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A study of the preparation and mechanism of the ambient temperature curing of acrylic latex with epoxy resins*

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A method for the ambient temperature curing of acrylic emulsions with epoxy resins has been developed. The results show that an acrylic resin can be effectively cured at room temperature through the addition of between 5 and 20 wt% of epoxy resin to the acrylic monomers. The resulting cured polymers have a degree of reticulation of the order of 75%. It is shown that the tensile strength, and water and alkali resistance are greatly increased compared to those of uncured resins, while the elongation rate decreases sharply. The reticulation reaction was demonstrated to be a result of a reaction between epoxy and carboxyl groups, and was favoured when the amine concentration (curing agent) was low with respect to the concentration of epoxy groups, and when the amine was carboxylated by the acrylic monomers. It was also found that a grafting reaction took place between the acrylic monomers and the epoxy resins via an esterification of the carboxyl groups during the emulsion polymerization step. © 1997 Elsevier Science Ltd.

(Keywords: ambient temperature curing; epoxy resin; curing mechanism)

INTRODUCTION

A polymer latex is commonly reticulated in order to improve physical properties such as their cohesion, mechanical strength, water and solvent resistance, etc. In general, very few latices can be reticulated at ambient temperatures. Therefore their reticulation is often carried out at relatively high temperatures (>130°C). Industrially, this is accomplished by using reactive monomers, such as derivatives of (meth)acrylic acids or esters, and combining the latex with an amine resin. However, reticulation of these products at high temperatures can be expensive in terms of energy costs, and lower temperature reticulation would also offer the advantage of increasing the range of application where heating is not practical or possible.

There are relatively few experimental or theoretical studies treating reticulation of polymers at room temperature, despite its industrial importance[1-4]. The principle methods for doing so generally consist of either (1) combining a multi-isocyanate with a latex containing either an –OH and/or –COOH group[4-6]; (2) introducing an epoxy resin into a latex containing carboxyl or amine groups[7-9]; (3) using special active monomers[10-12]; or (4) using latexes with carboxyl groups plus metal ions[13,14]. However, for reasons of high cost and technical difficulty, only the first technique has been used significantly on an industrial scale. Furthermore, the latices obtained in this manner are generally used only as adhesives in woodworking applications, and the pot life of the latex is limited to approximately 2 h after the addition of multi-isocyanate. The use of carboxylated latex plus metal ions has the limitations of being reversible at ambient temperatures and is not particularly efficient. The other techniques are essentially limited to laboratory studies. It is therefore of significant interest to develop an efficient reticulation process that can be used at ambient temperature.

A new method for the reticulation of acrylic latex containing epoxy side groups using amine-containing cross-linking agents at ambient temperature is presented in this work. The two components, mixed at the time of use to provide a reticulating system that can be transported easily, are used at room temperature. The feasibility of this two-component process, and the improvement in physical properties that it provides, are examined. The role of each component in the reticulation process is also examined in order to try to understand more clearly the mechanism by which the reticulation takes place.

EXPERIMENTAL

Materials

Ethyl acrylate (EA), methyl acrylate (MA), methyl methacrylate (MMA), and acrylic acid (AA) were supplied by the East China Chemical Company (Beijing,

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China), and were purified by distillation before use. Epoxy Resin 618, with a molecular weight of 388.4 was supplied by Shell Chemicals (UK). Emulsifiers OP (polyoxyethylene alkylphenyl ether), OS (the sodium salt of the succinic acid half ester of polyoxyethylene alkylphenyl ether) and sodium lauryl sulfate (SLS) were obtained from the Shanghai Auxiliary Chemical Company (Shanghai, China) and used as received. Pure reagent grade ammonium persulfate (APS), *n*-methylol acrylamide (NMA), disodium hydrogen phosphate, benzoyl peroxide (BPO), tetraethylenepentamine (TEPA), T31 (amine) and ammonia solutions were also obtained from the Shanghai Auxiliary Chemical Company, and reagent grade dimethyl benzylamine (DMBA) was obtained from Merck (New Jersey, USA). All were used as received. Deionized water was used in all experiments.

