

Film Formation of Vinyl Acrylic Latexes; Effects of Surfactant Type, Water and Latex Particle Size

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INTRODUCTION

The process of film formation from a polymer latex is often described by a three-step mechanism.¹⁻⁴ The stages are successively those in which the latex particles are mobile in the bulk water phase, pack into an ordered array and coalesce, and maturation of the latex film as a result of polymer diffusion across the original particle boundaries. The T_g of the latex must be at or below the film temperature for coalescence to occur.

A number of forces exist during the film formation process. The forces which cause film formation are the polymer-water and polymer-air interfacial tensions and capillary forces, while film formation is resisted by the temperature-dependent elasticity and viscosity of the polymer.^{5,6} The polymer-water and polymer-air interfacial forces have been studied by a number of authors to determine the extent to which these forces contribute to the overall coalescence process.⁷⁻⁹ These forces are said to come into play after the particles are forced together due to water evaporation.

Recently some doubt has been placed on the significance of the water-polymer interfacial tension during coalescence. Dobler¹⁰⁻¹² and co-workers designed experiments which allowed latexes to coalesce in the presence of water but in the absence of evaporating water. They concluded that the forces due to polymer-water interfacial tensions were very small and thus most of the forces in coalescence were exerted during the evaporation of water. They also noted that a considerable resistive force was exerted by stabilizing moieties consisting of poly(methacrylic acid), in this case, and attributed this to a loss of conformational entropy. When the particles were significantly compressed, elastic resistance of the stabilizing moieties was also expected to become a factor. Also, the energy of hydration of the shell was thought to prevent total coalescence of the latex particles in the absence of evaporation. Although forces are also needed to break the steric or electrostatic barrier on latex particles during coalescence, they have been considered but not included in coalescing models.

The process of film formation from an 85/15 vinyl acetate/butyl acrylate latex was studied with respect to the effects of particle size and surfactant type on minimum film formation temperature (MFFT), glass transition temperature (T_g), drying rates, and optical clarity of the coalesced films.

Water plasticizes this polymer and thus only wet viscoelastic parameters and T_g values are realistic in film formation theories. The polymer is plasticized by ethoxylated alkylphenol non-ionic surfactants. The surfactants with shorter ethylene oxide chains are better plasticizers and poorer steric stabilizers than their longer analogs. The type and concentration of stabilizing entities on the latex particle surfaces have very significant effects on the drying and coalescence properties of these latexes. Coalescence is somewhat faster with smaller latex particle sizes but larger particle size products dry at a faster rate than smaller ones in the absence of surfactant effects.

Capillary forces have also been studied in relation to the coalescing process. Water in the capillaries between particles produces forces which are calculated to contribute to the film formation process in proportion to the air-water interfacial tension and inversely proportional to the size of the capillary formed.^{5,6,9,13,14} Agreement among various authors as to the magnitude of capillary forces is lacking. This is because it is difficult to define surface energetics of polymer latexes. Latex complexity

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Table 1—Recipes for Monodisperse Vinyl Acrylic Latexes

Recipe (charge amount in grams)	M1	M2
Deionized water	380.0	380.0
DS10 ^a	0.15	0.04
Ammonium persulfate	0.30	0.30
DS10 ^a	0.10	0.10
Deionized water	158.0	158.0
Butyl acrylate	63.5	63.5
Vinyl acetate	360.5	360.5
Sodium bicarbonate	0.85	0.85
Deionized water	15.0	15.0
Deionized water	20.0	20.0
Ammonium persulfate	0.52	0.52

(a) Sodium dodecyl benzene sulfonate (Rhône-Poulenc).

as well as nonhomogeneous film formation increases the surface analysis difficulties. Both Sheetz¹⁴ and Okubo¹⁵ report that in improperly stabilized latexes, surface particles coalesce before the bulk material (skinning), increasing the complexity of the mechanism of film formation.

The forces resisting coalescence must also be properly defined. As previously mentioned, stabilizing moieties resist obliteration of particle boundaries. Work by Winnik et al.¹⁶ was aimed at defining the final stages of film formation, the interdiffusion of polymer chains, using energy transfer measurements. They determined that carboxylic acid functionality at the surface of the latex particles can hinder the interparticle polymer diffusion. The viscoelastic properties of the polymer also resist deformation of the particles. The polymer modulus is significantly reduced at temperatures above the T_g of the material. Bertha and Ikeda¹⁷ studied the coalescence of dried latexes in air and reported that coalescence occurred exothermically at temperatures above the T_g of the polymer.

Eckersley and Rudin⁵ have summarized the historical progression of film formation models. These authors proposed a theory in which capillary and interfacial forces act in tandem to promote film coalescence. The interfacial forces may involve dry and/or wet sintering, depending on the details of the drying process. The model was shown to predict the time dependence of coalescence of an acrylic latex system.

Further work by van Tent and te Nijenhuis¹⁸ using transmission spectrophotometry has aided in determining the internal structure of concentrated latex dispersions. Rayleigh scattering equations and multi-layer interference patterns were used to describe the size of the water domains and the time of coalescence of the particles, respectively.

It has been substantially documented that water can plasticize a polymer^{4,6,19-24} and thus change its viscoelastic properties and its resistance to coalescence. As a result the dried latex moduli are not necessarily representative of the moduli of the polymer in a wet latex. It is suggested that polar and acidic groups associate²⁵ causing pseudo crosslinks to form, raising the T_g which is a function of the viscoelastic properties of the latex. Water can plasticize these regions, lowering the T_g . Tradition-

ally, dry latex viscoelastic properties and T_g s have been used in describing latex film forming mechanisms^{11,26-28} and as a result, higher forces were ascribed to capillary and interfacial tension effects than were necessary for the coalescence of a latex.

Very recently, Sperry et al.²⁹ have shed further light on the film formation of latexes. By comparing the MFFT of pre-dried latexes with that of wet latexes they reported that, for given polymer compositions, the capillary forces present during the drying of latex films contribute little if anything to the forces involved with coalescing.

Surfactants can also plasticize latex particles. Bradford and Vanderhoff report that film integration of styrene butadiene copolymer latexes increased with decreasing ethylene oxide (EO) chain length of nonyl phenol ethoxylates.^{30,31} They also stated that EO chain lengths of 15 or less were more compatible with the film than longer nonyl phenol EO chains. Snuparek³² noted that water adsorption of carboxylated butyl methacrylate/butyl acrylate copolymer latexes increased significantly when the nonyl phenol ethoxylate stabilizer chain length was 20 or more units. He attributed it to decreased compatibility of the more hydrophilic emulsifiers allowing them to more easily adsorb water at the surface of the particle. This decreased compatibility is similar to that observed by Bradford. Vijayendran, Bone, and Sawyer²⁶ showed that surfactants markedly reduced the MFFT and T_g of vinyl acrylic latexes. They also report that higher hydrophilic lipophilic balance (HLB) non-ionic surfactants are better agents at plasticizing, on a weight basis, than lower HLB nonionic surfactants due to their superior compatibility with the relatively polar vinyl acrylic latex. Nonionic surfactants have also been reported to plasticize acrylic latex polymers.²⁴ The exudation rate of these surfactants from a latex film was determined by Winnik et al.³³ to be enhanced through the use of coalescing aids.

