

Interfacial Aspects of Strength Development in Poly(methyl methacrylate)-Based Latex Systems

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SYNOPSIS

Film formation from poly(methyl methacrylate) (PMMA) latex and PMMA copolymer latexes incorporating *N*-(iso-butoxymethyl)acrylamide (IBMA) or methacrylic acid (MAA) has been investigated in terms of the development of tensile strength as a function of annealing time and temperature. Tensile strength is developed through a combination of macromolecular interdiffusion and interfacial crosslinking. The relative rates of interdiffusion vs. crosslinking reactions were studied as a function of temperature and the chemical nature and concentration of the IBMA and MAA functional groups. For low concentrations of these two functional monomers it appears that polymer chain interdiffusion between adjacent latex particles during the film formation process dominates the kinetics of strength development. However, at higher IBMA and MAA concentrations, the higher glass transition temperature at the latex particle surface and intraparticle crosslinking hinders interdiffusion, as reflected by differences in the power law exponent values obtained from the log-log dependence of tensile strength on annealing time. The power law exponents were higher in the case of PMMA than for both IBMA- and MAA-containing copolymers. There was a greater influence of annealing temperature on the tensile behavior for the MAA copolymer system as compared to the IBMA copolymer. In the interfacially crosslinked latex polymer system, there is competition between the interdiffusion and crosslinking mechanisms in determining the final mechanical strength of films during the annealing process. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Emulsion polymers are primarily used for technologically important applications such as coatings, adhesives, and thermoplastics, where polymer films with good mechanical strength are often required. Film formation from latexes and the subsequent development of cohesive strength occurs after intimate contact between adjacent latex particle surfaces is achieved. Often, there are two mechanisms for tensile strength development: (1) molecular interdiffusion of polymer chains from one particle to another across an interphase region and their entanglement, and/or (2) interfacial crosslinking. In the

first case, the particle interface eventually disappears, but ultimate strength is developed before then. In the case of interfacial crosslinking, the particles retain their original boundaries, the shapes of the particles are distorted from the spherical to dodecahedron shape, and strength results from "spot welds" originating from functional groups present on the latex particle surfaces, which are capable of chemical crosslinking or physical bonding.

There are several models describing the molecular interdiffusion of polymer chains across an interface based on deGennes' reptation theory.¹⁻⁸ Scaling laws for the number of bridges crossing the interface by molecular interdiffusion as a function of annealing time has been derived by Prager and Tirrell²⁻⁶ and Wool.^{7,8} Kim⁹ has found that the tensile strength increased with the annealing time to the one-fourth power, confirming the scaling law predictions.

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There are many instances in latex technology where functional groups are chemically incorporated into the latex particle, often at the surface of the particles. Many of these groups are capable of associating with one another, through ionic, covalent, or hydrogen bonding mechanisms to form a cross-linked network. For example, the effects of interfacial crosslinking was examined by Yeliseeva,^{10,11} who studied the mechanical strength of air-dried and thermally cured latex films prepared from copolymers of ethyl acrylate with *n*-methylolmethacrylamide (MMAA) or glycidyl methacrylate. For the more polar crosslinking monomer, MMAA, the air-dried copolymer exhibited tensile strengths that were 10 times higher than those synthesized with the less polar glycidyl methacrylate. This increase was attributed to the high surface concentrations and orientation of the polar MMAA moieties, which were capable of strong hydrogen bonding at room temperature, forming an interfacial crosslink. In the present study, a model latex system was synthesized, which was comprised of poly(methyl methacrylate) (PMMA) homopolymer or copolymers with the functional comonomers *N*-(iso-butoxymethyl)acrylamide (IBMA), or methacrylic acid (MAA) incorporated into the latex particles. IBMA is capable of self-condensation reactions at temperatures ranging from approximately 120°C upwards,¹² while MAA is capable of hydrogen bonding.

