Isocyanate-Functionalized Latexes: Film Formation and Tensile Properties

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ABSTRACT: Latexes functionalized with isocyanate groups were prepared by carrying out the emulsion terpolymerization of dimethyl meta-isopropenyl benzyl isocyanate (TMI®) with methyl methacrylate and *n*-butyl acrylate. The film formation of these latexes and the tensile properties of the resulting latex films were studied. The effect of TMI concentration on the film properties was investigated. The locus of the isocyanate groups in the latex particles was controlled by using different polymerization processes. The locus of the functional groups was found to greatly influence the tensile properties of the latex films. Triethyl amine was used as an external catalyst to cure the TMI polymer films. One-component self-curable systems capable of undergoing crosslinking at ambient temperatures were developed by incorporating small amounts of methacrylic acid into the recipe. These systems exhibited significant improvement in tensile properties upon curing. In addition, the shelf-stability of these latexes was found to be excellent. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66**: 1869–1884, 1997

Key words: ambient curing latexes; TMI; tensile properties

INTRODUCTION

A previous publication dealt with the emulsion terpolymerization of dimethyl meta-isopropenyl benzyl isocyanate (TMI) with the acrylic monomers methyl methacrylate (MMA) and *n*-butyl acrylate (BA).[1] The kinetics of the single-stage emulsion polymerization process were discussed. This article describes the film formation and behavior of these TMI-functionalized latexes. The ability of these latexes to undergo crosslinking reactions after film formation is also discussed. Waterborne resins capable of being cured after the polymerization step have gained significant industrial importance. The demand for solvent-free crosslinkable polymers has also increased as a result of increasingly stringent environmental

stipulations. Such systems are typically prepared by incorporating monomers containing functional groups. These functional monomers are capable of undergoing crosslinking reactions at room temperature after the polymerization step.

A number of functional monomers are available as reviewed by Daniels and Klein.[2] The development of mechanical properties of films from polymer latexes has been reviewed recently by Zosel.[3] Monomers with methylol groups and their derivatives form a popular family of functional monomers. These monomers include self-condensable methylol amides such as *N*-methylol acrylamide (NMA), *N*-(isobutoxymethyl) acrylamide (IBMA), and hydroxymethylated diacetone acrylamide. These monomers are copolymerized in emulsion with conventional monomers such as acrylates, vinyl acetate, etc., to obtain thermally curable polymer latexes. Bonardi and colleagues[4] investigated the properties of copolymers of BA and MMA, and BA and styrene (S) functionalized with NMA. The latex pH was found to

have a significant effect on the cure kinetics. The copolymerization of BA with IBMA and the more polar reactive monomer NMA has also been investigated.[3] The effect of the water solubility of the functional monomer on the distribution of crosslinking sites in the polymer particles was reported. Similar studies were also carried out by Hidalgo and associates,[5,6] who copolymerized BA with IBMA and other amide-type functional monomers of higher water solubilities.

Functional monomers containing carboxyl moieties are used to carry out both covalent[7,8] and ionic[9–11] crosslinking reactions. This family of monomers includes acrylic acid, methacrylic acid (MAA), and itaconic acid. Carboxyl groups can react with epoxy or acrylamide derivatives and isocyanate-functionalized latexes in order to form covalent linkages. They can also associate via hydrogen bonding to form reversible physical networks. Chelation of carboxyl groups with multivalent cations results in ionically crosslinked polymers. Other types of functional monomers include alkoxysilane derivatives,[12] thiirane monomers,[13] maleimide acceptors,[14] and monomers with hydroxyl functionalities.[15–17] Functional monomers such as glycidyl methacrylate or glycidyl acrylate are also copolymerized with acrylics to obtain latexes with epoxy groups. These latexes can be cured with amine curing agents.[18]

Isocyanates react with a variety of functional groups such as amine, carboxyl, and hydroxyl moieties. They also react with water at room temperature. Therefore, if polymer chains were to be functionalized with isocyanate groups, room temperature-curable systems can be developed which can be crosslinked in the presence of atmospheric moisture. Recently, Tramontano and Blank[19] described a low-temperature-curable polyurethane–aliphatic system. Renk and Swartz[20] have described the formulation of two-component waterborne polyurethanes for the wood industry. The two components of the coating consisted of a hydroxyl-functional acrylic latex and a water-dispersible polyisocyanate.

TMI is a novel bifunctional monomer[21,22] with a reactive double bond and a tertiary aliphatic isocyanate (NCO) group. TMI can be introduced into the polymer backbone via copolymerization with conventional monomers such as MMA, BA, S, etc. The emulsion copolymerization of TMI facilitates the preparation of a waterborne NCO-functionalized polymer in a single stage. Several such formulations are described in the patent literature.[23,24] The open literature also lists several studies on the emulsion copolymerization of TMI. Parker and coworkers[25] utilized a blocked derivative of TMI to develop reactively curable diene elastomers. Inaba and colleagues,[26] carried out the terpolymerization of TMI with S and BA using conventional and miniemulsion polymerizations. The crosslinking of latex films containing TMI and a combination of TMI and MAA was studied. Wang and Thames[27] described coating formulations containing vinyl acrylic and acrylic latexes functionalized with TMI. We recently reported[1] the process development and kinetics of the emulsion terpolymerization of MMA/BA/TMI.

The following sections describe the effect of different variables—such as the TMI concentration, polymerization process, locus of NCO groups in the polymer particles, etc.—on the film formation behavior of TMI latexes and the mechanical properties of the latex films.

EXPERIMENTAL

Materials

MMA and BA (both from Aldrich, Milwaukee, WI) were cleaned using an inhibitor-removal column (Aldrich) and stored at −2°C before use. All other reagents were used as received. Ammonium persulfate, potassium metabisulfite, and ammonium iron(II) sulfate hexahydrate (AISH) (all from Aldrich) were stored in the dark prior to use. TMI and sodium dihexyl sulfosuccinate surfactant (Aerosol MA 80) were received from Cytec Industries (Stamford, CT). MAA and triethyl amine (TEA) were also obtained from Aldrich. Distilled–deionized (DDI) water was used in all experiments.

Polymerizations

The details of the process development and kinetics of the emulsion terpolymerization of MMA/BA/TMI have been described elsewhere.[1] Batch polymerizations were carried out in 4-oz bottles at 40°C. Redox initiators comprising ammonium persulfate (oxidant), potassium metabisulfite (reductant), and AISH (activator) were used. All of the surfactant was introduced into the bottles, along with most of the DDI water. Separate aqueous solutions of the oxidant, reductant, and activator were prepared with the remainder of the

water charge. The activator solution and the monomers were added to the bottles and the contents purged with nitrogen. The reductant and oxidant solutions were then introduced, in that order. The bottles were then placed in a bottle polymerizer maintained at 40°C. The bottles were tumbled end-over-end for a period of 12 h.

Larger-scale batch polymerizations were carried out in a 250-mL glass reactor as described earlier.[1] Seeded polymerizations were also carried out in 250-mL glass reactors. Seed latex was introduced into the reactor, along with some of the DDI water charge, and purged with nitrogen while being maintained at 40°C. The second-stage monomers were then introduced and the seed latex swelled for 30 min with constant stirring. Thirty-three percent of the reductant and oxidant were added as aqueous solutions at 15-min intervals to start the polymerization. The remaining initiator was fed as two separate streams (of reductant and oxidant) using a syringe pump over a period of 5 h. The polymerization was then continued for an additional hour. Additional surfactant was not added during the second-stage polymerization.

