

Characterization of Two-Stage Latexes Using Dynamic Mechanical Thermal Analysis

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INTRODUCTION

Background-Composite Latexes

In an attempt to reduce volatile organic compounds (VOCs), coatings manufacturers, and their customers, are increasingly utilizing water-based technologies. Using emulsion polymers, or latexes, high molecular weight polymeric coatings can be obtained that require minimal amounts of solvent.

With polymeric materials, a wider range of physical and chemical properties is commonly achieved by incorporating several monomers into the polymer backbone. In emulsion polymerization, addition of several monomers often results in an extremely complex polymerization, and a multi-phase, or "composite" latex product. As the name implies, composite particles contain distinct regions, composed of different material. Due to their unique properties, these latexes are often highly desirable.¹

Composite latexes can be produced from either a single or multi-stage emulsion polymerization. In a single-stage emulsion polymerization, copolymerization of monomers with different reactivity ratios results in compositionally heterogeneous copolymers. Early in the reaction, the more reactive monomer preferentially polymerizes, producing a polymer rich in the more reactive monomer. Later in the polymerization, this monomer becomes depleted; and a polymer rich in the less reactive monomer is produced. If these heterogeneous copolymers are incompatible, phase separation occurs resulting in composite latex particles. Typically, "core-shell" morphologies are produced, with the more hydrophilic polymer occupying outer regions of the particles while the more hydrophobic polymer is confined to internal regions.^{2,3} Additionally, composite particles can be produced using two-stage emulsion polymerizations.²⁻⁴ In the first stage, a hydrophilic "seed" particle is polymerized. In the second stage, this seed is swollen with another monomer(s); and a second polymer is polymerized within the seed. Depending on monomer selection and reaction conditions, a wide variety of particle morphologies can be obtained ("core-shell," "in-

Coatings prepared from two-stage acrylic latexes were characterized using dynamic mechanical thermal analysis (DMTA). The DMTA data, in conjunction with additional supporting data (differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and particle size analysis), provided detailed information on copolymer compositions, latex particle morphologies, and coating morphologies.

Depending on monomer selection and monomer order of addition during polymerization, one of three different particle morphologies was obtained: two particles of different composition, two-phase particles, or interpenetrating polymer network (IPN) particles. Coating performance was highly dependent on latex and coating morphologies, as well as monomer composition. IPN latex morphologies produced coatings with superior mechanical properties and chemical resistance.

verted core-shell," "acorns," "raspberries," etc.).⁴ Particle morphology is controlled by both thermodynamics and kinetics.⁴ If the two polymers are incompatible, phase separation occurs resulting in multi-phase particles, where the more hydrophilic polymer occupies outer regions of the particles. Additionally, particle morphology can be controlled by kinetics. Thermodynamically, incompatible polymers may want to phase separate and/or migrate to a specific area within the particles. However, migration and/or phase separation can be hindered or eliminated by reducing polymer mobility through internal crosslinks^{1,4} or lower reaction temperatures.⁵

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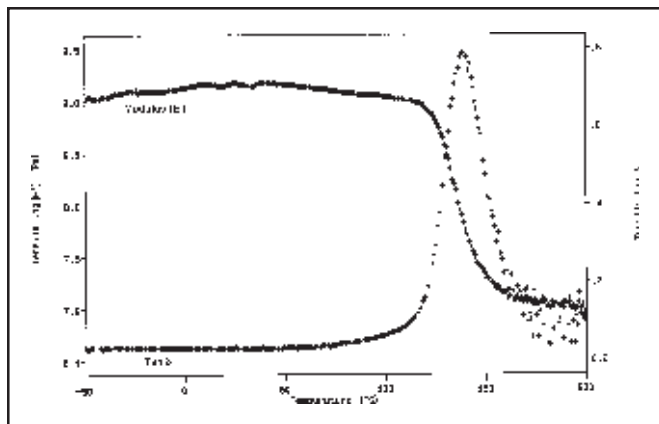


Figure 1—DSC results for Stage 1 and Stage 2 "only" polymers (free film samples).

