

Film Formation from Pigmented Latex Systems: Mechanical and Surface Properties of Ground Calcium Carbonate/Functionalized Poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) Latex Blend Films

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ABSTRACT: The mechanical and surface properties of films prepared from model latex/pigment blends were studied using tensile tests, surface gloss measurements, and atomic force microscopy. Functionalized poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) [P(BMA/BA)] and ground calcium carbonate (GCC) were used as latex and extender pigment particles, respectively. The critical pigment volume concentration of this pigment/latex blend system was found to be between 50 and 60 vol % as determined by surface gloss measurement and tensile testing of the blend films. As the pigment volume concentration increased in the blends, the Young's modulus of the films increased. Nielsen's equations were found to fit the experimental data very well. When the surface coverage of carboxyl groups on the latex particles was increased, the yield strength and Young's modulus of the films both increased, indicating better adhesion at the interfaces between the GCC and latex particles. When the carboxyl groups were neutralized during the film formation process, regions with reduced chain mobility

were formed. These regions acted as a filler to improve the modulus of the copolymer matrix and the modulus of the resulting films. The carboxyl groups on the latex particle surfaces increased the surface smoothness of the films as determined by surface gloss measurement. When the initial stabilizer coverage of the latex particles was increased, the mechanical strength of the resulting films increased. At the same time, rougher film surfaces also were observed because of the migration of the stabilizer to the surface during film formation. With smaller-sized latex particles, the pigment/latex blends had higher yield strength and Young's modulus. Higher film formation temperatures strengthen the resulting films and also influence their surface morphology. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4550–4560, 2006

Key words: mechanical properties; functionalization of polymers; surfaces; blends; latices

INTRODUCTION

Latex particles with diameters of a few hundred nanometers are widely used as binders in coatings in a variety of applications including paints and coated papers.¹ Such applications usually contain a large amount of pigments bound by latex polymers. These are usually high modulus inorganic particles such as TiO₂ and CaCO₃.² In the commonly employed pigment/polymer latex blend systems, the soft latex particles deform during the film formation process, whereas the hard particles, that is, the pigment particles, do not deform but retain their original shapes and serve as reinforcing fillers for the coalesced soft-polymer matrix. Therefore, latex/pigment blend films can be considered two-phase systems, having a con-

tinuous phase and a dispersed phase. The mechanical properties of such systems will depend on the properties of the components, the shape of the filler phase, the morphology of the system, the nature of the interface between the phases, and the composition of each component.

In this study the mechanical and surface properties of GCC pigment/functionalized poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) [P(BMA/BA)] latex blend films were studied as a function of latex surface functionality, amount of polymeric stabilizer, latex particle size, and film formation temperature.

EXPERIMENTAL

Materials

n-Butyl methacrylate (BMA), *n*-butyl acrylate (BA), and methacrylic acid (MAA) monomers (Sigma-Aldrich, Milwaukee, WI; reagent grade) were purified by passing them through columns filled with an appro-

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TABLE I
Recipe Used to Synthesize ≈ 150 nm Noncarboxylated Seed P(BMA/BA) Latex Particles at 80°C

Seed		Second-stage feed seeded polymerization
BMA (g)	26.25	215.0
BA (g)	8.75	71.70
Deionized (DI) water (g)	450.00	50.00
KPS (g)	0.40	0.40
SLS (g)	1.00	2.44

BMA, *n*-butyl methacrylate; BA, *n*-butyl acrylate; KPS, potassium persulfate; SLS, sodium lauryl sulfate.

appropriate inhibitor-removal packing material (Sigma-Aldrich, Somerville, NJ). Sodium lauryl sulfate (SLS; Fisher Scientific, Fair Lawn, NJ; reagent grade) and potassium persulfate (KPS; Fisher Scientific, Fair Lawn, NJ; reagent grade) were used as received without further purification. A cationic ion-exchange resin (20- to 50-mesh; AG 50W-X4, Bio-Rad Co., Hercules, CA) and an anionic ion-exchange resin (20- to 50-mesh; AG 1-X4, Bio-Rad Co., Hercules, CA) were cleaned according to the method suggested by van den Hul and Vanderhoff.³ Ammonia hydroxide (NH₄OH; Fisher Scientific, Fair Lawn, NJ; reagent grade), sodium polyacrylate (NaPA, molecular weight (M_w) = 5100 g/mol; Aldrich, Milwaukee, WI), and ultrafine ground calcium carbonate (GCC; Covercarb[®] HP, Omya, Proctor, VT; particle size = 650 nm with a broad size distribution) were used as received.

Latex synthesis and basic characterization

Monodispersed latex particles of varying particle size, varying degrees of carboxylation, and controlled

glass-transition temperatures (T_g) were prepared via a designed semicontinuous emulsion copolymerization procedure. The appropriate comonomer feeding rates could be adjusted to control the uniformity of both particle size and copolymer composition.⁴ Table I shows the recipe used to prepare approximately 150 nm of P(BMA-*co*-MA) noncarboxylated seed latex particles, whereas Table II shows the recipe used to prepare 250 nm of functionalized latices by a seeded emulsion polymerization process. For both, polymerization was carried out at 80°C in a 1-L four-necked flask outfitted with a reflux condenser and a nitrogen gas inlet tube in order to keep the reaction blanketed with an inert atmosphere during polymerization. The reactants were stirred using a half-moon polytetrafluoroethylene impeller at a speed of 230 rpm. First, 150 nm of seed latex particles were prepared in a separate reaction (Table I). This latex was then used as seed that could be grown to a final amount of latex particles of 250 nm in a subsequent reaction by feeding in comonomer (BMA/BA for the noncarboxylated latex or BMA/BA/MAA for the carboxylated latex) into the reactor for varying durations using a syringe pump (Harvard Apparatus, Model 22M, Holliston, MA; Table II). A separate syringe pump was used to feed a separate surfactant (SLS) solution in parallel with the comonomer feed in order to maintain latex stability during the polymerization. The reaction was allowed to proceed for an additional 2 h once the monomer and surfactant feeds were complete in order to achieve complete conversion.

