

Role of Particle Size on Latex Deformation During Film Formation

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INTRODUCTION

The film formation behavior of latex-based coatings is an important property affecting many end-use applications. High T_g latexes are often used in applications which require film hardness. In order to achieve latex coalescence at ambient temperature, co-solvents or coalescent aids are frequently added to plasticize the latex to lower the film forming temperature. Due to environmental and health concerns and stricter emission regulations, there is a strong desire by the coating industries to minimize the use of volatile organic compounds (VOC) in coating applications. Therefore, coating systems that exhibit both good film formation and end-use properties with little or no VOCs in the formulations are desired. A better understanding of the fundamental aspects of film formation is important towards the design of optimal coating systems. Recently, there has been renewed research interest to study all aspects of film formation. Dobler and Holl,¹ Winnik,² Visschers and co-workers,³ and Keddie⁴ have reviewed the literature on latex film formation. New experimental techniques such as small angle neutron scattering,⁵⁻⁷ small angle X-ray scattering,⁸ and atomic force microscopy⁹⁻¹⁵ have been applied to study aspects of film formation.

In the latex film formation process, particles deform to eliminate interstitial air voids and coalesce to form an integral film. There are many hypotheses proposed to account for the origin of the deforming forces. Dillon and co-workers¹⁶ first proposed that latex coalescence is due to surface tension forces following the evaporation of water. This is referred to as the dry sintering theory. Brown¹⁷ suggested that the capillary forces, due to the water/air interfacial tension generated during water evaporation, are responsible for the deformation of the latex particles and film formation. Vanderhoff and co-workers¹⁸ proposed another theory suggesting that the deforming forces are due to the pressure generated by the water/latex interfacial tension. This is referred to as the wet sintering process. Sheetz¹⁹ concluded that the capillary forces and wet sintering are confined to the early stages of the coalescence process and cannot account for the forces present throughout the entire film formation process. He suggested that the surface layer of latex dries first forming a membrane. Subsequent water evaporates by diffusion through the membrane

The ability of latex particles to deform and coalesce to form an integral film upon drying is an important property in many latex coating applications. Many theories have been proposed to account for the origin of the deformation forces. The capillary forces which depend inversely on particle size have been accepted as important for latex deformation and film formation. The minimum film forming temperature (MFFT) has been found to be a function of the particle size of latexes and has been used as evidence that the capillary forces are responsible for film formation.

In this study, the deforming force at MFFT has been determined from the moduli of water-equilibrated latex polymers. No particle size dependence was observed. The magnitude of the deforming forces was at least an order of magnitude lower than that predicted by the capillary force theory. Electron microscopy of film formed below the MFFT, a condition that corresponds to early stage film formation, showed significant deformation, indicating that at the beginning of film formation, forces of magnitude predicted by the capillary force theory are present. However, the magnitude of the forces decreases rapidly as film formation progresses. The MFFT particle size dependency can be explained by the difference in the degree of water plasticization. Evidence that latexes of different particle size were plasticized by water to different extents was determined from the T_g s of the latex emulsions.

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exerting a compressive force on the latex particles until the latex film is dry. Kendall and Padget²⁰ later proposed that the adhesive forces, as described by the Johnson, Kendall, and Roberts theory (JKR theory), are the origin of the forces deforming latex particles in the film formation process.

In Brown's capillary force theory¹⁷ and Kendall and Padget's adhesive force theory,²⁰ the forces exerted on the latex particles were predicted to be a function of the latex particle size. Brodnyan and Konen²¹ first studied the effect of particle size on the minimum film formation temperature (MFFT). However, their study was inconclusive. Eckersley and Rudin,²² and Jensen and Morgan²³ measured the MFFT of a series of acrylate latexes with different particle sizes and found the MFFT increased as a function of the particle size. This was taken as evidence that the deforming force is a function of the latex particle size. Sperry and co-workers,²⁴ however, recently observed insignificant particle size effect on MFFT with a series of poly(butylmethacrylate) latexes. Vanderhoff and co-workers¹⁸ suggested that capillary forces are important only during the early stages of film formation. Doblér and co-workers²⁵ found that the MFFT of a series of latexes are similar with and without added surfactants at various humidities and concluded that capillary forces alone cannot account for the film formation. Brown¹⁷ suggested that the magnitude of the deforming forces can be determined by measuring the modulus of the "water-saturated" latex film at conditions corresponding to the film formation process. Brodnyan and Konen²¹ determined that the shear modulus, G' , at film formation ranges from 2.7×10^6 to 3.5×10^8 Pa for the series of latexes. Kan²⁶ determined the deforming forces responsible for film formation of a series of carboxylated styrene/butadiene (S/B) latexes to be in the range of $1.5\text{--}3.0 \times 10^6$ Pa. However, due to the limited particle size range, no conclusion could be made concerning the effect of particle size on the deforming forces.