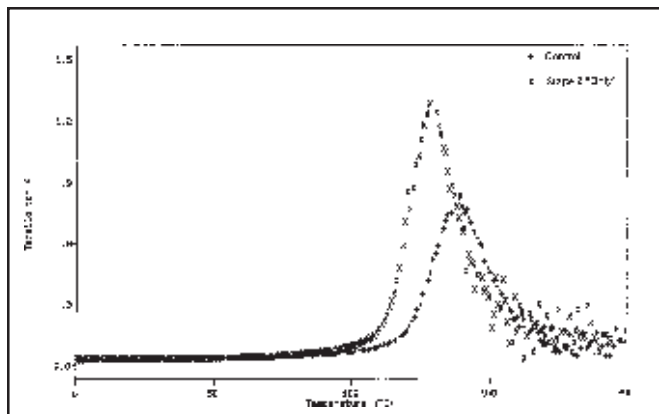


Figure 2—Characteristic TMA results for several experimental coatings.

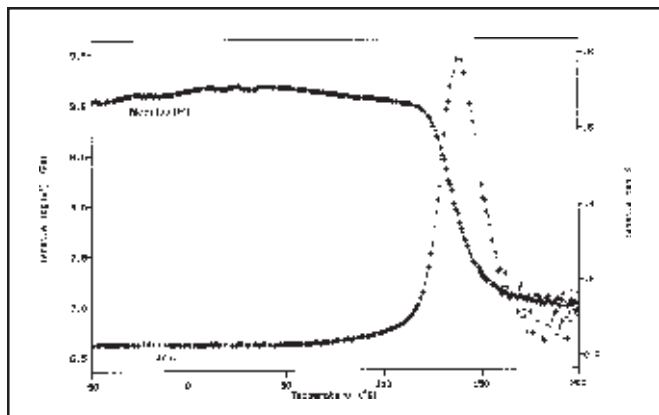


Figure 3—DMTA results for the control latex.

Background Characterization of Latex Morphology Using Dynamic Mechanical Thermal Analysis (DMTA)

DMTA is a powerful polymer characterization technique. Complete discussions of theoretical fundamentals and applications of DMTA have been presented elsewhere.⁶⁻⁸

In a typical DMTA experiment, a small sinusoidal stress is applied to a prestressed polymeric sample; and, the resulting strain is measured as a function of temperature or frequency. Since polymers exhibit some degree of viscoelasticity, measured strains are between 0° and 90° out-of-phase with applied sinusoidal stresses. By quantifying this lag, or phase angle, complex viscoelastic behavior can be separated into elastic [elastic modulus (E')] and viscous [loss modulus (E'')] components. The ratio of the loss and elastic moduli (loss factor, or $\tan \delta$) is proportional to damping, or energy dissipated within the material.

Considerable information on structure of a polymeric material can be extracted from the modulus and $\tan \delta$ data: homopolymer/copolymer glass transitions (T_g); frequency dependence of transitions; copolymer compositions; crosslink densities; number of polymer phases present; assignment of continuous and dispersed phases; and homogeneity of phases present.

In several studies, coalesced latex films have been examined using DMTA.^{1,9-11} In these studies, DMTA data provided information on latex T_g values and copolymer compositions, as well as latex particle morphologies.

In this study, DMTA, and several other supporting techniques were used to characterize coatings produced from extremely complex latexes, synthesized using multiple reaction stages and monomers. This data was used to establish relationships between latex composition, latex structure, coating structure, and coating performance.

