The Influence of Latex Blend Composition on Crosslinking and Mechanical Properties

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ABSTRACT: Model reactive latices were synthesized by semicontinuous emulsion copolymerization of *n*-butyl methacrylate and acetoacetoxyethyl methacrylate or dimethylaminoethyl methacrylate. The two functional latices were then blended in various ratios to study the influence of blend composition on crosslinking and mechanical properties of the resulting films. Crosslinking was quantified through swelling measurements. It was found that the crosslink density increased with increasing amounts of acetoacetoxy-functional polymer. In addition, the crosslink density exhibited two maxima, at 30/70 and 70/30 (acetoacetoxy-functional latex/amino-functional latex) blend compositions. The mechanical properties of the films were quantified by dynamic mechanical analysis (DMA). It was shown that optimal mechanical properties occurred when the particles packed most efficiently at the 30/70 and 70/30 blend compositions. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3774–3779, 2007

Key words: latex blend; film formation; reactive latex; crosslinking; mechanical properties

INTRODUCTION

Latex blends have a great deal of industrial importance. Blends can be used to control mechanical properties, avoid the use of plasticizers by utilizing a blend of high and low glass transition temperature (T_g) polymers,[1] reduce material costs through the addition of low-cost fillers,[2] and control interfacial crosslinking reactions through the use of a two-component crosslinker. One of the major advantages of utilizing latex blends is that a film or coating prepared from a latex blend can exhibit mechanical properties that are superior to the properties of the individual latices by themselves.

A common problem when dealing with polymer blends is polymer–polymer compatibility. Many pairs of polymers are thermodynamically incompatible and blends of these polymers often phase separate. However, Xu et al. showed that crosslinking can be used to overcome polymer miscibility issues to produce cohesive films from incompatible polymers.[3] In addition to compatibilizing polymers, crosslinking is used in latex blends to improve the mechanical properties of the resulting film. Latex blends can offer more control over crosslinking reactions by separating the reactive components into different latex particles. As a result, intraparticle crosslinking can be reduced in blend systems if the reactive components are not capable of crosslinking by themselves.

Crosslinking in polymer blends has received significant attention in the literature. For example, Collins and Taylor showed how acetoacetoxy-functional groups could be incorporated into otherwise inert latex particles and then stabilized through the formation of a polymeric (polyamino) enamine (PPAE) crosslink.[4] Stockl, Collins, and Taylor then showed that PPAE could be blended with acetoacetoxy functional polymers for adhesive applications.[5] In addition, epoxy and carboxyl groups have received a great deal of attention in the literature.[6–8]

Although the influence of crosslinking on mechanical properties in latex blends has been studied previously,[9] little attention has been given to the significant influence that the blend composition and latex particle packing behavior has on crosslinking. To address this issue, an acetoacetoxy-amine system was chosen to model a two-component reactive latex blend. This particular system was selected for several reasons. First, the functional groups are both commercially available as methacrylic monomers that can be easily incorporated into a latex by copolymerization with an otherwise inert backbone polymer such as *n*-butyl methacrylate. Second, neither the acetoacetoxy nor amino function groups are subject to appreciable hydrolysis by the aqueous phase of an emulsion under the conditions that were investigated during this study.

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TABLE I
Summary of Polymerization Recipes

	Amount of ingredient	
	Seed stage	Feed stage
n-BMA[a] (g)	21.00	189.00
AAEM[b] or DMAEM[c] (g)	0.00	15.00
Deionized (DI) H_2O (g)	500.00	0.0
IGEPAL CO-880 (g)	23.8	0.0
V-50 Solution[d] (mL)	5	20
Time (h)	0.5	10

[a] *n*-Butyl Methacrylate.
[b] Acetoacetoxyethyl Methacrylate.
[c] Dimethylaminoethyl Methacrylate.
[d] V-50 solution was prepared by dissolving 2.1 g of V-50 in 20 mL of DI H_2O and diluting to 25 mL.