The importance of the role of water plasticization on latex properties and, therefore, film formation has been recognized.^{27,28} Kan²⁶ reported on the viscoelastic properties of water saturated latex polymer film. Lee and co-workers²⁹ used microcalorimetry to determine the glass transition behavior of latex emulsions. The effect of water on the depression of glass transition temperature (T_g) of latexes depends on the hydrophilicity of the polymer. There are many studies of the MFFT of different polymer latexes. Eckersley and Rudin²² found the MFFTs of a series of poly(methyl methacrylate-butyl acrylate-methacrylic acid) (MMA/BA/MAA) latexes to be higher than their dry polymer T_g s. Jensen and Morgan²³ found the MFFTs of a series of poly(methyl methacrylate-ethyl acrylate-methacrylic acid) (MMA/EA/MAA) latexes to be lower than their dry polymer T_g s. Li³⁰ studied the MFFTs of a series of poly(styrene-methyl methacrylate-ethyl acrylate-methacrylic acid) (S/MMA/EA/MAA) latexes, varying the S/MMA ratio. He found the MFFT of poly(S/EA/MAA) latex to be 17°C higher than the corresponding MMA/EA/MAA latex, even though the dry T_g s of the two polymers were similar. Sperry and co-workers²⁴ have presented similar results. They also suggested that a surface layer enriched with hydrophilic material that varies with particle size might be respon-

sible for the sometime-observed particle size effect on MFFT.

The difference in latex hydrophilicity can also be important in end-use performance in addition to film formation. Smith and Wagner,³¹ for example, attributed the better dirt pickup performance of poly(styrene-acrylate) coatings when compared to poly(methyl methacrylate-acrylate) coatings to the lower hydrophilicity of S versus MMA.

In this paper, the role of latex particle size on film formation will be examined. The magnitude of the deforming forces experienced by latex particles during film formation will be determined using two series of acrylate latexes with particle size ranging from 76 to 960 nm. The magnitude of the deforming forces in the early stage of film formation will also be studied by examining the deformation of latex particles in films formed at conditions below the MFFT. The role of water plasticization on the T_g s of latex emulsions, referred to as wet T_g s in this paper, will be determined using microcalorimetry in order to study the effect of particle size of the latex on MFFT. The role of different monomers on water plasticization and MFFT will also be discussed.

EXPERIMENTAL

Materials

Two series of latexes were made using semi-continuous emulsion polymerization. In the first series, latexes were prepared using MMA, EA, and acrylic acid (AA) as monomers. In the second series, MMA, BA, and MAA were used. Latexes of different particle size were prepared.

Preparation of Unseeded Latexes

The emulsion polymerization procedure used to prepare unseeded latexes was as follows. A solution containing 0.50 parts of sodium lauryl sulfate (SLS), based on 100 parts of monomer, 0.25 parts of ammonium persulfate, and 150 parts of deionized water was added to a stirred 0.5 gal reactor. The reactor was heated to 80°C. Ten parts of a monomer mix consisting of 48.5 parts MMA, 48.5 parts EA, and 3 parts AA were added to the reactor and allowed to react for 10 min. The remaining 90 parts of monomer mix were added over 60 min, concurrent with the addition of a separate aqueous stream consisting of 38.5 parts of deionized water and 0.05 parts of sodium hydroxide. After the monomer mix and aqueous mix were added, the reaction mixture was maintained at 80°C for an additional 60 min. Another unseeded latex was also made using a monomer mix consisting of 48.5 parts MMA, 48.5 parts BA, and 3 parts MAA.

Preparation of Seeded Latexes

The procedure used to prepare seeded latexes is similar to the procedure used to prepare the unseeded latexes. An initial charge consisting of the seed latex, 0.01

parts of a 1% solution of Versenol 120, a trisodium salt of N-(carboxymethyl)-(2-hydroxyethyl)-N,N'-ethylene-diglycine from The Dow Chemical Company, and deionized water was added to the reactor and heated to 80°C. The monomer mix was added in 180 min. The aqueous feed, consisting of 25 parts of deionized water, 0.5 parts of ammonium persulfate, and 0.05 parts of sodium hydroxide was added to the reactor in 210 min. For latexes with particle sizes below 600 nm, 0.25 parts of Dowfax 2EP, a sodium salt of dodecylated sulfonated phenyl ether from The Dow Chemical Company, was also added in the aqueous feed stream. The reactor was held for 60 min longer at 80°C after the aqueous feed was completed. Two series of latexes were made based on MMA/EA/AA and MMA/BA/MAA. The particle size of the MMA/EA/AA series ranged from 196.5 nm to 809.7 nm. The particle size of the MMA/BA/MAA series ranged from 158.3 to 958.2 nm. Particle sizes were determined by hydrodynamic chromatography. The volume median diameter and polydispersity were reported. Glass transition temperature of the dried latex films was obtained by differential scanning calorimetry using a DuPont Model 912 instrument and a 10°C/min heating rate. The precision of the T_g measurement is determined to be $\pm 1^\circ\text{C}$.

Minimum Film Formation Temperature

The MFFT of latexes was determined using an apparatus similar to that described by Protzman and Brown,³² manufactured by Modern Metalcraft, Midland, MI (Type 991). Three 5 mil thick latex films were drawn down on a 92 gauge Type S Mylar film. A forced air hood was placed over the drawdowns. The times for the latexes to reach film formation at the MFFT were determined visually. The MFFT was taken as the point at which cracks of the latex film ceased. The standard deviation (1σ) was determined to be $\pm 1^\circ\text{C}$.