Two major parameters of interest for interfacial crosslinking studies are the concentration of the reacting moieties in the interphase region and the relative rates of polymer chain interdiffusion to that of the crosslinking reaction. More information is needed as to the relative rates of interdiffusion vs. the interfacial crosslinking reaction as a function of particle morphology, annealing time, temperature, and the chemical nature of the reactive functional groups.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) monomer (Polysciences, Inc.) was purified by passing it through an inhibitor removal column (Aldrich Chemical Company, Inc.) to remove residual hydroquinone inhibitor. Methacrylic acid (MAA) monomer (Aldrich) was distilled under vacuum (8 mmHg at 55°C). The other reactants, *N*-(iso-butoxymethyl)acrylamide monomer (IBMA; Polysciences, Inc.), sodium bi-

carbonate buffer (Fisher Scientific), Aerosol MA surfactant (sodium dihexyl sulfosuccinate; Cytec Industries), and ammonium persulfate initiator (FMC) were used as received.

Emulsion Polymerization

All syntheses were carried out in a 500 mL, four-necked glass reactor fitted with a condenser and a stirrer at 60°C. The reactions were carried out under a nitrogen blanket at a stirring rate of approximately 100 rpm over a 2-hr period. A batch emulsion polymerization technique was used to synthesize model poly(methyl methacrylate) (PMMA) latexes according to the recipe given in Table I. In this procedure, all reactants except for initiator were charged into the reactor, degassed, and heated to reaction temperature over a 20–30 min period; initiator solution was then added to begin the polymerization. PMMA latexes that contained varying amounts of *N*-(iso-butoxymethyl acrylamide) (IBMA) were synthesized through two different processes: either a batch or shot growth emulsion polymerization procedure. For the batch process, the experimental technique was the same as that described for the PMMA latex synthesis. Three latexes with IBMA contents of 0.85%, 4.25%, and 8.5% (wt % based on the total amount of MMA) were synthesized by the batch polymerization technique. These batch polymerizations were conducted in an attempt to obtain latexes with more homogeneous compositions. In comparison, a shot growth process¹³ (see Table II for a typical recipe) was employed to synthesize PMMA/IBMA latexes with a higher surface concentration of the IBMA functional groups. The first step of the shot growth process consisted of first polymerizing MMA through a batch process as previously described. A second shot consisting of a mixture of IBMA monomer with distilled-deionized (DDI) water, additional Aerosol MA surfactant, sodium bicarbonate buffer, ammonium persulfate initiator, and MMA monomer was immediately added to the reactor when the first stage MMA polymer-

Table I Recipe for the Batch Emulsion Polymerization of PMMA Model Latexes at 60°C

Ingredient	Amount (g)
Methyl Methacrylate	60.00
Aerosol MA 80	0.45
Ammonium Persulfate	0.24
Sodium Bicarbonate	0.24
Distilled-deionized (DDI) Water	240.00

Table II Typical Recipe for the Preparation of PMMA/IBMA Latexes by Batch and Shot Growth Emulsion Polymerization (0.85 or 1% IBMA) at 60°C

	Batch (0.5% IBMA)		Shot Growth (1% IBMA)	
	1st Shot	2nd Shot	1st Shot	2nd Shot
Methyl methacrylate (MMA)	60 g	—	60 g	2.07
<i>N</i> -(Iso-butoxymethyl) acrylamide (IBMA; 85%)	0.6 g	—	0 g	0.73 g
Aerosol MA 80	0.45 g	—	0.45 g	0.02 g
Sodium bicarbonate	0.24 g	—	0.24 g	0.01 g
Ammonium persulfate	0.24 g	—	0.24 g	0.005 g
Distilled-deionized (DDI) water	240 g	—	240 g	10 g

ization had reached 90% conversion. The ratio of IBMA/MMA added in the second shot was kept constant at 30%, and the ratio of IBMA/total amount of MMA present in the latex formulation was varied at 1, 5, or 8.5%. PMMA latexes that incorporated methacrylic acid (MAA) were synthesized in the same manner (with the same functional monomer concentrations) as the PMMA/IBMA (batch) model latexes. However, the reaction temperature was increased to 75°C for all polymerizations carried out with MAA.

Particle Size Analysis of Latex

The latex particle size was measured by photon correlation spectroscopy using a Nicomp Submicron Particle Size Analyzer (Model 370; Pacific Scientific Instruments). The mean diameter and standard

deviation of the latex particles is reported in Table III.

