

# Crosslinking of Isocyanate Functional Acrylic Latex with Telechelic Polybutadiene. II. Film Formation/Crosslinking

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**ABSTRACT:** The mechanism of film formation and crosslinking in a poly(methyl methacrylate/*n*-butyl acrylate/TMI<sup>®</sup>) (PMBT) and amino-telechelic polybutadiene (PBD-NH<sub>2</sub>) latex blend was studied. Films cast from the latex blends were ultramicrotomed and examined by transmission electron microscopy. The PBD-NH<sub>2</sub> was found to be located primarily at the surface of the PMBT particles due to a crosslinking reaction. Without the possibility of crosslinking (when TMI was absent in the acrylic copolymer), the PBD-NH<sub>2</sub> only formed segregated phases in the acrylic polymer matrix due to the incompatibility of the two polymers. While this PBD-NH<sub>2</sub> could be extracted with toluene, the PBD-NH<sub>2</sub> crosslinked at the PMBT particle surfaces was not extractable. FTIR results showed that the isocyanate groups in the PMBT were completely consumed when the PBD-NH<sub>2</sub> concentration was sufficiently high, indicating that the PBD-NH<sub>2</sub> had diffused and reacted inside the PMBT particles. Thus, the crosslinking reaction was considered to be the driving force for the diffusion of the PBD-NH<sub>2</sub> into the PMBT particles. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 977–984, 1998

**Key words:** latex blend; telechelic polybutadiene; poly(methyl methacrylate/*n*-butyl acrylate/TMI); latex film formation; crosslinking

## INTRODUCTION

Film formation from a single component latex can be generally divided into three stages: (1) evaporation of water until the particles are densely packed, (2) deformation and coalescence of the polymer particles until a continuous and pore-free polymer film is formed, and (3) cohesive strength development by further gradual coalescence of adjacent latex particles and the interdiffusion of polymer chains from adjacent particles.<sup>1–6</sup> Crosslinking is often introduced to stage (3) in order to enhance film properties such as cohesion or mechanical strength.

Most crosslinking latices are formulated by

mixing a single functional latex with a small molecule crosslinking agent such as melamine formaldehyde,<sup>7</sup> or by copolymerizing two functional monomers into a single latex.<sup>8</sup> The crosslinking occurs either at the interfaces of adjacent particles or throughout the whole particle, depending on the location of the functional groups. We reported previously the preparation and characterization of an ambient curable, isocyanate-functional acrylic latex synthesized by incorporating dimethyl meta-isopropenyl benzyl isocyanate (TMI<sup>®</sup>), an isocyanate monomer, into styrene/*n*-butyl acrylate copolymer latex particles.<sup>9</sup> We also reported the preparation of functionalized telechelic polybutadiene,<sup>10</sup> which was subsequently transformed into an artificial latex for use as a crosslinking agent for the TMI-containing acrylic copolymer; these two latices were blended and films were cast and characterized. This system contains two incompatible polymers: acrylic poly-

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mer and polybutadiene. Thus, the film formation and crosslinking may not follow the conventional mechanism stated above. The present article is intended to provide some understanding of this process.

## EXPERIMENTAL

### Materials

Dimethyl meta-isopropenyl benzyl isocyanate (TMI<sup>®</sup>, Cytec Industries), 1,12-diaminedodecane (Aldrich), potassium persulfate ( $K_2S_2O_8$ , Aldrich), potassium metabisulfite ( $K_2S_2O_5$ , Aldrich), and Aerosol MA 80 (sodium dihexyl sulfosuccinate, Cytec Industries) were used as received. Poly(methyl methacrylate/*n*-butyl acrylate/TMI) (designated PMBT) latex and the amino-terminated telechelic polybutadiene (designated PBD-NH<sub>2</sub>) artificial latex were prepared as reported previously.<sup>9</sup>

### Core (PMBT)/Shell (PMB) Latex Preparation

The following were charged into a 250 mL three-neck flask fitted with a condenser and a stirrer under nitrogen atmosphere at 40°C: 35.00 g of the PMBT latex described previously<sup>9</sup> (TMI content 2% based on monomers; particle size 81 nm; solids content 30%), 0.220 g of the reductant (potassium metabisulfite), 0.500 g of the anionic surfactant (Aerosol MA 80), and 31.50 g of water. Twenty-nine grams of the monomers (methyl methacrylate/*n*-butyl acrylate = 1 : 1) and 0.220 g of the oxidant (potassium persulfate) in 31.0 g of water were fed into the flask at a rate of 0.05 mL/min. After the completion of the feed, polymerization was continued until no more monomers were detected by gas chromatography (GC). A final solids content of 29.4% was determined gravimetrically. This latex had a volume average particle size ( $D_v$ ) of 137 nm ( $D_n = 135$  nm;  $D_w = 139$  nm) as determined by capillary hydrodynamic fractionation (CHDF).<sup>9</sup>

### Latex Film Formation

Latex films were formed by casting the latex onto a glass plate at room temperature and drying for more than 7 days. The amount of the latex used and the area of the plate were determined by the solids content of the latex in order to obtain a dry film thickness of ~ 0.3–0.6 mm.