EXPERIMENTAL

Materials

Monomethylether hydroquinone (MEHQ) inhibitor was removed from *n*-butyl methacrylate (*n*-BMA; Sigma-Aldrich, Milwaukee, WI) and dimethylaminoethyl methacrylate (DMAEM; Sigma-Aldrich, Milwaukee, WI) by passing the monomers through an inhibitor removal column (Sigma-Aldrich, Milwaukee, WI) before use. Acetoacetoxyethyl methacrylate (AAEM; Eastman Chemical, Kingsport, TN), IGEPAL CO-880 ($[C_2H_4O]_nC_{15}H_{24}O$; $n = 20–30$; Rhodia, Cranbury, NJ), V-50 (2,2′-azobis(2-methylpropionamidine) dihydrochloride; Wako, Osaka, Japan), and toluene (VWR Scientific, Bridgeport, NJ) were used as received without further purification. Water was deionized and purged of oxygen by bubbling nitrogen through it before use.

Latex synthesis and characterization

n-BMA latices containing acetoacetoxy or amino functional groups were prepared by semicontinuous emulsion polymerization processes. Table I shows the recipes used for the syntheses of the two types of latices. All reactions were carried out in a 4-neck 1 L reaction flask immersed in a thermostated water bath maintained at 60°C. The flask was equipped with a half-moon Teflon® stirring paddle and a Friedrichs condenser. The stirring rate was approximately 200 rpm. The flask was also continuously purged with nitrogen to prevent oxygen from inhibiting the polymerization. The seed stage reactants were charged to the flask and held at 60°C for 30 min. The feed stage *n*-BMA and functional monomer (AAEM or DMAEM) were thoroughly mixed and fed using a Teflon® feed line and a Harvard apparatus (model 22M, Holliston, MA) syringe pump over the course of 10 h. The feed-stage initiator solution was fed in parallel with the monomer using a separate feed line and Harvard apparatus (model 22M) syringe pump over the course of 10 h. All reactions had an 18-h postfeed time at 60°C to ensure complete conversion (100%).

Swelling measurements

Blends of the two functional latices (*n*-BMA-*co*-AAEM or *n*-BMA-*co*-DMAEM) were prepared according to Table II. Films were prepared by drying the latex blends on glass plates covered with Dupont Tedlar® film at 90°C until a plateau in crosslink density was achieved. The evolution of the molecular weight between crosslinks (M_c) and crosslink density (ρ_c) as a function of the cure time were determined. Pieces of the crosslinked films were cut and weighed, placed in a preweighed wide mouth bottle, and immersed in toluene at approximately 100 times the weight of the film. The bottles were then sealed and slowly rotated end-over-end at 30 rpm for 48 h. The swollen film was then removed, blotted dry, and quickly weighed. The sample was then allowed to dry to constant weight in a fume hood. The molecular weight between crosslinks and crosslink density were calculated using eqs. (1)–(5).[10]

$$\chi_1 = \frac{V_1(\delta_s - \delta_p)^2}{RT} \tag{1}$$

$$V_s = \frac{W_o}{\rho_p} + \frac{W_s - W_o}{\rho_s} \tag{2}$$

$$c = \frac{W_o}{\rho_p V_s} \tag{3}$$

$$M_c = \frac{-V_1 \rho_p (c^{1/3} - c/2)}{\ln(1-c) + c + \chi_1 c^2} \tag{4}$$

$$\rho_c = \frac{\rho_p}{M_c} \tag{5}$$

where χ_1 is the Flory Chi parameter, V_1 (cm^3/mol) is the molar volume of the solvent, ρ_p (g/cm^3) and ρ_s