Determination of the Glass Transition Temperature of PMMA, PMMA/IBMA, and PMMA/MAA Copolymers

The glass transition temperatures (T_g) of PMMA homopolymer and its copolymers with IBMA and MAA were measured using a Mettler TA 3000 dynamic scanning calorimeter (DSC). The DSC scans were carried out over a temperature range from 60 to 150°C at a heating rate of 10°C/min.

Determination of the Molecular Weight of PMMA Homopolymer and PMMA/MAA Copolymers

The molecular weight of the PMMA homopolymer was determined by dilute polymer solution viscom-

Table III Particle Size Characteristics of Latexes

Latex Composition	Polymerization Process	Mean Diameter (nm)	Standard Deviation (%)
PMMA	Batch	301	8
PMMA/0.85% IBMA	Batch	332	12
PMMA/4.25% IBMA	Batch	300	5
PMMA/8.5% IBMA	Batch	327	12
PMMA/1% IBMA	Shot Growth	310	11
PMMA/5% IBMA	Shot Growth	330	9
PMMA/8.5% IBMA	Shot Growth	342	8
PMMA/0.85% MAA	Batch	290	11
PMMA/4.25% MAA	Batch	320	10
PMMA/8.5% MAA	Batch	290	7
PMMA/0.85% MAA	Shot Growth	280	12
PMMA/4.25% MAA	Shot Growth	206	9
PMMA/8.5% MAA	Shot Growth	N/A	N/A

etry measurements using an Ubbelohde viscometer maintained at 30°C. The Mark-Houwink coefficients (a and K) used to calculate the viscosity average molecular weight were 0.7 and 7.7×10^{-3} mL/g, respectively (PMMA in acetone at 30°C).¹⁴

Cleaning of Latex Polymers

The technique used for the purification of the latex polymers described previously (prior to compression molding them in the preparation of microtensile specimens) consisted of drying the latex in a 60°C oven to evaporate off all of the water, followed by grinding the resulting polymer into a fine powder with a mortar and pestle. This powder was then dispersed into methanol and stirred for 30 min at room temperature. The dispersion was then sonicated for 5 min in order to break apart larger flocs and facilitate the extraction of residual polymerization recipe components (e.g., surfactant, initiator, buffers, and oligomers) from the polymer. The methanol was then removed by vacuum filtration using a fritted glass filter in a Büchner funnel. The polymer cake was then immediately flushed with hot water, followed by DDI water at room temperature. The cake was then air dried at 65°C and ground into powder once again.

Mechanical Testing of Latex Polymer Films

In order to verify the mechanism of mechanical strength development during the latex film formation process, the experimental conditions for processing time, temperature, and pressure needed to be established. Fully dense films (i.e., free of voids) should be prepared in which individual latex particles remain in contact with one another by sintering the polymer powder. At this point, minimal polymer chain interdiffusion should occur between adjacent polymer particles. After this sintering stage, the film needs to be annealed under conditions where the extent of interdiffusion of polymer chains between adjoining particles may be controlled. For the PMMA/IBMA system, IBMA self-condenses at temperatures beginning around 120°C (optimum at approximately 150°C¹¹ with the T_g of the copolymer being close to 120°C (T_g of IBMA homopolymer is approximately 30°C).¹⁵ The film formation process has to take place at a temperature where the rate of the IBMA condensation reaction is slow or negligible compared to the rate of interdiffusion. The sintering criterion that was used in this study is that the temperature during the film formation stage remained below the temperature for the self-condensation of

IBMA, but still at a sufficiently high temperature (above the T_g of the copolymer) for minimal macromolecular interdiffusion to occur.

A compression molding technique was used to prepare the latex polymer films at 135°C and 20 MPa pressure for various sintering times using a Carver hot press. In order to satisfy the conditions that minimal chain interdiffusion was taking place between adjacent latex particles, the optimum processing time for preparing fully sintered films with minimal chain interdiffusion was determined to be 12 min, which included a 5-min period to preheat the powder and 7 min to mold the powder. This was determined to be the minimum time to form fully dense films without forming voids. The mold was constructed of a 13 cm \times 13 cm \times 0.6 cm thick aluminum plate that had four identical rectangular slots of 6 cm \times 1 cm machined into the mold. Latex polymer powder (0.65 g) was placed into these cavities sandwiched between rectangular spacers (6 cm \times 1 cm \times 0.3 cm thick) and compression molded at 135°C for various times to obtain a specimen that was 1 mm in thickness. The compression-molded samples were shaped to an ASTM standard-type microtensile "dogbone-shaped" specimen (ASTM D638M, with a type MIII specimen) using a Dremel grinding device. The overall specimen was 60 mm long and 10 mm wide. The tapered neck of the specimen (over which the specimen breaks during the tensile test) was 10 mm long and 2.5 mm wide. These specimens were subsequently annealed at 175°C for various lengths of time, from 0 to 1000 min. The individual samples were tested using an Instron Tensile tester at a strain rate of 10 mm/min. Three specimens were used for each tensile strength measurement; the median value was used as the tensile strength reported in this article. Specimens that had broken in the jaws of the tensile tester during testing were discarded, and their values were not included in the tensile strength results.