Emulsion polymerization

The polymerization of the acrylic polymer was carried out in a glass reactor equipped with a reflux condenser, an anchor-type agitator, a thermocouple, a nitrogen stream and two feed streams. The reactions were carried out semi-batchwise, and the basic recipes used are outlined in *Table 1*.

The initial charge was fed into the reactor under nitrogen and heated to 70°C. The temperature was maintained for 30 min, the reactor contents were then heated to 75°C. The reactor was then fed with two separate streams: the first contained the pre-emulsion, and the second, an aqueous solution of initiator. The feed stream flow rates were adjusted in order to finish the addition in 2.5 h. The reactor temperature was then increased to 85°C, and the reaction was continued batch-wise for another hour.

Table 1 Preparation of acrylic latex (component masses, reported in grams)

Component	Initial charge	Stream 1	Stream 2
H_2O	220	Variable	6.0
OP	4.0	3.0	
OS	1.0	1.0	
SLS	1.0		
Epoxy resin		Variable	
EA	13.4	120.6	
MA	5.2	46.8	
AA		10.0	
NMA		4.0	
Na_2HPO_4	0.6		
NH_4OH (26%)		2.3	
Catalyst		Variable	
APS	0.3		0.6

The quantity of epoxy resin used varied between 5 and 20 wt% (with respect to the total mass of the monomers plus epoxy resin). The resin was added prior to polymerization in most cases with the exception of latex ERa-20 and ERNAa-20 where it was added afterwards. The catalyst and epoxy resin (except for the two cases above) were dissolved in the monomer mixture before beginning the polymerization.

The different latex formulations (co-acrylate formulations, type and quantity of catalyst used, etc.) produced in this fashion and used in the reticulum experiments are shown in *Table 2*. For reasons of comparison, one latex (NER) was prepared using no epoxy resin. Furthermore, when 20 wt% (mass of monomer + epoxy) of epoxy is added to NER, a latex (ERa-2) is obtained that has the same formulation as ER-20, but a different method of introduction. This allows us to identify the importance of the grafting of epoxy and acrylic resins during the polymerization stage.

In order to investigate the effect of the presence of acrylic acid on the reticulation of the latex, the acrylic acid component of the monomer mixture was replaced by MMA in two cases: ERNA-20 (20% w/w epoxy resin added during polymerization) and ERNAa-20 (20% w/w epoxy added after polymerization).

Two types of catalyst were also used in this study (BPO and DMBA) in order to study the mechanism by which grafting takes place between epoxy and the acrylic latex. The type and quantity of catalyst used are also given in *Table 2*.

Latex properties

The physical properties of the different latex used in this work are summarized in *Table 3*. The epoxy group content was evaluated by the method previously outlined by Bell[15]. The intrinsic viscosity was measured as described in ref. 16, using N,N-dimethylformamide as the solvent. In order to determine its carboxyl content, a latex was first dissolved in a mixture of ethanol and isopropyanol (1/1 by weight), and then titrated with a

Table 2 Latex formulation

Latex name	Ratio of epoxy resin to co-acrylate	Catalyst type and quantity[b]	Co-acrylate formulation. EA/MA/AA/NMA/MMA (molar equivalents)
NER	0/100	0	67/26/5/2/0
ER-20	20/80	0	67/26/5/2/0
ER-10	10/90	0	67/26/5/2/0
ER-5	5/95	0	67/26/5/2/0
ERa-20[a]	20/80	0	67/26/5/2/0
ERB-1.5	20/80	BPO, 0.15%	67/26/5/2/0
ERB-3	20/80	BPO, 0.30%	67/26/5/2/0
ERDM-26	20/80	DMBA, 0.26%	67/26/5/2/0
ERDM-43	20/80	DMBA, 0.43%	67/26/5/2/0
ERNA-20	20/80	0	67/26/0/2/5
ERNAa-20[a]	20/80	0	67/26/0/2/5

[a] Epoxy resin added after polymerization. Resin added prior for all other cases
[b] With respect to mass of monomer