### Stress–Strain Behavior

An Instron universal tensile testing machine (Model 1011) was used for measuring the stress–strain behavior of the latex films. Standard microtensile test specimens were used according to the ASTM D1708-84 method. A 500 N load cell was employed, and the experiments were carried out at a crosshead speed of 25 mm/min.

### Cryoultramicrotoming and TEM

The cryoultramicrotome technique was employed to prepare ultrathin (90–150 nm) sections of the PMBT/PBD-NH<sub>2</sub> films for transmission electron microscope (TEM) examination. The films were cryoultramicrotomed with a diamond knife in an RMC MT6000-XL ultramicrotome equipped with a CR-2000 cryosectioning unit. The sections were collected on copper grids and vapor stained by a 2% aqueous solution of osmium tetroxide for 2 h before being examined in a Philips 400 transmission electron microscope.

## RESULTS AND DISCUSSION

A PMBT latex containing 2% TMI based on solids and having a volume average diameter of 81 nm ( $D_n = 78$  nm;  $D_w = 84$  nm) was mixed with different amounts of PBD-NH<sub>2</sub> artificial latex (particle size ~ 70 nm). Four latex films ~ 0.5 mm thick with different PMBT/PBD-NH<sub>2</sub> ratios were prepared by casting the PMBT/PBD-NH<sub>2</sub> latex blends onto glass plates and air drying for 10 days. The compositions of the four latex films and the percent NCO consumed by the PBD-NH<sub>2</sub> are listed in Table I.

### Solvent Test

In a solvent test, a circular piece of the latex film with a 14 mm diameter was placed in toluene for 48 h. The swelling ratio of the film was taken as  $W/W_0$ , where  $W_0$  and  $W$  are the weights of the film before and after being swollen in toluene, respectively. The PMBT film (03071), without PBD-NH<sub>2</sub> in it, dissolved completely in the toluene, indicating that there was no crosslinking in the film. The PMBT/PBD-NH<sub>2</sub> films (03072, 03073, 03074), however, did not dissolve. The swelling ratio varied with the ratio of PBD-NH<sub>2</sub> to PMBT, and thus the NH<sub>2</sub>/TMI ratio, as shown in Figure 1. In relation to the FTIR results (Table

**Table I** Compositions of Four Latex Films and the Percent NCO Consumed by the PBD-NH<sub>2</sub>

Film Code	03071 <sup>b</sup>	03072	03073	03074
PBD-NH <sub>2</sub> /PMBT (wt)	0	0.058	0.115	0.345
NH <sub>2</sub> /TMI (mol)	0	0.5	1.0	3.0
% NCO consumed by PBD-NH <sub>2</sub> <sup>a</sup>	0	10	25	100

<sup>a</sup> Determined by FTIR after 10 days' curing.

<sup>b</sup> Film cast from PMBT without the addition of PBD-NH<sub>2</sub>.

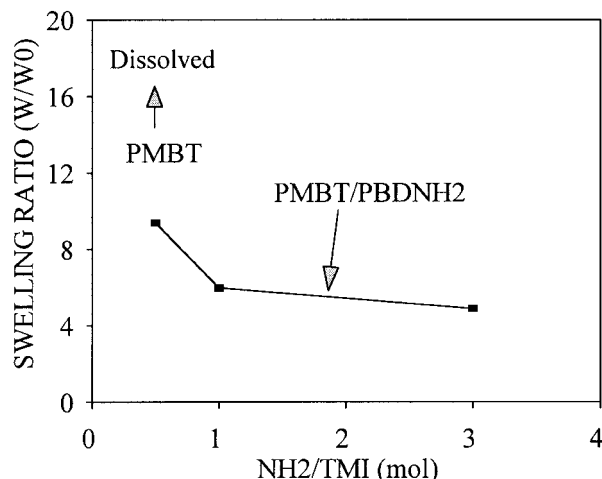
I), it can be seen that the greater the amount of the NCO that was consumed by the PBD-NH<sub>2</sub>, the lower was the swelling ratio and the higher the degree of crosslinking. The crosslinking, due to the incorporation of the PBD-NH<sub>2</sub>, resulted in improved solvent resistance properties of the acrylic latex films.