Three other polymerization processes were utilized: (1) Seeded polymerization: Seed latex of poly(MMA/BA) was used to carry out the second-stage polymerization of MMA/BA/TMI. (2) Inverse seeded polymerization was carried out by using poly(MMA/BA/TMI) (obtained via single-stage polymerization) as the seed latex. Seeded polymerization of MMA/BA was then carried out. (3) Shot growth polymerization: Batch emulsion copolymerization of MMA/BA was carried out to approximately 90% conversion. At this time, a second shot of monomer feed (consisting of MMA/BA/TMI) was added, and the polymerization taken to completion. The details of these processes are discussed in the relevant portions of the Results and Discussion section.

Film Formation

Films were formed by drying the latexes at room temperature. Latexes were cast on rectangular glass plates kept under a glass enclosure in order to prevent the formation of ripples on the polymer film as a result of air currents. The polymer films were removed from the glass plates after 3 days and dried for an additional week at ambient temperature. Smooth films of constant thickness were obtained. The thickness of the films was around 0.35 mm. Under suitable conditions, TMI polymers crosslink in the presence of moisture. The NCO group reacts with water to form an amine with the liberation of carbon dioxide. The amine reacts with another NCO group to form a urea linkage.[28]

Determination of Crosslink Density

Swelling experiments were carried out on crosslinked films using acetone as the solvent. Polymer films were weighed and then allowed to swell overnight in acetone. The weights of the swollen samples were determined. The ratio of the weights of the swollen film (W_s) and the dry film (W_o) samples was used to determine the crosslink density. According to the equilibrium swelling theory of Flory and Rehner[29]:

$$M_x = \frac{-V_1 \rho_p \left[v_2^{1/3} - \dfrac{v_2}{2} \right]}{\ln(1 - v_2) + v_2 + \chi v_2^2} \qquad (1)$$

$$v_2 = \frac{W_o}{\rho_s V_s} \qquad (2)$$

$$V_s = \frac{W_o}{\rho_p} + \frac{W_s - W_o}{\rho_s} \qquad (3)$$

$$\chi = \beta_1 + V_1(\delta_s - \delta_p)^2 / RT \qquad (4)$$

where χ is the Flory–Huggins interaction parameter; β_1 is the lattice constant of entropic origin; V_1 is the molar volume of the solvent; δ_s and δ_p are the solubility parameters of the solvent and polymer, respectively; V_s is the volume of the swollen polymer; v_2 is the volume fraction of polymer in the swollen gel; M_x is the number-average molecular weight between crosslinks; and ρ_s and ρ_p are the densities of the polymer and solvent, respectively.

The crosslink density (ρ_p / M_x) was calculated using eqs. (1)–(4). In order to determine the solubility parameter of the polymer, the films were swollen in a series of solvents with different solubility parameters. The swelling ratio of the polymer was plotted against the solubility parameter of the individual solvents. The maximum of this plot was taken as the solubility parameter of the polymer. The δ_p was determined to be equal to 9.9. The χ parameter for the polymer–acetone system was calculated from eq. (4) to be 0.12. The value of β_1 was assumed to be zero.[30]

Table I   Recipe for the Batch Emulsion Terpolymerization of MMA/BA/TMI

Component	Amount (g)
Methyl methacrylate	12.9–7.5
n-Butyl acrylate	16.50
TMI	0.6–6.0[a]
Aerosol MA 80[b]	1.80 (31.2 mM)[c]
Ammonium persulfate	0.1575 (5.9 mM)[c]
Potassium metabisulfite	0.1575 (5.8 mM)[c]
Ammonium iron(II) sulfate	
hexadehydrate	0.0015
DDI water	117.84

Polymerization temperature: 40°C.
[a] 2–20 wt % based on total monomer.
[b] 80% solids.
[c] Based on water.

Tensile Testing

The tensile properties of the latex films were determined using an Instron universal tensile testing machine. Standard microtensile test specimens were cut from the latex films using a metallic die. The stress–strain data was generated according to the ASTM D1708-84 method. A 500-N load cell was employed, and the experiments were run at a crosshead speed of 25 mm/min. The tensile strength, yield stress, and strain at fracture were calculated. At least five specimens were tested for each sample and the average values determined. Typical standard deviation values were found to vary between 10 and 15%. The toughness of the polymer, which is the fracture energy per unit volume of the sample, is given by the area under the stress–strain curves. Due to the small gauge length of the microtensile samples, this is not the most suitable method for determining the absolute values of the moduli.[31] However, the values of Young's modulus are reported for the sake of comparison between different samples.

RESULTS AND DISCUSSION

Crosslinking of TMI Latexes

Emulsion polymerization of MMA/BA/TMI (40/55/5) was carried out according to the procedure described earlier.[1] The polymerization recipe is shown in Table I. The surfactant level was above the critical micelle concentration. Redox initiators were used and the polymerization carried out at 40°C. Almost complete conversion was obtained.

Latex films were obtained by drying a latex containing 5% TMI at room temperature. The films were found to be soluble in acetone, indicating the lack of crosslinking. The fresh latex was acidic in nature with a pH of 3.2. The effect of pH on the crosslinking reaction was studied. The pH of the latex was increased by adding sodium hydroxide or sodium bicarbonate just before film formation. In another experiment, a tin catalyst (dibutyl tin dilaurate) was added to the latex and the films were cast. The films obtained from these latexes were found to be crosslinked as shown in Table II. It can be observed that the higher pH accelerates the crosslinking reaction to a different extent. Although the fresh latex was observed to dissolve in acetone, crosslinked films were obtained when the pH of the same sample was raised to 7.5 or 8.2 by adding either sodium bicarbonate or sodium hydroxide prior to film formation. The crosslink density at pH 7.5 was higher. This could be due to the presence of an active hydrogen in the bicarbonate which contributes to the NCO curing reaction. The highest degree of crosslinking was obtained when the catalyst, dibutyl tin dilaurate, was added before film formation. However, the catalyst could not be dispersed homogeneously in the latex because of its hydrophobicity.

Since dibutyl tin dilaurate could not be dispersed well in the latex, a more hydrophilic catalyst, TEA, was chosen for other experiments. TEA

Table II   Effect of Latex pH and Catalyst on the Crosslinking of Poly(MMA/BA/TMI) (40/55/5)

Sample	Latex pH	Additive	Crosslink Density (mole crosslink/cc)
1	3.2	None	Dissolved
2	7.5	NaHCO$_3$	42.1×10^{-5}
3	8.2	NaOH	13.5×10^{-5}
4	3.2	Tin catalyst	63.5×10^{-5}

Table III   Effect of TEA Concentration on the Crosslinking of Poly(MMA/BA/TMI) (43/55/2)

TEA Concentrations (wt %)	Crosslink Density (mole crosslink/cc)
0.25	1.99×10^{-5}
0.50	8.55×10^{-5}
0.75	20.4×10^{-5}
1.00	26.8×10^{-5}

