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Effect of Ionomeric Behavior on the Viscoelastic Properties and Morphology of Carboxylated Latex Films

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ABSTRACT: The viscoelastic properties of a series of carboxylated styrene/butadiene latexes were determined using dynamic mechanical spectroscopy. The viscoelastic properties of the latex films were found to depend on the pH of the latex and the type of neutralization ions present in the latex. This change in the viscoelastic properties is explained by the change in the ionomeric characteristics of the latex and a change of morphology of the latex film as determined using transmission electron microscopy. At low pH, the low-T_g (glass-transition temperature) essentially noncarboxylated bulk polymer phase is often the continuous phase with the high-T_g carboxylated interfacial polymer as the dispersed phase. As the mobility of the interfacial polymer decreases with increasing ionomeric characteristic with increasing pH, the morphology changes to one in which the high-T_g carboxylated interfacial polymer is the continuous phase.

Introduction

Emulsion polymers, such as carboxylated styrene/butadiene (S/B) copolymer latexes, are used widely in water-based binder and coating systems. The viscoelastic behavior of the latex films affects the performance of many end-use applications and is therefore a critical design parameter to achieve optimum properties.[1] It is well-known that the glass-transition temperature (T_g), molecular weight, and degree of cross-linking of the latex affect the viscoelastic properties of the latex films.[2,3] With copolymer latexes, the monomer composition during polymerization can also affect the morphology of the latex particle and, therefore, the viscoelastic properties of the latex films.[4−6] The different degrees of hydrophilicity of the comonomers can also result in a copolymer composition gradient at different locations in the latex particle. Films of carboxylated latexes often show honeycomb-like structures because the more hydrophilic carboxylic acid groups concentrate near the particle surface.[7,8]

Zosel and co-workers studied the effect of acrylic acid on the viscoelastic properties and morphology of butyl acrylate latexes. Both the viscoelastic properties and electron microscopy of the latex films suggested the presence of two polymer phases. The high T_g phase, despite being a small volume fraction of the total polymer, formed a honeycomb-like structure and had a very pronounced effect on the viscoelastic properties of the latex films.[9] Richard and Maquet studied the ionomeric behavior of carboxylated S/B latexes and found that the degree of neutralization and the size of the neutralizing ions affect the viscoelastic properties of the latex films.[10]

The effects of metal ions on the viscoelastic properties of acid-containing polymers have been studied extensively.[11−13] Vaughan and co-workers,[14,15] Macknight,[16] Otocka,[17] and others studied the effect of metal ions on the viscoelastic behavior of crystalline copolymers, such as poly(ethylene−acrylic acid) and poly(ethylene−methacrylic acid). Fitzgerald and Nielsen[18] and Erdi and Morawetz[19] pioneered the study of the viscoelastic properties of styrene-based ionomers. Eisenberg and King[20] reviewed the extensive studies of the viscoelastic behavior of the styrene-based ionomers. Cooper[21] studied the effect of various divalent ions on the mechanical properties of butadiene−acrylic acid and butadiene−methacrylic acid copolymers. Other butadiene-based ionomers have also been studied.[22] Other than the studies of Richard and co-worker,[9,10] there appears to be no systematic study of the effect of metal ions on the viscoelastic properties of carboxylated S/B latex polymers.

The latex film formation process has been a subject of extensive research and has been reviewed.[23−25] The film formation process of latex is usually divided into three stages. During stage 1, the latex concentrates by water evaporation until particles form a close packing configuration. In stage 2, latex particles deform and coalesce to form a continuous and void-free film. Recently, Chevalier and co-workers studied the transformation of the dispersed latex particles into a continuous film using small-angle neutron scattering (SANS).[26] In stage 3, the latex film undergoes further gradual coalescence by interdiffusion. The interdiffusion of polymer chains has been studied using SANS[27,28] and a nonradiative energy transfer technique.[29,30] In the film formation process of carboxylated latexes, the carboxylic acid-rich polymer phase that concentrates at the particle surface will be forced to occupy the spaces between the deformed latex particles. Therefore, at least initially, the carboxylate-rich interfacial polymer is the continuous phase of the film. Due to the difference in polarity between the carboxylate-rich polymer and the bulk polymer, there is significant interfacial tension between the two phases. Thermodynamics provides the driving force for rearrangement to minimize interfacial surface area in order to achieve the lowest interfacial tension. If the carboxylated interfacial polymer chains have sufficient mobility, a re-

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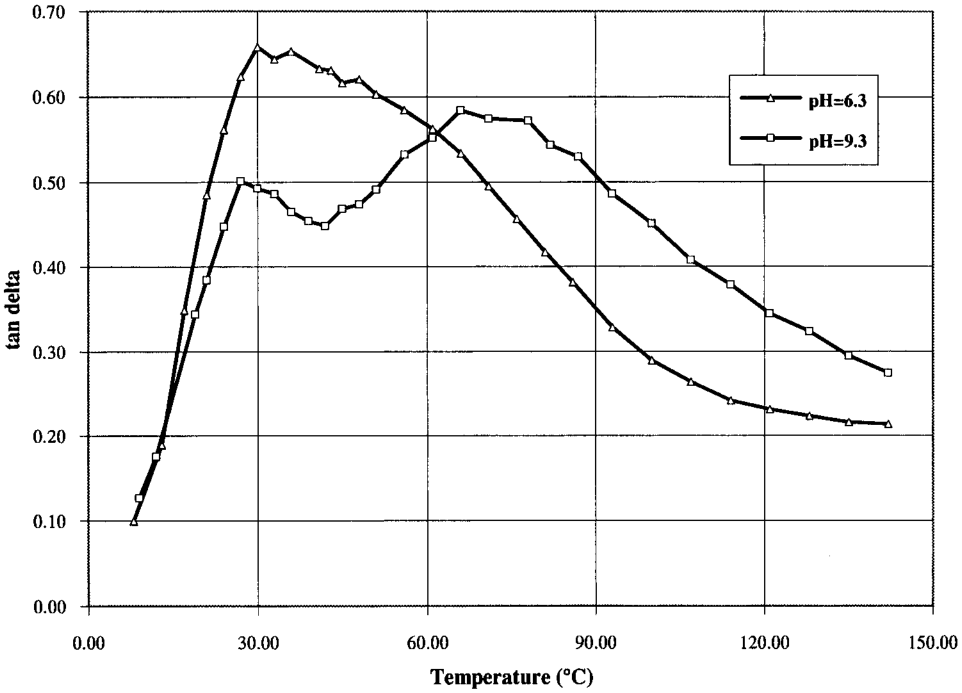


Figure 1. Dynamic mechanical spectrum of carboxylated styrene/butadiene latex film: latex A containing 10 parts BOM acrylic acid. Plot of tan δ vs temperature.

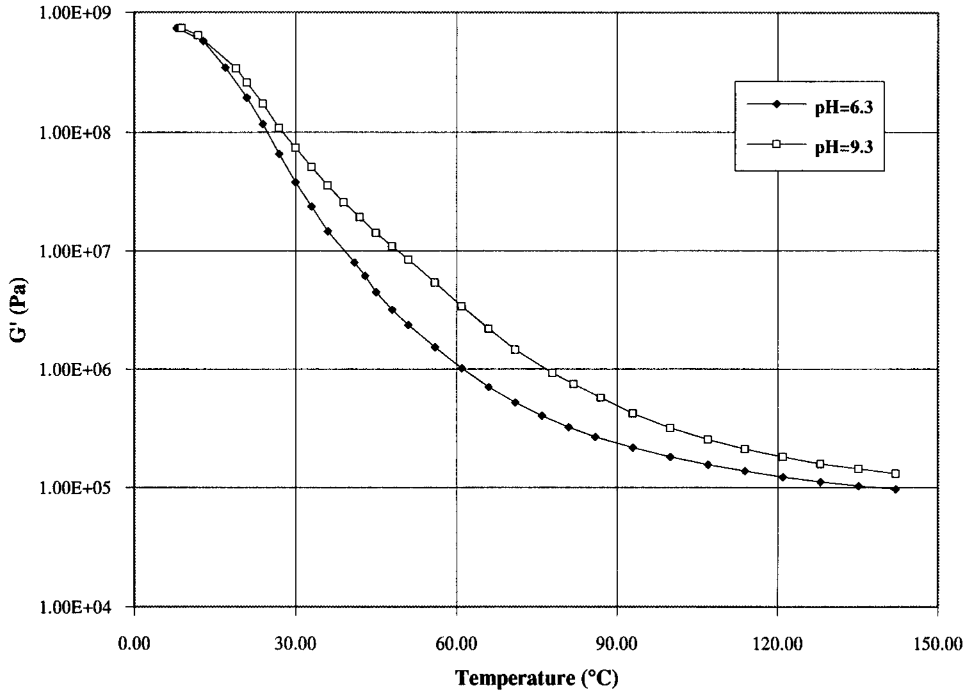


Figure 2. Dynamic mechanical spectrum of carboxylated styrene/butadiene latex film: latex A containing 10 parts BOM acrylic acid. Plot of G' vs temperature.

arrangement of morphology from honeycomb-like structure to an isolated domain-like structure will occur. This rearrangement corresponds to a form of phase inversion. As the carboxylated interfacial polymer chains retreat into interstices between latex particles, the bulk polymer phase becomes the continuous phase. This change in morphology will be reflected in the viscoelastic properties of the latex films. The role of morphology on the viscoelastic properties of blends and multiphase polymers, such as block copolymers, are well-known.[31] Richard and co-worker[3,10] have shown the effect of the ionomeric character of carboxylated S/B latexes on the viscoelastic properties of the latex films. Recently, Kim and Winnik[32] reported on the effect of the neutralizing ion has on the polymer diffusion rate.