The effect of the particle size of the latex on the film formation process has also been disputed. While some authors have found that increasing the particle size increases the MFFT of the latex,^{5,6,25,26} others have not.³⁴ Theoretical arguments have been put forth to support both sides. Vanderhoff³¹ maintained that decreasing the particle size should decrease the MFFT since capillaries formed in the drying process are smaller, therefore increasing the forces on the particles and allowing the particles to coalesce at a higher modulus and thus a lower temperature. Mason,¹³ on the other hand, determined that particle size may have no effect since as particles coalesced the capillaries would decrease in size, increasing the force of coalescence. Thus, if materials are not too rigid, the latexes will always form a film, a conclusion which is independent of particle size. Some of the apparent conflict may reflect the use of polydisperse latex samples in most studies.

A number of attempts have been made to explain the phenomenon of film formation and all have met with varying degrees of success. It is agreed that a number of forces contribute to the film formation process but the extent to which each force participates is contested and may, in fact, vary between different latex types. Vinyl

acetate based latexes are the largest class of latex polymers used in coatings applications.³⁵ It is the purpose of this study to further clarify the factors involved in the film formation of vinyl acrylic latexes. These areas include plasticization of the latex by water and surfactants, and the effect of stabilizer surface groups on the film formation process. While studies of this kind have been performed on vinyl acrylic latexes before, this is the first work where the parameters are examined using a series of monodisperse latexes as well as a series of nonyl phenol surfactants.

The effects of surface groups on the film formation process were studied by the addition of surfactants to so-called "surfactant free" latexes. The topics examined are the effect of particle size and surfactant type on the MFFT, T_g , optical clarity, and drying rates of the latex.

The latexes used in this study were composed of 85 wt% vinyl and acetate and 15 wt% butyl acrylate. The stabilizing moieties were generated *in situ* from the reaction of the ammonium persulfate initiator with the monomer. These latexes were manufactured in a number of monodisperse sizes ranging from approximately 200 to 1800 nm.

EXPERIMENTAL

Latex Production Apparatus

The polymerizations were carried out in a one-liter reactor with a four-port glass lid. The reactor was fitted with an overhead condenser. The stirring rate was adjusted so that monomer did not pool on the surface of the reaction mixture (200-400 rpm). The reactor contents were maintained at the appropriate temperature through the use of a thermostatted water bath. Monomers were fed into the reactor using an FMI lab pump, model RP-SY at a prescribed rate. Water soluble initiators were fed into the reactor using a Sage Instruments Model 355 syringe pump.

Production of Monodisperse Latexes³⁷

Monodisperse latexes were produced at 42% solids using the following reaction scheme (Table 1, M1). The

reactor was charged with deionized water, 380.0 g, and surfactant, 0.15 g (DS10, sodium dodecyl benzene sulfonate, 98%, from Rhône Poulenc). The critical micelle concentration (CMC) of DS10 is 0.4 g/L. The CMC is defined as the point where further increases in the amount of surfactant added to water will not significantly decrease the surface tension. This is thought to be the point at which the surfactant begins to aggregate into micelles. The water and surfactant were purged with nitrogen and then heated to 70°C.

A pre-emulsion of monomer in water was prepared as follows: Vinyl acetate, 360.5 g (from Aldrich Chemical Co. Inc., 99+%, inhibited with 3-5 ppm of hydroquinone), and butyl acrylate, 63.5 g (from Aldrich, 99+%, inhibited with 10-50 ppm of methyl ether hydroquinone [MEHQ]), were slowly added to a stirred solution of 0.1 g DS10 in 158.0 g deionized water.

Ammonium persulfate, 0.30 g (from Aldrich, 98+%), was added to the reactor. At this time 30.0 g of the pre-emulsion was also added. The contents of the reactor were then heated to 80°C over the next 20 min.

Sodium bicarbonate, 0.85 g (from Aldrich), dissolved in 15.0 g water was then added to the remaining portion of the pre-emulsion. The pre-emulsion was then added to the reactor over a period of three hours using a lab pump. The emulsion addition rate was increased stepwise every 1/2 hr starting at a rate of 1.2 mL/min to a final rate of 7.0 mL/min. The initiator solution of 0.52 g of ammonium persulfate dissolved in 20.0 g of deionized water was added concurrently with the monomer at a constant rate using a syringe pump. This feed method ensured the production of a homogeneous copolymer and provides conversions of at least 99.75%.

A lightly larger particle size latex was made using less surfactant, 0.04 g, in the pre-charge (Table 1, M2).

Seeded Monodisperse Latexes

Further increases in particle size were accomplished through seeded reactions as listed in Table 2 (M3-M7). The reaction scheme is virtually the same as for the latex described earlier except for the following changes. For reaction M3, the reactor is initially charged with 200.0 g of a seed latex which was manufactured in reaction M2.

Table 2—Seeded Reactions

Charge Amount in Grams	M3	M4	M5	M6	M7
Seed latex	200.0 ^a	200.0 ^b	300.0 ^c	400.0 ^d	400.0 ^e
Deionized water	100.0	100.0	—	—	—
DS10 ^f	0.14	0.14	0.12	0.07	0.07
Deionized water	448.0	448.0	411.0	274.0	274.0
Sodium bicarbonate	0.85	0.85	0.64	0.43	0.43
Butyl acrylate	63.5	63.5	47.6	31.8	31.8
Vinyl acetate	360.5	360.5	270.4	180.3	180.3
Deionized water	25.0	25.0	18.75	13.0	13.0
Ammonium persulfate	0.85	0.85	0.62	0.41	0.41

(a) From M2

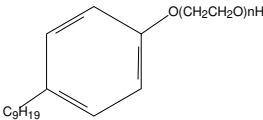
(b) From M3

(c) From M4

(d) From M5

(e) From M6

(f) Sodium dodecyl benzene sulfonate (Rhône Poulenc).

Table 3—Nonyl Phenol Ethoxylates Used for Blending with Monodisperse Latexes


Ethylene Oxide Units (n)	Average Molecular Weight	Moles Added per 100g Latex (x10 ³)
4	397	5.04
6	485	4.12
9	617	3.24
15	881	2.27
20	1101	1.82
40	1982	1.01

Water is also added (100.0 g). This is purged with N₂ for 30 min and heated to 80°C.