TABLE II
Summary of Blend Ratios

	Blend composition	
Blend	Acetoacetoxy : amino weight ratio	Weight % acetoacetoxy group in the blend
9–91	1 : 10	8.8
20–80	1 : 4	20.0
29–71	1 : 2.5	28.6
40–60	1 : 1.5	40.0
50–50	1 : 1	49.8
62–48	1 : 0.6	62.5
77–23	1 : 0.3	76.9
91–9	1 : 0.1	90.9
95–5	1 : 0.05	95.0
100–0	1 : 0	100

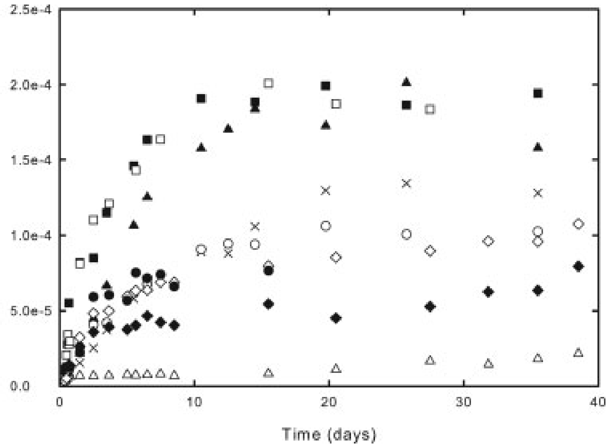

Figure 1 Evolution of crosslink density (ρ_c) of films prepared with different AAEM-BMA and DAEMA-BMA latex blend ratios with time: (△) 9–91; (◆) 20–80; (◇) 29–71; (○) 40–60; (×) 50–50; (▲) 62–48; (■) 77–23; (□) 91–9; (●) 95–5.

(g/cm^3) are the densities of the polymer and solvent, respectively, δ_p (J/cm^3)$^{1/2}$ and δ_s (J/cm^3)$^{1/2}$ are the solubility parameters of the polymer and solvent, respectively, W_o (g) and W_s (g) are the weights of the unswollen and swollen films, respectively, V_s (cm^3) is the volume of solvent in the swollen film, c is the concentration of solvent in the polymer, M_c (g/mol) is the molecular weight between crosslinks, and ρ_c (mol/cm^3) is the crosslink density. The values for δ_p and ρ_p were assumed to be the same as poly(*n*-BMA) since no literature values were available for the copolymers.

Mechanical characterization

Dynamic mechanical analysis (DMA, TA Instruments, Advanced Rheometric Expansion System (ARES), Newark, DE) was used to determine the shear storage modulus (G') of the latex films. Experiments were performed at a strain of 0.1%, a frequency of 1 Hz, and a temperature range from −105°C to 100°C at a heating rate of 5°C/min. Films were prepared by freeze-drying the latex blends and compression molding the resulting powder into uniform films. A small amount of the freeze-dried powder was placed in a silicone rubber mold. The mold was covered with a sheet of heavy gauge aluminum foil and placed in a hydraulic press (Carver Model C, Fred S. Carver, Inc., Menomonee Falls, WI) and pressed at 5000 psi and 50°C for 10 min. After 10 min, the pressure was dropped to 1000 psi and the temperature was increased to 90°C. The film was then annealed at 90°C and 1000 psi for 4 h. After annealing, the film was cooled back down to room temperature before releasing the pressure and removing the film from the press.

RESULTS AND DISCUSSION

Figure 1 shows the results obtained from the swelling measurements for several of the different blend compositions illustrating the range of different crosslink density plateau values that can occur. A plot of the plateau values of the crosslink density as a function of latex blend composition is shown in Figure 2, illustrating the trend that the crosslink density increases as the fraction of acetoacetoxy-functional polymer increases up to a certain point (∼ 95%) and then falls off. The increase in crosslink density results from the mechanism of crosslinking being an amine-catalyzed aldol condensation/dehydration reaction of the acetoacetoxy functional groups as illustrated in Figure 3.[11] The drop after 95% acetoacetoxy functionality indicates that at very high acetoacetoxy weight fractions, there are not enough amino functional groups present to catalyze the reaction (and thus the crosslink density is much lower due to the lack of catalyst).