In this paper, the role of the ionomeric character of carboxylated S/B latexes on the morphology and the viscoelastic properties of the latex films will be reported. The propensity of the carboxylic acid-rich interfacial polymer to rearrange from the honeycomb-like morphology to a domain-like structure depends on the interfacial tension between the interfacial and bulk polymer phases and the kinetic mobility of the polymer chain. The polymer chain mobility is a function of T_g, molecular weight, degree of cross-linking, and the ionomeric character of the carboxylic acid-containing polymer.

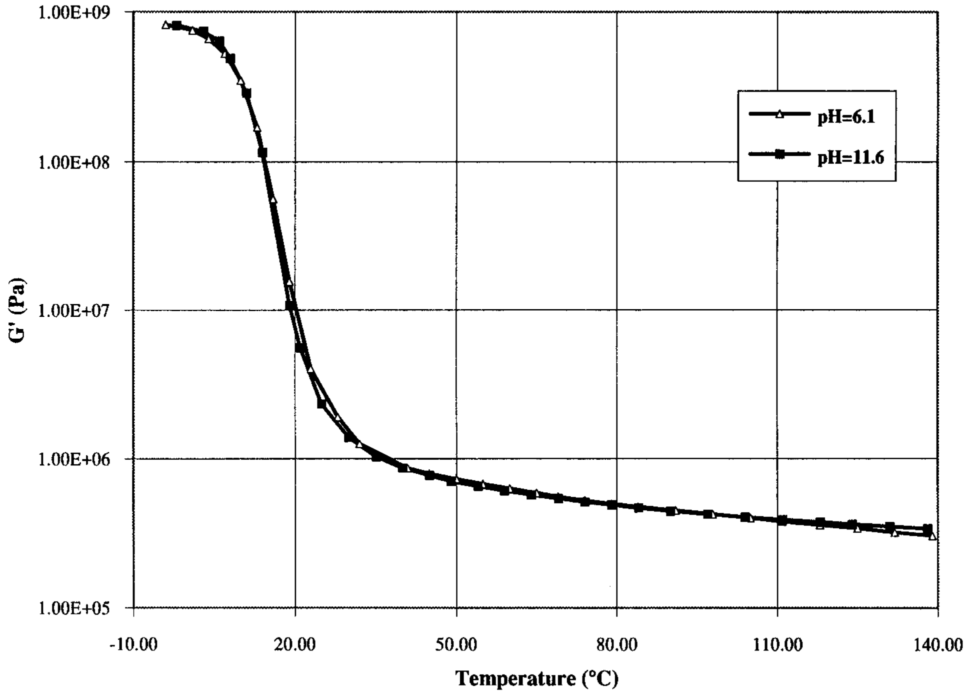


Figure 3. Dynamic mechanical spectrum of noncarboxylated styrene/butadiene latex film: latex B. Effect of pH on *G*′.

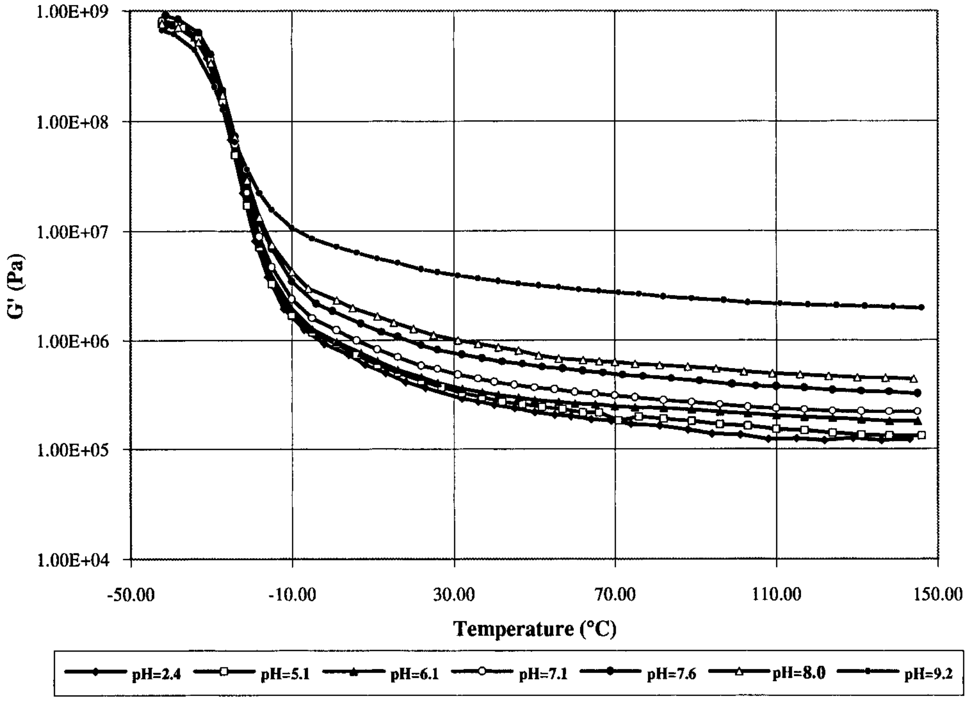


Figure 4. Dynamic mechanical spectrum of carboxylated styrene/butadiene latex film: latex C containing 3 parts BOM itaconic acid. Effect of pH on *G*′.

Therefore, the morphology of some latex films can be controlled by adjusting the ionomeric characteristics of the carboxylic acid-rich interfacial polymer. The change in morphology can be detected using transmission electron microscopy and inferred from the viscoelastic properties of the latex films.

Experimental Section

Latexes. Carboxylated S/B latexes of various compositions were used in this study. A typical procedure, similar to that described in the literature,[33] was used to prepare the latexes. A mixture containing 1975.6 g of deionized water, 99.7 g of a 1% solution of the trisodium salt of *N*-(carboxymethyl)-*N*′-(2-hydroxyethyl)-*N*,*N*′-ethylenediglycine, and 10.8 g of a 28.7% polystyrene polymer seed having an average diameter of 23.6 nm was charged into a stainless steel jacketed reactor. The reactor was purged with nitrogen and heated under agitation to 92 °C. Monomers composed of 1443.7 g of styrene, 1012.4 g of butadiene, and 9.5 g of *tert*-dodecylmercaptan were continuously added to the reactor in 270 min. Also, 423.9 g of deionized water, 14.5 g of sodium persulfate, and 13.7 g of a 20% solution of sodium hydroxide were continuously added to the reactor in 300 min. Also, 37.5 g of fumaric acid, 18.7 g of a 30% solution of sodium lauryl sulfate, and 12.5 g of a 45% percent solution of sodium dodecyl diphenyloxide disulfonate were continuously added to the reactor in 225 min. The reactor vessel was maintained at 92 °C during the additions and for 20 min thereafter. The latex was then steam distilled

