

Crosslinkable Emulsion Polymers by Autoxidation. II

FUNG-BOR CHEN* and B. GEORGE BUFKIN,[†] *Polymer Science
Department, University of Southern Mississippi, Hattiesburg,
Mississippi 39401*

Synopsis

The physicochemical properties, molecular weights, glass transition temperatures, and crosslinking mechanisms of fatty acrylate copolymers consisting of unsaturated bonds in the side chain were studied. The kinetics of the crosslinking mechanism of polymer films was analyzed by isothermal differential scanning calorimetry. The crosslinking rate was slow and influenced more by cobalt catalyst than by lead catalyst. The different physical properties displayed by the polymer films with and without catalysts demonstrated the occurrence of autoxidation. In general, 60 min at 100°C or 2 weeks at room temperature was sufficient time for polymer films reported here to obtain constant physical properties, such as tensile strength, swelling ratios, and percent insoluble polymers. The enhanced tensile strength from crosslinking was not large enough to overcome the lowering of the tensile strength due to plasticization with crosslinkable monomers such as linolenyl acrylate, linoleyl acrylate, and oleyl acrylate. However, non-crosslinkable lauryl acrylate showed better coalescence at room temperature.

INTRODUCTION

In Part I of this series was reported that the study of the fatty acrylates included (1) linolenyl acrylate (LA3), (2) linoleyl acrylate (LA2), (3) oleyl acrylate (OA) and (4) lauryl acrylate (LA). The above acrylates were prepared from the reaction of fatty alcohols with acryloyl chloride. The purity of the acrylates was checked by gas chromatography, infrared spectroscopy, and nuclear magnetic resonance. The Kelen-Tüdös and the integrated transformation methods were applied to determine the reactivity ratios of comonomers of ethyl acrylate or methyl methacrylate with LA3, LA2, or OA.

In this paper the pre-emulsion technique will be used to prepare the higher conversion (> 98%) emulsion polymers for this study, and the physicochemical properties, molecular weight, glass transition temperatures, and crosslinking mechanisms of the emulsion polymers will be discussed.

EXPERIMENTAL

Preparation of Emulsion Polymers

The formulation used to prepare the emulsion polymers is outlined in Table I and the detailed procedure is as follows: A pre-emulsion was prepared with items g-j. A 500-mL flask was charged with items a-e. Nitrogen

*Present address: Deseret Medical, Inc., 9450 South State, Sandy, UT 84070.

[†]Present address: Sherwin-Williams Co., P.O. Box 6027, Cleveland, OH 44101.

TABLE I
Pre-Emulsion Formulation for Preparing Emulsion Polymers

Items	Reactants	Parts by weight
a	Triton N-101 ^a	0.5
b	Triton X-200 ^a	1.0
c	Distilled water	66.0
d	Sodium metapersulfite	0.2
e	Ferrous sulfate	0.01
f	Ammonium persulfate	0.2
g	Distilled water ^b	25.0
h	Triton N-101 ^b	1.5
i	Triton X-200 ^b	5.5
j	Monomers ^b	50.0

^a Emulsifiers from Rohm and Haas Co.

^b Pre-emulsified before polymerization.

was bubbled into the flask for 15 min. The 15.4 g of pre-emulsion was added concomitantly with one fifth of item f. After a few minutes, the reaction temperature reached its maximum (about 50°C) and then dropped. At that time, the reaction was allowed to cool down to 25°C. The rest of the pre-emulsion and item f were continuously added over 2 h. The reaction temperature was maintained at 30°C for 1 h after addition of monomers.

The monomer compositions and general physical properties of the emulsion polymers prepared are included in Tables II-V.

Determination of Conversion and Coagulation of Emulsion Polymers

A 300 μm filtered emulsion (1-2 g) was weighed into a clean, dry aluminum dish. The dish and contents were heated in an oven at 150°C until constant weight was obtained. The conversion and coagulation were defined by the following:

$$\text{conversion (\%)} = N/T \times 100$$

$$\text{coagulation (\%)} = C/M \times 100$$

where N = nonvolatile matter (%), T = theoretical nonvolatile content (%), C = precipitate on a filter cloth (g), and M = total monomer weight (g).

TABLE II
General Properties of Emulsion Polymers of LA3

Expt no.	E-0	E-1	E-2	E-3	E-4
LA3 (%) ^a	0	2	4	6	8
EA (%) ^a	60	58.8	57.6	56.4	55.2
MMA (%) ^a	40	39.2	38.4	37.6	36.8
pH	2.2	2.3	2.3	2.2	2.2
Conversion (%)	99.9	99.9	98.9	98.3	98.2
Coagulation (%) ^a	0	0	0	0	0

^a Based on monomer weights; LA3 = linolenyl acrylate, EA = ethyl acrylate, and MMA = methyl methacrylate.

TABLE III
General Properties of Emulsion Polymers of LA2

Expt no.	E-5	E-6	E-7	E-8
LA2 (%) ^a	2	4	6	8
EA (%) ^a	58.8	57.6	56.4	55.2
MMA (%) ^a	39.2	38.4	37.6	36.8
pH	2.3	2.2	2.3	2.3
Conversion (%)	99.6	99.3	99.0	98.5
Coagulation (%) ^a	0	0	0	0

^a Based on monomer weights; LA2 = linoleyl acrylate, EA = ethyl acrylate, and MMA = methyl methacrylate.

Glass Transition Temperature

A DuPont 910 DSC was used to determine the glass transition temperatures of the polymers. The conditions for analysis were

progress rate 10°C/min
temperature range -20-30°C

Determination of Molecular Weights

A Knauer Vapor Pressure Osmometer was used to determine the number-average molecular weight of polymers using toluene as the solvent and a temperature of 37°C. The emulsion polymers were precipitated by methanol, then washed with water, and dissolved by acetone three times. Polymers were dried about 2 h under vacuum pressure and the desired polymer solutions were prepared.