The density of surface functional groups on the particles was quantified by time-dependent conductometric titration experiments developed by Nishida et al.⁵ The latex was first cleaned using mixed ion-exchange resins in order to remove any adsorbed sur-

TABLE II
Recipe Used to Synthesize Noncarboxylated and Carboxylated P(BMA/BA) Latex Particles by a Seeded Emulsion Polymerization Process with a Designed Size of ≈ 250 nm at 80°C

	Before comonomer feed stage				
≈ 150 nm seed latex (g)	89.40				
Deionized (DI) water (g)	428.28				
KPS (g)	0.03				
	Feed stage				
	Without MAA	1% MAA	3% MAA	6% MAA	10% MAA
BMA (g)	188.87	179.25	165.36	144.37	116.38
BA (g)	62.96	70.06	79.08	92.51	110.42
MAA (g)	0.00	2.52	7.56	15.12	25.20
DI water (g)	50.0	50.0	50.0	50.00	50.00
KPS (g)	0.10	0.10	0.10	0.10	0.10
SLS (g)	0.45	0.45	0.45	0.45	0.45

BMA, *n*-butyl methacrylate; BA, *n*-butyl acrylate; MAA, methacrylic acid; KPS, potassium persulfate; SLS, sodium lauryl sulfate.

TABLE III
Characterization Results of Model P(BMA/BA) Latex Particles Used in the Study of Film Formation from Pigmented Latex Systems

Sample	1	2	3	4	5
D_w (nm)	243.8	251.9	247.1	240.1	259.3
D_n (nm)	239.6	238.8	225.6	231.9	254.7
PDI (= D_w/D_n)	1.02	1.06	1.09	1.04	1.02
Wt % of MAA ^a	0	1	3	6	10
COOH surface coverage (%) ^b	0.0	9.8	23.1	56.4	100.0
T_g (K)	272.3	271.8	273.5	274.0	272.9

^a Based on the weight of the P(BMA/BA) copolymer.

^b Cross-sectional area of each carboxyl groups is $20\text{\AA}^{2.22}$. D_w , weight-average diameter; D_n , number-average diameter; PDI (= D_w/D_n), polydispersity index.

factants and electrolytes. The latex was then diluted to 1% solids and placed into a 250-mL beaker and stirred with a magnetic stir bar. The contents of the beaker were blanketed with inert argon gas during the conductometric titration measurement to eliminate any contribution from dissolved CO_2 in the diluted latex. The latex was first forward-titrated with 0.02N NaOH solution (Fisher Scientific, Pittsburgh, PA) at a feed rate of 1.0 mL/min and then back-titrated with 0.02N HCl solution (Fisher Scientific, Pittsburgh, PA) at a feed rate of 2 mL/min.

The time-dependent titration results revealed that surface coverage of the carboxyl groups varied from 0% to 100% as the MAA amount was increased from 0 to 10 wt %, based on BMA/BA comonomer, during the semicontinuous polymerization process. Table III lists the basic characterization results of model P(BMA/BA) latex particles with a particle size about 250 nm in diameter.

Preparation of GCC/P(BMA/BA) pigmented latex films

Pigmented latex films were cast from a pigment slurry/latex blend consisting of GCC pigment particles and cleaned P(BMA/BA) latex particles (vol % GCC varied from 0% to 60%, and surface coverage of carboxyl groups on P(BMA/BA) latex particles varied from 0% to 100%). The detailed latex cleaning process was reported previously.⁶ The pH and the aqueous phase concentration of NaPA were both controlled during the preparation of the pigment slurry/latex blends. It should be noted that the pH of the cleaned latex was adjusted to 9 by adding an aqueous ammonia hydroxide (NH_4OH) solution drop by drop into the latex. Before film formation, the pigment slurry/latex blend had an overall pH of 9, as measured with a pH meter (model 125, Corning, Medfield, MA). After using a Rotavapor apparatus (Büchi, model EL 131, Flawil, Switzerland) to remove enough water to attain the

specific solids content of 15% solids, pigmented latex films were cast by drying the latex/pigment blends at room temperature on clean glass plates covered with Tedlar[®] [poly(vinyl fluoride); DuPont, Wilmington, DE] films.

Characterization of GCC/P(BMA/BA) blend films

Stress-strain tests were performed a week after the blend films were totally dry. The dried pigmented latex films, with a thickness between 0.25 and 0.28 mm, were cut into dumbbell-shaped specimens according to ASTM Standard D1708-96, and tensile tests were performed with an Instron Universal Testing Machine (Model 5567, Canton, MA) with a crosshead speed of 25 mm/min and a 500N load cell. At least five specimens of each film were tested, and the results were averaged. The specimens were tested at 25°C and a relative humidity of 50%. Relative surface gloss of the P(BMA/BA)/GCC blend films was measured with a Glossmeter (Novo-Gloss, Rhopoint, Bexhill, UK) at incident angles of 20°, 60°, and 75° (only the 75° results are reported here). Each film was measured at seven points on the film surface in order to obtain an average gloss value and the standard deviation. The glass-transition temperatures of the polymers in the resulting films were measured with a differential scanning calorimeter (DSC; DSC 2920 scanning calorimeter, TA Instruments, New Castle, DE). Experiments were performed over a temperature range of -20°C–100°C with a heating rate of 10°C/min. Surface morphology was examined with an atomic force microscope (AFM; Topometrix, Explorer[™], Santa Barbara, CA) operated in the noncontact mode.

RESULTS AND DISCUSSION

Critical pigment volume concentration of blend system

The concept of critical pigment volume concentration (CPVC) of a paint system, that is, the volume concentration of pigment particles at which the binder just fills the interstices between the pigment particles, was introduced by Van Loo and Asbeck in 1949.⁷ CPVC represents the densest degree of packing of the pigment particles in the dispersion system. It is a transition point at which some dramatic changes in paint properties including permeability and optical properties occur, and therefore, conversely, these marked changes in film properties can be used to determine the CPVC.