### Stress-Strain Measurements and Morphology Studies

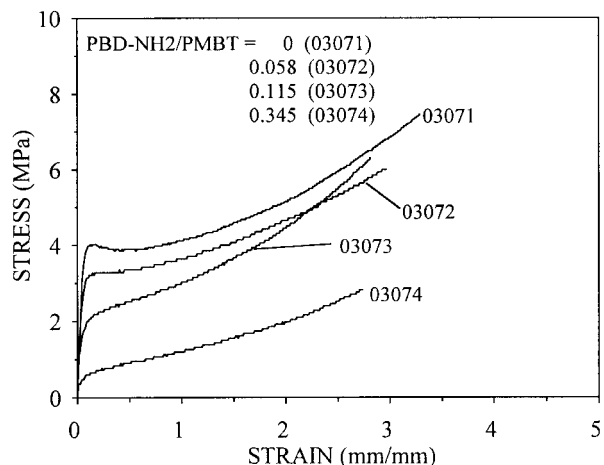
Figure 2 shows the stress-strain behavior of the PMBT film (03071) and three PMBT/PBD-NH<sub>2</sub> films (03072, 03073, and 03074). The crosslinked films exhibited lower tensile strengths (stress at break) and toughness (area under the curve) compared to the uncrosslinked one. This was due to the incompatibility of the PBD and the PMBT, resulting in phase separation in the film.

Figure 3 shows TEM micrographs of the four cryoultramicrotomed films, which clearly reveal the presence of phase separation. When there was no PBD-NH<sub>2</sub> present (03071), the pure PMBT

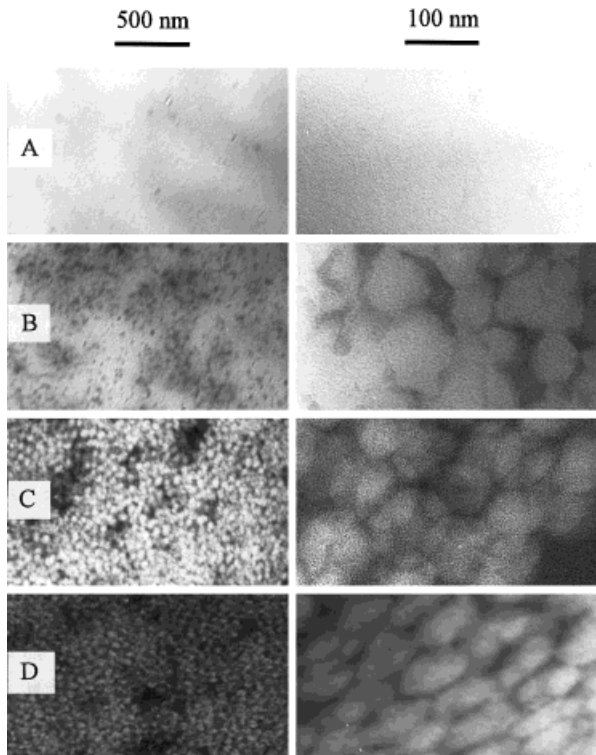
film was not stained by the osmium tetroxide and no PMBT particle contours could be observed. In the PMBT/PBD-NH<sub>2</sub> films (03072, 03073, and 03074), however, the PBD-NH<sub>2</sub> was stained by the osmium tetroxide vapor and appears dark in the micrographs. When the PBD-NH<sub>2</sub>/PMBT weight ratio was 0.058 (03072), the amount of PBD-NH<sub>2</sub> was not sufficient (stained dark areas) to surround all the PMBT particles (bright areas, unstained), and indeed, only some of the PMBT particle contours are visible; partial coalescence of PMBT particles occurred. However, a certain amount of the PBD formed isolated, phase-separated (dark) pockets in the film. When the PBD-NH<sub>2</sub>/PMBT weight ratio was 0.115 (03073), the PMBT particles appeared to be completely surrounded by the PBD-NH<sub>2</sub>, and the PBD-NH<sub>2</sub> pockets increased in size and number compared to film 03072. When the PBD-NH<sub>2</sub>/PMBT weight ratio increased to its maximum of 0.345 (03074), all the PMBT particles appeared to be surrounded by the PBD-NH<sub>2</sub> and there were larger PBD pockets present. It should be pointed out that since the FTIR results indicated the complete consump-



**Figure 1** Swelling ratio of the PMBT/PBD-NH<sub>2</sub> latex films as a function of the ratio of NH<sub>2</sub> to TMI in the two latices.



