

Study of the Consumption of TMI[®] in Latex Using Attenuated Total Reflectance FTIR (ATR-FTIR)

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ABSTRACT: Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was used to study the mechanism for consumption of isocyanate groups from a dimethyl *meta*-isopropenyl benzyl isocyanate (TMI[®]) monomer. A series of polystyrene/poly(butyl acrylate-*co*-TMI) [PS/P(BA-TMI)] core/shell structured latexes with different core/shell ratios were prepared by seeded emulsion polymerization techniques. These latexes were air-dried on ATR-FTIR germanium (Ge) discs while the FTIR spectra were taken during the film-formation process. The amounts of isocyanate moieties which were reacted during polymerization and the film-formation process were determined quantitatively using the FTIR data combined with titration calibration of the isocyanate groups. The thickness of the shell in which the TMI monomer was incorporated was found to be very important in determining the extent of consumption (hydrolysis) of the isocyanate groups during either polymerization or film formation. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1967-1973, 1997

Key words: latex particles; latex films; interfacial crosslinking; ATR-FTIR

INTRODUCTION

Among a number of functional monomers that can undergo crosslinking reactions during the latex film-formation process, the dimethyl *meta*-isopropenyl benzyl isocyanate (TMI[®]; Cytec Industries) monomer is of considerable commercial interest. The two reactive moieties in the TMI monomer, i.e., via the vinyl double bond and the aliphatic isocyanate group, can be reacted independently, i.e., copolymerization with other vinyl monomers through the vinyl group or reaction of the isocyanate groups with some active hydrogen-containing compounds.^{1,2} An unusual property of the TMI monomer is its ability to undergo emulsion copolymerization in an aqueous medium with only a small fraction of the isocyanate groups being hydrolyzed. The isocyanate moieties which remain inside the latex particles (or on the particle

surfaces) could then undergo crosslinking reactions during the film-formation process. Obviously, it is very important to quantify the fractions of isocyanate groups which have reacted during polymerization and film formation. Any premature crosslinking of the isocyanate groups inside the latex particles during the emulsion polymerization process would hinder the molecular interdiffusion of polymer chains during the film-formation process^{3,4} and would usually degrade the mechanical properties of the latex film. On the other hand, the reactions of the isocyanate groups during the film-formation process, especially during the cohesive strength development stage, would tend to form interfacial crosslinks between adjacent latex particles, which could greatly enhance the mechanical properties of the latex film.⁵⁻⁸

The attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy technique has been successfully applied to the study of polyurethane foam systems by monitoring isocyanate absorption near a 2250 cm⁻¹ wave-

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number.^{9,12} ATR techniques have also been used to study surfactant migration behavior during latex film formation¹³ and in determining suspended material in polymer latexes.¹⁴

The amount of isocyanate groups remaining in a latex film was determined by FTIR in our laboratory some time ago.¹⁵ However, since the FTIR spectra were determined on latex film samples, the information obtained described the amount of isocyanate groups remaining in the final latex film. It has been hard to distinguish the consumption of the isocyanate groups in latex particles themselves and in the latex film. The ATR technique is a rather new tool for monitoring the consumption of the isocyanate groups during the entire latex film-formation process.

In the present work, we report studies which show that ATR-FTIR spectroscopy is an appropriate method for studying the latex film-formation process. A series of polystyrene/poly(*n*-butyl acrylate-*co*-TMI) [PS/P(BA-TMI)] core/shell structured latexes with different core/shell ratios were prepared by seeded emulsion polymerization techniques. The freshly prepared latexes were cast on a germanium (Ge) ATR-FTIR disc while the FTIR spectra were taken during the entire film-formation process. A decreased pattern of water absorption clearly showed the different stages of film formation. Combined with titration calibration of the isocyanate groups, the amount of isocyanate moieties in the latex particles before film formation occurred, which could reflect the consumption of the isocyanate groups during the emulsion polymerization process, and the amount consumed after the final stage of film formation, i.e., the cohesive strength development stage, were determined quantitatively.

EXPERIMENTAL

Materials

The *n*-butyl acrylate (BA) monomer (Fisher Scientific) was treated by passing it through an inhibitor-removal column. The TMI[®] monomer (Cytac Industries) was used as received. Ammonium persulfate (APS) and potassium metabisulfite (PMBS), all analytical grade (Fisher Scientific), and sodium dihexyl sulfosuccinate surfactant (Aerosol MA 80; Cytac Industries) were used as received. Polystyrene (PS) seed latex (LS-1039-E, Dow Chemicals; particle size = 93 nm, PDI

= 1.004) was used as received. Distilled-deionized (DDI) water was used in all polymerizations.