Table 3 Latex properties and quantity of curing agent used per latex

Latex	Solids (% mass)	Viscosity at 20°C (mPa.s)	pH	Carboxyl content[a]	% Epoxy groups (mass)	(η)	T31[b]	TEPA[b]
NER	36.2	85	4.0	14.7	0	–		
ERa-20	36.1	45	4.1	11.8	1.51	0.92	2.7	1.27
ER-20	36.0	38	4.2	11.6	1.45	1.22	2.6	1.22
ER-10	36.1	43	4.2	–	–	–	1.3	0.61
ER-5	36.1	50	4.1	–	–	–	0.65	0.31
ERB-1.5[a]	36.1	33	4.2	11.8	1.45	1.06	2.6	1.22
ERB-3[a]	36.0	30	4.2	12.1	1.46	0.98	2.6	1.22
ERDM-3[a]	36.0	35	4.1	11.2	1.34	1.31	2.6	1.22
ERDM-5[a]	36.1	35	4.1	11.0	1.28	1.56	2.6	1.22
ERNAa-20[a]	36.1	30	5.3	–	–	–	2.7	1.27
ERNA-20	36.0	25	5.5	–	–	–	2.7	1.27

[a] mg KOH/100 g polymer
[b] % of latex by weight

KOH/ethanol solution. The viscosity of the latex was measured in a Brookfield rotary viscometer at 30 rpm at 20°C.

Preparation of latex films and property evaluations

Film preparation. Two different curing agents were used in the experiments reported here: TEPA (tetraethylenepentamine) and T_{31} (a reaction product of $C_6H_6OH + HCHO + (CH_2NH_2)_2$ which has an H activity equivalent of 62.5). The quantities of each of the curing agents used in the various experiments are also reported in *Table 3*. Latex and curing agents were mixed, poured into a Teflon mould, dried at ambient temperature for 2 days, and then placed under vacuum for an additional 2–3 days. The films thus formed were between 0.7 and 0.8 mm thick. Curing time is defined to begin at the moment the two components are mixed.

Stress–strain tests. Samples of the latex films were cut into strips, the shape and dimensions of which are shown in *Figure 1*. The stress–strain tests were conducted on a model XLL-50 apparatus from the Guangzhou Material Test Machine Co. (Guangzhou, China) at a speed of 100 mm min^{-1}.

Gel content. A sample weighing from 0.5–0.8 g was placed in an extractor and extracted with acetone for 8 h. The fraction remaining in the test cell was said to represent the gel content of the latex.

Water and alkali absorption. Samples of the latex films were cut into 4 cm × 4cm squares which were left to soak in either deionized water, or a 0.05 N NaOH solution (both at 15°C) for 48 h. The weight gain was measured and reported in terms of a percentage of the original sample mass.

I.r. spectra. I.r. spectra were obtained using a Nicolet 170SX *FT*i.r. spectrometer.

D.s.c. scans. D.s.c. scans were performed in a Perkin-Elmer DSC 2C at a rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

The experimental results reported below concern three major issues: (1) a demonstration of the feasibility and effectiveness of the method of reticulating acrylic latex at ambient temperature; (2) an investigation of the mechanism of the partial grafting of the acrylic resin with the epoxy resin during the reticulation; and (3) an examination of the mechanism of reticulation of the acrylic latex containing the epoxy resin in the presence of amine co-curing agents.

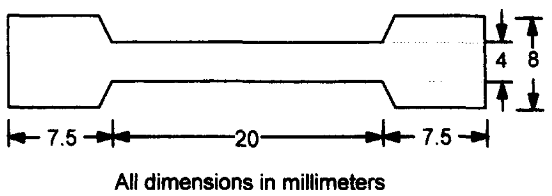


Figure 1 Shape of tests strips for use in stress–strain tests

Reticulation at ambient temperature

Reticulation is a useful method of improving the properties of a latex, including water, solvent and alkali resistance, as well as mechanical strength. It is thus of interest to investigate the evolution of these properties during the reticulation of different products. The results of the reticulation study are summarized in *Table 4*, and *Figures 2*, *3* and *4*.

The evolution of the gel content of the ER-20 latex, using both curing agents, is shown as a function of time in *Figure 2*. It was found that reticulation was essentially complete after approximately 15 days.