RESULTS AND DISCUSSION

Particle Size

The particle size of all of the latexes, whether they were prepared by batch or shot growth, and regardless if IBMA or MMA was copolymerized with MMA, all exhibited particle sizes in the 300 nm range (Table III). No clear-cut trend in particle size with increasing amounts of functional monomer was observed. Because all particle sizes were approximately the same within experimental error, any ef-

Table IV Glass Transition Temperatures for PMMA, PMMA/IBMA, and PMMA/MAA Copolymers

Polymer Composition	T_g ($^{\circ}\text{C}$)
PMMA	120.8
PMMA/MAA (0.85%; batch)	117.7
PMMA/MAA (4.25%; batch)	115.0
PMMA/MAA (8.5%; batch)	122.9
PMMA/MAA (0.85%; shot growth)	120.3
PMMA/MAA (4.25%; shot growth)	117.9
PMMA/MAA (8.5%; shot growth)	114.0
PMMA/IBMA (0.85%; batch)	119.2
PMMA/IBMA (4.25%; batch)	117.4
PMMA/IBMA (8.5%; batch)	114.3
PMMA/IBMA (1%; shot growth)	122.0
PMMA/IBMA (5%; shot growth)	120.5
PMMA/IBMA (8.5%; shot growth)	117.7

fect of particle size on strength development was negated.

Glass Transition Temperature

The glass transition temperatures (T_g) of the PMMA homopolymer and the copolymers with both IBMA and MAA are given in Table IV. The T_g of PMMA homopolymer was determined to be 120.8 $^{\circ}\text{C}$ (obtained at a heating rate of 10 $^{\circ}\text{C}/\text{min}$). The T_g of the copolymers all fell within the same range, again, regardless of the amount of functional monomer or the polymerization method (either batch or shot growth).

Tensile Strength

The tensile strengths for the PMMA specimen, as well as the PMMA/IBMA and PMMA/MAA copolymers, whether prepared by batch or shot growth emulsion polymerization processes, increased with increasing annealing times at 175 $^{\circ}\text{C}$ for low comonomer concentrations (i.e., 0.85 or 1%) (Figs. 1 and 2). The rate of tensile strength development as a function of annealing time for the PMMA/IBMA copolymers (Fig. 1) whether prepared by the batch or shot growth methods was lower than that of the PMMA homopolymer or the PMMA/MAA copolymers and exhibited lower tensile plateau values. This implies that even at low concentrations of IBMA comonomer, intraparticle crosslinking occurs during polymerization, which hinders the extent of macromolecular interdiffusion during film formation and leads to lower tensile strengths. However, the

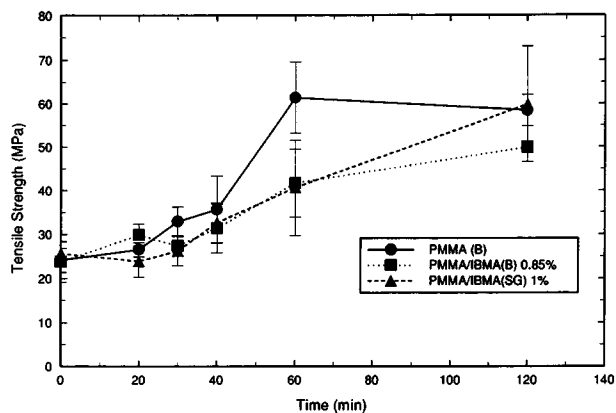


Figure 1 Tensile strength development of PMMA homopolymer and PMMA/IBMA copolymers as a function of annealing time at 175 $^{\circ}\text{C}$; B = batch emulsion polymerization; SG = shot growth emulsion polymerization. The ultimate elongation for these specimens ranged from approximately 0.2 to 0.5.

tensile strengths of the PMMA/MAA copolymers, prepared from either the batch or shot growth method, at a concentration of 0.85%, increased faster than for PMMA. Higher tensile plateau values were also attained (Fig. 2). This indicates that polymer chain interdiffusion, at low MAA concentration (0.85%), was not significantly inhibited.