Dynamic Mechanical Spectroscopy

Sample preparation of latex film used to determine the viscoelastic properties is as follows. A three-inch diameter Teflon® O-ring was taped along the outer edge onto a flat Teflon surface. The flat Teflon surface was maintained at a temperature sufficiently high to facilitate film formation. Approximately 15 g of latex were poured into the area defined by the O-ring. Care was taken to exclude air bubbles. When the sample was dried, it was removed from the Teflon surface. The sample was dried further in a forced air oven at 80°C until completely dry. A sample of 1 to 2 mm thickness was obtained. The "water-saturated" polymer was obtained by soaking the sample in water at 80°C for at least 72 hr.

The viscoelastic properties of the "water-saturated" polymers were determined using the parallel plate geometry in the compression mode on a Rheometrics Solid Analyzer RSA II. Experimental details have been described before.²⁶ A rubber dam was fitted onto the lower plate and filled with water to immerse the sample. The sample was placed at the center of the lower 4.75 mm parallel plate. The upper plate was then lowered so that it was in contact with the sample with approximately

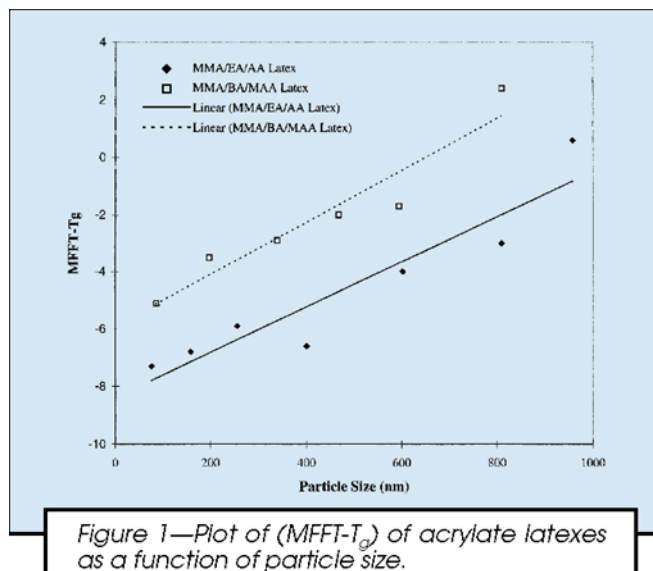


Figure 1—Plot of $(MFFT-T_g)$ of acrylate latexes as a function of particle size.

10 g compression force. The viscoelastic properties were determined at a frequency of 1 rad/sec from -5° to 95°C .

Glass Transition Temperature of Latex Emulsion

The glass transition temperatures of the latexes in the emulsion state (wet T_g s) were determined using a MicroCal MC-2 scanning calorimeter. The T_g was determined from the difference in heat capacity (ΔC_p) of a five percent degassed latex compared to a water reference under a nitrogen pressure of 30 psi. The ΔC_p was determined from -5° to 105°C at a heating rate of $1^\circ\text{C}/\text{min}$. The standard deviation (1σ) was $\pm 1^\circ\text{C}$. The experimental details have been published elsewhere.²⁹

RESULTS AND DISCUSSION

At the MFFT of the latex, the deformation forces are just sufficient to overcome the resistance to deform, i.e., the modulus of the latex, to form an integral film. There are

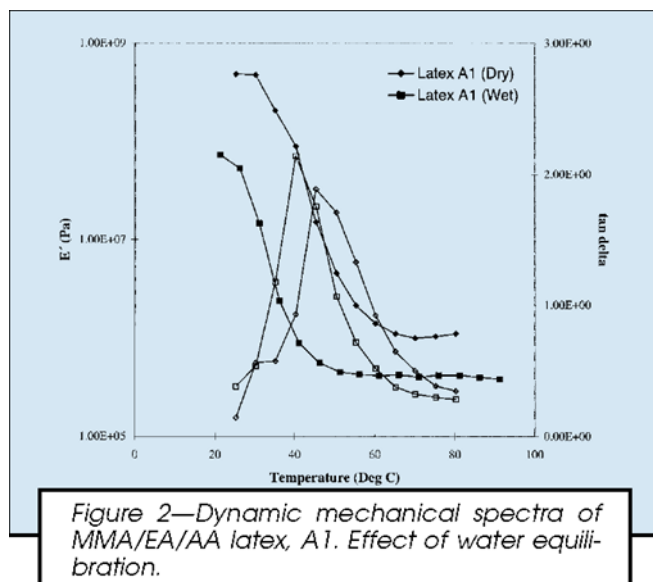


Figure 2—Dynamic mechanical spectra of MMA/EA/AA latex, A1. Effect of water equilibration.

