

Crosslinking of Isocyanate Functional Acrylic Latex with Telechelic Polybutadiene. III. Application of a Diffusion Model

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ABSTRACT: The diffusion and reaction of amino-telechelic polybutadiene (PBD-NH₂) in poly(styrene/*n*-butyl acrylate/TMI®) (PSBT) was studied. A monodisperse poly(St/BA/TMI) seed latex was prepared by semicontinuous emulsion polymerization. Two core/shell latices were also prepared semicontinuously, using the seed latex as the core and poly(St/BA) as the shell. These monodisperse latices were mixed with equivalent amounts of the telechelic PBD-NH₂ artificial latex before casting into films. The consumption of the TMI in these films was monitored by FTIR as a function of time and the NH₂/TMI ratio. The results showed that without the PSB shell, the PSBT particles (80 nm radius) could be penetrated by the PBD-NH₂ completely. A 24 nm PSB shell was found to act effectively as a barrier to preventing the penetration of the PBD-NH₂ inside the particles. This was consistent with previous TEM results, indicating that the crosslinking between the isocyanate in the PSBT particles and the amine in the PBD-NH₂ particles provided the driving force for the chain diffusion. A diffusion model was established for the PSBT/PBD-NH₂ system. Assuming steady-state diffusion, the effective diffusion coefficients were calculated based on the experimental data. This led to the estimation of the surface coverage of the PBD-NH₂ on the PSBT particles in the latex films. A film formation and crosslinking mechanism was proposed for the PSBT/PBD-NH₂ latex blend system. In the absence of crosslinking reactions, the two incompatible polymers tended to completely phase separate during the film formation. However, with the crosslinking reactions, the PBD-NH₂ will be bound to the PSBT particle surfaces, forming a PSBT-PBD copolymer interphase. This interphase facilitates the diffusion of the PBD-NH₂ into the PSBT particles. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 985–993, 1998

Key words: latex blend; telechelic polybutadiene; reaction-diffusion; crosslinking

INTRODUCTION

The development of an ambient curable, isocyanate-functional acrylic latex blend consisting of a poly(styrene/*n*-butyl acrylate/TMI® (dimethyl

meta-isopropenyl benzyl isocyanate, Cytec Industries)) (PSBT) latex and an amino-telechelic polybutadiene (PBD-NH₂) latex was reported previously.^{1,2} The transmission electron micrographs revealed the morphology of the PMBT/PBD-NH₂ latex films, the PBD-NH₂ covered the surface of the PMBT particles.² Since the reaction between the TMI isocyanate and the PBD-NH₂ is much faster than the mutual diffusion of the two species, the crosslinking process was considered to

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be diffusion-controlled. A theoretical model to describe the diffusion process was derived based on one initially developed to describe the burning of charcoal³ as follows. Consider a partially reacted particle. Both reactant A and the boundary of the unreacted core move inward toward the center of the particle. With the steady-state assumption, the rate of reaction of A at any time t is given by its rate of diffusion to the reaction surface, or

$$-dN_A/dt = 4\pi r^2 Q_A = 4\pi R^2 Q_{As} = 4\pi r_c^2 Q_{Ac} \quad (1)$$

where N_A is the moles of fluid reactant A ; Q_A is the flux of A through a surface of any radius r ; Q_{As} is the flux of A through the exterior surface of the particle with a radius of R ; and Q_{Ac} is the flux of A through the reaction surface with a radius of r_c (this will be described later in Fig. 4).

Using Fick's law, we have

$$Q_A = D_e(dC_A/dr) \quad (2)$$

where D_e is the effective diffusion coefficient of the reactant (PBD-NH₂) in the layer containing reacted material (analogous to the ash layer). Combining eqs. (1) and (2),

$$-dN_A/dt = 4\pi r^2 D_e(dC_A/dr) = \text{constant} \quad (3)$$

Integrating across the reacted layer from R to r_c ,

$$-dN_A/dt(1/r_c - 1/R) = 4\pi D_e C_{As} \quad (4)$$

This model had been previously applied to simulate alkali-neutralization of carboxylated latex particles⁴; and it was found that the diffusion coefficient, D_e , decreased as a function of diffusion time. A similar diffusion model for the PSBT/PBD-NH₂ system will be applied to aid in the understanding of the film formation and cross-linking mechanism as proposed in the present article.