is a tertiary amine which is known to catalyze the isocyanate–water reaction. TEA, in the form of a dilute aqueous solution, was added just prior to film formation to a latex containing 2 wt % TMI. The amine concentration was varied between 0.25 and 1 wt %, based on the latex polymer. All of the films were found to be crosslinked after a week. The crosslink densities are shown in Table III, and the tensile properties for two samples are compared with the control sample without TMI present in Figure 1. The degree of crosslinking was found to increase with the concentration of TEA external curing agent; however, a concomitant improvement in the tensile properties was not observed. Within experimental error, all three of these films were substantially identical. The lack of improvement in the properties of these films could result either from premature crosslinking which occurred before particle coalescence or from plasticization due to the presence of the amine. In order to check the latter hypothesis, the
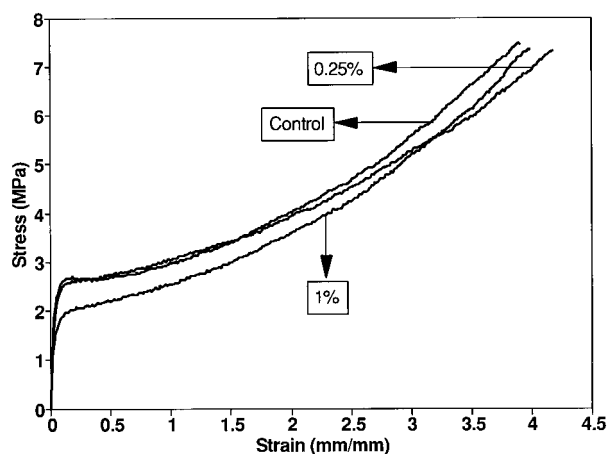
Figure 1   Effect of the amount of TEA catalyst on the tensile properties of poly(MMA/BA/TMI) (43/55/2); catalyst added before film formation at room temperature.
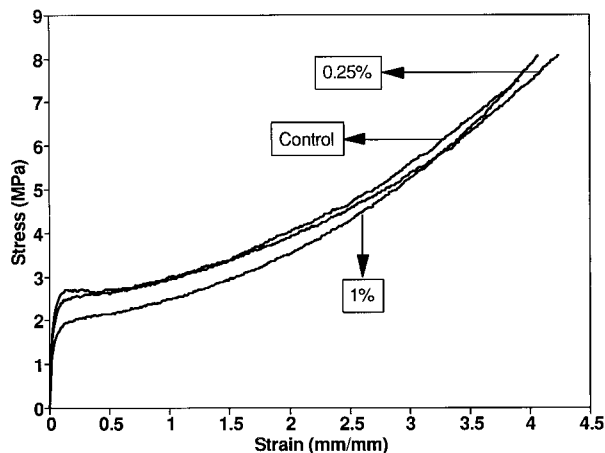
Figure 2   Effect of the amount of TEA catalyst on the tensile properties of poly(MMA/BA/TMI) (43/55/2); catalyst added before film formation at room temperature; films cured at 75°C for 4 h before tensile tests.

films were dried at 75°C for 4 h in order to drive away any amine remaining in the samples. The tensile tests were again carried out on these films (Fig. 2). Again, identical results were obtained for all samples. This indicates that the plasticization of the films was not the reason for the lack of improvement of the properties. The lack of improvement was probably due to premature crosslinking which occurred before the particle coalescence step of film formation. This hindered the strength-development process of polymer chain interdiffusion, thereby leading to a loosely fused film of individually crosslinked latex particles. Therefore, despite the crosslinking, these films did not exhibit improved mechanical properties.

Latent Crosslinking After Film Formation

Addition of TEA before film formation was found to result in inferior mechanical properties due to premature crosslinking. In order to overcome this problem, the film was cured *after* film formation. Films were first cast on glass plates from freshly prepared latexes obtained via batch polymerization (Table I). Latexes containing 2, 5, 10, and 20% TMI were dried at room temperature for 3 days. They were then removed from the glass plates and dried for an additional 7 days. The dry films were immersed in a 1% aqueous solution of TEA and heated at 70°C for 30 min. The films were then removed from the solution and dried in an oven at the same temperature for 2, 3, 4, and 6 h. The films thus cured were found to be cross-

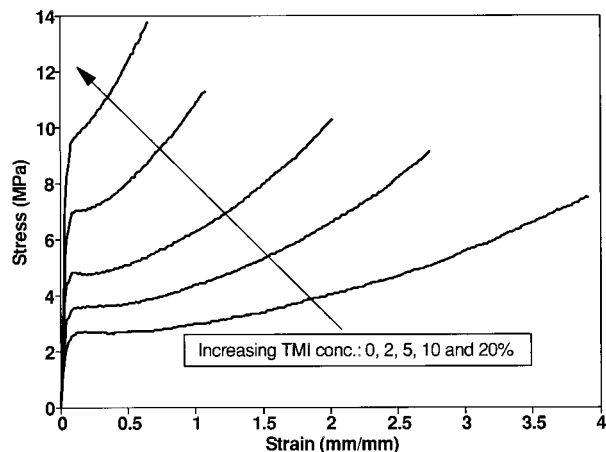**Table Table IV   Effect of TMI Concentration on the Tensile Properties of Poly(MMA/BA/TMI)**

TMI Concentration (%)	Crosslink Density (mole crosslink/cc)	M_x[a] (mole/g)	Young's Modulus (MPa)
0	—	—	130.8
2	42.1×10^{-5}	2376	142.0
5	60.2×10^{-5}	1662	162.3
10	83.4×10^{-5}	1200	186.3
20	194.8×10^{-5}	513	238.1

TMI Concentration (%)	Yield Stress (MPa)	Tensile Strength (MPa)	Toughness (MPa)
0	2.54	7.14	16.83
2	3.43	9.12	15.03
5	4.56	10.22	13.43
10	6.91	10.47	9.14
20	9.60	13.78	7.04

[a] M_x, molecular weight between crosslinks.

linked. The degree of crosslinking was found to be independent of the drying time. The curing was therefore assumed to have taken place only in the presence of the TEA solution. Hence, a drying time of 2 h was used in all subsequent experiments. The degree of crosslinking was determined (Table IV). The stress–strain curves are shown in Figure 3. The reported values of Young's modulus are in the range of leathery materials. As expected, the degree of crosslinking increased with increasing TMI concentration. At the higher TMI concentrations, the yield stress and tensile strength increased, as compared with the control

Figure 3   Effect of TMI concentration on tensile properties of poly(MMA/BA/TMI); films were cured in a 1% aqueous solution of TEA for 30 min at 70°C.

sample. However, the ultimate strain at fracture decreased. An increase in the crosslink density makes the polymer more rigid (higher Young's modulus), resulting in a less-flexible film. The table and the figure also show that a high concentration of TMI is not required for significantly improving the mechanical properties. In fact, a higher concentration of TMI ($>5\%$) may be detrimental, due to excessive crosslinking resulting in highly rigid films that fracture at low extensions. The toughness of these films was found to be much lower than that of the control sample. A good combination of modulus, tensile strength, and toughness is required in order to obtain optimal properties.

All of the above samples exhibited a yield point which is characteristic of a two-phase structure. The two-phase structure might be due to the formation of an MMA-rich terpolymer during the initial stages of the polymerization. As discussed in the previous publication,[1] the order of incorporation of the three monomers into the polymer is MMA > TMI > BA. Due to the difference in the composition of the terpolymer chains formed during the different stages of the polymerization, a two-phase structure is obtained in the final latex film. The initial portions of the tensile curves exhibit elastic deformation up to the yield point. This is due to the more-rigid phase which increases with the degree of crosslinking. Therefore, both Young's modulus and the yield stress increase and the elongation at break decreases as
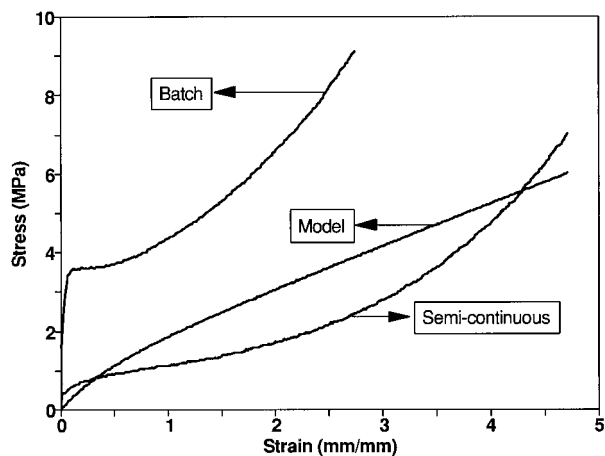
Figure 4 Effect of terpolymer composition on tensile properties of poly(MMA/BA/TMI) (43/55/2); films were cured in a 1% aqueous solution of TEA for 30 min at 70°C. The model curve was generated based on the theory of rubber elasticity, $\sigma = nRT(\alpha - 1/\alpha^2)$, where $\alpha = \varepsilon + 1$ and $n = 42.1 \times 10^{-5}$ mole crosslink/cc, obtained by swelling the batch sample in acetone and application of the Flory–Rehner equation.

the level of TMI, and thereby the crosslink density, is increased. The slope of the tensile curves beyond the yield point also increases with increasing crosslink density. This is because of the restriction against stretching of the polymer chains induced by the chemical crosslinks.

