

Synthesis and Characterization of Core/Shell Ionomeric Latexes. I. Latex and Film Properties

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SYNOPSIS

This research work involved studies on the synthesis and characterization of core/shell ionomeric latexes in order to understand the process of ionic aggregate formation. The core/shell structure of the ionomeric latexes prepared in this study confines the ionic domains to the copolymeric matrix within the shell polymer, and in addition, benefits from the ionomeric properties and core/shell structure simultaneously. Core/shell ionomeric latexes with polystyrene cores and styrene/*n*-butyl acrylate/methacrylic acid terpolymer shells were synthesized by a semicontinuous seeded emulsion copolymerization process. The distribution of the methacrylic acid in the core/shell latexes was determined using conductometric titration techniques. The results of the conductometric titration analysis indicate that the principal locus of the carboxyl groups in the core/shell latexes is at the particle surface, but specific information about the differences in the distribution of methacrylic acid inside the latex particles could not be obtained. Mechanical characterization of the core/shell ionomeric latex films was carried out to understand the structure–property relationships using Dynamic Mechanical Analysis (DMA) and tensile testing. It was discovered that the core/shell latexes exhibited significantly different properties, owing to the differences in the overall carboxyl content and surface loading. Extensive studies were carried out to study the effect of water plasticization on the mechanical behavior of the core/shell ionomeric latex films; water adsorption causes the solvation of ionic aggregates. A preliminary investigation of the effect of the type of counterion used for the neutralization of carboxyl groups on the properties of core/shell ionomeric latex films was also carried out.

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INTRODUCTION

Copolymers containing hydrophobic backbone chains and a small number of ionic groups attached on the backbones, side chains, or on the backbone terminals are termed ionomers. Upon the introduction of an ionic comonomer into the base polymer, profound changes are observed relative to the non-ionic parent polymer. Ionomers exhibit unique solid-state and solution properties that include a dramatic increase in modulus,¹ adhesive strength,² tear and abrasion resistance,³ melt viscosity,⁴ and impact

strength.⁵ Much research has been directed towards understanding the microstructure of ionomers in order to comprehend their physical properties. Although the concept of a so-called “ionic crosslink” has been recognized for over 40 years,⁶ the exact spatial arrangement of ions and attached chain segments within the domain structure of ionomers is still not understood. Many models have been put forth to describe the morphology of ionomers,^{7–9} but, unfortunately, they are often system specific because the placement of the ions along the polymer chain can profoundly affect the nature of the ionic aggregates.

Evidence for ionic aggregation is plentiful. The increase in the glass transition temperature of ionomers with ion content may be directly related to the presence of aggregates, which are expected to

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diminish the mobility of the segments in a manner similar to that of covalent crosslinks. The very large increase in melt viscosity of ionomers with increasing ion content may be attributed to the ionic interactions between the chains that persist even at temperatures far above the glass transition temperatures of these systems.¹⁰ Dynamic mechanical measurements also display features that may be attributed to the presence of aggregates. The loss tangent curves usually show an additional peak at a temperature above the glass transition temperature of the system that has been associated with a transition of the ion-rich phase.¹¹ Several other techniques such as x-ray diffraction,¹² infrared spectroscopy,¹³ electron microscopy,¹⁴ and small-angle x-ray scattering⁵ have been used to provide evidence for the existence of local structure.

Despite the considerable industrial and academic effort that has been expended on the study of ionomers, there is still a lack of general agreement about their structure. In particular, the central question concerning the distribution of the salt groups in the bulk polymer has not been definitely answered. In most ionomers, the ionic groups are spaced randomly along a high molecular weight polymer chain. In contrast, there has recently been a strong interest in synthesizing ionomers with ionic groups at specified locations on the polymer backbone. Some recent investigations include telechelic polyisoprene ionomers containing ionic groups only at the ends by Broze et al,¹⁵ and three-arm star sulfonated polyisobutylenes prepared by Bagordia et al.¹⁶ The idea behind synthesizing specially tailored ionomers is that in ionomers, wherein the ionic sites are randomly distributed along the polymer backbone, a large fraction of the ionic groups may remain dispersed in the matrix due to topological constraints imposed by the polymer chain. However, well defined placement of ionic groups in specifically tailored ionomers should allow for greater phase separation.

Carboxyl-containing functional monomers, e.g., acrylic or methacrylic acid, are usually incorporated into emulsion polymerization recipes to enhance the colloidal stability of the latex particles. Some carboxylated latexes are used as rheological modifiers because of their alkali swellability at high pH. Another function of the carboxyl groups is to provide sites for crosslinking by further reaction with other species in the latex. The carboxylic functionality incorporated into a latex system offers still other possibilities for film curing through the formation of ionic aggregate formation in a manner analogous to that of conventional ionomers because of the heterogeneous distribution of ionic functional groups

in the latex particles. It is the intention of this article to describe the synthesis and characterization of these ionomeric core/shell latexes where ionic aggregation may occur in the interphase region between neutralized carboxyl groups present in the shell copolymers between adjacent latex particles resulting from the latex film formation process (see Fig. 1).

EXPERIMENTAL

Materials

All monomers used were distilled under vacuum. Styrene (Aldrich Chemical Company, Inc.) and *n*-butyl acrylate (Aldrich Chemical Company, Inc.)