EXPERIMENTAL

Materials

Styrene (St, Aldrich) and *n*-butyl acrylate (BA, Aldrich) monomers were passed through inhibitor removal columns (Aldrich Cat. #30, 631-2 for BA and 30, 632-0 for St) before use. Dimethyl meta-isopropenyl benzyl isocyanate (TMI®, Cytec In-

Table I Recipe for Preparation of Monodisperse PSBT Latex by Semicontinuous Emulsion Polymerization at 40°C

Component	Seed (g)	Feed (g)	Total	
			(g)	% on Oil Phase
St	4.000	4.000	8.000	48.25
<i>n</i> -BA	4.000	4.000	8.000	48.25
TMI	0.2058	0.2058	0.4115	2.50
EGDM	0.0850	0.0850	0.1700	1.00
AMA80 ^a	0.6000	0	0.6000	3.61
K ₂ S ₂ O ₅ (reductant)	0.1200	0.0800	0.2000	1.20
K ₂ S ₂ O ₈ (oxidant)	0.1200	0.0800	0.2000	1.20
DDI H ₂ O	80.00	20	100	—

^a AMA80: Aerosol MA80 anionic surfactant, sodium dihexyl sulfosuccinate, 78–80% in a mixture of isopropanol and water, CMC = 24.5 mM = 1.19%, Cytec Industries.

dustries) and ethylene glycol dimethacrylate (EGDM; 98% Aldrich), Aerosol MA (sodium dihexyl sulfosuccinate, Cytec Industries), potassium persulfate (K₂S₂O₈, Aldrich), and potassium metabisulfite (K₂S₂O₅, Aldrich) were used as received. Water was distilled and deionized (DDI).

Preparation of Monodisperse PSBT Latex (PSBT160)

Fifty percent of the monomers (styrene, *n*-butyl acrylate, TMI, and ethylene glycol dimethacrylate, EGDM), 100% of the surfactant (Aerosol MA 80), 60% of the initiator (potassium metabisulfite and potassium persulfate), and 80% of the water were added to a 250 mL flask fitted with a stirrer and a condenser under a nitrogen atmosphere at 40°C. The rest of the recipe was fed after 30 min, using three syringes, one for the monomers, one for the reductant/H₂O, and the other for the oxidant/H₂O, at a rate of 0.08 mL/min using a syringe pump (Harvard Apparatus, Model 22). The recipe is listed in Table I. EGDM (1.0%) based on monomers was used to moderately crosslink the PSBT copolymer to prevent migration of the TMI into the subsequent shell layer. After the completion of the feed, the polymerization was continued until no measurable monomers remained in the system [checked by gas chromatography (GC)].

Table II Recipe for the Preparation of Core/Shell Latices by Seeded Emulsion Polymerization at 40°C

Component	PSBT160-PSB24	PSBT160-PSB42
PSBT160 seed (g)	30.00*	20.00*
St (g)	2.500	3.400
BA (g)	2.500	3.400
Aerosol MA80 (g)	0.1000	0.1500
Potassium metabisulfite (g)	0.1300	0.1600
Potassium persulfate (g)	0.1300	0.1600
DDI Water (g)	22.00	30.60

* 30.00 g of PSBT160 latex contained 4.269 g solids; 20.00 g of PSBT160 latex contained 2.846 g solids.

Preparation of PSBT-PSB Core/Shell Latices (PSBT160-PSB24 and PSBT160-PSB42)

The PSBT160 seed latex and Aerosol MA80/H₂O were placed in a flask with a stirrer and a condenser, under nitrogen atmosphere, at 40°C. The monomers, the reductant/H₂O, and the oxidant/H₂O were fed with three syringes at a rate of 0.08 mL/min. The completion of the polymerization was checked by GC. The recipes used are shown in Table II.