Figure 2 also shows that there are two regions centered around the 30/70 and 70/30 blend compositions where the value of crosslink density remains constant over several blend compositions. These two plateau regions can be explained by examining the packing of the latex particles in the film. Optimal packing of the latex particles will theoretically occur when one type of particle is surrounded by the other because the contact between the different functional groups would be maximized (fewest unused functional groups). If hexagonal packing of the latex particles is assumed, the particles will pack according to the schematic diagrams presented in Figure 4. The darkened particles correspond to the maximum number of particles that can be present in a hexagonal cell and still maintain optimal packing (i.e., one type of particle completely surrounded by the other). This fraction corresponds to 5 of 17 particles or approximately a 30/70 weight % blend (assuming uniform particle size). The plateau

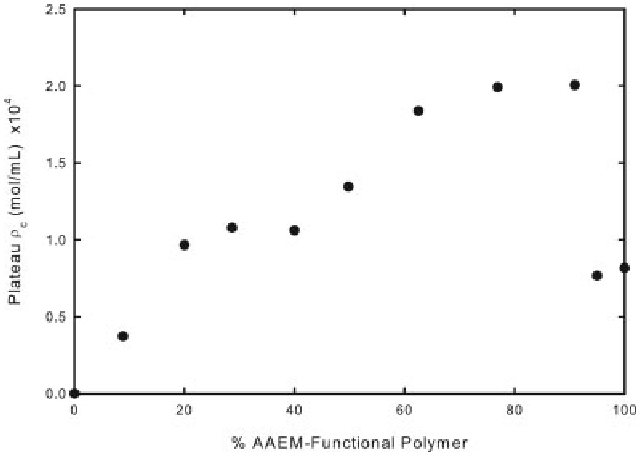

Figure 2 Correlation of plateau values of crosslink density (ρ_c) with blend composition.

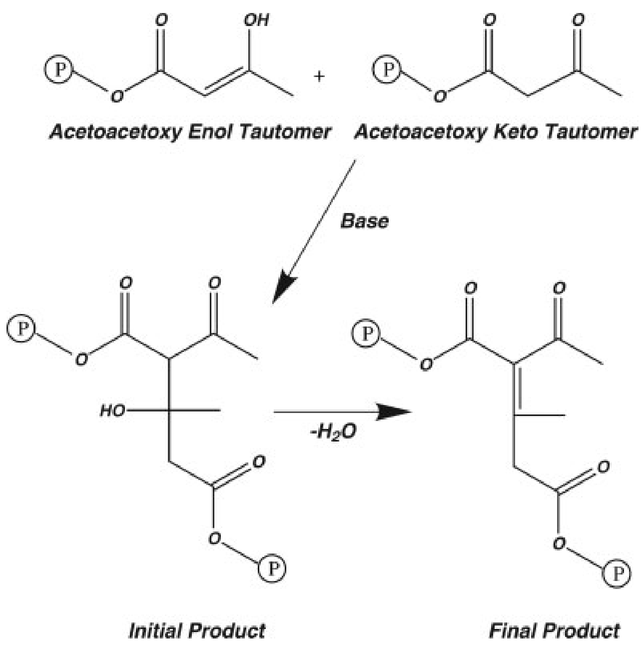

Figure 3 Schematic representation of the aldol condensation and dehydration reactions for self-crosslinking of AAEM-functionalized *n*-BMA copolymer and dehydration of the initial product. P represents the remainder of the polymer chain.

regions in Figure 2 correspond roughly to the 70/30 and 30/70 blends. At these two points, the mixing of the different particle types is maximized resulting in the smallest number of unused functional groups.