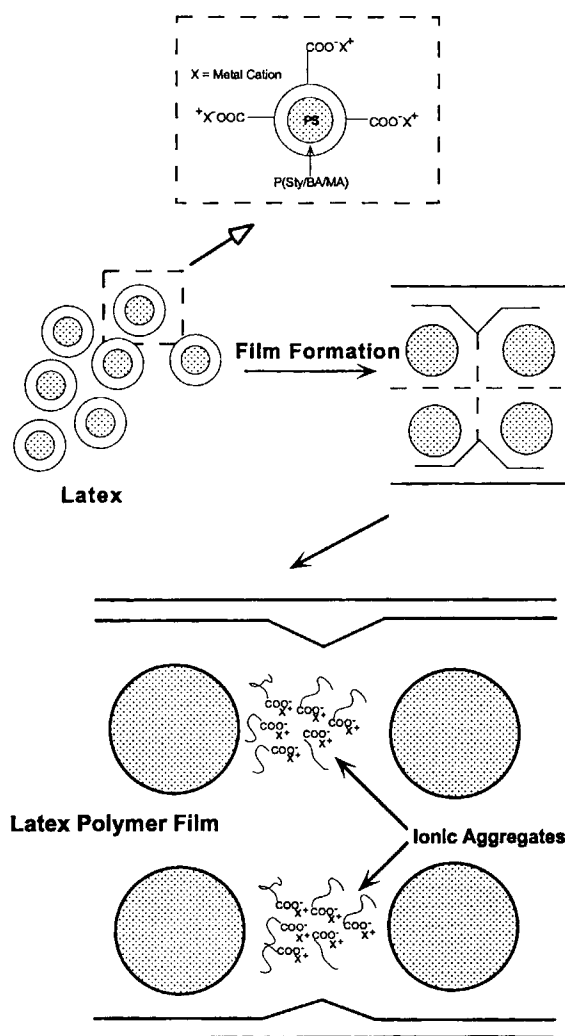


Figure 1 Schematic representation of the proposed film formation mechanism from the core/shell ionomeric latexes.

were washed with 10% aqueous sodium hydroxide solution to remove the inhibitor, washed with distilled-deionized (DDI) water several times to remove the residual base, dried with anhydrous sodium sulfate, and then distilled under vacuum (12 mmHg at 40°C for *n*-butyl acrylate, 50 mmHg at 70°C for styrene). Methacrylic acid was dried with anhydrous sodium sulfate and then distilled under vacuum (8 mmHg at 55°C).

Distilled-deionized water was degassed before use by boiling for 20–30 min and then cooled under nitrogen gas. Aerosol MA 80 anionic surfactant (dihexyl ester of sodium sulfosuccinic acid; Cytec Industries), Igepal CO-880 nonionic surfactant (nonylphenoxy poly(ethyleneoxy)glycol; GAF Corp.), potassium persulfate initiator ($K_2S_2O_8$; Fisher Scientific), and sodium bicarbonate buffer ($NaHCO_3$; Fisher Scientific) were used as received without any further purification. A monodisperse polystyrene latex with a particle diameter of 190 nm (LS1102A; Dow Chemical) was used as seed. The seed latex was used without further cleaning.

Emulsion Polymerization

Seeded emulsion copolymerization was carried out in a 500 mL glass reactor, equipped with a reflux condenser, a stirrer, and a thermometer. A typical recipe used to prepare these core/shell latexes is shown in Table I. The reactor was maintained at 70°C in a thermostated water bath and the polymerization was carried out under an inert nitrogen atmosphere. Seed latex, DDI water and anionic emulsifier (Aerosol MA) were introduced into the reactor and were allowed to equilibrate for 10 min, followed by the addition of the initiator and buffer. The comonomer mixture and the aqueous solution of nonionic surfactant Igepal CO-880 (0.0352 g/mL) were added over a 9-h period using separate syringes, both at the same feed rate of 0.04 mL/min. The system was allowed to react for an additional 3-h period to achieve high conversion once the addition of comonomer and Igepal surfactant was complete. The amount of methacrylic acid and styrene added in the second stage monomer mixture was varied to determine the optimal amount of carboxylic monomer required to achieve ionomeric properties while the *n*-butyl acrylate was held constant. Two core/shell latexes with compositions of 29/56/15 (wt) of styrene (Sty)/*n*-butyl acrylate (*n*-BA)/methacrylic acid (MAA) or 14/56/30 Sty/*n*-BA/MAA were synthesized and characterized in this study.

Table I Recipe for the Seeded Emulsion Copolymerization of 14/56/30 (Wt) Styrene/*n*-Butyl Acrylate/Methacrylic Acid

Ingredient	Amount (g)
Distilled-deionized water	160.00
Aerosol MA 80 ^a	0.083
Potassium persulfate initiator	0.08
Sodium bicarbonate buffer	0.08
Igepal CO-880 ^b	0.92
Polystyrene Seed Latex (30% solids)	20.0
<i>n</i> -Butyl Acrylate	11.2
Styrene	5.8
Methacrylic Acid	3.0

^a Aerosol MA 80 is a dihexylester of sodium sulfosuccinic acid (Cytec Industries).

^b Igepal CO-880 is a nonylphenoxy poly(ethyleneoxy)ethanol (GAF Corp.).

Aqueous Phase Polymerization of Methacrylic Acid

Although methacrylic acid is more hydrophobic than acrylic acid and itaconic acid, a significant amount of methacrylic acid may polymerize in the aqueous phase if the reaction is not adequately monomer starved. The complete incorporation of methacrylic acid into the latex particles is a major point of interest. The amount of methacrylic acid in the serum, either as free monomer or polymer, might adversely affect the mechanical properties of the film. The amount of carboxyl groups in the serum was determined using a potentiometric titration technique.