**Figure 2** Effect of the PBD-NH<sub>2</sub> to PMBT ratio on the stress-strain behavior of PMBT/PBD-NH<sub>2</sub> films as measured with an Instron universal testing machine.



**Figure 3** TEM micrographs of latex films. (A) 03071, (B) 03072, (C) 03073, (D) 03074 (PBD-NH<sub>2</sub>/PMBT = 0, 0.058, 0.115, and 0.345, respectively). The particle size of the PMBT was 81 nm. The films were dried from latices for 30 days, cryoultramicrotomed, and positively stained with OsO<sub>4</sub> vapor (dark = PBD-NH<sub>2</sub>, bright = PMBT).

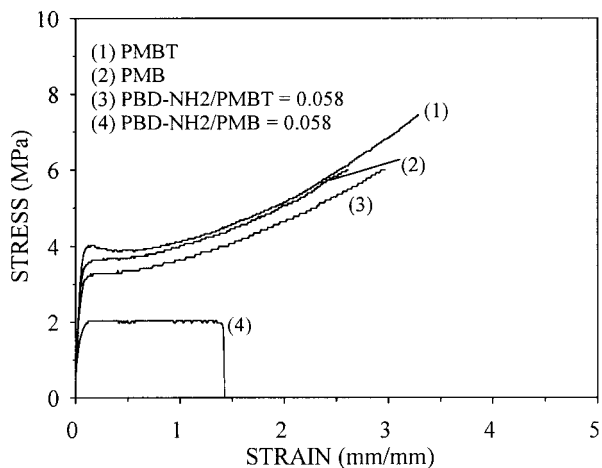
tion of the NCO groups in the PMBT particles in film 03074, the PBD-NH<sub>2</sub> must have diffused completely into the PMBT particles (or at least the mutual diffusion of the NCO groups and the NH<sub>2</sub> groups was complete). Due to the relatively low concentration of the PBD-NH<sub>2</sub> inside the PMBT particles, the osmium tetroxide staining could not provide further proof of the existence of the PBD-NH<sub>2</sub> inside the PMBT particles; the PMBT particles appeared brighter than the surrounding PBD-NH<sub>2</sub>.

In another system consisting of an interpenetrating elastomer network of poly(urethane-urea) and a polyacrylate, Klemperer, Frisch, and Frisch<sup>11</sup> encountered a similar decrease in the tensile strength with increasing polyacrylate content, reaching a minimum near 20% polyacrylate. The authors attributed this minimum to the plasticizing effect of the polyacrylate in this concentration range.

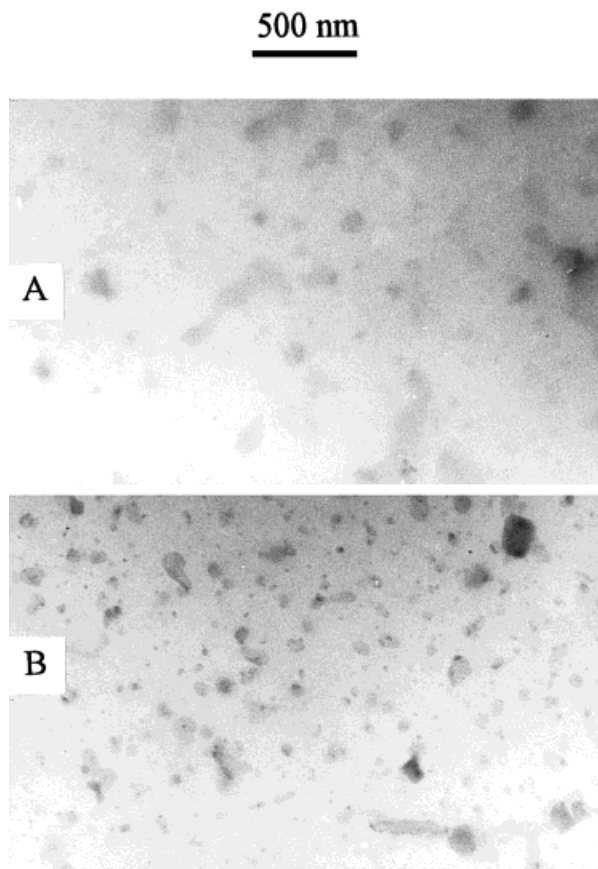
The TEM film morphology study indicated that it is the incompatibility of the PBD and the PMBT

