Mechanical Properties of Films Prepared from Model High-Glass-Transition-Temperature/Low-Glass-Transition-Temperature Latex Blends

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ABSTRACT: The mechanical properties of films prepared from model high-glass-transition-temperature (T_g)/low-T_g latex blends were investigated with tensile testing and dynamic mechanical analysis. Polystyrene (PS; carboxylated and noncarboxylated) and poly(*n*-butyl methacrylate-co-*n*-butyl acrylate) [P(BMA/BA); noncarboxylated] were used as the model high-T_g and low-T_g latexes, respectively. Carboxyl groups were incorporated into the PS latex particles to alter their surface properties. It was found that the presence of carboxyl groups on the high-T_g latex particles enhanced the Young's moduli and the yield strength of the PS/P(BMA/BA) latex blend films but did not influence ultimate properties, such as the stress at break and maximum elongation. These phenomena could be explained by the maximum packing density of the PS latex particles, the particle–particle interfacial adhesion, and the formation of a "glassy" interphase. The dynamic mechanical properties of the latex blend films were also investigated in terms of the carboxyl group coverage on the PS latex particles; these results confirmed that the carboxyl groups significantly influenced the modulus through the mechanism of a glassy interphase formation. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2788–2801, 2002

Key words: emulsion polymerization; blends; mechanical properties

INTRODUCTION

The enhancement of the mechanical properties of films cast from a low-glass-transition-temperature (T_g) polymer latex blended with a high-T_g polymer latex is one of the most important advantages of using this type of latex blend. The use of this type of latex blend offers a powerful strategy for eliminating volatile organic compounds (VOCs) from coatings formulations. However, adhesion between such incompatible polymers is poor in general, causing mechanical weakness in the resulting film.[1,2] Coagulation of the low-T_g latex particles causes the high-T_g latex particles to become distributed nonrandomly, a condition that may be improved via surface modification of the polystyrene (PS) latexes. Unfortunately, few researchers have explored the influence of the degree of adhesion between the two polymer phases and the distribution of the high-T_g particles within the low-T_g copolymer matrix on the mechanical properties of the latex blend films. The main focus of the publications in this area has been on the relationship between the volume fraction of the high-T_g particles and the mechanical properties of the latex blend films.[3–5]

High-T_g/low-T_g latex blend films provide an excellent example of two-phase systems with one continuous phase and one dispersed phase. The mechanical properties of these composite materials are determined by 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. Research on the mechanical properties of two-phase mixture systems began long ago.[6–12] However, the main parameters that were considered in the previous research were the mechanical properties of the component materials and the composition of the two-phase mixtures. As latex blending was found to be a good strategy for eliminating VOCs from latex systems, a detailed investigation of the mechanical properties of latex blend films was required. Thus, research in this area was triggered. Again, most of the previous publications have focused on the volume fraction of the filler particles in the latex blend films,[5,13,14] although some attention has been paid to the interfacial properties.[15–18]

In this study, the mechanical properties of high-T_g/low-T_g latex blend films were examined, with an emphasis on the surface properties of the latex particles,

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TABLE I
Characteristics of the High-T_g and Low-T_g Latex Particles Used in this Study

	Latex polymer P(BMA/BA)[a]	PS						
D_n (nm)	122.9	123.1	123.2	125.8	128.8	127.5	125.8	125.3
D_w (nm)	126.2	127.4	126.6	127.5	130.2	129.8	129.6	128.6
PDI	1.027	1.035	1.028	1.014	1.011	1.018	1.030	1.026
σ_{COOH}[b] (%)	0.0	0.0	7.6	12.9	19.1	29.7	43.0	65.8
T_g (°C)	0	105	105	105	105	105	105	105

D_n = number-average diameter; D_w = weight-average diameter; PDI = polydispersity index (D_w/D_n).
[a] Statistical copolymer consisting of 75 wt % of BMA and 25 wt % BA.
[b] Particle surface area covered by carboxyl groups, choosing the cross-sectional area of each carboxyl group as 9 Å^2 on the basis of a theoretical calculation.[20]

which were altered by the inclusion of carboxyl groups. We developed an approach to understand the mechanism by which the carboxyl groups present on the latex particle surface influenced the yield strength, Young's modulus, and ultimate mechanical properties (i.e., maximum stress and maximum elongation) of the high-T_g/low-T_g latex blend films when all the other variables, such as phase volume ratio and particle size, remained unchanged.

EXPERIMENTAL

Materials

We purified n-butyl methacrylate (BMA), n-butyl acrylate (BA), styrene (St), and methacrylic acid (MAA) monomers (Aldrich, Milwaukee, WI; reagent grade) by passing them through columns filled with an appropriate inhibitor-removal packing material (Aldrich). Sodium dodecyl sulfate (SDS; Fisher Scientific; reagent grade) and potassium persulfate (KPS; Aldrich, Pittsburgh, PA; reagent grade) were used as received. Carboxylated and noncarboxylated high-T_g PS and noncarboxylated low-T_g poly(n-butyl methacrylate-co-n-butyl acrylate) [P(BMA/BA)] model latex particles were synthesized, cleaned, and characterized according to methods published earlier.[19] The characteristics of the latex particles used for the work described in this article are listed in Table I.

Preparation of latex films

Films were cast from latex blends consisting of cleaned PS and P(BMA/BA) latex particles (PS = 0–60 vol %) to eliminate any possible influence of water-soluble oligomers, surfactant, or other additives on the properties of the resulting films. A previous publication described the cleaning process.[19] For the films used for mechanical tests, an initial solids content of 6 wt % was used, and the latex blends were dried under controlled conditions (temperature = 22 ± 0.5°C; relative humidity = 50 ± 0.5%) on poly(vinyl fluoride) films (Tedlar; DuPont, Wilmington, DE) for 10 days.

The thickness of these films ranged from 0.20 to 0.25 mm. For the films used for gloss or transparency measurements, 1 g of the latex blend with a solids content of 4.0 wt % was dried under the same conditions as mentioned previously. The thickness of the dried films was around 20 μm.

Measurements of mechanical properties

Stress–strain test

The latex blend films were cut into dumbbell-shaped specimens according to ASTM Standard D 1708-96, and tensile tests were carried out with an Instron universal testing machine (model 5567) (Canton, MA) with a crosshead speed of 200 mm/min. A 500 N load cell was used. At least five specimens were tested for each film, and averaged values are reported. Figure 1 represents a typical stress–strain curve for the latex blend system (average of five samples).

Dynamic mechanical analysis (DMA)

The storage (E′) and loss moduli (E″) of the PS/P(BMA/BA) latex blend films were measured in tension with a Rheometrics solid analyzer (RSA II, Rheometric Scientific, Piscataway, NJ). The films were cut into specimens with dimensions of 55 mm in length and 6 mm in width using a die. The frequency used for the DMA measurements was 1 Hz. A temperature step method was used for all DMA measurements. Data were obtained in 6°C increments from −100 to 200°C, with a soak time of 1 min at each temperature to ensure isothermal conditions. The strain was initially set at 0.05% when the specimen was cold and was increased to a maximum of 1.0% as the sample became soft.