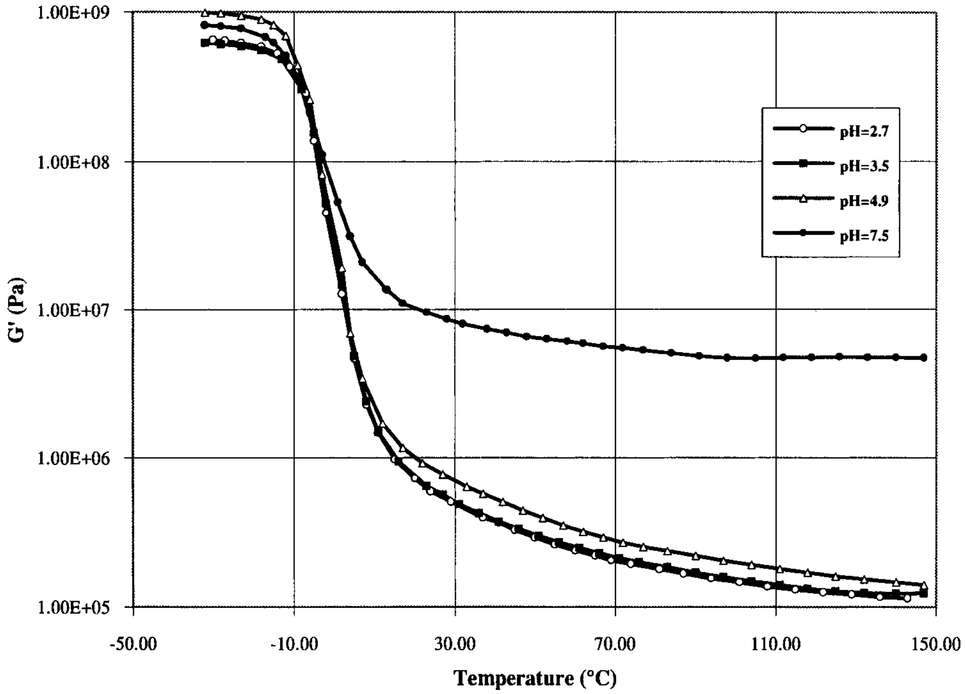


Figure 5. Dynamic mechanical spectrum of carboxylated styrene/butadiene latex film: latex D containing 1.75 parts BOM fumaric acid. Effect of pH on *G*′.

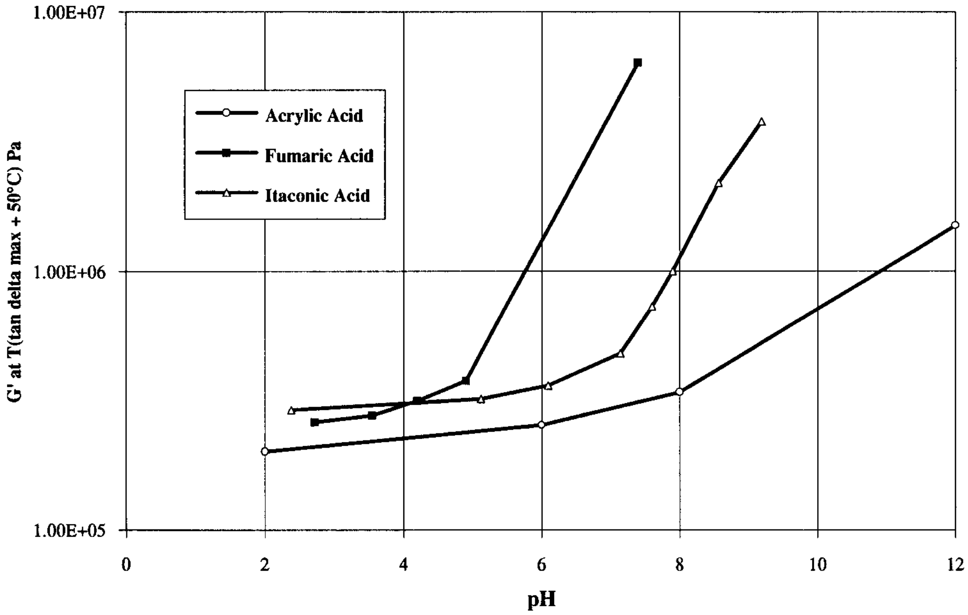


Figure 6. Plot of $G'(T_{\tan\delta_{\max}+50\,°C})$ vs pH. Effect of carboxylic acid type.

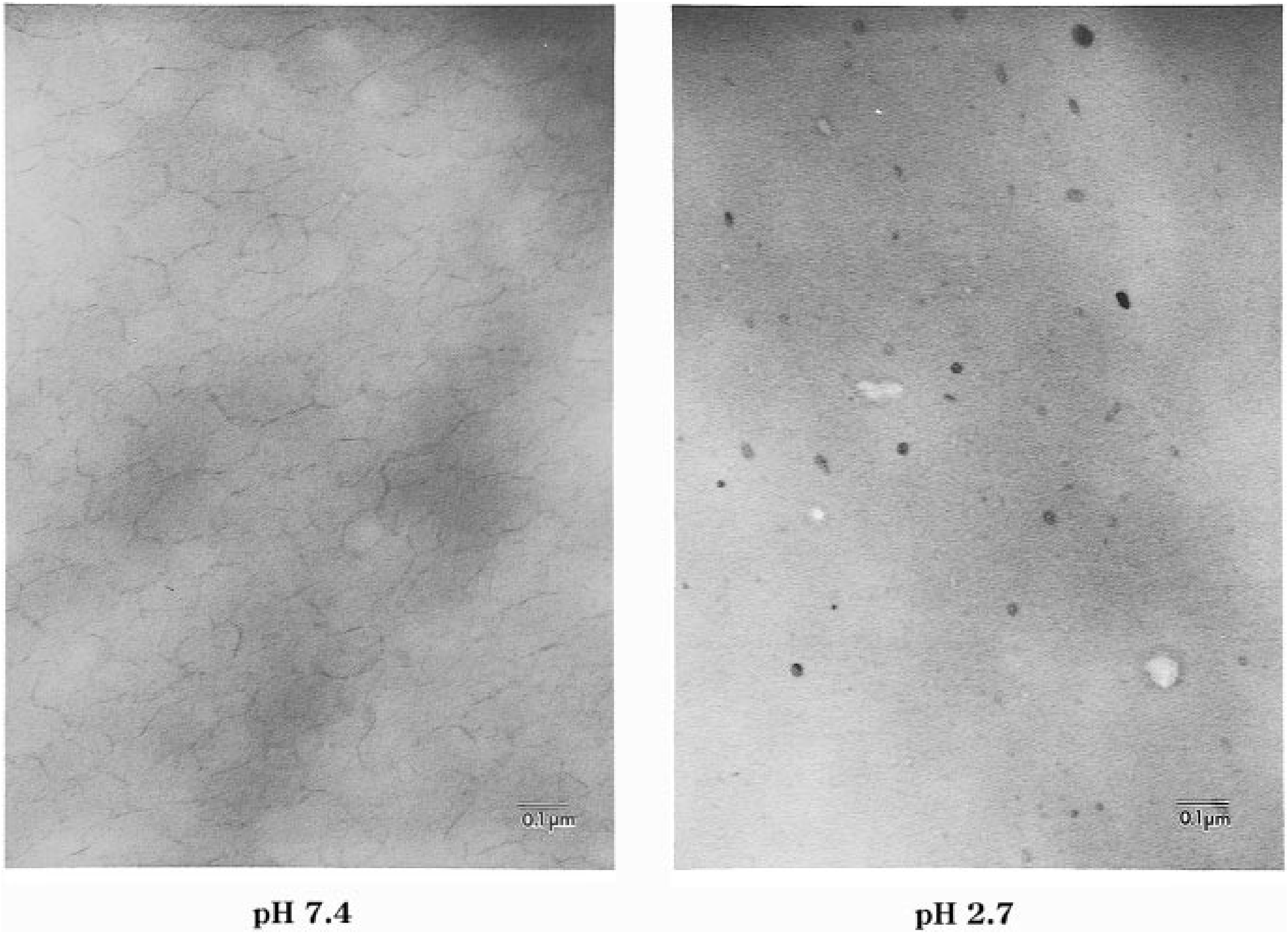
to remove unreacted monomers and subsequently neutralized to the desired pH with base as noted below.

Sample Preparation. In order to study the effect of postformulated pH on the morphology and the viscoelastic properties of the latex films, the pH of the latexes was carefully measured using a pH meter and adjusted to the desired value using the neutralant being studied. This was usually a 10% NaOH solution unless otherwise noted. Latexes with lower pH values were obtained by first treating the latexes with DOWEX MR-3-C, a mixed bed ion exchange resin from The Dow Chemical Co., followed by addition of base to reach the desired pH.

The latex films were prepared as follows. Three-inch diameter Teflon O-rings were taped onto a flat Teflon surface. The temperature of the Teflon surface was maintained between 35 and 40 °C. Sufficient latexes were poured into the area defined by the O-ring. Care was taken to exclude air bubbles. When the samples were dried, they were removed from the Teflon surface. The samples were dried further in a forced-air oven at 80 °C until completely dry. Samples of 1−2 mm thickness were obtained.

Dynamic Mechanical Spectroscopy. The viscoelastic properties of latex films were determined using the parallel plate geometry on a Rheometrics RDS-II dynamic mechanical spectrometer. The sample was carefully placed at the center of the lower 7.9 mm plate. The upper plate was then lowered so that it was in contact with the sample. The temperature was increased so that the sample would adhere to the plates. It was important to ensure good adhesion between the plates and the sample since any slippage would result in an erroneous modulus measurement. The thickness of the sample was then determined. The moduli of the latex films were determined in the linear viscoelastic regime as a function of temperature, starting at a temperature lower than the T_g of the film to approximately 150 °C, at a frequency of 0.16 Hz.