Table 1—Particle Size of MMA/EA/AA Latexes

Latex	Particle Size (nm)	Volume Sigma (1 σ) nm
A1	76	55
A2	158	22
A3	256	31
A4	401	109
A5	602	84
A6	810	98
A7	958	121

Table 2—Particle Size of MMA/BA/MAA Latexes

Latex	Particle Size (nm)	Volume Sigma (1 σ) nm
B1	86	14
B2	197	25
B3	339	46
B4	468	44
B5	595	80
B6	824	94

many hypotheses proposed to account for the origin of the deforming forces. Brown¹⁷ proposed that the capillary force is the origin of the deformation forces responsible for latex film formation. He suggested that for film formation to occur, the elastic shear modulus, G' , of the polymer must be lower than the capillary forces present equation (1).

$$G' < 35\gamma_w/r \quad (1)$$

where γ_w is the water surface tension and r is the radius of the latex particle. In this paper, Young's moduli of latex films, E' , were determined instead of shear moduli, G' . However, Young's modulus can be related to the shear modulus,³⁴ using equation (2).

$$E' = 2G'(1+\nu) \quad (2)$$

where ν is the Poisson ratio. For materials with ν equals 0.5, E' equals $3G'$. Therefore, E' of the latex film has to be lower than $105\gamma_w/r$. With γ_w in the range of 30 to 70 dynes/cm, the magnitude of the deforming forces is in the range of $315/r$ to $735/r$ Pa. Kendall and Padgett's adhesive force theory²¹ predicted that deformation forces can be described by equation (3).

$$E < 9\pi\gamma(1-\nu^2)/4r \quad (3)$$

where γ is the specific contact energy between latex particles. The value of γ has been previously estimated to be 24 dynes/cm.²⁶ Therefore, with Poisson ratio, ν , having a value of 0.5, E in equation (3) has to be less than $12.7/r$ Pa. Both Brown's and Kendall and Padgett's theories also predicted that the deforming force is inversely proportional to the size of the latex particle. Eckersley and Rudin,²² and Jensen and Morgan²³ determined the MFFT of a series of acrylate latexes and found the MFFT to be a function of the particle size: increasing with the diameter of the particle. This was used as evidence that the deformation forces exerted on the particles were dependent on the size of the latex particles. In a previous

study,²⁶ the deforming forces responsible for film formation of a series of carboxylated styrene/butadiene (S/B) latexes were determined. The magnitudes of the forces were found to range from 1.5 to 3×10^6 Pa. The magnitudes of the deforming forces were lower than would be predicted by Brown's theory, but were in the range as predicted by Kendall and Padgett's theory. However, due to the limited range of the latex particle size, no conclusion could be made as to the effect of particle size on the deforming forces.

Effect of Particle Size on MFFT

The film formation behavior of two series of acrylate latexes of particle size ranging from 76 to 960 nm was determined in order to study the effect of particle size on deforming forces. A series of latexes containing 48.5 parts MMA, 48.5 parts EA, and 3 parts AA of different particle sizes was prepared. The latex, A1, made with unseeded latex recipe had a particle size of 76 nm. Latexes of increasing particle sizes were prepared using a portion of the previous latex as seed. The latexes are described in Table 1. Another series of latexes based on 48.5 parts MMA/48.5 parts BA/3 parts MAA was also prepared in a similar fashion (Table 2). The MFFTs and T_g s of these two series of latexes were determined. The results are shown in Tables 3 and 4.

The effect of particle size on the MFFT of the latexes can be seen in Figure 1, where (MFFT- T_g) was plotted versus latex particle size. It is necessary to plot (MFFT- T_g) instead of just MFFT because there are small differences in the T_g of the latexes in the series. The (MFFT- T_g) of the latexes increased as a function of particle size. This is in agreement with the findings of Eckersley and Rudin,²² and Jensen and Morgan.²³ The (MFFT- T_g) increases by 0.8-0.9°C per 100 nm in the particle size range studied, with R^2 equal to 0.88 and 0.92 for the MMA/EA/AA and MMA/BA/MAA latexes, respectively. The (MFFT- T_g) of MMA/EA/AA latexes were approximately 2°C lower than MMA/BA/MAA latexes throughout the entire particle size range. The (MFFT- T_g) of the MMA/

Table 3—Minimum Film Formation Temperature of MMA/EA/AA Latexes

Latex	Particle Size (nm)	T_g (°C)	MFFT (°C)	MFFT- T_g (°C)
A1	76	35.3	28 ± 1	-7.3
A2	158	35.8	29 ± 1	-6.8
A3	256	34.9	29 ± 1	-5.9
A4	401	36.6	30 ± 1	-6.6
A5	602	35.0	31 ± 2	-4.0
A6	810	36.0	33 ± 1	-3.0
A7	958	35.4	36 ± 1	+0.6

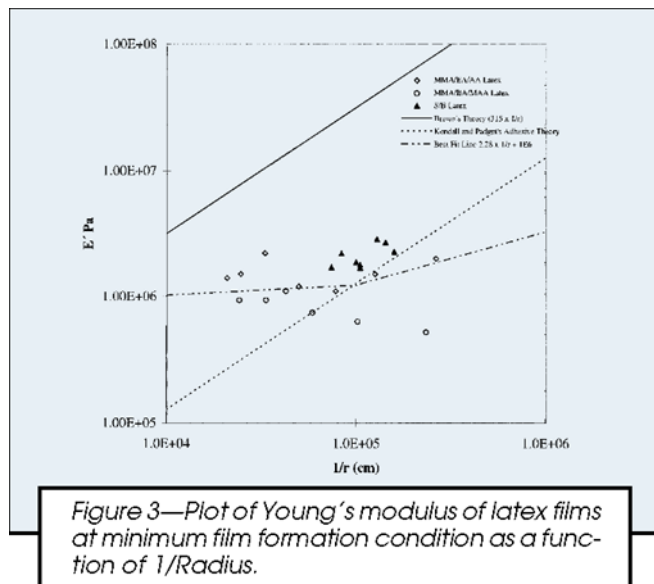
Table 4—Minimum Film Formation Temperature of MMA/BA/MAA Latexes