A pre-emulsion of monomer in water was prepared as follows. Vinyl acetate, 360.5 g, and butyl acrylate, 63.5 g, were slowly added to a stirred solution of 0.14 g DS10 and 0.85 g sodium bicarbonate in 458.0 g deionized water. The surfactant, DS10, was below its CMC.

The pre-emulsion was then added to the reactor over a period of three hours using a lab pump. The emulsion addition rate was increased stepwise every 1/2 hr starting at a rate of 1.2 mL/min to a final rate of 12.0 mL/min. The initiator solution of 0.85 g of ammonium persulfate dissolved in 25.0 g of deionized water was added concurrently with the monomer at a constant rate using a syringe pump.

Further reactions (Table 2, M4-M7) were performed as for M3 to obtain even larger particles. The amount of seed latex and the amount of monomer added varied to produce the appropriate particle sizes.

A narrower range of particles was produced for the drying rates and optical clarity experiments. The reactions were carried out as mentioned previously with the following exceptions. Reaction M2 was repeated and used as a seed to build larger particles using reaction scheme M5. The latex obtained in this reaction was then used again as a seed for the subsequent reaction all the time using reaction scheme M5. In all cases, a solids concentration of approximately 42% was obtained.

Addition of Surfactants to Latexes

The surfactants used in the study were nonyl phenol ethoxylates (Table 3), which are common steric stabilizers for vinyl acrylic latexes used in the manufacture of interior latex paints. The surfactants were added to the latexes by first diluting them in water and subsequently adding them to the latex under agitation. Agitation was continued for at least one hour. The final solids content of the latex was 20% with a 4.8% surfactant loading based on polymer, for the T_g and MFFT data, while for drying rates and clarity studies a two percent surfactant loading was used.

The lower ethoxylate surfactants (4EO and 6EO) were only very slightly soluble in water. Therefore they were

briefly heated in water to aid in dissolving them. Upon cooling, a fine suspension appeared. This suspension was subsequently added to the latex.

Conversion

The monomer concentration in the vinyl acrylic latexes was determined using a Hewlett Packard 5890 Series II gas chromatograph and recorded on a Hewlett Packard HP 3396A Integrator. Pressures for the air, hydrogen, and helium were 35, 17, and 40 psi, respectively. The oven temperature was 80°C, and the column was a six foot, 10% Carbowax 20M-TPA, Chromsorb W-DMCS, 60-80 mesh column. The detector was a flame ionization detector. Samples were drawn from the reactor during and at the end of specific reactions, by syringe, through a septum. The latex was diluted 1/10 with deionized water and injected directly into the gas chromatograph. The injector port contained a removable glass tube to facilitate cleaning.

Particle Size and Distribution Measurements

The particle size and size distribution of the latexes was measured using an ICI-Joyce Loebl disk centrifuge. The output was recorded by a Brookhaven Instruments DCP-100 data system. Water was used as the spin fluid and the density gradient was produced using methanol. The latexes were diluted to 0.25 to 0.5 wt% in a mixture of 80/20 water/methanol by weight.³⁸

The densities of the copolymeric latexes were calculated using a weighted average of the densities of the homopolymers. The rotational speed of the disc was selected so that the particles passed the detector after one minute. For the longer analysis times, the spin fluid was put into the disc and 1 mL of dodecane was added to the top of the spin fluid. This inhibited the evaporation of methanol from the top of the spin fluid and thus prevented the breakdown of the spin fluid gradient, especially on humid days.

Particle sizes below 80 nm are not reliably measured on the disc centrifuge and particles below 40 nm may not even be detected. Smaller particles can be detected however, by the visual observation of the spinning disc soon after the injection of the concentrated latex onto the disc. The larger particles rapidly migrate to the edge of the disc while the small second generation particles form a faint blue ring. The sizes of small particles cannot be measured but this procedure allows for their detection and indication of a second generation of particles in monodisperse latex systems.

Differential Scanning Calorimetry

The T_g of the latexes was analyzed using a DuPont Instruments 910 differential scanning calorimeter. The latexes were dried for 10 days at room temperature to ensure the elimination of any moisture, where required. Each sample was then analyzed twice; the first run was performed to eliminate any thermal history while the second run was used to measure the T_g of the latexes. The scanning range was varied depending on the T_g of

Table 4—Particle Size and Distribution of Latexes Produced from Recipes in Tables 1 and 2 for Stabilizer and Surfactant Effects

Recipe	Particle Size Dn (nm)	Projected (nm)	Polydispersity (Dw/Dn)	Coefficient of Variation (%)
M2	208	—	1.013	6.7
M3	384	379	1.028	9.3
M4	686	699	1.014	6.9
M5	1.26	1043	1.007	5.0
M6	1367	1344	1.007	5.1
M7	1791	1791	1.018	7.9

Dn = number average diameter.
Dw = weight average diameter.

the latex. The scanning rate for all samples was 10°C/min. The T_g was taken to be the onset of the transition.

To determine the T_g of wet latexes as a function of water content, a sample was partially dried overnight in a polyethylene lined petri dish. A portion of the sample was then put into an aluminum pan. The scanning range started at -30°C and ended at 100°C. The 100°C final temperature aided in driving off some of the water. The scans were repeated until all of the water was driven off and a constant T_g was obtained.

Dynamic Mechanical Measurements

A Rheometrics dynamic mechanical spectrometer was used to confirm the T_g measurements of the wet and dry latex films. A known amount of latex (50 g at 42% solids) was allowed to dry in a polyethylene lined petri dish (total surface area for petri dish = 165.1 cm²). After one day, the incompletely dried film was removed from the dish and cut into rectangular pieces using a die (5.9 cm × 1.25 cm) on a hydraulic press. The film was allowed to fully dry for 10 days. To obtain the T_g of a wet latex a dried specimen was soaked overnight in water.

The dynamic mechanical tests were performed using a torsion rectangular configuration at a constant frequency of 20 Hz and a strain rate of one percent. The temperature was increased from -30° to 65°C.

Minimum Film Forming Temperature

The minimum film forming temperature (MFFT) of the latexes was obtained through the use of an MFFT bar. This bar consisted of a stainless steel plate with slight depressions milled into it to contain the latex. One end was cooled using two 12-volt ceramic thermoelectric cooling modules while the other end remained at room temperature creating a temperature gradient from 0° to 20°C along the bar. The temperature gradient on the bar was measured using eight thermocouples placed at equal intervals along the bar. The bar was covered with a glass plate and nitrogen was passed between the bar and glass cover at a rate of 2 L/min to facilitate drying and to maintain a constant humidity. The latex was applied to the bar and the temperature profile of the bar was monitored during the drying of the latex.³⁹

The MFFT of the latex was considered to be the temperature at which the film turned from a clear, well coalesced film, to a cloudy or cracked uncoalesced film. The error in the measurements is ±5%.