RESULTS AND DISCUSSION

Monodisperse PSBT Latex

The PSBT seed latex (designated PSBT160) prepared by semicontinuous emulsion polymeriza-

tion of St, BA, and TMI had a narrow particle size distribution as indicated by the statistics given in Table III. Two core/shell structured PSBT/PSB latex particles (designated PSBT160-PSBS24 and PSBT160-PSB42) with different shell thicknesses were prepared from this seed so that the isocyanate groups would be contained in a core; these will be used to study the extent of chain interdiffusion of the telechelic PBD through shell layers of varying thickness. The characteristics of the three latices PSBT160, PSBT160-PSBS24, and PSBT160-PSB42, are summarized in Table III. The predicted diameters of the core/shell particles were calculated with eq. (5):

$$D_2/D_1 = (1 + w_2\rho_2/w_1\rho_1)^{1/3} \quad (5)$$

where D_1 and D_2 are the diameters of the core particles and the core/shell particles, respectively; w_1 and w_2 are the masses of the core polymer(s) and shell polymer(s); and ρ_1 and ρ_2 are the densities of the core polymer(s) and the shell polymer(s).

Crosslinking Between PSBT and PBD-NH₂

In order to study the reaction of the amino-terminated telechelic PBD with the TMI in the three latices described above, blends of the two latices were prepared in which the amounts of the PSBT latices were adjusted to maintain the same TMI/PBD-NH₂ ratios; that is, the amount of the TMI-containing particles was the same in terms of the

Table III Characteristics of PSBT160, PSBT-160-PSB24, and PSBT160-PSB42 Latices

Characteristic	PSBT160	PSBT160-PSB24	PSBT160-PSB42
% Solids	14.23	15.44	16.93
% TMI based on solids ^a	2.24	1.05	0.67
Particle size determined by CHDF (nm)			
D_n	159	209	243
D_w	169	211	247
PDI	1.05	1.02	1.02
D_v	161	208	244
Particle size calculated (nm)	—	210	245
Thickness of the shell (nm)	0	24	42
Volume ratio of core/shell	1/0	1/1.24	1/2.53

^a The %TMI based on monomers in the recipe was 2.35% for the PSBT160 latex. Assuming 5% of the TMI was lost due to hydrolysis during the polymerization, the %TMI based on solids in the latex was 2.24%.

Table IV PSBT/PBD-NH₂ Latex Blends

PBD-NH ₂ /PSBT160 (g/g)	PBD-NH ₂ /PSBT160-PSB24 (g/g)	PBD-NH ₂ /PSBT160-PSB42 (g/g)	NH ₂ /TMI (mol/mol)
0/0.250	0/0.520	0/0.745	0
0.100/0.250	0.100/0.520	0.100/0.745	0.55
0.200/0.250	0.200/0.520	0.200/0.745	1.1
0.300/0.250	0.300/0.520	0.300/0.745	1.66
0.500/0.250	0.500/0.520	0.500/0.745	2.78

number of particles while their total mass increased with increasing size from the seed to the core/shell particles with varying shell thickness. For example, 1 g of the PSBT160 particles was equivalent to 2.075 g of the PSBT160-PSB24 particles and 2.979 g of the PSBT160-PSB42 particles; all three were comprised of 6.51×10^{13} particles.

Several series of latex blends were prepared according to Table IV, where the NH₂/TMI ratio was varied for all three TMI-containing latices. The preparation and characterization of the PBD-NH₂ artificial latex was reported previously.¹ The 15 latex blends listed in Table IV were cast on FTIR disks and dried at room temperature. FTIR spectra were taken at different time intervals to determine the consumption of NCO in the films as a function of time. The results are shown in Figures 1–3. It is clear from these plots that (1) the consumption of NCO by the amino-PBD was most significant within the first 24 h, after which the films were basically dry, and the decrease in the NCO content was significantly slowed; (2) the higher the NH₂/TMI ratio, the more NCO was

consumed; (3) PBD reacted with NCO more readily in the case of the PSBT160 particles than in the core/shell particles (PSBT160-PSB24 and PSBT160-PSB42); the thicker the shell, the less NCO was consumed (for example, when NH₂/TMI = 1.66 (mole ratio), more than 90% of the NCO was consumed in the PSBT160 particles after 5 days, while only ~ 50% of the NCO was consumed in the PSBT160-PSB24 particles, and ~ 30% in the PSBT160-PSB42) particles; (4) given a sufficient amount of the PBD-NH₂, the mutual diffusion of the two types of polymer allowed reaction of all NCO groups with the NH₂. This is shown in Figure 1 with the curve representing a NH₂/TMI mole ratio of 2.78. However, when a PSB shell was present, the TMI was not consumed completely even at the highest NH₂/TMI ratio, even though the shells were far thinner than 80 nm, the radius of the core particles (PSBT160). When these results are correlated with the TEM morphology studies in the previous article, it is clear that the PBD-NH₂ could penetrate the 80 nm radius of the PSBT160 particles because the reaction between the NH₂ and the TMI provided