Characterization

The particle size and particle size distribution were measured by capillary hydrodynamic fractionation (CHDF; model 1100, Matec Applied Sciences, North-
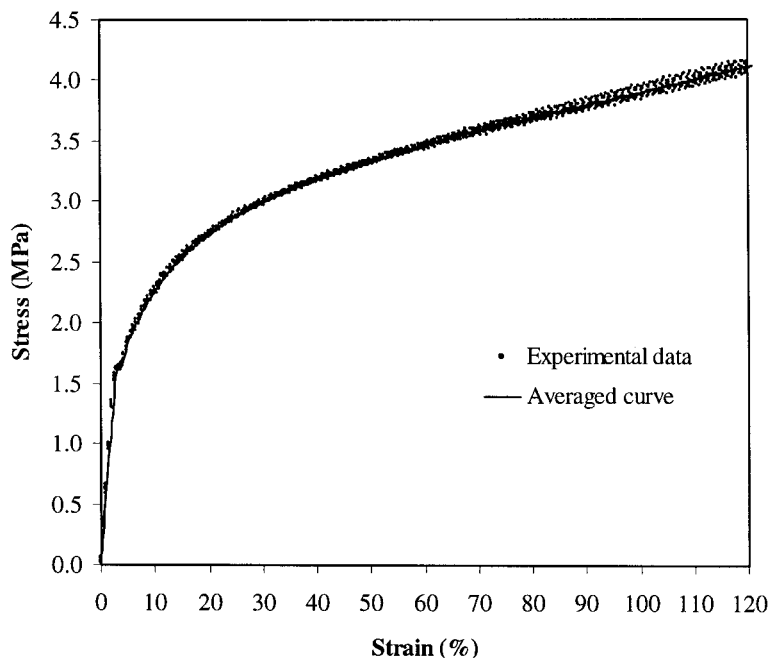
Figure 1 Sample stress–strain curve of the high-T_g (105°C)/low-T_g (0°C) latex blend films: volume fraction of the PS particles $\phi_2 = 0.35$; particle size of both latex particles = 125 nm.

borough, MA). Surface gloss and transparency were measured with a glossmeter (Novo-Gloss, Rhopoint Instrumentation Ltd., Surrey, England) at an incident angle of 75° and a densitometer (X-Rite, model 48, Grandville, MI), respectively. Gloss and transparency measurements were obtained at three different points on the film surface, and we measured at least two films for each sample to obtain the average gloss value and standard deviation. For bulk morphology observations, we microtomed film samples at −80°C with a CY2000 microtoming instrument (RMC, Inc. Microtomy & Cryobiology Products, Tucson, AZ) to obtain thin sections around 90 nm in thickness; these sections were then imaged with a transmission electron microscope (Phillips EM400T, Eindhoven, The Netherlands) with an accelerating voltage of 100 kV.

RESULTS AND DISCUSSION

Critical pigment volume concentration (CPVC) of PS/P(BMA/BA) latex blend systems

The CPVC of a paint system, as defined by Asbeck and van Loo,[21] is the transition point above or below which substantial differences in the appearance and behavior of a paint film will be encountered. It is that point in a pigment vehicle system at which just sufficient binder is present to completely fill the voids remaining between the pigment particles incorporated in the film after volatilization of thinner. It represents the densest degree of packing of the pigment particles in the dispersion system. The practical significance of determining this property is that the CPVC is a tran-

sition point; many properties of the paint undergo a marked change through the CPVC. Thus, one can use many methods to determine the CPVC of a composite dispersion system by monitoring the change in appropriate physical properties against the change of the pigment volume concentration (PVC).[22–26] The CPVC value is undoubtedly very important in the latex blend system in which the high-T_g latex particles are treated as organic pigments because coherent latex blend films may only be obtained below the CPVC of the system. Furthermore, the CPVC represents the point where the high-T_g particles just come into contact. Therefore, the value of the CPVC of a latex blend system is related to the maximum packing of the high-T_g latex particles in latex blend films.[27]

In this work, we used three methods (gloss, transparency, and tensile strength) to determine the CPVC of the PS/P(BMA/BA) latex blends. The results are shown in Figures 2 and 3. In all three series of measurements, the gloss, transparency, and tensile strength all dropped sharply after reaching 50 vol % PS in the PS/P(BMA/BA) latex blend films, indicating that the CPVC of this system was between 50 and 60 vol %.

Stress–strain behavior of the PS/P(BMA/BA) latex blend films

Stress–strain testing is the most widely used of all mechanical test methods and is described by ASTM standard test protocols such as D 638, D 1708, D 882, and D 412. However, the relationship of this test to
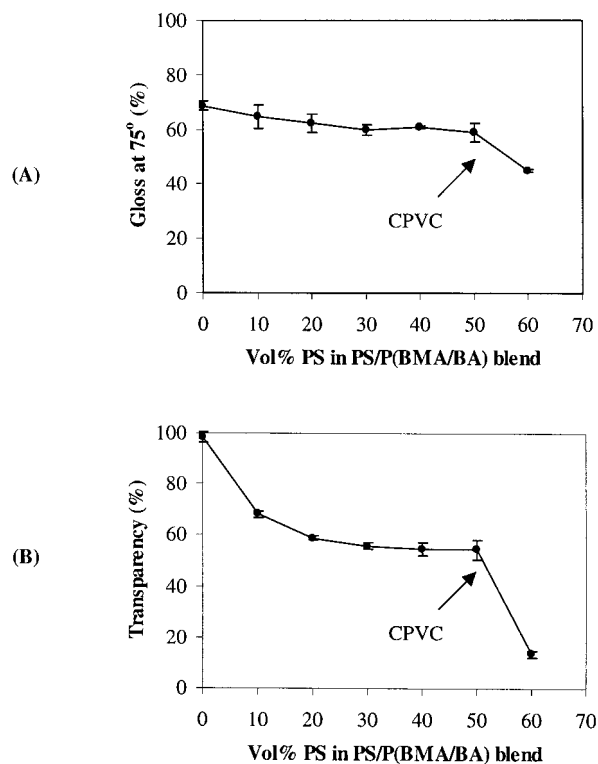
Figure 2 (A) Gloss and (B) transparency versus the volume concentration of the PS latex particles in the PS/P(BMA/BA) latex blend films; none of the latex particles were carboxylated.

end use applications is not as clear as is generally assumed, especially for two-phase mixtures such as latex blend films.

By comparing the stress–strain curves of films cast from high-T_g/low-T_g latex blends containing various volume concentrations of the high-T_g PS latex particles (Fig. 4), we could see that the mechanical strength of the latex blend film was substantially increased by the addition of the PS latex particles into the P(BMA/BA) latex copolymer matrix. This result again indicates that latex blends could be substituted for films prepared by coalescing high-T_g latexes with coalescing aids. The stress–strain curves gradually changed from those obtained for typical elastomers to a tough material and eventually to a brittle plastic material as the volume concentration of the PS particles increased from 0 to 60 vol %. An interesting feature of the stress–strain curves obtained from the latex blend films was a rapid decrease in the slope for each of the curves with a PVC lower than their CPVC in the range of 10–40% strain. This point where the slope (i.e., the tangent to each curve) rapidly decreased arose from the yielding of the latex blend films, which was regarded mainly as matrix-inclusion debonding.[3,28] However, there was no such point on the curve of the latex blend film with 60 vol % PS (>CPVC) because this film broke before reaching its yield point.

The influence of the presence of carboxyl groups on the surface of the PS latex particles on the mechanical properties of the latex blend film was also investigated. Figure 5 shows the stress–strain curves for the latex blend films containing different concentrations of carboxyl groups on the PS latex particles at the same volume percentage of PS. As discussed earlier, the yield point on each stress–strain curve indicated debonding of the P(BMA/BA) copolymer from the PS particles. Figure 5 shows that the yield strength of the latex blend films increased as the carboxyl group coverage on the PS particles increased, indicating that the adhesion of the interface between the PS particles and the P(BMA/BA) copolymer matrix was improved by the presence of the carboxyl groups on the PS particles. The enhancement in yield strength could be attributed to the hydrogen bonding between the carboxyl groups present on the PS particles and the carbonyl groups in the P(BMA/BA) copolymer matrix. The following calculations might support this explanation.