Potentiometric Titrations

A L8-55M Beckman preparative ultracentrifuge was used to separate the serum phase from the latex. Optimum conditions, i.e., 20,000 rpm at 4°C for 2 h, were determined for the centrifugation, so as to yield a clear serum. The serum was decanted, and appropriate amounts of DDI water were added to the sediment to obtain a redispersed latex. This redispersed latex was magnetically stirred over a period of 24 h and the resulting latex was subjected to centrifugation again. This cycle was repeated 3–4 times. The serum collected each time was cation-exchanged with Bio-Rad AG 50W-X4 purified ion exchange resin for 2 h and then potentiometrically titrated with NaOH solution to determine the amount of methacrylic acid. To a known quantity of the serum, 0.002 *N* NaOH solution was added dropwise through a burette and the pH of the serum was recorded after each addition of base. The pH of the solution was plotted as a function of the amount

of NaOH solution added, and the amount of 0.002 *N* NaOH required to neutralize the serum was determined from the inflection point on this curve. In this way, the quantity of carboxyl groups in the serum phase of the core/shell latexes was determined. It was found that no significant amount of methacrylic acid was present in the serum collected during the third and fourth centrifugation cycle, and thereafter, two centrifugation cycles were used as a benchmark to determine the amount of methacrylic acid present in the serum phase. It should be noted that the methacrylic acid that was titrated in the serum represented polymeric acid. Gas chromatography analysis of the latex showed no detectable residual monomeric acid.

The feed rate for the second stage comonomer mixture had to be reduced from an original feed rate of 0.056 mL/min. to 0.04 mL/min, based on potentiometric titration results, in order to minimize the amount of methacrylic acid polymerizing in the aqueous phase. After this modification was carried out, the amount of methacrylic acid polymerizing in the aqueous phase was less than 2–3% of the total methacrylic acid added in each polymerization recipe.

Distribution of Carboxyl Groups by Conductometric Titration

A modified conductometric titration technique was used to characterize the carboxyl group distribution of the core/shell latexes. The modified conductometric titration was developed by Nishida.¹⁷ This technique assumes that the locus of the carboxyl groups in the latex particles is a function of the diffusion of the counterions. By adding an excess of base, the neutralization of the carboxyl groups can be measured as function of time by following the decay in conductance. The initial drop in conductivity can be considered a measure of the quantity of carboxyl groups on the latex particle surface, and the subsequent drop in conductivity can be considered a measure of the carboxyl groups that are buried inside the particle. Ultracentrifugation was used to separate the serum phase from the latexes. The redispersed latex obtained after two ultracentrifugation/redispersion cycles at 20,000 rpm at 4°C for 2 h was used to determine the distribution of carboxyl groups in the core/shell latex particles. The redispersed latex obtained after two centrifugation cycles was cation-exchanged with Bio-Rad AG 50W-X4 resin for 2 h and subjected to conductometric titration. The distribution of carboxyl groups was estimated by adding a large excess of 0.02 *N* sodium

hydroxide solution to 0.5% (wt) of redispersed latex in DDI water and measuring the instantaneous drop in conductivity and the additional drop after a period of 24 h. A calibration curve was prepared to quantitatively relate this initial drop in conductivity to the amount of carboxyl groups on the surface. A mass balance on the total amount of methacrylic acid present in the latex particles or in the serum accounted for 97–98% of the acid charged into the reactor. The missing 2–3% of acid could result from the adsorption of poly(methacrylic acid) onto the ion exchange resin from the surface of the latex particles or from the latex serum during the cleaning process.

Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) was used to obtain morphological evidence for the existence of the core/shell structure. TEM was also used in the earlier stages of the recipe development process to detect any secondary generation of particles. Transmission electron microscopy was performed using a Phillips EM 300 instrument. The core/shell latex was stained with phosphotungstic acid (PTA; negative stain) to protect the polymer particles from deforming under the electron beam and ruthenium tetroxide (RuO₄) to stain the polystyrene-rich regions. Electron microscopy was performed in the frozen state by cooling the sample with liquid nitrogen in a cold-stage attachment to the TEM. Electron microscopy analysis confirmed the formation of an uniform Sty/*n*-BA/MAA terpolymer shell layer around the polystyrene seed latex without the presence of a secondary crop of particles. The final particle size of these composite latexes was approximately 240 nm.

Analysis of Latex Polymer Films

The carboxyl groups present in the core/shell latexes were neutralized with stoichiometric amounts of sodium hydroxide and were then freeze dried into powders. Previous attempts to dry the neutralized latexes at room temperature yielded brittle films because of the high methacrylic acid content and the presence of the glassy polystyrene core. Further attempts to compression mold these air-dried films were unsuccessful, owing to their extremely high melt viscosities. Freeze drying of the neutralized latexes resulted in the formation of powders that could easily be compression molded. These powders were compression molded at 11,000 psi at 120°C for 10 min into flat rectangular bars (6 × 1 × 0.2 cm).

Compression-molded bars were annealed at 90°C for 48 h and stored in a vacuum desiccator until testing to avoid the absorption of water from the atmosphere by the films.

Dynamic Mechanical Analysis

The viscoelastic behavior of the core/shell ionomeric latex films was investigated to determine the effect of ionic crosslinking on the mechanical properties at elevated temperatures. The dynamic mechanical analysis was performed on compression molded and annealed core/shell latex films of rectangular shape ($6 \times 1 \times 0.2$ cm) using a Rheovibron DDV II instrument at a frequency of 110 Hz.

