

# Elastomeric Films from Structured Latexes

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**ABSTRACT:** A model structured latex that is capable of forming a self-curable elastomeric film under mild temperature conditions was developed. In this model latex system, a small amount of dimethyl meta-isopropenyl benzyl isocyanate (TMI<sup>®</sup>) was copolymerized with *n*-butyl acrylate (BA) onto poly(butadiene-*co*-styrene) [(P(Bd-S)] seed latex particles. In the final stage of the film formation process, the latex particles coalesce with each other, and interdiffusion of PBA-based polymer chains in the shell layers of adjacent structured particles occurs. At this stage, the isocyanate groups in the P(BA-TMI) shell layer would begin to crosslink by either a moisture-cure reaction via trace amounts of water remaining in the latex film or by a post-added crosslinker that contains amine groups. Improved elastomeric properties of the latex film are expected from this kind of "interphase" crosslinking structure. However, latex films prepared from the model P(Bd-S)/P(BA-TMI) core/shell latexes were cracked and brittle, which was explained by the formation of a highly crosslinked/grafted core/shell interphase zone. Saturation of the residual double bonds in the P(Bd-S) seed latex particles by hydrogenation was found to be an effective way to reduce the development of the interphase zone and the degree of crosslinking during the second-stage polymerization. An elastomeric film with good mechanical and anti-aging properties was formed from this hydrogenated-P(Bd-S)/P(BA-TMI) structured latex. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1143-1152, 1997

**Key words:** latex particles; elastomeric films; latex films; interfacial crosslinking

## INTRODUCTION

The applications for film-forming latexes are of great interest in industry. The mechanism of film formation from latexes has been studied extensively.<sup>1-4</sup> A great deal of attention has been focused on the final stage of the film formation process, i.e., the development of cohesive strength in the film. In this stage, latex particles begin to coalesce with each other through either molecular interdiffusion<sup>3,5,6</sup> or interfacial crosslinking<sup>7-13</sup> (if appropriate crosslinking groups are available), or both. The molecular interdiffusion of polymer chains between adjacent latex particles has been shown to be of critical importance to the develop-

ment of the final mechanical properties of latex polymer films. However, the extent of the polymer chain interdiffusion greatly depends on the mobility of the polymer chains, i.e., the rigidity of the polymer chains themselves, their molecular weight, the degree of crosslinking, and the conditions of film formation, such as temperature and the presence of external additives. For example, a relatively high degree of crosslinking of the polymer chains inside the latex particles, e.g., rubber particles, would greatly hinder interdiffusion between adjacent particles.<sup>14</sup> Interfacial crosslinking, as compared with molecular interdiffusion, can be a more effective method to strengthen the latex film, and at the same time allows for more process control by varying the type, the concentration, and the distribution of the crosslinkable functional groups within the latex particles. With the increasing demand for aqueous-based latex

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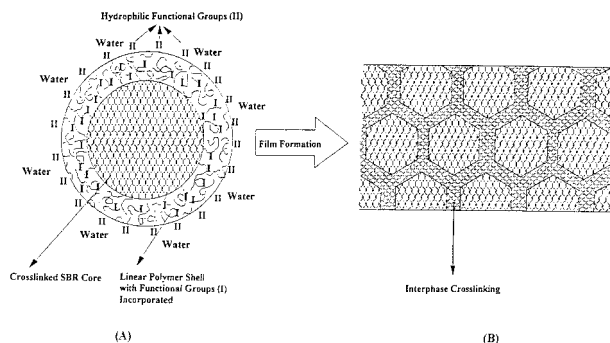
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polymer systems in such applications as paints, coatings, and elastomers, interfacially crosslinkable latex films are of great commercial interest.

One of the most extensively used methods to achieve interfacial crosslinking is to modify the latex particles by incorporating a small amount of functional groups via copolymerization into the latex particles. These functional groups are capable of associating with one another through ionic, hydrogen, or covalent bond mechanisms. It has been demonstrated by numerous studies<sup>11,12,15,16</sup> that a high concentration of functional groups in the particle surface layer is a key parameter to attain interfacial crosslinking. It is relatively easy to concentrate hydrophilic functional groups at the particle surfaces via emulsion polymerization. A typical functional group which is capable of ionic or hydrogen bonding is the carboxyl moiety, which can be incorporated into the particle structure by copolymerizing a small fraction of functional monomer, such as acrylic acid, methacrylic acid, or itaconic acid.<sup>6-8</sup> In these cases, however, because of the presence of the highly hydrophilic carboxyl groups, the films formed from these latexes do not exhibit strong resistance to alkaline aqueous solutions, such as detergents.