Latex	Particle Size (nm)	T_g (°C)	MFFT (°C)	MFFT- T_g (°C)
B1	86	23.1	18 ± 1	-5.1
B2	197	22.5	19 ± 1	-3.5
B3	339	22.9	20 ± 1	-2.9
B4	468	22.0	20 ± 1	-2.0
B5	595	21.7	20 ± 2	-1.7
B6	824	20.6	23 ± 1	+2.4

EA/MAA latexes in Jensen and Morgan's study is in the same range as in the present study. However, the (MFFT- T_g) of the MMA/BA/MAA latexes in Eckersley and Rudin's study were 8° to 10°C higher throughout the entire particle size range than found in the present study. Part of the discrepancy is due to the method used to measure T_g . In Eckersley and Rudin's study, the T_g s were determined at a heating rate of 1°C/min. In the present study, the heating rate was 10°C/min. It is known that the value of T_g is dependent on the heating rate. A lower heating rate will result in a lowering of the T_g . It is expected that lowering the heating rate by one order of magnitude will result in lowering the T_g by approximately 3 to 5°C.³³ However, the (MFFT- T_g s) of the latexes in Eckersley and Rudin's study were still larger even after accounting for the possible difference due to lower heating rate. It is likely that the difference in (MFFT- T_g) between the two series of latexes studied in this paper, and the latexes studied by Jean and Morgan, and Eckersley and Rudin is due to differences in the degree of water plasticization of the latexes and its effect on MFFT of the latexes. This will be discussed in more detail later. It is also important to note that in their recent study, Sperry and co-workers²⁴ failed to find a particle size effect on MFFT for their series of latexes.

Estimation of Deformation Force in Film Formation Process

In order to determine the magnitude of the deformation forces responsible for film formation, the modulus of the "water-equilibrated" latex film that corresponds to the minimum film forming condition has to be measured. In this study the viscoelastic properties of the "water-equilibrated" latex films were determined using a Rheometrics RSA-II spectrometer. Figure 2 shows the dynamic mechanical spectra of latex A1. The effect of water on the viscoelastic properties of the latex film resulted in both a lowering of the Young's modulus, E' , and the temperature of $\tan \delta_{max}$. From the MFFT and the drying time, the appropriate viscoelastic properties that correspond to the minimum film forming condition can



be determined using the Williams-Landel-Ferry time temperature superposition theory (WLF theory). The detail of the calculation has been described before.²⁶ The storage moduli of the two series of "water-equilibrated" latex films were measured at 1 rad/sec at temperatures that correspond to the MFFT. The results are tabulated in Tables 5 and 6.

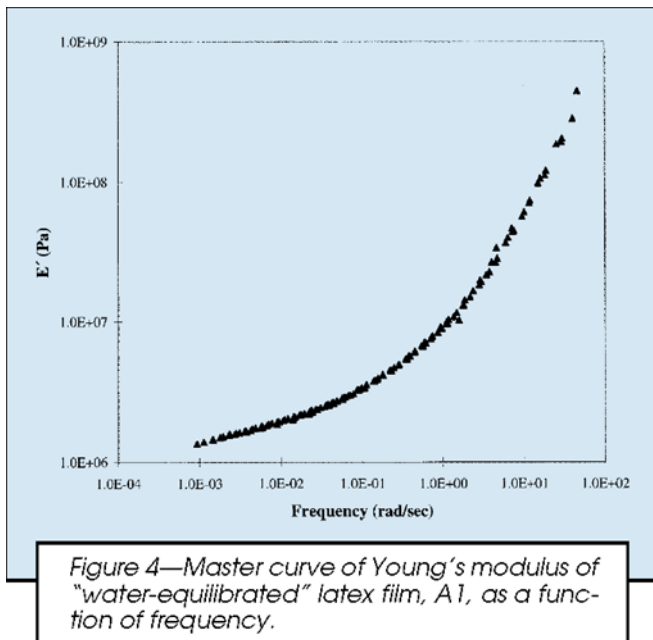
Figure 3 shows the plot of the storage moduli of the "water-equilibrated" latex films at film formation condition as a function of 1/particle radius. Data of carboxylated S/B latexes reported before are also included.²⁶ It can be seen from the data that the magnitudes of the deforming force for the two series of acrylate latexes are similar, in the range of 0.5 - 2 x 10⁶ Pa. The magnitudes of the deformation forces are also similar to those of the S/B latexes reported previously. Brown's capillary force theory overestimated the force by at least an order of magnitude. It is also clear from the data that Kendall and Padgett's theory does not predict the deforming force well, especially in the large particle size range. The de-