EXPERIMENTAL PROCEDURE

Latex Preparation

Two-stage acrylic latexes were prepared using the following procedure. In Stage 1, the reactor was charged with water, acrylic monomers, anionic surfactant, and ammonium hydroxide. This emulsion was stabilized by both the anionic surfactant and neutralized acid monomers (with the ammonium hydroxide). After introduction of the free radical initiator, the monomers were polymerized at 80°C for 2 hr, forming the Stage 1 polymer. Next, a second charge of initiator was added to the reactor, and another mixture of acrylic monomers was added to the reactor over a two-hour period, followed by a two-hour hold. This second monomer mixture formed the Stage 2 polymer. All monomers were converted into a latex polymer with a solids content of approximately 25%.

Latex particles were composed of four different types of ethylenically unsaturated monomers: "hard," or high T_g monomers; "soft," or lower T_g monomers; acid functional monomers; and internal crosslinker monomers. All internal crosslinker monomers were multi-functional,

Table 1—Composition of Experimental Two-Stage Latexes

Latex Variable	Stage 1 Composition	Stage 2 Composition
	35% (Latex Solids)	65% (Latex Solids)
Control	Hard (60%) Acid (40%)	Hard (90%) Internal Crosslinker (10%)
Stage 1 modified	Soft (60%) Acid (40%)	Hard (90%) Internal Crosslinker (10%)
Stage 2 modified	Hard (60%) Acid (40%)	Hard (45%) Soft (45%) Internal Crosslinker (10%)
Stage 2 modified No internal crosslinkers	Hard (60%) Acid (40%)	Hard (50%) Soft (50%)

producing polymer network formation through free radical or step-growth polymerization. Generalized latex compositions are summarized in *Table 1*.

DMTA-Sample Preparation

DMTA required “free” film samples. Acceptable coating free films (0.5–0.8 mil) were obtained using the following procedure. Fully formulated latexes were drawn down on thin aluminum foil (0.25 mil) using a #40 wire bar. All coatings then received an identical thermal treatment: baked at 400°F for 2 min and “slow cooled” to room temperature. After cooling, rectangular samples were cut from the coated foil (approximately 12.5 × 35.0 mm). The coated aluminum samples were then placed in an aqueous copper sulfate solution to remove the aluminum from the coating. After removal of the aluminum, the free films were washed in water, using an ultrasonic bath to remove any residual material. All samples were placed between glass microscope slides, for storage, and dried in a vacuum desiccator.

DMTA-Testing

Free film samples were tested in tension using a Polymer Labs MKIII DMTA unit. Data was obtained from –50 to 200°C at 1 Hz using a heating rate of 5°C/min.

DSC-Sample Preparation and Testing

DSC samples were prepared using two different forms of coating material: free films and resin droplets. Using coating free films, only low sample weights could be achieved (4 to 5 mg), resulting in fairly weak transitions. On the other hand, higher weight samples (7 to 11 mg) were prepared using resin droplets. A small droplet of resin was placed in an aluminum sample pan; and, specimens were then dried slowly (overnight in a laboratory

hood) to maximize contact between the resin and pan. All analysis was performed using a DuPont Instruments Model 912 DSC unit. T_g values were measured using a heating rate of 20°C/min.

TMA-Sample Preparation and Testing

Softening points (T_g) of all free films samples were determined using a TA Instruments 2940 TMA unit at a heating rate of 10°C/min. Softening points were defined as the maximum rate of probe penetration into the coating samples.

Particle Size Analysis

Particle sizes were determined using a Horiba Light Scattering Particle Size Distribution Analyzer.

RESULTS AND DISCUSSION

Coating and latex physical properties are summarized in *Table 2*. Characteristic DSC and TMA curves are presented in *Figures 1* and *2*, respectively. DMTA results are presented in *Figures 3–7*.

Control Latex

For this “hard” latex containing all high T_g monomers and internal crosslinker monomers, mean particle size increased from Stage 1 to Stage 2 of the polymerization (*Table 2*). This increase indicated that the Stage 1 particles acted as “seeds” for the Stage 2 monomers, resulting in the formation of composite latex particles.