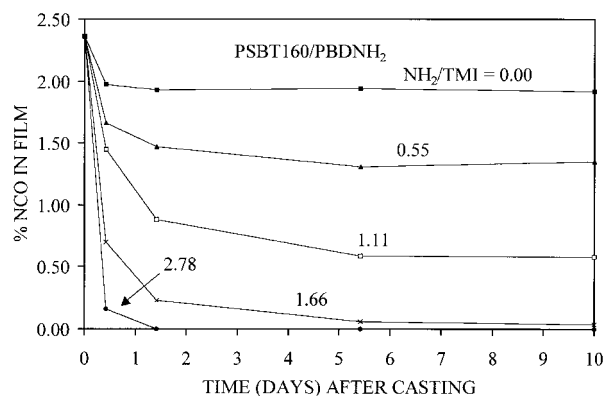


Figure 1 Percent NCO in PSBT160 and PSBT160/PBD-NH₂ latex films as a function of time and NH₂/TMI ratio as determined by FTIR spectroscopy.

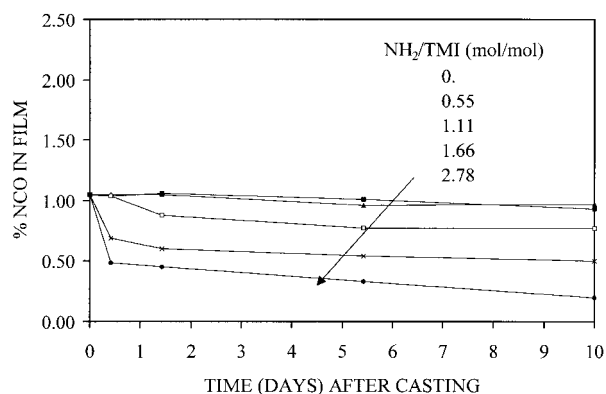


Figure 2 Percent NCO in PSBT160-PSB24 and PSBT160-PSB24/PBD-NH₂ latex films as a function of time and NH₂/TMI ratio.

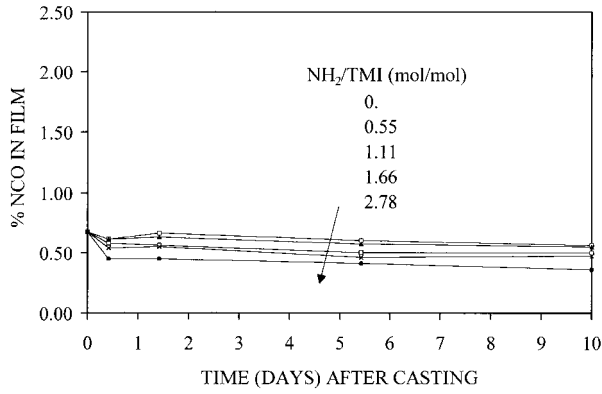


Figure 3 Percent NCO in PSBT160-PSB42 and PSBT160-PSB42/PBD-NH₂ latex films as a function of time and NH₂/TMI ratio.

the driving force, while the PBD-NH₂ had more difficulty penetrating the shells on the PSBT160-PSB24 and PSBT160-PSB42 particles because this driving force was not as strong.

The diffusion process of the PSBT160/PBD-NH₂ can be illustrated as in Figure 4, where the PBD-NH₂ forms a continuous phase on the PSBT particle surface. The PBD-NH₂ diffuses into the PSBT particle and reacts with the TMI in it, forming a crosslinked layer having a thickness of $(R - r_c)$, where R is the particle radius (80×10^{-7} cm); and r_c is the shrinking radius of the unreacted core. When the diffusion model described above is applied to the PSBT160/PBD-NH₂ system, the diffusion coefficient of the PBD-NH₂ in the crosslinked layer of the PSBT particles, D_e , can be expressed as

$$D_e = [1/(4\pi C)](dN_T/dt)(1/r_c - 1/R) \quad (6)$$

where C is the concentration of the PBD-NH₂ on the PSBT particle surface, N_T is the moles of the TMI in one PSBT particle, and t is the time of the diffusion process. N_T can be expressed as

