatures (MFTs) of these particles were expected to vary with core and shell characteristics in the following order: soft/hard > medium/medium > hard/soft. In fact, this order was observed only if the shell thickness was greater than a certain minimum value that depends on the diameter of the core polymer. Thinner, softer shells on harder cores may require higher drying temperatures than thicker shells with the same composition because the former are required to deform more to produce void-free films.

INTRODUCTION

The properties of emulsion copolymers may vary widely, even at fixed comonomer composition.¹⁻³ When staged feeds of monomers or monomer mixtures are employed, the composition of the latex particles can be different across the particle cross section. The properties of such polymer particles will reflect their particular morphology, as well as their chemical composition. Reports from other workers have described the effects of particle structure on various properties. The dependence of particle size on pH,⁴ particle shape,⁵ mechanical and optical properties of cast films,⁶ and surface reactivity⁷ have been reported. Several recent papers have reviewed the different emulsion particle structures that may be realized.^{8,9}

Morgan¹⁰ studied the effect of monomer feed sequence on the minimum film temperature (MFT) of film-forming latexes. The MFT is the minimum temperature at which the latex will coalesce sufficiently well to form a clear film on drying. At lower temperatures the dried film is hazy or cracked. MFT depends on the latex particle size, composition, and particle morphology. In this case MFT correlated with shell thicknesses, which were calculated, but not measured. Differences were observed between the products of seeded and unseeded sequential monomer addition polymerizations and the behavior of some latexes were found to be unstable with time.

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This article is a further contribution to the study of the effects of latex particle morphology on MFT. In our case, all products were intended to have the same overall polymer composition, but this objective was changed later when shell thicknesses were varied, on a common core polymer. Particle sizes were measured at all stages of the sequential polymerization procedure. Evidence is adduced for the actual production of core-and-shell morphologies. Our results extend those of Morgan and help to clarify some of the unexplained features in his work.

The methyl methacrylate/butyl acrylate system studied here was polymerized to produce particles with a variety of structures. The MFT was varied over a wide temperature range to study the effects of the various particle morphologies. Two surfactants, sodium dodecyl benzene sulfonate and pectin, were used separately in this work. These two surfactants were chosen because they differ in surface activity in water. Polymerization recipes were adjusted to produce particles with the same sizes, using the two surfactants. All polymerizations with dodecyl benzene sulfonate as emulsifier were seeded, while those with pectin were not. As shown below, the products behaved in a similar manner, despite the differences in polymerization procedures and surfactants.

EXPERIMENTAL

Materials

Commercial polymerization-grade monomers were used as received in all the copolymerizations. Materials used include: methyl methacrylate (MMA), butyl acrylate (BA), sodium dodecyl benzene sulfonate (Alcolac DS-10), ammonium persulfate, distilled deionized water, and partially methoxylated polygalacturonic acid (pectin). The emulsion copolymerizations were carried out in a half-liter thermostatted glass reactor, fitted with stirrer, reflux condenser, and two inlets for nitrogen and for other ingredients. Typical recipes are given below (Tables I-V) for preparation of the seed, core, and core-shell latices. The emulsifier concentration in these polymerizations was kept low to avoid the production of second generation particles. Each finished latex was filtered through a mesh screen to remove any coagulum and the pH was adjusted to 9.

Polymerization conditions are given here for the production of homogeneous particles and core-shell structures. Homogeneous particles also employed the same staged polymerization sequence used for core-shell products. In the former case, however, the composition of the shell comonomer mixture was the same as that of the core monomer mixture. The two surfactants were used separately. Some reactions were performed only with the anionic emulsifier, sodium dodecyl benzene sulfonate, while others relied on the protective colloid, pectin, as the sole surfactant. Both procedures are described. Descriptions below are for 50/50 ratios of methyl methacrylate and butyl acrylate. The variations to change this ratio and to change the ratio of shell to core masses are obvious.

The distilled water and surfactant (DS-10) were added to the reactor under a nitrogen blanket and the mixture was heated to 80°C. The initiator and 5 g of the preemulsion were then added to the reactor. After 30 min, the addition

TABLE I
Seed Recipe
(Using Sodium Dodecyl Benzene Sulfonate)

Ingredient	Weight (g)
Water	290.0
Sodium dodecyl benzene sulfonate (DS-10)	0.20
Initiator (ammonium persulfate)	0.30
Preemulsion	
DS-10	0.04
Water	26.40
MMA	39.00
BA	39.00

of the remaining monomer preemulsion was commenced. Seed latices were prepared at 20% solids concentration. The seed latex, the distilled water, and the initiator were charged to the reactor, under a nitrogen blanket, and the mixture was heated to 80°C. The preemulsion was added slowly to the reactor over approximately 3 h. The core latices were prepared at 40% solids.