Transmission Electron Microscopy. The morphology of the latex films was examined without heavy metal staining



pH 7.4 pH 2.7

Figure 7. Transmission electron micrograph of carboxylated styrene/butadiene latex film: latex D containing 1.75 parts BOM fumaric acid. Effect of pH on morphology.

using transmission electron microscopy. Thin sections (approximately 80 nm in thickness) were produced by cryoultramicrotomy at a temperature of approximately −120 °C, collected on unsupported 600 mesh copper grids, and examined in a JEOL 2000FX TEM operating at 200 kV accelerating voltage. Elemental analysis was performed using a Link Analytical ultrathin windowed energy dispersive X-ray spectrometer (EDS).

Results and Discussion

The viscoelastic properties and morphology of emulsion polymers, such as carboxylated S/B latexes, and the resultant films are affected by many parameters of the emulsion polymerization process. Indeed, Bassett and Hoy have suggested that emulsion polymers can be called “products by process”.[4] They studied the location of carboxylic acid on the latex particles using conductometric titration. They concluded from their experiments that the carboxylic acid is concentrated in a hydrated shell surrounding a compact polymer core in the carboxylated latex particle. A two-phase morphology in the films of carboxylated latexes consisting of polymer cores surrounded by carboxylic acid-rich shells can be expected, provided that the interdiffusion of polymer chains is restricted to the interfacial acid-rich region and do not occur to an extent that would result in a homogeneous one-phase morphology. Indeed, Distler and Kanig[7] presented electron micrographs of acrylate latexes with a two-phase honeycomb-like morphology. Two-phase morphology was also observed in poly(vinyl acetate) latexes when poly(vinyl alcohol) was present.[25,34,35] However, Zosel and co-workers[9] also showed electron micrographs of butyl acrylate/methacrylic acid copolymer latex films where the honeycomb-like structure was not observed. Richard and coworker[3,10] were the first to publish studies of the viscoelastic properties of carboxylated S/B latexes. The roles of pH and neutralizing ion on the viscoelastic properties of the latex films were also reported.

Dynamic Mechanical Spectroscopy of Carboxylated S/B Latex. The viscoelastic properties of a series of carboxylated S/B latexes were studied using dynamic mechanical spectroscopy. Zosel[2] and Richard[10] found that Williams−Landel−Ferry (WLF) time temperature superposition theory[39] is applicable to the acrylic latexes and carboxylated S/B latexes in their studies. It was found that the carboxylated S/B latexes studied here also follow the WLF theory. In this paper, only the isochronal temperature dependence viscoelastic properties at a frequency of 0.16 Hz will be presented. Information on the viscoelastic properties at other frequencies can readily be determined using the WLF theory.

Figure 1 shows the dynamic mechanical spectrum (DMS) of latex A, a carboxylated S/B latex film of a latex containing 10 parts, based on total monomer (BOM), of acrylic acid. The pH of the wet latex was adjusted to a value of 6.3 with NaOH. The tan δ_{max} occurred at 30°C. The tan δ_{max} is qualitatively indicative of the glass transition of the polymer. There is a shoulder on the tan δ curve on the high temperature side. When the pH of the latex was adjusted to a value of 9.3, the tan δ curve of the latex film showed two peaks at 30 and 70 °C. Since polyacrylic acid and polysodium acrylate have reported T_g values of 104 and 230 °C,[36] respectively, it is reasonable to expect a shift of the tan δ peak to higher temperature as Na$^+$ concentration increases if the tan δ peak is associated with acrylic acid present in the latex. The fact that the lower temperature tan δ peak remained constant at 30 °C suggests that the polymer associated with this tan δ peak contains little or no acrylic acid and is, therefore, predominately styrene/butadiene copolymer. An alternative explanation might be that the Na$^+$ ions were not given sufficient time to diffuse into the bulk of the latex particles to neutralize the acrylic acid present. However, this is not likely to be the case. Figure 2 shows the effect of adjusting the pH with NaOH on the storage modulus (G') of the films of latex A. The storage modulus of the film prepared with latex at a pH value of 9.3 is higher than that prepared from latex with a pH value of 6.3. This is in accord with the observation reported by Richard and Maquet.[10] This is in contrast with the viscoelastic behavior of a noncarboxylated S/B latex, latex B. Figure 3 shows that changing the pH of the latex from 6.1 to 11.6 with NaOH resulted in essentially no effect on the storage modulus of the latex films.

The effect of adjusting the pH of the latex with NaOH on the viscoelastic properties of latex films can be depicted by plotting the rubbery plateau modulus of the latex film as a function of pH. Figures 4 and 5 show the effect of pH of latex on the storage modulus of latex films of latex C, which contains 3 parts BOM itaconic acid, and latex D, which contains 1.75 parts BOM fumaric acid. Figure 6 plots G' at a temperature 50 °C above the tan $\delta_{\max}$, $T_{\tan\delta_{\max}+50°\mathrm{C}}$, in the rubbery plateau region, as a function of the pH of the latexes. It can be seen that for latex C, G' at $T_{\tan\delta_{\max}+50°\mathrm{C}}$ increased slowly when the pH was increased to 7. At pH higher than 7, G', at $T_{\tan\delta_{\max}+50°\mathrm{C}}$ increased rapidly with changes in pH. Similar behavior was also observed with latex D. The storage modulus, G', at $T_{\tan\delta_{\max}+50°\mathrm{C}}$ increased slightly as a function of pH below 5. A sharp increase in G' at $T_{\tan\delta_{\max}+50°\mathrm{C}}$ was observed when the pH was increased from 5 to 7. Figure 6 also shows G' dependence on the pH of latex E, a latex containing 4 parts BOM acrylic acid. The increase in G' at $T_{\tan\delta_{\max}+50°\mathrm{C}}$ as the pH increased for latex E is not as sharp as with latexes C and D. The difference in pH dependence can be explained by the difference in the apparent dissociation constant, pK_{app}, of different carboxylic acids in the latexes. In order to reach the same degree of neutralization, 50% for instance, the pH has to be at $\sim$7.5, 5.5, and 4.5 for latexes containing acrylic acid, itaconic acid, and fumaric acid, respectively.[37] Therefore, it is reasonable to expect that the pH at which G' in the rubbery plateau region undergoes rapid increase will be related to the dissociation constant of the copolymeric carboxylic acids in the latexes.

Transmission Electron Microscopy of Latex Films. Figure 7 shows the transmission electron micrographs of latex films prepared using latex D (with fumaric acid) at pH values of 2.7 and 7.4. The honeycomb-like morphology can clearly be seen in the electron micrograph of the latex film cast at a pH value of 7.4. The honeycomb-like structure is not apparent in the latex film cast at a pH value of 2.7. Instead, some electron-dense domains were seen. The chemical nature of the electron-dense areas in the honeycomb-like region of the latex film at high pH and the domain-like region of the latex film at low pH were determined using electron dispersive spectroscopy. The spectra are shown