that led to the decrease in the film strength. However, the solvent swelling measurements and the FTIR results clearly showed that crosslinking was present in the PMBT/PBD-NH<sub>2</sub> films. In order to clearly indicate the effect of crosslinking on the film morphology, a poly(MMA/BA) (designated PMB, i.e., no TMI) film and a PMB/PBD-NH<sub>2</sub> film were prepared as control samples and their stress-strain behavior and TEM morphology were examined. The PMB latex was synthesized in the same way as the PMBT latex; the resulting particle size of the PMB latex was the same as the PMBT latex (81 nm).

Figure 4 shows that the PMB/PBD-NH<sub>2</sub> film (PBD-NH<sub>2</sub>/PMB = 0.058) showed a much lower tensile strength than the comparable film cast from the latex containing the isocyanate groups (03072; PBD-NH<sub>2</sub>/PMBT = 0.058). Since there was no TMI in the PMB, the PBD-NH<sub>2</sub> could not act as a crosslinker, and thus there was no crosslinking in the film. The TEM morphology study of the PMB/PBD-NH<sub>2</sub> films (Fig. 5) indicated that no separate PMB particles could be identified, even when the ratio of the PBD-NH<sub>2</sub> to the PMB was increased to 0.115 (when this ratio was increased to 0.345, the latex blend did not form a uniform film, but resulted in massive phase separation of the PMB and PBD-NH<sub>2</sub> in the film). The PBD-NH<sub>2</sub> did not surround the acrylic particles as it did in the PMBT/PBD-NH<sub>2</sub> films (Fig. 3). The PBD-NH<sub>2</sub> (dark areas) only formed separated phases in the PMB matrix. The obvious difference between the PMB/PBD-NH<sub>2</sub> film and the PMBT/PBD-NH<sub>2</sub> films suggests that the crosslinking re-



**Figure 4** Stress-strain behavior of PMB and PMBT/PBD-NH<sub>2</sub> films in comparison with PMBT and PMBT/PBD-NH<sub>2</sub> films.



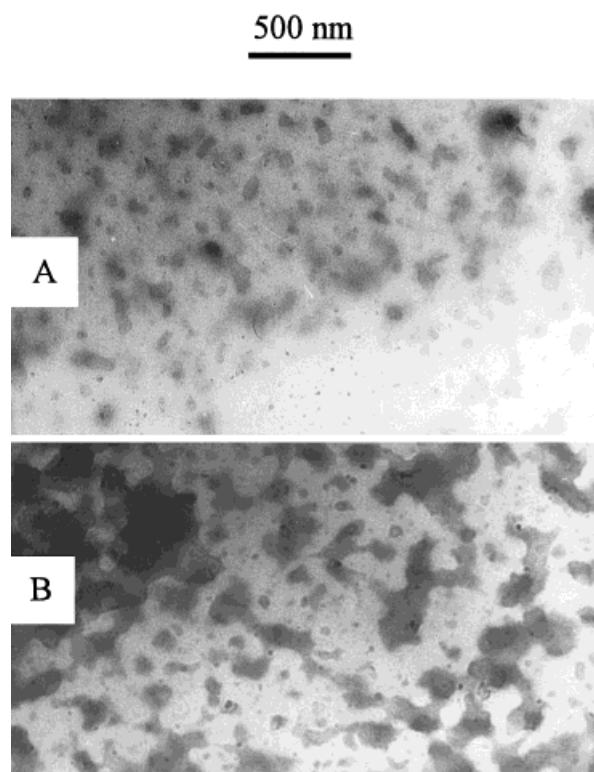
**Figure 5** TEM micrographs of PMB/PBD-NH<sub>2</sub> films. (A) PBD-NH<sub>2</sub>/PMB = 0.058; (B) PBD-NH<sub>2</sub>/PMB = 0.115. The particle size of the PMB latex was 81 nm. The films were dried for 30 days, cryoultramicrotomed, and stained with osmium tetroxide (OsO<sub>4</sub>) vapor (dark = PBD-NH<sub>2</sub>, bright = PMB).

action between the TMI and the amino-telechelic PBD provided a means of “compatibilizing” the two polymers creating a “driving force” for the incompatible PBD to diffuse into the PMBT acrylic particles.