Compared with ionic and hydrogen bonding interparticle associations, interfacial crosslinking through covalent bonding could greatly improve both the mechanical and the environmental resistance properties of the latex film. Some of the commonly used functional monomers capable of undergoing condensation reactions are *N*-methylolacrylamide, glycidyl methacrylate, and *N*-(isobutoxymethyl)acrylamide.<sup>11-13</sup> These functional monomers either are self-condensable or may react with other types of functional groups. The main disadvantage for these types of functional monomers is that a relatively high temperature thermal curing period (usually higher than 100°C and longer than 20 min) is required, which is energy intensive and may not be feasible in many applications, such as architectural paints.

The synthesis of interfacially crosslinkable latex films under mild curing conditions has been of great interest. One example of this type of latex is an isopropenyloxazoline-based copolymer latex<sup>17</sup> developed by Dow Chemical Company. Oxazoline groups are readily reacted with acid groups at room temperature. By blending latexes containing oxazoline groups with carboxylated latexes, an interfacially crosslinked latex film could be formed at room temperature. However, be-



**Figure 1** Schematic representation of (A) the structured latex particle and (B) the elastomeric film formed from the particles.

cause two types of latexes are utilized in this blending/curing process, i.e., a so-called “two-pot” system, and crosslinking can only occur between different types of latex particles, it would be difficult to achieve uniform interfacial crosslinking.

In order to develop a “one-pot” low-temperature self-curable latex film, a model structured latex was developed in this study. In the model core/shell structured latex particles, the crosslinkable functional groups are effectively distributed in the shell layer via core/shell polymer phase separation. This approach is especially significant for those highly hydrophobic functional monomers which tend to be distributed throughout the latex particle. As shown in Figure 1, two types of crosslinkable functional groups (I and II) are separately distributed in the inner side of the shell and the outer surface of the core/shell particle. Functional group I can be incorporated in the shell layer by copolymerizing the functional monomer with a second-stage monomer. A surfactant which contains multiple hydrophilic functional groups (II) such as carboxyl, hydroxyl, or amine groups, is postadded. This surfactant (which acts in the role of a crosslinking agent) would then tend to absorb onto the particle surfaces with their functional groups facing toward the water phase because of their hydrophilicity. In this way, through the control of the addition sequence and the large difference in the hydrophilicity (or hydrophobicity) of the two types of functional groups, these I and II functional groups are separated from one another in the shell layer of the structured particles as long as the particles remain surrounded by a water medium, as shown in Figure 1(A). In the final stage of the film formation process, water, as the bulk phase, disappears, and the latex particles start to interact by

coalescing with each other. The two types of functional groups would then approach one another and react via molecular interdiffusion, as shown in Figure 1(B). By controlling the distribution of functional groups, an "interphase" crosslinked network separating the core particles could be formed.

To the best of our knowledge, most of the polymers used to prepare core/shell structured latexes for the production of elastomers have been acrylic polymers. Considering the excellent elastomeric properties of polybutadiene (PBd)-based materials, and more important, from an economic point of view (i.e., the price of butadiene is about one-ninth of that for most of the acrylic monomers), it is very meaningful to modify PBd-based latexes to develop high-performance elastomeric materials.

Poly(butadiene-*co*-styrene) [P(Bd-S)] (known as SBR for certain copolymer compositions) is a widely used elastomer. The most widely applied method to process P(Bd-S) is through a coagulation-vulcanization process, where the crosslinking process for the P(Bd-S) polymer has to be carried out during or after the shaping of the coagulated P(Bd-S) crumb. This procedure requires a very low degree of crosslinking of the original P(Bd-S) latex before the coagulation, and the vulcanization temperature is usually higher than 150°C.<sup>18</sup> These kinds of conditions are not suitable when P(Bd-S) is processed as an elastomeric film formed by the direct casting of the latex under mild temperature conditions. In these applications, a certain degree of precrosslinking in the latex particles is required to form an elastomeric film. Nevertheless, crosslinking inside the latex particles would hinder the interdiffusion of polymer chains between adjacent particles during film formation.<sup>14</sup> Actually, an elastomeric film cannot be formed by simply casting the P(Bd-S) latex, which is highly crosslinked. Through the modification of the pre-crosslinked P(Bd-S) latex particles with another linear or lightly crosslinked rubbery polymer to form a core/shell latex particle by utilizing the model structured latex particle approach, the properties of the latex film might be improved. However, an unavoidable problem that occurs when a PBd-based seed latex is used is that the large numbers of residual double bonds in the P(Bd-S) seed particles are highly active to radical reactions and are able to continue reacting among themselves, and with the second-stage monomers during second-stage polymerization. In our companion article,<sup>16</sup> we reported that the

composite latex particles became greatly hardened from the development of a highly crosslinked/grafted core/shell interphase zone in a P(Bd-S)/poly(butyl acrylate) (PBA) latex system. Very little fusion of these particles occurred during the film formation process in air at either room temperature or elevated temperature (e.g., 70°C), and the resulting films were cracked and brittle, although both types of polymers were originally soft (i.e., possessed a low glass transition temperature).