The area under a stress–strain curve represents the energy to displace or break the sample tested. Thus, the energy necessary for yielding of the latex blend film can be calculated by integration of the stress–strain curve between the original and the yield point. The difference between the integrated area under the stress–strain curve of the latex blend film without carboxyl groups present and the area under the curve of the latex blend film with a specific amount of carboxyl group present on the PS particles (e.g., 12.9% carboxyl group coverage) should represent the extra energy necessary for overcoming the extra strength caused by the presence of the carboxyl groups in the latex blend films (Fig. 5). If this extra energy resulted
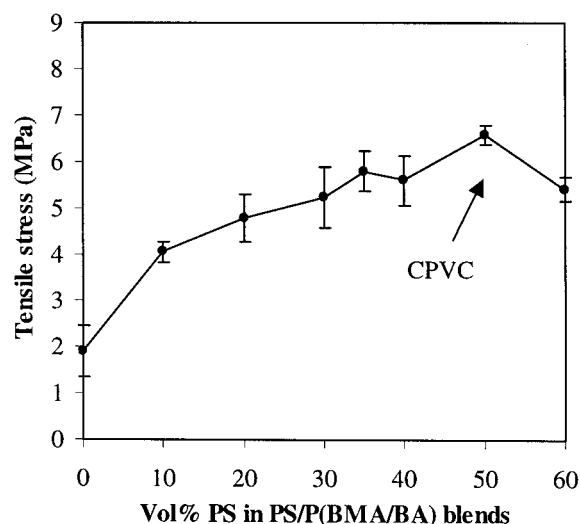

Figure 3 Ultimate tensile strength versus volume concentration of the PS latex particles in the PS/P(BMA/BA) latex blend films; none of the latex particles were carboxylated.
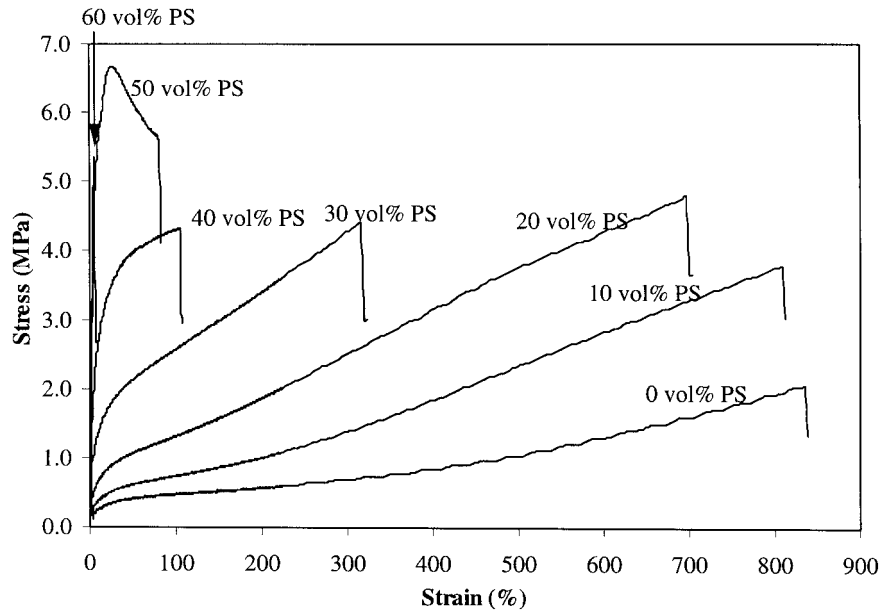
Figure 4 Stress–strain curves of the PS/P(BMA/BA) latex blend films with different volume concentrations of the PS latex particles; none of the latex particles were carboxylated. Plots of the latex blend films containing 40–60 vol % PS represent the entire stress–strain curves; the other curves show the stress–strain results obtained between 0 and 300% strain.

from the formation of hydrogen bonds, the increase in this energy should have been close to the energy of hydrogen bond formation. To check whether the extra energy was generated by the formation of hydrogen bonds or not, we performed an example calculation using the curve of 0% carboxyl group coverage and the one of 12.9% carboxyl coverage in Figure 5. The calculated extra energy needed for yielding of the carboxylated latex blend films was 1.66 kcal/mol of carboxyl groups present on the PS particles. Because
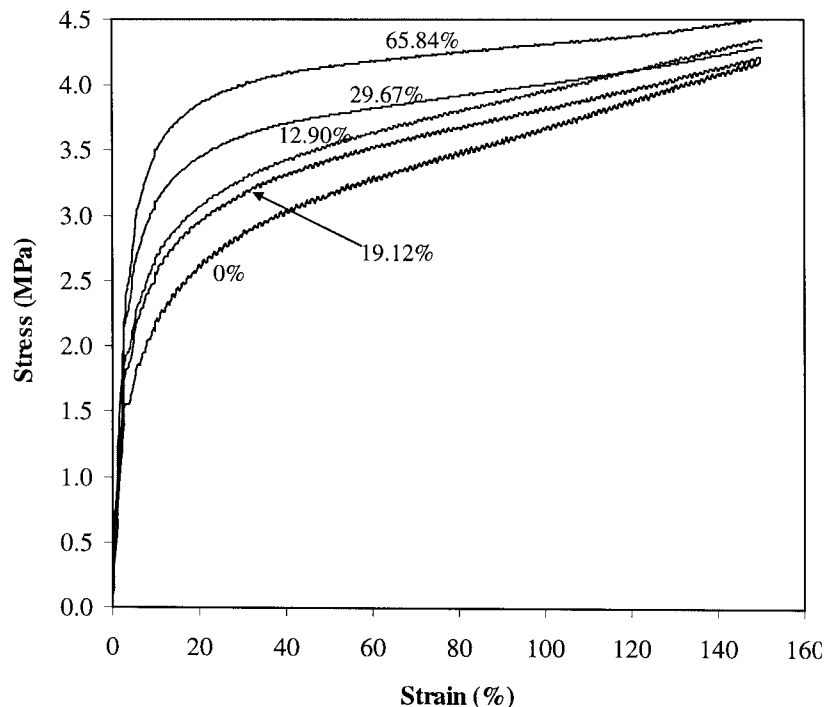

Figure 5 Stress–strain curves of the PS/P(BMA/BA) latex blend films with different carboxyl group coverage on the PS latex particles; PS = 35 vol %. The plots shown here depict only part of the stress–strain curves (i.e., strain from 0–150%). The percentage value given on each curve represents the carboxyl group coverage on the PS latex particles. No carboxyl groups were present on the P(BMA/BA) latex particles.

cavitation (caused by matrix-inclusion debonding) between the PS/P(BMA/BA) particle interphase only occurred in the direction of the tensile test, approximately one-third of the PS surface was debonded after the yield point. Thus, the calculated extra energy needed to be multiplied by a factor of 3, yielding a value of 4.98 kcal/mol of carboxyl groups. Comparison of this calculated value with the literature value for the energy of hydrogen-bond formation, which lies in the range of 1–10 kcal/mol,[29] suggested that the enhancement in yield strength resulted from the hydrogen-bond formation between the carboxyl groups present on the PS particles and the carbonyl groups present in the low-T_g P(BMA/BA) copolymer matrix.

An interesting phenomenon was that the yield strength of the latex blend films did not always increase with an increase in the carboxyl coverage on the PS latex particles. The yield strength of the latex blend film with 19.1% carboxyl coverage on the PS particles exhibited a lower yield strength than the film with 12.9% carboxyl coverage.