Effect of Terpolymer Composition

In order to study the effect of the terpolymer composition on the tensile properties, two latexes of poly(MMA/BA/TMI) (43/55/2) were prepared. The first latex was prepared via batch emulsion polymerization, while the second was obtained using semicontinuous polymerization under monomer-starved conditions. The processes are described in detail elsewhere.[1] The terpolymer composition of the first latex was dictated by the reactivity ratios of the three monomers, as discussed in the previous section. The terpolymer prepared using the semicontinuous process was, however, expected to have a more homogeneous composition (almost the same as that of the monomer feed) as the polymerization was carried out under monomer-starved conditions. Films were cast at room temperature from the two latexes and cured in TEA solutions, as discussed in the previous section. The tensile properties are compared in Figure 4. The batch terpolymer exhibited

a yield point indicating the presence of two segregated components: a rigid phase accounting for the initial rapid build in stress at small elongations, and an elastomeric phase which causes the polymer film to elongate further beyond the yield point. The rigid phase consists predominantly of MMA-rich terpolymer obtained as a result of compositional drift during batch polymerization. On the other hand, the terpolymer with the homogeneous composition (obtained via semicontinuous polymerization) showed a gradual increase in both the stress and strain up to the break point due to the presence of a single phase. The behavior is closer to that predicted by the theory of rubber elasticity (Fig. 4) as compared with the sample obtained via batch polymerization. The tensile strength was lower than that of the batch polymer, while the extension at break was higher. These results are similar to those reported recently by Canche-Escamilla and colleagues[32] for poly(MMA/BA) copolymers obtained via different polymerization processes.

Effect of the Locus of NCO Groups

The locus of NCO groups in the latex particles can be controlled by using different emulsion polymerization processes. The locus of these functional groups is very important because it controls the type of crosslinking occurring during film formation. A uniform distribution of functional groups leads to homogeneous crosslinking. A preponderance of crosslinking sites at the surface of the latex particles results in interfacial crosslinking. In this case, a continuous network of crosslinked polymer is obtained as a result of crosslinking at the interface between adjacent latex particles. The NCO groups can be concentrated at the surface of the particles by using a seeded polymerization technique. Using a poly(MMA/BA) (45/55) seed latex of 150 nm diameter, the second-stage polymerization of MMA/BA/TMI was carried out. The concentration of TMI in the final two-stage polymer was adjusted to 2%. A final particle size of 200 nm, with an NCO-rich shell of approximately 25 nm, was obtained. The details of the seeded polymerization process will be described in detail in a separate publication. In order to achieve thinner shells (5 nm), shot growth polymerization was utilized. First, the emulsion copolymerization of MMA/BA was carried out using 80% of the total acrylic monomers in the recipe. When the conversion reached approximately 90%,

Batch polymerization

Shot-growth polymerization

Seeded polymerization
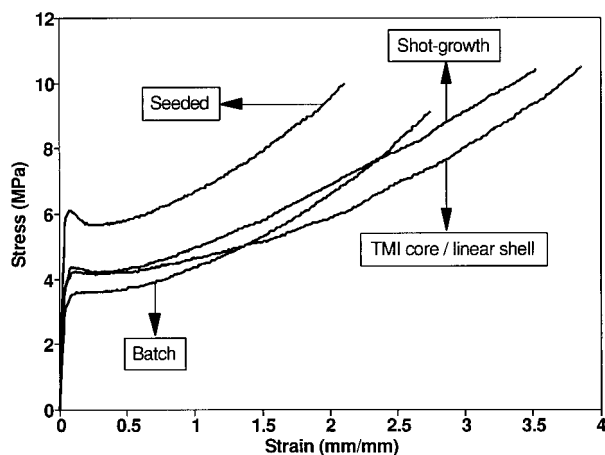
TMI core - linear shell
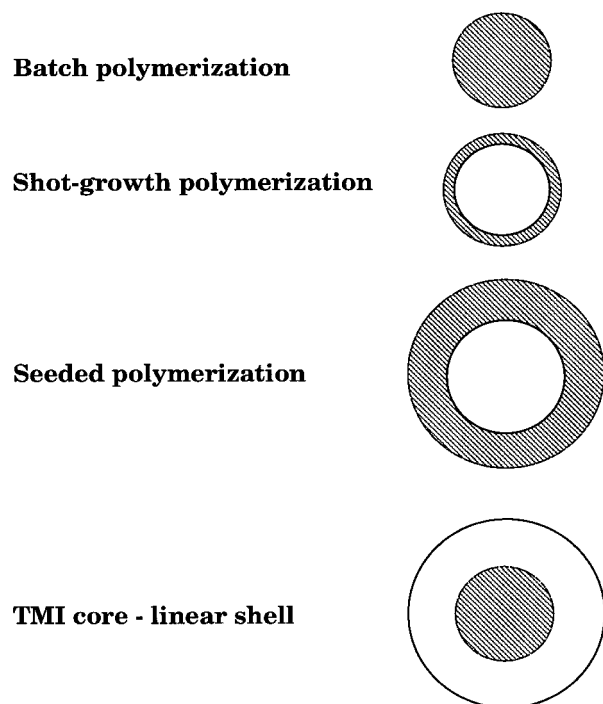
Figure 5 Schematic representation of latex particles obtained via different emulsion polymerization processes; shaded area represents the locus of NCO groups. The TMI core−linear shell sample was prepared by carrying out the seeded polymerization of MMA/BA in the presence of a seed latex of poly(MMA/BA/TMI).

TMI was added along with the remaining acrylic monomer charge as a second shot, and the polymerization was taken to completion.

Single-stage polymerization of MMA/BA/TMI is expected to yield latex particles with isocyanate groups distributed throughout the particle volume. A different type of morphology (inverse seeded) was obtained by using this TMI-containing latex as the core and carrying out the seeded polymerization of MMA/BA. The NCO groups were distributed in the core region (about 150 nm), surrounded by a noncrosslinkable copolymer of MMA and BA. The final particle size was 200 nm. The loci of NCO in the latex particles obtained using different processes are shown schematically in Figure 5. Fresh latexes containing 2% TMI were cast on glass plates in order to obtain polymer films which were soluble in acetone. These films were then cured by immersing them in 1% TEA solutions as described in the previous sections. Tensile tests were carried out to study the effect of the locus of the NCO groups on the film properties. The results are compared in

Table V and Figure 6. All the samples exhibited yield points indicating the presence of a two-phase structure. The yield point of the sample obtained via seeded polymerization was the most prominent, and the yield stress value the highest. This signifies the presence of a continuous rigid component which can be attributed to interfacial crosslinking. Due to the presence of the NCO groups at the surface of the particles, the curing leads to a continuous rigid crosslinked network structure at the particle boundaries. This interfacial crosslinking results in a higher modulus, as compared with the other samples. Although the shot growth sample also had a preponderance of NCO groups at the surface of the particles, the shell was not thick enough to maintain its integrity during the film formation process. As a result, interfacial crosslinking could not occur in this case, and no significant improvement in the yield stress and Young's modulus could be observed. The film obtained via batch polymerization exhibited the lowest yield stress and tensile strength. The films obtained via the shot growth and linear shell techniques showed similar properties. Both of these films had significant amounts of MMA/BA copolymers (without TMI, and therefore more elastomeric). As a result, the ultimate strain at fracture and the toughness values were high.