Optimal Concentration of Catalyst for Crosslinking

A Perkin-Elmer DSC-1 was used to select the appropriate amount of catalysts for autoxidation. Three polymer films of polymer E-8 containing the described amount of catalysts in Table VI were prepared. After 1 day's drying, these samples were isothermally run at the desired temperature on the DSC.

TABLE IV
General Properties of Emulsion Polymers of OA

Expt no.	E-9	E-10	E-11	E-12
OA (%) ^a	2	4	6	8
EA (%) ^a	58.8	57.6	56.4	55.2
MMA (%) ^a	39.2	38.4	37.6	36.8
pH	2.2	2.3	2.3	2.3
Conversion (%)	99.7	99.3	99.0	98.9
Coagulation (%) ^a	0	0	0	0

^a Based on monomer weights; OA = oleyl acrylate, EA = ethyl acrylate, and MMA = methyl methacrylate.

TABLE V
General Properties of Emulsion Polymers of LA

Expt no.	E-13	E-14	E-15	E-16
LA (%) ^a	2	4	6	8
EA (%) ^a	58.8	57.6	56.4	55.2
MMA (%) ^a	39.2	38.4	37.6	36.8
pH	2.3	2.3	2.2	2.3
Conversion (%)	99.8	99.5	99.6	99.4
Coagulation (%)	0	0	0	0

^a Based on monomer weights; LA = lauryl acrylate, and MMA = methyl methacrylate.

Film Thickness

The films were prepared by drawing down the emulsion polymer containing the optimal amount of catalysts on a smooth glass. The thickness of the dried film was measured with a micrometer after the film was free from the glass.

Swelling Ratio

The swelling ration of a crosslinked polymer is the percent volume increase of the polymer in a solvent.¹

Tensile Strength and Percent Elongation

The tensile strength and percent elongation of the film were determined with an Instron 1130 Tensile Tester. The specimens possessed a width of 2.5 m, a thickness of 0.2–0.3 m and a gauge length of 15 m. The crosshead speed was 10 cm/min.

In most cases, the data represents the average of those four samples showing the highest tensile strength among 10 measurements. The average standard deviation is about 10%

Percent Insoluble Polymers

The percent insoluble polymer is the percent ratio of the weights of polymers films after to that before extracted by tetrahydrofuran.

Alkali, Acid and Water Resistance

Alkali, acid, and water resistance was indicated by the swelling ratios in desired solvents.

TABLE VI
Three Polymer Films of Polymer E-8 Containing Various Amount of Catalysts

Expt no.	D-1	D-2	D-3
Cobalt (%) ^a	0.1	0.08	0.065
Lead (%) ^a	0.98	0.057	0.35

^a Metal dry weight of Troy water-dispersion metal oleate driers to the weight of monomer LA2.

RESULTS AND DISCUSSION

The general properties displayed by the emulsion polymers based on LA3, LA2, OA, and LA are listed in Tables II-V. The results show the high conversion of the polymer produced and negligible coagulation levels. Polymer E-4 has the lowest conversion among these polymerization, but this conversion level is acceptable for the preparation of the emulsion.

Glass Transition Temperature (T_g)

The results of T_g analysis measured via DSC are included in Figure 1. The higher concentration of fatty acrylates and unsaturated functionalities in polymers lowers T_g . There are two reasons: First, an internal plasticization results from the long side chain to increase segmental mobility.² Second, saturated long side chains are extended in a linear zig-zag fashion and fit together rather well. The introduction of unsaturation simply bends the side chain and causes the side chain fitting each other badly. The looser the molecules fit, the weaker the intermolecular forces, and the lower the T_g . This type of influence of unsaturation is similar to lowering the melting point of fat by the introduction of unsaturation.³

Molecular Weight Analysis (M_n)

The results of M_n analysis measured via the vapor pressure osmometer (VPO) as shown in Figure 2 show the effect of allylic methylene hydrogens on the number-average molecular weight. The higher concentrations of allylic methylene hydrogens increase the retardation and/or chain transfer and lower M_n . Also, the pre-emulsion technique often results in a broadened molecular weight distribution, thereby giving rise to an increased number

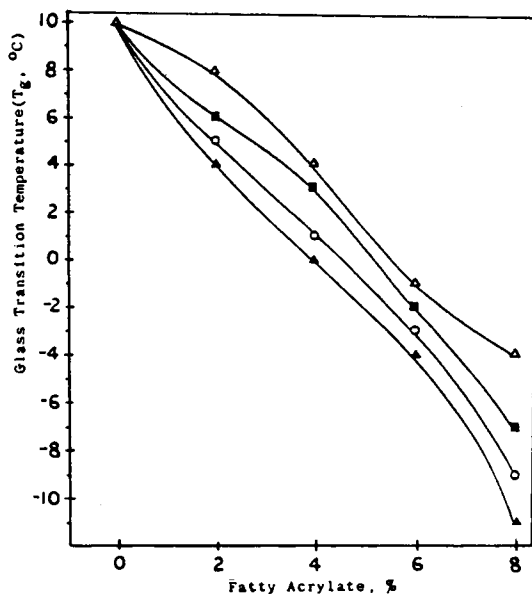


Fig. 1. Glass transition temperatures as a function of fatty acrylate concentrations emulsion polymers: (Δ) LA; (\blacksquare) OA; (\circ) LA2; (\blacktriangle) LA3.

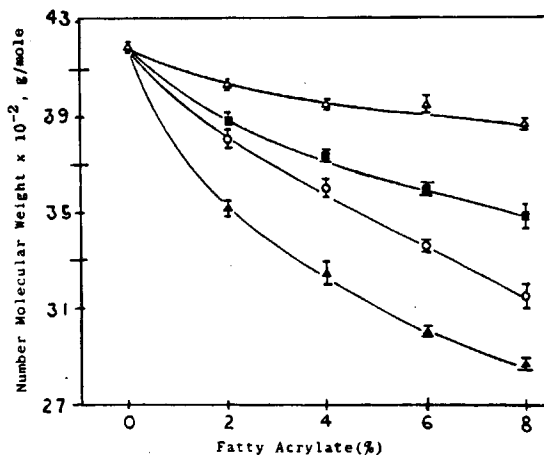


Fig. 2. Number-average molecular weights as a function of fatty acrylate concentrations in emulsion polymers: (Δ) LA; (■) OA; (○) LA2; (▲) LA3.

of low molecular weight fragment.⁴ Since the number-average molecular weight is characterized by its sensitivity to a small weight fraction of constituents of low molecular weight,⁵ polymers prepared by this technique would have low number-average molecular weight. This was found to be the case in EA-MMA, polymer E-0.