To explain this phenomenon, the morphology of the latex blend films containing different carboxyl group coverages on the PS particles was examined. As discussed in an earlier publication,[30] the uniformity of the PS latex particle distribution within the low-T_g P(BMA/BA) copolymer matrix was improved when the carboxyl group coverage on the PS latex particles was low, and the uniformity became worse as the carboxyl coverage on the high-T_g particles increased in a range of high carboxyl group coverages. The optimum point for the best uniformity was around 12.9% carboxyl group coverage. The phenomenon was also observed in the bulk of the latex blend films with transmission electron microscopy (TEM) plus cryo-ultramicrotomy techniques (Fig. 6). In the latex blend film where the carboxyl group coverage on the surface of the PS latex particles was 12.9% [Fig. 6(A)], the PS particles were uniformly distributed within the P(BMA/BA) copolymer matrix, whereas the PS latex particles were unevenly distributed in the matrix when the carboxyl group coverage on the PS particles was high [e.g., 65.8%; Fig. 6(B)]. It was proposed previously[30] that the phase compatibility between PS and P(BMA/BA) was improved in the presence of carboxyl groups on the PS particles, which was the driving force to improve the uniformity of the PS particle distribution. Hydrogen bonding between the carboxyl groups present at high concentration on the PS particles can also be the driving force that decreases the uniformity of the PS particle distribution in the low-T_g copolymer matrix. Based on the morphology study described earlier,[30] the relationship between the yield strength and the carboxyl group coverage could be explained as follows. The yield strength is a function of the density of the hydrogen bonds that were formed between the carboxyl groups present on the PS parti-
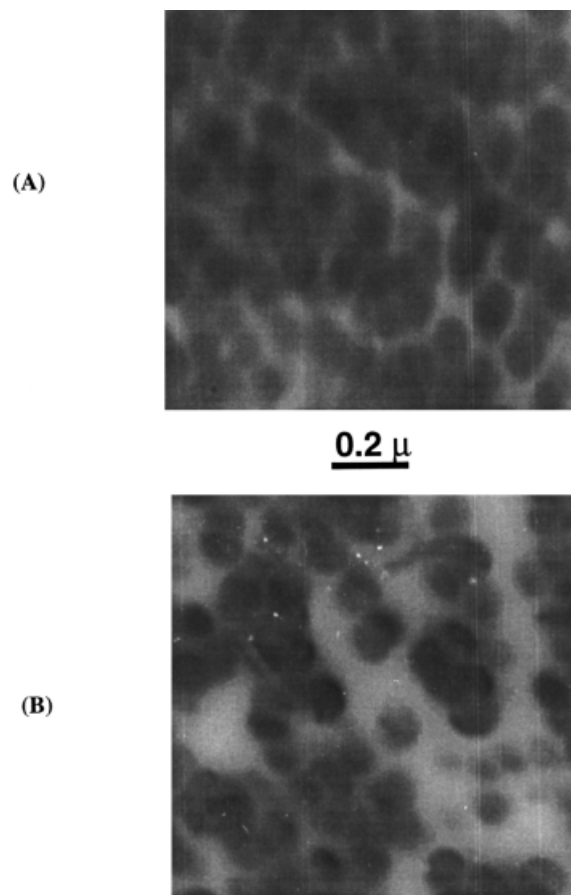

(A)

0.2 μ

(B)

Figure 6 TEM micrographs of the cryo-ultramicrotomed thin sections of the PS/P(BMA/BA) latex blend films with (A) 12.9% carboxyl group coverage on the PS particles and (B) 65.8% carboxyl group coverage on the PS particles: PS = 35 vol %.

cles and the carbonyl groups present in the low-T_g P(BMA/BA) copolymer matrix. The increase in the carboxyl group coverage on the PS particles should have increased the density of hydrogen bonding between the low- and high-T_g polymer phases. However, it also may have increased the degree of clustering of the PS particles through carboxyl group hydrogen bonding between the PS particles, resulting in some loss of reinforcement. These clustering effects may have offset the increase in the yield strength due to the increase in the concentration of the hydrogen bonds resulting from the higher coverage of the carboxyl groups present in the PS particles.

Young's modulus of the PS/P(BMA/BA) latex blend films

Young's modulus (E) is one of the most important parameters commonly used to characterize the mechanical properties of materials. Many methods have been used to measure elastic modulus. Probably, the most widely used method is the tensile stress–strain
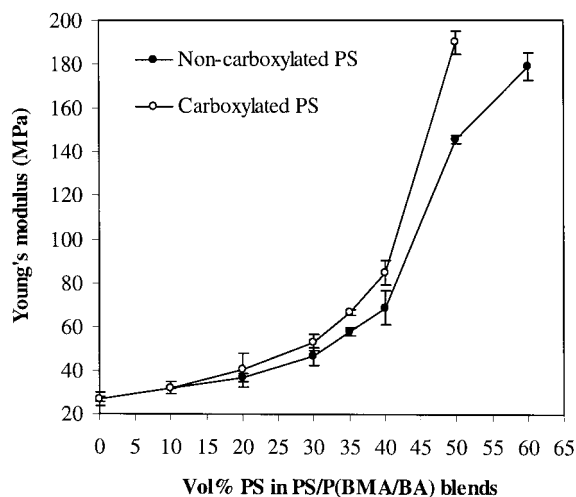
Figure 7 Young's modulus versus volume concentration of PS latex particles in PS/P(BMA/BA) latex blend films: (●) none of the latex particles contained carboxyl groups and (○) carboxyl group coverage on the PS particles = 12.9% and no carboxyl groups were present in the P(BMA/BA) particles.

test.[31,32] Young's modulus is represented by the initial slope of the stress versus strain curve.

Similar to the yield strength (Fig. 4), the Young's modulus of the PS/P(BMA/BA) latex blend films increased as the volume concentration of the PS particles was increased (Fig. 7). Young's modulus as a function of the volume percentage of PS is also plotted in Figure 7 for the PS/P(BMA/BA) latex blend films containing carboxylated PS latex particles. The modulus of the carboxylated latex blend film was higher than that of the noncarboxylated latex blend films at the same volume percentage of PS, indicating that the presence of the carboxyl groups on the PS particles improved the Young's modulus of the PS/P(BMA/BA) latex blend films.

As discussed previously, the presence of the carboxyl groups on the PS latex particles increased the yield strength of the latex blend films through the mechanism of interfacial adhesion, which was enhanced by the formation of hydrogen bonds between the carboxyl groups present on the PS particles and the carbonyl groups present in the copolymer matrix. However, as all of the moduli were measured before the yield point was reached, the enhanced interfacial adhesion may not have been the most important factor that increased the Young's modulus. The modulus may have been enhanced by another mechanism. The mechanism proposed here is the formation of a glassy interphase. This interphase was formed between the PS particles and the P(BMA/BA) copolymer matrix because of the formation of hydrogen bonds, which is illustrated in Figure 8. The carboxyl groups present on the PS latex particles formed hydrogen bonds with the carbonyl groups in the low-T_g P(BMA/BA) copolymer

matrix. Domains resulting from the formation of the hydrogen bonds would have been formed around each PS particle [Fig. 8(A)]. In each of the domains, the P(BMA/BA) molecular chains were crosslinked by these hydrogen bonds, resulting in a higher modulus than that of the low-T_g P(BMA/BA) copolymer matrix. These domains may have served as high-T_g fillers and increased the Young's modulus of the PS/P(BMA/BA) latex blend films. The proposed glassy interphase mechanism served as the basis for the development of quantitative equations, which correlated the Young's modulus of the PS/P(BMA/BA) latex blend films to the carboxyl group coverage on the PS latex particles.[33]

The results shown in Figure 7 demonstrate that the presence of the carboxyl groups on the high-T_g PS latex particles significantly influenced the modulus of the latex blend film. Thus, we carried out further experiments to investigate the influence of the carboxyl groups on Young's modulus over a wider range. Figure 9 shows these results. A general trend was noted in which the modulus first increased as the carboxyl group coverage on the PS latex particles increased. However, there was then a sudden drop in the modulus between 12.9 and 19.1% carboxyl group coverage on the PS particles. This phenomenon could be explained by the combined effects of the glassy interphase and the PS particle packing, which was reported previously.[33] The formation of the glassy interphase, whose volume increased with the increase in the carboxyl group coverage on the PS particles, would have contributed to the enhancement of Young's modulus, whereas the sudden drop of Young's modulus between 12.9 and 19.1% carboxyl group coverage may have been due to the change of the packing of the PS particles from a body-centered cubic to a hexagonal close-packed array.

Ultimate properties of PS/P(BMA/BA) latex blend films

The modulus of a composite material can be accurately predicted with well-developed theories.[6,9,33,34] However, the modeling of ultimate properties, such as maximum elongation and ultimate tensile strength, is less reliable because ultimate properties are much harder to model than modulus or transport properties.