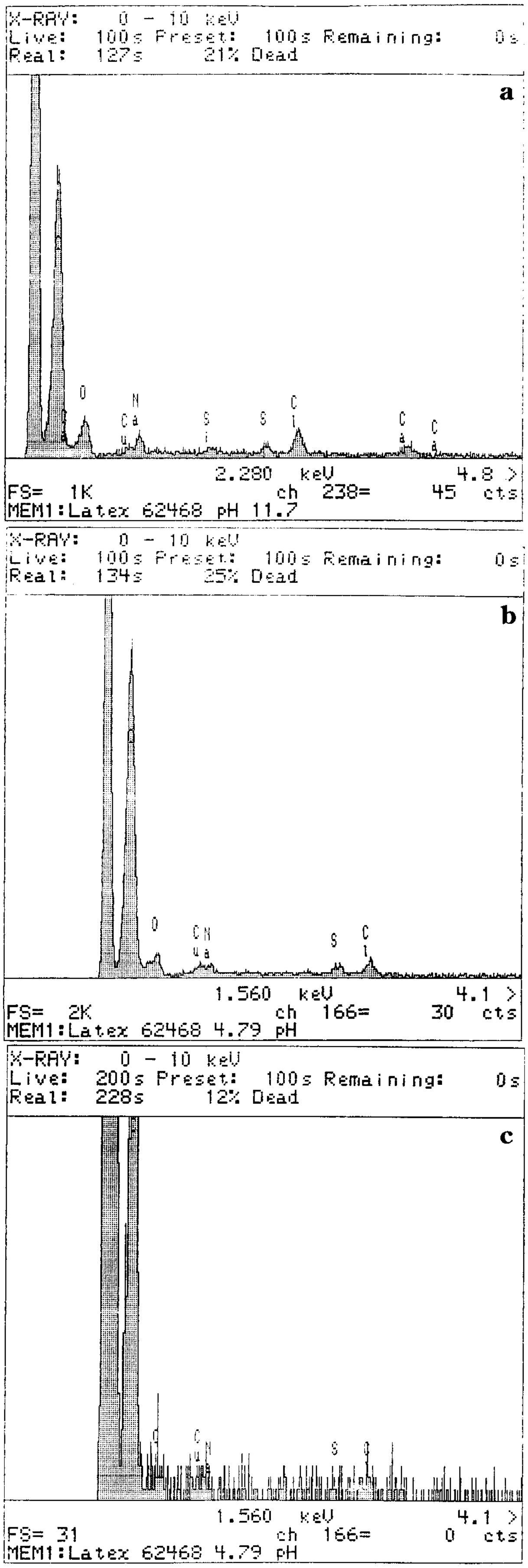


Figure 8. Electron dispersive spectra of carboxylated styrene/butadiene latex: electron-dense area of latex film cast at (a) high pH and (b) low pH and (c) an area away from electron-dense area of latex film cast at low pH.

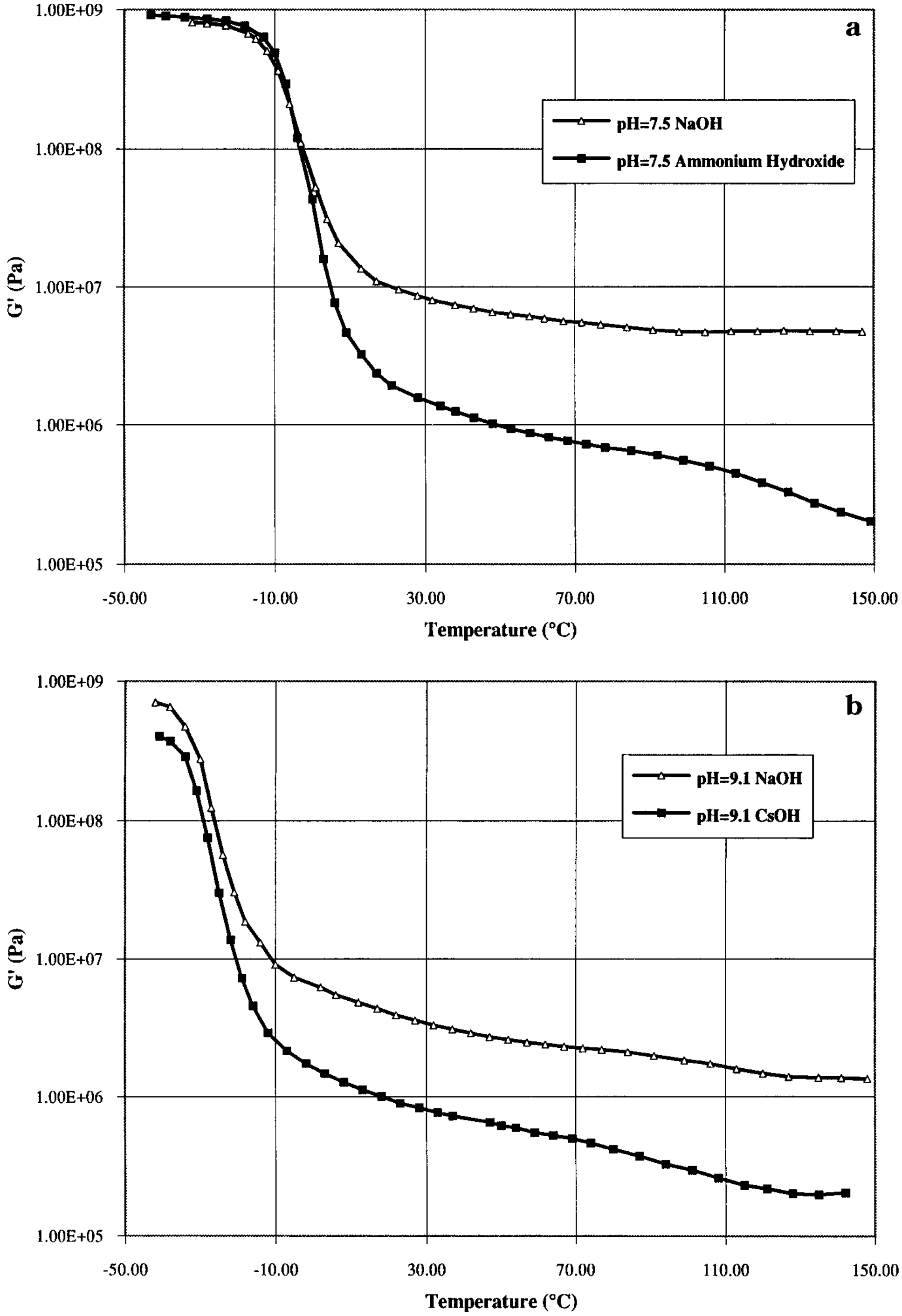


Figure 9. Dynamic mechanical spectrum of carboxylated styrene/butadiene latex film to study the effect of cation on G': (a) latex D containing 1.75 parts BOM fumaric acid, Na^+ vs NH_4^+, (b) latex C containing 3 parts BOM itaconic acid, Na^+ vs Cs^+.

as Figure 8. It can be seen that the chemical nature of the two electron-dense areas are similar. The origin of carbon, oxygen, sodium, and sulfur are probably from the acid-rich sodium hydroxide-neutralized interfacial polymers. Sodium persulfate used as initiator and sodium dodecyl diphenyloxide disulfonate, the surfactant used in this latex, could also contribute toward the sodium and sulfur detected. The chemical nature of an area off the electron-dense region of the latex film cast at low pH was also obtained. The spectrum is also shown in Figure 8. No significant amount of elements other than carbon was detected. This indicates that the areas off the electron-dense region are due to polymer consisting mainly of hydrocarbons, such as styrene and butadiene.

Effect of Ionomeric Characteristics of Latex Polymers on Film Morphology and Viscoelastic Properties. The change in latex film morphology as a function of pH supports the observed change in the viscoelastic behavior. The increase in the storage modulus is both a result of increased ionomeric character of the latex film and a change of film morphology from domain-like to honeycomb-like structure. Dickie[38] calculated the expected moduli of two-phase polymer systems. His results indicated that, at the same phase composition, there is an increase in modulus in the rubbery plateau region when the higher T_g polymer becomes the continuous phase. Therefore, it is possible that, with latex D (with fumaric acid), the polymer chains at low values of pH are sufficiently mobile that a phase morphology change from the honeycomb-like structure to the more thermodynamically favorable domain-like structure occurred during the film formation process. When the latexes are neutralized with NaOH to higher pH values, the T_g of the acid-rich interfacial polymer increases, thus decreasing the mobility of the polymer chains. This decrease in mobility of the polymer chains retards the formation of the preferred domain-like morphology within the time scale of the present experiments. Furthermore, neutralization probably increases the polarity difference between the interfacial and the bulk polymer and decreases miscibility, causing more discrete definition of the interfacial domains.

Since the honeycomb-like structure is hypothesized to be morphologically metastable, it is possible that the morphology of the film would change as a function of time, eventually to the domain-like structure. It was found that no morphological change occurred after the films were conditioned at 80 °C for 24 h. It is therefore reasonable to regard, for all practical purposes, that the phase morphology of the film and the associated viscoelastic properties will remain constant for most latex end-use applications.

Effect of Cation on the Viscoelastic Properties of Carboxylated Latexes. Navratil and Eisenberg[40] have discussed the effect of the nature of the counterion on the stability of the ion multiplets and the viscoelastic properties of the styrene/methacrylic acid ionomers. They theorized that the size of the ion would have some effect on the stability of the ion multiplets. They found Cs^+ ion formed less stable cross-links than Na^+ ion, as shown by the lowering of the rubbery plateau modulus. The effect of different counterions on the viscoelastic behavior of carboxylated S/B latexes was studied. The latexes used in these experiments were first ion exchanged to remove the counterions. The pH of the ion-exchanged latexes was in the range of 2−3. Figure 9a compares the storage modulus of latex D at pH 7.5 neutralized with Na^+ or NH_4^+ ions. It can be seen that the storage modulus of the NH_4^+-neutralized latex was lower than the Na^+-neutralized latex. Similar results were obtained when comparing the storage modulus of Na^+- and Cs^+-neutralized latex C at pH 9.04. The Cs^+-neutralized sample exhibited a lower rubbery plateau modulus than the Na^+-neutralized sample, as seen in Figure 9b. The effect of Li^+ on the storage modulus of latex C in the pH range from 2.38 to 9.07 has also been examined (Figure 10). The effect of Li^+ on the storage modulus of latex C is similar to that of the Na^+ ion. A slight increase in the storage modulus was observed in the pH range from 2 to 7. The modulus increased at a much faster rate as a function of pH at pH values above 7. It is perhaps surprising to find that the rubbery plateau modulus of Li^+-neutralized samples was lower than that of the Na^+-neutralized samples at the same pH value since the size of the Li^+ ion is expected to be smaller than the Na^+ ion. However, it has been noted that the size of hydrated Li^+ is larger than hydrated Na^+ ion.[41] The latex samples were dried under mild conditions. It is likely that not all the water of hydration has been eliminated.