Attempts were made to confirm the morphology of the latex particles using transmission electron

Figure 6 Effect of the locus of NCO groups on the tensile properties of poly(MMA/BA/TMI) (43/55/2); films were cured in a 1% aqueous solution of TEA for 30 min at 70°C. The TMI core−linear shell sample was prepared by carrying out the seeded polymerization of MMA/BA in the presence of a seed latex of poly(MMA/BA/TMI).

**Table V   Effect of the Type of Polymerization Process on the Tensile Properties of Poly(MMA/BA/TMI) (43/55/2)**

Polymerization Process	Young's Modulus (MPa)	Yield Stress (MPa)	Tensile Strength (MPa)	Toughness (MPa)
Batch	142	3.43	9.12	14.96
Seeded	230	6.10	9.92	15.18
Inverse	183	3.98	10.52	24.25
Shot	162	3.21	10.40	21.32

microscopy. The TMI concentration was too low (2%) to preferentially stain the NCO phase; however, indirect evidence is presented that supports the morphologies described above. In both the seeded polymerization (linear core−TMI shell) and the inverse core−shell cases, the particle size increased from 150 nm to 200 nm as predicted by theoretical calculations based on the seed latex diameter. The increase in particle size after the introduction of the second shot of monomer in shot growth polymerization also followed the predicted pattern. The shelf storage stability of the batch-polymerized and the inverse core−shell polymers (TMI core) was excellent. However, the seeded polymerization (TMI in the shell layer) and shot growth samples coagulated after 2 weeks of storage. This could be due to the proximity of the NCO groups to water as a result of being concentrated at the surface of the latex particles. These NCO groups hydrolyze in the presence of water, resulting in the loss of colloidal stability. In the case of the batch polymerized and inverse core−shell samples, the NCO groups are buried inside the particles and therefore protected from hydrolysis. The shelf storage stability of these samples was excellent. Moreover, the significant increase in the modulus and tensile strength of the seeded polymerization sample further supports the hypothesis of the NCO groups being concentrated at the particle surface, thereby leading to interfacial crosslinking.

The presence of NCO groups at the surface of the latex particles significantly increases the rigidity and tensile strength of the polymer films as a result of interfacial crosslinking. The effect of TMI concentration on the interfacial crosslinking is shown in Figure 7. Samples containing 2 and 5% TMI in the shell were obtained via seeded polymerization. They were cured immediately after film formation by immersion in a 1% TEA solution at 70°C. The modulus and tensile strength were found to improve significantly as

compared with the control sample prepared without TMI. The sample with 5% TMI showed higher stress values for any given strain. Young's moduli for the seeded polymerization samples with 2 and 5% TMI were found to be similar (230 and 233 MPa, respectively). However, the final strain at fracture was lower than that for the 2% sample which, as a result, had a higher final tensile strength value. Thus, utilizing seeded polymerization, one can obtain a modulus for polymers with 2% TMI which is comparable to that obtained using 20% TMI in a single-stage process (Tables IV and V). In order to further investigate the importance of the locus of the NCO groups on the tensile properties, the following experiment was carried out. Two films were cast from a latex prepared via seeded polymerization. The latex contained 2% TMI, with the NCO groups concentrated in the shell layer. Both films were linear (not crosslinked) at this stage. One of the films was dissolved in acetone and recast from the solution. Both of the films (latex-cast and solution-cast) were then immersed in a 1% aqueous solu-
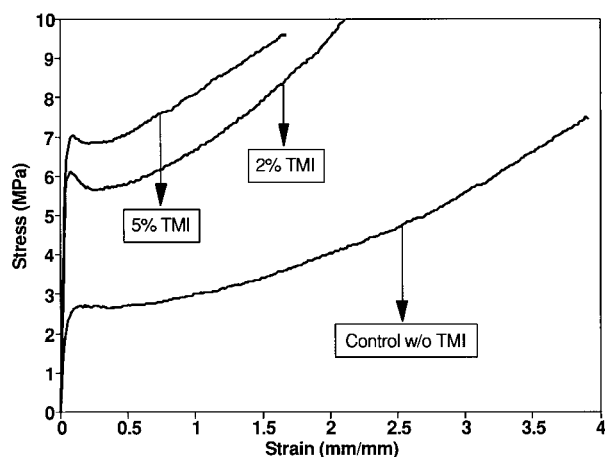
Figure 7   Effect of TMI concentration on interfacial crosslinking of poly(MMA/BA/TMI); films were cured in 1% aqueous solution of TEA for 30 min at 70°C.
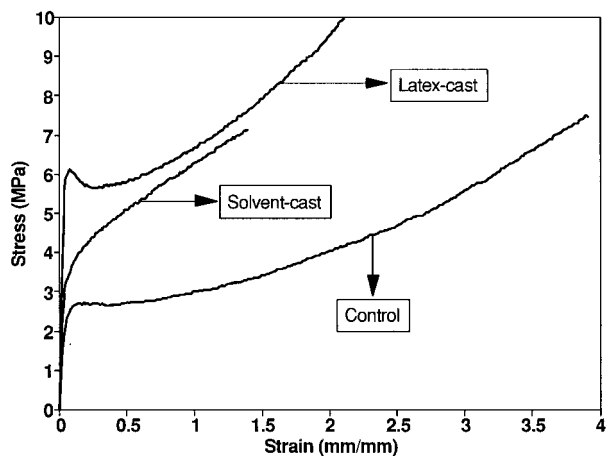
Figure 8 Effect of the locus of NCO groups on the tensile properties of poly(MMA/BA/TMI); films were cured in 1% aqueous solution of TEA for 30 min at 70°C; TMI = 2%.

tion of TEA and cured for 30 min at 70°C. The tensile properties of the crosslinked films thus obtained were studied and are compared in Figure 8. It is clear that the latex-cast film exhibits tensile properties that are greatly superior to those of the film cast from solution. A striking difference between the two tensile curves is the lack of a distinct yield point in the solvent-cast film. The other film was cast from latex particles in which the functional NCO groups were concentrated at the surface and therefore resulted in interfacial crosslinking during the curing process. As a consequence, a continuous rigid crosslinked network was formed at the particle interface upon curing. The seemingly two-phase structure causes the polymer film to exhibit a prominent yield point. In contrast, the solvent-cast film loses its two-phase structure when dissolved in acetone. Moreover, by dissolving the second film in acetone, the locus of the NCO groups was disrupted. As a result, interfacial crosslinking, which forms a continuous network of crosslinked polymer in the film, could not occur. This resulted in lower tensile strength and toughness.

Room Temperature-Curable Latexes

The reaction of TMI with water is quite slow. This is an advantage during the emulsion polymerization process because it minimizes the risk of premature crosslinking due to hydrolysis. However, as a result of the slow reaction of the NCO groups of TMI with water, external catalysts (such as

TEA) are required to carry out the crosslinking. Isocyanates are known to react with other functional moieties such as hydroxyl, amino, and carboxyl groups. Hence it was felt that incorporation of such functional monomers in the polymer chain along with TMI would enhance the crosslinking reaction at room temperature. Previous studies in our laboratory[26] had indicated that the copolymerization of TMI with MAA catalyzes the moisture-curing reaction at room temperature. Therefore, in order to develop one-pack, room temperature-curable systems, the incorporation of monomers with other functional groups was investigated. Emulsion polymerization was carried out in 4-oz glass bottles as described in the Experimental section. A typical recipe is shown in Table VI.