Tensile Properties

Compression molded and annealed samples ($6 \times 1 \times 0.2$ cm) were tested for their tensile properties using an Instron Tensile Testing Machine using a crosshead speed of 0.5 in/min. Special care was taken to keep the samples in a dry state before testing to avoid water absorption and subsequent plasticization of the polymer films.

Effects of Water Plasticization

The core/shell ionomeric latexes fully neutralized with Na^+ were freeze dried and compression molded, as mentioned earlier. After annealing, the compression molded samples were weighed and stored in a sealed glass chamber that contained water in order to maintain an environment with approximately 100% relative humidity, to allow the films to absorb moisture from water vapor present inside of the chamber. After 48 h, the samples were removed and weighed again to determine the amount of water absorbed. The film prepared from the core/shell latex with 29/56/15 Sty/*n*-BA/MAA in the shell incorporated 8.4 wt % water, while the film with 14/56/30 Sty/*n*-BA/MAA in the shell absorbed 16.2 wt % water; both significant amounts of water.

Effect of Counterion Type

The core/shell latex with a shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA was neutralized with stoichiometric amounts of monovalent cations (Na^+ , from sodium hydroxide, or Cs^+ , from cesium hydroxide), or divalent cation (Zn^{2+} , from zinc acetate). The neutralized core/shell latexes were freeze dried, compression molded, and annealed as described earlier.

RESULTS AND DISCUSSION

Distribution of Carboxyl Groups by Conductometric Titration Analysis

Nishida,¹⁷ in his work, had originally assigned four arbitrary locations to the carboxyl groups inside the latex particles; however, in this work, it was observed that the drop in conductivity after 10 min and 1 h of the addition of excess base was very small. This instantaneous drop in conductivity observed after the addition of excess NaOH was assigned to the carboxyl groups present at the latex particle surface. The subsequent drop in conductivity after a period of 24 h was assigned to the carboxyl groups that are buried inside the latex particles. The quantity of carboxyl groups corresponding to these two drops in conductivity was determined by using a calibration curve. The amount of carboxyl groups in the serum phase of the core/shell latexes was determined using the potentiometric titration technique discussed previously. Both of the latexes (with shell compositions of 29/56/15 or 14/56/30 (wt) Sty/*n*-BA/MAA) were found to have a majority of the carboxyl groups located at the latex particle surface (91 and 92% on the surface, respectively), compared to the serum (3 and 2%, respectively) or buried within the particles (6% for either case).

Film Properties of Core/Shell Ionomeric Latexes

Previously it was discussed that the ionic aggregate formation takes place upon neutralization of the carboxyl groups and yields interesting mechanical and thermal properties. The core/shell structure of the latex particles prepared in this study has made it possible to confine the ionic domains to the polymer matrix around the polystyrene cores in the core/shell latex films (Fig. 1). This unique feature makes these core/shell ionomeric films remarkably different from the ionomers synthesized through bulk polymerization. Moreover, the ionomeric latex films benefit from both the core/shell structure and ionomeric properties. These special attributes are expected to impart interesting mechanical properties to the film. Extensive studies involving mechanical characterization were carried out to investigate the structure-property relationships for the core/shell latex films. Experiments were carried out to characterize the effect of methacrylic acid content and distribution, the type of counterion, and the influence of plasticization with water on the mechanical properties of the core/shell latex polymer film.

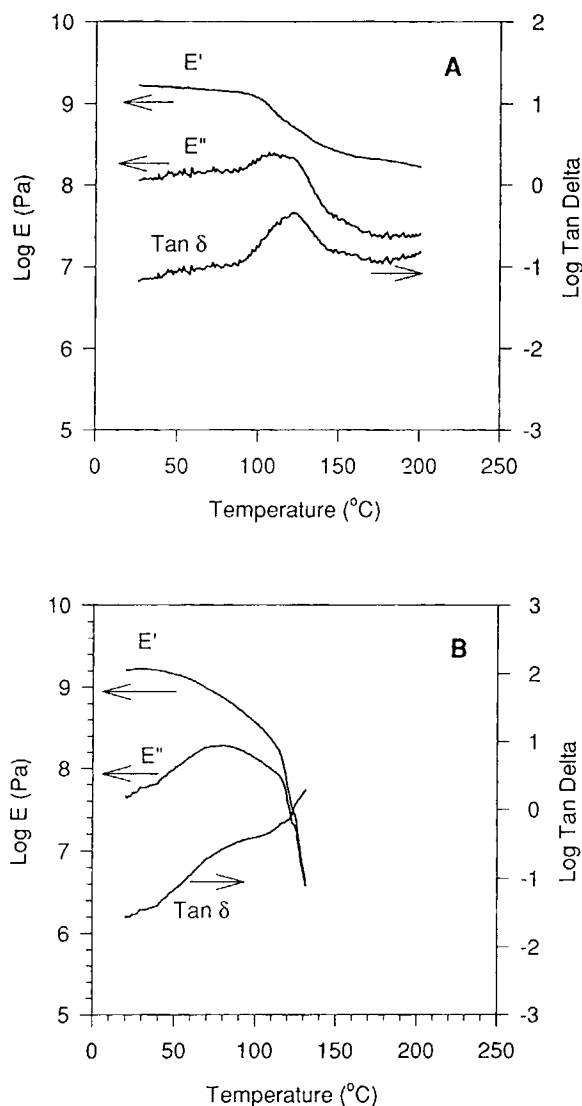


Figure 2 Dynamic mechanical behavior of the core/shell latex film with a shell composition of 14/56/30 (wt) styrene/*n*-butyl acrylate/methacrylic acid: (A) neutralized with a Na⁺ cation; and (B) in its acid form (H⁺).