Emulsion Polymerization

Emulsion polymerizations of BA and TMI were carried out in a four-neck 250-mL flask at 40°C, according to the recipes shown in Table I. Runs 1–3 were carried out in the presence of PS seed latex, while Run 4 was conducted without PS seed latex. In Run 4, 10% of the total monomers and initiator, all of the surfactant, and 80% of the DDI water were initially charged in the flask and allowed to react for 1 h. A semicontinuous process was utilized for the addition of the second-stage monomers and initiator for Runs 1–3, and the remaining monomers and initiator for Run 4, at a constant rate of 0.028 mL/min using a syringe pump.

ATR-FTIR Spectroscopy

The IR spectra were obtained on a React IR-2000 Fourier transform spectrometer (Applied Systems Inc.), by averaging 64 scans with a resolution of 4 cm⁻¹. One spectrum was recorded every 30 min during the entire latex film formation process over a 24 h period.

Titration of Isocyanate Groups in P(BA-TMI)

A series of P(BA-TMI) latexes were prepared following the same procedure described for Run 4 of Table I. The concentrations of TMI monomer used in the copolymers varied from 0.4 to 3.2 wt % of the total copolymer. Latex films were cast at room temperature, dried for 4 days, and then dried in a vacuum oven for 24 h. The titration was carried out as follows: (1) Approximately 8.0 g of latex film samples were dissolved in 150 mL THF and mixed by tumbling for 48 h; (2) solutions were filtered to remove large insoluble gels (for systems with high TMI contents); (3) the solids contents for each filtered solution sample was determined gravimetrically; 100.00 g of each solution was then transferred to an Erlenmeyer flask; (4) appropriate amounts of dibutylamine (DBA) (0.05*N* in THF) were added into each solution and stirred for 3 min before each titration; three drops of a Bromothymol Blue indicator were added and the solution exhibited a light blue color; (5) 40 mL isopropanol was added into the solution to ensure the solubility of HCl in the system; and (6) the solution was titrated with HCl (0.02*N*); some ad-

Table I Emulsion Polymerization Recipes Used to Prepare Latex Samples Used in the ATR-FTIR Film-Formation Study

Component (g)	Run 1	Run 2	Run 3	Run 4
Polystyrene seed ^a	50.0	50.0	50.0	—
<i>n</i> -Butyl acrylate	5.0	10.0	20.0	20.0
TMI®	0.15	0.3	0.6	0.6
Ammonium persulfate	0.06	0.12	0.24	0.24
Potassium persulfate	0.06	0.12	0.24	0.24
Aerosol MA 80 ^b	—	—	—	0.80
Distilled-deionized (DDI) water	10.0	20.0	40.0	80.0

^a 20% solids content; particle size = 93 nm; PDI = 1.004.

^b Sodium dihexyl sulfosuccinate, 78–80% solution in a mixture of isopropanol and water.

ditional isopropanol was added when the system exhibited any cloudiness; an end point was shown by the sharp transition of the light blue to light yellow color when the titration was completed. In step (4), to make the final amount of HCl (0.02*N*) consumed during the titration to be around 10–20 mL, the amount of DBA used should be about 0.2–0.4 mmol in excess, which corresponded to the amount of isocyanate from the recipe in each solution sample.

RESULTS AND DISCUSSION

A schematic representation of the ATR-FTIR is shown in Figure 1. The latex sample is deposited on the germanium (Ge) disc, and the IR beam undergoes a series of total reflections at the Ge/sample interface, which would then pass to the detector. The depth that the IR beam can probe into the sample is about 100 nm. In other words, the thickness of the sample detected by the IR beam would be fixed and would remain close to the Ge/sample interface. Since the IR spectrum was recorded during the whole film-formation pro-

cess, the change in the concentration for each functional group in the system can be followed.

Figure 2 shows typical ATR-FTIR spectra obtained during a 24-h period of time in which a film is being formed from a PS/P(BA-TMI) core/shell (1/1, w/w) latex system. An individual IR spectrum was determined every 30 min. Three peaks of interest at wavenumbers of 1640, 1750, and 2259 cm^{-1} represent water, carbonyl (—CO—), and isocyanate (—NCO) groups, respectively. From this series of spectra, profiles of the absorbance with time for each of these three peaks can be plotted. It should be noted that the same film specimen was used during the entire 24-h IR analysis period. Since the IR beam used in this study was of low power, it was felt that the IR beam itself did not contribute significantly to the rate of drying, the rate of hydrolysis, or the rate of the —NCO consumption.