$$N_T = W_T/M_T = (1/M_T)(4/3)\pi R^3\rho T \quad (7)$$

where W_T is the weight of the TMI in one particle; M_T is the molecular weight of the TMI, 201.3 g/mol; ρ is the density of the poly(St/BA/TMI), 1.05 g/cm³; and T is the TMI content (g) per gram of solids in the PSBT particle (unitless), obtained from the experimental data. Thus,

$$dN_T/dt = (1/3M_T)4\pi R^3\rho(dT/dt) \quad (8)$$

Substituting (8) into (6), we have

$$D_e = [R^3\rho/(3M_T C)](dT/dt)(1/r_c - 1/R) \quad (9)$$

From a mass balance, we also have

$$\begin{aligned} \Delta T = T_0 - T &= 4\pi n \rho_T \int_{r_c}^R r^2 dr \\ &= (4\pi/3)n \rho_T (R^3 - r_c^3) \end{aligned} \quad (10)$$

where T_0 is the initial TMI content (g) per gram of solids (at $t = 0$ or $r = R$); ΔT is the TMI consumption (g) per gram of solids at time t (unitless); n is the number of particles per gram of solids (1/g):

$$n = 3/(4\pi R^3\rho) \quad (11)$$

ρ_T is the TMI density in the particle solids (g/cm³):

$$\rho_T = T_0\rho \quad (12)$$

From the above three equations, we obtain

$$\begin{aligned} r_c &= [R^3 - 3\Delta T/(4\pi n \rho_T)]^{1/3} \\ &= R(1 - \Delta T/T_0)^{1/3} = R(T/T_0)^{1/3} \end{aligned} \quad (13)$$

Thus, the diffusion coefficient can be expressed as

$$D_e = [R^2\rho/(3M_T C)](dT/dt)[(T_0/T)^{1/3} - 1] \quad (14)$$

While T_0 , T , and dT/dt are obtained from the

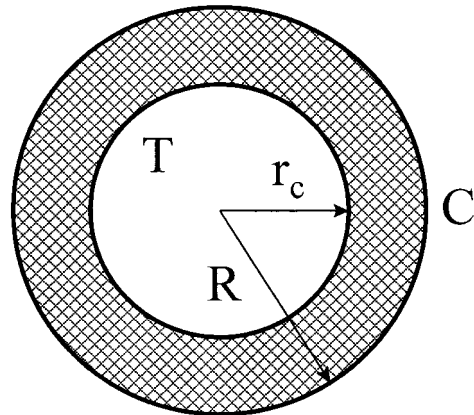


Figure 4 Diffusion model of the PSBT160/PBD-NH₂ system. T is the TMI content (g) per gram of solids; C is the concentration of the PBD-NH₂ on the PSBT particle surface; R is the particle radius; r_c is the shrinking radius of the unreacted core.

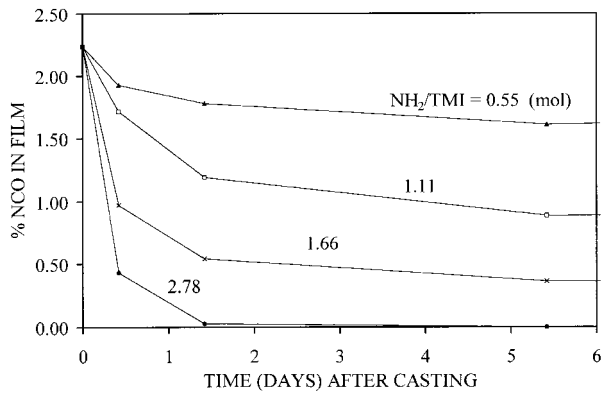


Figure 5 Percent NCO (%*T*) as a function of time for the PSBT160/PBD-NH₂ latex films.