The CPVC of a pigment/latex blend system is important not only because coherent pigmented latex systems can only be obtained below the CPVC of the system, but also because the CPVC represents the point at which pigment particles just come into con-

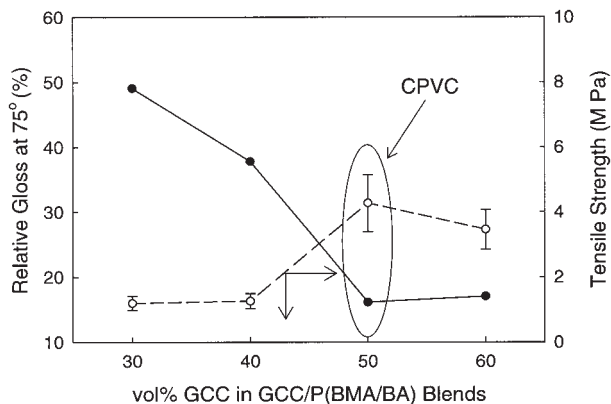


Figure 1 Determination of the CPVC of GCC/P(BMA/BA) blend systems from measurement of relative surface gloss at 75° and tensile strength. Note: in these experiments the latex particles were not carboxylated.

tact. Therefore, the CPVC of a pigment/latex blend system is related to the maximum packing of the pigment particles in the pigmented latex films. In this work, two methods, surface gloss measurement and tensile testing, were utilized to determine the CPVC of the GCC pigment/P(BMA/BA) latex blends. The CPVC results are shown in Figure 1. It can be seen from Figure 1 that both gloss and tensile strength dropped dramatically after reaching 50 vol % GCC in the GCC/P(BMA/BA) blend films, indicating that the CPVC of the system was between 50% and 60%.

Effect of pigment volume concentration on mechanical properties of GCC/P(BMA/BA) blend films

Stress–strain curves of the films cast from GCC/P(BMA/BA) latex blends containing various volume concentrations of the GCC pigment particles are shown in Figure 2(a). It can be seen that the ultimate tensile strength of the blend film increased dramatically when the volume fraction of the pigment particles increased. As the pigment volume concentration (PVC) increased from 30% to 60%, the stress–strain curves gradually changed from those characteristically obtained for typical elastomers to those of a brittle plastic material.

The slope of the initial straight-line portion of the stress–strain curve was the elastic modulus of the material under testing. In a tensile test this modulus is the Young’s modulus,

$$E = \frac{d\sigma}{d\varepsilon} \tag{1}$$

where E , σ , and ε are the Young’s modulus (MPa), stress (MPa), and percent strain (%), respectively. Young’s modulus usually is one of the most important

parameters used in the evaluation of the mechanical properties of a material.

From Figure 2(b), it can be seen that the Young’s modulus of the GCC/P(BMA/BA) blend films increased as the volume concentration of the GCC particles was increased.

Many equations are available for predicting the Young’s modulus of a two-phase mixture consisting of a continuous phase and a dispersed phase as the volume fraction of the hard (dispersed) phase changes. In the simplest models the modulus of the composite can be obtained by assuming either uniform strain (the Voigt average) or uniform stress (the Reuss average). The upper and lower bounds of the modulus can be calculated by these two means.

The upper bound (equal strain model) is

$$E_c = \phi_h E_h + \phi_s E_s \tag{2}$$

The lower bound (equal stress model) is

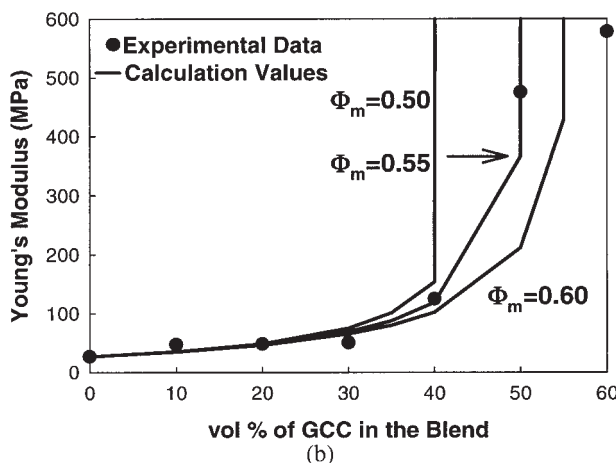
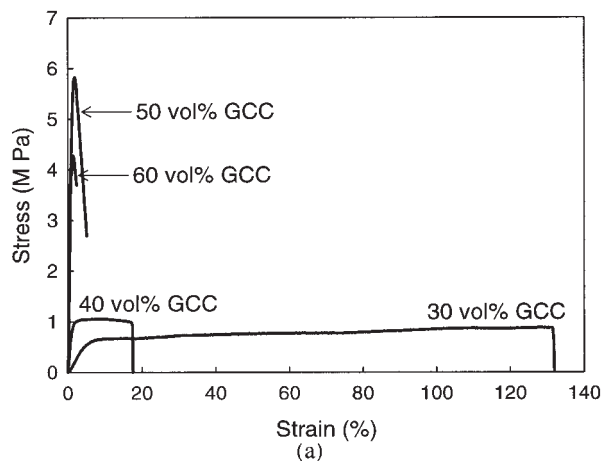


Figure 2 (a) Stress–strain curves of GCC/P(BMA/BA) blend films with different concentrations of GCC pigment particles; (b) Young’s modulus versus volume concentration of GCC/P(BMA/BA) blend films (the latex particles were not carboxylated in these experiments).

$$E_c = \frac{E_s E_h}{(E_s \phi_h + E_h \phi_s)} \quad (3)$$

where E_i and ϕ_i are the moduli and volume fraction, respectively, of $i = c$, the composite; $i = h$, the filler (hard phase); and $i = s$, the soft matrix; and $\phi_h + \phi_s = 1$. In most cases the observed values fell within these bounds. Using Einstein's theory [only valid at very low concentrations ($\leq 10\%$) of filler], Guth⁸ developed an equation for use with higher filler concentrations (valid at concentrations up to 30 vol %).

$$E_c = E_s(1 + 2.5\phi_h + 14.1\phi_h^2) \quad (4)$$

Kim et al.⁹ modified the Guth equation to make it applicable with a filler concentration of up to 45 vol %.