DMTA results from a cured free film of the control latex are presented in *Figure 3*. Both modulus and $\tan \delta$

Table 2—Physical Properties of Coatings from Two-Stage Latexes (Average Value ± Standard Deviation)

Sample Description	Particle Size (after Stage 1 and Stage 2) (nm)	DMTA T_g (°C)	TMA Softening Point (°C)
Control	1) 120 2) 250	138 ± 2	112 ± 2
Stage 1 modified	1) 191 2) 195	–75 130	104 ± 2
Stage 1 modified	1) 214 2) 253	2 128	106 ± 2
Stage 2 modified	1) 121 2) 342	119	79 ± 2
Stage 2 modified	1) 119 2) 13,580	108	71 ± 2
Stage 2 modified	1) 111 2) 219	81 ± 2 143 ± 1	64 ± 2
Stage 2 modified	1) 142 2) 570	52 ± 1 142 ± 1	37 ± 2

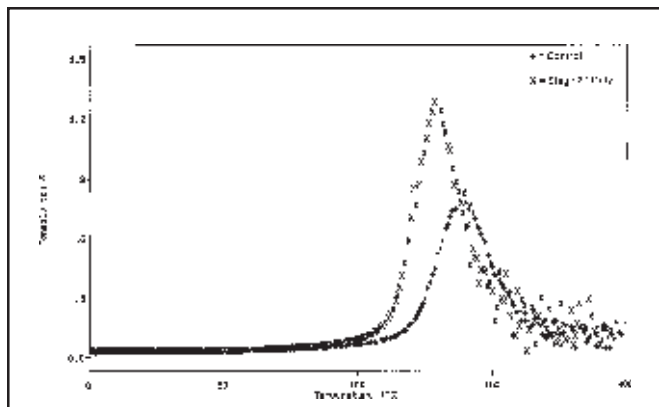


Figure 4—DMTA results for the control and Stage 2 “only” latexes.

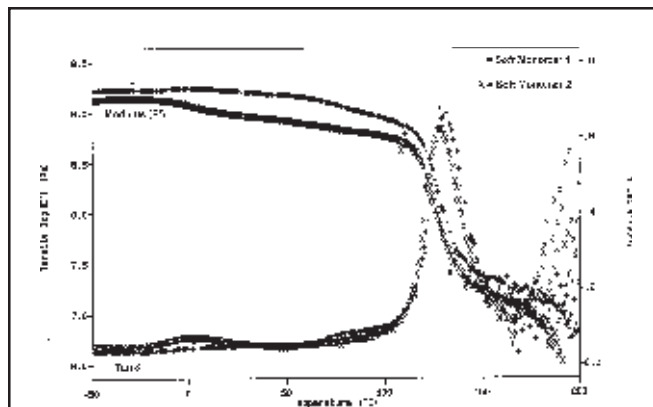


Figure 5—DMTA results for Stage 1 modified latexes (soft monomer).

curves showed a single, narrow transition ($T_g = 138^\circ\text{C}$). This type of DMTA trace usually indicates that the polymer is a fairly homogeneous, single phase material.

Homopolymer T_g values and monomer weight fractions were used to calculate theoretical T_g values of polymers formed during the two-stage polymerization. Theoretical T_g values of the Stage 1 “only” and Stage 2 “only” polymers were substantially different (Table 3). These differences were confirmed by DSC and DMTA experiments on “model,” single-stage latexes made from Stage 1 or Stage 2 monomers (Figures 1 and 4, Table 3). It should be noted that the differences between experimental and calculated T_g values are due to the frequency dependence of T_g . Since DMTA is a “dynamic” characterization technique, experimental T_g values are higher than calculated, “static” values.