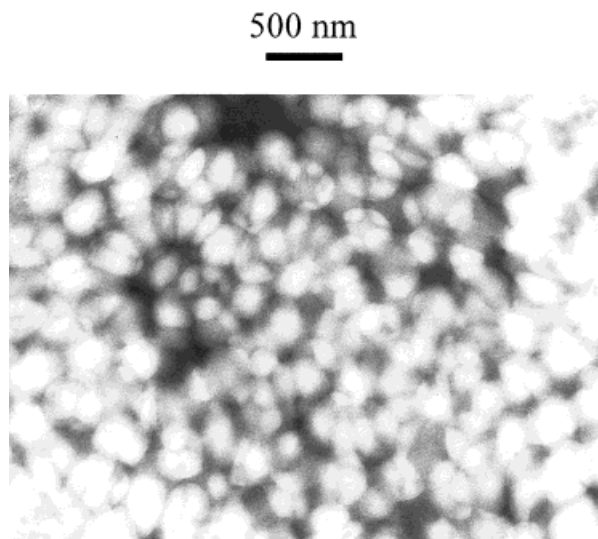
This phenomenon is further illustrated in the following experiment. A core/shell latex with the PMBT (2% TMI based on solids; 81 nm particle size) as the core and a 28 nm PMB shell was prepared. No TMI was incorporated into the shell formulation. This core/shell latex was mixed with the PBD-NH<sub>2</sub> artificial latex in two different ratios; latex films were cast and examined by TEM. Figure 6 shows the same morphology pattern as in Figure 5: no acrylic particle contours can be identified, the PBD-NH<sub>2</sub> did not surround the acrylic particles but only formed separated phases. This was because there was no TMI in the shell of the acrylic particles; thus, the PBD-

NH<sub>2</sub> could not reach the TMI inside the core of the acrylic particles due to polymer incompatibility. Since there was no chemical reaction, there was no driving force for the incompatible PBD to enter into the acrylic particles.

The particle size of the core/shell particles (136 nm) was larger than the previously studied PMBT particles (80 nm) due to the added shell thickness. Could the difference in particle size have resulted the difference in film morphology? To eliminate this possibility, a PMBT latex having a larger particle size (280 nm) was prepared and mixed with the PBD-NH<sub>2</sub> latex and its film was examined by TEM. The micrograph in Figure 7 shows that the film morphology was the same as the previous three films (03072, 03073, and 03074) in Figure 3, independent of the latex particle size. The PMBT particle contours can be clearly identified, especially in the case of the high PBD-NH<sub>2</sub>/PMBT ratio. The PBD-NH<sub>2</sub> can enter into the acrylic particles as long as they have TMI on or close to the surface, regardless of their particle size.



**Figure 6** TEM micrographs of the PMBT (core)-PMB (shell)/PBD-NH<sub>2</sub> films. (A) PBD-NH<sub>2</sub>/PMBT-PMB = 0.058; (B) PBD-NH<sub>2</sub>/PMBT-PMB = 0.345. The films were dried for 30 days, cryoultramicrotomed, and stained with osmium tetroxide (OsO<sub>4</sub>) vapor (dark = PBD-NH<sub>2</sub>, bright = PMBT).



**Figure 7** TEM micrograph of the PMBT/PBD-NH<sub>2</sub> film in which the PMBT particle size was 280 nm. PBD-NH<sub>2</sub>/PMBT = 0.345. The film was dried for 30 days, cryoultramicrotomed, and stained with osmium tetroxide (OsO<sub>4</sub>) vapor (dark = PBD-NH<sub>2</sub>, bright = PMBT).