Optimizing Catalyst Concentration

Differential scanning calorimetry (DSC) is a technique widely used in the study of curing kinetics and reaction mechanisms of thermosetting resins.⁶ The DSC was successfully applied in this research to study the rate of crosslinking as a function of various catalysts compositions.

Three polymer films of polymer E-8 containing the amount and type of catalysts described in Table VI were prepared. These films were studied in a temperature range of 100–190°C. Typical curves from the isothermal DSC are shown in Figure 3. Because the curves contain plateaus instead of sharp peaks, the crosslinking rate is revealed to be slow. In order to understand the efficiency of the added catalysts, Figure 4 was obtained.

Since cobalt catalysts are active driers,^{7,8} the heat expelled from polymers D-1, D-2, and D-3 shown in Figure 4 should depend on the amount of cobalt catalysts and adhere to the decreasing order as follow: D-1 (cobalt, 0.1%) > D-2 (cobalt, 0.08%) > D-3 (cobalt, 0.065%). At higher temperatures the heat expelled by all three polymers followed the above expected order. At lower temperatures the heat expelled from polymers D-1 and D-2 is the same regardless of the cobalt content. This may be explained by the fact that there exists a maximum effective catalyst concentration for crosslinking at a specific temperature. As a result, excessive concentrations of cobalt catalysts do not improve crosslinking rate. On the other hand, the dependence of the heat expelled on the amount of lead catalysts was not observed to adhere to the decreasing order: D-1 (lead, 0.98%) > D-3 (lead, 0.35%) > D-2 (lead, 0.057%). This is due to the fact that lead catalysts are auxiliary driers and do not significantly promote crosslinking rate.^{7,8}

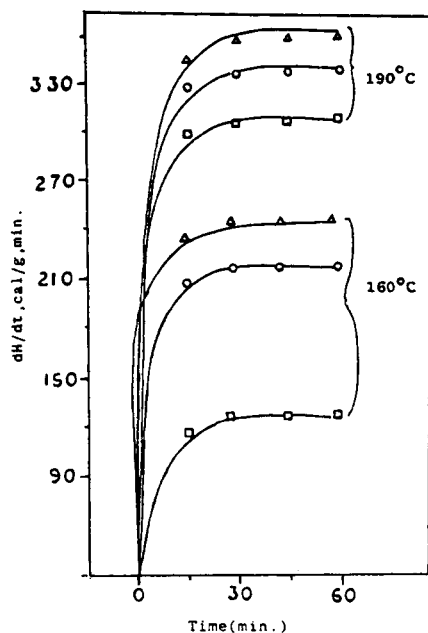


Fig. 3. Kinetics curves from isothermal DSC: (Δ) D-1; (\circ) D-2; (\square) D-3.

From the DSC study, it was found that in the temperature range of 100–130°C, polymers D-1 and D-2 have the highest crosslinking rates, and polymer D-2 is preferable to polymer D-1 due to its lower catalyst content. All other polymer films made and studied in this project which contain catalysts

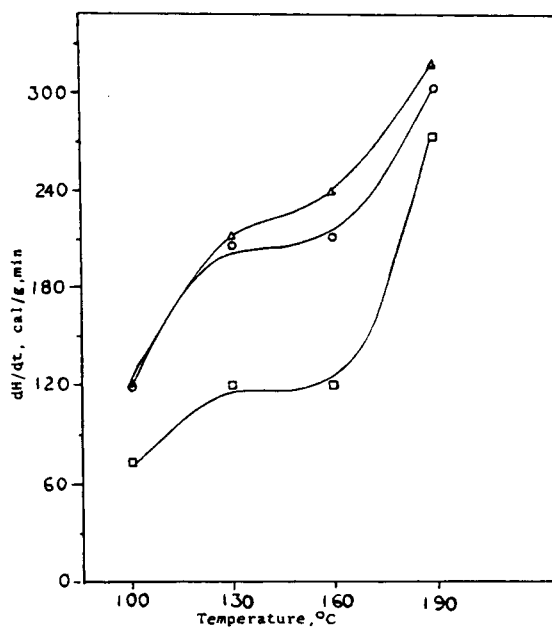


Fig. 4. Heat expelled from polymers D-1 to D-3 on isothermal DSC at various temperatures: (Δ) D-1 (0.1% Co, 0.98% Pb); (\circ) D-2 (0.08% Co, 0.057% Pb); (\square) D-3 (0.065% Co, 0.35% Pb).

were therefore made using the catalyst composition employed in experiment D-2.

Evidence of Autoxidation

Two polymer films derived from polymer E-6 were prepared. One contains the catalyst as described in experiment D-2, and the other does not. The latex containing catalyst is expected to have a higher crosslink density than the one without catalyst, thereby yielding a greater percent insoluble polymers, greater tensile strength and hardness, and lower elongation and swelling ratios.

Figures 5-9 illustrate the results obtained in terms of percent insoluble polymers, tensile strength, swelling ratio, hardness, and percent elongation. The insoluble portions of the films increase with the use of catalysts and longer crosslinking times. Of course, more crosslinking results in a more densely crosslinked network from which the solubility of polymer films is decreased, and the percent insoluble polymer is increased. The development of a network also contributes to an increased tensile strength, lower swelling ratios, lower percent elongation, and increased hardness which are observed with catalyzed polymer E-6.