$$E_c = E_s(1 + 2.5\phi_h + 16.2\phi_h^2) \quad (5)$$

Nielsen¹⁰ proposed a generalized equation to account for the maximum packing fraction, ϕ_m , of the filler:

$$E_c = E_s \frac{1 + AB\phi_h}{1 - B\psi\phi_h} \quad (6)$$

$$B = \frac{\frac{E_h}{E_s} - 1}{\frac{E_h}{E_s} + A} \quad (7)$$

$$\psi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2} \right) \phi_h \quad (8)$$

where ϕ_m is the maximum packing fraction of the hard dispersed phase, A and B are constants, and ψ is the factor that enables the use of a reduced concentration scale to take into account the maximum packing fraction of the particles. The constant A is related to the generalized Einstein coefficient, K_E , by

$$A = K_E - 1 \quad (9)$$

where K_E equals 2.5 for spheres. From eq. (7), it is known that B is close to 1 when the filler is much more rigid than the soft continuous phase. The typical Young's modulus for GCC is about 35,000 MPa.¹¹ The Young's modulus for noncarboxylated P(BMA/BA) was determined to be about 27 MPa. Applying Nielsen's equations [eqs. (6)–(8)] to calculating the moduli of the GCC/P(BMA/BA) blend films showed that the theoretical curves fit the experimental data quite well, as shown in Figure 2(b).

Figure 2(b) shows three theoretical curves representing different values of ϕ_m . Of the three predic-

tions, $\phi_m = 0.55$ showed the best fit of the experimental data. This result was not unexpected because of the CPVC for this system. As previously mentioned, the CPVC represents the densest degree of packing of the pigment particles in the dispersion. Experimental results have shown that the CPVC of this pigmented latex system is between 50% and 60%. Therefore, a reasonable assumption was that the maximum packing fraction (ϕ_m) of the pigment used in this study was between 0.5 and 0.6.

Influence of carboxyl groups on soft P(BMA/BA) latex particles on mechanical properties of GCC/P(BMA/BA) blend films

The effects of carboxyl groups on the surface of the P(BMA/BA) latex particles on the mechanical properties also were studied. The stress–strain curves for the pigmented latex films containing different concentrations of carboxyl groups on the latex particles at the same PVC are shown in Figure 3(a). It can be seen from Figure 3(a) that the ultimate tensile strength of the pigmented latex films increased as carboxyl group coverage of the P(BMA/BA) latex particles increased.

The tensile yield strength of the pigmented latex films was also found to increase as the carboxyl group coverage on the latex particles was increased. The yield point can be either a distinct maximum or a region of strong curvature approaching the zero slope in the stress–strain curve. Tensile yield stress depends on the morphology of the polymer, and in heterogeneous polymer systems, in addition to structure, it can be related to the interaction of the components. The separation of interfaces (i.e., debonding or dewetting) very is often the dominating deformation mechanism in particulate-filled polymers.^{12–14} Tang found similar results in a polystyrene (PS)/P(BMA/BA) latex blend system.¹⁵ He interpreted increased yield strength increase as improved adhesion of the interface between the hard PS particles and the soft P(BMA/BA) copolymer matrix because of carboxyl groups on the surface of the PS latex particles. This is likely to be the case in the GCC/P(BMA/BA) blend system as well, that is, increased adhesion of the interface between GCC particles and the P(BMA/BA) matrix as the carboxyl group coverage increased. Granier and Sartre¹⁶ observed the ordering and adhesion of latex particles on model inorganic surfaces using AFM. They found that increasing the acid content of the latex particles enhanced particle spreading.

Young's modulus as a function of carboxyl group coverage of the latex particles is plotted in Figure 3(b). It can be seen that the Young's modulus of the pigmented latex films increased with increasing carboxyl group coverage of the P(BMA/BA) latex particle surface while maintaining a constant pigment volume concentration. Nielsen's equations [eqs. (6)–(8)] indi-

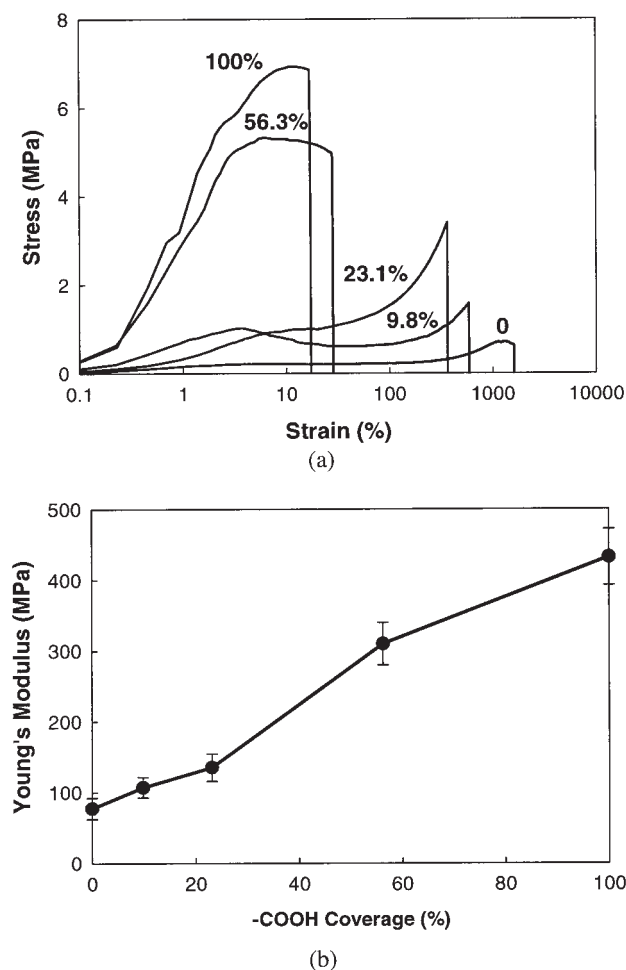


Figure 3 (a) Stress-strain curves of GCC/P(BMA/BA) blend films [the percentage on each curve represents the carboxyl group coverage on the P(BMA/BA) latex particles]; (b) Young's modulus versus carboxyl group surface coverage on the P(BMA/BA) soft latex particle surface (vol % GCC = 17.35%, pH = 9 for film formation).

cated that this increase in Young's modulus of the pigmented latex films might result from an increase in the Young's modulus of the soft-polymer matrix, E_s , because all the other parameters on the right-hand side of eq. (6) would remain unchanged. To further investigate this, DSC measurement of the pigmented latex films was performed.