Maximum elongation

Although it is difficult to model the ultimate properties of two-phase mixtures such as latex blend films, efforts continue to achieve better predictive models. Some theories predicting the ultimate properties (e.g., maximum elongation) of particulate-filled polymers can be extended to include films cast from latex blends consisting of phase-separated high- and low-T_g latex
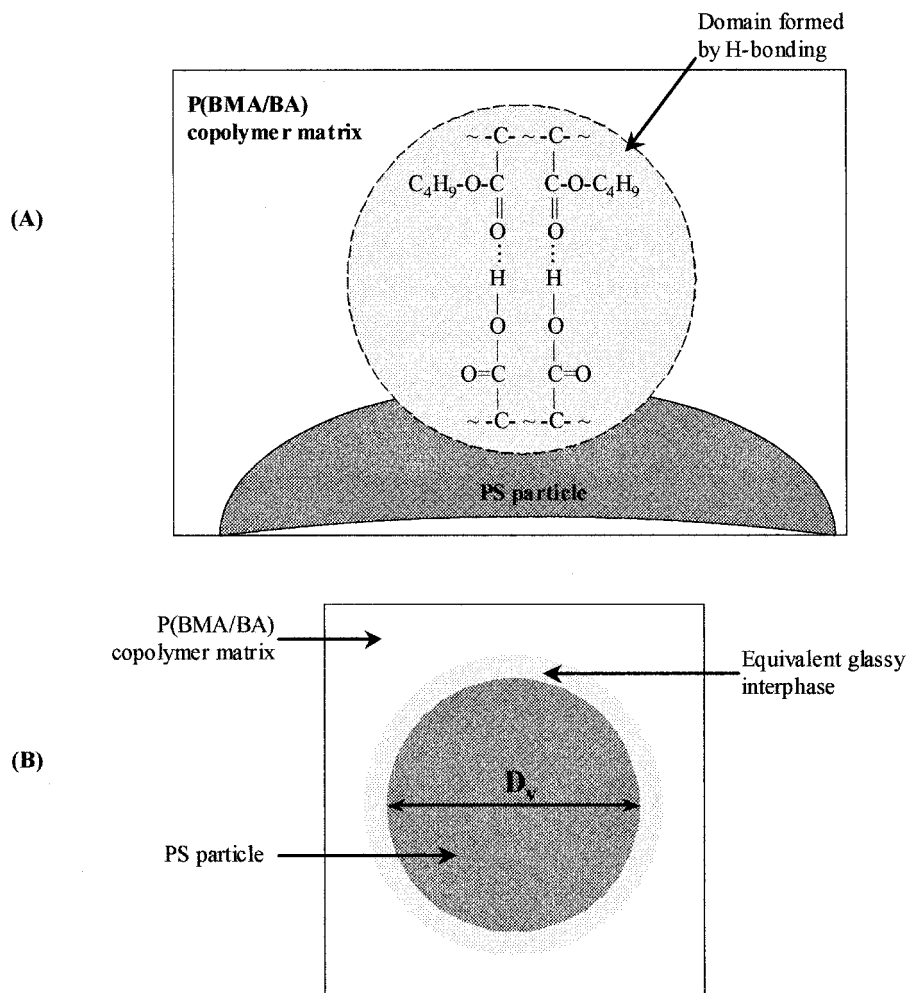
Figure 8 Schematic representations of (A) high-T_g domains resulting from the formation of hydrogen bonds between the carboxyl groups present on the PS particles and the carbonyl groups in the P(BMA/BA) copolymer matrix and (B) an equivalent glassy interphase that formed between the PS latex particles and the P(BMA/BA) copolymer matrix resulting from the formation hydrogen bonds.

particles. For example, Nielsen proposed a model to predict the maximum elongation of composite materials (ε_b) from the volume fraction of the high-T_g dispersed phase (ϕ_2) and the maximum elongation of the pure low-T_g matrix (ε_{b0}).[35] This model is expressed by eq. (1):

$$\varepsilon_b = \varepsilon_{b0}(1 - \phi_2^{1/3}) \tag{1}$$

This model usually predicts values of maximum elongation that are lower than the corresponding experimental data, which is commonly thought to be caused by the assumption of perfect adhesion between the two particle phases because many composites do not possess perfect adhesion.

Another model that has been used to predict the maximum elongation of a filled polymer system is the strain amplification model,[3,36] which is presented in eq. (2). This model predicts that in composites comprised of high-T_g particles (spheres) dispersed in a
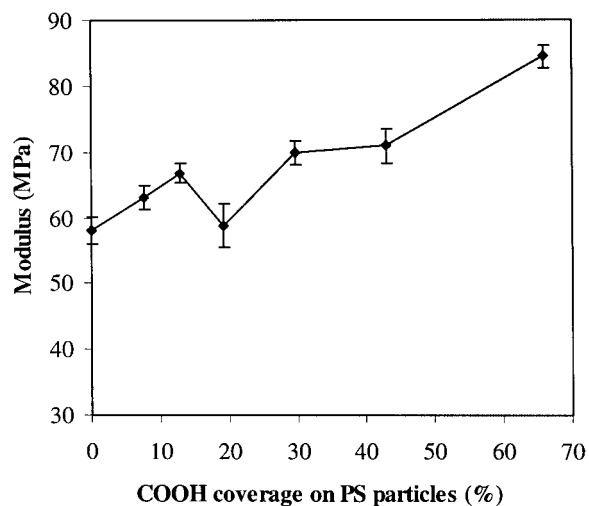

Figure 9 Young's modulus versus the carboxyl group coverage on the PS latex particles in PS/P(BMA/BA) latex blend films: volume fraction of PS $\phi_2 = 0.35$. No carboxyl groups were present in P(BMA/BA) latex particles.
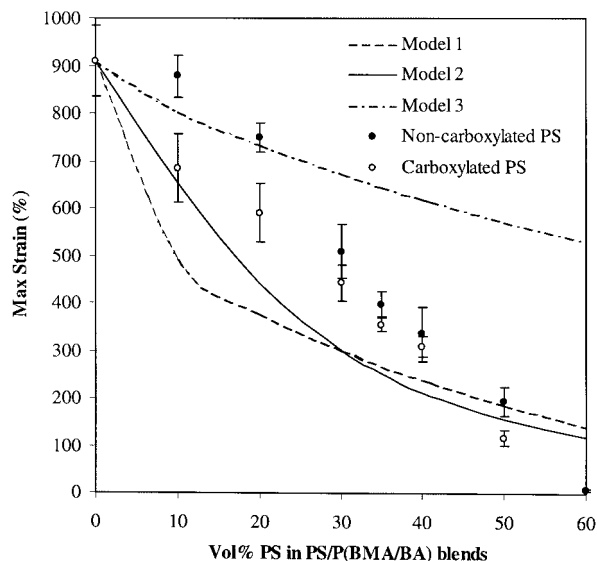
Figure 10 Maximum strain versus volume concentration of the PS latex particles in the PS/P(BMA/BA) latex blends: (model 1) predicted by Nielsen's model , (model 2) predicted by the strain amplification model , (model 3) predicted by Sato and Furukawa's no-adhesion model, (●) experimental data obtained with the latex blend films without any carboxyl groups present, and (○) experimental data obtained with the latex blend films containing PS latex particles with 12.9% carboxyl group coverage.

low-T_g matrix, the average local strain of the low-T_g (continuous) matrix is higher than the macroscopic strain of the composite film:

$$\varepsilon_L = \varepsilon_M(1 + 2.5\phi_2 + 14.1\phi_2^2) \tag{2}$$

where ε_L is the average local strain of the low-T_g matrix and ε_M is the macroscopic strain of the biphasic film.