Table 5—Storage Moduli of "Water Equilibrated" MMA/EA/AA Latex Films at MFFT

Latex	MFFT (°C)	Drying Time (min)	T (equivalent) (°C)	1/r (cm ⁻¹)	E'(Pa), x10 ⁶
A1	28 ± 1	6 ± 1	46	264000	2.0
A2	29 ± 1	9 ± 2	47	126000	1.5
A3	29 ± 1	12 ± 2	47	78200	1.1
A4	30 ± 1	16 ± 7	49	49900	1.2
A5	31 ± 2	9 ± 1	51	33200	2.2
A6	33 ± 1	9 ± 1	54	24700	1.5
A7	36 ± 1	11 ± 4	60	20900	1.4

Table 6—Storage Moduli of "Water Equilibrated" MMA/BA/MAA Latex Films at MFFT

Latex	MFFT (°C)	Drying Time (min)	T (equivalent) (°C)	1/r (cm ⁻¹)	E'(Pa), x10 ⁵
B1	18 ± 1	13 ± 6	33	234000	5.2
B2	19 ± 1	24 ± 5	38	102000	6.3
B3	20 ± 1	22 ± 9	40	59000	7.4
B4	20 ± 1	24 ± 3	40	42800	11.0
B5	20 ± 2	20 ± 6	43	33600	9.3
B6	23 ± 1	21 ± 8	45	24300	9.3



forming force's particle size dependency is at least an order of magnitude lower than that predicted by the Kendall and Padgett's theory. In fact, particle size of the latexes was found to have minimal effect on the magnitude of the deforming forces. Therefore the MFFT's dependency on particle size is not due to differences in deformation force. The cause of the MFFT dependency on particle size will be discussed further.

Sheetz¹⁹ proposed that during film formation, a thin layer of coalesced particles closes the surface of the drying latex. The remaining water evaporates by diffusion through this latex membrane. The compressive force generated would result in the coalescence of the latex film. Sheetz further noted that the maximum compressive pressure generated cannot exceed the tenacity of water, which is of the order of 4×10^6 Pa. The results in the present study do not contradict Sheetz's theory.

Deformation Forces in Early Stage of Film Formation

It is reasonable to expect the magnitude of the deformation forces to change during the course of film formation. Calculation by Vanderhoff and co-workers¹⁸ showed that the magnitude of these capillary forces decreases as coalescence progresses. Therefore, capillary forces may be responsible for the initiation of coalescence, but cannot account for the entire coalescence process. There are relatively few studies concerning the early stage of film formation after the latex particles come into close contact. Recently, atomic force microscopy has been used to study latex morphology of a drying latex film.³⁵ In this study, information of the deforming behavior of the latex particles at the early stage of film formation is gained by studying the extent of latex particle deformation at conditions below the MFFT, taking advantage of the Williams-Landel-Ferry (WLF) time temperature superposition theory.

WLF time temperature superposition theory states that the temperature and time dependencies of the viscoelastic behavior of polymers can be described using equations (4) and (5).

$$\text{Log } a_T = -C_1(T-T_r)/(C_2+T-T_r) \quad (4)$$

$$f_1 a_{T1} = f_2 a_{T2} \quad (5)$$

where a_T is the shift factor at temperature T , C_1 and C_2 are constants, T_1 and T_2 are the temperatures at conditions 1 and 2, T_r is the reference temperature at which a_T 's are determined, f_1 and f_2 are the frequencies of deformation under conditions 1 and 2. From equations (4) and (5), it can be seen that the viscoelastic properties of latex at early stage of forming a film can be characterized by examining the latex film formed at low temperature. The viscoelastic behavior of "water-equilibrated" carboxylated latex films have been found to obey WLF theory.²⁶ The WLF constants, C_1 and C_2 , of a "water-equilibrated" latex films were determined by shifting

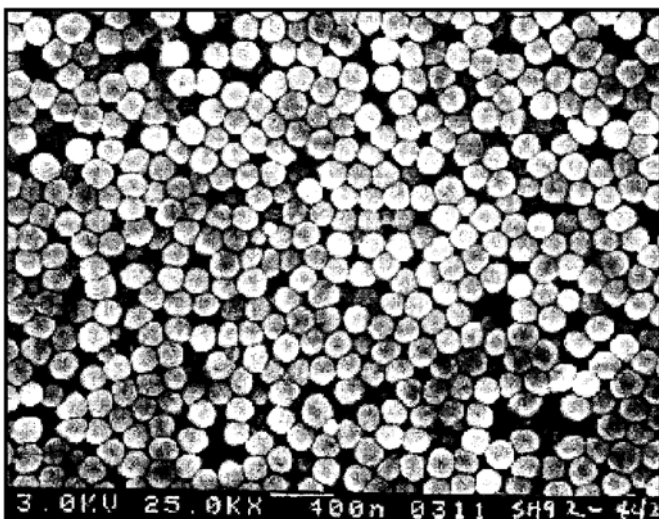


Figure 5—Scanning electron micrograph of carboxylated S/B latex. Film formed at 21°C and 10 min drying time.