The DSC results, shown in Table IV, indicated two glass transitions in the copolymer matrix of the pigmented latex films if the soft latex particles were carboxylated. When the carboxyl group coverage of the latex particles surfaces were 9.8%, 23.1%, and 56.4%, the first glass transition occurred at about 0°C which was the designed T_g of the copolymer, whereas a second glass transition took place at about 25°C. When the carboxyl group coverage was 100%, other than the first glass transition, around 0°C (T_g of the copolymer), the second glass transition temperature appeared at 38°C.

The origin of the second glass transition in the polymer phase of the pigmented latex films is believed to have resulted from neutralization of the carboxyl groups during the film formation process. According to Eisenberg and Kim,¹⁷ when a polymer has ionic groups, there is a strong driving force (ionomers) in the polymer matrix for the formation of ion-counterion associations, ion pair-ion pair associations, and even higher aggregates (multiplets). The Eisenberg-Hird-Moore (EHM) model¹⁸ suggests that: (1) the mobility of the material immediately surrounding multiplets is reduced relative to that of the bulk material; (2) isolated multiplets should not exhibit their own T_g ; and (3) when the number of multiplets increases to the point at which substantial overlap of regions of reduced mobility is encountered, these overlapping regions of restricted mobility, called clusters, become large enough to exceed the threshold for independent phase behavior (50–100 Å) and thus exhibit their own T_g . As a result of this structural change, two glass transitions, one from the matrix and the other from the region with reduced mobility, and an increase in the moduli of the materials can be observed.

Similarly, carboxylated film-forming latex particles also can form regions that have reduced chain mobility between particles, either between latex and pigment particles or between individual latex particles, and will exhibit their own glass transitions. These regions can explain the observed increase in Young's modulus of the pigmented latex films as carboxyl group coverage was increased on the soft latex particles, as shown in the stress-strain test results. According to Eisenberg et al.,¹⁷ between the two glass transitions, the overlapping regions with reduced mobility (the cluster) would act as a filler that would, in turn, increase the modulus of the polymer matrix dramatically. As mentioned previously, from the time-dependent conductometric titration measurements of the latex particles, it was found that there were a large number of carboxyl groups on the latex particle surface, depending on the amount of MAA used in the synthesis recipe. This feature helped the formation of regions with reduced chain mobility because of ionic

TABLE IV
Glass-Transition Temperature (T_g) of Latex Polymer Before and After Neutralization in Film Formation Process

COOH Coverage (%)	T_g of Latex polymer (°C)	T_g of Polymer in film (°C)	
		1st	2nd
0	-0.7	2.2	—
9.8	-1.2	-1.9	25.9
23.1	0.5	1.7	23.7
56.4	-1.0	1.9	23.7
100	-0.1	0.5	37.5

TABLE V
Calculated Young's Modulus of Polymer Matrix
Obtained from Nielsen's Equations and Calculated
Volume Fraction of Regions with Reduced Chain
Mobility Using the Modified Guth Equation

Carboxyl group coverage of P(BMA/BA) latex particle surface (%)	E_p (MPa)	Volume fraction of regions with reduced chain mobility (%)
0	27.01	0
9.8	37.40	4.4
23.1	47.21	13.2
56.4	108.03	26.3
100	150.68	48.3

$$E_h = 35,000 \text{ MPa}, B = 1, A = 1.5, \phi_m = 0.52, \phi_h = 0.1735.$$

interactions, which occurred during the film formation process when the system was neutralized. These regions acted as fillers to increase the modulus of the soft-polymer matrix.

To determine the moduli of the polymer matrix with different degrees of carboxylation and the moduli of regions with reduced mobility and their volume fraction in the polymer matrix of the pigmented latex films, Nielsen's equations [eqs. (6)–(8)] and a modified Guth equation [eq. (5)] were used to analyze the Young's moduli of the resulting films. First, the Nielsen equations were employed to calculate the moduli of different carboxylated latex polymer phases (E_p). The calculated results are listed in Table V.

Because the Young's modulus of different carboxylated latex polymer phases have been obtained, the volume fraction of the regions with reduced chain mobility in the soft copolymer matrix can be calculated. Here, the modified Guth equation [eq. (5)] was applied instead of Nielsen's equations. The modified Guth equation was used because not enough information about the shape and size of the regions with reduced chain mobility was available to allow the use of Nielsen's equations, which have maximum packing fraction (ϕ_m) as a required parameter. A nonlinear least-squares method was applied to calculate the volume fraction of the regions with reduced chain mobility. The calculated volume fraction values of the regions with reduced chain mobility for latex particles with various degrees of carboxylation also are listed in Table V.

The modulus of the regions with reduced chain mobility was estimated from eq. (2) to be 286.68 MPa. This indicated that the copolymer matrix, now considered a composite of the copolymer with the regions of reduced chain mobility, fell within the upper bound of the Young's modulus if the region of reduced mobility had a modulus of 286.68 MPa. Figure 4 shows the calculated Young's modulus of the copolymer matrix with different degrees of carboxylation obtained from

Nielsen's equations and from the modified Guth equation.