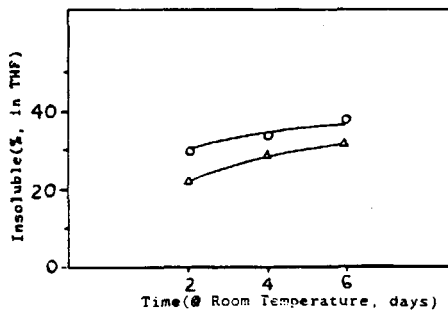


Fig. 5. Percent insoluble polymer of polymer E-6 as a function of catalysts and cure time at room temperature: (○) with catalyst; (△) without catalyst.

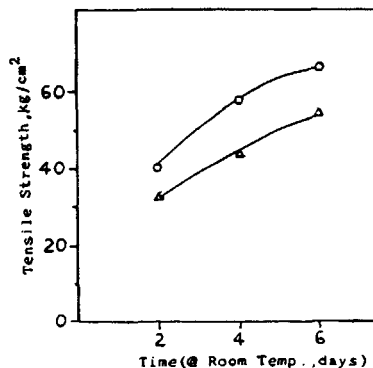


Fig. 6. Tensile strength of polymer E-6 as a function of catalysts and cure time at room temperature: (○) with catalyst; (△) without catalyst.

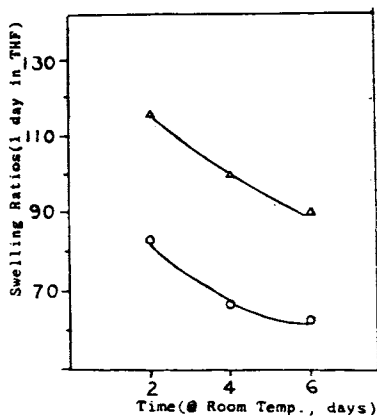


Fig. 7. Swelling ratios of polymer E-6 as a function of catalysts and cure time at room temperature: (○) with catalyst; (△) without catalyst.

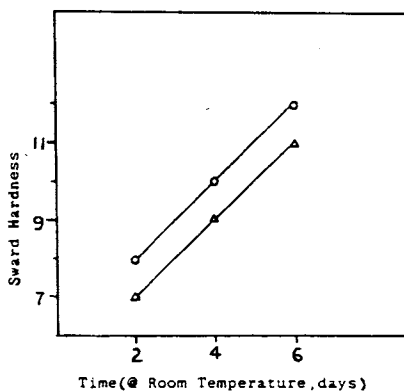


Fig. 8. Sward hardness of polymer E-6 as a function of catalysts and cure time at room temperature: (○) with catalyst; (△) without catalyst.

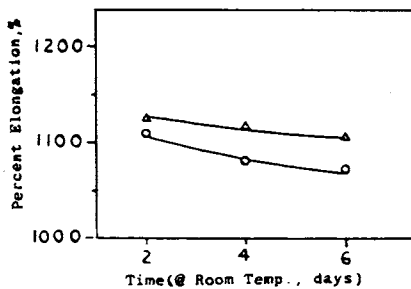


Fig. 9. Percent elongation of polymer E-6 as a function of catalyst and cure time at room temperature: (○) with catalyst; (△) without catalyst.

Latex of Linolenyl Acrylate (LA3)

Latexes with linolenyl acrylate concentrations of 0–8% by weight were investigated. From the tensile strength results as shown in Figure 10, it is clear that EA/MMA copolymer, polymer E-0, has a greater tensile strength than any of the crosslinked polymers containing LA3. In fact, increasing the crosslinkable monomer, LA3, does not simply increase the tensile strength within the E-1–E-4 polymer series. During crosslinking at 100°C, latexes become crosslinked gels, thereby increasing the tensile strength if the system performs as expected. This crosslinking should compensate for the lowering of the tensile strength resulting from the plasticization of the side chains and the decreased molecular weight, thereby giving increased overall tensile strengths. The effect of these factors occurring simultaneously makes interpretation of these data complex. Thus the trend toward an increased tensile strength with increasing concentration of LA3 is too complicated to conclude from the tensile strength data alone. However, the swelling ratio, as shown in Figure 11, and percent insoluble polymers, as indicated in Figure 12, lead supporting evidence to the fact that there is increased crosslinking with increased LA3 concentration.

The swelling ratio decreases with increased LA3 concentration. Two factors control the swelling occurrence. One is the elastic force developing from crosslinking, and the other is entropy.⁹ The lower swelling ratio indicates a better developed network assuming the solubility difference between polymers is negligible. Polymer E-4, containing 8% concentration of LA3, dominates other polymers in terms of crosslink density. On the other hand, Polymer E-1 with 2% concentration of LA3 shows far less crosslink-

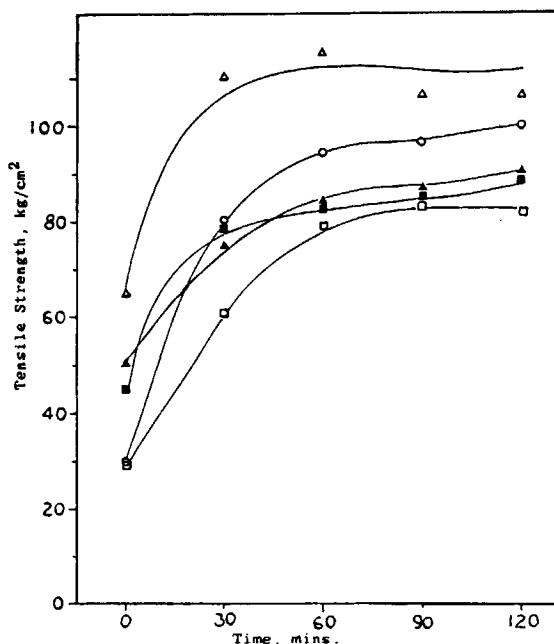


Fig. 10. Tensile strength of polymers E-0–E-4 as a function of cure time at 100°C. LA3 (wt %): (△) E-0,0; (■) E-1,2; (▲) E-2,4; (□) E-3,6; (○) E-4,8