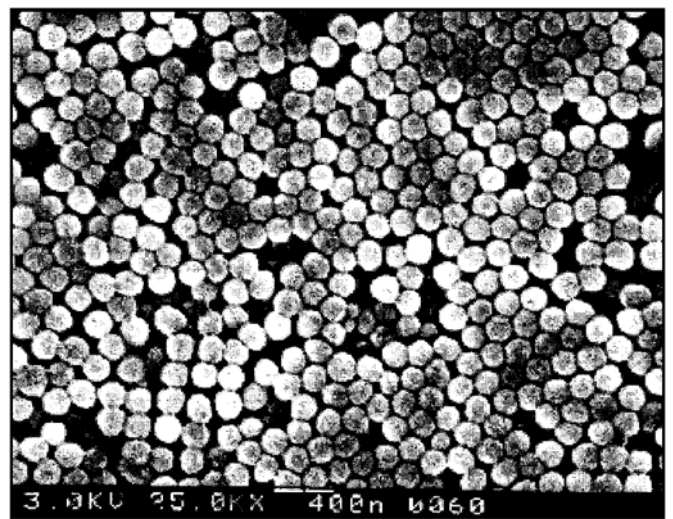


Figure 6—Scanning electron micrograph of carboxylated S/B latex. Film formed at -2°C and 4 min drying time.

Table 7—Glass Transition Temperature and Minimum Film Formation Temperature of Acrylate Latexes

Latex	Type	Composition	Particle Size (nm)	Dry T_g (°C)	Wet T_g (°C)	ΔT_g (°C)	MFFT (°C)	MFFT-Dry T_g (°C)	MFFT-Wet T_g (°C)
C1	MMA/BA/AA	54/42/4	330	34	17	17	31	-3	14
C2	S/BA/AA	54/42/4	330	37	31	6	41	4	10
C3	MMA/EA/AA	54/42/4	290	47	25	22	41	-6	16
C4	S/EA/AA	49/47/4	330	51	40	11	54	3	14
C5	MMA/EA/AA	57/42/1	240	44	29	15	38	-6	9
C6	S/EA/AA	52/47/1	290	47	40	7	47	0	7

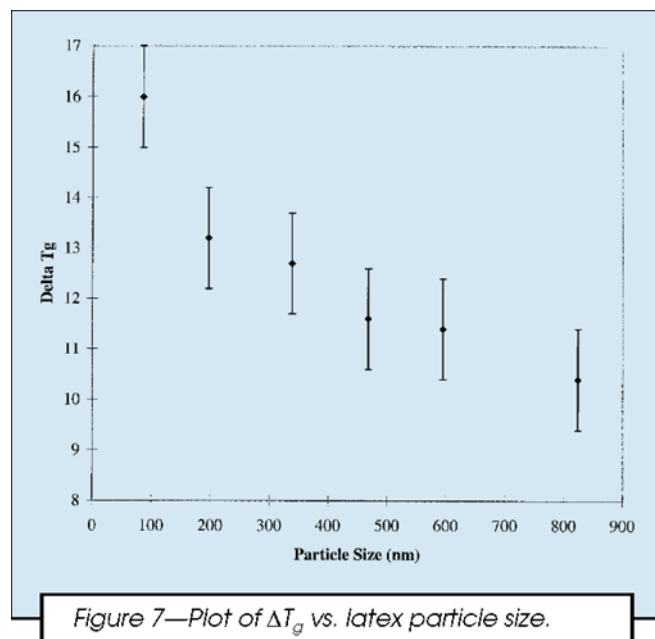
Table 8—Glass Transition Temperature of MMA/BA/MAA Latexes

Latex	Particle Size (nm)	MFFT (°C)	Dry T_g (°C)	Wet T_g (°C)	ΔT_g (°C)	MFFT-Dry T_g (°C)	MFFT-Wet T_g (°C)
B1	86	18	23.1	7.1	16.0	-5.1	10.9
B2	197	19	22.5	9.3	13.2	-3.5	9.7
B3	339	20	22.9	10.2	12.7	-2.9	9.8
B4	468	20	22.0	10.4	11.6	-2.0	9.6
B5	595	20	21.7	10.3	11.4	-1.7	9.7
B6	824	23	20.6	10.3	10.4	2.4	12.7

the frequency plots of Young's moduli, E' , at various temperatures to form a superimposed master curve. Figure 4 shows a plot of the time temperature superimposed Young's modulus of latex film A1 as a function of frequency, using the data at 29°C as the Tr. It can be seen from the degree of fit of the data that WLF theory is applicable to describe the viscoelastic properties of "water-equilibrated" latex film.

The early stage film formation behavior was studied using a carboxylated S/B latex with a MFFT of 45°C. The particle size of this latex was 190 nm. The extent of particle deformation of a latex film formed below MFFT, at 21°C with a drying time of 10 min was examined using scanning electron microscopy (SEM). C_1 and C_2 of this latex were determined to be 13.2 and 104.4, respectively, at a Tr, of 46°C. For this latex, film formation at 21°C reflects the condition experienced by the latex particles during film formation at MFFT, 45°C, 0.05 sec after the latex particles reach the close packing configuration. Figure 5 shows the SEM of the latex film formed at 21°C, with a drying time of 10 min. The deforming force experienced by the latex particles 0.05 sec into the film formation process can be determined from the Young's modulus of this latex at conditions corresponding to 0.05 sec at 45°C. E' , and therefore, the deforming force, was found to be $\sim 1.4 \times 10^8$ Pa. According to Brown's theory, the capillary force experience by a 190 nm particle is $\sim 3 \times 10^7$ Pa. If Mason's modification of Brown's theory is incorporated,³⁶ the capillary forces can be as high as $\sim 2 \times 10^8$ Pa, in the range of the forces determined in the present study. Figure 6 shows the SEM of the same latex dried at -2°C, a temperature 47°C below the MFFT, with a drying time of four minutes. It can be seen readily from the SEM that even at this temperature, significant latex particle deformation was observed.