Effect of Methacrylic Acid Content and Distribution

The overall content of the ionic functionality is of crucial importance in ionomers. The impact on the thermal and mechanical properties of even a few ionic groups per chain can be formidable.¹⁸ The primary effects of the ionic character of a polymer are to increase the glass transition temperatures, the melt viscosity, and the characteristic relaxation times. Tant and Wilkes¹⁹ recently reviewed the properties of ionomers and concluded that the formation of microphase separated, ion-rich aggregates, called ionic clusters, is a direct consequence of the

amount of ionic functionality. The core/shell latexes prepared in this study are significantly different in terms of the overall content of methacrylic acid in the surface and subsurface loadings of the carboxyl groups. The mechanical properties of these core/shell latexes were investigated in order to understand their structure-property relationships.

Dynamic Mechanical Analysis

As was mentioned earlier, upon neutralization of the methacrylic acid in the core/shell latex, there is ionic aggregate formation that serves to physically crosslink the polymer chains. These interchain associations of the ionic groups can even persist at elevated temperatures, especially for ionomers containing high amounts of functional groups, and improved mechanical properties can be obtained. The impact of ionic groups on the viscoelastic behavior of the polymer films can be significant.

The dynamic mechanical behavior of the core/shell latex film with a shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, which was neutralized with a Na⁺ cation, is shown in Figure 2A. Figure 2B shows the dynamic mechanical behavior of the core/shell latex film with a shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, in its acid form (H⁺). Figure 3 compares the tensile storage modulus (E') vs. temperature behavior for the core/shell latex films with a shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, in its neutralized (with Na⁺) and acid form (H⁺).

It can be noted from Figure 2B that the core/shell latex film with the shell composition of 14/56/

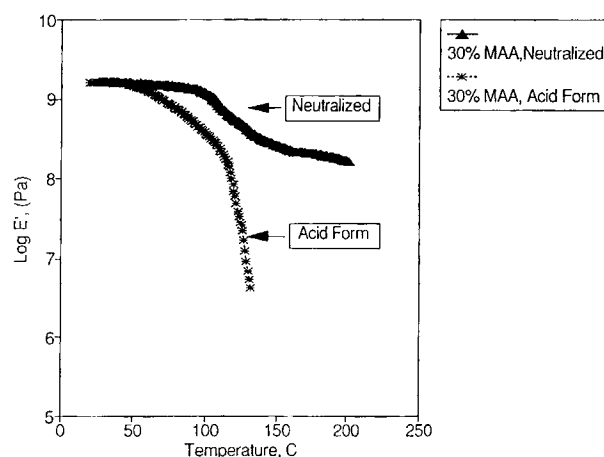


Figure 3 Comparison of the dynamic mechanical behavior of the core/shell latex films with a shell composition of 14/56/30 (wt) styrene/*n*-butyl acrylate/methacrylic acid, in its neutralized (with Na⁺) and acid form (H⁺).

30 (wt) Sty/*n*-BA/MAA in its acid form, exhibits two large drops in the modulus corresponding to the terpolymer shell (70°C) and the polystyrene core (115°C). The neutralized (with Na⁺) core/shell latex film with a shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA (Fig. 2A), exhibits only one large drop in modulus corresponding to the glass transition temperature of polystyrene (115°C). It also exhibits a large crosslinked plateau that remains almost unchanged up to the temperature limit of the instrument (200°C). This crosslinked plateau confirms the presence of strong ionic interactions, which act as physical crosslinks.

The dynamic mechanical behavior of the core/shell latex film with a shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA, neutralized with Na⁺ (using NaOH) is shown in Figure 4. The tensile storage modulus (*E'*) vs. temperature behavior of the core/shell latex film with a shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, neutralized with Na⁺, the core/shell film with a shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA, also neutralized with Na⁺, and the core/shell latex film with a shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, in its acid form (H⁺) are compared in Figure 5. It can be seen from Figures 4 and 5 that the core/shell latex film with a shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA, neutralized with Na⁺, does not exhibit the large crosslinked plateau characteristic of ionomeric systems that was exhibited by the core/shell latex film with the shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, neutralized with Na⁺.

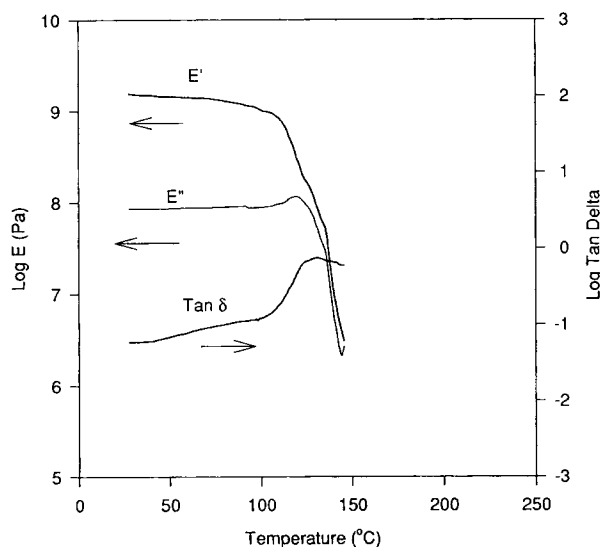


Figure 4 Dynamic mechanical behavior of the core/shell latex film with a shell composition of 29/56/15 (wt) styrene/*n*-butyl acrylate/methacrylic acid, neutralized with Na⁺.