In addition to particle packing in the films, latex particle clustering (the formation of particle multiplets) will also influence particle-particle contact. Theoretical calculations using Monte Carlo block plotting simulations have been carried out by Zerlaut and Kaye[12] to determine the number and size of clusters ranging from 1 to 17 particles present in a dispersion of monodisperse spherical particles. The probability of a particle singlet calculated from the simulations is only 35.6% indicating that the majority of the particles will exist as multiplets, thus reducing the fraction of particles in direct contact with particles of the opposite type. As a result, films cast from uniformly-mixed latex blends will not be perfectly homogeneous. While the 70/30 and 30/70 compositions correspond to one type of particle being surrounded by the other, this cannot be the case if particle clustering occurs because clusters consisting of particles of the same type will prevent maximum contact. As a result, the crosslink density does not go through a maximum at optimal packing, but rather exhibits a plateau where the contact between the particle types is approximately the same.

The trend where the crosslink density was found to increase with increasing acetoacetoxy functionality can also be explained through probability analysis of the latex blends. If the number of particles that an acetoacetoxy-functional particle can chemically bond to through crosslinking is treated as a random variable, then for any given blend composition, the expected number of bonds that any acetoacetoxy-functional particle can form will only be a function of the fraction of particles that contain acetoacetoxy functional groups (blend composition) and the packing coordination number (12 for hexagonal packing and 10 for close random packing). To calculate the expected number of particles chemically bonded to each other, a single acetoacetoxy-functional particle is examined, and the probability of it bonding to itself or any of its acetoacetoxy-functional neighbors (assuming that at least one neighbor is amino-functional to act as the catalyst) is summed. This summation is broken into 2 terms as given in eq. (6)

$$E(\text{Bonds}) = \left\{ \frac{\sum_i^n \frac{n!}{i!(n-i)!} p^{n-i}(1-p)^i}{2} + [1-(1-p)^n] \right\} \times (1-p) \quad (6)$$

where E(Bonds) is the expected number of bonds per acetoacetoxy-functional particle, n is the coordination number for the system, i is the number of acetoacetoxy-functional neighbors that a single acetoacetoxy-

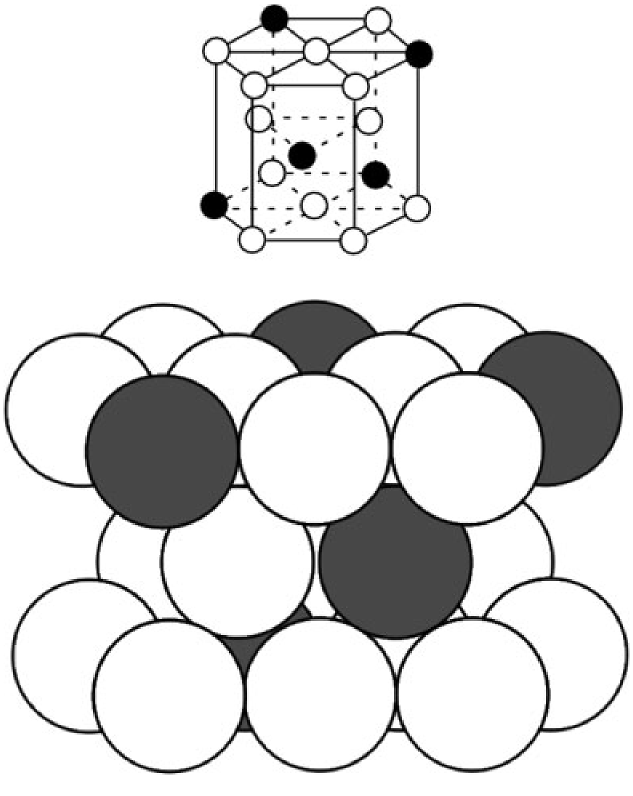

Figure 4 Schematic diagrams of a hexagonal closed-packed (HCP) unit cell; white and black particles represent how two different types of particles would have to pack to have one type of particle completely surrounded by the opposite type.