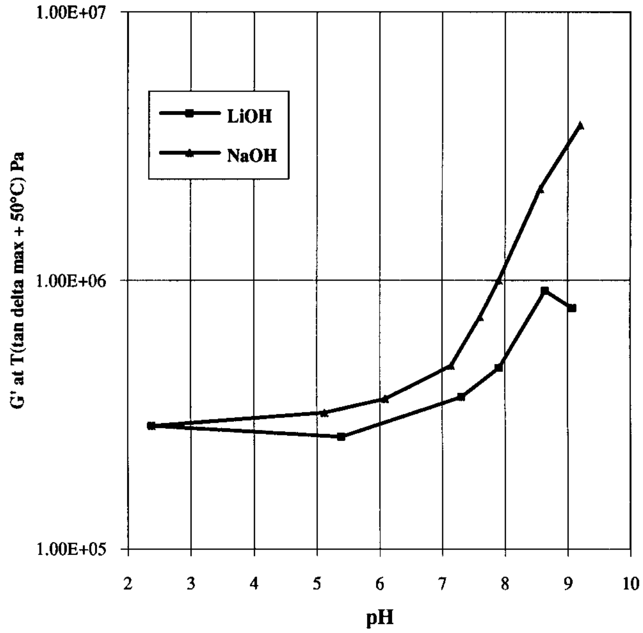
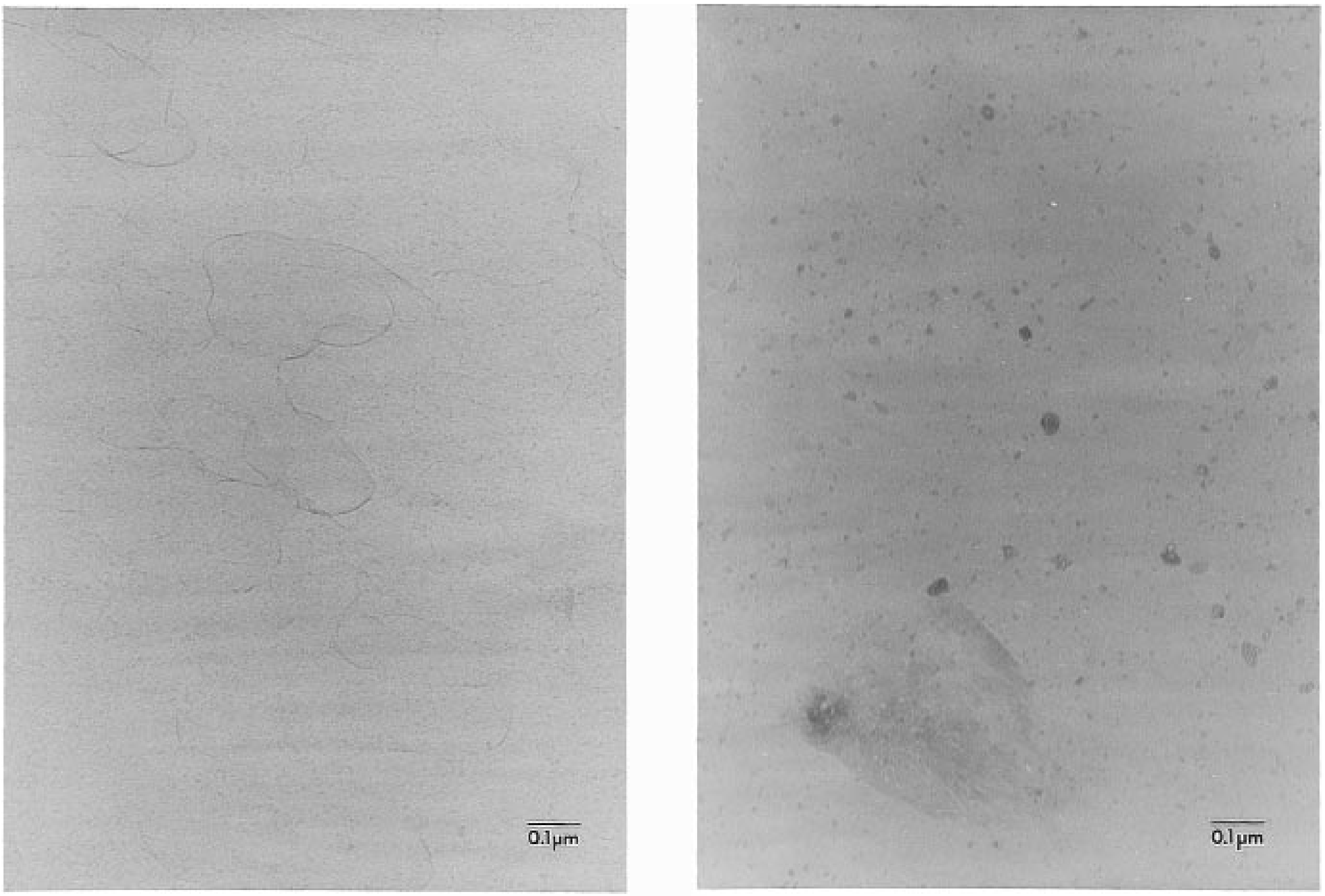


Figure 10. Plot of $G'(T_{\tan\delta_{\max}+50°C})$ vs pH. Effect of cation, Li^+ vs Na^+.

Effect of the Amount of Chain Transfer Agent on the Morphology of Carboxylated Latex Film. The molecular weight and the molecular weight between cross-links of latexes can be controlled by the amount of chain transfer agent added. The molecular weight and the molecular weight between cross-links will affect the mobility of the polymer chains. The effect of chain transfer agent on the latex film morphology and viscoelastic properties as a function of pH was studied by comparing the behavior of latexes D and F prepared with 0.38 part and 1 part *tert*-dodecylmercaptan (tDDM) as chain transfer agent, respectively. The morphologies of films of latex F cast from latex having pH values of 2.8 and 9.7 were examined using TEM (Figure 11). The domain-like morphology was observed in the film cast from latex at pH 2.8. This morphology is similar to that observed with the film cast from latex D at pH 2.7 (Figure 7). Irregular thread-like discontinuous electron dense areas were observed in the film of latex F cast at a latex pH value of 9.7. This is to be compared with the regular honeycomb-like structure observed in the film cast from latex D at pH 7.4 (Figure 7). Figure 12 compares the effect of pH on the rubbery plateau modulus, G', of the latex films at $T_{\tan\delta_{\max}+50°C}$. The effect of increasing pH on the rubbery plateau modulus of latex F, the latex made with 1 part tDDM, is relatively small in the pH range from 2 to 10. This is in contrast to the behavior of films cast with latex D. In the pH range from 2 to 5, the rate of modulus increase with pH is similar to that of latex F. A sharp increase in modulus was observed when the latex pH was increased from 5 to 7.4. The sharp increase is attributed to the change of morphology, as discussed before. The change in morphology of the cast film of latex F as a function of the latex pH was not as distinct as in the case of latex D. The irregular string-like structure observed in the latex film of latex F at high pH as shown in the TEM did not appear to be the continuous phase in the film, hence, resulting in little modulus increase.

Degradation of Honeycomb-like Structure. It is proposed that the honeycomb-like structure is present in some latex films because there is insufficient mobility or thermodynamic driving force to permit the rearrangement to domain-like structure during the time scale of the experiment. Therefore, if the mobility of the acid-rich interfacial polymer is increased, the rearrangement of the honeycomb structure to domain-like structure will be facilitated. For example, mobility of



pH 9.7

pH 2.8

Figure 11. Transmission electron micrograph of carboxylated styrene/butadiene latex film: latex F containing 1.75 parts BOM fumaric acid.