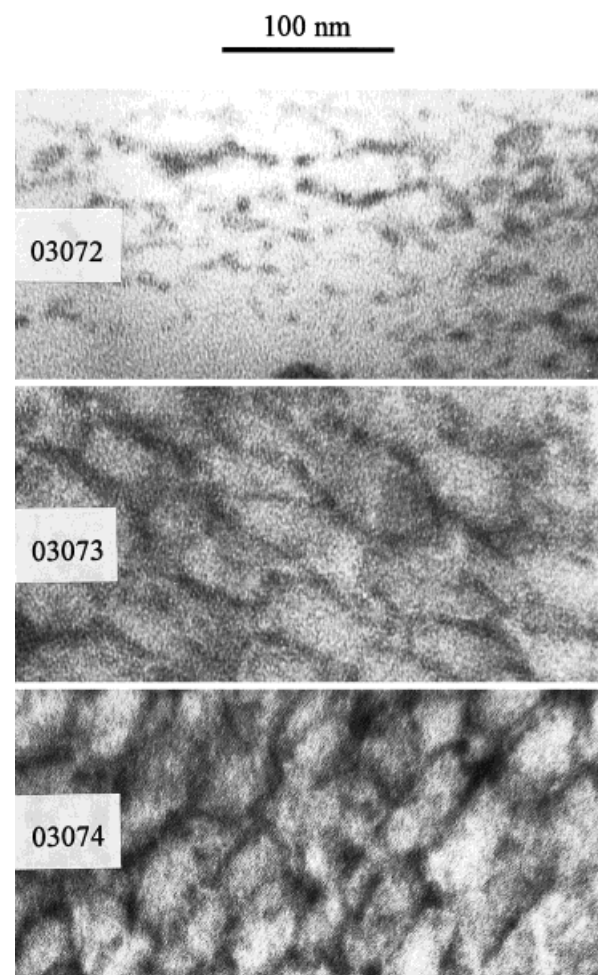
#### Extraction Experiment

The above results showed that in the PMBT/PBD-NH<sub>2</sub> films, some of the PBD-NH<sub>2</sub> diffused into the PMBT particles and crosslinked with the TMI, while the rest of the PBD-NH<sub>2</sub> formed separated phases or pockets in the film. The ratio of the crosslinked amount to the remainder of the PBD-NH<sub>2</sub> depended on the PMBT/PBD-NH<sub>2</sub> ratio. If the phase separated PBD-NH<sub>2</sub> could be removed from the film, the ratio of the reacted PBD-NH<sub>2</sub> to the phase separated PBD-NH<sub>2</sub> could be quantified and the film strength should be expected to increase. The following experiment was intended to discover this relationship.

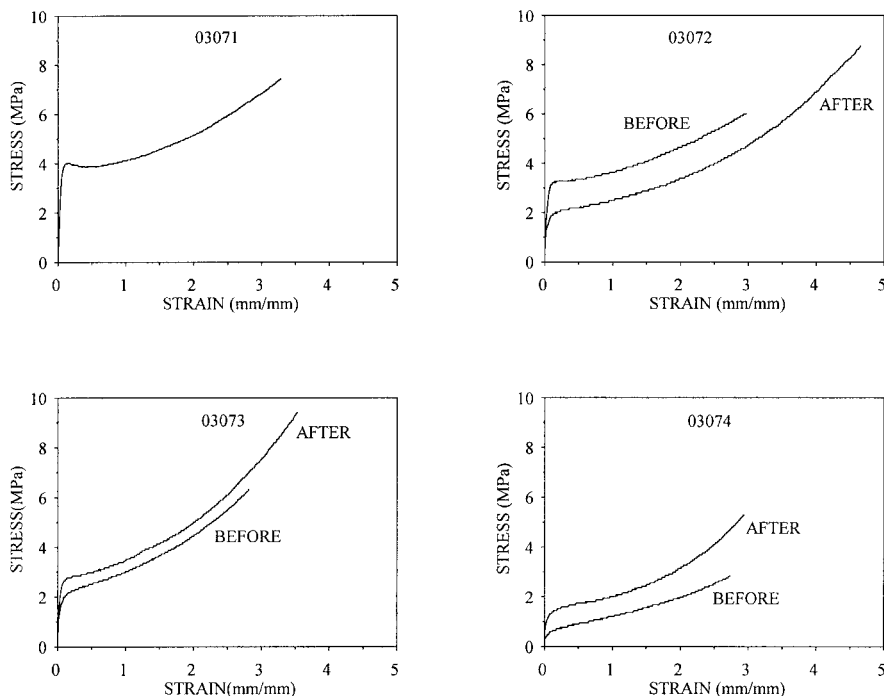
The PMBT/PBD-NH<sub>2</sub> films (03072, 03073, and 03074) were placed in toluene for 15 days in order to extract the uncrosslinked PBD-NH<sub>2</sub> from the films. Then the films were left under vacuum for 24 h to evaporate the toluene. The toluene treated films were again cryo-ultramicrotomed and examined by TEM. Figure 8 shows the TEM micrographs of the three toluene treated films. It can be seen that most but not all of the phase separated PBD-NH<sub>2</sub> domains were removed by the toluene extraction. The PMBT particles, however, were still clearly identified by the stained PBD-NH<sub>2</sub> surrounding them. The toluene could not remove the reacted PBD-NH<sub>2</sub>.