Three different types of functional monomers were used: hydroxyethyl acrylate (HEA) (hydroxyl groups), MAA (carboxyl groups), and 2-(diethylamino)ethyl methacrylate (DEM) (amino groups). Almost complete conversions (>98%) were obtained in all three cases.

Incorporation of Hydroxyl and Amino Groups

The polymer containing TMI and HEA was found to be soluble in acetone after film formation at room temperature. Heating the polymer films at 75°C for 4 h also did not result in any crosslinking. DEM has a tertiary amino group and was expected to act as an internal catalyst for the crosslinking of the latexes through the reaction of the isocyanate group with moisture. Some amount of

Table VI   Recipe for the Batch Emulsion Polymerization of MMA, BA, TMI, and a Functional Monomer (HEA, MAA, or DEM)

Component	Amount (g)
Methyl methacrylate	7.79
n-Butyl acrylate	10.45
TMI	0.38[a]
Functional monomer[b]	0.38[a]
Aerosol MA 80	1.14 (31.2 mM)
Ammonium persulfate	0.0950
Potassium metabisulfite	0.0950
Ammonium iron(II) sulfate hexahydrate	0.0007
DDI water	76.00

Polymerization temperature: 40°C.
[a] 2% based on total monomer.
[b] HEA, MAA, or DEM.
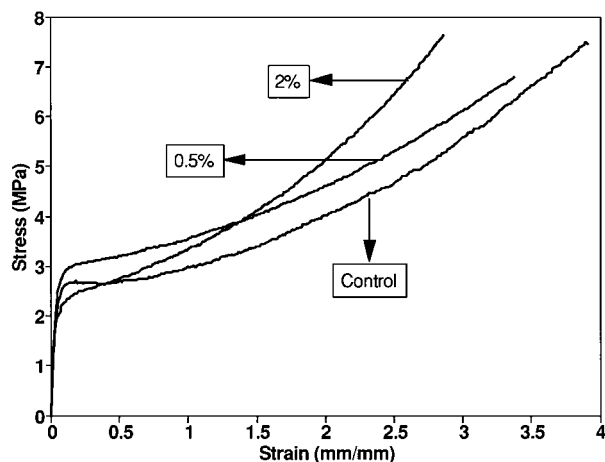
Figure 9 Effect of DEM on the mechanical properties of poly(MMA/BA/TMI/DEM); films were cured at room temperature for 10 days.

coagulum was observed on the walls on the polymerization bottles during the copolymerization with DEM. This could be due to the hydrolysis of TMI during the polymerization step in the presence of the amine-functionalized monomer. Two different concentrations of DEM (0.5 and 2%) were used. The films obtained from both these latexes were found to be crosslinked. The films were cast from fresh latexes on glass plates at room temperature and dried for 10 days. The crosslink densities were 4.6×10^{-5} and 11.1×10^{-5} mole crosslink/cc, respectively. The tensile properties of these films were determined as shown in Figure 9. The presence of DEM did not improve the mechanical properties over the control sample without TMI and DEM, although it did enhance the crosslinking reaction. This could be due to the crosslinking occurring prematurely during the polymerization step instead of during or after film formation. This leads to a weak film of loosely fused individual crosslinked particles instead of a strong, coalesced film. Young's moduli of the films with 0.5 and 2% DEM (109.3 and 102.8 MPa, respectively) were found to be lower than that of the control sample (130.8 MPa).

Effect of Carboxyl Groups on Crosslinking of TMI Latexes

Latexes containing 5% functional monomers (3% TMI and 2% MAA) were prepared using a recipe similar to the one shown in Table VI. The crosslinking properties of this latex were compared with those of a latex prepared with 5% TMI (with-

out MAA). Films were obtained by drying the latexes at room temperature for 10 days. While the film prepared in the absence of MAA dissolved in acetone, the sample containing 3% TMI and 2% MAA was found to be crosslinked. The mechanical properties of the latter film were determined and are compared with the control MMA/BA copolymer in Figure 10. A significant improvement was observed in the mechanical properties of the carboxylated TMI latex. In order to verify whether this improvement in tensile properties was indeed due to the crosslinking via the NCO group and not due to the carboxyl groups alone, a sample containing 2% MAA but no TMI was also prepared for comparison. The tensile properties of this sample (not shown in the figure, for the sake of clarity) were determined to be quite similar to the control sample: this sample did not exhibit any crosslinking and it dissolved readily in acetone. It can therefore be concluded that the crosslinking is due to the isocyanate groups. In order to further confirm this conclusion, the Fourier transform infrared (FTIR) spectrum of the film was taken. Unlike the TMI polymer without MAA, the spectrum of the above film did not reveal any peak in the 2260 cm^{-1} wave number range, which is characteristic of the isocyanate group. This again indicated that the isocyanate groups were consumed during the crosslinking reaction at room temperature. Further curing of the film at elevated temperatures did not result in any significant increase in the tensile properties. Therefore, the crosslinking occurred either during the polymerization step itself or during the film formation
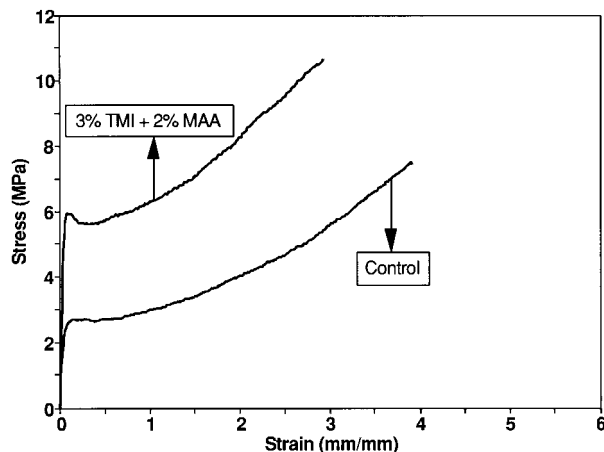
Figure 10 Effect of MAA on the mechanical properties of poly(MMA/BA/TMI/MAA) (40/55/3/2); films were dried at room temperature for 10 days.

Table VII   Effect of MAA Concentration on the Tensile Properties of Poly(MMA/BA/TMI/MAA)

MAA Concentration (%)	Crosslink Density (mole crosslink/cc)	M_x[a] (mole/g)	Young's Modulus (MPa)
0.0	—	—	130.8
0.5	5.1×10^{-5}	19648	115.5
1.0	20.4×10^{-5}	4892	152.5
2.0	24.0×10^{-5}	4160	194.0
4.0	4.8×10^{-5}	20660	208.0

MAA Concentration (%)	Yield Stress (MPa)	Tensile Strength (MPa)	Toughness (MPa)
0.0	2.54	7.14	16.83
0.5	5.19	10.85	23.83
1.0	6.64	11.72	21.28
2.0	8.15	13.36	23.20
4.0	9.19	13.27	20.71

[a] M_x, molecular weight between crosslinks.

stage. Had the crosslinking taken place prematurely during the polymerization step, a loosely fused film of crosslinked properties with poor mechanical strength would have been obtained. However, the tensile strength of the above film was significantly better than that of the control sample. Therefore it can be concluded that the crosslinking took place predominantly during the film formation stage. Since carboxyl groups are lower in the reactivity hierarchy with NCO groups as compared with water,[28] it is believed that the function of MAA is to catalyze the NCO–water reaction. Addition of free MAA monomer to a poly(MMA/BA/TMI) latex prior to film formation was also found to enhance the crosslinking. However, films cast from latex blends of poly(MMA/BA/TMI) and poly(MMA/BA/MAA) were found to be soluble in acetone. In this case, the crosslinking did not occur because the carboxyl moieties were not in close proximity with the isocyanate groups, the two functionalities being on separate latex particles.