Drying Rates of Latexes Using a UV/VIS Spectrometer

The drying rates of the latexes were measured as a function of opacity of the sample. The opacity was monitored by measuring the transmittance of visible light (500 nm) using a Perkin-Elmer UV/VIS spectrometer. A known amount of latex (0.6 g at 42% solids) was applied to a glass slide (7.5 cm × 1.3 cm). This configuration gives a sample coverage of 0.061 g/cm². The latex was allowed to air dry in still air conditions until it would not flow when the glass slide was held vertically. A clean glass slide was used as a blank and then the glass slide with the latex was inserted into the UV/VIS spectrometer and the transmittance monitored until a constant transmittance of close to 100% was obtained.

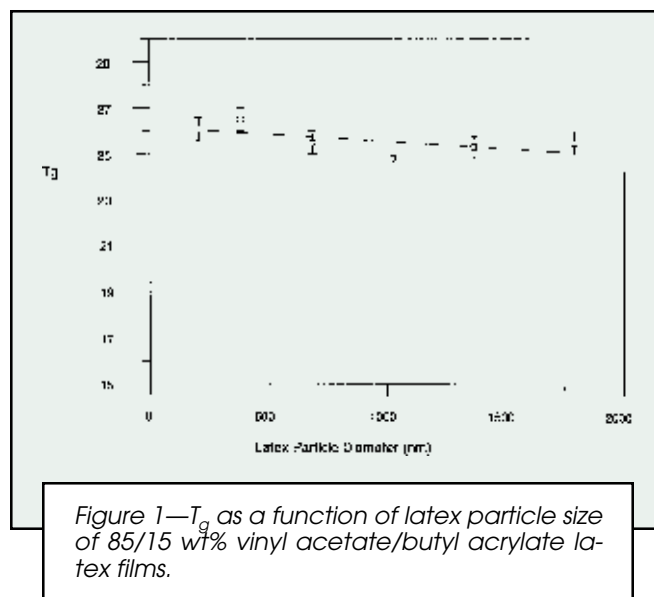
Drying of Latexes Using Gravimetric Analysis

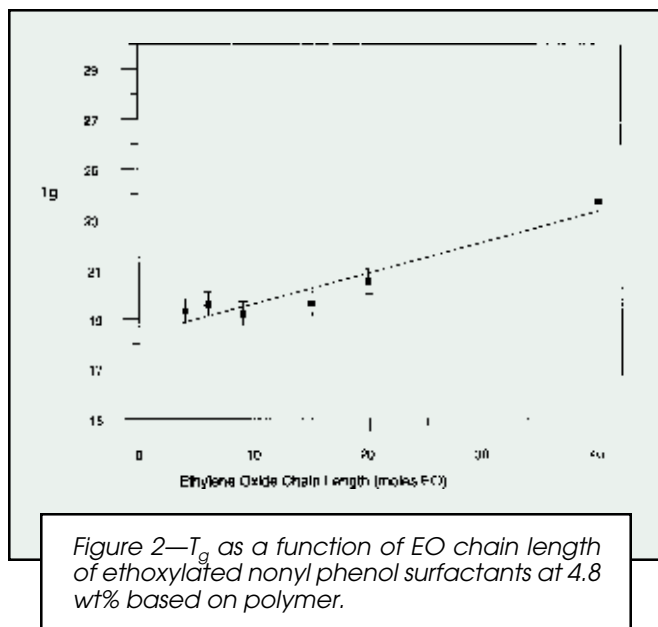
Drying rates were also confirmed using gravimetric analysis. A known quantity of latex (10.0 g) or latex paint (7.6 g) was allowed to dry in a petri dish (total surface area for latex petri dish = 165.1 cm² and 124.7 cm² for paint petri dish). This configuration also gives a sample coverage of 0.061 g/cm². The weight was monitored until a constant weight was obtained. All latexes in a series were dried at the same time to reduce humidity and temperature effects on drying rates between samples. The temperature was 20°C while the humidity was at 40%.

RESULTS AND DISCUSSION

Stabilizer and Surfactant Effects on the T_g and Minimum Film Forming Temperatures of Latexes

The mean particle sizes and distributions of the latexes obtained are listed in Table 4. The T_g of the latex films made from these surfactant-free latexes was measured and plotted with respect to the particle size of the latex (Figure 1). These measurements were done in order to

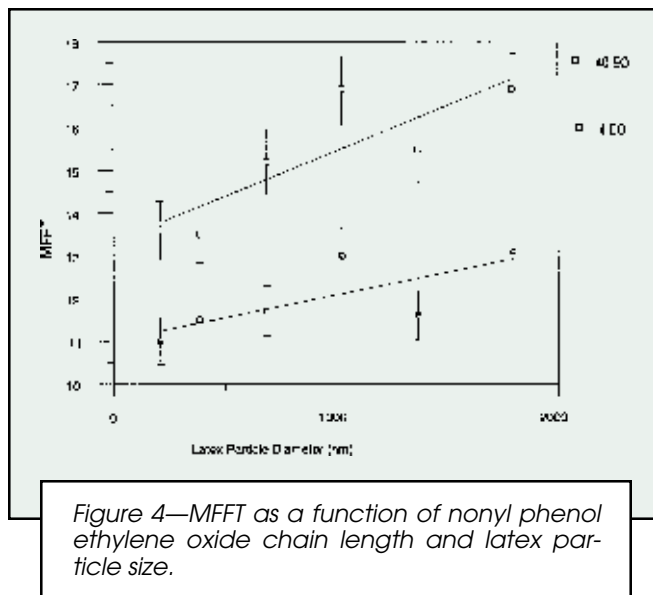
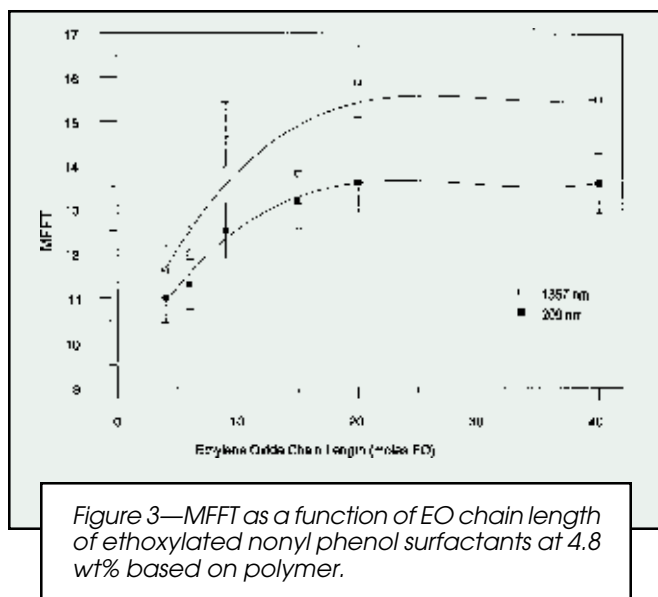




establish a baseline from which all other plasticizing effects were to be compared. As illustrated in Figure 3, the T_g of the latex films was approximately 26°C. The T_g is thus not a function of particle size, as expected, since each latex was produced to be homogeneous. (The error bars, representing an error of 1°C, were obtained by finding the error associated with measuring five T_g s of the same sample and then applying this error to all samples.)