the particle size of latex influences the MFFT. However, there are also studies that showed latex particle size has little or no effect on MFFT.^{21,24} One important underlying assumption when studying the effect of the particle size of latex on MFFT is that the latex mechanical properties remain constant when different particle size latexes were prepared. The T_g s of the dried polymers are used as the supporting evidence. However, during film formation, the latex particles are equilibrated with water and therefore the MFFT should depend on the wet T_g s rather than the dry T_g s of the latexes. It has been shown that there is no necessary correlation between the dry T_g and the wet T_g of a latex. Lee and co-workers²⁹ showed that the difference between dry and wet T_g s (ΔT_g) can be attributed to the extent of water plasticization and is dependent on the hydrophilicity of the latex polymers. It can be seen from Table 7 that for latexes containing the more hydrophilic monomer, MMA, the difference between dry and wet T_g is larger than the corresponding S



Effect of Latex Particle Size on the Glass Transition Temperature of Latex Emulsions

It is clear from the present study and results from Eckersley and Rudin,²² and Jensen and Morgan²³ that

containing latexes indicating that the MMA containing latexes are plasticized by water to a greater extent than the corresponding S containing latexes. The MFFT of the MMA containing latexes are below the dry T_g s of the latexes and the MFFT of the S containing latexes are above the dry T_g s of the latexes; whereas the MFFT is above the wet T_g s of all the latexes.

The effect of latex particle size on the extent of water plasticization was determined using the series of latexes B1-B6. Results are shown in Table 8. The data indicated that ΔT_g is a function of particle size of the latex, suggesting that water plasticization is dependent on the surface area of the latex particles (Figure 7). It is known that carboxylic acid concentrates in a hydrophilic polymer shell around the latex particles.³⁷ Therefore, it is possible that there are more carboxylic acid groups in the surface layer for the smaller particle size latex resulting in a larger extent of water plasticization.

It has also been suggested that the T_g of the polymer at the surface can be lower than the bulk polymer. Keddie and co-workers³⁸ determined the T_g of thin polystyrene (PS) films as a function of film thickness and suggested that at the surface of the glassy PS film is a liquid-like layer. The T_g of PS film was found to decrease from 102°C for film of thickness 100 nm to -70°C for 10 nm thick film. Forrest and co-workers,³⁹ and Meyers and co-workers⁴⁰ have come to similar conclusions. Since the smaller particle size latex will have larger surface area, the surface effect on lowering T_g will be more significant. The dry T_g was usually determined using coalesced latex film, the surface area is much reduced. Therefore, the effect of surface reduction of T_g is expected to be minimal for coalesced latex films. However, since the particle size effect on MFFT sometimes is not observed,^{21,24} this would indicate that the role of surface effect on T_g is probably not important. Rather, it is more likely due to the difference in the amount of hydrophilic polymer on the latex surface as a function of particle size. In studies where no particle size effect was observed, it is probably due to either little hydrophilic polymer on the latex surface, or the amount of hydrophilic polymer on the surfaces of the latexes is similar regardless of latex particle size.

SUMMARY

The dependency of MFFT on the latex particle size has been taken in previous studies as evidence that the deforming forces experienced by the particles during film formation are functions of particle size, as predicted by the capillary force theory or the JKR theory. In this study, the deformation forces experienced by latex particles were determined from the viscoelastic properties of the "water-equilibrated" latex films at conditions corresponding to the film formation process. The magnitude of the deformation forces were found to be lower than what would be expected from capillary forces, in the range of 5×10^5 to 2×10^6 Pa. and independent of particle size. Significant latex deformation was observed using SEM at conditions below MFFT, a condition corresponding to the early state of film formation, indicating that deformation forces of magnitude in the range of 10^8 Pa.

were present during the early stage of film formation. These forces decrease rapidly as film formation progresses. Therefore, capillary forces are probably present during the early stages of film formation, initiating the particle deformation process. However, the magnitude of the forces at the later stages of film formation is much lower than the capillary forces, indicating that capillary forces play a minor role towards the completion of film formation. The magnitude of the forces towards the completion of film formation is in the range predicted by Kendall and Padgett's adhesive force model in certain particle size range or Sheetz's compressive force model. The lack of particle size effect on the magnitude of the force would argue against the importance of the adhesive force model.

Since the magnitude of the deforming force responsible for the completion of film formation was found to be constant independent of particle size, the MFFT should not show a particle size dependence. However, it is clear that MFFT of the series of latexes studied is indeed a function of particle size. This can be explained by the difference in the degree of water plasticization. The hydrophilicity of latex was characterized by comparing the T_g of the dry latex polymer with that of the latex emulsion. It was found that the wet T_g s of the smaller particle size latex emulsions were lower than the corresponding latex emulsions of larger particle size for a series of latexes with similar dry T_g s, indicating that water plasticizes the smaller particle size to a greater extent. Therefore, the MFFT dependency on particle size can be explained by the difference in the T_g of the latex emulsions due to the difference in degree of water plasticization.

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