Figure 3 shows the profiles for these three peaks for this specific system. At the beginning of the film-formation process ($t = 0$), the high absorbance intensity of water reflects the high concentration of water in the polymer dispersion, while both organic peaks (—CO— and —NCO)

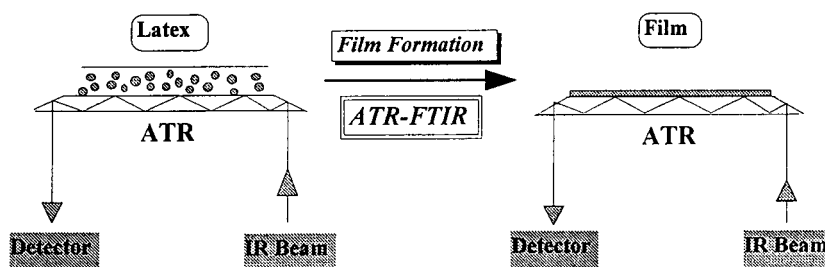


Figure 1 A schematic illustration for ATR-FTIR for the *in situ* study of the latex film-formation process.

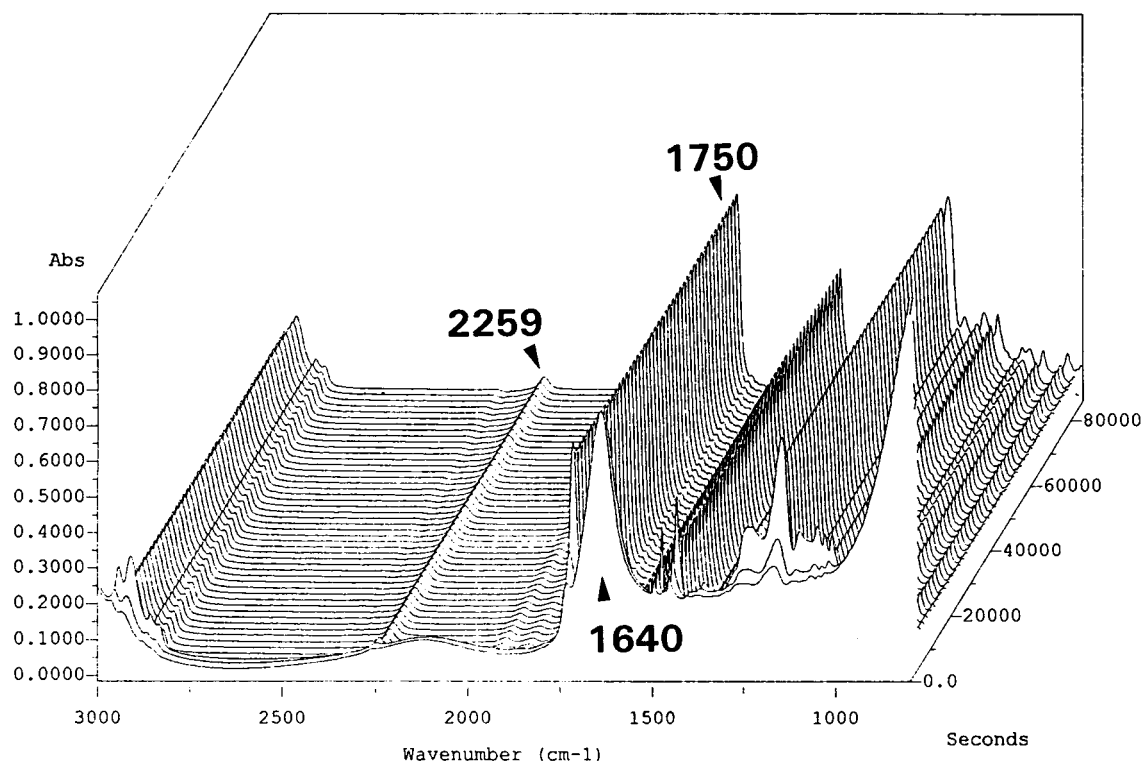


Figure 2 Time-dependent ATR-FTIR spectra recorded during the film-formation process for 1/1 (w/w) PS/P(BA-TMI) core/shell latex over a 24-h period.