Two different latex morphologies could explain a single, intermediate DMTA transition for the combination of Stage 1 and Stage 2 polymers. First, Stage 1 and Stage 2 polymers could be miscible, resulting in a blend with a single, intermediate T_g . Second, Stage 1 and Stage 2 polymers may be incompatible; however, incorporation of internal crosslinkers into Stage 2 may have resulted in a microheterogeneous, or IPN, particle morphology. An IPN is an intimate polymer mixture, where a network polymer(s) is formed in the presence of another polymer.^{12,13} In an IPN, the individual polymers may be incompatible; however, crosslinking one or both polymers restricts mobility and phase separation, forcing a degree of miscibility between the two polymers.^{1,12,13}

In order to test these theories, an attempt was made to remove all internal crosslinkers from this control poly-

mer. Unfortunately, this latex could not be successfully synthesized, and the previously discussed theories could not be tested. However, analysis of the Stage 1 “only” and Stage 2 “only” polymers provided critical information. These two polymers had different T_g values than the control latex, indicating that some degree of mixing/interaction between the Stage 1 and Stage 2 polymers was present in the latex particles and in the cured coatings.

Latex Modified in Stage 1

In an attempt to increase coating flexibility, latexes incorporating one of two different lower T_g , or “soft,” monomers were synthesized. These modifying monomers have homopolymer T_g values of 20°C and -55°C , respectively. DMTA modulus/tan δ curves for Stage 1 modified polymers are presented in Figure 5. Both sets of curves showed two distinct transitions, indicating a two-phase coating morphology was present. Additionally, modulus data was used to determine the relative positions of these two phases within the coatings. DMTA showed that coating remained rigid at temperatures well above the T_g of the softer phase. In fact, these coatings remained rigid to temperatures near the T_g of the harder phase (Table 2). This was true for both Stage 1 modified coatings, indicating that the higher T_g material formed the continuous phase and the lower T_g material was dispersed within this matrix. TMA results supported this theory. In TMA, softening point values are highly dependent on T_g of the continuous phase.^{14,15} Softening points (Figure 2 and Table 2) of the control and of both Stage 1 modified coatings were almost identical, again indicating that the higher T_g material formed the continuous phase.

Particle size data provided additional details on the latex and coating morphologies. Contrary to the previous case, Stage 1 and Stage 2 particles were nearly identical in size, indicating that the Stage 1 particle did not act as “seeds” for the Stage 2 polymerization. Thus, at each stage of the reaction, separate particles were formed, resulting in

Table 3—Experimental and Theoretical T_g Values for Stage 1 and Stage 2 Only Polymers

Sample Description	DMTA T_g ($^\circ\text{C}$)	DSC T_g “Free” Film ($^\circ\text{C}$)	DSC T_g Resin ($^\circ\text{C}$)	Theoretical T_g ($^\circ\text{C}$)
Control	138 ± 2	115 ± 2	104 ± 1	~ 109
Stage 1 only	—	115 ± 2	126 ± 2	~ 121
Stage 2 only	129	102 ± 1	103 ± 1	~ 103

Table 4—Effect of Latex/Coating Microstructure on Coating Performance

Coating Modification	Latex Microstructure	Coating Microstructure	Coating Flexibility ^a	Coating Resistance ^b
Control	IPN	IPN	Pass	Pass
Stage 1 modified	Mixture of hard and soft-acid particles	Cont. phase- hard Disp. phase soft-acid	Fail	Fail
Stage 2 modified	IPN	IPN	Pass	Pass

(a) Falling Weight Impact Test. Failure determined from change in coating electrical resistance.
(b) Water (low pH) Immersion Test. Failure determined from change in coating electrical resistance.

a latex containing a mixture of soft and hard particles. Coalescence of these two particle types produced two-phase coatings. Hard Stage 2 particles, the major component in the mixture (65%), formed the coatings' continuous phase, while soft, Stage 1 particles formed the dispersed phase.

DMTA T_g data supported this two-particle theory. For coatings from Stage 1 modified latexes (low T_g monomers), hard phase T_g values (130° and 128°C, for the two different modifying monomers) were identical to the T_g of Stage 2 only coatings (128°C). Thus, coating hard phases were composed of the Stage 2 monomers. Additionally, soft phase T_g values were close to theoretical values for Stage 1 copolymers, consisting of only the acid functional monomer and the low T_g modifying monomer.