Influence of carboxyl groups on soft P(BMA/BA) latex particles on the surface gloss of GCC/P(BMA/BA) blend films

Gloss is one of the most important optical properties of a coating. The appearance of a surface depends on the manner in which incident light is reflected, absorbed, or transmitted by the surface. Gloss is expected to increase with: (1) an increase in the refractive index of the surface, (2) an increase in the specular angle at which the measurement is made, and (3) an increase in the microsmoothness of the surface of the film. Specular gloss (incident angle between 20° and 85°) is influenced primarily by the refractive index and the smoothness of the surface, but the latter has a greater effect if the incident angle is fixed.¹⁹ Relative surface gloss can be defined as follows:

Relative Gloss (%)

$$= \text{Gloss of the film} / \text{Gloss of the blank glass slide} \quad (10)$$

Three angles were employed in the measurements, 20°, 60°, and 75°. Figure 5 shows the effects of the degree of carboxylation on the 75° surface gloss of the pigmented films. It can be seen that the gloss of the poly(BMA-co-BA)/GCC pigment blend films increased significantly with the degree of carboxylation of the latex particles. This increase in gloss might be attributed to the increased smoothness of the film surface. This finding was similar to the results obtained by Tang.¹⁵

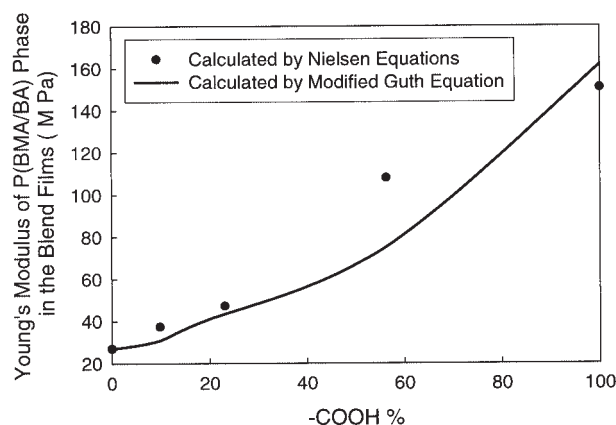


Figure 4 Young's modulus of the P(BMA/BA) phase in the GCC/P(BMA/BA) blend films versus degree of carboxylation of soft P(BMA/BA) latex particles.

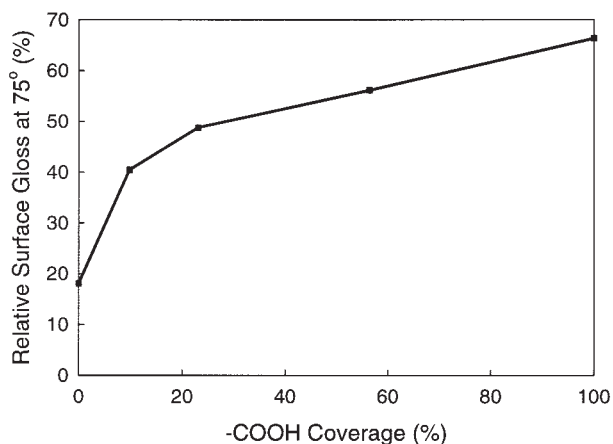


Figure 5 Surface gloss of GCC/P(BMA/BA) blend films as a function of carboxyl group surface coverage on P(BMA/BA) latex particles.

Influence of amount of NaPA stabilizer on latex particle surface on mechanical properties and surface gloss of GCC/P(BMA/BA) blend films

Sodium polyacrylate (NaPA) was added as stabilizer before film formation was carried out in order to maintain the stability of both pigment particles and latex particles prior to their being blended together. Many researchers have noted that during the film formation process the existence of surfactant or stabilizer can influence the drying behavior, surface morphology, and many other properties of the resulting films. For instance, Feng and Winnik²⁰ found that films obtained from surfactant-free latex blend systems had a much more uniform thickness over the surface area that did the corresponding surfactant-containing films. They also found that granules of surfactant would be exuded to the surface during the film formation process. Therefore, it would be interesting to check the effects of the amount of NaPA adsorbed on P(BMA/BA) latex particle surfaces on the mechanical and surface properties of the pigmented latex films.

With knowledge of the adsorption of NaPA in the cleaned P(BMA/BA) latex particles, reported elsewhere,⁶ it becomes easy to change the surface coverage of NaPA on the latex particles by following the adsorption isotherms. NaPA coverage of the latex particles varied from 8% to 18% and finally to 36%. Other parameters such as pH, surface coverage of NaPA on the pigment particles, and volume concentration of pigment remained unchanged.

Figure 6(a) shows the stress-strain curves of GCC/P(BMA/BA) pigmented films with different initial NaPA coverage of the P(BMA/BA) latex particles. It can be seen that the yield strength of the pigmented latex films increased as the initial coverage of NaPA on the soft latex particles increased from 8% to 18%.

After this point, the yield strength at 36% of the initial coverage was lower. Tensile strength also followed the same pattern. This indicated that at a NaPA initial coverage of the latex particles of 18%, the blend system had the highest adhesion in the interface between GCC and polymer matrix in the resulting films. Young's modulus as a function of initial NaPA coverage is shown in Figure 6(b). The Young's modulus was found to increase as the NaPA coverage of the P(BMA/BA) latex particles was increased. This was expected because when more NaPA was present in the blend system, after reaching surface saturation as the system became more concentrated, more free NaPA would remain in the film-forming aggregates. This free NaPA (aggregates) would act as filler because NaPA is a polymer that is quite rigid with a rather high T_g (503 K).²¹

Figure 6(b) also shows the results of surface gloss measurement of the three pigmented latex films, each with different initial NaPA coverage of the