All the polymerizations involved use of the same seed, followed by a hard core/soft shell or a soft core/hard shell sequence. The hard component contained 40 parts butyl acrylate and 60 parts methyl methacrylate. These proportions were reversed in the monomer mixture used to produce the soft component. The hard copolymer contained more methyl methacrylate and was more hydrophilic than the softer copolymer. It was conceivable, therefore, that the more hydrophobic soft shell could be formed inside the preexisting hard core, rather than on the exterior, as intended.⁵ In order to vary the surface energy of the system, and perhaps therefore to control the location of the more hydrophobic copolymer, polymerizations were conducted in which the particular surfactant, dodecyl benzene sulfonate, was replaced by pectin. The pectin reactions are summarized below. Emulsion polymerizations that used pectin were not seeded.

The distilled water and initiator were added to the reactor under a nitrogen blanket and the mixture was heated to 80°C. Twenty grams of the preemulsion were added to the reactor and polymerized for 20 mins, after which the remaining monomer preemulsion was added at a rate of 2 g/min. The core

TABLE II
Core Recipe
(Using Sodium Dodecyl Benzene Sulfonate)

Ingredient	Weight (g)
Seed Emulsion (20% solids)	12.40
Water	20.50
Initiator	0.84
Preemulsion	
Water	47.00
DS-10	0.16
MMA	70.00
BA	70.00

TABLE III
Core-Shell Recipe
(Using Sodium Dodecyl Benzene Sulfonate)

Ingredient	Weight
Core latex (40% solids)	250.00
Water	50.00
Initiator	0.50
Preemulsion	
Water	33.00
DS-10	0.10
MMA	41.60
BA	41.60

TABLE IV
Core Recipe (Using Pectin)

Ingredient	Weight (g)
Water	150
Initiator	0.8
Preemulsion	
Pectin (6% solids)	90
Water	100
MMA	48
BA	32

latex was added to the reactor with the water and the nitrogen and the mixture was heated to 60°C. The monomer was added dropwise over 2 hrs.

Particle size measurements were performed with an ICI-Joyce LoebL disk centrifuge. Centrifuge speeds were chosen so that particles passed the detector between 1 and 25 mins after injection. Samples were diluted to between 0.25 and 0.5% weight concentrations with a 80% water-20% methanol mixture. The spin fluid was water and the density gradient within the spin fluid was formed with methanol. In all cases stable sedimentation conditions were achieved. MFT measurements were conducted by casting the latexes on a temperature gradient bar and allowing the latex to dry overnight. The temperature at which the dried film was clear was recorded as the MFT.

Differential scanning calorimetry was used to determine the glass transition temperatures of the polymer films. The heating rate for these measurements was 10°C/min. The copolymer compositions used can be classified as hard or

TABLE V
Core Shell Recipe (Using Pectin)

Ingredient	Weight (g)
Core latex (20% solids)	300
Water	60
Monomer	
MMA	24
BA	36

soft based on their glass transitions (i.e., 60/40 MMA/BA = hard, 40/60 MMA/BA = soft).

RESULTS

Table VI lists the characteristics of the various latexes produced. Here D_n and D_w are experimental diameters. The shell thickness reported is also a measured value. The projected diameter is the experimental D_n plus the increase in D_n if perfect layering would have taken place. The mass of core polymer is equal to the mass of shell polymer in latexes 6–10C and the overall composition is the same (i.e., MMA/BA = 50/50). It can be seen that a soft copolymer shell on a hard core causes the MFT to decrease while the opposite trend is observed for a hard polymer shell on a soft core. This is true only, however, for shells with adequate thicknesses. The cores used in this work had diameters between 330 and 350 nm. In this case, the expected MFT of the particles with soft shells is lower than that of the hard shell analogs only when shell thicknesses were at least approximately 80 nm. Morgan's data¹⁰ show a similar trend, although he was not able to measure core and shell thicknesses. Interpolation of his data indicate that the overall particle diame-

