The Effect of Synthesis Methods on the Mechanical Properties of Self-Crosslinkable Poly(*n*-butyl methacrylate-*co*-N-methylolacrylamide) Films

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ABSTRACT: The effects of particle size and parent polymer characteristics on the mechanical properties, gel fraction, and swelling index of self-crosslinkable poly(*n*-butyl methacrylate-co-*N*-methylolacrylamide) films made by two-stage emulsion or microemulsion polymerization in the presence of variable amounts of the chain transfer agent, *n*-butyl mercaptan, are reported here. In films prepared with latexes made by microemulsion polymerization, the crosslinking degree increased greatly on curing; by contrast, in those made by emulsion polymerization, the crosslinking degree practically did not increase after curing. Stress–strain tests of uncured and cured films indicate that microemulsion-made films are tougher than the emulsion-made films. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1669–1674, 2011

Key words: mechanical properties; crosslinking; films; swelling; polymer synthesis; characterization

INTRODUCTION

Polymeric latexes have many applications such as binders in coatings.[1–3] In this application, the colloidal dispersion of polymer particles is transformed into a polymer film.[4] The formation of a continuous, stable film is the result of latex particle packing, particle deformation and cohesion, and polymer chain interdiffusion (coalescence of polymer particles).[3,4] The purpose of forming a crosslinked film is to upgrade its properties such as solvent and chemical resistance, hardness and toughness compared with those of the noncrosslinked polymer films.[4–10] The crosslinking reaction can take place before the coalescence of polymer particles,[5–7,9,10] parallel to the polymer chain interparticle diffusion[8,10] or after particle film formation.[7]

To improve mechanical properties of films and to increase the adhesion to substrates, vinyl and acrylic polymers are usually modified with small amounts of a functional monomer such as *N*-methylolacrylamide (NMA), acrylic acid, or methacrylic acid.[7,11–17] When NMA is used as the functional monomer, self-crosslinkable latexes are obtained that form films with higher tensile strength, toughness, abrasion, and solvent resistance with respect to the noncrosslinked films.[16,17] To produce though and mechanically strong films, it is necessary to reduce the microgel content (i.e., the amount of crosslinked polymer chains) in the parent latex particles; these particles should contain long chains that can diffuse across particle–particle interfaces during film formation.[4–9] In particular, when NMA is employed, the crosslinking can be achieved after film formation by thermal treatment.[7]

Similarly to its emulsion counterpart, microemulsion polymerization allows the synthesis of colloidal dispersions of high-molar mass polymer particles with fast reaction rates, but in the nanometer range.[18,19] However, the mechanism of polymerization is different for the two processes and often polymers with different physicochemical characteristics or morphology from the ones produced by emulsion polymerization are obtained by microemulsion polymerization.[20–26]

Recently Krishnan et al.[7] reported the synthesis of copolymers of *n*-butyl methacrylate (BMA) and NMA by a two-stage emulsion polymerization process in the presence of varying amounts of the chain transfer agent, carbon tetrabromide. Films prepared with these copolymers had low crosslinking degree (low gel content) before curing and higher crosslinking degree (higher gel content) after thermal curing.

These authors reported gel contents and swelling indexes (SIs) of the uncured and cured films but not their mechanical properties.

In this work, the synthesis of BMA and NMA copolymers made by two-stage emulsion or microemulsion polymerization processes with *n*-butyl mercaptan (*n*-BM) as chain transfer agent to produce self-crosslinkable films with improved mechanical properties is reported. The aim is to determine the effect of the different methods of preparation on the characteristics (gel content and SI) and mechanical properties of uncured (made by casting) and thermally cured films.

EXPERIMENTAL SECTION

BMA, 99% pure from Aldrich (Milwaukee, WI), was passed through a DHR-4 column (Scientific Polymer Products , Ontario, NY) to remove the inhibitor. NMA, TCI America (Portland, OR), was used as received. *n*-BM was 99% pure from Aldrich. Sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were both 99% pure from Aldrich. Potassium persulfate, 99% pure from Aldrich, and 2,2-azobis(2-methylpropionamidine) dihydrochloride (V-50), 99% pure from Wako Chemicals (Richmond, VA), were the initiators. HPLC-grade tetrahydrofurane (THF) and toluene (99% pure) were from Aldrich. Methanol reagent grade was purchased from Fermont (Monterrey México). Deionized and bi-distilled water was used. Sodium bicarbonate, 95% pure from Fermont, was employed as a buffer to maintain the pH at 6.5–7.0.