The effects of comonomer concentration on the development of tensile strengths of the copolymer specimens are compared in Figure 3 for the case of PMMA/IBMA and in Figure 4 for the PMMA/MAA copolymers. In both cases, the rates of tensile strength development were significantly reduced as

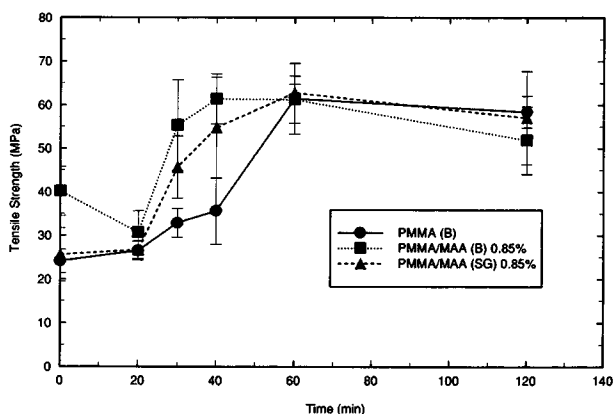


Figure 2 Tensile strength development of PMMA homopolymer and PMMA/MAA copolymers as a function of annealing time at 175 $^{\circ}\text{C}$; B = batch emulsion polymerization; SG = shot growth emulsion polymerization. The ultimate elongation for these specimens ranged from approximately 0.2 to 0.4.

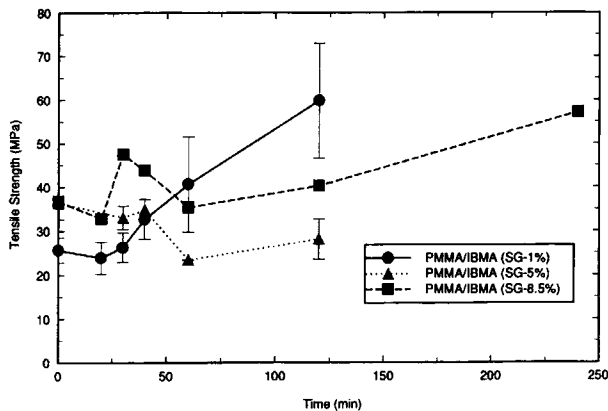


Figure 3 Tensile strength development of PMMA/IBMA copolymers annealed at 175°C as a function of IBMA content; B = batch emulsion polymerization; SG = shot growth emulsion polymerization. The ultimate elongation for these specimens ranged from approximately 0.2 to 0.6.

the concentration of functional groups increased (1, 5, or 8.5% for IBMA; and 0.85, 4.25, and 8.5% for MAA). All functional monomers were incorporated using the shot growth technique. There was a decreased rate of tensile strength development for the copolymer containing 5% IBMA, which suggests that intraparticle crosslinking had occurred. The plateau tensile strength achieved with the copolymer with 4.25% MAA was the same as that with 0.85% MAA. The inclusion of 4.25% MAA in the copolymer was not sufficient to reduce the plateau tensile strength. A concentration of at least 8.5% MAA was required to retard molecular interdiffusion in the PMMA/MAA copolymer films.

The PMMA homopolymer and the PMMA/IBMA and PMMA/MAA copolymers (with 0.85–1% IBMA or MAA) were annealed at two different temperatures, i.e., 145 and 175°C (Figs. 5, 6, and 7). The tensile strength development rates for the films annealed at 145°C were lower than those for the films annealed at 175°C; it also took longer to reach the ultimate tensile strength plateau values at 145°C.