TABLE VI
Latex MFTs

Emulsion composition surfactant	Core shell ^a	D_n (nm)	D_w/D_n (nm)	Shell thickness (nm)	MFT (°C)	Projected diameter (nm)	
1	DS-10	Soft/—	344	1.04	—	< 1	
2	DS-10	Med/—	346	1.05	—	13	
3	DS-10	Hard/—	329	1.06	—	> 20	
4	Pectin	Soft/—	332	1.06	—	< 1	
5	Pectin	Hard/—	347	1.07	—	30	
6	DS-10	Soft/hard	418	1.04	37	18	433
7	Pectin	Soft/hard	460	1.03	64	18	418
8	DS-10	Med/med	444	1.06	49	11	436
9	Pectin	Hard/soft	428	1.09	41	20	437
10 ^b	DS-10	Hard/soft	405	1.07	38	19	415
10 ^c	DS-10	Hard/soft	—	—	—	20	
10 ^d	DS-10	Hard/soft	—	—	—	22	
11	Pectin	Hard/soft	545	1.14	99	8	539
12	Pectin	Soft/hard	543	1.19	106	25	580
13	Pectin	Hard/soft	377	1.11	15	26	377
14	Pectin	Soft/hard	360	1.04	14	10	380
15	Pectin	Hard/soft	522	1.14	88	10	533
16	Pectin	Soft/hard	472	1.06	70	28	

^aSoft — MMA/BA = 40/60, hard — MMA/BA = 60/40, med — MAA/BA = 50/50.

^bShell polymerized at 80°C.

^cShell polymerized at 60°C with continuous addition of monomer and separate, continuous addition of surfactant and initiator.

^dShell polymerized at 22°C with ammonium persulfate/sodium bisulfite redox system.

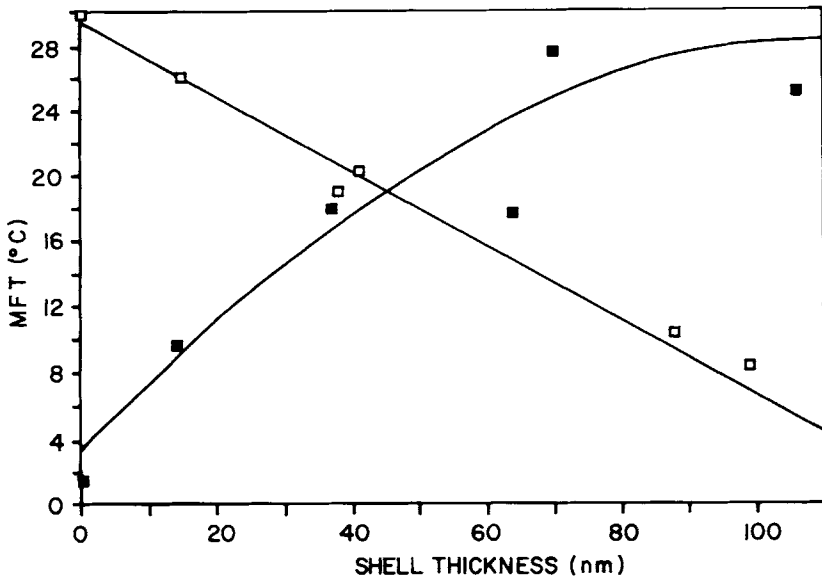


Fig. 1. MFT vs. shell thickness: (□) hard core (MMA/BA = 60/40 in core; MMA/BA = 40/60 in shell); (■) soft core (MMA/BA = 40/60 in core; MMA/BA = 60/40 in shell).

ters were generally less than 100 nm, which is much smaller than those in our study. In Morgan's case, the minimum shell thickness for observation of the expected effect of MFT on shell composition is apparently less than 10 nm (Fig. 2 of ref. 10). This is equivalent to about 20% of the total particle diameter. In our study, with a different copolymer composition, the critical shell thickness is similar, at about 15% of the total particle diameter.