In order to determine the effect of nonyl phenol surfactant type on T_g , a 686 nm latex was dosed with a series of nonyl phenol surfactants. Latex films were produced by allowing the latexes to air dry for 10 days at ambient temperatures. DSC measurements were performed to determine the effect of surfactant type on the T_g .

As illustrated in Figure 2, the type of surfactant dramatically affects the T_g of the latex film. All of the surfactant types reduced the T_g of the latex. While 40EO decreased the T_g of the latexes by only 3°C, the lower



ethoxylated surfactants decreased it by 5° to 7°C. It should be noted that while all surfactant additions were equal on a weight basis they varied significantly on a molar basis. The higher ethoxylates have a much higher molecular weight and therefore fewer moles of surfactant were added than with lower ethoxylates.

Vijayendran's²⁶ results are in direct conflict with the results presented in this work. While the trend presented in Figure 2 indicates better plasticizing with lower ethoxylate chain lengths, Vijayendran's results indicate the opposite. Since he used only two relatively hydrophilic surfactant types (20EO and 50EO) a trend is difficult to establish. His values for the T_g of the latex are further suspect since he used a batch polymerization technique to produce the copolymer latex.⁴⁰ This technique will most certainly produce heterogeneous particles and thus more than one T_g or a broad range for the T_g should be reported.⁴¹

MFFT measurements were performed on two surfactant modified latexes (208 nm and 1367 nm). Surfactants were added as described. Figure 3 illustrates the results. (The error bars, representing an error of $\pm 5\%$, were obtained by finding the error associated with measuring five MFFTs of the same sample and then applying this error to all samples.) For both the large and small latex, the MFFT remains relatively unchanged for 20EO and 40EO. As the EO chain length in the surfactant is decreased, the MFFT drops off sharply. In the present work, as the EO chain length was reduced, the driving force for coalescence increased since it results in an increase in the interfacial energies of the system. At the same time, the T_g and the modulus were reduced, thus lowering the MFFT.

In work done by Eckersley and Rudin²⁴ on acrylic latexes, they also found that a nonionic ethoxylated alkyl phenol surfactant plasticized a latex of a 49:49:2 poly(methyl methacrylate-co-butyl acrylate-co-methacrylic acid) polymer. However, the MFFT was independent of the nonionic surfactant concentration. This is presumably because of two counteracting efforts. Since only the concentration of surfactant was varied and not

the type, the plasticization of the polymer by the surfactant reduced the resistance of the material to flow and coalescence as explained earlier; but with this surfactant, the driving force for coalescence was decreased since the total EO content increased resulting in a reduction in the interfacial energies of the system.

Another series of latex samples were made in which two different types of ethoxylated nonyl phenol surfactants were added to a range of particle sizes (Figure 4, error $\pm 5\%$). Here the effect of particle size can be observed. With both of the surfactant types, MFFT increases with increasing particle size.

Figure 5 illustrates some of the same data as Figure 4 but with a complete range of particles to which the complete range of surfactants have been added (error bars have been omitted for 6EO and 20E for clarity). The data are difficult to resolve, but the MFFT data appear to increase with increasing particle size for all surfactant types. This was expected since although surfactants plasticize the latex polymer, they also reduce the aqueous surface tension and polymer/water interfacial energy.

It should be noted that MFFTs of so-called "surfactant free" latexes also increase with particle size. The total surface area of a large particle size latex is less than that of a small particle size latex at equivalent solids concentrations. These latexes contain sulfate ions from the initiator at equivalent solids concentrations. These latexes contain sulfate ions from the initiator at the ends of the polymer chains which act as stabilizers. Since these stabilizers are hydrophilic and the T_g of the polymer is below the reaction temperature during the production of these latexes, the ionic groups can migrate to the surface of the latex particle.³⁹ Larger particle size latexes will thus have a higher concentration of stabilizing moieties on their surface than smaller ones and thus are expected to resist coalescing to a greater degree. As a result, larger particles will also have lower latex-water interfacial tensions, reducing the forces favoring coalescence and, as a result, produce higher MFFTs.

Drying Rates of Latexes

The latex particle size and size distributions for this set of experiments are listed in Table 5.

There appears to be a relationship between particle size and the drying rate of latexes. The clarity of a latex film was used as a criterion for the loss of water from a latex film. This was accomplished by monitoring the transmittance of a latex as it dried using a UV/VIS spectrometer at a wavelength of 500 nm. It is realized that the phenomenon measured reflects both the loss of water from between the latex particles and polymer coalescence.

The larger particle size, "surfactant free" latexes dried at a faster rate than smaller particle size latexes (Figure 6). It is suggested that the larger particles dried faster since the density of stabilizing entities on the surface of the latex is much greater than on the smaller latex particles, thus increasing the resistance to coalescence and allowing more rapid water evaporation from the latex film.

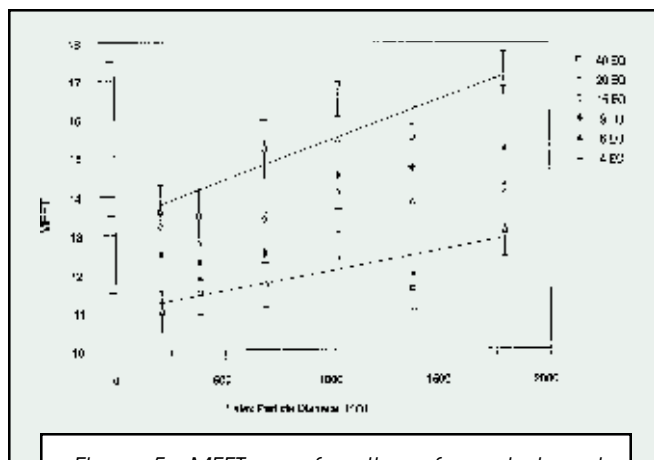


Figure 5—MFFT as a function of nonyl phenol ethylene oxide chain length and latex particle size.

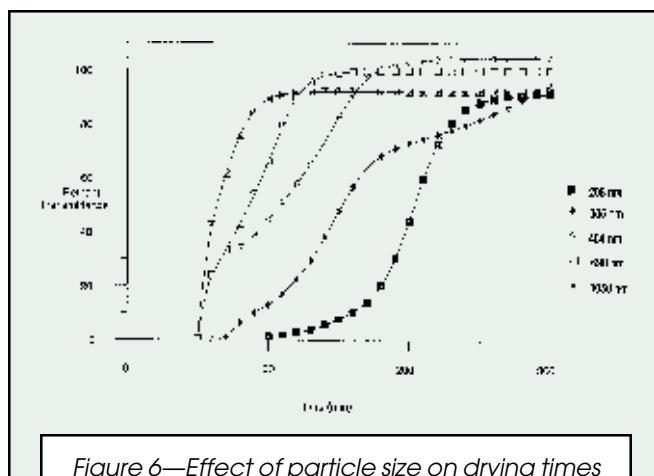


Figure 6—Effect of particle size on drying times of latexes.