For the 0.85% and 1% PMMA/IBMA copolymers (Fig. 6) prepared by the batch and shot growth method, respectively, the rate of tensile strength development as a function of annealing time at 145°C was significantly lower than that for the PMMA homopolymer (Fig. 5) or the PMMA/MAA copolymer (Fig. 7); these IBMA copolymers also exhibited lower plateau tensile values. This indicates that even at low concentrations (0.85% and 1%) of IBMA comonomer, interfacial crosslinking occurs at the particle surface, which slows macromolecular inter-

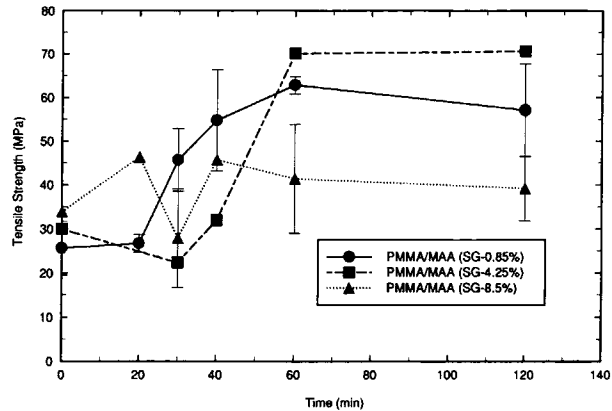


Figure 4 Tensile strength development of PMMA/MAA copolymers annealed at 175°C as a function of MAA content; B = batch emulsion polymerization; SG = shot growth emulsion polymerization. The ultimate elongation for these specimens ranged from approximately 0.2 to 0.4.

diffusion. Meanwhile, the rate of tensile strength development for the PMMA/MAA copolymers (Fig. 7) prepared from the batch or shot growth method at a MAA concentration of 0.85% was slightly lower than the rate for the PMMA homopolymer (Fig. 5). However, the PMMA/MAA (0.85%) copolymer films did not have a sufficiently high glass transition temperature, which could have retarded the macromolecular interdiffusion during the annealing process.

It is possible to calculate the power law dependence of tensile strength on annealing time from the slopes of plots (i.e., the ascending linear portions of these curves) of $\log(\text{tensile strength})$ vs. $\log(\text{annealing time})$. The slopes of these plots (representing the power law exponents) remained the

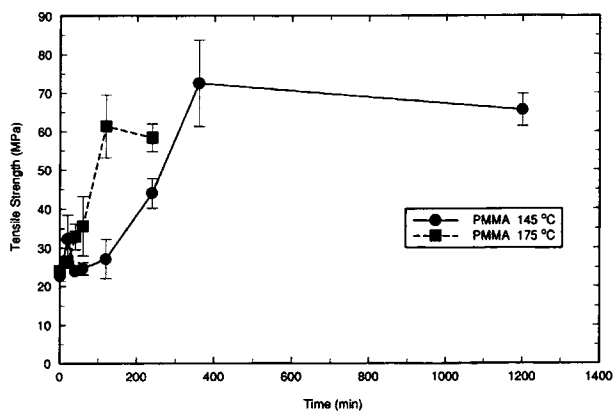


Figure 5 Tensile strength development of PMMA homopolymer as a function of annealing temperature. The ultimate elongation for these specimens ranged from approximately 0.2 to 0.5.

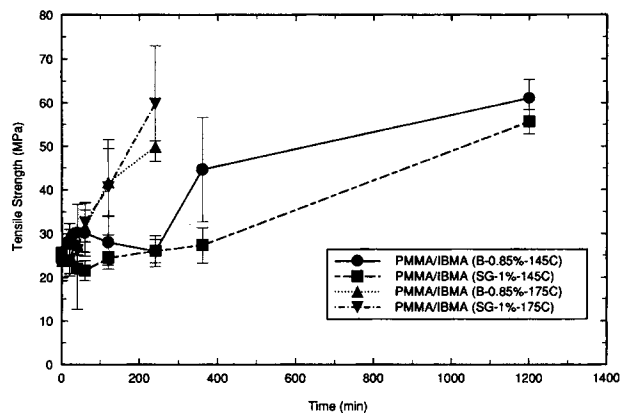


Figure 6 Tensile strength development of PMMA/IBMA copolymer as a function of annealing temperature; B = batch emulsion polymerization; SG = shot growth emulsion polymerization. The ultimate elongation for these specimens ranged from approximately 0.2 to 0.5.