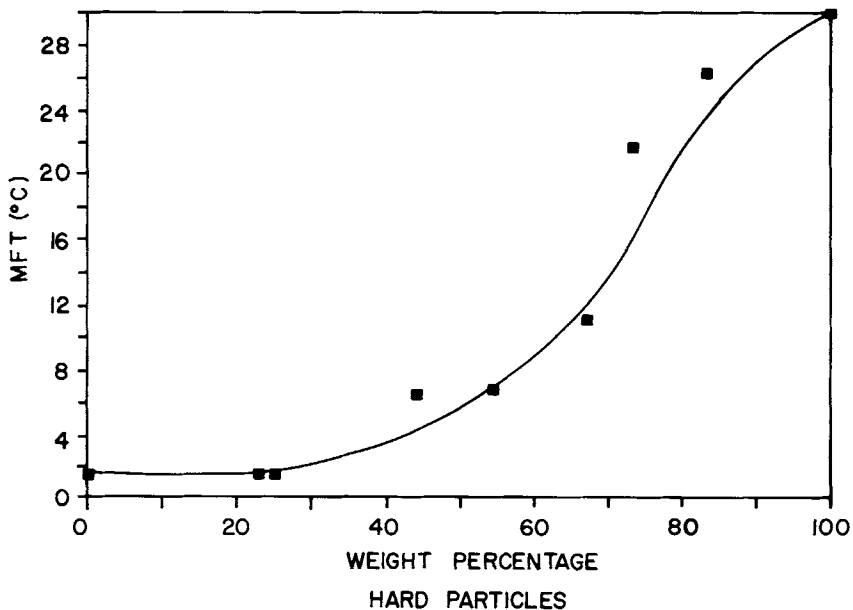


Fig. 2. MFT vs. weight percentage hard particles in a mixture.

TABLE VII
Glass Transitions

Latex	T_g (°C) (estimated)	T_g (°C) (measured) (10°C/min)
4	-6.3	6.0
5	26.4	31.0
14	—	3 and 37
13	—	9 and 22

In Figure 1, MFT is plotted against shell thickness for the hard core/soft shell and soft core/hard shell latexes. The MFT of these latices is directly related to the amount and type of polymer in the shell. In Figure 2, MFT is plotted against the weight percentage of hard particles in a mixture of latex 4 (core latex with 40/60 MMA/BA composition) with latex 5 (core latex with 60/40 MMA/BA composition). The MFT of the mixture of hard and soft particles appears to be independent of composition when the soft particle is the more abundant component of the mixture. In the region of 50–80 wt % hard particles the curve breaks to higher MFT. This is an indication that the hard particles essentially act as a filler in the soft film.

The MFTs of the mixed latices also differ from those of the core-shell latexes of the same overall composition. The core-shell latices have a higher MFT. This can presumably be attributed to the structure of the polymer particles. The core-shell particles did not form films as readily because the ability of the shell polymer to flow is restricted by its attachment to the harder core.

Table VII compares the measured glass transitions of the soft and hard cores and for two of the core-shell latexes to the glass transition calculated from the Fox equation:

$$\frac{1}{T_g} = \frac{w_a}{T_{ga}} + \frac{w_b}{T_{gb}} \quad (1)$$

where T_g , T_{ga} , and T_{gb} are the glass transition temperatures of the copolymer and homopolymers of monomer a and monomer b, respectively. The copolymer composition is represented by the weight fractions, w_a and w_b of the two comonomers. The presence of two glass transitions for the core-shell latexes is evidence that our polymerizations produce structured particles. The effects of the surfactant choice on the surface tension of water and of the latex serum are shown in Table VIII. DS-10 decreases the surface tension of the water and

TABLE VIII
Surface Tensions of Surfactant Solutions (dyn cm)

Surfactant (g/40 g solution)	In water		In soft core/hard shell latex	
	DS-10	Pectin	DS-10	Pectin
0	—	—	57	57
0.1	36	76	33	57
0.2	35	75	32	61
0.3	34	78	34	68

the latex but pectin does not. It is conceivable, however, that pectin could become surface-active during the polymerization, due to grafting reactions.

DISCUSSION AND CONCLUSIONS

The expected order of minimum film temperatures for latexes of the same overall compositions but different morphologies is soft/hard > 50/50 > hard/soft. The observed order, in latexes 6–10C, is, however, soft/hard = hard/soft > 50/50. This is due to the fact that the core polymer has an influence on the MFT which in this case is sufficient to offset the higher film forming ability of the softer shell polymer when the two types of polymers are present in equal amounts. It is obvious that the MFT depends on both the morphology of the latex and the volume of polymer in the shell relative to that in the core. This is discussed further below.

Three polymerizations of the hard/soft latex were carried out to study the effects of reaction conditions on MFT. Since the relative hydrophobicity of the soft and hard polymers is different (due to the higher aliphatic character content of the butyl acrylate rich polymer) an intended hydrophobic soft shell (rich in BA) could conceivably polymerize inside the more hydrophilic harder core. Changes to the reaction temperature could affect this process because a decrease in temperature reduces the mobility of the polymer particles in the core.⁶ A completely immobile core would prevent any core-shell inversion from taking place during polymerization. However, no effect of reaction temperature has been observed. A comparison between the latex prepared at 80°C (10a) to latexes prepared at 60 and 22°C (10b and 10c, respectively) shows the MFT is of these products to be essentially the same.