Saturation of the residual double bonds in P(Bd-S) seed latex particles by hydrogenation<sup>19,20</sup> has been found to be an effective way to reduce the formation of the interphase zone, and at the same time reduce the effect of aging (i.e., oxidation of residual double bonds) that usually deteriorates PBd-based polymer materials. Elastomeric films were produced from modified hydrogenated P(Bd-S) [H-P(Bd-S)] latex by the use of the model structured particle concept.

## MODEL STRUCTURED LATEXES USED FOR THE STUDY

A small amount of dimethyl meta-isopropenyl benzyl isocyanate (TMI<sup>®</sup>, Cytec Industries) was copolymerized with *n*-butyl acrylate (BA) onto P(Bd-S) seed latex particles to prepare the model structured latexes. Because the isocyanate groups from the TMI monomer are relatively stable to hydrolysis during emulsion polymerization<sup>21</sup> under certain conditions, and because of the relatively high hydrophobicity of the TMI monomer unit, it is possible to control the loci of the isocyanate groups (functional group I) so that they are distributed in the interior portion of the PBA-based shell layer nearest to the core P(Bd-S) polymer. Several types of functional groups with active hydrogens can possibly be used as the second functional group. Generally, the order of the reactivity of these functional groups to the isocyanate group is: amine > hydroxide > carboxylate.<sup>22</sup> The amine group rapidly reacts with the isocyanate group, while some metal catalyst is usually needed for the other two types of functional groups. Surfactants or water-soluble polymers that contain such functional groups can be post-added as the surfactant (crosslinker). In a related article,<sup>23</sup> the crosslinking mechanism of the structured latex particles containing isocyanate groups was studied by use of the attenuated total reflectance (ATR)-FTIR technique. It was shown

**Table I Characteristics of Seed Latexes**

Parameter	P(Bd-S)-S	H-P(Bd-S)-1	H-P(Bd-S)-2	LPH-7382
Particle size (nm)	80	80	80	50
Gel fraction before hydrogenation (%) <sup>a</sup>	41	41	41	13
Gel fraction after hydrogenation (%) <sup>a</sup>		53	60	52
Hydrogenation (%)	0	74	93	95

<sup>a</sup> Measured by toluene extraction at 23°C.

that most of the isocyanate groups, e.g., 80–90% for some systems, will remain intact during the emulsion polymerization process and will become incorporated inside the latex particles. The shell thickness in which the isocyanate groups are incorporated was found to be an important parameter influencing the hydrolysis of the isocyanate groups during the polymerization and the film formation process. For this specific structured latex system, in the final stage of film formation, trace amounts of water molecules remaining in the latex film could effectively react with the isocyanate groups to form amines and, hence, to cure the film through the isocyanate-amine reactions, i.e., a two-step water molecule-curing mechanism. The focus of this study is on the preparation of the structured latexes and the mechanical properties of the latex films formed through the moisture-curing mechanism.

## EXPERIMENTAL

### Materials

BA (Fisher Scientific) was treated by being passed through an inhibitor removal column, while TMI<sup>®</sup> was used as received. Ammonium persulfate (APS) and potassium metabisulfite (PMBS), both analytical grade (Fisher Scientific), were used as received. Three kinds of hydrogenated P(Bd-S) latexes were used; H-P(Bd-S)-1 and H-P(Bd-S)-2 were prepared by hydrogenating P(Bd-S)-S prepared in this laboratory, while Chemisat HSBR LPH-7382X (abbreviated as HSBR hereafter) was kindly supplied by The Goodyear Tire & Rubber Company.

### Treatments of Hydrogenated P(Bd-S) Seed Latexes

Both non-hydrogenated and hydrogenated P(Bd-S) [H-P(Bd-S)] latexes were used as seeds in the second-stage polymerization. The particle sizes, gel fractions, and degrees of hydrogenation of these latexes are listed in Table I. The prepara-

tion, hydrogenation of P(Bd-S)-S latex, and characterization of these latexes are described in companion articles.<sup>16,20</sup>