The emulsion and microemulsion copolymer latexes were prepared in two stages in a 250-mL glass reactor. The first stage consisted in the batch polymerization of BMA (seed stage), whereas the second one was carried out semicontinuously under monomers (BMA and NMA) starved conditions to produce a copolymer shell (feed stage). The compositions of the emulsion and the microemulsion are indicated in Table I. In the first stage, the batch polymerization of BMA was carried out for both processes for 45 min at 70°C under N$_2$-atmosphere. In the second stage, a mixture of water, NMA, BMA, *n*-BM (in variable concentration), and SDS (for emulsion) or CTAB (for microemulsion) were fed at 0.7 cm^3/min rate (Table I). For conversion, measured by gravimetry, the polymer was precipitated by adding excess methanol, recovered by filtration, washed several times with excess water to remove adsorbed surfactant, subjected to dialysis, and dried in an oven to constant weight. Final latexes at the end of both stages were also collected for particle size and polymer molar mass determination.

Intensity average particle size (D_{pz}) was measured at 25°C and at 90° in a Malvern 4700 quasielastic

TABLE I
Recipes for Latex Preparation

Component	Amount (g)	
	First stage	Second stage
Emulsion		
Water	88.5	19.3
BMA	10.5	79.8
NMA	–	2.4
SDS	0.1278	0.66
KPS	0.0735	–
NaHCO$_3$	0.0725	–
n-Butyl mercaptan[a]	–	0%, 0.1%, and 0.3%
Microemulsion		
Water	88.5	38.75
BMA	10.5	27.5
NMA	–	0.82
CTAB	1.92	1.5
V-50	0.105	–
NaHCO$_3$	0.072	–
n-Butyl mercaptan[a]	–	0%, 0.1%, and 0.3%

[a] Weight percentage based on BMA added in the second stage.

light scattering apparatus equipped with a He–Ne laser ($\lambda = 664$ nm). Latexes were diluted 100-times with water to minimize particle–particle interactions and to reduce multiple light scattering. D_{pz} is given by the sixth moment divided by the fifth moment for the size distribution, according to:

$$D_{pz} = \frac{\sum_{i=1}^{n} n_i D_{pi}^6}{\sum_{i=1}^{n} n_i D_{pi}^5}. \tag{1}$$

For measuring molar mass distribution (MMD) and average molar masses of the soluble fraction, the gel formed during the polymerization was removed from the surfactant-free copolymer recovered by the procedure described above. To remove the gel fraction, samples were placed in separated vials with THF for 1 week, filtered, and the solvent from the filtrate were evaporated to obtain the sol fraction. Then the sol fraction was dissolved in THF (3 mg/cm^3) and injected into a PerkinElmer LC-30 gel permeation chromatograph equipped with a refractive index detector and a multiangle light scattering detector with the specific refractive index increment (d_n/d_c) value of 0.083 mL/g[27] for PBMA and THF, to determine molar mass and MMD.

The gel fraction and the SI of the uncured and cured films were determined gravimetrically. Latex samples were dried at 40°C in a Petri dish to produce the uncured films (1.2–1.4 mm in thickness). This temperature is above the glass transition temperatures of the BMA–NMA copolymers prepared here, which are 33 and 35°C for the emulsion and the microemulsion-made, respectively.[28] For the

TABLE II
Particle Size, Weight Average Molar Masses and Polydispersity for Both Polymerization Methods as a Function of *n*-Butyl Mercaptan Concentration

	Emulsion				Microemulsion			
n-BM (wt %)	$D_{pz}{}^a$ (nm)	$D_{pz}{}^b$ (nm)	$M_w \times 10^{-3}$ (Dalton)	M_w/M_n	$D_{pz}{}^a$ (nm)	$D_{pz}{}^b$ (nm)	$M_w \times 10^{-3}$ (Dalton)	M_w/M_n
0	113	250	3000	1.1	42	65	946	1.5
0.1	110	237	170	1.2	40	70	470	3.7
0.3	100	234	83	2.5	44	64	421	6.1

[a] Particle size measured by QLS (Average in Intensity, D_{pz}) at the end of the seed stage.
[b] Particle size measured by QLS (Average in Intensity, D_{pz}) at the end of the Feed Stage.

curing process, a sample of each film was heated at 150°C during 30 min. The uncured and cured films were placed in vials with toluene in a film-to-solvent weight ratio of 1/100 for 1 week. The suspensions were filtered using 2 μm pore-size membranes. The swollen gels (fraction retained in the filter) were weighted and then dried to constant weight. The gel fraction was calculated as the mass of the dried gel weight divided by the original mass of the polymer sample. The SI was calculated as the ratio of the mass of the swollen gel to that of the dry gel.

