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The effects of latex coalescence and interfacial crosslinking on the mechanical properties of latex films

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Abstract

The effects of latex coalescence and interfacial crosslinking on the mechanical properties of latex films were extensively investigated by means of several series of model latexes with varying backbone polymer crosslinking density and interfacial crosslinking functional groups. It was found that the tensile strength of crosslinked model latex films increased with increasing gel content (i.e. crosslinking density) of latex backbone polymers up to about 75% and then decreased with further increase in gel, while their elongation at break steadily decreased with increasing gel content. These findings showed that latex particle coalescence was retarded above a gel content of about 75% so that the limited coalescence of latex particles containing gel contents higher than 75% prevented the tensile strength of crosslinked latex films from increasing by further crosslinking the latex backbone polymers. This was contrary to the theory of rubber elasticity that the tensile strength increases with increasing molecular weight and crosslinking density. This limitation was found to be overcome by the interfacial crosslinking among latex particles during film formation and curing. This paper will discuss the effects of both latex backbone polymer and interfacial crosslinking on latex film properties. It will also discuss the development of self-curable latex blends and structured latexes containing co-reactive groups: oxazoline and carboxylic groups.

Keywords: Latex coalescence; Backbone polymer crosslinking; Interfacial crosslinking

1. Introduction

For many applications of latexes, latex film properties, such as film modulus, tensile strength, %elongation at break, wet strength, and solvent resistance, are very important. Therefore, it is highly desirable to be able to either control or improve these properties. It is well known that these properties depend on the chemistries of latex backbone monomers, the glass transition temperatures (T_g's), molecular weights, and crosslinking densities of backbone polymers, particle size, surfactant level, the extent of coalescence, particle surface functional groups, interfacial crosslinking, film-forming and curing temperatures and conditions, etc. Among these properties, this work studied the mechanical properties (tensile strength and %elongation at break obtainable from the stress–strain curves) of dry and wet latex films as a function of backbone polymer and interfacial crosslinking as well as curing temperatures.

Unlike well-mixed and molded polymer films, latex films achieve their integrity and strengths only by coalescence through the particle interfaces in the absence of any interfacial bonds, such as hydrogen bonding, ionic bonding or covalent bonds. This understanding suggested that the tensile strength of latex films would increase with increasing backbone polymer crosslinking [1], until too much crosslinking would retard the extent of coalescence. For this reason, it was decided to study the effect of backbone polymer crosslinking on both the strength of latex films and the extent of coalescence with a series of low T_g, non-functionalized model latexes by varying the backbone polymer crosslinking.

Since the strength of latex films could not be increased by increasing the crosslinking density of backbone polymers beyond the critical value at which the coalescence would be limited, it was speculated that the interfacial bonding or crosslinking would overcome this limitation, if its strength would be equal to or greater than the strength of the

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crosslinked backbone polymers. As a matter of fact, this concept was thought to achieve a homogeneous crosslinking of latex films by interfacially crosslinking the crosslinked latex particles. For this reason, it was further decided to test this concept with a series of carboxylated latexes by varying the backbone polymer crosslinking, and then to develop self-curable latex blends and structured latxes containing 2-isopropenyl-2-oxazoline (IPO) and vinyl acids [2,3].

2. Experimental

2.1. Crosslinked model latexes

A series of n-butyl acrylate/styrene (BA/S: 65/35) model latexes was prepared with varying amounts of allylmethacrylate (AMA) as a crosslinking monomer and sodium persulfate as an initiator by a seeded semi-continuous emulsion polymerization at 90 °C. The particle size was 120 nm. They were cast on Teflon-coated glass plates and dried at room temperature, and then these latex films were tested for tensile strength and %elongation at break. Fig. 1 shows the tensile strength and %elongation at break as a function of AMA level.