experimental data, the value of *C* has yet to be defined. Let us tentatively assume that the PSBT160 particles are fully covered by the PBD-NH₂. During the diffusion process, the total amount of the PBD-NH₂ decreases. Since the PBD-NH₂ forms a continuous phase on the PSBT particles, the decrease in the PBD-NH₂ only decreases the domain size of the PBD-NH₂ phase; the concentration of the PBD-NH₂ does not change. Thus, the *C* can be considered to be a constant and can be calculated as for a pure polybutadiene:

$$C = d/M = 0.95/3100 = 3.06 \times 10^{-4} \text{ (mol/cm}^3\text{)} \quad (15)$$

where *d* is the density of polybutadiene (0.95 g/

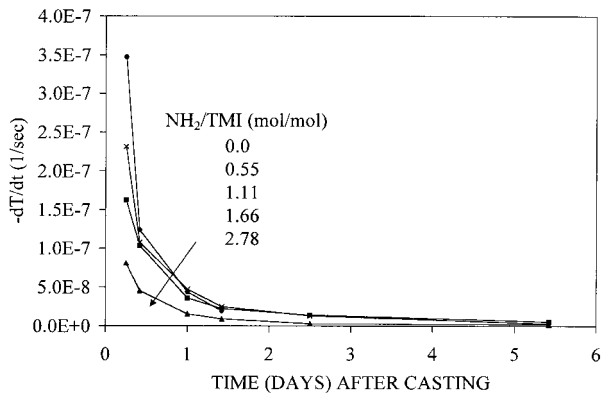


Figure 6 *dT/dt* as a function of time for the PSBT160/PBD-NH₂ latex films.

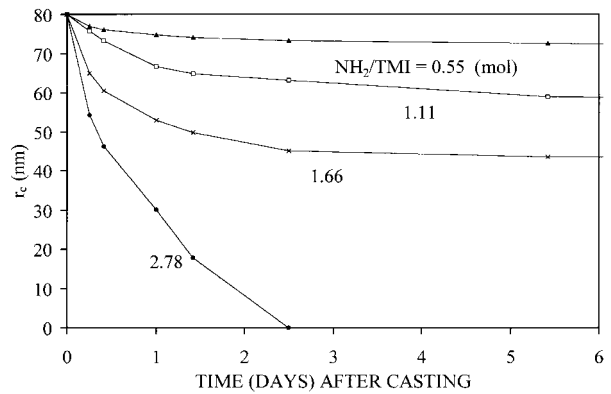


Figure 7 *r_c* as a function of time for the PSBT160/PBD-NH₂ latex films.

cm³); and *M* is the molar mass of the PBD-NH₂ (3100 g/mol).

By deducting the disappearance of the NCO's by water hydrolysis (deducting the %NCO of the curve representing NH₂/TMI = 0 from the rest of the curves in Fig. 1), the percent *T* values corresponding to the above equations can be plotted as a function of time, as in Figure 5. The *dT/dt* values as a function of time (obtained from the slopes of the curves in Fig. 5), and the *r_c* values as a function of time, are plotted in Figure 6 and Figure 7, respectively. Finally, the diffusion coefficients, *D_e*, are calculated and plotted in Figure 8.

It can be seen from Figure 8 that as the concentration of the PBD-NH₂ decreases (decreasing NH₂/TMI ratio), the diffusion coefficient decreases. However, by definition, *D_e* is independent of the concentration of the diffusing component.

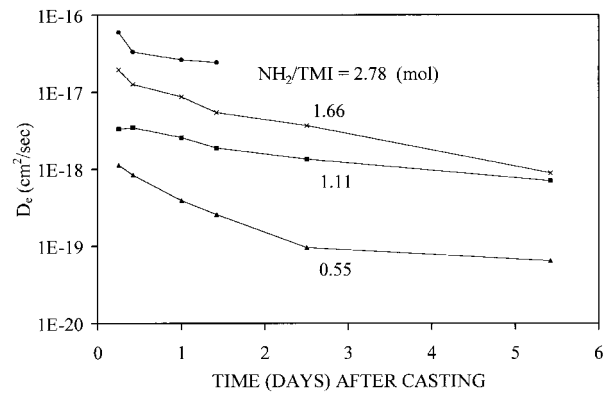


Figure 8 Diffusion coefficients as a function of time for the PSBT160/PBD-NH₂ latex films.