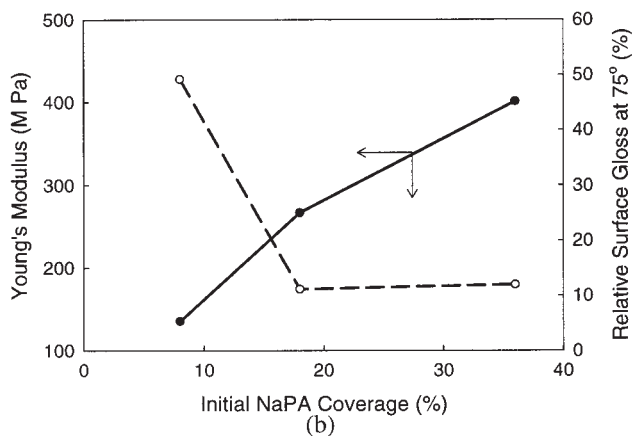
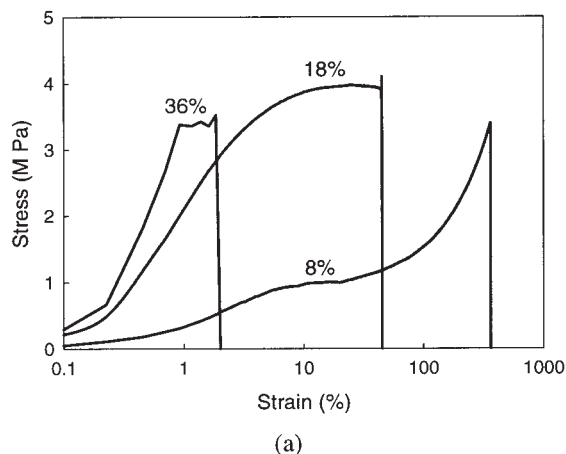
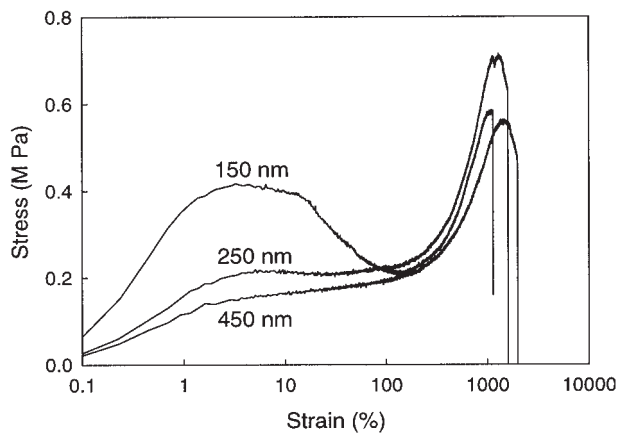
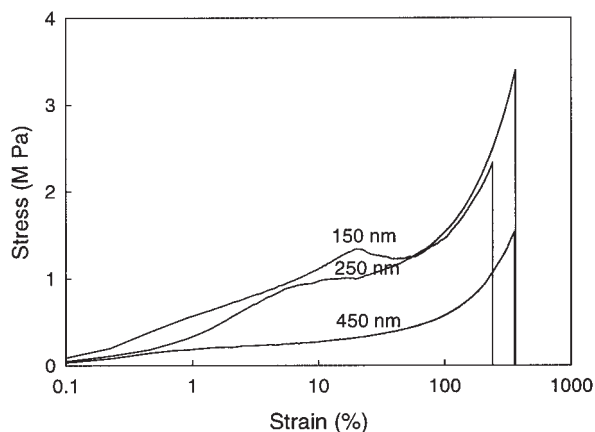


Figure 6 Effect of initial NaPA surface coverage on GCC/P(BMA/BA) blend films: (a) stress-strain curve and (b) Young's modulus and surface gloss at 75° [vol % GCC = 17.35%; carboxyl group coverage on the P(BM/BA) latex particles = 23.1%; percentage on each curve represents the NaPA coverage on the P(BMA/BA) latex particles].



(a)



(b)

Figure 7 Stress-strain curves of the GCC/P(BMA/BA) blend films prepared with different-sized latex particles: (a) carboxyl group coverage on the P(BMA/BA) latex particles = 0; (b) carboxyl group coverage on the P(BMA/BA) latex particles = 23.1% (vol % GCC = 17.35%; pH = 9 for the pigment/latex blend before film formation).

P(BMA/BA) latex particles. Relative surface gloss was found to decrease when NaPA coverage increased from 8% to 18% and then leveled off until reaching 36% NaPA coverage. As pointed out by Simpson,¹⁹ surface gloss is influenced primarily by the refractive index and the smoothness of the surface; however, the latter has a greater effect if the incident angle is fixed. The results suggested there was a rougher surface when a greater amount of NaPA was initially present on the surface of the latex particles in the GCC/P(BMA/BA) blend films. This rougher surface can be explained by the presence of free NaPA (or perhaps NaPA aggregates). Some of these NaPA aggregates would tend to migrate to the film surface during the film formation process, causing the surface to be rougher.

Influence of latex particle size on mechanical properties of GCC/P(BMA/BA) blend films

In many surface coatings systems, such as paper coating, it has been found that latex particle size influences many coating properties such as peel strength and viscosity. In this section, the tensile test results obtained from pigment/latex blend films with different-sized latex particles.

Stress-strain curves of two series of blend samples with different-sized latex particle are shown in Figure 7 (numbers beside the curves indicate the average diameters of the latex particles). It can be clearly seen that the pigmented latex blend films achieved higher yield strength when utilizing smaller latex particles. As described previously, higher yield strength is an indication of better adhesion of interfaces between the hard and soft phases of a blend system. Smaller latex particles can help the system achieve better interactions (e.g., better adhesion) between GCC pigment particles and latex particles because of larger total surface area. It also can be seen in Figure 7 that the Young's modulus of the blend films increased with decreasing latex particle size. At the same time, maximum percent strain increased with increasing latex particle size.

Influence of film formation temperature on mechanical properties and surface morphology of GCC/P(BMA/BA) blend films

The effects of film formation temperature on the mechanical properties and surface morphology of pigmented latex films also were studied. From Figure 8 it can be seen that a film formed at a higher temperature possessed greater mechanical strength (both yield strength and tensile strength). This indicates that ad-

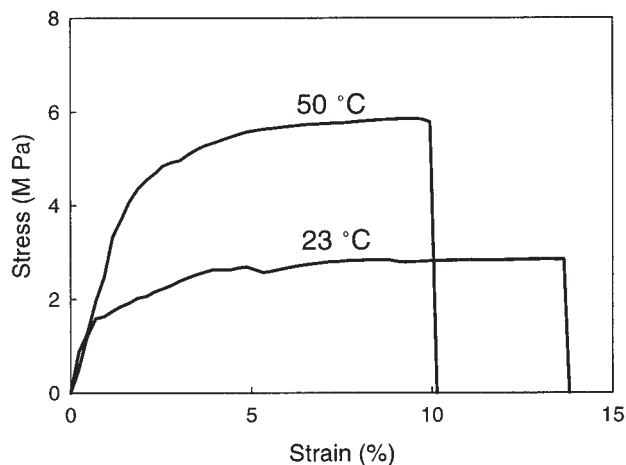


Figure 8 (a) Stress-strain curves of GCC/P(BMA/BA) blend films formed at 50 °C and at room temperature [vol % GCC = 30%, carboxyl group coverage on the P(BMA/BA) latex particles = 100%].