The %gels and swelling indexes of the above model latex films were determined by a solvent swelling and extraction method. Small film pieces (~1 g each) were inserted into centrifuge tubes and toluene was added to them, and then these tubes were shaken for 24 h. After this swelling and extraction step, the tubes were centrifuged at high speeds for 2 h and the polymer solutions were separated from the swollen gels. After these swollen gels were weighed and dried, the weights of the dried gels were measured, and then %gels and swelling indexes were calculated. Fig. 2 shows the %gels and swelling indexes of these latex films in toluene as a function of AMA level.

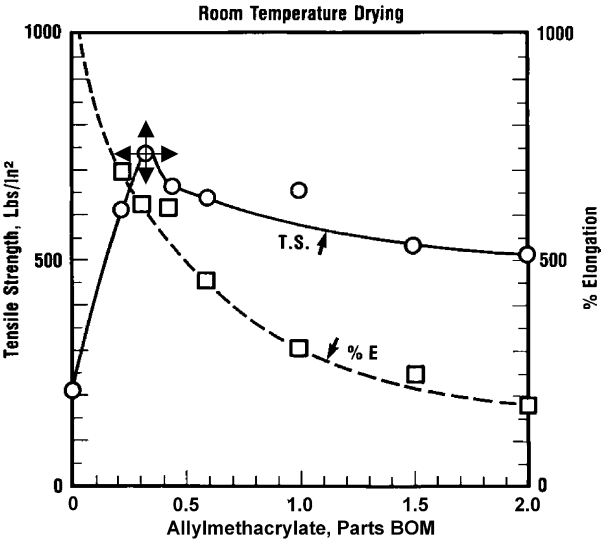

Fig. 1. The effect of latex backbone polymer crosslinking on the tensile strength and %elongation at break of latex films: latex polymer compositions {BA/S/AMA [65/(35−X)/X]}; particle size (120 nm); latex films were dried at room temperature.

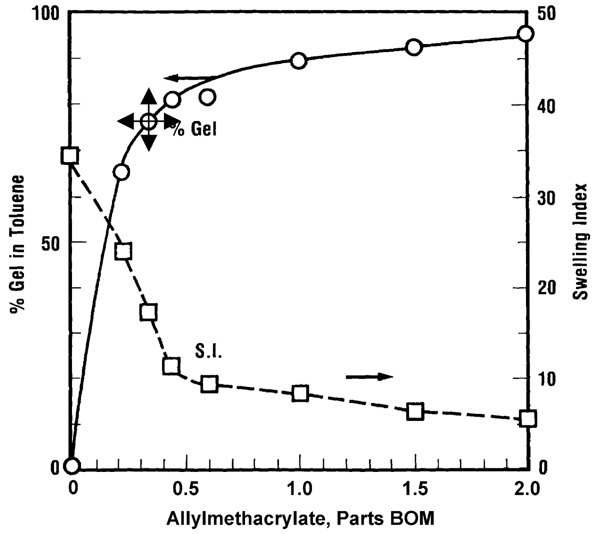

Fig. 2. The effect of latex backbone polymer crosslinking on %gel and swelling index of latex films: latex polymer compositions {BA/S/AMA [65/(35−X)/X]}; particle size (120 nm); latex films were dried at room temperature.

2.2. Non-crosslinked, carboxylated model latexes

To test the effect of interfacial bonding on the mechanical properties of latex films, a series of non-crosslinked, carboxylated model latexes [BA/S/AA: 65/(35−X)/X] was prepared by varying the amount of acrylic acid as an ionic and hydrogen bonding-capable functional monomer.