Polymerizations were carried out with a low surface tension surfactant and a high surface tension surfactant. The surface tension of the surfactant is important in determining the amount of monomer that will absorb into the latex particle. The free energy change during mixing favors the absorption of unlimited amounts of monomer into the particle if the mixing process is exothermic. This effect is counteracted, however, by the increase in surface energy as the particle size increases. Monomer concentrations in the particles are directly related to surface tension of the surfactant¹¹ and the radius of the particle. The chemical potential difference (μ) between the spheres having finite (r) and infinite radii is given by¹¹

$$\mu_s = \mu(r) - \mu(\infty) = 2V_m\tau/r \quad (2)$$

where V_m is the molar volume of the monomer, τ is the interfacial tension, and r is the swollen particle radius. Swelling of a latex particle by a soluble monomer increases with increasing radius and decreasing interfacial tension. A high surface tension surfactant therefore should lead to a more core-shell-like morphology, since swelling of the core by the shell monomers is expected to be less. The difference between the emulsions containing pectin and those containing DS-10 is imperceptible, however, suggesting that both products are core-shell particles.

It is also a matter of concern to determine whether second and third stage polymerizations yielded new particles. This complication can be of great importance, since the MFT of latexes that are polydisperse in particular size is apparently a function of D_n .¹² Generation of new, small particles in the later steps of the polymerization sequence could evidently confound the obscure relations between shell composition and film forming behavior of the latex particles. This problem could not be addressed directly in the earliest work cited above.¹⁰ In our case, the disc centrifuge failed to detect the presence of any second-generation particles. All intermediate and final latexes were unimodal and generally monodisperse in particle size, as shown in Table VI. The same table lists projected values of particle diameters, as calculated from the masses and densities of the copolymers deposited in the various stages of particle buildup. It can be seen that the measured and estimated sizes agree within experimental error.

Morgan¹⁰ noted that only seeded core-shell latexes had MFTs that varied as expected with regard to shell composition. No explanation was offered. In our study, film-forming characteristics of the latexes were independent of the presence or absence of seed particles. The seed diameter was a much greater proportion of the core size in the case of Morgan's work, however, and the character of the seed may have been reflected in the observed behavior of the shell in his study.

The fact that pectin and dodecyl benzene sulfonate both gave the same products, regardless of the differences in the surface tensions of their aqueous solutions, suggests that core/shell morphology was obtained in both cases. It has been shown that the differences in interfacial activity may influence the structure of composite particles very strongly.¹³

As mentioned above, a minimum shell thickness is required in order for the observed MFTs to vary inversely with shell polymer T_g , as expected. This requirement is readily understood when it is remembered that the shell polymer must flow to fill the voids between the initial, discrete latex particles as the latex dries.

To visualize this requirement, consider core/shell latex particles with rigid cores and softer shells. Each particle has a radius r_T , and the radius of the core is r_c . Then, the projected area of a particle is Πr_T^2 , the projected area of the core is Πr_c^2 , and the projected area of the shell polymer is $\Pi(r_T^2 - r_c^2)$. Consider a square with sides = $2Xr_T$. The area of this square is $4X^2r_T^2$. A total of X^2 uniform core/shell particles can be packed into this square. In that case, the projected area between particles equals $4X^2r_T^2 - \Pi X^2r_T^2 = (4 - \Pi)X^2r_T^2$. In order for the particles to form a void-free film, the deformable shell polymer must flow to cover this unoccupied area, more or less. Thus, the shell polymer in a single particle, which had an initial projected area = $\Pi(r_T^2 - r_c^2)$ must cover an area = $(4 - \Pi)X^2r_T^2/X^2 = (4 - \Pi)r_T^2$ after the latex has dried. The relative expansion of the projected area of each shell is then $(4 - \Pi)r_T^2/\Pi(r_T^2 - r_c^2)$. Evidently, the thinner the shell (i.e., the smaller is $r_T - r_c$), the more unlikely it will be for the latex to be able to form a void-free film under given drying conditions. It can be expected, then, that the minimum shell thickness needed for the expected parallel between shell composition and MFT will vary directly with the size of the immobile core in the core/shell particle. In the present work, with core radii of about 170 nm,

the minimum value for $r_T - r_c$ was 80 nm. Thinner shells required higher drying temperatures than thicker shells with the same composition because they were required to deform more to produce void-free films.

An alternate model could assume that the core remains spherical in the film (hardly ever true) and that the shell must fill the void space between the core globules during the continuous film formation. If the monodisperse core globules are in random close packing in the film, occupying 63% volume fraction, the shell thickness would have to be at least 14% of the final diameter to satisfy these rather extreme criteria. Obviously, much larger shell thickness is needed for a completely shell-dominated MFT value. Otherwise, film formation is a cooperative process involving both core and shell deformation.

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