Table V Surface Coverage of PBD-NH₂ on PSBT160 Particles

NH ₂ /TMI (mol)	Effective PBD Surface Concn. ($\times 10^5$ mol/cm ³)	% Surface Coverage
0.55	0.533	2
1.11	2.57	8
1.66	9.67	32
2.78	30.6	100 (assumed)

This contradiction is actually due to the improper assumption that in all cases the PSBT particles are fully covered by the PBD-NH₂, with a concentration, C , of 3.06×10^{-4} mol/cm³. The TEM morphology studies presented previously² showed that only at high PBD-NH₂/PMBT ratios (≥ 0.345 weight ratio or ≥ 3.0 mole ratio) were the PMBT particles fully covered by the PBD-NH₂. Thus, in the present PSBT160/PBD-NH₂ system, only the curve where NH₂/TMI equals 2.78 is close to full coverage of the PBD-NH₂ on the PSBT160 particles. In the cases where NH₂/TMI equals 1.66, 1.10, and 0.55, there was not enough PBD-NH₂ to completely cover the PSBT160 particles, and thus the "effective" surface concentration of the PBD-NH₂, C , was lower than 3.06×10^{-4} mol/cm³. Assuming that the diffusion coefficient was actually the same for all four NH₂/TMI ratios and equal to that for the 2.78 NH₂/TMI ratio ($D_e \sim 10^{-17}$ cm²/s⁻¹), the "effective" surface concentration of the PBD-NH₂ in the other three cases can be calculated and from these values the percentage surface coverage can be estimated. Table V lists the effective surface concentration, C , assuming it to be 3.06×10^{-4} mol/cm³ for the 2.78 NH₂/TMI ratio. The estimated percent surface coverages of the PSBT160 particles by the PBD-NH₂ at the four NH₂/TMI ratios is also given. This is an approximation of the surface coverage, since even for the NH₂/TMI ratio of 2.78, the effective concentration of the PBD-NH₂ may still be less than 3.06×10^{-4} mol/cm³ and the coverage may be less than 100%. The decrease of D_e as a function of time in the curve obtained for the 2.78 NH₂/TMI ratio (Fig. 8) may be due to the increasing diffusional resistance of the crosslinked layer toward the telechelic PBD, but may also be due to a decrease in the concentration of the PBD-NH₂ as the phase separation of the two polymers can also progress with time. Nevertheless, the results presented in Table V are still interesting in that

Table VI Comparison of Self-Diffusion Coefficients of Polystyrene

Temp. (°C)	D_e (cm ² /s)
120	1.3×10^{-17}
130	3.7×10^{-16}
135	2.4×10^{-16}
136	2.0×10^{-15}
160	4.8×10^{-14}
212	6.6×10^{-12}

See ref. 5.

they show how the surface coverage may be substantially decreased when the NH₂/TMI ratio is decreased.

The magnitude of the estimated D_e values is on the order of 10^{-17} cm²/s⁻¹. The self-diffusion coefficients of polystyrene at several temperatures have been compared,⁵ as shown in Table VI. Similar results were found for the deuterated polystyrene/protonated polystyrene system.⁶ From these data the diffusion coefficient at 25°C could be extrapolated to be $\sim 10^{-25}$ cm²/s⁻¹. Obviously, the diffusion coefficient depends upon the nature of the material. Poly(St/BA/TMI) and polybutadiene have much lower T_g 's than polystyrene; thus, it is reasonable that D_e for the PSBT/PBD-NH₂ system should be higher than for polystyrene.

The film forming process of the PSBT/PBD-NH₂ latex blend system can be illustrated as in Figure 9. The first stage in the process, water evaporation, is the same as for any common latex system described in the literature. The differences arise in the second stage. For common latex sys-

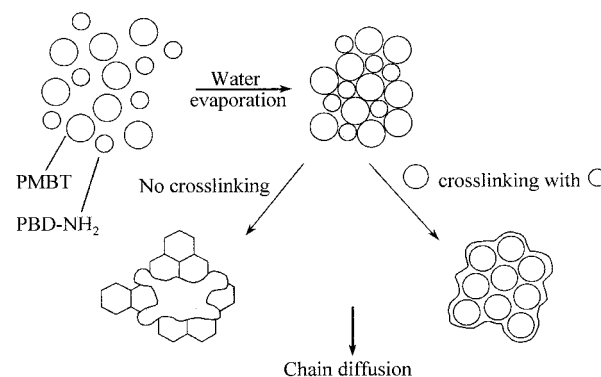


Figure 9 Schematic representation of the film formation process in the PSBT (or PMBT)/PBD-NH₂ latex blends.