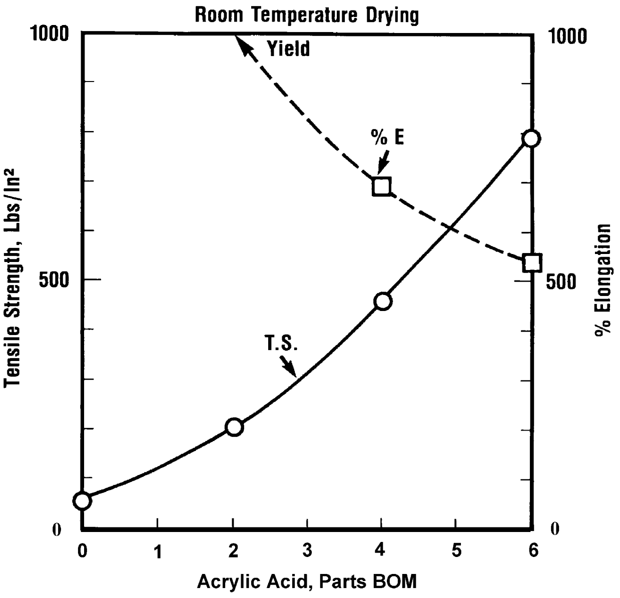

Fig. 3. The effect of vinyl acid level on the tensile strength and %elongation at break of latex films: latex polymer compositions {BA/S/AA [65/(35−X)/X]}; particle size (120 nm); latex films were dried at room temperature.

The tensile strengths and %elongations at break of non-crosslinked, carboxylated model latex films are plotted against the acrylic acid level in Fig. 3. The %gels and swelling indexes of non-crosslinked, carboxylated latex films were determined in toluene, as described previously. They are shown in Fig. 4.

2.3. Non-crosslinked, carboxylated model latexes with varying carboxylation and particle size

To study the effects of carboxylation and particle size on the strength of latex films, a series of carboxylated latexes (BA/S/AA) was prepared by varying the amount of acrylic acid (2, 4, and 6 parts) and particle size from 80 to 160 nm. The tensile strengths of these latex films are plotted against the particle size with the acrylic acid level as a parameter in Fig. 5.

2.4. Crosslinked, carboxylated model latexes

To test the concept of overcoming the limitation preventing the strength of crosslinked latex films from increasing by further crosslinking latex backbone polymers beyond the critical crosslinking density by means of the interfacial crosslinking, a series of crosslinked, carboxylated model latexes [BA/S/AA/AMA: 65/(31 − X)/4/X)] was prepared by varying the amount of allymethacrylate from 0 to 1 part per 100 parts monomers at the interval of 0.2 part. The tensile strength and %elongation at break of these crosslinked, carboxylated model latex films were measured. Their %gels and swelling indexes were also determined. The tensile strength and %elongation of these crosslinked, carboxylated latex films are plotted against allylmethacrylate in Fig. 6. Their %gels and swelling indexes are shown as a function of allylmethacrylate in Fig. 7.

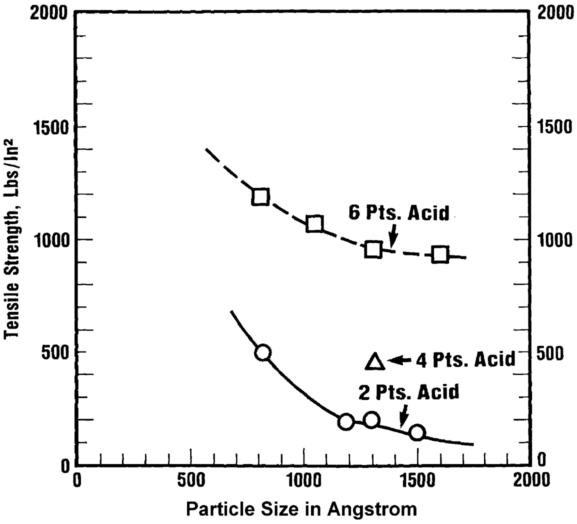

Fig. 5. The effects of vinyl acid level and particle size on the tensile strength of carboxylated latex films: latex polymer compositions {BA/S/AA [65/(35 − X)/X]}; latex films were dried at room temperature.

2.5. Wet strength of carboxylated latex films

The wet film strengths of a carboxylated latex were evaluated as a function of curing temperatures and compared with its dry film strengths. The results are shown in Fig. 8.