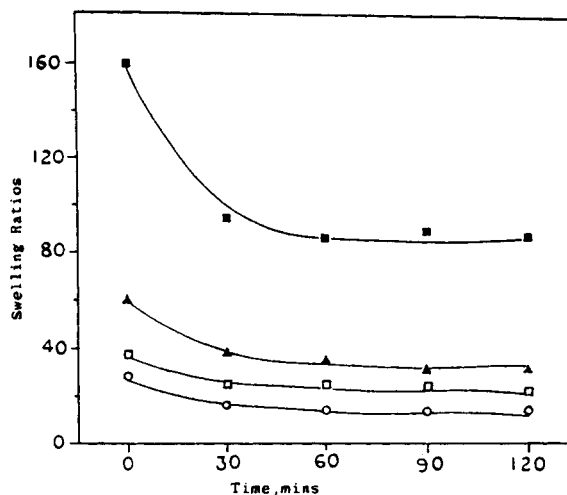


Fig. 11. Swelling ratios of polymer films E-1-E-4 as a function of cure time at 100°C. LA3 (wt %): (■) E-1,2; (▲) E-2,4; (□) E-3,6; (○) E-4,8.

ing. This can be explained by the lower LA3 concentration which dramatically decreases the crosslink density. From swelling ratio analysis it is obvious that LA3 provides suitable crosslinking for the formation of polymer films when incorporated in a minimum amount of 4% by weight or above.

Because the polymer solubility decreases with increased crosslinking, percent insoluble polymers increase as LA3 concentration increases. On the other hand, percent elongation as shown in Figure 13 is decreased with increased LA3 concentration, because crosslinking will limit the expansion of polymers.¹⁰

The optimum crosslinking time at 100°C is about 60 min. Beyond this time of cure, the previously mentioned physical properties were not ob-

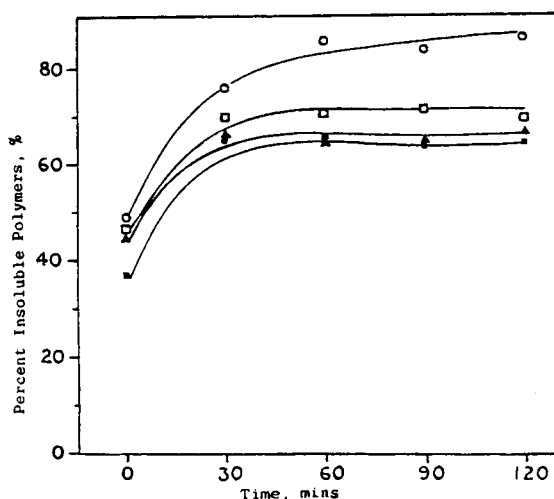


Fig. 12. Percent insoluble polymers of polymer films E-1-E-4 as a function of cure at 100°C. LA3 (wt %): (■) E-1,2; (▲) E-2,4; (□) E-3, 6; (○) E-4,8.

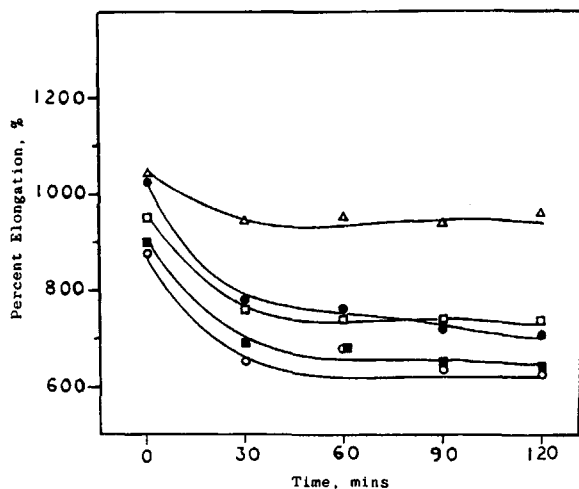


Fig. 13. Percent elongation of polymer films E-0-E-4 as a function of cure time at 100°C. LA3 (wt %): (Δ) E-0,0; (\bullet) E-1,2; (\square) E-2,4; (\blacksquare) E-3,6; (\circ) E-4,8.

served to greatly improve. This may be due to most of the crosslinking sites having reacted.

At room temperature, the results as described in Figure 14 show that the tensile strength, except for polymer E-1, is increased with the amount of LA3 introduced. It is clear from these data that the increased tensile strength from crosslinking dominates other mentioned factors, such as plasticization and molecular weight changes. Polymer E-1 has few crosslinking sites, so that the increased tensile strength is not significant.

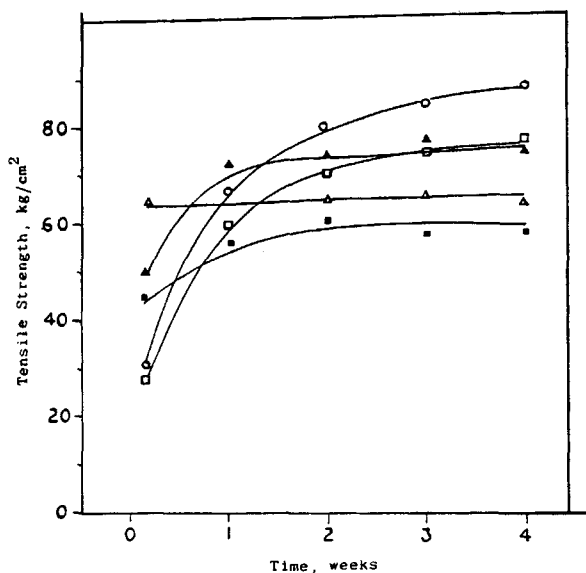


Fig. 14. Tensile strength of polymer films E-0-E-4 as a function of cure time at room temperature. LA3 (wt %): (Δ) E-0,0; (\blacksquare) E-1,2; (\blacktriangle) E-2,4; (\square) E-3,6; (\circ) E-4,8.