Mechanical (stress–strain) tests of uncured and cured film samples were carried out at 15 ± 1°C and a displacement rate of 5 mm/min in an SFM-10 United universal testing machine, according to the ASTM D-882 standard. Tests for each film were repeated at least 10 times to provide the average values and standard deviations of the Young modulus and other mechanical parameters.

RESULTS AND DISCUSSION

In both emulsion and microemulsion polymerization processes, conversions were high (≥90%) at the end of the seed (first) and feed (second) stages. Final particle size for both polymerization processes is practically independent of the amount of chain transfer agent (*n*-BM) used (Table II). Particle size at the end of the seed stage was on the order of 42 (±3) nm for the microemulsion process and ∼ 113 (±3) nm for the emulsion process; during the feed stage, particles grew to approximately 65 (±2) and 250 (±15) nm for the microemulsion and emulsion processes, respectively (Table II). Particle growth in all cases, indicate that both monomers (BMA and NMA) added during the second stage were incorporated in the particles. Because of the monomer-starved conditions, both monomers can be incorporated over the particles and polymerize there to form a core-shell, where the shell is made of the functionalized copolymer. Krishnan et al.[7] demonstrated by transmission electron microscopy and atomic force microscopy of the copolymer particles and of the thermally cured films that a core-shell structure develops due to the

monomer-starved conditions in the feed stage and to the hydrophilicity of NMA. However, according to Winnik and coworkers,[6] it is difficult that the locus of the polymerization be outer the seed particles if the core and the shell have similar compositions, then because of the low amount of NMA used in the second stage, some of the monomers should diffuse inside the particles and polymerize there. In any case, either of these two mechanisms should lead to particle growth during the second stage.

Weight-average molar masses (M_w) and polydispersity (M_w/M_n) of the sol fraction obtained at the end of the second stage for both processes are reported in Table II. The addition of *n*-BM decreases the molecular mass of the soluble fraction; this effect is larger in the emulsion-made copolymers than in the microemulsion-made ones. This could be the result of the much larger particle number density in the microemulsion polymerization process when compared with that in the emulsion one, which leads to a much lower local concentration ratio of chain transfer agent-to-monomer into the particles in the former. However, this issue has not been addressed in the literature, as far as we know.

Table III reports the gel fraction and the SIs for both uncured and cured films. As expected from the results of Krishnan et al.,[7] both the uncured and cured cast films made with the latexes prepared by emulsion polymerization in the absence of chain

TABLE III
n-Butyl Mercaptan Concentration Effect on Gel Fraction and Swelling Index

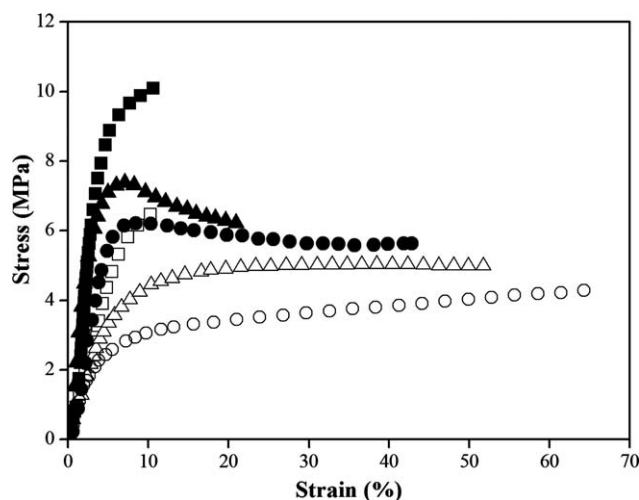|	Emulsion		Microemulsion	
n-BM (wt %)	Gel fraction	Swelling index	Gel fraction	Swelling index
Uncured films				
0	0.85 ± 0.01	5.2 ± 0.25	0.21 ± 0.02	2.1 ± 0.20
0.1	0.18 ± 0.01	2.3 ± 0.03	0.15 ± 0.03	1.4 ± 0.15
0.3	0.12 ± 0.01	1.5 ± 0.02	0.10 ± 0.03	1.2 ± 0.15
Films cured at 150 °C for 30 min				
0	0.86 ± 0.01	5.3 ± 0.26	0.78 ± 0.02	35.2 ± 0.60
0.1	0.21 ± 0.02	3.6 ± 0.03	0.60 ± 0.01	28.6 ± 1.05
0.3	0.12 ± 0.01	3.0 ± 0.14	0.50 ± 0.03	27.7 ± 1.62