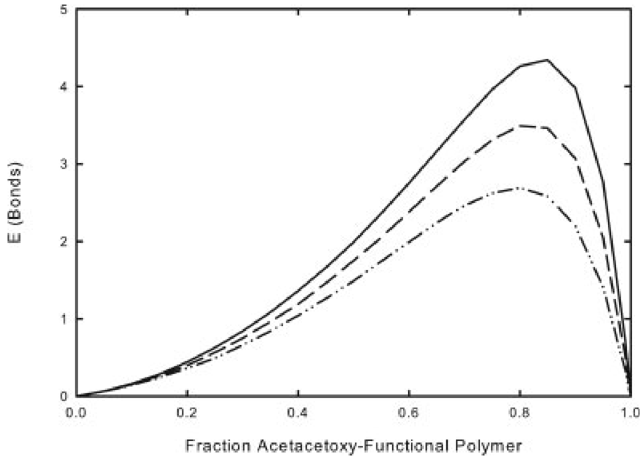

Figure 5 Expected number of acetoacetoxy-functional particles chemically bonded to each other for different coordination numbers (CN); CN = 12 (–), CN = 10 (- -), CN = 8 (-···-).

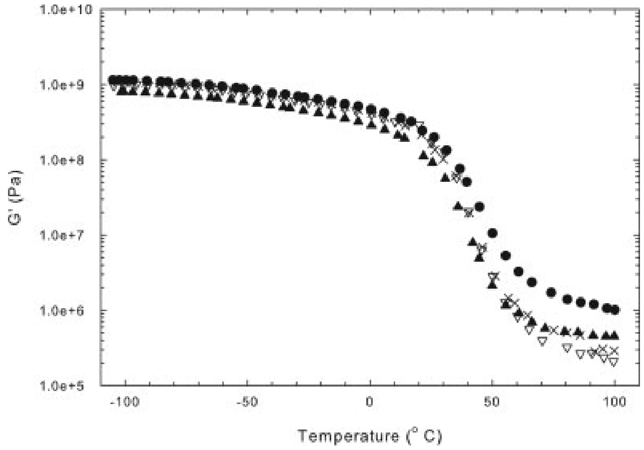

Figure 6 G' versus temperature for films cast from different blends and cured for 4 h: (▽) *n*BMA homopolymer; (▲) 50–50; (×) 62–48; (●) 77–23; scans were performed from −105 to 100 °C with a heating rate of 5°C/min; γ = 0.1%, and ω = 1 Hz.

functional particle can have (from 0 to n), and p is the fraction of amino-functional particles in the blend. The first half of eq. (6) is a summation over a binomial distribution to count the bonds between a particle and any one of its acetoacetoxy-functional neighbors. The summation is then divided in half to prevent double counting of bonds. The second half of eq. (6) accounts for an acetoacetoxy-functional particle forming intraparticle bonds (the only way that a particular particle would not be able to form intraparticle bonds would be if a particle and all of its neighbors were acetoacetoxy-functional). Lastly, the entire equation is multiplied by the acetoacetoxy-fraction to normalize the expected number of particles that are chemically bonded. The only assumption necessary to apply eq. (6) is that if any neighbor of an acetoacetoxy-functional particle is an amino-functional particle, then the probability of the acetoacetoxy-functional particle forming bonds with itself and any of its acetoacetoxy-functional neighbors is constant.

Figure 5 is a plot of eq. (6) against blend composition for several coordination numbers. The graph shows that a maximum value is attained near an acetoacetoxy fraction of 0.8, which is in agreement with the observed crosslink density trend. This implies that the second plateau region in Figure 2 is due not only to optimal packing of the particles (resulting in the fewest number of unused functional groups), but also to the maximum number of bonds as determined by the statistical expectation.