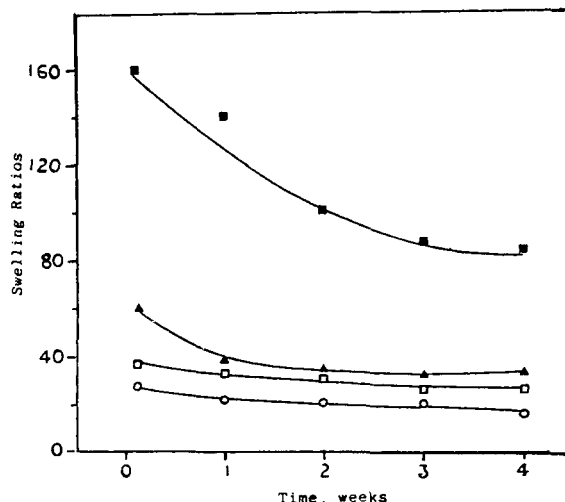


Fig. 15. Swelling ratios of polymer films E-1-E-4 as a function of cure time at room temperature. LA3 (wt %): (■) E-1,2; (▲) E-2,4; (□) E-3,6; (○) E-4,8.

The swelling ratio trends shown in Figure 15, percent insoluble polymers indicated in Figure 16, and percent elongation described in Figure 17 are similar to those at 100°C observed with the same polymers. The explanations mentioned are applied here and extend to polymers containing LA2 or OA if no special mention is given later herein.

After 2 weeks, swelling ratios, percent insoluble polymers, and percent elongation are not significantly changed. This would indicate that most crosslinking sites have been consumed or at least sufficient crosslinking has occurred that no physical property improvement is observed. Thus, in general, 2 weeks may be enough time for latexes of this type to obtain constant properties resulting from crosslinking.

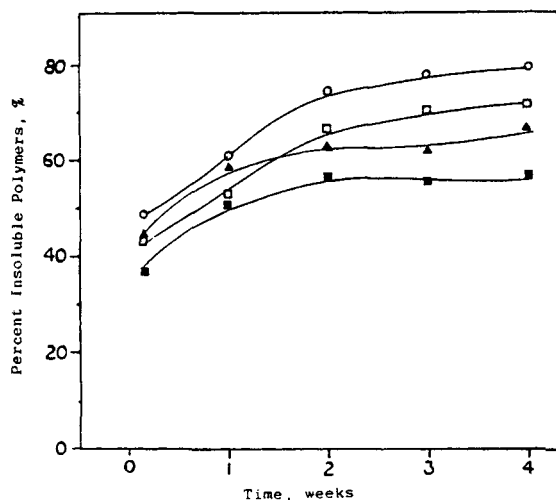


Fig. 16. Percent insoluble polymers of polymer films E-1-E-4 as a function of cure time at room temperature. LA3 (wt %): (■) E-1,2; (▲) E-2,4; (□) E-3,6; (○) E-4,8.

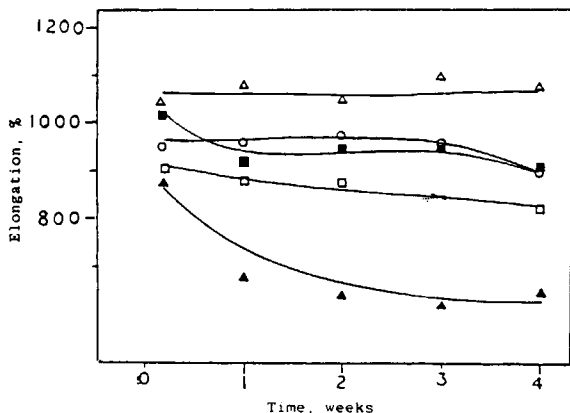


Fig. 17. Percent elongation of polymer films E-0-E-4 as a function of cure time at room temperature. LA3 (wt %): (Δ) E-0,0; (\blacksquare) E-1,2; (\circ) E-2,4; (\square) E-3,6; (\blacktriangle) E-4,8.

Latexes of Linoleyl Acrylate (LA2)

When crosslinked at 100°C, the latexes do not follow a trend toward an increased tensile strength with the increase of LA2 concentrations. Similarly, molecular weight changes and plasticization occur simultaneously. As a result, the tensile strength of polymers E-5-E-8 seems to be inferior to that of polymer E-0. At room temperature, the results show that the tensile strength among polymers E-5-E-8 is increased with the amount of LA2 introduced.

The swelling ratios and percent insoluble polymers support the aforementioned time to obtain constant physical properties from crosslinking at 100°C or at room temperature and the increased crosslinking along with increased LA2 concentrations.

Latexes of Oleyl Acrylate (OA)

The tensile strength of polymers E-9-E-12 is below the value obtained from polymer E-0, when crosslinked at 100°C or at room temperature. This lowered tensile strength is due to the inability of crosslinking to overcome the plasticization effect of the long side chains.

The crosslinking of a polymer film of polymer E-9 at 100°C shows a large but measurable swelling ratio, but at room temperature its swelling ratio is not experimentally detected. Because heat usually can improve crosslinking,⁶ the results point out that 100°C is more effective in polymer E-9.

The optimum time for obtaining constant crosslinking properties is concluded to be 60 min at 100°C or 2 weeks at room temperature. The increased crosslinking along with increased OA concentration was observed to be in agreement with the decreased swelling ratios and increased percent insoluble polymers.

Latexes of Lauryl Acrylate (LA)

The tensile strength derived from LA containing polymer films after 2 weeks at room temperature or after 60 min at 100°C becomes constant. These curing periods appear to be sufficient for improved coalescence of the polymer films and for obtaining constant physical properties.