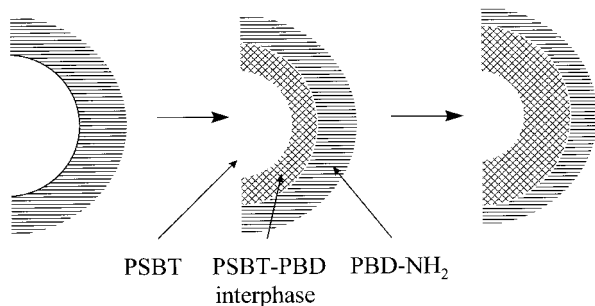


Figure 10 Schematic representation of the crosslinking and diffusion process in the PSBT/PBD-NH₂ system in which the PBD-NH₂ chains diffuse into a PSBT-PBD copolymer interphase.

tems, all particles are basically the same and easily form a honeycomb-patterned structure. For the PSBT/PBD-NH₂ blend, however, the PBD-NH₂ artificial latex particles interfere with the packing of the acrylic particles. The PBD-NH₂ polymer is a viscous fluid and its particles are highly deformable and are squeezed by the harder acrylic particles during the drying and packing process. If there is no chemical reaction between the polymer in the acrylic particles and the PBD-NH₂ polymer, the PBD-NH₂ particles tend to coalesce with themselves, forming segregated domains in the acrylic matrix. When there is chemical reaction between the acrylic and the PBD-NH₂ polymers, the squeezed PBD-NH₂ particles remain in between the acrylic particles due to the chemical bonding between the PBD-NH₂ and the acrylic particles. This chemical bonding tends to prevent the PBD-NH₂ particles from coalescing by themselves and forming separated domains. Once the chemical bonds are formed, an interphase is established which is neither the PSBT polymer nor the PBD-NH₂ polymer alone, but a PSBT-PBD copolymer. This copolymer is more compatible with the PSBT than the PBD-NH₂, and likewise more compatible with the PBD-NH₂ than the PSBT. While it is difficult for the PBD-NH₂ to diffuse into the PSBT polymer, it is certainly easier for it to diffuse into the copolymer. Once a PBD-NH₂ chain penetrates the copolymer interphase, it reacts further with an NCO in the PSBT polymer forming more copolymer, thus increasing the thickness of the interphase. This stage of film formation is different from the common mechanism described in the literature, for it is not simply chain interdiffusion between neigh-

boring particles but a process of interfacial crosslinking and interphase formation. The PBD-NH₂ polymer chains do not diffuse far into the PSBT polymer directly, but primarily diffuse into the interphase copolymer. Figure 10 illustrates this process. The TEM micrograph of cryoultramicrotomed sections of the PMBT/PBD-NH₂ latex film in Figure 11 clearly shows the stained dark area of the PBD-NH₂, the unstained bright area of the PMBT, and the partially stained gray area of the PMBT-PBD-NH₂ interphase.

CONCLUSIONS

A diffusion model was established for film crosslinking in the PSBT160/PBD-NH₂ system. Assuming steady-state diffusion, the diffusion coefficients were calculated based on experimental data. This led to a rough estimation of the surface coverage of the PBD-NH₂ on the PSBT160 particles in the latex films. It was found that while the PSBT160 particles were completely covered with the PBD-NH₂ when the NH₂/TMI ratio was above 2.78, only 32% of the PSBT particle surface area was covered by the PBD-NH₂ when the NH₂/TMI ratio was 1.66. The surface coverage was even less when the NH₂/TMI ratio was lower. These results were consistent with the TEM morphology studies shown in the preceding article in this series.



Figure 11 TEM micrograph of the PMBT/PBD-NH₂ latex film. The PMBT particle size was 280 nm. The black area is the PBD-NH₂ (stained by osmium tetroxide). The bright area is the PMBT. The gray area is the PMBT/PBD-NH₂ interphase.

A film formation and crosslinking mechanism was proposed for the PSBT (or PMBT)/PBD-NH₂ latex blends. Without crosslinking, the two incompatible polymers tend to phase separate during film formation. With crosslinking, the PBD-NH₂ will be bound to the PSBT particles, forming a PSBT-PBD copolymer interphase. This interphase facilitates the diffusion of the PBD-NH₂ into the PSBT particles. The crosslinking reaction provides the driving force for the diffusion of the PBD-NH₂ into the acrylic polymer.

The TEM work on the latex films by Ms. O. L. Shaffer is greatly appreciated.

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