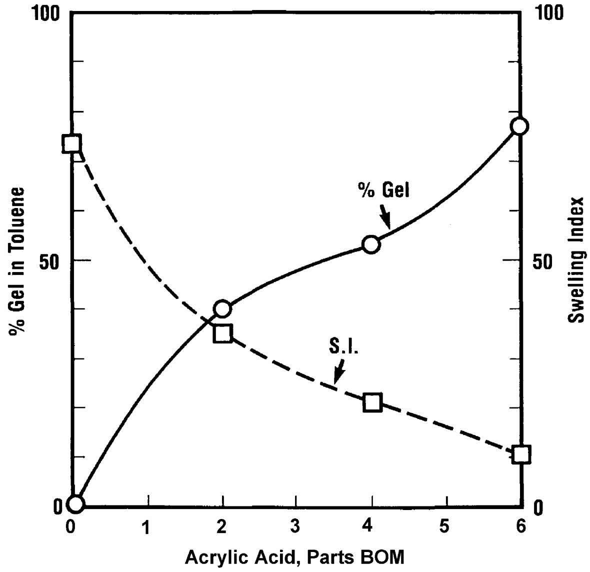

Fig. 4. The effect of vinyl acid level on %gel and swelling index of latex films: latex polymer compositions {BA/S/AA [65/(35 − X)/X]}; particle size (120 nm); latex films were dried at room temperature; %gel and swelling index were measured in toluene.

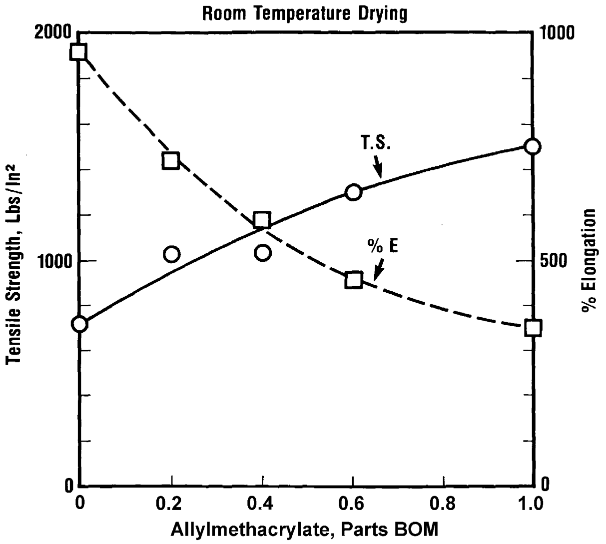

Fig. 6. The effect of latex backbone polymer crosslinking on the tensile strength and %elongation at break of carboxylated latex films: latex polymer compositions {BA/S/AA/AMA [65/(31 − X)/4/X]}; particle size (120 nm); latex films were dried at room temperature.

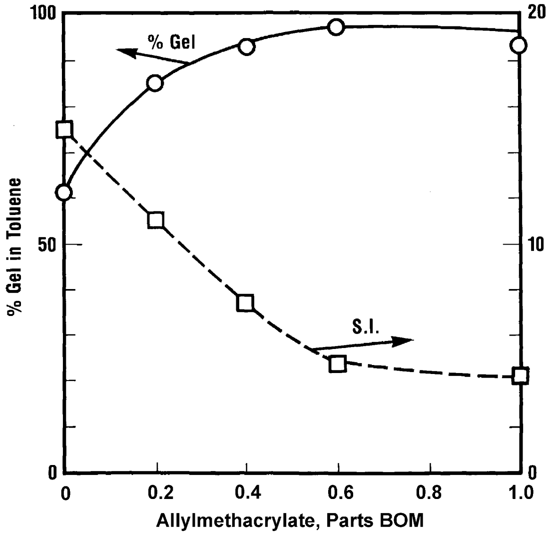

Fig. 7. The effect of latex backbone polymer crosslinking on %gel and swelling index of carboxylated latex films: latex polymer compositions {BA/S/AA/AMA [65/(31 − X)/4/X]}; particle size (120 nm); latex films were dried at room temperature.