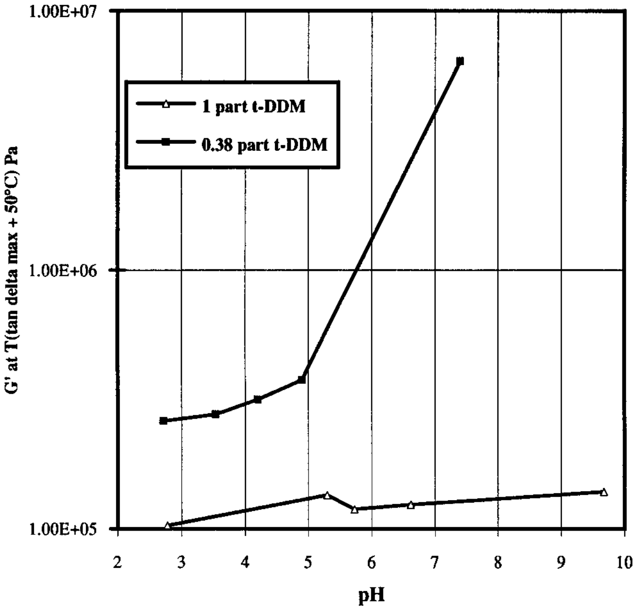
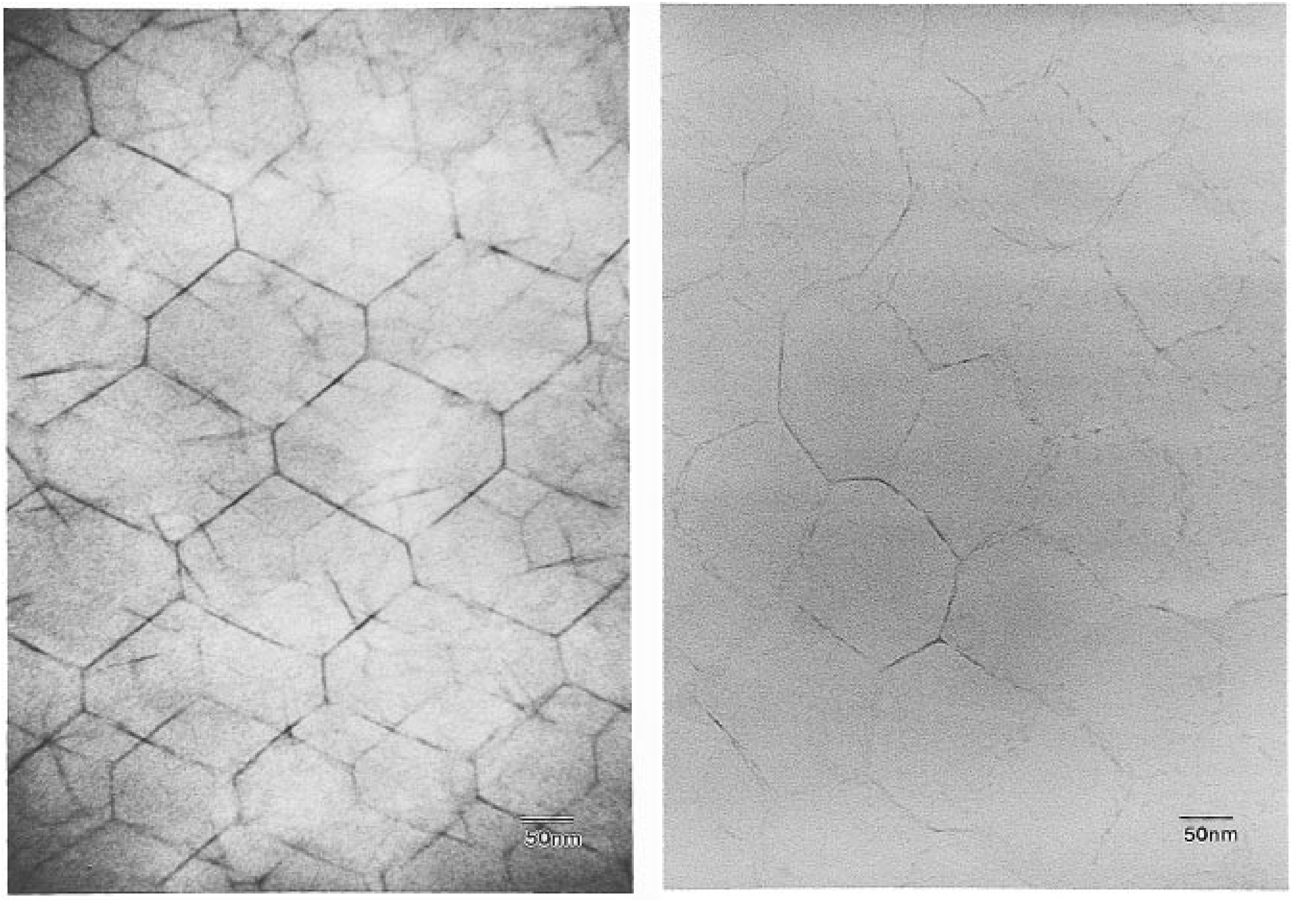


Figure 12. Plot of $G'(T_{\tan\delta_{\max}+50°C})$ vs pH. Effect of the amount of chain transfer agent.

polymer chains can be increased by incorporation of a higher amount of chain transfer agent, as already discussed.

The effect of increased polymer chain mobility on the morphology of a latex film can be demonstrated in another way. In an experiment, latex films prepared from a latex containing 3 parts fumaric acid BOM, latex G, at pH values of 4.9 and 8.5 were soaked in water at 80°C for 48 h. The hydrophilic acid-rich interfacial polymer should be plasticized by water and the mobility of the polymer chain increased. The latex films were then dried. The morphology of the latex films and dynamic mechanical properties were determined and compared with the films without soaking. Figure 13 shows the TEM of latex film cast with latex G at pH 8.5 before and after soaking in water. Deformation of the honeycomb-like structure occurred when the latex film was soaked in water. There are indications that disruption of the continuous nature of the interfacial polymer had started, rearranging to a domain-like structure. Figure 14 shows the dynamic mechanical spectra of the latex films cast with latex G at pH 8.5 with and without water soaking. A modulus decrease of 2 orders of magnitude in the rubbery plateau region was observed after the latex film was soaked in water. This large decrease in modulus can be explained in part by the disruption of the high-T_g acid-rich interfacial polymer continuous phase, as indicated by the TEM.

A decrease in Na^+ in the acid-rich interfacial polymer will result in a decrease of the T_g of the interfacial polymer, contributing to the decrease of the rubbery plateau modulus. This is shown by the behavior of the latex film cast with latex G at pH 4.9 to be less significant. Little modulus difference in the rubbery plateau region was observed with the latex films at pH 4.9 with and without water soaking. Since the acid-rich interfacial polymer in the latex film at pH 4.9 before



no water soak water soak

Figure 13. Transmission electron micrograph of carboxylated styrene/butadiene latex film: latex G containing 3 parts BOM fumaric acid at pH 8.5. Effect of water soak.