The physical properties of the ER-20 and NER latex films, before (no curing agent) and after reticulation, are summarized in *Table 4*. It can be seen clearly from the results that reticulation of latex with epoxy resins can be carried out effectively at ambient temperature, and that this reticulation has significant effects on the physical properties of the latex such as the glass transition temperature (T_g), and water and solvent resistance of the latex films. Before reticulation, neither latex had any detectable degree of reticulation. After curing for 20 days at 288 K, the degree of reticulation of the ER-20 latex was 88.6% when T_{31} was used, and 79.8% in the presence of TEPA. No noticeable reticulation was obtained in the absence of epoxy resin (NER).

As expected, reticulation increases the glass transition temperature of the acrylic latex by 10–13 K. The uncured ER-20 film has a lower T_g than that of NER because of the plasticizing effect of the epoxy resin, which is compatible with the acrylic resin. It can also be seen from *Table 4* that, at complete reticulation, the water and

Table 4 Effect of ambient temperature reticulation on latex properties. Reticulation conditions: 20 days, 288 K

	NER			ER-20		
	Before ret.	After ret. with T_{31}	After ret. with TEPA	Before ret.	After ret. with T_{31}	After ret. with TEPA
% Ret.	0	0	0	0	88.6	79.8
T_g (K)	284.3	–	–	276.2	289.4	286.4
% H_2O absorbed	347.8	–	–	242.2	23.1	25.2
% NaOH absorbed	>1000	–		467.0	126.0	198.0

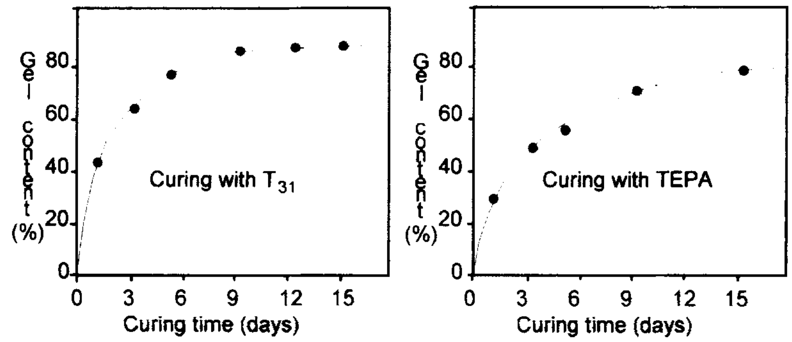


Figure 2 Kinetics of the reticulation of latex ER-20 with T_{31} and TEPA

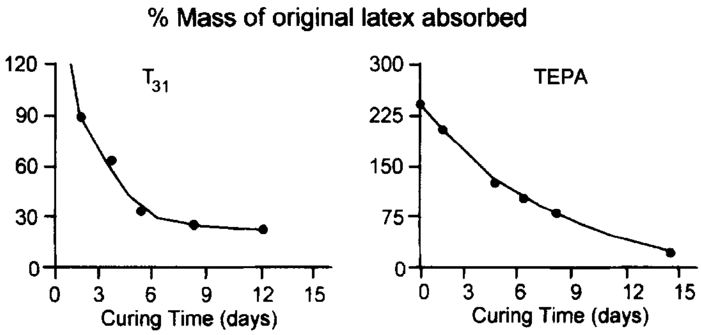


Figure 3 Reduction of water absorption of reticulating ER-20 film as a function of reticulation times for T_{31}-cured (left) and TEPA-cured (right) films at 15°C