TABLE VI
Surface Gloss and AFM Roughness Data for Pigmented Latex Films Formed at Different Temperatures

	Relative surface gloss at 75°	AFM: scanning length = 26 μm	
		<i>R_a</i> (nm)	<i>RMS</i> (nm)
FFT = 23°C	51.68	20.98	31.10
FFT = 50°C	35.30	46.41	61.69

GCC = 30 vol %; the carboxyl group coverage of the latex particles was 100%.

hesion at the interface between the hard particles and the soft copolymer matrix was improved when the film formation temperature was increased.

The surface gloss measurements and the AFM images both reflected a rougher surface morphology at a higher film formation temperature. Table VI and Figure 9 show the results of gloss measurement and the AFM images, respectively. In the AFM analysis, average roughness (*R_a*) was defined as the arithmetic average deviation from the center line (at 1/2 *L*):

$$R_a = \frac{1}{L} \int_{x=0}^{x=L} |y| dx \tag{11}$$

where *L* and *y* are the sampling length and ordinate of the curve of the profile, respectively. Root mean square (RMS) roughness was given by

$$RMS = \left(\frac{1}{L} \int_{x=0}^{x=L} y^2 dx \right)^{1/2} \tag{12}$$

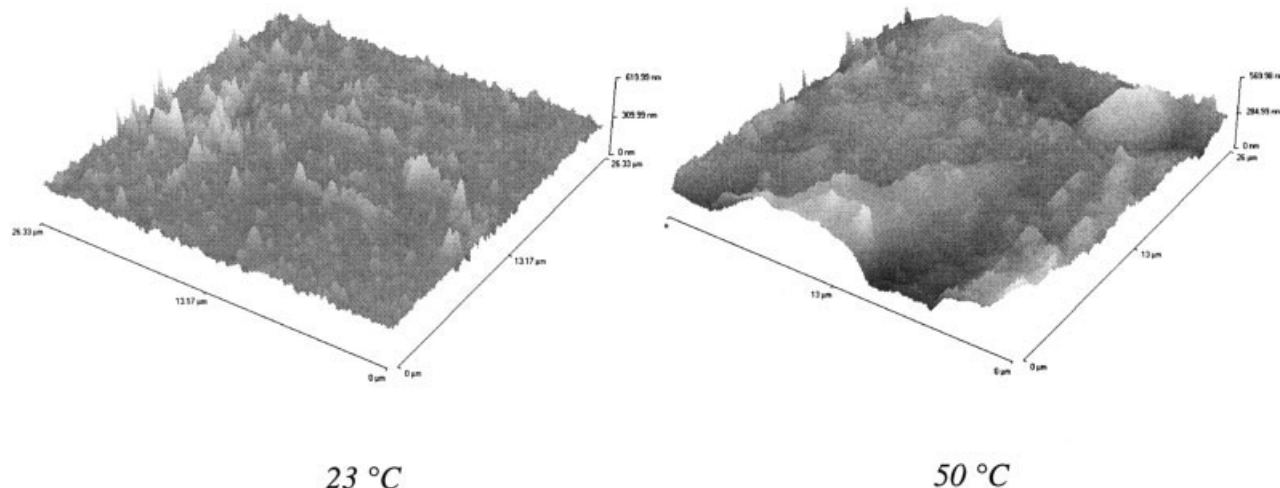


Figure 9 AFM topographical images of films formed at different temperatures [vol % GCC = 30%, carboxyl group coverage on the P(BMA/BA) latex particles = 100%, scanning length = 26 μm, pH = 9 of the pigment/latex blend before film formation].

The rougher surface at a higher film formation temperature may have been caused by a greater migration speed of the free NaPA to the film surfaces during the film formation process. As a result, more free NaPA or NaPA aggregates would appear on the film surface, making the roughness value larger when the film formation temperature was higher.

CONCLUSIONS

In this study, surface gloss measurement, tensile testing, and AFM analysis were performed on films prepared from model P(BMA/BA)latex/GCC pigment blend systems in order to investigate the effects of pigment volume concentration, surface carboxyl group coverage of latex particles, amount of NaPA stabilizer, latex particle size, and film formation temperature on the surface and mechanical properties of the film.

The critical pigment volume concentration (CPVC) of the pigment/latex blend system was found to be between 50 and 60 vol % using both tensile tests and surface gloss measurements. The Young’s modulus of the films was shown to increase along with the increase of PVC in the GCC/P(BMA/BA) blends. Nielsen’s equations were found to fit the experimental data very well.

As the surface carboxyl group coverage of the latex particles increased, both the yield strength and Young’s modulus of the films increased, indicating better adhesion between the GCC and latex particles at the interface. The increase in Young’s modulus of the films as the carboxyl group coverage of the latex particles increased resulted from an increase in the Young’s modulus of the copolymer matrix itself. When the carboxyl groups were neutralized during the film formation process, regions with reduced chain

mobility were formed that acted as filler to improve the modulus of the copolymer matrix. The surface gloss increased with the increasing carboxyl group surface coverage of the latex particles in the blended films, indicating a smoother surface of the resulting films.

If the initial NaPA coverage of the latex particles increased, the resulting films exhibited an increased Young's modulus. In addition, rougher film surfaces were observed because of the migration of the stabilizer to the film surface during the film formation process. A smaller latex particle size had the effect of increasing the mechanical strength of the resulting blend films. Higher film formation temperatures strengthened the films and led to a rougher surface morphology.

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