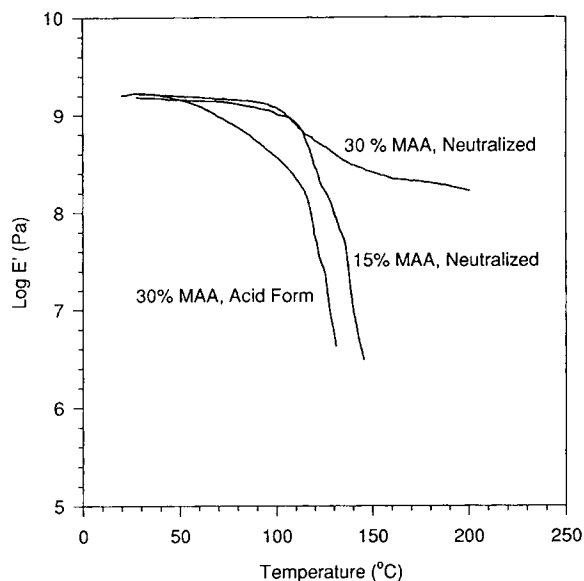


Figure 5 Comparison of the tensile storage modulus (*E'*) vs. temperature behavior of the core/shell latex film with a shell composition of 14/56/30 (wt) Styrene (Sty)/*n*-Butyl acrylate (BA)/methacrylic acid (MAA), neutralized with Na⁺, the core/shell latex film with the shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA, neutralized with Na⁺, and the core/shell latex film with the shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, in the acid form (H⁺).

It is also interesting to compare these results in light of the distribution of carboxyl groups for these core/shell latexes as determined by the x-ray photoelectron spectroscopy (XPS) analysis (discussed in Part II). It was found that the core/shell latex with the shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA exhibited a much higher concentration of the carboxyl groups in the surface and subsurface layers than the core/shell latex with the shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA. This difference must have resulted in a much stronger ionic association in the core/shell latex with the shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, when neutralized with Na⁺. It was mentioned previously that Eisenberg⁹ suggested that above a critical ion content, cluster formation occurs, which results in a greater extent of microphase separation. It appears that there has been a much greater degree of microphase separation in the core/shell latex with a shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, neutralized with Na⁺, than in the core/shell latex with the shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA, which was also neutralized with Na⁺.

However, it should also be mentioned that Dynamic Mechanical Analysis (DMA) measures the

viscoelastic response with temperature. The presence of small ionic associations in the core/shell latex film with the shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA, neutralized with Na⁺, was not significant enough to withstand the strains at elevated temperatures during the dynamic mechanical analysis. However, this small amount of physical crosslinking might have a noticeable effect on the tensile properties of the core/shell latex films at room temperature. Thus, with this motivation, the tensile properties of both the core/shell latex films in the acid (H⁺) and neutralized (Na⁺) forms were also investigated.

Tensile Properties

The stress-strain behavior of the core/shell latex films in the neutralized (with Na⁺) and acid form (H⁺) was determined and the results are shown in Figure 6. The core/shell latex films were very brittle and exhibited very small strain values. It can be inferred that there is a significant increase in the tensile strength and the stress at maximum load values for the neutralized films. The core/shell latex with the shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA neutralized with Na⁺, exhibited the highest value of the tensile modulus and the stress at maximum load. The core/shell latex film with the shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA neutralized with Na⁺, also exhibits a considerable increase in the tensile modulus as compared with the film in its acid form. It should be noted here that the core/shell latex film with the shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, neutralized with Na⁺, exhibited a higher MAA/*n*-BA ratio in the surface and subsurface layers of the shell and consists of a higher overall methacrylic acid content, which has resulted in much stronger ionic interactions that are manifested by the higher tensile modulus of that film.

Effect of Water Plasticization

It was mentioned earlier that the incorporation of an ionic functional group into a macromolecule exerts a profound effect on its physical properties. These effects have strongly supported the idea that coulombic interactions cause aggregation of the ionic groups, resulting in the formation of ion-rich microdomains, which are, in turn, responsible for the superior physical properties of the ionomers. However, this ionic aggregation also leads to processing problems due to elevated glass transition temperatures and higher melt viscosities. To circumvent

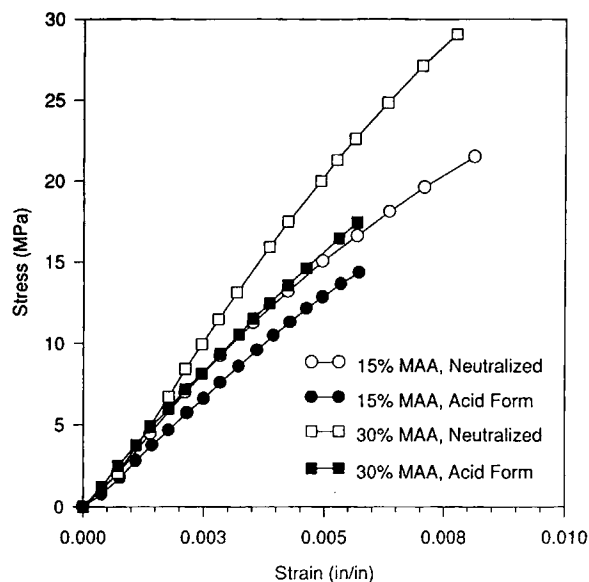


Figure 6 Comparison of the tensile behavior of the core/shell latex film with a shell composition of 14/56/30 (wt) styrene/*n*-butyl acrylate/methacrylic acid, in its acid form (H⁺, unneutralized) and neutralized form (with Na⁺), and the core/shell latex film with a shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA, in its acid form (H⁺, unneutralized) and in the neutralized form (with Na⁺).