Figures 6 and 7 show the results from DMA tests carried out on six of the blends as well as the poly(*n*BMA) homopolymer. As mentioned previously, crosslink density of films cast from different blends increases with increasing acetoacetoxy functionality. Consequently, the films with greater acetoacetoxy functionality present should exhibit a higher shear storage modulus (G') resulting from crosslinking. This is consistent for the blends with more than 50% by weight acetoacetoxy-functional polymer (shown in Fig. 6). When the amount of acetoacetoxy-functional polymer is reduced below 50% by weight (Fig. 6), the values for G' show a slight decrease with increasing crosslink density. This unexpected trend is due to the crosslinking reaction proceeding too quickly and prematurely preventing polymer chain interdiffusion. Because poly(*n*BMA) homopolymer has a significant entanglement contribution to mechanical properties (the results presented here are comparable to those found in the literature)[13] premature termination of chain interdiffusion by a fast crosslinking reaction

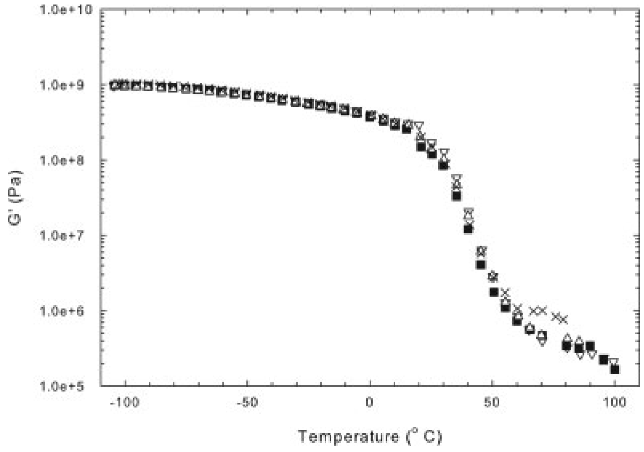

Figure 7 G' versus temperature for films cast from different blends and cured for 4 h: (▽) *n*BMA homopolymer; (■) 9–91; (△) 20–80; (□) 29–71; scans were performed from −105 to 100°C with a heating rate of 5°C/min; γ = 0.1%, and ω = 1 Hz.

results in a film with fewer crosslinks (chemical and physical combined) compared to a film with only physical entanglements. In addition, below 50%, the acetoacetoxy-functional particles are likely to be isolated from each other, and therefore, the crosslinked portions of the film are likely to be separated into domains. At higher amounts of acetoacetoxy-functional polymer, the crosslinked polymer is more likely to become the continuous phase of the film resulting in the higher values of G′ that were observed. Figures 6 and 7 also illustrate the influence of particle packing on mechanical properties. Blends 77–23 and 29–71 both show an increase in the plateau value of G′ due to optimal packing of the particles at these blend compositions.

CONCLUSIONS

The study of the influence of the AAEM-DMAEM blend fraction on crosslink density and the mechanical properties of films cast from the corresponding latex blends showed that the crosslink density increased with larger amounts of acetoacetoxy-functional polymer (up to 95% by weight acetoacetoxy-functional polymer). The crosslink density also showed two relative maxima/plateau regions centered around the 30/70 and 70/30 blend compositions. The relative maxima were due to optimal packing of the particles resulting in maximum contact between the two different functional groups. The observed plateaus resulted from clustering of the particles in the latex resulting in composition ranges with approximately the same amount of contact between the different particle types. In addition, the maximum value observed around 70% AAEM-functional polymer was consistent with the maximum number of bonds calculated using a statistical expectation.

DMA measurements performed on several of the blends showed that at lower amounts of acetoacetoxy-functional polymer (less than 50% by weight), the crosslinked films were weaker than poly(*n*BMA) homopolymer since the crosslinking reaction stopped polymer chain interdiffusion too quickly and prevented any significant entanglement contribution to the mechanical properties. When the amount of acetoacetoxy-functional polymer was increased above 50%, the film showed improved mechanical properties compared to the poly(*n*BMA) homopolymer because the films now had sufficient crosslinks to make up for the loss of the entanglement contribution to mechanical properties.

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