2.6. ZnO-crosslinking of carboxylated latexes

In this study, ZnO was studied as a potential ambient temperature interfacial crosslinking agent. Although ZnO is sparingly soluble in water, it has been found that it neutralizes carboxylated latexes in the wet state rather fast and cures them upon drying. It has been speculated that despite very low dissolution of ZnO in water (i.e. a few ppm), Zn^{++} ions in equilibrium with ZnO (source) are chelated away by carboxylated latex particles (sink). So ZnO dissolves rather quickly by a source and sink coupling between ZnO and carboxylated latex particles until all carboxylic groups are neutralized. Dispersions of small ZnO particles were used in this study. The dry strength of a carboxylated latex film is shown as a function of increasing %neutralization with ZnO in Fig. 9.

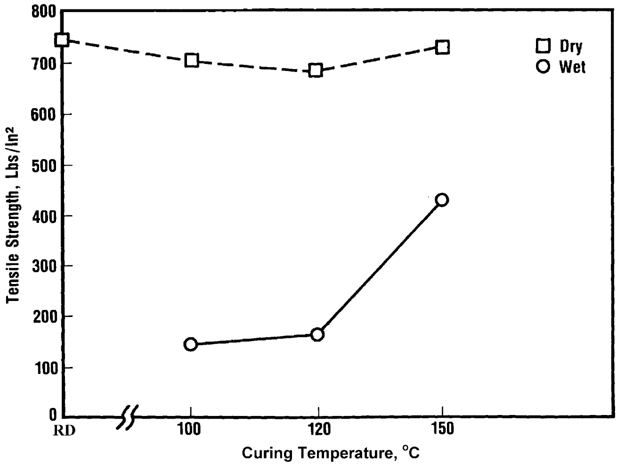

Fig. 8. The tensile strength of dry and wet carboxylated latex films vs. curing temperature: latex polymer composition [BA/S/AA (65/31/4)]; particle size (120 nm); latex films were dried at room temperature, and then cured at each curing temperature for 5 min; RD stands for room dried films; wet latex film samples were soaked in a 1% aerosol OT solution for 5 min.

2.7. Development of self-curable latex blends and structured latexes

Based on the above-described studies, it was decided to develop self-curable latexes using reactive monomers: 2-isopropenyl-2-oxazoline (IPO) and acrylic acid (AA). Since oxazoline and carboxylic groups react at low pH's even in the wet state, two different synthesis approaches were designed to develop self-curable latexes: blending and structured latexes [2,3], as shown in Fig. 10.

For the blending approach, carboxylated latexes (BA/S/AA: 65/31/4) were prepared at low pH's (e.g. 3–4), while IPO-containing latexes (BA/S/IPO: 65/30/5) were prepared at high pH's (e.g. 8–9). These AA-containing and IPO-containing latexes were subsequently blended at 50/50. For the structured latex approach [4–7], the first stage of 80 parts BA/S/AA/DVB (65/30.7/4/0.3) monomers was carried out at low pH's by a seeded semi-continuous emulsion polymerization and the reactor pH was raised from 8 to 9 with ammonium hydroxide, then the second stage of 20 parts BA/S/IPO (65/25/10) monomers was carried out, as shown in Fig. 11. All latexes were prepared at 90 °C.

A self-curable latex blend was tested for its dry and wet tensile strengths as a function of curing temperatures. The results are shown in Fig. 12. A self-curable structured latex was also tested for dry and wet tensile strengths. Fig. 13 shows the tensile strengths of dry and wet self-curable structured and control latex films as a function of curing temperatures, respectively. The control latex was a carboxylated latex.