After the hydrogenation of P(Bd-S) latexes by the hydrazine/hydrogen peroxide redox system was complete, a small amount of either hydrazine reductant or hydrogen peroxide oxidant, depending on the ratio of both components used for the hydrogenation, would still remain in the latex system. Because any trace amount of either component would greatly inhibit the second-stage polymerization using a redox initiator system, excesses of hydrazine or hydrogen peroxide must be removed from the system. Usually, the hydrazine/hydrogen peroxide ratio used in the hydrogenation was controlled in such a way that a slight excess amount of hydrazine remained in the system after the hydrogenation was complete. The remaining hydrazine in the HSBR latex had been removed by treatment with ozone gas. The method used in this laboratory to treat the H-P(Bd-S) latexes is described as follows: 1) 5 mL of the latex sample (at approximately 20% solids) was diluted to 20 mL with distilled-deionized (DDI) water, and a few drops of a 10% aqueous solution of CuSO<sub>4</sub>/Dowfax 2A-1 surfactant (1/10, w/w) were added; 2) ferrothiocyanate indicator was added to the system (ferrothiocyanate can detect hydrogen peroxide down to 0.001%, which involves conversion of colorless ferrothiocyanate to red ferrithiocyanates); and 3) the diluted latex was titrated with hydrogen peroxide (50% solution) until the equivalence point was reached, at which point the color of the latex became red. The addition of the copper ion in step 1) can greatly increase the reaction rate between hydrazine and hydrogen peroxide to obtain a sharp equivalence point. Because iron and copper ions introduced into the system could influence the stability of the latex, Dowfax 2A-1 surfactant (sodium dodecyl diphenyl ether disulfonate, Dow Chemical) was used to stabilize the latex system during the titration process. The amount of hydrogen peroxide

**Table II** Recipe for the Second-Stage Polymerization at 40°C

Component	Wt (g)
Seed latex (20.0% solids content) <sup>a</sup>	50
<i>n</i> -BA	10
TMI <sup>®</sup>	None, 0.1, and 0.3
Redox initiator <sup>b</sup>	0.15
DDI water	20

<sup>a</sup> Seed latexes used for Runs 1–4 are P(Bd-S)-S, H-P(Bd-S)-1, H-P(Bd-S)-2, and LPH-7382, respectively. (see Table I for their characteristics).

<sup>b</sup> Redox system: PMBS and APS (Fisher Scientific), 1/1, w/w.

used right before the equivalence point is considered to be suitable to minimize the amount of hydrazine remaining in this latex. To further remove trace amounts of the remaining hydrazine, the latex was bubbled with air with stirring for 24 h.

For the HSBR latex, although remaining hydrazine had been removed during the manufacturing process, some unknown additives, i.e., inhibitor and antioxidants, may be present in this industrial latex sample. Very low conversions were obtained when using this latex directly as the seed latex in the second-stage polymerization, especially when redox initiator was used. To compensate for the presence of any remaining polymerization-retarding agents (i.e., carried into the reactor via the seed latex) in the subsequent second-stage seeded polymerization with BA and TMI, the HSBR latex was first treated as follows before the second-stage polymerization was carried out: 1) 0.5 g of the second-stage BA monomer was added to 50 g of HSBR latex (at 20% solids content) and stirred for 8 h at 15°C; 2) the temperature of the system was then raised to 80°C and 0.1 g of potassium persulfate was added; and 3) the system was kept at this temperature for 24 h to ensure that any inhibitor left in the system would be consumed during this polymerization step. After this time, the remaining BA and TMI monomers would be added to the reactor along with initiator to complete the second-stage polymerization at 40°C, as shown in Table II.

### Seeded Emulsion Polymerization

A series of second-stage emulsion polymerizations with different seed latexes were carried out at 40°C with a redox initiator system according to the recipe shown in Table II. Two modes of addi-

tion of the second-stage monomers to the seed latex particles were utilized: 1) an equilibrium-swelling process was used for Run 1 only [seed: P(Bd-S)-S], in which the monomer was allowed to swell the seed particles for 24 h at room temperature before the seeded emulsion polymerization was started; and 2) a semicontinuous process for all of the other runs, in which 5 wt % of the monomer and the initiator were added to the seed latexes at the beginning of the second-stage polymerization, and the remaining monomer and initiator were added continuously to the reaction flask with a syringe pump at a constant rate of 0.028 mL/min.

### Preparation of Latex Films

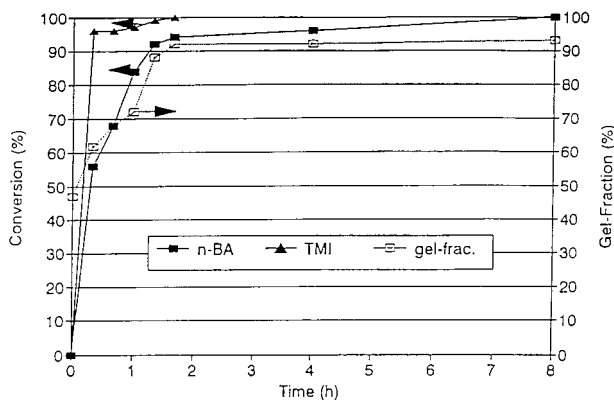
Latex films were cast on a clean glass plate and dried in an oven. The film formation temperatures used in this study were 25, 45, and 65°C. The thickness of the latex films used in this work ranged from 0.50 to 0.65 mm. The film was considered to be completely dried when its weight did not change appreciably (drying usually took 1–3 days, depending on the oven temperature).