Both of the previous models assume perfect adhesion between the high-T_g dispersed phase and the low-T_g continuous phase. Sato and Furukawa developed a model to predict the maximum elongation of two-phase mixtures with no adhesion between the high-T_g and low-T_g phases.[37,38]

The predicted values of maximum elongation with the Nielsen, strain amplification, and Sato and Furukawa models are plotted along with the experimental data in Figure 10. Comparison of the experimental data with the predicted values showed that the high-T_g/low-T_g phases of the PS/P(BMA/BA) latex blend films possessed an intermediate level of adhesion before break because most of the experimental data fell between the strain amplification curve (model 2) and the no-adhesion curve (model 3). These results also showed that the presence of carboxyl groups on the PS particles did not significantly increase the maximum elongations of the latex blend films for most of the experimental points. These results were different from

those obtained from the yield strength results, which were substantially improved by the presence of the carboxyl groups. This could be explained by the fact that yielding occurred before the films broke.[3] After the yield point, cavitation could be induced between the high-T_g particles and the low-T_g matrix,[37,38] which resulted in poor adhesion in the direction of the tensile test. Thus, the presence of the carboxyl groups on the PS latex particles would not influence the maximum elongation but could substantially enhance the yield strength and Young's modulus of the latex blend films.

Changing the carboxyl group coverage over a larger range (from 0 to 66% coverage) resulted in only a slight decrease in the maximum elongation (strain;
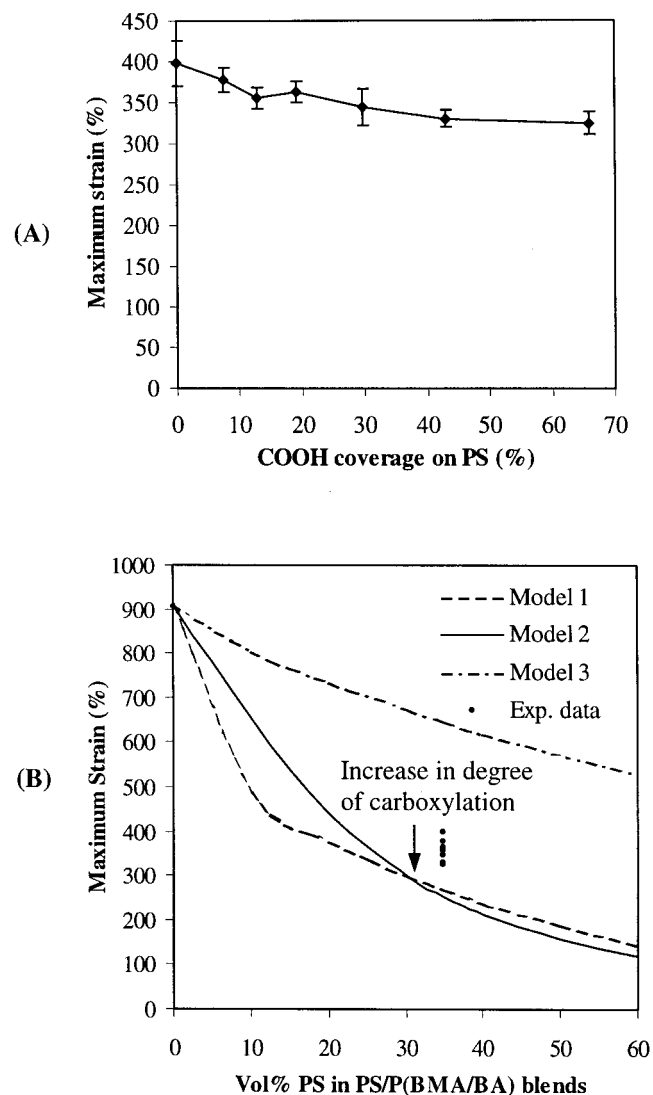

(A)

(B)

Figure 11 (A) Maximum strain versus carboxyl group coverage on the PS latex particles in the PS/P(BMA/BA) latex blends: PS = 35 vol %, and (B) maximum strain versus volume percentage PS: (●) experimental data obtained when the carboxyl coverage on the PS particles was increased from 0 to 66%.

Fig. 11). These results could be interpreted by strong adhesion between the particle/particle interface in the direction perpendicular to the tensile testing direction after the yield point. If particle/particle adhesion is strong, polymer chain interdiffusion is limited, and the sample would break at a lower elongation. Because the carboxyl groups can increase the particle/particle adhesion through hydrogen bonding, the presence of the carboxyl groups would decrease the maximum elongation. Because it is known that the breaking point occurs after the debonding point in this system, where the particle/particle bonding in the direction of the tensile testing is disrupted, the presence of the carboxyl groups can only increase the particle/particle adhesion perpendicular to the tensile testing direction, which also contributes to a decrease in the maximum elongation.

Tensile strength

The equivalent box model (EBM) is a recently proposed model that may be used to predict the tensile strength of two-phase mixtures,[16] which represents a combination of parallel and series models. The ultimate tensile strength is predicted by eq. (3):

$$\sigma_u = (\sigma_{u1}\phi_{1p} + \sigma_{u2}\phi_{2p}) + A\sigma_{u1}\phi_s \qquad (3)$$

where σ_u, σ_{u1}, and σ_{u2} are the tensile strength of the two-phase mixtures, the continuous phase, and the dispersed phase, respectively; ϕ_{1p} and ϕ_{2p} are the parallel contributions of polymer phase 1 and 2 to the volume fraction; ϕ_s is the series volume fraction contribution of the lower strength component, and A represents the interfacial adhesion, where A lies between 0 (no adhesion) and 1 (perfect adhesion). ϕ_{1p} and ϕ_{2p} are calculated with eqs. (4–6):

$$\phi_{1p} = [(\phi_1 - \phi_{1cr})/(1 - \phi_{1cr})]^{D_1} \text{ and } \phi_{s1} = \phi_1 - \phi_{1p} \qquad (4)$$

$$\phi_{2p} = [(\phi_2 - \phi_{2cr})/(1 - \phi_{2cr})]^{D_2} \text{ and } \phi_{s2} = \phi_2 - \phi_{2p} \qquad (5)$$

$$\phi_{cr} = \phi_{1cr} + \phi_{2cr} \qquad (6)$$

where ϕ_{cr} is the percolation threshold volume fraction and D is the critical universal exponent. ϕ_{1cr}, ϕ_{2cr}, D_1, and D_2 can be considered to be adjustable parameters. As an approximation, $\phi_{1cr} = \phi_{2cr} = 0.156$ and $D_1 = D_2 = 0.1833$.[16] The predicted EBM curves are plotted along with the experimental data in Figure 12. The deviation of the predicted values from the experimental data was large, indicating that the EBM model was not applicable for the prediction of the tensile strength of the PS/P(BMA/BA) latex blend films. However, some useful information could still be drawn from the EBM model. As shown in Figure 12, the ultimate tensile strength in the case of perfect adhesion (i.e., A
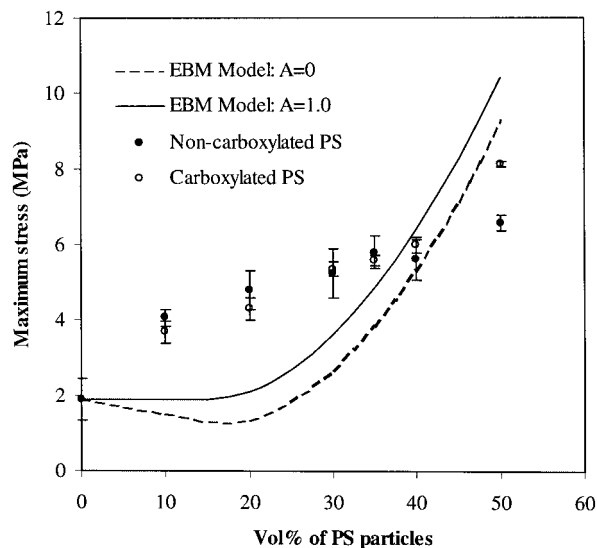

Figure 12 Tensile strength versus volume concentration of the PS/P(BMA/BA) latex particles in the PS/P(BMA/BA) latex blends: (○) experimental data obtained with PS/P(BMA/BA) latex blend films containing the latex particles with 12.9% carboxyl group coverage and (●) neither the PS nor the P(BMA/BA) latex particles contained carboxyl groups.