exhibit relatively low absorbance values due to their low concentration at this stage. With the evaporation of water from the latex during film formation, the absorbance for the water peak decreases rapidly to a minimum value, while the absorbances for both organic peaks increase to their respective maximum values. The film-for-

mation process could be roughly divided into two stages by monitoring the different decreasing rates of water absorbance during the drying process. The rapid decrease in water peak absorbance in the first stage of film formation from time 0 to 60 min indicates that water, as the continuous phase of the system, evaporates quickly. When the latex system becomes highly concentrated and massive coalescence is occurring among latex particles, the continuous phase changes from a water phase to a polymer phase. At the same time, the absorbance for the carbonyl (—CO—) groups, which should not be consumed by any reaction during the film-formation process, reaches its maximum absorbance value and remains at this value thereafter. Thus, it is reasonable to define this time as the point at which an extremely concentrated latex changes into a latex film. In other words, the maximum absorbance of the carbonyl group could be used to represent the carbonyl concentration in the latex right before the formation of the latex film. The absorbance for the isocyanate group, on the other hand, reaches its maximum value at the same time (about 60 min) as the carbonyl group, decreases rapidly in a short time period, and then decreases gradually there-

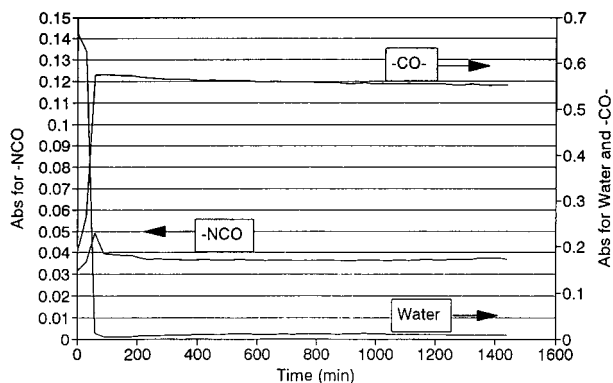


Figure 3 Profiles for the intensities of water, carbonyl (—CO—), and isocyanate (—NCO—) functional groups at wavenumbers of 1640, 1750, and 2259 cm^{-1} , respectively, from ATR-FTIR measurements during a 24-h film-formation process.

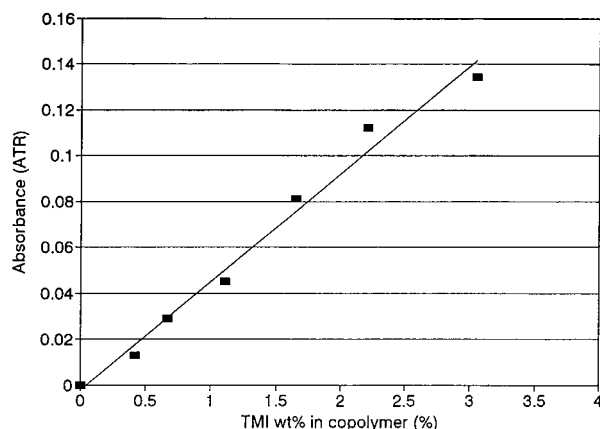


Figure 4 ATR-FTIR absorbance calibration curve for the isocyanate groups in P(BA-TMI) copolymer and its corresponding weight concentration as determined by titration.

after. This decrease suggests that the isocyanate moieties are consumed by chemical reactions, i.e., hydrolysis and addition reactions between the isocyanate groups and newly formed amine groups from the hydrolysis, during this stage. By setting up the analysis method shown above, the relative consumption of the isocyanate groups during the film-formation process can be monitored. However, to quantitatively understand the consumption mechanism for the isocyanate groups during both the polymerization and film-formation processes, a calibration between the ATR-FTIR absorbance and absolute concentration of isocyanate groups is needed. It should be noted that it is possible for reactions of the —NCO groups to occur with hydroxyl (generated from reactions of the sulfate radicals from the initiator with water) or carboxyl groups (from oxidation of the hydroxyl groups) during the polymerization itself. These reactions may also result in the consumption of the NCO groups. However, previous experiments¹⁶ have shown that only a small amount (i.e., less than 2%) of the —NCO groups are consumed during the polymerization for the lower TMI concentrations (i.e., 2 wt % TMI), and, therefore, it is believed that the vast majority of the —NCO group consumption results from hydrolysis reactions.