The effect of the concentration of copolymerized MAA on the crosslinking and mechanical properties of TMI latexes was investigated. The amount of TMI in the latex was fixed at 2%, and the MAA concentration varied between 0.5 and 4%. The latex films were found to crosslink over a period of 1–4 weeks at room temperature. The tensile properties were determined after curing the films at room temperature for 4 wk; these are compared in Table VII and Figure 11. The modulus and tensile strength of the polymer films were found to increase with MAA concentration, while the ultimate strain decreased. However, the degree of crosslinking was first found to increase and then decrease with increasing MAA concentration. The low degree of crosslinking for the first sample (MAA = 0.5%) was due to the films not being cured completely after 4 weeks. The degree of crosslinking increased to 4.8×10^{-5} mole crosslink/cc after the film was cured for an additional 2 months. As a result, the modulus was lower than that for the other samples. The films with 1 and 2% MAA exhibited similar degrees of cross-
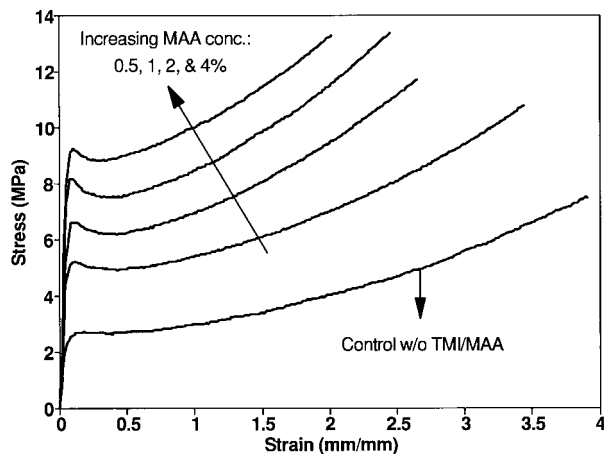
Figure 11   Effect of MAA concentration on the tensile properties of poly(MMA/BA/TMI/MAA) containing 2% TMI; films were cured at room temperature for 4 weeks.

linking. The sample with the highest MAA level again had a low degree of crosslinking. MAA acts as a catalyst for the NCO–water reaction. The high concentration of MAA might have resulted in the loss of some TMI monomer due to hydrolysis during the polymerization step, resulting in the low final degree of crosslinking. However, the hydrolysis was not significant enough to deteriorate the final film properties.

Yield stress and tensile strength values obtained in the presence of MAA were higher than those obtained via the two-step seed polymerization process. In the latter process, high tensile strengths were observed as a result of interfacial crosslinking due to the preponderance of crosslinking sites at the surface of the latex particles. A similar mechanism may be in effect in the presence of MAA as well. At high concentrations of the more hydrophilic MAA, the carboxyl groups which are instrumental in catalyzing the NCO–water reaction tend to stay at the surface of the latex particles. As a result, the major locus of the crosslinking reaction is at the interparticle boundaries, resulting in interfacial crosslinking. This leads to the development of a rigid network across the particle–particle interface, which increases the film rigidity (higher Young's modulus). The development of a continuous crosslinked network is also backed by the increasing prominence of the yield point with MAA concentration. The yield stress increased and the yield point became sharper as the concentration of the carboxyl groups was increased. Another interesting feature of these latex systems is that not only the modulus but also the toughness of the polymer films increased at higher MAA concentrations (Table VII) as compared with the control sample.

Room temperature-curable TMI latexes can be developed by incorporating small amounts of MAA into the polymer. The presence of MAA in the polymer chain helps to catalyze the NCO–water crosslinking reaction. A self-curable system that crosslinks in the presence of moisture can thus be obtained.

Latex Pot-Life Stability

It was shown in the previous sections that TMI can be used to prepare latexes capable of undergoing latent crosslinking. Latexes that undergo curing at ambient temperature can also be obtained by copolymerizing small amounts of MAA along
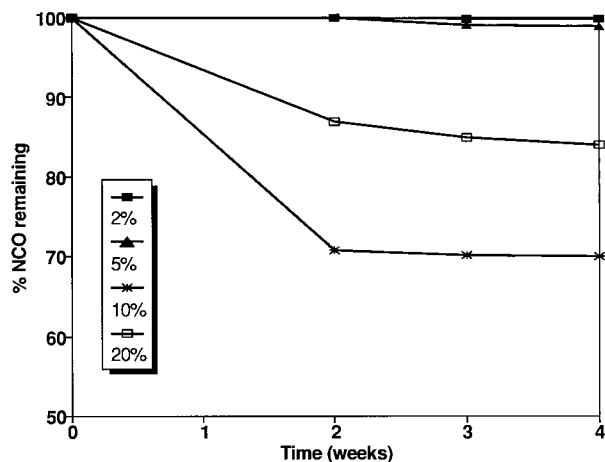

Figure 12 Shelf stability of the NCO group in poly(MMA/BA/TMI) latexes stored for different intervals of time, as determined by FTIR spectroscopy; thin films of stored latexes were cast on ZnSe disks for FTIR analysis of NCO groups.

with TMI. The isocyanate group of TMI was determined[1] to be quite stable toward hydrolysis during the emulsion polymerization process (at 40°C), which typically lasts for 2–4 h. However, most applications of crosslinkable latexes require shelf storage for more than 6 months. It was therefore felt necessary to study the fate of the isocyanate group of TMI polymers stored in the latex form for an extended period of time.

Stability of the NCO Group in Latex Form

The polymer particles in a latex are in constant contact with water. Although TMI is much more stable than conventional isocyanates toward hydrolysis, it does react slowly with water during latex storage. The extent of hydrolysis depends mainly on the locus of the NCO groups in the polymer particles. Latexes prepared via seeded polymerization had a preponderance of NCO groups at the surface of the latex particles, i.e., in close proximity to the continuous water phase. As a result, these latexes were found to hydrolyze and coagulate after 2 weeks of storage at room temperature. The shelf stability of latexes prepared via single-stage polymerization was studied using FTIR spectroscopy. These latexes had a more homogeneous distribution of the NCO groups. FTIR spectra of latexes stored for different periods of time were taken and compared with those of the fresh latex. Thin films of diluted latexes were cast on ZnSe disks for the spectroscopic
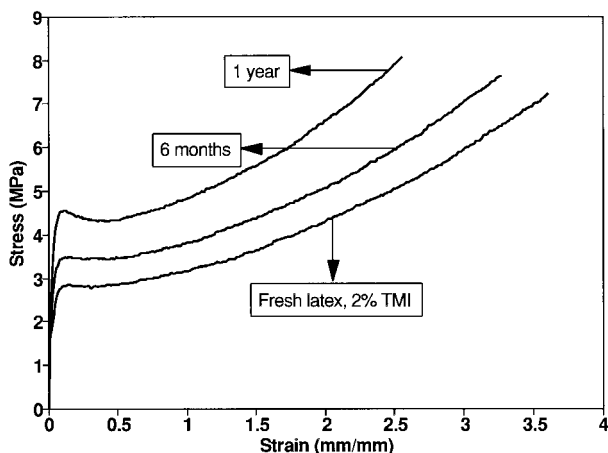
Figure 13 Tensile properties of polymer films obtained from poly(MMA/BA/TMI) (43/55/2) latexes stored at room temperature for different intervals of time (6 months, 1 year); films were dried at room temperature from the stored latexes for 10 days prior to testing.

measurements. The absorbance of the isocyanate peak (around 2260 cm^{-1}) was followed in order to quantify the amount of NCO present in the latex. The results are shown in Figure 12 for four different TMI concentrations (2–20%). It can be observed that a significant loss of the NCO groups (up to 30%) occurs for the high TMI-content (10–20%) latexes. This is due to hydrolysis during storage in the aqueous latex. However, the loss of NCO is minimal for latexes containing 2 and 5% TMI. It was discussed in the previous sections that a TMI concentration less than 5% is sufficient in order to obtain substantial improvement in the mechanical properties of the polymer films. For these latexes, the stability of the isocyanate group over a period of 1 mo was excellent.