The summation of the final results with respect to LA concentration is plotted in Figure 18. It can be seen that the tensile strength obtained at room temperature initially increases with the introduction of a small amount of LA. When LA is continuously added, the tensile strength gradually drops. This can be explained by the fact that the coalescence of polymer films is improved by the increased freedom of motion when a small amount of LA is present. After a larger amount of LA is added, the plasticization due to side chains was observed.¹¹⁻¹⁵ Yet, in reviewing the results from higher temperatures in Figure 18, better coalescence of polymer films observed at room temperature was not observed. The higher temperature apparently enhances the coalescence of the polymer film of E-O giving rise to a higher tensile strength. Thus, the introduction of LA simply softens the film. As a result, the typical plasticization resulting from LA was observed.

At a lower concentration of LA the polymer has a higher T_g , and the emulsion particles do not coalesce as completely as those samples with a higher percentage of LA. Annealing improves the coalescence of the film and therefore the tensile strength. At higher concentrations of LA the difference in tensile strength is less between the annealed and unannealed films because coalescence is more complete at room temperature due to the lower T_g and bulk viscosity.

Alkali, Acid, and Water Resistance

Table VII demonstrates that polymers E-O-E-16 have similar alkali resistance. The introduction of fatty acrylates does not greatly affect the alkali resistance. Similarly, the same trend was observed in water resistance. In comparison with the water resistance, the polymers exhibit better resistance

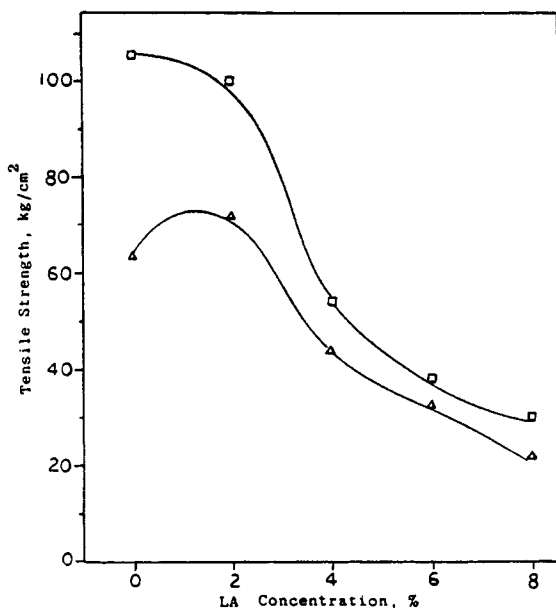


Fig. 18. Comparison of tensile strength between polymer films annealed at 100°C (□) for 2 h and those cured at room temperature (△) for 4 weeks.

TABLE VII
Swelling Ratios of Polymer Films^a in Various Solutions

Polymer	E-0	E-1	E-2	E-3	E-4	E-5	E-6	E-7	E-8	E-9	E-10	E-11	E-12	E-13	E-14	E-15	E-16
5% NaOH ^b	1.12	1.14	1.18	1.13	1.15	1.17	1.14	1.14	1.15	1.12	1.18	1.14	1.16	1.16	1.17	1.20	1.18
Water ^c	1.61	1.61	1.67	1.61	1.68	1.63	1.62	1.63	1.68	1.67	1.63	1.65	1.67	1.62	1.63	1.65	1.61
5% AA ^d	1.97	1.74	1.77	1.76	1.73	1.73	1.76	1.79	1.75	2.41	2.45	2.48	2.02	2.16	2.05	2.71	3.01

^aThe polymer films were dried at room temperature for 4 weeks.

^b5% NaOH by weight in deionized water solution.

^cDeionized water.

^d5% acetic acid by weight in deionized water solution.

in the alkali solution. Thus it appears that ions in the solution limit the expansion of polymer films containing negative charges due to anionic surfactants.¹⁶ On the contrary, in acidic solutions, acetic acid which acts not only as a charge neutralizer but also as an organic solvent results in higher swelling ratios. Compared to polymers E-O and E-9-E-16, polymers E-1-E-8 show improved crosslinking properties and display better acid resistance.

Comparison of Physical Properties

Room Temperature Cure for 4 Week

In Figure 19, a plot of tensile strength against fatty acrylate concentrations is shown. There exists an unexpected relationship between tensile strength and increasing amounts of crosslinkable monomers. This has been discussed earlier. Inclusion of low concentrations of fatty acrylates simply softens the film and decreases the tensile strength. On the other hand, at higher concentrations of fatty acrylates, crosslinking sites are increased as is crosslinking density. Thus, the tensile strength goes up again.

Figure 19 also shows that the tensile strength depends on the type of monomer included in the polymer. It would be expected that a larger degree of unsaturation would be readily attacked by oxygen and give a higher degree of crosslinking to yield a hard film.¹⁷ OA with a single double bond (four allylic hydrogens) in the side chains does not provide enough crosslinking sites at low concentrations to give high crosslinking density films. Increasing the OA concentration increases the number of crosslinking sites, but the film becomes plasticized before a high crosslink density polymer film is reached. The tensile strength of OA containing polymers is therefore always lower than the others.

Swelling ratios as shown in Figure 20 indicate that the increasing concentrations of fatty acrylates give decreasing values of swelling ratios. Poly-

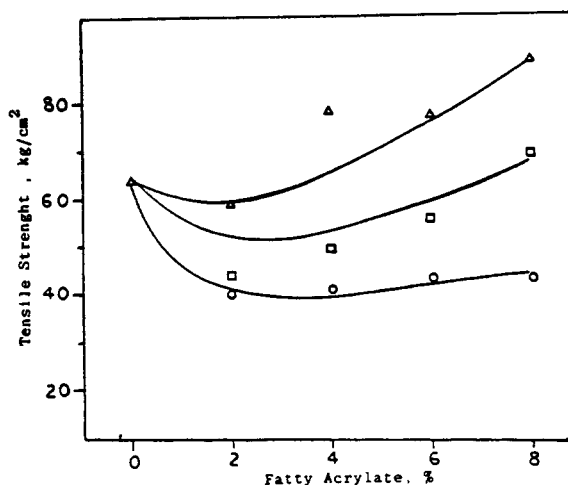


Fig. 19. Comparison of tensile strength as a function of fatty acrylate concentrations in emulsion polymers; (Δ) LA3; (\square) LA2; (\circ) OA.