Figure 4 shows the ATR-FTIR absorbance calibration curve and the absolute concentration of isocyanate groups as obtained by titration. A well-fitted linear calibration relationship was obtained. It should be emphasized that all macrogel was removed from the sample solutions prior to titration, which accounted for the sharp end-

points. Therefore, any residual gel did not significantly impact on the calibration curve.

To investigate the influence of the structure of the latex particles on the consumption of isocyanate groups during the polymerization and film-formation process, a series of latexes with shells of varying thickness (in which isocyanate groups were incorporated) were prepared according to recipes shown in Runs 1–3 in Table I. To avoid the formation of any core/shell interphase zone and obtain a relatively sharp core/shell interface, a polystyrene seed latex with a narrowly distributed particle diameter of 93 nm (PDI = 1.004) was used to carry out the second-stage polymerization of BA/TMI (97.1/2.9, w/w). In this way, the theoretical shell thickness could be controlled and calculated in various PS/P(BA-TMI) latexes with different core/shell ratios. A P(BA-TMI) latex (Run 4 of Table I) with a particle diameter of 180 nm was also used to represent the largest “shell” thickness of 90 nm (=particle radius). Figure 5 shows the results. The calculated shell thickness for the PS/P(BA-TMI) latexes with core/shell ratios of 1/2, 1/1, and 1/0.5 (w/w) are 20, 12, and 7 nm, respectively.

The percentages of NCO groups remaining at the maximum of each curve were obtained from values determined by the calibration curve shown in Figure 4 divided by the total amount of TMI which was initially added. First of all, from the percentage values shown at the maximum points for each curve, it is seen that the isocyanate groups present in the latex did undergo some degree of hydrolysis before the latex films were formed. Since these experiments were carried out a short time (less than 1 day) after the latexes were prepared, these values should indicate the percentage of isocyanate moieties remaining right after the emulsion polymerization was complete. Obvious differences in these values were seen for each system. It seems that the larger the domain size or the shell thickness in which the isocyanate moieties are incorporated, the lower the percentage of the isocyanate groups which were hydrolyzed, and the greater number of isocyanate groups which remained in the latex particles after the polymerization. The hydrolysis percentage of the isocyanate groups after an emulsion polymerization is also dependent on some other polymerization parameters, such as temperature, pH value, and the mode of addition of the monomers, i.e., batch or semicontinuous. It was found that the average percentage of hydrolysis of isocyanate groups from the TMI monomer after a 10-h batch

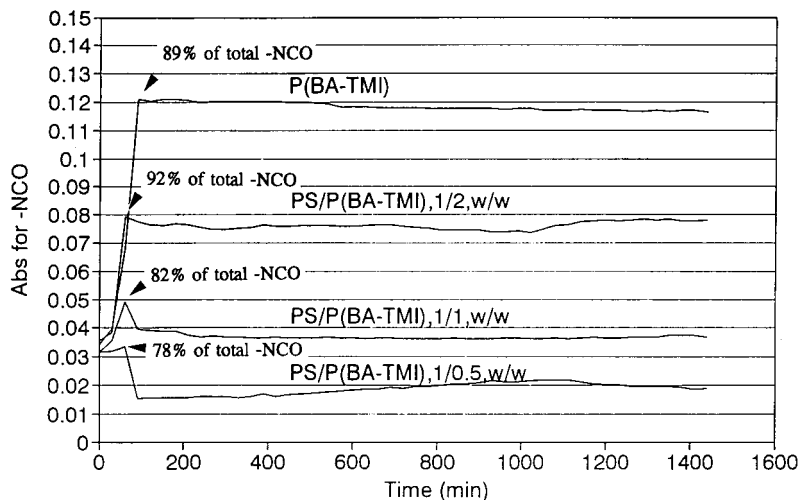


Figure 5 ATR-FTIR absorbance profiles of the isocyanate group in P(BA-TMI) (180 nm) latex and a series of PS/P(BA-TMI) core/shell latexes with shell thicknesses of 20, 12, and 7 nm obtained during a 24-h film-formation process.

emulsion polymerization of BA/TMI (3 wt % TMI) at 40°C is around 5%.