Figure 9 shows the stress–strain behavior of the three toluene treated films in comparison with

the PMBT film (03071; it could not be treated with toluene due to its solubility). All three toluene-treated films showed higher tensile strengths and toughness than the original, untreated films. When the PBD-NH<sub>2</sub>/PMBT ratio was 0.058 (film 03072), the toluene-treated film was softer (the yield point of the curve is lower) than both the PMBT film and the original untreated PMBT/PBD-NH<sub>2</sub> film. This might be due to the loss of PMBT in the film. Recall that the TEM micrographs showed that in this film only a part of the PMBT particles were surrounded by the PBD-NH<sub>2</sub>. The toluene most probably extracted not only the uncrosslinked PBD-NH<sub>2</sub>, but also the uncrosslinked PMBT. Nevertheless, the tensile strength and the elongation at break of the toluene-treated PMBT/PBD-NH<sub>2</sub> film was higher



**Figure 8** TEM micrographs of the toluene-treated PMBT/PBD-NH<sub>2</sub> films 03072, 03073, and 03074. The films were dried for 30 days, cryoultramicrotomed, and stained with osmium tetroxide (OsO<sub>4</sub>) vapor (dark = PBD-NH<sub>2</sub>, bright = PMBT).



**Figure 9** Stress–strain behavior of the toluene-treated PMBT/PBD-NH<sub>2</sub> films compared with the PMBT film (top left).

than both the PMBT film and the original untreated PMBT/PBD-NH<sub>2</sub> film. The film strength improvement was even greater when the PBD-NH<sub>2</sub>/PMBT ratio was 0.115 (film 03073), due to the increased degree of crosslinking. The toluene-treated PMBT/PBD-NH<sub>2</sub> film showed a higher tensile strength than the PMBT film and was even harder than the original untreated PMBT/PBD-NH<sub>2</sub> film because of the removal of the excess PBD-NH<sub>2</sub> by the toluene. When the PBD-NH<sub>2</sub>/PMBT ratio was increased to 0.345 (film 03074), however, the film became significantly softer and weaker than the PMBT film, even after it was treated with toluene. This film still contained a significant number of domains of PBD, which have a much lower  $T_g$  ( $\sim -100^\circ\text{C}$ ) than the PMBT ( $\sim 10^\circ\text{C}$ ). These results suggest that the ratio of PMBT to PBD-NH<sub>2</sub> is critical to the film strength development, having an optimum range.

The toluene extract separated from the films contained not only the uncrosslinked PBD-NH<sub>2</sub>, but also part of the uncrosslinked PMBT. Evaporating the solvent yielded the total amount of the uncrosslinked PBD-NH<sub>2</sub> and PMBT. These solids were then extracted with acetone, which only dissolves the PMBT, not the PBD-NH<sub>2</sub>. This yielded the uncrosslinked PMBT and the PBD-NH<sub>2</sub> separately. Table II shows the results. It should be pointed out that these results can only be evaluated qualitatively. The solvent treatment was not only an extraction process, but also a process in which polymer chain reptation was facilitated by swelling. Therefore, further chain interdiffusion between particles and further crosslinking were likely to occur in parallel with the extraction process. Nonetheless, these results show that the uncrosslinked PMBT decreased with increasing amount of crosslinking PBD-NH<sub>2</sub>, although pro-

**Table II** Results of Toluene and Acetone Extractions of the PMBT/PBD-NH<sub>2</sub> Films

	03072	03073	03074
PBD-NH <sub>2</sub> /PMBT (weight ratio)	0.058	0.115	0.345
% Uncrosslinked PMBT	12	6	4
% Uncrosslinked PBD-NH <sub>2</sub>	24	25	36

portionately less of the latter was involved in the crosslinking (lowered efficiency).

## CONCLUSIONS

Different film morphologies were found for different PBD-NH<sub>2</sub>/PMBT compositions in the latex blend. The crosslinking reaction of the TMI with the amino-telechelic PBD was the driving force for the incompatible PBD to enter and react inside the acrylic particles. Without such crosslinking, the PBD would only form phase-separated domains within the acrylic matrix. Removing the uncrosslinked PBD-NH<sub>2</sub> phase from the PBD-NH<sub>2</sub>/PMBT films by toluene extraction changed the film morphology and improved the mechanical properties. The ratio of the crosslinked to the uncrosslinked PBD-NH<sub>2</sub> and PMBT in films were semiquantitatively determined by toluene/acetone extractions.

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