Shelf Stability Over Extended Periods of Time

The FTIR data indicated that the isocyanate groups did not hydrolyze after a month of storage. The shelf stability of the latexes over extended periods of time was studied by determining the tensile properties of the latexes. Polymer films were cast from latexes stored for different intervals of time, and the mechanical properties were compared with those of the fresh latex.

Figure 13 compares the tensile properties of polymer films obtained from latexes and stored for different periods of time. Films were cast from a fresh latex containing 2% TMI. The same latex was then stored for periods of 6 months and 1 year.

Polymer films were cast from these latexes at the end of 6 months and 1 year. The film cast from the fresh latex was found to be soluble in acetone. The other two films, however, were crosslinked, the degree of crosslinking being greater for the latex sample stored for 1 year. The film obtained from the latex sample stored for 6 months was only slightly crosslinked; therefore, the final extension at fracture was almost the same as that of the fresh sample. The sample stored for 1 year exhibited the highest modulus (164 MPa as compared with the fresh-sample value of 138 MPa) and tensile strength; however, the ultimate strain at break was the lowest. These results indicate that the NCO groups do hydrolyze during latex storage at room temperature over an extended period of time. The extent of hydrolysis is low, especially during the first 6 months of storage. During this period, the tensile properties actually show a slight improvement over those of the fresh uncrosslinked sample. Hence it can be concluded that TMI latexes possess very good shelf-life stability. The latex stored for 1 year exhibited a higher and more prominent yield point as compared with the other samples. This may be due to the phase separation of terpolymers of different compositions during latex storage. The more hydrophilic MMA-rich polymer chains diffuse toward the surface of the latex particle. This rigid phase results in a higher yield stress of the latex film.

Shelf Stability of Carboxylated TMI Latexes

TMI latexes containing small amounts of MAA in the polymer backbone were found to exhibit
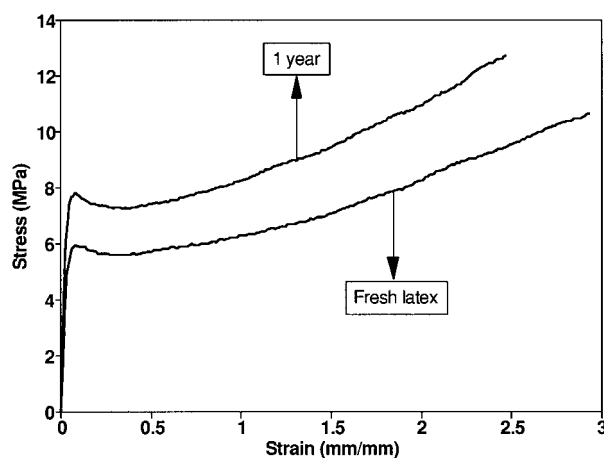
Figure 14 Tensile properties of poly(MMA/BA/TMI/MAA) latex stored at room temperature for 1 year compared with those of the fresh latex; TMI = 3%, MAA = 2%.

Table VIII   Recipe for the Batch Emulsion Polymerization of Poly(MMA/BA/TMI/MAA)

Component	Amount (g)
Methyl methacrylate	15.58
n-Butyl acrylate	20.90
TMI	0.76
Methacrylic acid	0.76
Aerosol MA 80	2.28 (82 mM)
Ammonium persulfate	0.19
Potassium metabisulfite	0.19
Ammonium iron(II) sulfate hexahydrate	0.0014
DDI water	57.00

Solids content: 40%; polymerization temperature: 40°C.

excellent tensile properties. Moreover, these latexes were self-curable at ambient temperatures. Such systems would be highly useful for industrial applications if the shelf stability of the latexes is good. Therefore, the storage life of these latexes was also investigated. Mechanical properties of films obtained from a fresh latex were compared with those of films cast from the same latex stored for a year at room temperature (Fig. 14). It can be observed that the mechanical properties of the sample stored for a year did not show any deterioration. The modulus (280 MPa) and tensile strength were actually higher than those for the fresh latex (modulus = 182 MPa). The degree of crosslinking for the former sample was slightly higher. The ultimate strain was lower, however, but not by a significant margin. The incorporation of small amounts of MAA (0.5 to 4%) in TMI latexes helps in catalyzing the crosslinking reaction of the NCO groups with water during film formation. As a result, single-pack systems capable of curing at ambient temperatures can be obtained. In addition to the advantage of being crosslinkable at room temperature, these latexes possess excellent shelf stability.

High-Solids-Content Crosslinkable Latexes

The latexes discussed in the previous sections were prepared at 20% solids content. Most practical applications require a higher concentration of polymer. Therefore the recipe for the carboxylated TMI latex was scaled up to 40% solids as shown in Table VIII. Batch polymerization was carried out at 40°C using redox initiators. A stable latex with good colloidal stability was obtained. No co-

agulation was observed even after storage of several months, unlike the results reported in a previous publication.[27] This could be due to a difference in the level of surfactant used. In the above case, the surfactant concentration was varied between 0.7 and 1.5%, based on monomer weight. In our case, the surfactant concentration was 4.8% based on total monomer. The tensile properties of films obtained from this latex were similar to those of polymer films obtained from latexes prepared at 20% solids content (Table VII) with 2% MAA.

CONCLUSIONS

The film formation behavior and mechanical properties of polymer latexes functionalized with TMI were studied. Films obtained from fresh latexes were found to be soluble in acetone and did not crosslink easily at ambient temperatures. The latexes were acidic in nature. Adjusting the pH to higher values before film formation seemed to enhance the crosslinking reaction. Addition of external curing agents such as TEA to the latexes also catalyzed the crosslinking at room temperature. However, this led to premature crosslinking of the latex particles before coalescence, thereby leading to loosely fused weak polymer films. Latent crosslinking after the completion of the film formation process resulted in strong polymer films with high tensile strengths. The degree of crosslinking, modulus, and tensile strength were found to increase with increasing TMI concentration. However, the ultimate strain at fracture decreased, and the films were brittle at high TMI contents. Employing TMI at a concentration of 2% (based on the monomer) was found to be adequate for significantly improving the tensile properties of the polymer films as compared with the control sample without TMI. The locus of NCO groups in the latex particles was determined to affect the mechanical properties. When the NCO groups were concentrated at the surface of the polymer particles using seeded polymerization, rigid films with high tensile strengths were obtained. This was ascribed to the development of continuous crosslinked network at the boundaries between individual particles as a result of interfacial crosslinking.

The incorporation of monomers with hydroxyl, amino, and carboxyl functionalities in TMI latexes was also studied. The hydroxyl monomers

did not affect the crosslinking reaction, whereas the amino monomer resulted in premature crosslinking. The introduction of carboxyl groups was found to catalyze the curing reaction at room temperature. A significant improvement in the mechanical properties was also observed. The shelf stability of the TMI latexes was found to be excellent. The carboxylated latexes were also found to be very stable even after a year of storage. These latexes are useful in developing single-pack systems capable of undergoing curing at room temperature in the presence of moisture.

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