Coatings from two-phase particles could have also produced similar T_g values. However, if two-phase particles were present, the observed coating continuous and dispersed phases should have been inverted. The acid copolymers would be expected to occupy outer regions of the particles, while the hydrophobic Stage 2 polymer would be stabilized in particle cores.⁴ Coalescence of these particles would produce a "soft" continuous phase and a "hard" dispersed phase, the opposite of what was observed experimentally.

Latexes Modified in Stage 2

Soft monomers were incorporated into the latex particles by substituting the same low T_g monomers used previously into Stage 2 of the polymerization. DMTA modulus/ $\tan \delta$ curves are presented in Figure 6.

Stage 2 substitutions produced completely different particle and coating morphologies. In these cases, cured coatings had a broad T_g , indicating that the polymer consisted of a single, fairly heterogeneous phase. DMTA and TMA results both showed that Stage 2 substitutions substantially lowered polymer T_g values (Table 2). Latex particle sizes also differed from the previous example. Particle size (Table 2) increased from Stage 1 to Stage 2, again indicating that Stage 1 particles acted as "seeds" for the Stage 2 polymerization.

Several particle morphologies could have produced the observed coating microstructures. First, particles with a wide range of compositions, and resulting T_g values, could be synthesized in the polymerization. Coalescence of these different particles would produce a fairly het-

erogeneous coating with a broad T_g . Second, particles of identical composition could be formed. In one scenario, the Stage 1 and Stage 2 polymers could be compatible, resulting in particles and coating films with a single, intermediate T_g value. In a second scenario, the Stage 1 and Stage 2 polymers may be incompatible. In this case, internal crosslinking within the particles could inhibit phase separation, resulting in an IPN particle morphology with a single, broad T_g .

Latexes Modified in Stage 2 with Soft Monomers and No Crosslinkers

In these resins, the high T_g , hard monomer in Stage 2 of the polymerization was replaced with the same low T_g monomers as described in the previous section. Additionally, all internal crosslinking monomers in Stage 2 were replaced by hard, non-crosslinking monomers.

Resin particle sizes were similar to the control and those discussed in the previous section. Again, particle size increased from Stage 1 to Stage 2, indicating that the Stage 1 particles acted as seeds for the Stage 2 polymerization.

DMTA modulus/ $\tan \delta$ curves are presented in Figure 7. Removal of the internal crosslinkers drastically changed coating morphologies. The broad, single transitions, seen with the Stage 2 modified coatings, separated into two distinct transitions, indicating that two phases were presented in the coatings.

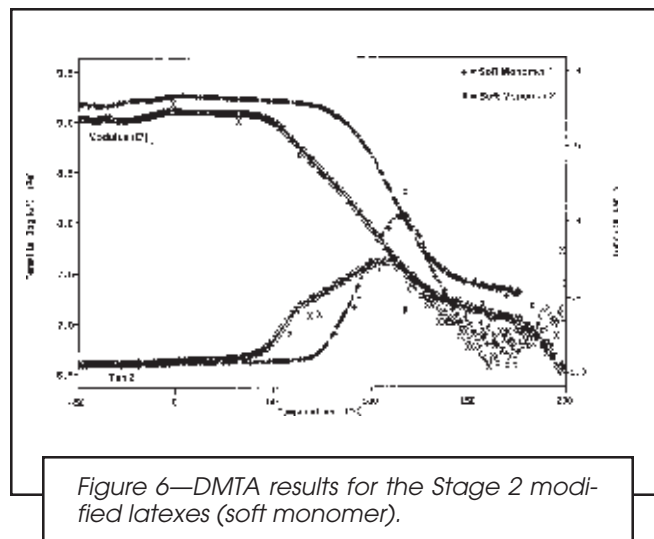


Figure 6—DMTA results for the Stage 2 modified latexes (soft monomer).