Figure 1 Stress–strain curves for non cured films made with emulsion or microemulsion latexes as a function of *n*-BM concentration: emulsion (□) 0 wt %, (△) 0.1 wt %, and (○) 0.3 wt % *n*-BM; microemulsion (■) 0 wt %, (▲) 0.1 wt %, (●) 0.3 wt % *n*-BM.

transfer agent contain large gel fraction, 0.85 and 0.86, respectively. Krishnan demonstrated that most of the copolymer produced in the feed stage was prematurely crosslinked even before the copolymer was thermally cured at elevated temperature and that the crosslinking was not only due to methylene bridge formation during the polymerization reaction but also by chain transfer of a free radical by abstraction of the α-atom of the NMA molecule, because of the high concentration of polymer in the latex particles during the feed stage. This process results in branching of the polymer chain, which may lead to crosslinking when two such branch ends meet and react. As expected, the addition of a chain transfer agent diminishes branching and the early crosslinking during the feed stage. The addition of *n*-BM reduces drastically the gel content of the uncured emulsion based films; however, as showed for the film made with latex prepared by emulsion polymerization in absence of *n*-BM, the gel content practically does not increase after curing. Moreover, the low SI of the cured emulsion-based films containing *n*-BM (Table III) indicates that the gel fraction has a high crosslinking density.

By contrast, the gel fraction of the uncured film made with latexes prepared by microemulsion polymerization in the absence of *n*-BM was much lower (0.21), and in the cured film increased substantially to 0.78 (Table III), demonstrating the advantage of microemulsion polymerization over emulsion polymerization, since in the microemulsion process, films with low premature crosslinking fraction can be obtained. As expected, the presence of *n*-BM also reduces the gel content in the uncured microemulsion-based films. The lower gel content of

the uncured films can be explained by their smaller particle size in the microemulsion-made latexes; because of their smaller size, they should have less polymer chains, and so the probability for chain transfer to polymer is much lower than in the larger particles obtained by emulsion polymerization. As a consequence, a lower crosslinking degree should be expected in the smaller particles. When the films are thermally cured, the OH groups of the polymer chains of adjacent particles can react to yield a film with higher crosslinking degree.

Figures 1 and 2 depict stress–strain tests performed in uncured and cured films, respectively. Table IV reports the Young modulus, tensile strength, elongation at break, and toughness for both types of films. The values reported are the average of at least 10 test pieces. The stress–strain curves for noncured films prepared from emulsion and microemulsion polymerization latexes at various *n*-BM concentrations are shown in Figure 1. In general, the mechanical response under unidirectional tensile tests of all samples is typical of hard, ductile polymers.[29,30] However, there are evident differences in the stress–strain curves of samples prepared by microemulsion compared with that made by emulsion polymerization: the shape of the stress–strain curves of samples prepared by emulsion polymerization reveals an uniform extension behavior and shows an apparent yield point, which decreases as the *n*-BM concentration increases, whereas for the microemulsion-based films, the stress–strain curves depict a yield point, after that the stress decreases as the strain increases to the break point (cold-drawing). Only the sample without *n*-BM shows a different mechanical response because the breaking point is very close to the yield point. The difference in stress–strain curves for
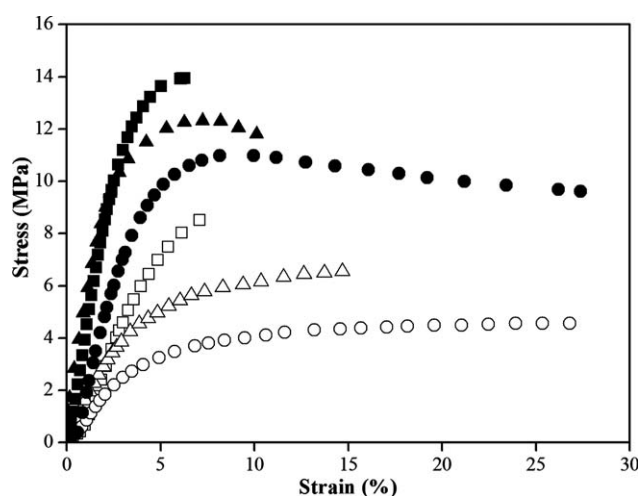