Compared to the percentage of hydrolysis (5%) after a batch emulsion polymerization, greater degrees of hydrolysis were found after emulsion polymerizations using a semicontinuous mode of addition of monomers, as shown in Figure 5. In a batch polymerization system, due to the hydrophobicity and the relatively high reactive rate (compared to BA monomer) of the TMI monomer, isocyanate moieties from the TMI units would tend to more likely be distributed in the inner side of the monomer-swollen polymer particles throughout the process of batch emulsion polymerization. On the other hand, during an emulsion polymerization using a semicontinuous mode of addition of monomers under monomer-starved conditions, the TMI units are distributed more uniformly in the latex particle and have a longer time to be exposed to the particle/water interfaces where the water concentration is much higher than the inner side of the latex particle. The dependence of the extent of hydrolysis on the shell thickness indicates that the isocyanate moieties in a "thick shell" would tend to stay far from the highly polar particle/water interface due to the relatively high hydrophobicity of the TMI unit, which could decrease the chance of exposure to water. In contrast, in a "thin shell," there is not much space for the isocyanate groups to stay away from the interface, and as a result, a greater degree of hydrolysis of the isocyanate groups would take place. However, despite the lower percentage

values of hydrolysis for the case of the thicker shell system, i.e., 1/2 core/shell ratio, the absolute amount of isocyanate groups which is hydrolyzed is still greater than that found for the thin shell system, i.e., 1/0.5 core/shell ratio, due to the larger amount of the total isocyanate groups. This is understandable because the thick shell had to grow gradually. During this shell growth process, more hydrolysis occurred at the beginning stages when the shell was still thin. A decreasing amount of hydrolysis would take place as the shell become thicker.

After the maximum absorbance values for each curve shown in Figure 5 were attained, the latex systems entered the film stage where polymer started to become the continuous phase. In this stage, although the bulky water phase has disappeared, large numbers of water molecules are still present in the film and are most likely present in the interfaces of the coalesced particles where surfactant molecules are localized. These water molecules would undergo diffusion in the latex film. This diffusion is restricted by the high viscosity of the polymer phase and the high polarity of surfactant, which should have a low tendency to diffuse. For this reason, if an isocyanate moiety is present at this interface, it would be in contact with water molecules for a much longer period of time since the mobilities for both of these species are relatively low. It is noted that relatively large amounts of isocyanate groups were consumed in a short period of time (~ 60 min) after the maxima of the curves for both of the "thin shell" la-

texes were reacted. The absorbances of isocyanate groups for PS/P(BA-TMI) latexes with core/shell ratios of 1/1 and 1/0.5 decreased 20 and 50%, respectively. The obvious higher reaction rates (compared with the rate during the emulsion polymerization) indicate that the water concentration in the interface regions between those coalesced particles is considerably higher during this short time period, i.e., the beginning of the second stage of latex film formation. Taking the latex system with the PS/P(BA-TMI) ratio of 1/1 as an example, the 20% decrease in isocyanate groups (i.e., absorbance of —NCO reduced from 0.05 to 0.04) can be assumed to result from the reactions of those isocyanate moieties that are distributed in a surface layer of the particle which takes up 20% of the entire volume of the shell. It can be easily calculated that the thickness of the surface layer is about 2 nm. Since the thickness of this "high water zone" is independent of particle size or shell thickness, the same 2 nm layer would take a higher volume fraction for a "thin shell" than for a "thick shell" and results in higher percentage of hydrolysis at this stage of the film formation. Since the hydrolysis at this stage occurs primarily at the interfaces of the latex particles, interfacial crosslinks would be formed via crosslinking reactions between isocyanate groups and amine groups that resulted from those hydrolysis reactions. For the same reason, if the isocyanate moieties are not close to these layers, which is the cases for the nonstructured latex particles with large particle size or "thick shell" particles, hydrolysis and interfacial crosslinking could not occur in a short time. Obvious differences are observed for each system shown in Figure 5. For the P(BA-TMI) latex system, the amount of isocyanate groups decreased only slightly when the film was formed. For the other three core/shell latex systems, the percentages of isocyanate groups hydrolyzed after the film formation, based on the amounts showed at the maximum absorbance values, are about 5, 20, and 50% for 20, 12, and 7 nm shell thickness, respectively.

SUMMARY

In summary, the consumption of isocyanate groups could occur either during polymerization and/or

the film-formation process. In most of the systems studied, the percentage of isocyanate groups consumed during the polymerization stage is less than 5% for batch emulsion polymerization and about 10–20%, depending on the particle size or the shell thickness in which the isocyanate groups are incorporated, for semicontinuous emulsion polymerizations under monomer-starved conditions. During the process of film formation, higher percentages of isocyanate moieties could be consumed for a thin shell layer latex system, some of which form interfacial crosslinks. When the particle size is larger than 60 nm, or the shell layer is thicker than 30 nm, interfacial crosslinking from the reactions of isocyanate groups would not take place in a short period of time.

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