3. Results and discussion

As can be seen from Figs. 1 and 2, the tensile strength of these crosslinked latex films increases with increasing AMA level up to 0.3 part per 100 parts monomers, corresponding to about 75% gel, and then decreases with further increasing AMA. This situation is unique to emulsion polymers whose film properties depend not only on the molecular weight and crosslinking density of latex backbone polymers, but also on the extent of coalescence in the absence of any interfacial bonding. From Figs. 1 and 2, it is quite evident that latex coalescence is limited for those latexes containing gel contents above about 75%. If we consider gels as a disperse phase in a continuous gel-free polymer phase, it is conceivable that the rheological behavior of such dispersions would be highly restricted above about 75% disperse phase. This finding is very important for designing latexes with good coalescence.

As can be seen from Fig. 3, the tensile strength of non-crosslinked, caboxylated model latex films increases with

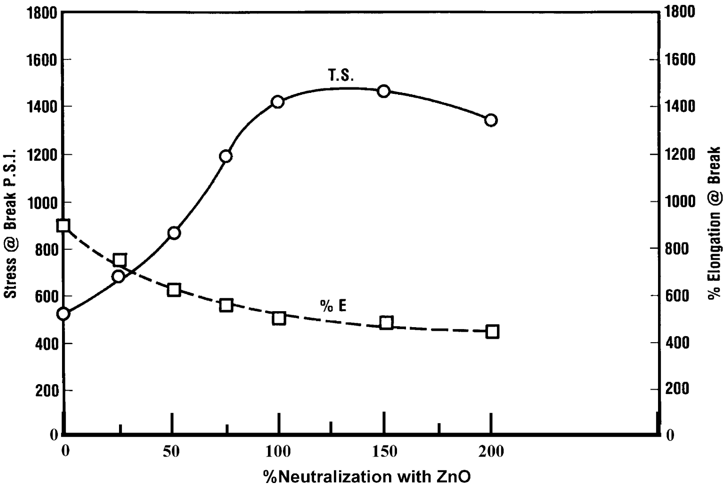

Fig. 9. The tensile strength and %elongation at break of a carboxylated latex film vs. ZnO neutralization: latex polymer composition [BA/S/AA (65/31/4)]; particle size (120 nm); latex films were dried at room temperature.

increasing carboxylation. Fig. 4 shows that the %gel of carboxylated latex films increases with increasing carboxylation, while their swelling index decreases, indicating that ionic and hydrogen bonds cause them to behave like crosslinked polymers in toluene. Undoubtedly, this is the reason why carboxylation increases the strength of carboxylated latex films, as shown in Fig. 3.

As expected, it can be seen from Fig. 5 that the tensile strength increases with increasing carboxylation, as already shown in Fig. 3, while their strength increases with decreasing particle size. This particle size effect on the film strength is intuitively obvious from the fact that the smaller the particle size, the larger the particle surface area, thus, the greater the interfacial crosslinking.

Figs. 3 and 5 clearly show that latex interfacial crosslinking is a powerful way to increase the strength of latex films. In fact, latex interfacial crosslinking is well known to produce latex films with reinforced honey-comb structures. This study also shows that the strength of these honey-comb structures achieved by latex carboxylation increases with increasing carboxylation and decreasing particle size, as shown in both Figs. 3 and 5. These results are consistent with the theory of rubber elasticity that tensile strength increases with increasing crosslinking density [1].

Figs. 6 and 7 clearly show that the strength of crosslinked, carboxylated latex films increases with increasing backbone polymer crosslinking density even well above a 75% gel content, suggesting that the combination of both backbone polymer and interfacial crosslinking is able to overcome the limited coalescence due to high gels and further increases the strength of latex films independently from the gel content. The finding that the strength of latex films can be increased by both latex backbone polymer and interfacial crosslinking is very important because the interfacial crosslinking of crosslinked latex particles would be able to match homogeneously crosslinked latex systems under relatively mild conditions.