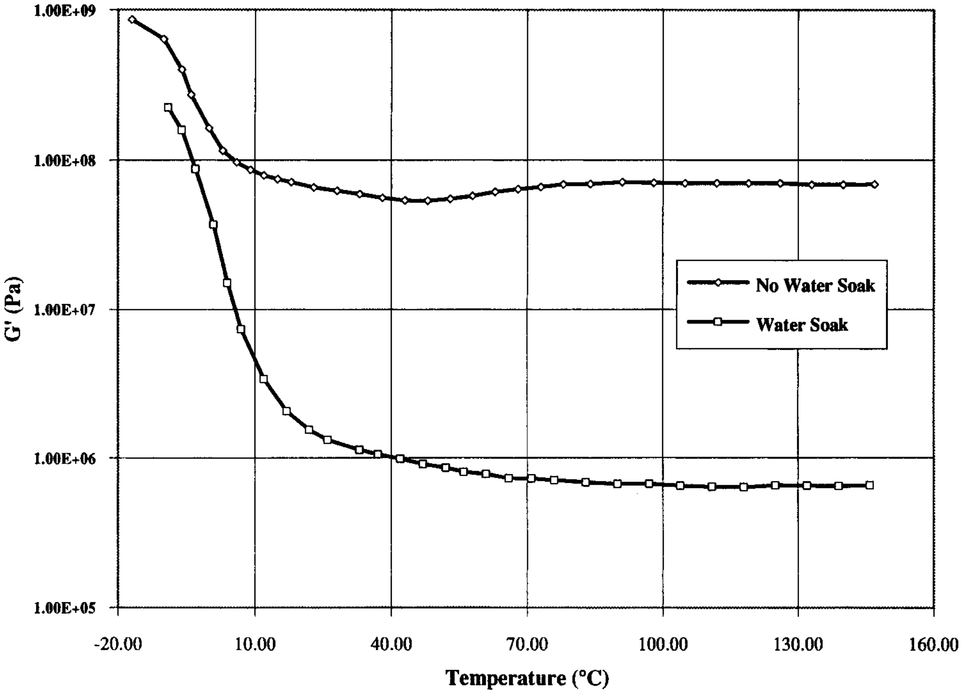
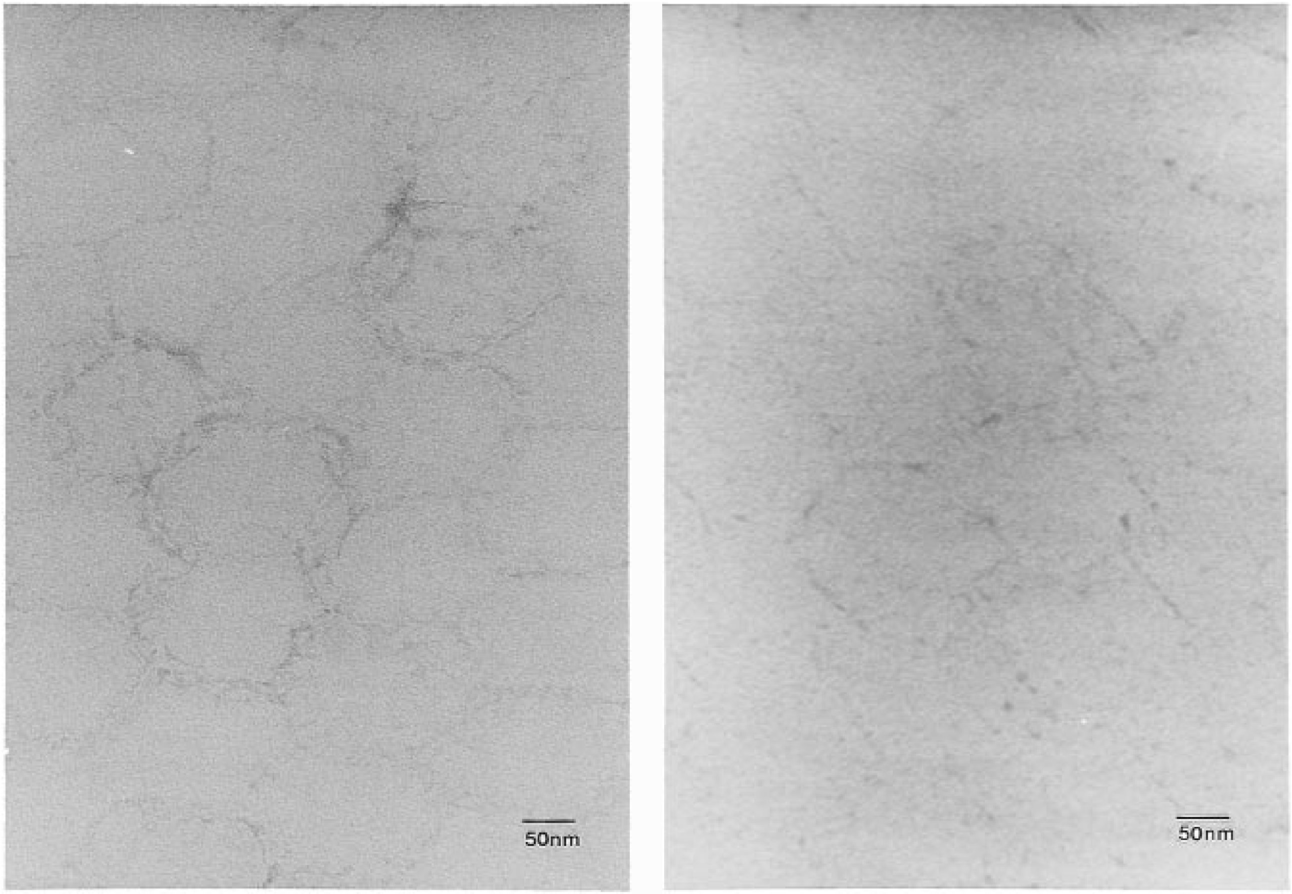


Figure 14. Dynamic mechanical spectrum of carboxylated styrene/butadiene latex film: latex G containing 3 parts BOM fumaric acid at pH 8.5. Effect of water soak.

water soaking was already in the transition stage between honeycomb-like and domain-like structures, no significant change in morphology was observed when the latex film was soaked in water (Figure 15). The slight decrease in the rubbery plateau modulus can be explained by either the slight difference in the morphology or the ionomeric nature of the interfacial polymer (Figure 16).



no water soak water soak

Figure 15. Transmission electron micrograph of carboxylated styrene/butadiene latex film: latex G containing 3 parts BOM fumaric acid at pH 4.9. Effect of water soak.

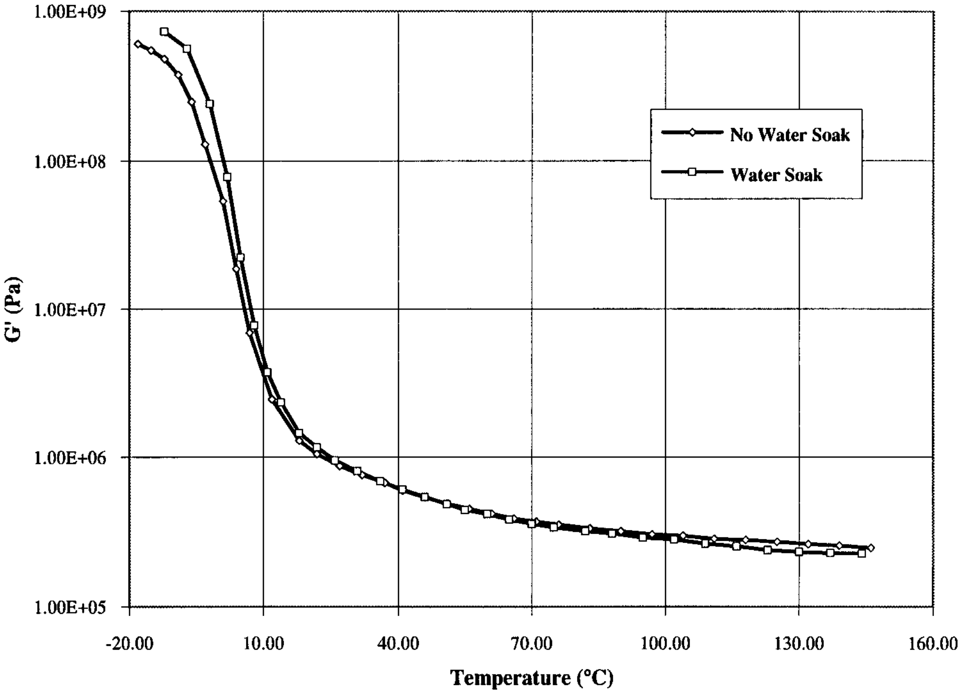


Figure 16. Dynamic mechanical spectrum of carboxylated styrene/butadiene latex film: latex G containing 3 parts BOM fumaric acid at pH 4.9. Effect of water soak.

Conclusions

The viscoelastic properties of carboxylated S/B latex films are affected by the ionomeric characteristics of the interfacial polymer. The rubbery plateau moduli increase when the pH of the latexes is adjusted to a higher value with monovalent metal bases. This behavior is distinct from the effect of divalent metal ions, such as Zn^{2+}, in which case ionic cross-linking is possible. Both the T_g of the acid-rich interfacial polymer and the morphology of the latex film are dependent on the ionomeric character of the interfacial polymer. The ionomeric character of the acid-rich interfacial polymer affects the T_g of the polymer and, concomitantly, the mobility of the polymer chains. The difference in the mobility of the polymer chains results in different morphologies. In the case where the interfacial polymer has restricted mobility either due to T_g or high molecular weight, a two-phase morphology with the interfacial polymer in a honeycomb-like structure is observed. Since the high-T_g interfacial polymer is the continuous phase, the viscoelastic properties of the interfacial polymer contribute significantly to the viscoleastic properties of the latex film, resulting in a film with high G' in the rubbery plateau region.

When the mobility of the interfacial polymer is increased, either by lowering the T_g or decreasing the molecular weight of the polymer, the interfacial polymer eventually attains a domain-like structure. In that case, viscoelastic properties of the latex film reflect predominately that of the continuous S/B phase. The effect of the interfacial polymer then resembles that of a filler. The ionomeric character of the interfacial polymer has less of an effect on the modulus of the latex film.

Supporting Information Available: The dynamic mechanical spectra presented in Figures 1, 2, 3, 4, 5, 9a,b, 14, and 16 are available in numerical form (10 pages). Ordering information is given on any current masthead page.

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