these problems, it would often be desirable to plasticize an ionomer with a low molecular weight diluent. Given the nature of the ionomers, i.e., ionic co-units in a nonpolar matrix, plasticizers can also be divided into two kinds: (1) those that plasticize the matrix, and (2) those that affect the ionic interactions such that they plasticize the ionic domains. Because an ionic cluster is more or less hydrophilic, it is severely affected by polar diluents such as water. The presence of water has been found to reduce the glass transition temperature.²⁰ It can greatly affect the results of the dynamic mechanical scans and cause the disappearance of the ionic peak in the small-angle x-ray scattering spectrum. With this motivation, some water plasticization studies were conducted to characterize the mechanical behavior of the water-plasticized core/shell ionomeric latex films.

Dynamic mechanical analysis of the core/shell latex film with the shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, neutralized with Na⁺, and then water plasticized, was carried out to see the effect of the volatilization of water during heating and the subsequent transient aggregate formation. Figure 7 compares the tensile storage modulus (*E'*) vs. temperature behavior of the core/shell latex film with the shell composition of 14/56/30 (wt) Sty/*n*-

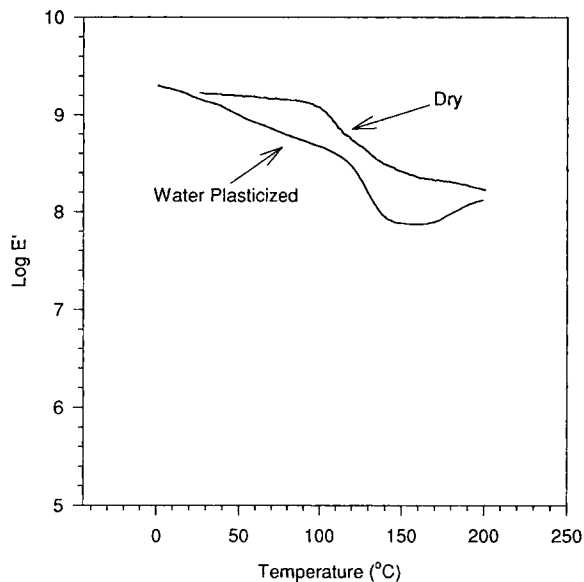


Figure 7 Comparison of the tensile storage modulus (E') vs. temperature behavior of the core/shell latex film with the shell composition of 14/56/30 (wt) styrene/*n*-butyl acrylate/methacrylic acid, neutralized with Na^+ ; in the water plasticized and dry state.

BA/MAA, neutralized with Na^+ , in the water-plasticized and dry state. Figure 7 exhibits some interesting features. This plot exhibits two drops in the tensile storage moduli (E') values that correspond to the glass transition temperatures of the polystyrene core and the terpolymer shell. It should be noted that the transition around 60°C also appeared in a DSC analysis, indicating that upon water absorption, the ionic aggregates have been solvated. One more interesting feature of the DMS behavior of this sample is a steady rise in modulus beyond 150°C . It should be mentioned here that although the water-plasticized sample exhibited an extremely low tensile strength before testing, the DMS run actually proceeded until 200°C , which is the maximum temperature attainable by the instrument. This can only be due to the loss of the water during the DMS run and subsequent ionic aggregate formation, because the core/shell latex film of the same sample in acid form could not undergo the dynamic mechanical analysis beyond 150°C (see Fig. 2B).

The tensile behavior of the core/shell latex films with shell compositions of 29/56/15 and 14/56/30 (wt) Sty/*n*-BA/MAA, respectively, neutralized with Na^+ and then plasticized with water, was measured with an Instron Tensile Testing machine at a cross-head speed of 0.5 in/min. The stress-strain behavior of the two samples is shown in Figure 8A and B.

It can be seen from Figure 8A and B that the absorption of moisture has had a dramatic effect on the mechanical properties of the core/shell latex films. The presence of water has completely solvated the ionic aggregates and resulted in a very low tensile strength of the materials. The values of the stress at maximum load and tensile modulus have been reduced approximately by one order of magnitude as compared to the dry core/shell ionomeric films (see Fig. 6). The effect on the strain to break values is even greater. The materials have been transformed from being extremely brittle in their dry state, into tough elastomeric films with strain to break values of 0.1 and 0.3 in/in for the core/shell latex films