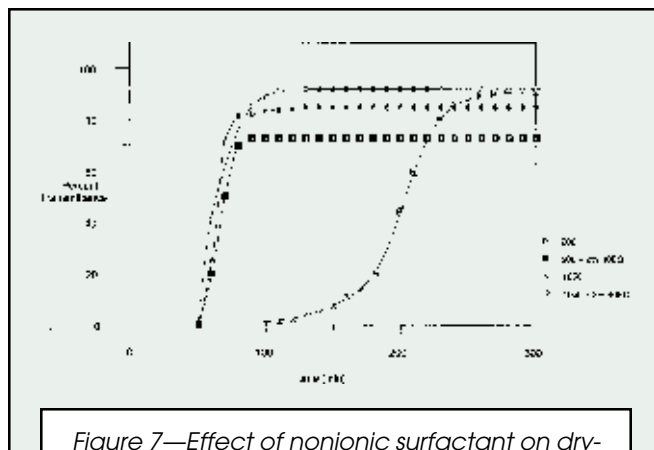


Figure 7—Effect of nonionic surfactant on drying time.

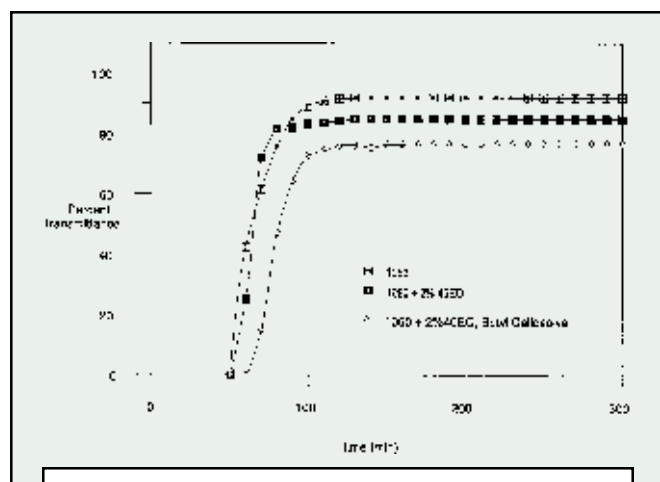


Figure 8—Effect of coalescing agent on drying time.

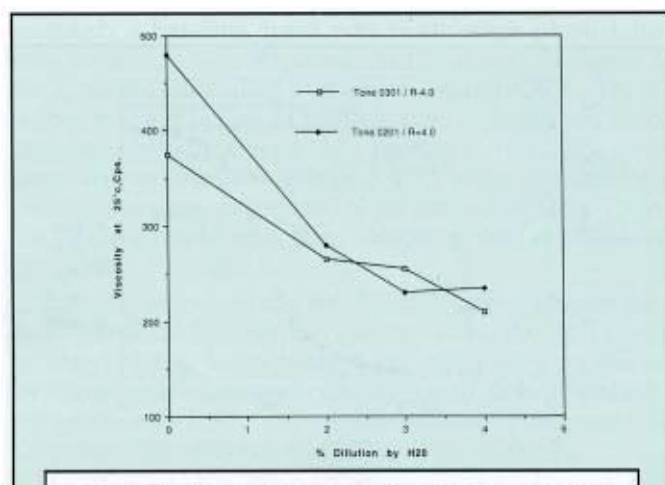


Figure 9—Drying rates as a function of particle size.

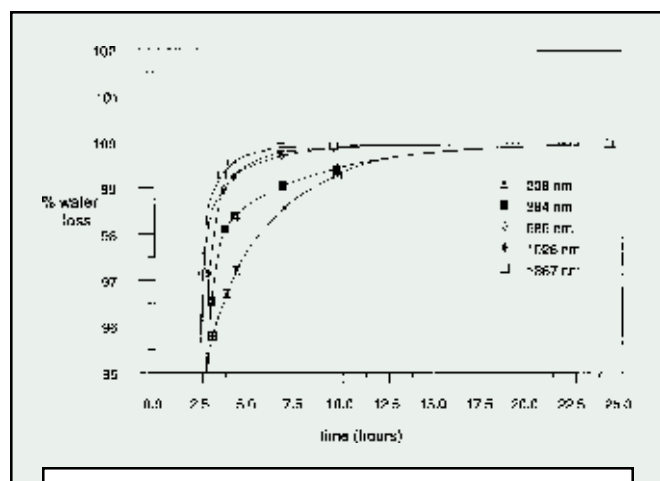


Figure 10—Drying rates as a function of particle size.

To test this hypothesis, the smallest (206 nm) and the largest (1050 nm) particle size latexes were stabilized with two wt%, based on polymer, of a 40EO surfactant and the drying rates were compared with those of their unstabilized counterparts (*Figure 7*). The addition of surfactant to the smallest particle size latex increased the drying rate to that of the largest size. The addition of surfactant to the largest particle size latex resulted in no discernible change in the drying rate. Thus, the effect of particle size appears to be a function of stabilizer concentration and not a function of particle size.

The addition of two wt% of a coalescing agent, butyl Cellosolve® (ethylene glycol monobutyl ether acetate from Union Carbide Corp.), did not significantly affect the drying time of the latex (*Figure 8*). This emphasizes the importance of the surface character of the latex particles on the drying rates. The butyl Cellosolve acts as a plasticizing agent, but it only affects the film formation process after the latex particles actually touch. The surfactants act as steric stabilizers, retard coalescence, and facilitate water loss.

Also notable in *Figures 6-8* are the final transmittance values. As illustrated in *Figure 6*, the largest and the smallest latexes produced the lowest transmittance levels at the end of the drying period while the 454 nm latex produced the highest transmittance. The latexes larger than the 454 nm latex became increasingly hazy as the particle size increased. This is speculated to be due to the increasing size of the interstitial domains in the larger particle size latexes which contain more hydrophilic material. As the domain size increased, the refraction of light at the boundaries increased, causing a hazy film to be produced. The latexes which were smaller than 454 nm produced films with surface irregularities. The concentration of irregularities increased as the particle size of the latex decreased. This produced films with lower final transmittance levels.