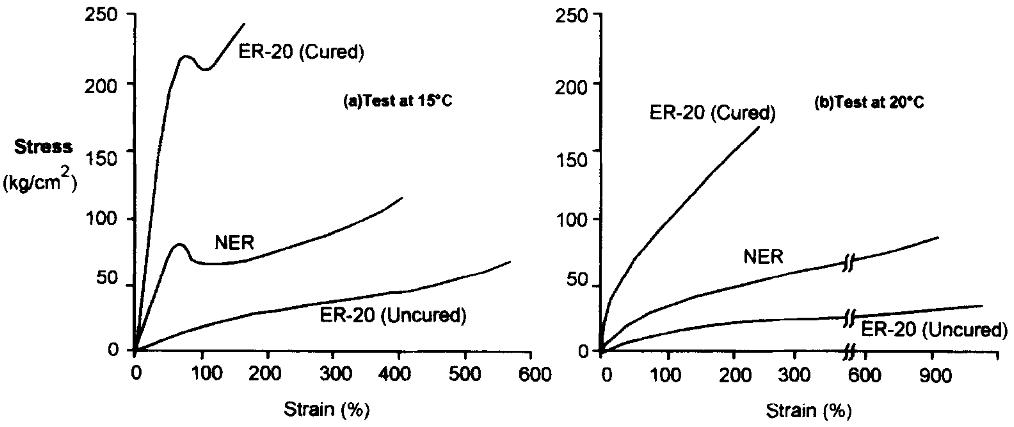


Figure 4 Stress–strain curves for latex NER and ER-20, cured at 15°C (a) and 20°C (b) for 20 days with T_{31}

alkali resistance of the ER-20 latex are significantly improved, with the quantity of water absorbed by the latex film decreasing by just over a factor of 10 in the case of reticulation by T_{31} and just under 10 with TEPA, and the alkali absorption decreasing by factors of 3.7 and 2.4 for T_{31} and TEPA respectively. The transient nature of the gain in water resistance is shown in *Figure 3*. It can be seen by comparing *Figures 2* and *3* that the ER-20 latex film's resistance to water absorption is roughly proportional to its degree of reticulation.

It is also interesting to note that the uncured ER-20 absorbs much less water and alkali solution than does NER. This can be explained by the fact that the epoxy resin is less hydrophilic than the acrylic resin which contains 5 wt% of acrylic acid and 2 wt% of methylol acrylate. Consequently, the introduction of the epoxy resin into the acrylic polymer reduces the hydrophilic nature of the resulting product. Secondly, the number of epoxy groups in the ER-20 latex is significantly higher than that of the carboxyl groups, and when the latex film was formed, most of the carboxyl groups were surrounded by the epoxy resin due to the low molecular weight, and thus higher diffusivity of the epoxy compounds, and also because the hydrogen of the carboxyl groups can form a hydrogen bond with the oxygen of the epoxy groups. This, too, leads to a reduction in the relative water and alkali absorption of the cured latex.

The different reticulating efficiencies of the two amine compounds, TEPA and T_{31}, will be discussed later.

The stress–strain relationships of the ER-20 and NER latex are shown in *Figure 4*. As expected, uncured ER-20 has a lower tensile strength and a higher elongation rate than NER because of the plasticization of the epoxy resin. After reticulation, the tensile strength increases sharply, and the elongation rate decreases correspondingly. In the test performed at 15°C, the yield points of both NER and the reticulated ER-20 are clearly visible at a strain of approximately 70%. The yield points are observable because the test was performed at a temperature just below the T_g of the two polymers. These points disappear when the test was performed at 20°C — just over the T_g.

The influence of the quantity of epoxy resin added to the acrylic latex (in terms of the mass of monomers plus epoxy resin) can be seen in *Figure 5*. Not only do relatively small quantities of epoxy lead to rapid gains in the degree of reticulation, but they can also have a significant impact on the different physical properties studied in this work, especially the water and alkali resistance of the reticulated films. All of these results point to the fact that reticulum at ambient temperatures is indeed possible, and can have a significant impact on the physical properties of acrylic latex.

Partial grafting between epoxy groups and acrylic chains

Before beginning the investigation of the actual reticulation mechanism, it is necessary to understand the structure of the polymer in the latex itself. It is likely that some slight amount of grafting between the epoxy and acrylic resins took place during the polymerization reaction itself since the epoxy resin was added to the polymerizing system before the reaction began. Evidence offered as proof of this grafting is shown in *Table 5*. Recall that ERa-20 has the same relative formulation as ER-20, except that the epoxy resin was added after the polymerization step in the case of ERa-20. It can be seen from *Table 5* that ER-20 has a higher intrinsic viscosity (and thus molecular weight) and T_g, both of which suggest that there has been some partial grafting in the case of ER-20. The slight reduction in the relative number of epoxy groups in the ER-20 latex also supports the idea that partial grafting takes place. This partial grafting would also explain the observed improvements in properties such as water and alkali resistance, and mechanical strength.