### Gel Fraction and Swelling Ratio Measurements

Gel fraction measurements were carried out by the use of a solvent extraction technique, the details of which have been described.<sup>16</sup> Briefly, this method involves dissolving 0.2 g of latex film, which is cast at room temperature and dried under vacuum for ten hours, in 25 mL of solvent, e.g., toluene or acetone, and mixing for 24 h. The dissolved portion, i.e., the non-gel part, is determined gravimetrically from the amount of solids remaining in the supernatant after the centrifugation of the swollen system at 5,000 rpm for 30 min. The gel fraction is the percentage of the insoluble polymer in the total film sample. The swelling ratio of a latex film was determined from the weight ratios of the film samples before and after a 24 h swelling process at room temperature.

### Stress-Strain Mechanical Properties

The latex films were cut into dumbbell shapes according to ASTM Standard D1708-84. Tensile tests were carried out with an Instron Universal Testing Machine (Model-1011) with a crosshead speed of 25 mm/min.



**Figure 2** Percentage of second-stage monomers converted and the total gel fraction (frac.) of the latex versus reaction time obtained with an SBR seed latex (Run 1 in Table II), which was polymerized to 57% conversion.

## RESULTS AND DISCUSSION

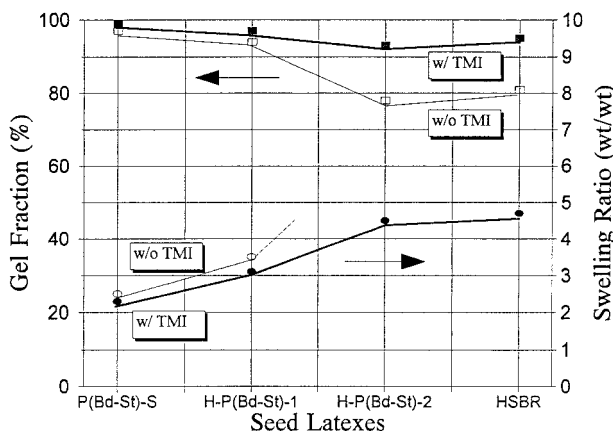
The reactions were carried out at 40°C with the redox initiator system to decrease the extent of hydrolysis of the isocyanate group in the TMI monomer during the second-stage polymerizations. It was found that there were almost no isocyanate groups left after polymerization at 70°C.

Seeded emulsion polymerization was first carried out after the equilibrium-swelling process of the second-stage monomers (Run 1, Table II). The film formed from the resulting latex was severely cracked and brittle. Figure 2 shows the conversions of the second-stage monomers and the increase in the gel fraction of the latex films formed from the latexes obtained at various conversions. The conversion of each monomer was measured by gas chromatography. The TMI monomer exhibited a much higher conversion compared with *n*-BA shortly after the reaction was started. After about 30 min, the conversion of TMI was 95%, while the conversion for *n*-BA was only about 55%. As shown in Figure 2, the gel fraction increased soon after the reaction started and eventually reached 93%. This indicates the occurrence of grafting/crosslinking reactions during the P(Bd-S) seeded emulsion polymerization of the second-stage monomers. The same tendency has been shown<sup>16</sup> for a P(Bd-S)/BA seeded emulsion polymerization system in the absence of the TMI monomer. Similar results were obtained when a low gel fraction (2%) P(Bd-S) seed latex was used, i.e., the final gel fraction was still higher than 90%, and the latex film was cracked and

brittle. In an attempt to search for a process that could be used to suppress the increase of the gel fraction, the reactions were also carried out with various addition rates of the second-stage monomers, e.g., from monomer flooded to monomer starved, or with the addition of a chain transfer agent such as *n*-dodecyl mercaptan. Nonetheless, the gel fractions of the latex films were always above 90%.

The process describing the development of the highly grafted/crosslinked core/shell interphase zone has been reported.<sup>16</sup> Because of the existence of a large number of residual double bonds, especially the vinyl double bonds, and allylic hydrogens in the P(Bd-S) seed latexes, the continuing reactions of these radical-reaction-active double bonds, which would cause crosslinking and graft formation on the P(Bd-S) polymer chains, seemed to be inevitable during the second-stage polymerization. Hydrogenation of these double bonds has been considered to be an effective means to control the development of the highly grafted/crosslinked interphase zone.