In *Figure 7*, where the nonionic surfactant 40EO was added, the transmittance level decreased when compared to the surfactant-free film. This is speculated to be due to surfactant regions or exudations^{42,43} causing the film to become hazy and reducing the final transmittance levels. Also in *Figure 8*, the addition of butyl Cellosolve caused the film to become even more hazy. Here the addition of butyl Cellosolve may have actually enhanced the exudation rate of the surfactant, causing the film to become more hazy than the latex film with no coalescing solvent added. This result was also obtained by Winnik et al.³³

The drying rates of latex films were also measured gravimetrically (*Figure 9*). Initially, the rate of water loss for large and small particles was identical up to 95% total water loss, which corresponds to a solids content of 93.5%. The drying rate during this period in time was $3.04 \times 10^{-4} \text{ g} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ which corresponds closely to the values of $2.5\text{--}2.9 \times 10^{-4} \text{ g} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ reported by Vanderhoff et al.¹ While Vanderhoff noticed a drop in the drying rate at about 60–75% solids, which corresponds to a solids concentration at which the particles are just touching, the drying rates for the latexes presented here did not decrease until 93.5 to 95.5% solids, depending on the particle size of the latex.

Table 5—Particle Size and Distribution of Latexes Produced from Recipes in Tables 1 and 2 for Drying Rates and Optical Clarity

Recipe	Particle Size Dn (nm)	Projected (nm)	Polydispersity (Dw/Dn)	Coefficient of Variation (%)
M2	206	—	1.035	10.5
M5 ^a	305	313	1.033	10.5
M5 ^b	454	464	1.029	9.6
M5 ^c	690	690	1.025	8.9
M5 ^d	1050	1049	1.010	5.9

(a) 206 nm seed.
 (b) 305 nm seed.
 (c) 454 nm seed.
 (d) 1050 nm seed.

Dn=number average diameter
 Dw=weight average diameter

These results fit a two-stage drying model,^{44,45} which has also been found to give a good picture of the drying behavior of acrylic latexes.⁴⁶ During the first drying stage, evaporation occurs from a water surface that retreats through the film, away from the air boundary, as the drying progresses. The water in the shrinking wet layer in contact with the substrate supplies water to maintain a constant evaporation rate. Total water loss is directly proportional to time until this reservoir of water is depleted. The second falling rate period begins long after the particles have packed into an irreversible array.

The percolation model^{44,45} implies that drying is complete before significant degrees of particle coalescence. It has been observed, however, that materials that coalesce more readily form a skin before the film is dry. It seems, therefore, that the newly formed coalesced films are sufficiently porous to allow essentially unimpeded transport of water.⁴⁶ The present results, with a different polymer, are consistent with this conclusion, since the addition of a coalescing agent did not affect the temporal development of a transparent film.

Close inspection of the curves at 95 to 100% water loss reveals similar trends to those seen with the UV/VIS spectrometer (Figure 10). The smaller particles take a much longer time to lose residual water. As the particle size increases, the residual water is lost more rapidly since the greater concentration of stabilizing moieties on the larger particles provides for better water transport.

Water as a Plasticizer

Another interesting aspect of the film formation of the "surfactant free" latexes is that, surprisingly, the MFFT values fall between the values for the 40EO and 4EO surfactants (Figure 11, error $\pm 5\%$). It was expected that the MFFT of the "surfactant-free" latex would be higher than that of the surfactant modified latexes since its T_g and, subsequently, its modulus is higher. Since the only other ingredient present was water, it was theorized that water must be plasticizing the latex.

The extent of water plasticization of latex polymers was examined using dynamic mechanical spectroscopy. The rheological behavior of a dry latex film was compared to that of a latex film which was soaked overnight in water (Figure 12). A one-percent strain was used since it allowed for the measurements to be done in the linear

viscoelastic region. The upper curves for G' , G'' , and $\tan \delta$ indicate the modulus for the wet latex film while the dry films are indicated by the lower curves of each set. The reason G' is higher for the wet latex is because the water in the wet latex is frozen at lower temperatures. As the temperature increases, the curves cross and G' wet dips below G' dry. This occurs since the water in the wet latex starts to melt above 0°C and plasticizes the latex.

The T_g of a partially dried latex was measured using DSC to verify the data obtained using dynamic mechanical spectroscopy. As illustrated in Figure 13, water significantly reduced the T_g of the latex. The lowest curve represents a latex with approximately five percent water. The large first order transition starting at approximately 0°C is indicative of the water melting. The second order transition, indicating the T_g of the latex, is at approximately 15°C for the lowest curve. As water is driven off, the size of the first order transition decreases (upper curves). The actual transition shifts to a lower temperature as the latex dries as well. This is probably due to a freezing point depression brought about by the higher concentration of initiator fragments and other ions which are soluble in the aqueous phase.²⁰

The T_g of the latex polymer also changes as it dries. It slowly shifts to higher temperatures at lower water concentrations. The third curve from the top represents a latex where there is no discrete water phase (no first order transition indicating the melting of water). The T_g of the polymer has increased, but is still less than that of the completely dried latex (top two curves). Upon further drying, the T_g shifts to its final temperature at 26°C (second curve from the top). This compares well with the room temperature dried latex which has a T_g of 26°C as well (top curve).

The Fox equation⁴⁷ can be used to calculate the glass transition temperature (T_g) of the latex (T_g of poly(butyl acrylate) = -54°C, T_g of poly(vinyl acetate) = 32°C).

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \quad (1)$$

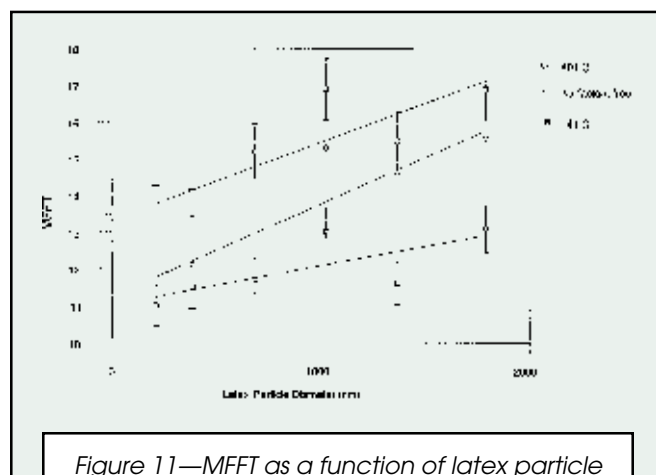


Figure 11—MFFT as a function of latex particle size of surfactant-free latexes and surfactant-free latexes blended with 4.8 wt% nonyl phenol ethoxylated surfactants based on polymer.