There are two likely mechanisms by which this grafting can take place: either via a radical pathway, in

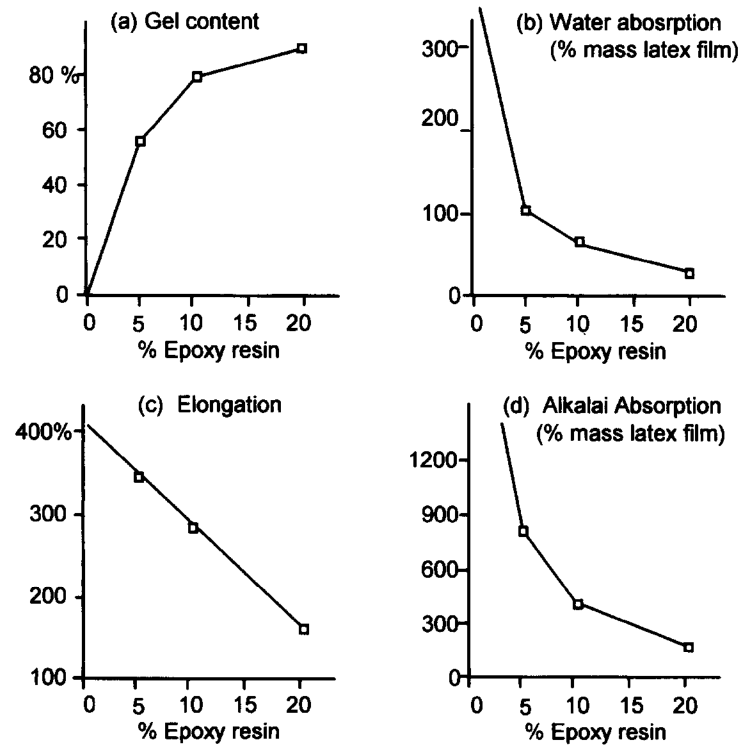


Figure 5 Effect of the quantity of epoxy resin (% by mass of monomer plus epoxy) on final latex properties reticulated with T_{31} at 15°C for 20 days. (a) Degree of reticulation as measured by % gel content, (b) water absorption (% mass of original latex film), (c) elongation at rupture, and (d) relative alkali absorption of latex (% mass of original latex film)

Table 5 Proof of partial grafting

	ER-20		ERa-20
Percent(mass) of epoxy groups left in solution after polymerization	1.45	<	1.51
Intrinsic viscosity	1.22	>	0.92
T_g (K)	276.2	>	274.7
Water absorption before reticulation (% mass of latex film)	242.2	<	294.2
Alkali absorption before reticulation (% mass of latex film)	467	<	558.0
Tensile strength before reticulation (kg cm^{-2})	68.2	>	58.0
Elongation (%) before reticulation	572	<	613

Table 6 Effect of type and quantity of catalyst on latex properties (pre-reticulation)

	Latex				
	ER-20	ERB-1.5	ERB-3	ERDM-26	ERDM-43
Catalyst and concentration (% mass of monomer)	None	BPO (0.15%)	BPO (0.3%)	DMBA (0.26%)	DMAB (0.43%)
Carboxyl content (mg KOH/100 g polymer)	11.6	11.8	12.1	11.2	11.0
% Mass epoxy groups	1.45	1.46	1.46	1.34	1.28
Intrinsic viscosity	1.22	1.06	0.98	1.31	1.56
H_2O absorption before reticulation (% mass original latex film)	242.4	265.3	289.1	213.8	205.0
H_2O absorption before reticulation (% mass original latex film)	467.0	492.2	573.1	350.1	319.4