= 1) was higher than that of zero adhesion (i.e., $A = 0$) as predicted by the EBM model, implying that the adhesion between the high-T_g and low-T_g particle phases in this system contributed to the increase in the tensile strength. However, Figure 12 indicates a different result, in that the tensile strength of the PS/P(BMA/BA) latex blend films consisting of carboxylated PS particles was not higher than that of the noncarboxylated latex blend films for most of the experimental points. The explanation for this observation was similar to that described previously for the maximum elongation results; that is, most of the samples broke after reaching the yield point. After this point, cavities created between the high-T_g and low-T_g particle phases disrupted the hydrogen bonding between the two phases. Thus, the presence of the carboxyl groups in the PS latex particles did not improve the tensile strength of the PS/P(BMA/BA) latex blend films. As discussed previously, there may have been some degree of adhesion remaining in the direction perpendicular to the direction of the tensile test, which resulted in a small decrease in the maximum elongation. However, this effect was small and did not contribute to the overall tensile strength. One exception occurred at 50 vol % PS, where a noticeable increase in the tensile strength was observed (Fig. 12). By comparing these results with the plots shown in Figure 4, we could see that the tensile strength at this point became the yield strength, which was enhanced in the presence of the carboxyl groups on the PS particles as discussed before. When a comparison was made between the stresses at break at 50 vol % PS, which were

TABLE II
Ultimate Tensile Strength and Stress at Break of the Films Prepared from PS/P(BMA/BA) Latex Blends Containing Carboxylated and Noncarboxylated PS Latex Particles

	Noncarboxylated latex blend film[a]		Carboxylated latex blend film[b]	
PS (vol %)	Maximum tensile strength (MPa)	Stress at break (MPa)	Maximum tensile strength (MPa)	Stress at break (MPa)
0.0	1.89 ± 0.54	1.89 ± 0.54	1.89 ± 0.54	1.89 ± 0.54
10.0	4.06 ± 0.22	4.06 ± 0.22	3.69 ± 0.30	3.69 ± 0.30
20.0	4.80 ± 0.52	4.80 ± 0.52	4.31 ± 0.29	4.31 ± 0.29
30.0	5.24 ± 0.65	5.24 ± 0.65	5.36 ± 0.19	5.36 ± 0.19
35.0	5.80 ± 0.43	5.80 ± 0.43	5.58 ± 0.13	5.58 ± 0.13
40.0	5.61 ± 0.53	5.61 ± 0.53	6.01 ± 0.20	6.01 ± 0.20
50.0	6.59 ± 0.20	5.04 ± 0.53	8.14 ± 0.06	5.44 ± 0.42

[a] None of the latex particles contained carboxyl groups.
[b] Carboxyl group coverage on the PS latex particles = 12.9%.

5.04 ± 0.53 MPa and 5.44 ± 0.42 MPa for the PS/P(BMA/BA) latex blend films containing noncarboxylated and carboxylated PS particles, respectively, the difference was negligible (Table II).

Further experiments were also carried out by variation of the carboxyl group coverage on the PS particles over a larger range (from 0 to 66%) to investigate the influence of the presence of carboxyl groups on the ultimate strength (i.e., the stress at break for the 35 vol % PS; Fig. 13). No noticeable change in the stress at break was observed as the carboxyl group coverage on the PS latex particles increased from 0 to 66%. Thus, it could be concluded that the strength at break of the PS/P(BMA/BA) latex blend films did not depend on the presence of the carboxyl groups on the PS latex particles.

Dynamic mechanical properties

DMA measures the modulus in a different manner from the stress–strain tests. Figure 14(A) shows the storage modulus of the PS/P(BMA/BA) latex blend films for different volume concentrations of the PS particles as a function of temperature. The figure shows that as the volume percentage of PS increased, the storage modulus increased, especially in the region where the temperature was higher than the T_g of the P(BMA/BA) copolymer matrix. The main reason that fillers had a larger effect in raising the modulus above the T_g of the rubbery phase rather than below it was the larger modulus ratio E_2/E_1 of the components when the polymer was in the rubbery state compared to the rigid glassy state. When comparing the storage modulus of the PS/P(BMA/BA) latex blend films with different carboxyl group coverage on the PS latex particles [Fig. 14(B)], we found that the storage mod-

ulus of the latex blend films increased in the high-temperature region ($>T_g$ of the copolymer matrix) of the curves as the carboxyl group coverage increased. As discussed before, this may have been due to the increase in the glassy interphase volume caused by the hydrogen bonding between the carboxyl groups on the PS particles and the carbonyl groups present in the P(BMA/BA) copolymer matrix.

Tan $\delta (G''/G')$ is the parameter that describes the ratio between shear energy loss modulus (damping) (G'') and shear energy storage modulus (G') of two-phase mixtures and is approximately equal to E''/E'. Fillers usually decrease the damping as long as there is some adhesion between the filler and the matrix.[39,40] The tan δ of the PS/P(BMA/BA) latex blend films versus the volume concentration curves at different temperatures are plotted in Figure 15(A). This plot shows a decrease in damping as the volume concentration of PS particles increased, indicating that there was some adhesion between the high-T_g and low-T_g phase. This conclusion is consistent with those discussed in the section on maximum elongation. The experimental data [Fig. 15(B)] showed a decrease in damping of the PS/P(BMA/BA) latex blend films as the carboxyl group coverage on the PS particles was increased. This implies that the presence of the carboxyl groups on the PS particles may have increased the equivalent volume of the PS phase and increased the extent of adhesion between the high- and low-T_g phases through a hydrogen bonding mechanism.