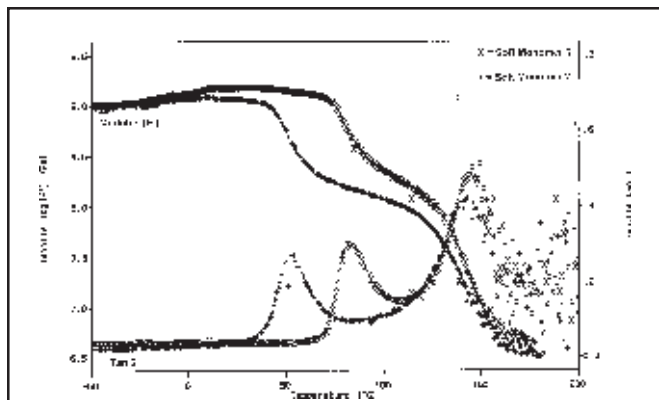


Figure 7—DMTA results for Stage 2 modified latexes (soft monomer, no internal crosslinkers).

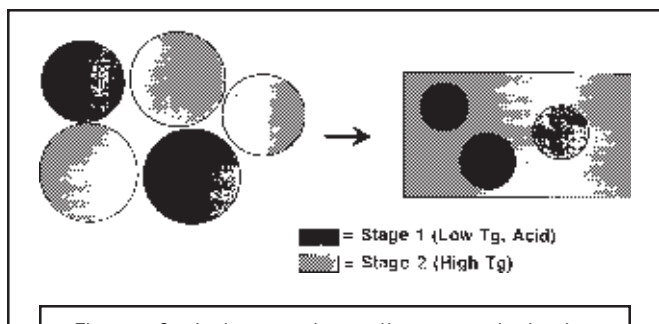


Figure 8—Latex and coating morphologies (Stage 1 modified).

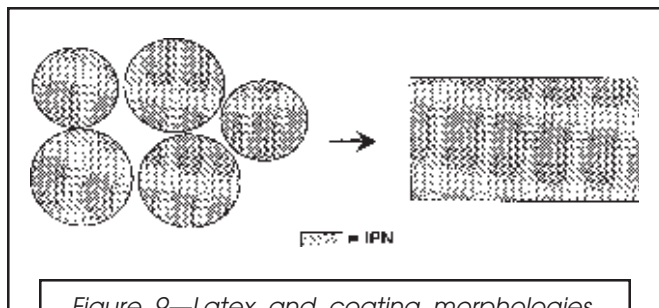


Figure 9—Latex and coating morphologies (control and Stage 2 modified).

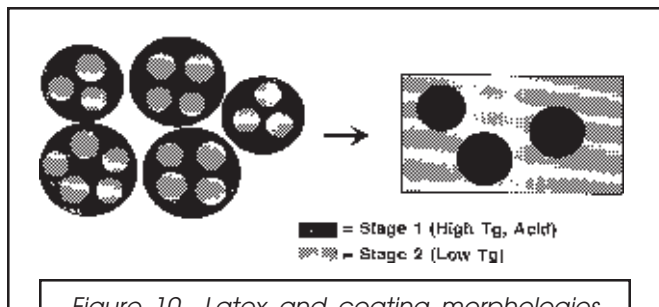


Figure 10—Latex and coating morphologies (Stage 2 modified—no internal crosslinkers).

DMTA and TMA data revealed the relative positions of these two phases within cured coatings. In both cases, coating rigidity decreased drastically at temperatures near the T_g of the softer phase (Table 2). This indicated that the lower T_g material (from Stage 2) formed the continuous phase and the higher T_g material (from Stage 1) formed a dispersed phase. To obtain this coating morphology, a “phase inversion” must have occurred during cure. Since the Stage 1 polymer (hard phase) contained acid functionality, it should have occupied regions of the latex particles, while the hydrophobic Stage 2 polymer (soft phase) occupied interior regions. Without internal crosslinks, these polymers could flow freely at elevated temperatures. Since the lower T_g material (Stage 2) was in excess (65%), it formed the coatings’ continuous phase. Similar inversion behavior has been observed in other latex systems.^{16,17} In latexes with high molecular mobility (low crosslinking densities), the hydrophilic particle shells fragment during coalescence and eventually become dispersed within a matrix of hydrophobic material.