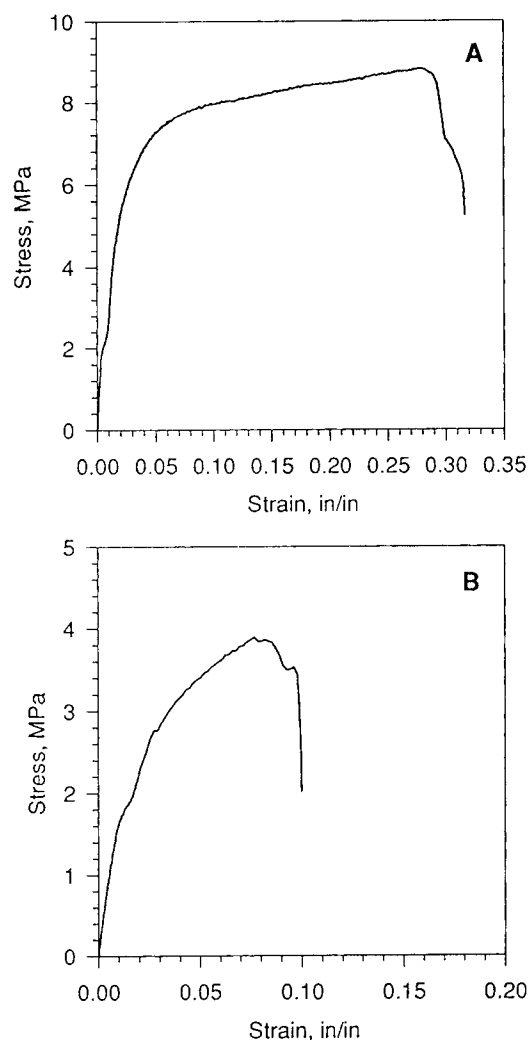


Figure 8 Stress-strain behavior of the core/shell latex film with a shell composition of: (A) 29/56/15 (wt) styrene/*n*-butyl acrylate/methacrylic acid, neutralized with Na^+ and then plasticized with water; and (B) 14/56/30 (wt) styrene/*n*-butyl acrylate/methacrylic acid, neutralized with Na^+ and then plasticized with water.

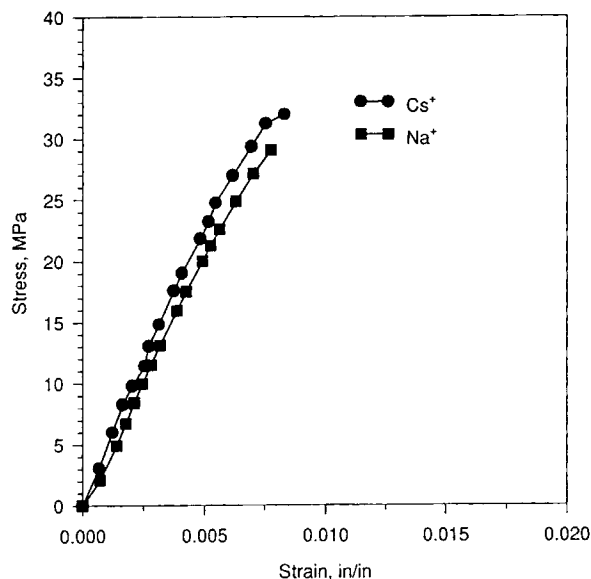


Figure 9 Comparison of the stress-strain behavior of the core/shell latex films with a shell composition 14/56/30 (wt) styrene/*n*-butyl acrylate/methacrylic acid, neutralized with Na⁺ and Cs⁺, respectively.

with the shell compositions of 14/56/30 (wt) and 29/56/15 (wt) Sty/*n*-BA/MAA, respectively, both neutralized and then plasticized with water. Taking into account the detrimental effect of water absorption on the properties of the core/shell ionomeric latex films, extreme care should be exercised during the testing of dry films in order to avoid getting inaccurate measurements.

Effect of Counterion Type

In the previous sections, the properties of the core/shell ionomeric latex films, neutralized with a sodium cation, were studied. The nature of the metal cation also has a significant effect on the strength of ionic interactions. This subject has recently received wide attention and has been the subject of some publications.^{21,22} For example, Hara et al.²¹ studied the effect of the counterion on the fatigue behavior of sulfonated polystyrene ionomers and discovered that, in general, divalent ions form stronger ionic bonds than monovalent ions. The fatigue performance for the sulfonated polystyrene ionomers neutralized with Ca²⁺, was three times better than that for the monovalent K⁺ and Cs⁺ salts. With this motivation, the effect of the cation type on the mechanical properties of the core/shell latex films was studied.

The core/shell ionomeric latex films with the shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, neutralized with Na⁺ and Cs⁺, were tested for their ten-

sile properties, and the result of the analysis is shown in Figure 9. It can be seen that there is no significant difference between the tensile behavior of the films neutralized with Na⁺ or Cs⁺. The core/shell latex film neutralized with Cs⁺ exhibited slightly higher values for the tensile modulus and stress at maximum load than the core/shell latex film neutralized with Na⁺. This can be explained on the basis of the smaller hydrated radius and lower hydration energy values for the Cs⁺ cation compared with Na⁺, which enables the Cs⁺ ion to penetrate deeper inside the carboxylated shell and cause greater neutralization of the carboxyl groups. In contrast, the core/shell latex films neutralized with Zn²⁺ were extremely brittle and could not be tested mechanically.

SUMMARY

Core/shell latexes with shell compositions of 14/56/30 (wt) and 29/56/15 (wt) Sty/*n*-BA/MAA, exhibited very different behaviors when analyzed with dynamic mechanical and tensile testing methods. The core/shell latex with a shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, exhibited a crosslinked plateau in the dynamic mechanical analysis and the highest tensile modulus value, which suggested the formation of stronger ionic interactions in that material. These results can be explained in the light of the overall methacrylic acid content and the carboxyl group distribution in this latex. The results obtained for the carboxyl group distributions in the core/shell latexes indicate that in both cases, the principal locus of the carboxyl groups is at the surface of the particles, and a very small fraction of the total carboxyl groups are buried inside the particles. It can be concluded that a higher surface concentration of carboxyl groups has resulted in a greater degree of microphase separation in this core/shell latex. The results of the water plasticization studies confirm that the presence of water results in the solvation of ionic aggregates. It was also observed that the plasticization by water is thermally reversible. The studies regarding the effect of the type of counterion suggest that because of a higher hydrated radius and hydration energy values, that the Zn²⁺ cation has not been able to penetrate as deeply inside the carboxylated shell as does the Na⁺ and Cs⁺ cations.

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