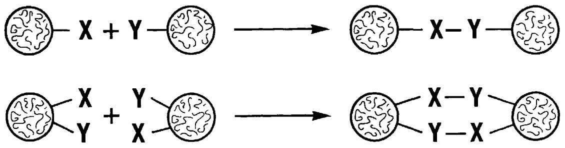

Fig. 10. Two different approaches for the development of self-curable latexes containing co-reactants, X and Y: blending X-containing and Y-containing latexes and structured latexes containing both X and Y; X: carboxylic group and Y: oxazoline group.

Although both series of non-crosslinked and crosslinked, carboxylated model latexes showed that latex interfacial crosslinking via carboxylic groups increased their dry film strengths, as shown in Figs. 3 and 5, their wet film strengths were significantly deteriorated except for the latex film cured at 150 °C, as shown in Fig. 8. These results are not surprising, since the hydrogen and ionic bonds are highly susceptible to water and weakened by it. Although the results are not reported here, it was also found that alkali-metal hydroxide-neutralized carboxylated latex films exhibited greater dry strengths than those of the un-neutralized

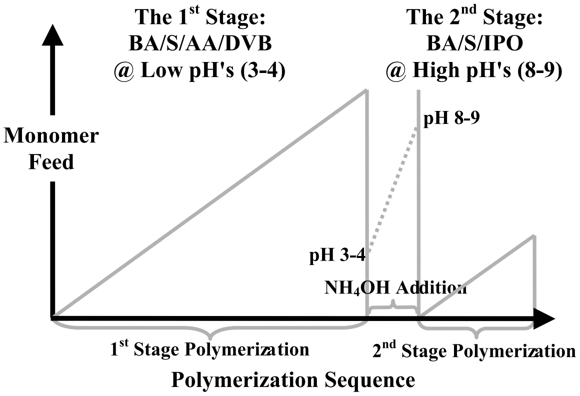

Fig. 11. Polymerization sequence for the preparation of self-curable structured latexes.

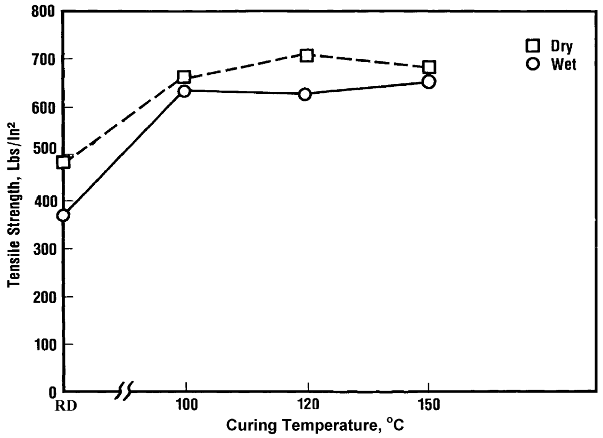

Fig. 12. The tensile strength of dry and wet self-curable latex blend films vs. curing temperature: latex blend of 50 IPO-containing latex [BA/S/IPO (65/30/5)] and 50 AA-containing latex [BA/S/AA (65/31/4)]; particle size (120 nm); latex films were dried at room temperature, and then cured at each curing temperature for 5 min; RD stands for room dried films; wet latex film samples were soaked in a 1% aerFosol OT solution for 5 min.

and fugitive base-neutralized counterparts, along with their higher gel contents in toluene, but their wet strengths were worse. For this reason, many crosslinking agents, such as melamine and urea formaldehyde resins, epoxy resins, multivalent metal ions, etc. have been studied in the literature to crosslink carboxylated latexes for both dry and wet strengths. Fig. 9 shows ZnO-crosslinking as an ambient temperature crosslinking agent. Unlike soluble divalent metal salts, such as $ZnCl_2$ and $CaCl_2$, ZnO is innocuous to the colloidal stability of latexes, but is almost as efficient as its soluble counterparts. Thus, ZnO is considered as one of the most innocuous and efficient ambient crosslinking agents for carboxylated latexes.