Separation of a single, broad transition into two narrow transitions strongly supported the IPN theory.^{1,13} Apparently, the Stage 1 and Stage 2 polymers were extremely incompatible. However, by polymerizing and crosslinking the Stage 2 polymer within swollen Stage 1 polymer particles, a highly intertwined structure was produced. The thermodynamically driven phase-separation of the Stage 1 and Stage 2 polymers was inhibited by the chain entanglements and chemical crosslinks, forcing a degree of compatibility between the two polymers.

Polymer compatibility may be further enhanced through a second mechanism. In addition to IPN formation, a small amount of grafting may be occurring between the Stage 1 and Stage 2 polymers. Graft copolymer “compatibilizers” are extremely effective in reducing phase separation in blends of incompatible polymers.¹⁸

Structural Models of Latexes and Coatings

Addition of a soft monomer to Stage 1 produced latex particles and coatings with the following characteristics:

- (1) These latexes were composed of a mixture of two distinct particle types. Each type of particle originated from a specific stage in the polymerization. Stage 1 particles had a lower T_g and contained acid functional monomers, while Stage 2 particles had a much higher T_g .
- (2) In the cured coatings, these particles coalesced to form two-phase coatings.
- (3) In the cured coatings, the higher T_g polymer (from Stage 2) formed the continuous phase while the lower T_g material (from Stage 1) formed the dispersed phase.

A schematic diagram describing particle and coating morphologies is presented in Figure 8.

On the other hand, addition of a soft monomer to Stage 2 produced entirely different particle and coating morphologies. In this case, the two-stage polymerization produced latex particles and coatings with the following characteristics:

(1) Polymerization produced only one type of latex particle. These particles contained two incompatible copolymers. However, phase-separation within the particles was inhibited by internal crosslinks, resulting in an IPN-type particle morphology.

(2) IPN particles had a single, broad intermediate T_g .

(3) After coalescence and cure, these particles were still structurally intact within the coatings.

A schematic diagram describing particle and coating morphologies is presented in *Figure 9*. Additionally, the experimental data indicated that control particles also had this morphology.

Lastly, addition of a soft monomer to Stage 2, while simultaneously removing the internal crosslinkers, produced particles and coatings with the following characteristics:

(1) Polymerization produced a single type of latex particles. In this case, the copolymers formed in Stage 1 and Stage 2 were incompatible, resulting in two-phase particles.

(2) Within these particles, the higher T_g polymer (Stage 1) formed the continuous phase while the lower T_g polymer (Stage 2) formed the dispersed phase.

(3) From these particles, two-phase coatings were produced. However, during cure, a phase inversion occurred, resulting in coatings with a continuous phase composed of the lower T_g material (Stage 2) and a dispersed phase composed of the higher T_g material (Stage 1).

A schematic diagram describing particle and coating morphologies is presented in *Figure 10*.

Coating performance was highly dependent on particle and coating morphologies. Performance data is summarized in *Table 4*.¹⁹ For a given monomer composition, the IPN morphology produced optimum coating flexibility and resistance.

CONCLUSIONS

DMTA was used to characterize coatings produced from two-stage latexes. From this, and other supporting data (TMA, DSC, and particle size analysis), several conclusions were made:

(1) For complex emulsion polymerizations, containing several monomers and reaction stages, DMTA provided detailed information on latex and coating structures/morphologies.

(2) Depending upon the monomer feed, these two-stage polymerizations produced several different particle morphologies: two particles of different composition, IPN particles, or two-phase particles.

(3) Coating performance was highly dependent on latex morphology, with the IPN morphology producing superior properties.

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