Figure 3 shows the gel fractions and swelling ratios of the films cast from the latexes obtained from the seeded emulsion polymerizations, in which the semicontinuous mode of addition of the second-stage monomers was used. The unfilled symbols represent the data for the control latex film samples in which no TMI monomer is present. Extremely high gel fractions for the latex films, prepared with or without the TMI present, were obtained when the nonhydrogenated P(Bd-S)-S seed latex was used. The low swelling ratios for this seed system indicate a very high degree



**Figure 3** Gel fractions and swelling ratios of the films cast from latexes obtained by using the different seed latexes with the second-stage monomer added via a semicontinuous polymerization technique.

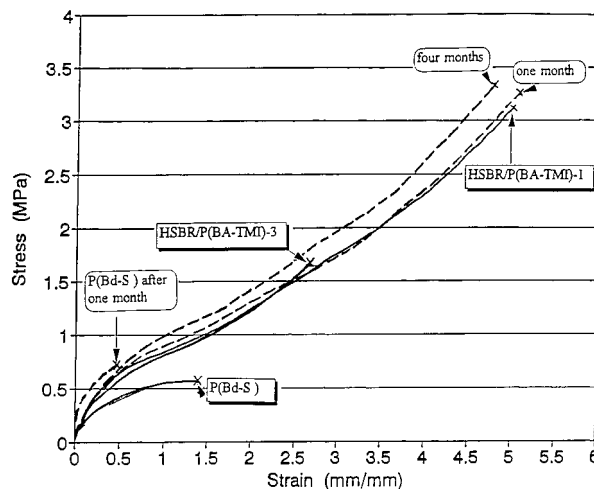
of crosslinking in the polymer. The latex films exhibited many cracks and were easily fragmented. When the modestly hydrogenated (74%) H-P(Bd-S)-1 latex was used as seed, the latex films exhibited a lower number of cracks but still did not exhibit any elasticity. This result suggests that even with a degree of hydrogenation of 74%, the remaining 26% of the double bonds in the H-P(Bd-S)-1 seed latex can still be crosslinked to such a high level that polymer chain interdiffusion is greatly restricted between adjacent particles and can prevent the formation of a continuous film.

By using the highly hydrogenated (> 90%) seed latexes, i.e., H-P(Bd-St)-2 and HSBR, the gel fractions of the control film samples decreased significantly. The gel fractions for the samples prepared with TMI present only decreased slightly, while the swelling ratios increased from 2.2 and 3.1 for the P(Bd-St)-S and H-P(Bd-St)-1 seed systems to 4.5 and 4.7 for the H-P(Bd-St)-2 and HSBR seed systems, respectively. The swelling ratios for the control film samples prepared by using the latter two seed latex systems were not obtainable because of the relatively high soluble fractions (> 20%). The swelling ratios were higher than 8 for the gel portion of these two film samples.

The mean molecular mass between two crosslinks,  $M_C$ , can be estimated from the well-known Flory-Rehner equation<sup>24,25</sup>:

$$\begin{aligned} \ln(1 - v_p) + v_p + \chi v_p^2 \\ + (\rho/M_C)V_1(v_p^{1/3} - v_p/2) = 0 \quad (1) \end{aligned}$$

where  $v_p$  is the volume fraction of the polymer in the swollen film,  $V_1$  is the molar volume of the solvent,  $\chi$  is the Flory-Huggins polymer-solvent parameter, and  $\rho$  is the density. For the swelling ratios obtained in this experiment, i.e., 2.2, 3.1, 4.5, and 4.7, the  $M_C$  values can be calculated as  $7 \times 10^2$ ,  $2 \times 10^3$ ,  $5 \times 10^3$ , and  $6 \times 10^3$  g/mol, respectively. It has been demonstrated<sup>14</sup> that latex films formed from particles so highly crosslinked that the  $M_C$  becomes smaller than the critical entanglement chain length,  $M_E$ , which is about  $3 \times 10^4$  g/mol,<sup>14,26,27</sup> remained brittle after annealing because the interdiffusion of polymer chains and the formation of interparticle entanglements were impossible in these films. It is noticeable that all of the  $M_C$  values obtained in this experiment are far below the  $M_E$  value. During the film formation process, additional crosslinks



**Figure 4** Stress-strain behavior for HSBR/P(BA-TMI) structured latex films and P(Bd-S) latex film; solid lines, freshly prepared latex film; dashed line, latex film after aging. The swelling ratios of the freshly prepared latex films are shown in Table III.

would form in those films with isocyanate groups incorporated, which would result in higher gel fractions and degrees of crosslinking, compared with the control film samples. The additional crosslinks which were formed during film formation could be either intraparticle (inside the latex particle) or interparticle, depending on the extent of interdiffusion of the polymer chains and/or the degree of crosslinking in the original particles for the systems where the polymer glass transition temperature is much lower than the film formation temperature. Polymer chains in highly crosslinked latex particles would undergo very little interdiffusion; thus, the majority of additional crosslinks arising from the isocyanate groups would result from “intraparticle crosslinking.” Consequently, the resulting films are as cracked and brittle as those latex films formed with P(Bd-S)-S and H-P(Bd-S)-1 as the seed latexes. On the other hand, the continuous films formed from the latexes prepared with H-P(Bd-S)-2 and HSBR as seeds exhibited good elasticity, which indicates that both chain interdiffusion and crosslinking via the isocyanate groups have played positive roles in the film formation process, i.e., the major part of the crosslinks derived from the isocyanate groups is formed among those polymer chains that have interdiffused beyond the original boundaries of particles, which would form “interparticle” crosslinks and strengthen the film.