CONCLUSIONS

The presence of carboxyl groups on the PS latex particles in the PS/P(BMA/BA) latex blend films significantly enhanced Young's modulus and the yield
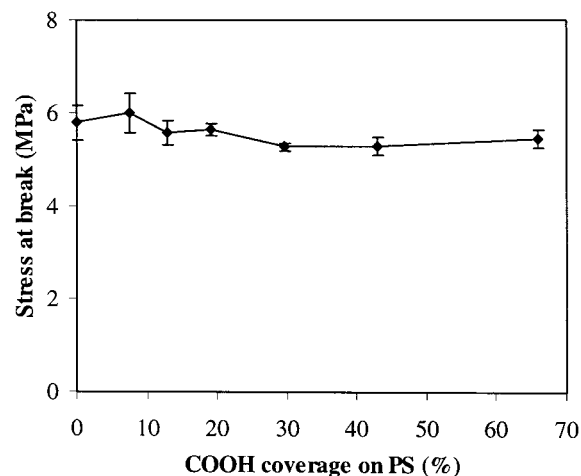
Figure 13 Stress at break versus the carboxyl group coverage on the PS latex particles in the PS/P(BMA/BA) latex blends; PS = 35 vol %. The P(BMA/BA) latex particles contained no carboxyl groups.
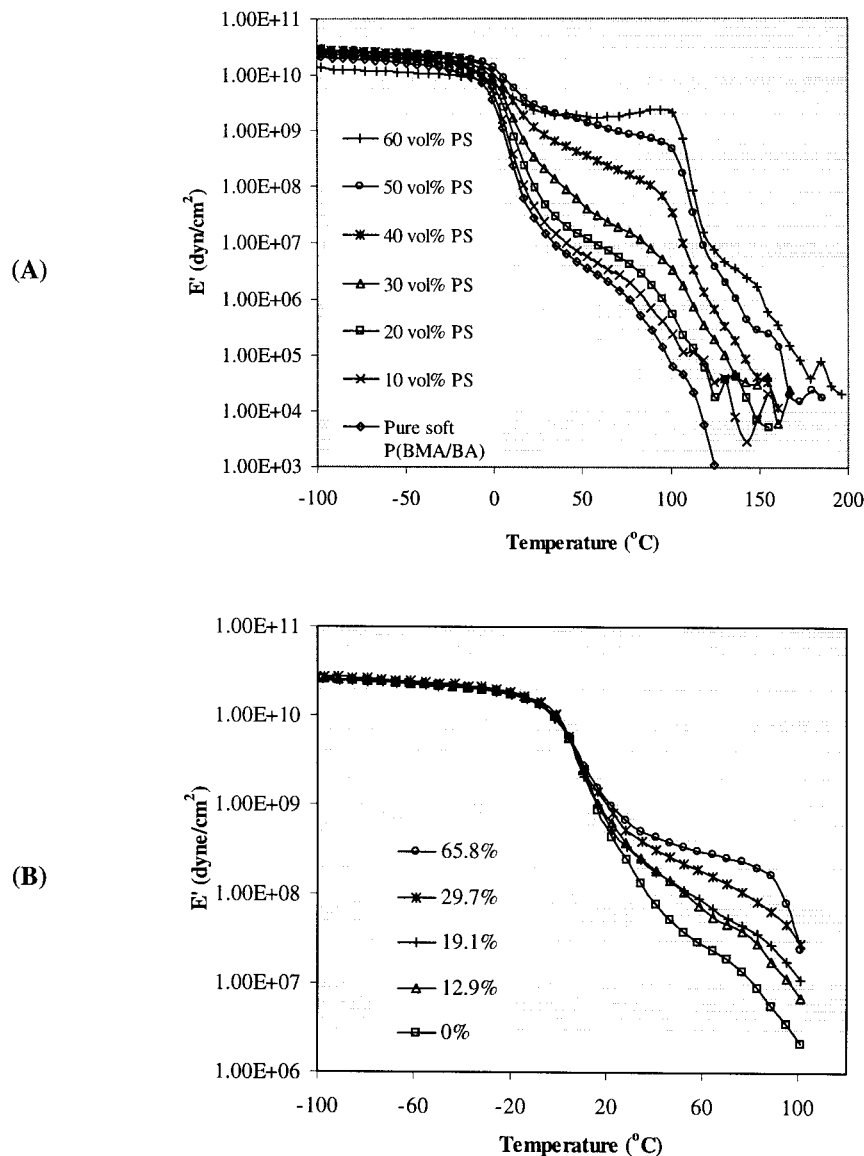
Figure 14 Storage modulus of the PS/P(BMA/BA) latex blend films with (A) different volume percentage of PS latex particles and carboxyl group coverage on the PS particles = 12.9% and (B) with different carboxyl group coverage on the PS particles: PS = 35 vol %. The percentages given in these plots indicate the carboxyl group coverage. No carboxyl groups were present on the P(BMA/BA) latex particles for both (A) and (B).

strength of the latex blend films. The carboxyl groups present on the PS latex particles would form hydrogen bonds with the carbonyl groups present in the P(BMA/BA) copolymer matrix or with the carboxyl groups present on adjacent PS particles (interparticle hydrogen bonding). The carboxyl groups present on the PS latex particles at a low concentration ($\leq 13\%$ coverage) primarily formed hydrogen bonds with the carbonyl groups present in the P(BMA/BA) copolymer matrix. This type of hydrogen bonding resulted in a random or body-centered cubic packing of the PS particles in their maximum packing state. When the carboxyl groups were present on the PS latex particles at a high concentration ($>13\%$ coverage), hydrogen bonding between the carboxyl groups on adjacent PS

particles could form. The formation of the interparticle hydrogen bonds induced an attractive force among the PS particles, resulting in tighter packing (hexagonal) of the PS particles at their maximum packing state. The presence of the carboxyl groups on the PS particles may have increased the yield strength of the PS/P(BMA/BA) latex blend films through the mechanism of interfacial adhesion, which was improved with the formation of hydrogen bonds between the particle/particle phases, whereas it may have enhanced the Young's modulus through the mechanism of a glassy interphase, which also resulted from the formation of these hydrogen bonds.

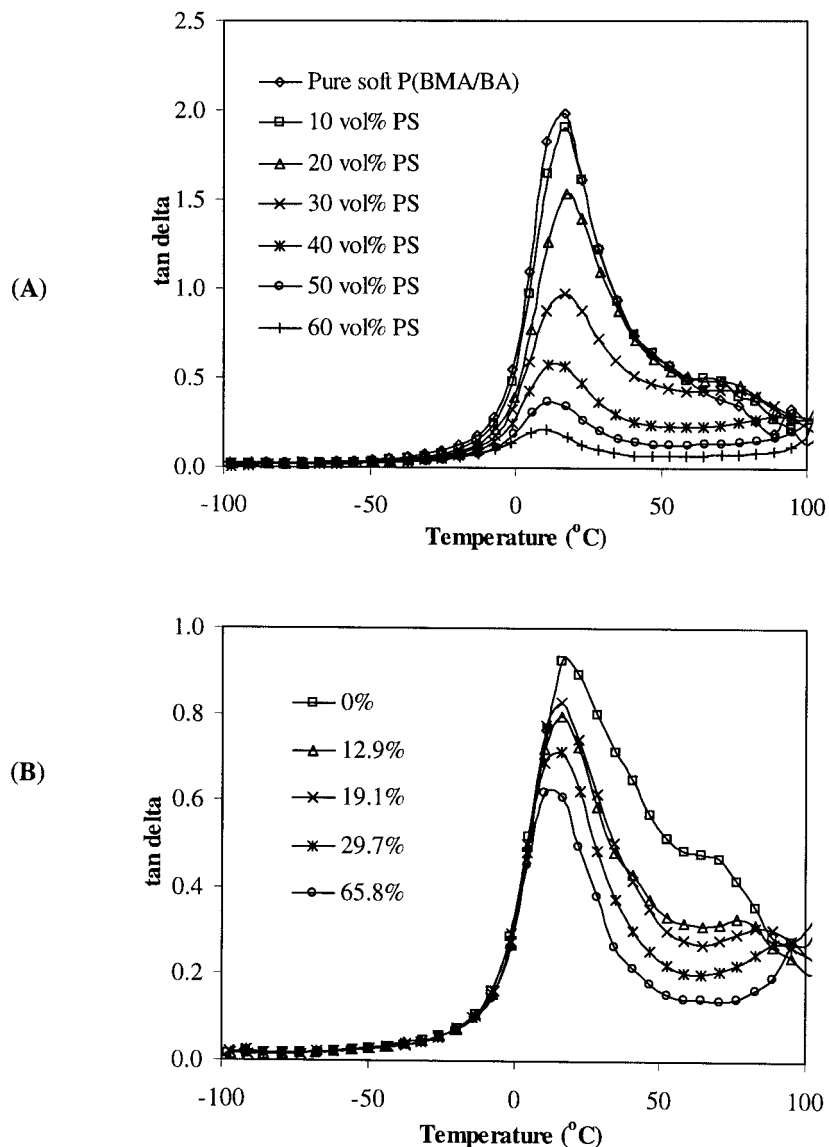After the yield point was reached, cavities occurred around the PS particles, separating the high-T_g and

Figure 15 Tan δ of the PS/P(BMA/BA) latex blend films with (A) different volume concentrations of the PS latex particles and carboxyl group coverage on the PS particles = 12.9% and (B) with different carboxyl group coverage on the PS particles: PS = 35 vol %. The percentages given in this plot indicate the carboxyl group coverage. No carboxyl groups were present on the P(BMA/BA) latex particles for both (A) and (B).

low-T_g particle phases; therefore, the surface properties of the PS particles did not significantly influence the ultimate mechanical properties. Thus, ultimate properties, such as stress at break and maximum elongation, of the PS/P(BMA/BA) latex blend films only slightly depended on the presence of the carboxyl groups on the PS particles if the films broke after reaching their yield points.

The DMA results confirmed the mechanism of the glassy interphase formed in the presence of the carboxyl groups on the PS particles, and the volume of the glassy interphase increased with an increase in the carboxyl group coverage on the PS particles, which significantly influenced the modulus of the latex blend films.

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