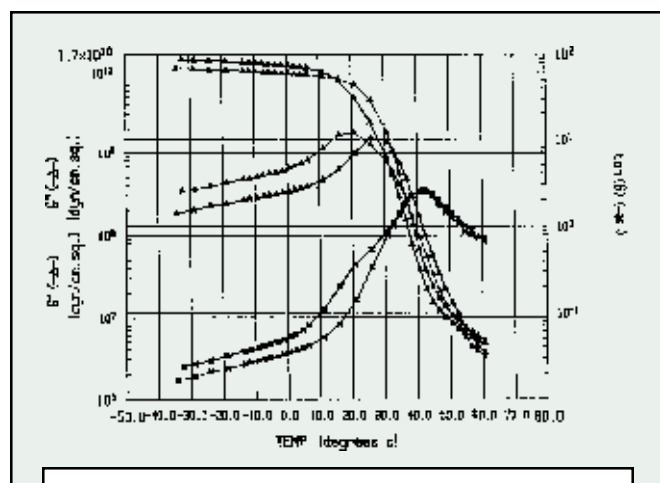


Figure 12—Dynamical mechanical properties of wet and dry vinyl acrylic latex films.

The values for T_{g1} and T_{g2} are in Kelvin for the homopolymers while T_g is the T_g of the copolymer. The values for w_1 and w_2 are the weight fractions of each polymer in the copolymer. The calculated T_g is 15°C.

Recall that the water plasticized latex has a T_g of 15°C, which equals the calculated T_g , while the dried latex has a T_g of 26°C. The Fox equation is not a noticeably accurate predictor, but one can use the discrepancy noted to speculate, as follows, on the surface character of the latex particles. Apparently the highly polar and ionic portions of the latex which include initiator sulfate ions on the ends of the polymer chains, small amounts of hydrolyzed poly(vinyl acetate) (i.e., poly(vinyl alcohol)) and other products,⁴⁸⁻⁵¹ possess a high T_g when dry, and can associate⁵² to form pseudo crosslinks raising the average T_g of the material. When water is present, the T_g is lowered since the water-soluble portions are solvated. It is suggested that water plasticization occurs significantly in the surface portions of the latex and to a lesser extent in the underlying polymer.

It is evident that major polymer types used for architectural coatings are plasticized by water. This is shown by earlier work^{21,24} with acrylic latexes and more dramatically by this study of vinyl acrylics. Water plasticization should therefore be included in any mechanistic study of coalescence of these latex types.

Combining Water and Surfactant Effects

Upon further examination of the data presented in this paper, one can see that the MFFT of the surfactant-free latex resides between those of the materials containing 4EO and the 40EO surfactants. The coincidence is approximately with the 9EO surfactant modified latex. This is interesting in that all surfactant types reduced the T_g of the latex yet only the latexes modified with surfactants with ethylene oxide lengths below 9EO actually reduced the MFFT of the latex. The explanation is rather simple when one looks at the structure of the surfactants used. The shorter EO surfactants are more hydrophobic than the longer ones and thus migrate further into the latex particle, a thermodynamically fa-

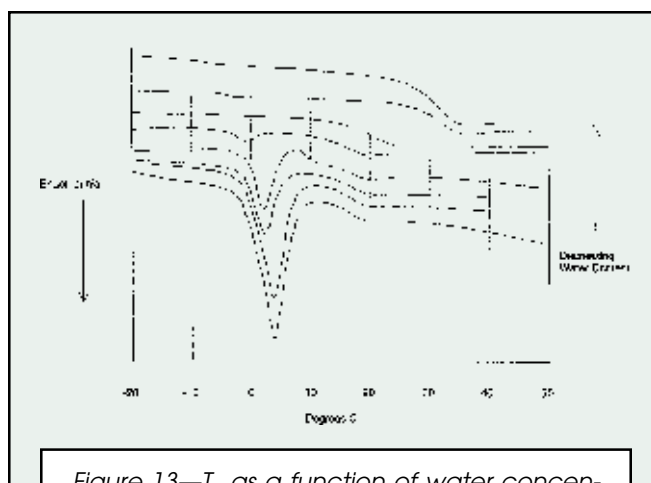


Figure 13— T_g as a function of water concentration in a vinyl acrylic latex.

vorable process studied and discussed by Bradford.³⁰ The longer EO surfactants extend further into the aqueous phase increasing the forces needed to cause the particles to come in contact with each other and coalesce.

The higher stabilizing ability of the longer EO surfactants was also evident in the storage stability of the wet latexes. The latexes formulated with 4EO and 6EO surfactants remained stable only one week while the latexes formulated with 20EO and 40EO surfactants were indefinitely stable.

A complementary or alternate reason for obtaining higher MFFTs with longer EO surfactants is that these surfactants are more hydrophilic than the shorter EO surfactants. This decreases the latex-water interfacial tension and thus reduces the force of coalescence, increasing the MFFT.

Thus, water plasticizes vinyl acrylic latexes decreasing T_g s and producing MFFTs which are significantly lower than the dry T_g s. Surfactants can either increase or decrease the MFFT depending on their relative ability to stabilize or plasticize latexes.

CONCLUSIONS

Water plays a large role in the film formation process of vinyl acrylic latexes. While many authors have considered the influence of water on the interfacial forces in latex film formation, not enough emphasis has been placed on its significance as a plasticizing agent. Clearly water plasticizes latexes and only wet viscoelastic moduli or T_g s should be used when modeling the film formation process.

A further influence in the film formation process is the type of stabilizer used. Ethoxylated nonyl phenol surfactants can plasticize polymer latex films. They also influence the MFFT of vinyl acrylic latexes by reducing the MFFT when ethoxylates of less than nine units in length are used. This is thought to be due to a plasticizing effect. While higher ethoxylates (20EO and 40EO) also plasticize latexes, the hydrophilic portion reduces

the latex-water interfacial tension and increases the steric barrier to coalescence, thus increasing the MFFT.

Increases in the particle size of latexes increase the concentration of surfactants on the surface of latex particles when surfactants are added on an equal polymer weight basis. A higher steric and ionic barrier to coalescence and a lower latex-water interfacial tension is then produced on larger latex particles, and as a result, the MFFT increases. The type and concentration of stabilizer on the surface of latex particles can alter the MFFT, even in surfactant-free latexes. As a result, particle size effects on the film formation process cannot be assumed without prior knowledge of the surface stabilizing type and concentration.

The vinyl-acrylic latexes used in this study were mono-disperse and were made without use of cellulosic stabilizers. These protective colloids are expected to undergo grafting and molecular weight degradation during the emulsion polymerization reaction. The presence of the products of such reactions on the latex particle surfaces will certainly exert an as yet undetermined effect on the coalescence and film properties of "real" vinyl acetate-butyl acrylic copolymer latexes. Drying rates of latexes are dependent on their stability. Vinyl acrylic latexes do not exhibit a reduction in drying rate until approximately 93.5% solids has been reached. The clarity of films produced from vinyl acrylic latexes increases with decreasing particle size to a maximum, and then decreases again. Clarity increase is due to the lowering of the surface stabilizer concentration on the particle surface, reducing surfactant domain size. The subsequent decrease of clarity from a maximum is attributed to the formation of surface defects in the film as it dries.

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