Figure 4 shows the tensile testing results for HSBR/P(BA-TMI)-1 and HSBR/P(BA-TMI)-3

**Table III Film Swelling Ratios for Samples Used in Stress-Strain Measurements (24 h in Toluene)**

Latex Films	Swelling Ratios ( $W_f/W_o$ ) <sup>a</sup>
Non-hydrogenated P(Bd-S)	5.1
HSBR/P(BA-TMI)-1	4.7
HSBR/P(BA-TMI)-3	4.0

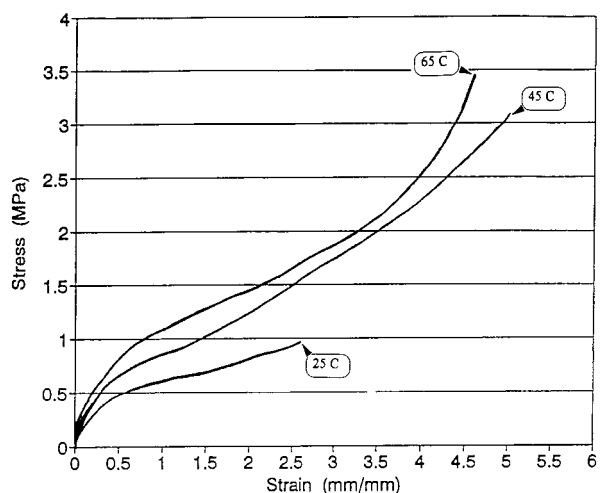
<sup>a</sup>  $W_o$  and  $W_f$  are weight of films before swelling and after 24 h of swelling in toluene, respectively.

(1 and 3 wt % of TMI in the shell, respectively). A non-hydrogenated P(Bd-S) latex film was also used as a control sample. A continuous film could not be formed from the unmodified HSBR seed latex in the temperature range used for casting films in this study (25–70°C), and thus, no testing was carried out with this latex. Table III lists the swelling ratios for film samples used in the tensile tests.

Figure 4 shows that both HSBR/P(BA-TMI) structured latex films exhibited typical stress-strain properties for elastomers, i.e., the stress increased gradually with an increase in strain without a yield point and the film samples were broken at the point where the highest stress was reached. The film having the lower TMI content (1% by wt) showed both higher stress and strain values than those obtained for the film with the higher TMI content (3% by wt). From the swelling ratio data in Table III, it is seen that the HSBR/P(BA-TMI)-3 latex film has a higher average degree of crosslinking (i.e., lower swelling ratio), which should normally result in a higher stress value or modulus in a uniformly crosslinked film. In the latex film systems using thermally crosslinkable functional monomers,<sup>11,12</sup> it has also been shown that both the stress and the modulus increased with an increase in the concentration of the functional monomers. However, unlike the thermal crosslinking system where the crosslinking resulting from the thermal activation of functional groups occurs during the annealing process after the formation of the latex film, in our latex system, both polymer chain interdiffusion and crosslinking (from reactions of isocyanate groups) occurred at the same time during the final stage of the film formation process. Thus, the relative extents of the intraparticle and interparticle crosslinking obtained via the isocyanate group are dependent on both the relative rates of polymer chain interdiffusion and the crosslinking reaction of the isocyanate groups. At high isocyanate con-

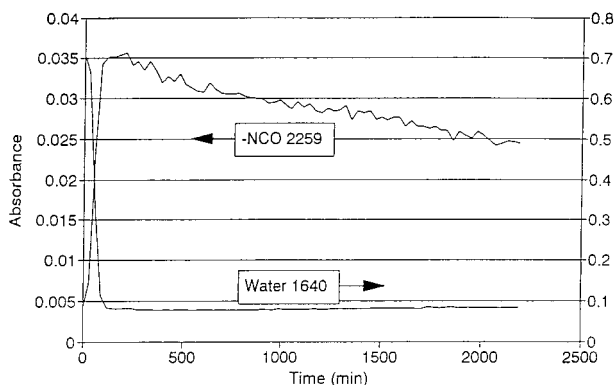
centrations, the crosslinking from the isocyanate groups during the film formation takes place too rapidly and polymer chain interdiffusion would be slowed. This premature crosslinking would restrict the further interdiffusion of polymer chains and reduce the extent of interparticle crosslinking. Therefore, the higher degree of crosslinking in the system with the higher TMI content is caused by an increased number of crosslinks inside the latex particles (formed before or during the film formation process). As a result, the HSBR/P(BA-TMI)-3 latex film has shown mechanical properties inferior to those of the HSBR/P(BA-TMI)-1 latex film.