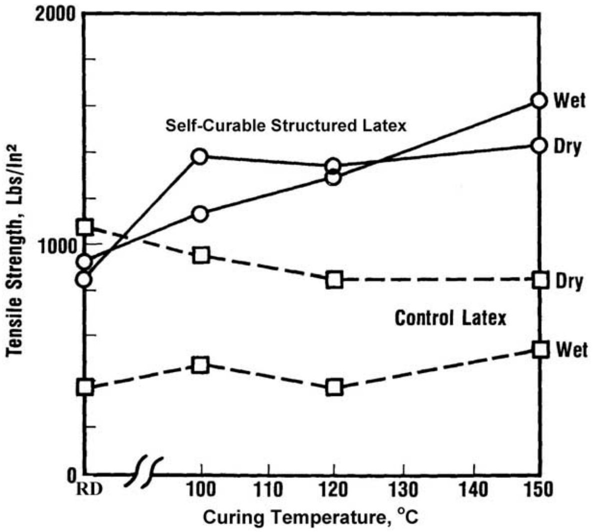

Fig. 13. The tensile strengths of self-curable structured and control latex films vs. curing temperature: self-curable structured latex [80 parts BA/S/AA/DVB (65/30.7/4/0.3)//20 Parts BA/S/IPO (65/25/10)] and control latex [BA/S/AA/DVB (65/30.7/4/0.3)]; particle size (120 nm); latex films were dried at room temperature, and then cured at each curing temperature for 5 min; RD stands for room dried films; wet latex film samples were soaked in a 1% aerosol OT solution for 5 min.

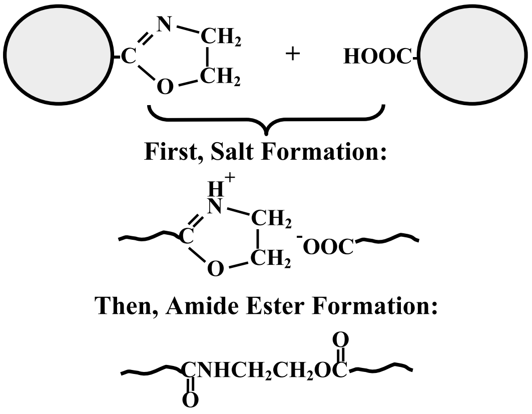

Fig. 14. The reaction between oxazoline and carboxylic groups leading to the formation of amide ester.

Fig. 10 depicts two approaches for the development of self-curable latex blends and structured latexes, respectively, by incorporating acrylic acid and 2-isopropenyl-2-oxazoline as co-reactants, while Fig. 11 shows how self-curable structured latexes can be prepared. Fig. 12 shows an excellent performance of a self-curable latex blend. Self-curable structured latexes containing both carboxylic and oxazoline groups on the same particles can lead to both inter-particle and intra-particle reactions. Although their intra-particle reactions would not result in the interfacial crosslinking, Fig. 13 shows that a structured latex has performed very well as a self-curable latex. The reaction of oxazoline and carboxylic groups first undergoes a salt formation, and then rearranges to form amide ester, as shown in Fig. 14. More importantly, oxazoline and carboxylic groups were found to be very efficient post-curing reactants even at relatively moderate curing temperatures in the presence of acid catalysts such as ammonium sulfate.

Since this work was done some years back, the recent literature has not been cited, but the results of this work have been found to be rather consistent with those of the papers contained in the ACS Symposium Series on ‘Film Formation in Waterborne Coatings [8]’ and more recent publications.

4. Conclusion

This study has clearly demonstrated that the mechanical properties of latex films depend not only on the crosslinking density of latex backbone polymers, but also on the interfacial crosslinking among the latex particles during film formation and curing. Self-curable blend and structured latexes containing both oxazoline and carboxylic groups were developed and required only relatively moderate curing temperatures for their interfacial crosslinking. With these self-curable latexes, it was possible to crosslink emulsion polymers under moderate curing conditions, as if they were homogeneously crosslinked.

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