Figure 2 Stress–strain curves for cured films made with emulsion or microemulsion latexes as a function of *n*-BM concentration: emulsion (□) 0 wt %, (△) 0.1 wt %, (○) 0.3 wt % *n*-BM; microemulsion (■) 0 wt %, (▲) 0.1 wt %, (●) 0.3 wt % *n*-BM.

TABLE IV
Summary of Tensile Properties [Young's Modulus (E), Tensile Strength (σ_p), Elongation at Break (ε_b), and Toughness]
of Films Prepared with the Emulsion or Microemulsion Latexes (At Least 10 Test Pieces were Used)

n-BM (wt %)	Emulsion				Microemulsion			
	E (MPa)	σ_p (MPa)	ε_b (%)	Toughness $\times 10^{-6}$ (J/m^3)	E (MPa)	σ_p (MPa)	ε_b (%)	Toughness $\times 10^{-6}$ (J/m^3)
Uncured films								
0	176 ± 8	6.9 ± 0.9	13 ± 2	0.6 ± 0.2	244 ± 17	10.6 ± 0.8	11 ± 1	0.8 ± 0.1
0.1	125 ± 6	3.9 ± 0.6	61 ± 8	1.9 ± 0.3	237 ± 11	8.2 ± 0.7	18 ± 5	1.3 ± 0.4
0.3	79 ± 5	3.3 ± 0.5	72 ± 7	2.0 ± 0.4	204 ± 9	7.1 ± 0.8	40 ± 7	2.4 ± 0.2
Films cured at 150 °C for 30 min								
0	225 ± 4	9.2 ± 0.7	9 ± 2	0.3 ± 0.1	315 ± 5	16.1 ± 0.7	11 ± 3	1.0 ± 0.4
0.1	196 ± 7	6.8 ± 0.9	18 ± 5	0.9 ± 0.2	295 ± 9	12.2 ± 0.5	12 ± 1	1.0 ± 0.4
0.3	181 ± 7	3.8 ± 0.4	27 ± 4	0.9 ± 0.2	272 ± 7	10.8 ± 0.6	29 ± 5	2.6 ± 0.6

samples prepared by the emulsion and microemulsion methods is a clear evidence of different morphological characteristics in these samples. The low toughness of the films prepared with latex obtained without the use of the chain transfer agent are related to the high gel content in the polymer particles that limits the interparticle diffusion and the healing of the interface between two or more particles. The decrease in ultimate and yield stress of the noncured films as the content of n-BM increases, observed in both emulsion- and microemulsion-made films (Figure 1), is a consequence of the lower molar masses (Table II) and the lower gel content induced for the augment of n-BM in the initial composition. The increase in toughness and elongation at break as the content of n-BM increases (Table IV) is a consequence of the smaller crosslink formation during polymerization, which results in a higher degree of polymer interparticle diffusion during the film formation.

The stress–strain curves of cured films samples are shown in Figure 2. As expected, the elongation at break decreases, whereas the tensile strength and Young modulus increase after the films are cured (compare Figs. 1 and 2; Table IV). This is a consequence of the additional crosslinking among the NMA-containing polymer chains, induced by the annealing at high temperature. After the thermal treatment, the toughness of the emulsion-based films decreases, whereas that of the microemulsion-based films increases. In the latter case, the increase of toughness is due to the formation of a network with low crosslinking density during the annealing (as suggested by the high SIs of these gels).

CONCLUSIONS

Here, it is shown that microemulsion polymerization reduces the premature crosslinking of the polymer chains. When n-BM is used, the gel content is decreased in both polymerization processes. However, only the films prepared with latex made by microemulsion polymerization increased greatly the crosslinking on curing. The mechanical tests indicate substantial differences in the mechanical response of the emulsion-made versus microemulsion-made films before and after curing. These differences are explained in terms of differences in molar masses of the soluble fraction, particle size, and degree of crosslinking before the film formation.

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