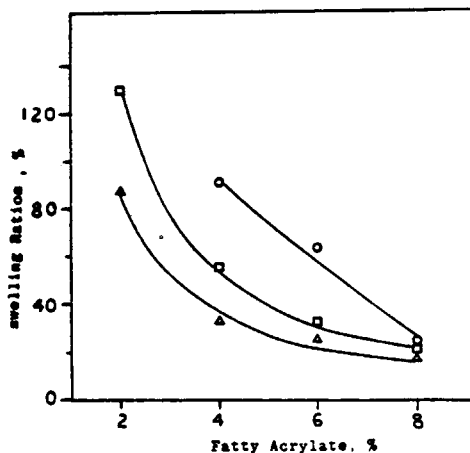


Fig. 20. Comparison of swelling ratios as a function of fatty acrylate concentrations in emulsion polymers: (Δ) LA3; (□) LA2; (○) OA.

mers containing LA3 were found to have the lowest swelling ratios. The degree of unsaturation can be used to explain this trend. Polymer E-9 containing a 2% concentration of OA does not crosslink well due to the low number of crosslinking sites. This gives rise to low crosslinking density and unmeasurable swelling ratios for those films. It was found upon further testing that high crosslink densities and low swelling ratios were not reached until the polymer contained at least 4% by weight of fatty acrylate. This percentage of monomer was the minimum amount required to provide adequate crosslinking sites to get high crosslinking density films, and therefore low swelling ratios.

It is seen in Figure 21 that the percent elongation decreases with increased amounts of fatty acrylate. This trend results from the increased amount of crosslinking with increased acrylate concentration. Increased crosslinking decreases the mobility of the molecular segments of the polymer and elongation is therefore decreased. All the fatty acrylate monomers studied reduce the percent elongation with only slight differences among

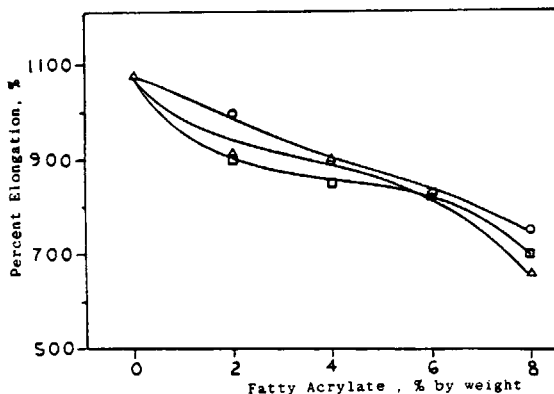


Fig. 21. Comparison of percent elongation as a function of fatty acrylate concentrations in emulsion polymers: (Δ) LA3; (□) LA2; (○) OA.

them when used in similar concentrations. The polymer generated here possesses both regions of crosslinked and thermoplastic domains as demonstrated by percent insoluble polymers far less 100%. Evidently the thermoplastic regions have an overriding effect over the crosslinked regions in effecting percent elongation. The degree of unsaturation of the fatty acrylates therefore has very little effect upon the percent elongation since crosslinking itself has little effect when thermoplastic regions are present.

Percent insoluble polymers as shown in Figure 22 increase with the amount of crosslinkable monomer used and depends on the type of fatty acrylates. This is due to the amount of unsaturation present and the number of crosslinking sites.

Curing at 100°C for 2 h

At high temperature polymer E-9 shows significant values of swelling ratios which have been discussed earlier. Other physical properties are similar to those derived from room temperature polymer films. The same explanation employed above can be applied here.

CONCLUSION

The results of T_g analysis indicate that a higher concentration of fatty acrylates in the emulsion polymers lowers T_g . Also, the molecular weight of the emulsion polymer was observed to decrease with an increase in concentration of LA3, LA2 or OA associated with retardation and/or chain transfer.

The kinetics of the crosslinking mechanism of the emulsion polymers were studied by isothermal differential scanning calorimetry over the temperature range of 100–190°C. Because the displayed curves contain plateaus instead of sharp peaks, the crosslinking rate was concluded to be slow. Since cobalt catalysts are active driers and lead catalysts are auxiliary driers, the results of crosslinking rate are influenced more by a cobalt-catalyzed system than a lead-catalyzed system.

The physical properties displayed by polymer films with or without catalysts are different. This information was used to support the occurrence of crosslinking at room temperature.

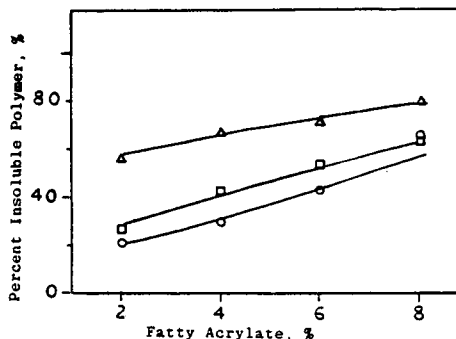


Fig. 22. Comparison of percent insoluble polymers as a function of fatty acrylate concentrations in emulsion polymers: (△) LA3; (□) LA2; (○) OA.

In general, 60 min at 100°C or 2 weeks at room temperature is sufficient time for polymer films to obtain constant physical properties, such as tensile strength, swelling ratios, and percent insoluble polymers. Longer periods of cure such as 120 min at 100°C or 4 weeks at room temperature do not result in an improvement in the physical properties to a significant extent.

The enhanced tensile strength from crosslinking in the polymer films is not large enough to dominate the deficiency of tensile strength due to plasticization by the introduction of crosslinkable monomers such as LA3, LA2, and OA. The dependency of tensile strength on the amount of the above monomers used must be recognized to be a function of plasticization, bulk viscosity, and crosslinking. At room temperature LA displays the characteristic of better coalescence.

The resistance of polymer films was found to be poorer in water and a 5% acetic acid solution, compared to a 5% NaOH solution. Polymers E-1-E-8 consisting of variable degrees of crosslinking display better resistance in the acidic solution than polymers E-O, E-9-E-16.

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