same for the PMMA homopolymer at two different annealing temperatures (145°C and 175°C) (with slopes of 0.88). The power law exponents of the PMMA/IBMA copolymers polymerized by a batch method were found to be 0.58 at 175°C and 0.49 at 145°C, while the copolymers prepared by the shot growth method exhibited power law exponents of 0.67 at 175°C and 0.48 at 145°C. The power law exponents of the PMMA/MAA copolymer films synthesized by the batch method were observed to be 0.75 at an annealing temperature of 175°C and 0.35 at 145°C, while those copolymer films prepared by the shot growth method exhibited power law exponents of 0.64 at 175°C and 0.31 at 145°C. In both copolymer cases, the decrease in the power law exponents at the lower annealing temperature indicates that interdiffusion is dependent upon temperature, reflecting lower rates of macromolecular interdiffusion at lower temperatures. The crosslinking reaction is less dependent upon temperature, although crosslinking can occur even at lower temperatures. Interfacial crosslinking (for the PMMA/IBMA copolymers) takes place faster than macromolecular interdiffusion at 145 or 175°C (i.e., less difference in exponents at the two temperatures compared to the case of PMMA/MAA copolymers), and prior buildup of a crosslinking network (i.e., intraparticle crosslinking that could occur during polymerization itself) hinders further macromolecular interdiffusion in the films. Both sets of exponents for the PMMA/IBMA and PMMA/MAA copolymers were lower than that obtained for the base PMMA homopolymer under the same annealing conditions, indicating that both copolymer systems

underwent a reduction in the rate of polymer chain interdiffusion during the annealing process.

The power law exponents were determined by Yoo et al.¹⁶ to be 0.69 for higher molecular weights (i.e., 2,000,000 g/mol) of polystyrene and 0.27 for lower molecular weights (250,000 g/mol) at an annealing temperature of 144°C. These researchers explained this difference based on the distribution of chain end groups, i.e., the higher the molecular weight, the greater the number of chain end groups located at the particle surface, which induced faster chain diffusion between adjacent particles. In the case of the PMMA homopolymer utilized in this study, the viscosity-average molecular weight was 2,500,000 g/mol, which corresponds to the higher molecular weight polystyrene; power law exponents in the same range as those for polystyrene were obtained.

CONCLUSIONS

It was inferred that higher concentrations of IBMA introduced into the PMMA/IBMA copolymer latex resulted in a increased degree of interfacial (and/or intraparticle) crosslinking, which was dominant as compared to the rate of macromolecular interdiffusion. The crosslinking reaction took place before molecular interdiffusion began and hindered further polymer chain interdiffusion. At low concentrations of MAA, it appears that the interdiffusional contribution governs the kinetics of strength development resulting from hydrogen bonding of the originally surface-rich carboxylic copolymer (i.e., PMMA/MAA) and contributed to the overall ten-

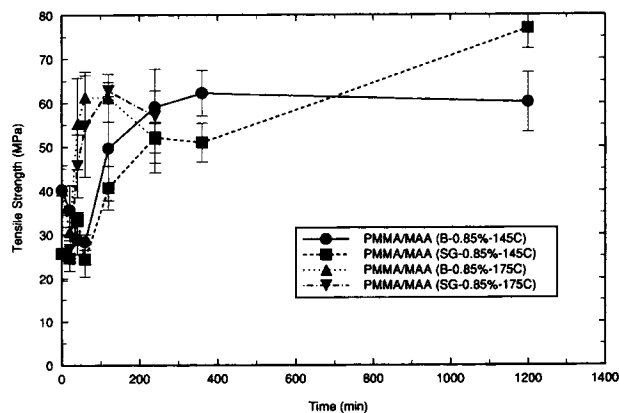


Figure 7 Tensile strength development of PMMA/MAA copolymer as a function of annealing temperature; B = batch emulsion polymerization; SG = shot growth emulsion polymerization. The ultimate elongation for these specimens ranged from approximately 0.2 to 0.6.

sile plateau strength. However, at higher comonomer concentrations, intraparticle and/or interfacial crosslinking (IBMA) and a high T_g particle surface reduced the extent of macromolecular interdiffusion, which resulted in decreased tensile properties.

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