Nonetheless, compared with the P(Bd-S) latex film, which was cast from the unmodified P(Bd-S) latex, both structured latex films showed much better properties. The P(Bd-S) latex film broke at low stress and strain values, although the average degree of crosslinking was lower than those obtained for the two structured latex films. An  $M_c$  of  $7 \times 10^3$  g/mol can be calculated by using eq. (1) from the swelling ratio data shown in Table III. Because there is no additional crosslinking which may arise from the presence of isocyanate groups in this latex film, this  $M_c$  value can be used to represent the  $M_c$  inside the original latex particles, which is much lower than the critical entanglement chain length  $M_E$  ( $\sim 3 \times 10^4$  g/mol). This indicates that the degree of crosslinking inside the P(Bd-S) latex particles is too high to develop enough molecular interdiffusion between adjacent particles. At the same time, it is further



**Figure 5** Stress-strain behavior for HSBR/P(BA-TMI)-1 structured latex films cast at various film formation temperatures with film formation times as follows: 4 days at 25°C, 1 day at 45°C and at 65°C.





**Figure 6** ATR-FTIR absorbance profiles of water and isocyanate groups in the HSBR/P(BA-TMI)-3 latex system during a 24 h film formation process.

shown that for both structured latex films, which have an even higher average degree of crosslinking (i.e., lower swelling ratio), there is a contribution from interfacial crosslinking which occurs during the film formation process.

Another significant difference between the modified HSBR latex film and the non-hydrogenated P(Bd-S) latex film is their aging properties. Obvious deteriorations in film properties were found for the P(Bd-S) film after 1 month of aging. On the other hand, there was very little change in the mechanical behavior of the HSBR/P(BA-TMI)-1 film after 1 month of aging; a slight improvement in the stress-strain properties was even observed after 4 months of aging.

Figure 5 shows the influence of the film formation temperature on the stress-strain properties of HSBR/P(BA-TMI)-1 latex films. Significant improvements in the mechanical properties were observed when the temperature was increased from 25 to higher than 45°C. The higher film formation temperature promoted better polymer chain interdiffusion and also enhanced interfacial crosslinking during the film formation process.

In a related article,<sup>23</sup> the consumption mechanism of the isocyanate groups from the TMI monomer was investigated by the use of an ATR-FTIR technique. By applying this technique, the infrared spectra are able to be recorded during the entire latex film formation process, and the change in the concentration of functional groups in the latex film system can be monitored.

Figure 6 shows the absorbance intensity profiles for the isocyanate groups and water during the film formation process of the HSBR/P(BA-TMI)-3 latex. After the time ( $\sim 60$  min) at which the absorbances of water and the —NCO group

reached their minimum and maximum points, respectively, the latex system became converted from an extremely concentrated latex into a latex film. After this point, the amount of water in the latex film remains almost constant, while on the other hand, the absorbance for the isocyanate group decreases gradually. This experiment demonstrates the formation of crosslinks (both intraparticle and interparticle) via isocyanate groups during the latex film formation process. Because the crosslinking network is formed in the entire shell polymer phase between core polymer domains, this kind of crosslinking may be, more appropriately, defined as “interphase crosslinking” to distinguish it from “interfacial crosslinking,” which is generally used to represent a rather thin crosslinked layer at the particle interfaces. Obviously, a more uniformly crosslinked latex film can be formed from the interphase crosslinking structure, which would lead to better elastomeric properties for the latex film.

## SUMMARY

In summary, the development of the highly grafted/crosslinked core/shell interphase zone in a PBd-based structured latex can effectively be suppressed by the hydrogenation of the PBd-based seed latex. A high degree of hydrogenation ( $> 90\%$ ) is necessary for the purpose of this study. Besides controlling the extent of crosslinking in the core/shell interface zone, another great benefit from the hydrogenation of the PBd-based seed latex is the significant improvement in the anti-aging properties of the latex film, which has been a severe problem in numerous applications with PBd-based latexes.

These model structured latex particles are appropriate for developing high-performance elastomeric films, in terms of the formation of an “interphase-crosslinked” network in the latex film. It is very important to have a controlled rate of crosslinking of the functional groups (not restricted to the functional groups used in this work) so that the crosslinking could occur primarily among interdiffused polymer chains. Premature crosslinking inside the latex particles themselves would greatly restrict interdiffusion and lead to the formation of poor latex films.

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