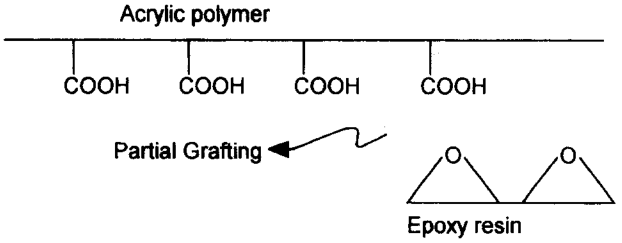


Figure 6 Schema of the mechanism of the partial grating between the acrylic polymer and the epoxy resin

which the addition of BPO would promote the observed amount of grafting; or via esterification of the carboxyl groups, in which event polymerization in the presence of DMBA would increase the amount of grafting. In the second case, DMBA would catalyse the esterification reaction between the carboxyl and epoxy groups.

The results shown in *Table 6* show the effect of the type and quantity of catalyst on the properties of the final latex. When 0.15% and 0.30% (w/w) of BPO are added to the polymerizing system, the number of carboxyl and epoxy groups is unaffected by changes in catalyst concentration. This indicates that BPO has no real effect on the grafting that might take place between the acrylic and epoxy resins. On the other hand, the intrinsic viscosity decreases with increasing quantities of BPO — this is to be expected in the case of a free radical polymerization reaction. The lower molecular weight might explain the increased water and alkali absorption which is also observed.

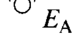
Contrarily, increasing the quantity of DMBA reduces the number of epoxy and carboxyl groups, and the more DMBA is added, the stronger the observed effect. This suggests that the DMBA is at least in part associated with an increased consumption of epoxy resin in the system, and hence has a positive effect on the partial grafting that could take place. The increasing intrinsic viscosity of the latex, and the improved absorption properties and tensile strength, can all be explained by the increased amount of grafting.

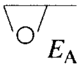
All of the results reported above point to the fact that the epoxy resin is partially grafted onto the carboxyl side groups during the polymerization via an esterification reaction as shown schematically in *Figure 6*.

Reticulation mechanism

When the latex are mixed with the amines, the three following reactions R1, R2 and R3 are possible:

(R1) $-COOH + H_2N- \rightarrow -COO^- \ NH_3^+-$

(R2) $-NH_2$ (or$=$NH) $+$  $\rightarrow -NHCH_2CH(OH)-$ $E_A = 12\text{–}14\,\mathrm{kcal\,mol^{-1}}$ [17-19]

(R3) $-COOH +$  $\rightarrow -COOCH_2CH(OH)-$ $E_A = 17\text{–}25\,\mathrm{kcal\,mol^{-1}}$ [20,21]

Of the three reactions, the first, R1, is by far and away the fastest (the formation of the amine salt). Of the other two, we wish to obtain reaction R3 in order to promote a maximum amount of reticulation (the same reaction as the partial grafting discussed above), however, because of the lower activation energy, R2 tends to proceed more rapidly. If R3 did not take place, latices to which the epoxy resins were added after polymerization (ERa-20) would reticulate only via the ionic route — a reaction which is reversible. For example, the treatment of resins reticulated in this manner would be degraded by the addition of NaOH. However, as shown in *Table 7*, this is not what is observed experimentally. It can be seen from the first two columns that the degree of reticulation does not decrease after treatment with NaOH. The slight

Table 7 Degree of reticulation of latex films. Reticulation conditions: 15°C, 20 days, curing agent = T_{31}

	Degree of reticulation:		
Latex	Before treatment	Treatment[a] with NaOH	Treatment[b] with NH_4OH
ERa-20	87.7	90.4	52.0
ER-20	88.6	91.2	61.4

[a] Treatment after reticulation. Latex film soaked in NaOH solution at 15°C for 48 h

[b] Treatment before reticulation. Quantity of NH_4OH = 110% equivalent of carboxyl content

Table 8 Reticulation of latex films with no AA (and no –COOH) Reticulation conditions: 15°C, 20 days, Curing agent = T_{31}

Latex	Degree of reticulation
ERNAa-20	18.9
ERNA-20	24.7

increase in its value was caused by the incorporation of Na into the reticulation network during treatment. If the latex are neutralized before being mixed with the amine in order to prevent the formation of ionic reticulation (latex film neutralized with NH_4OH at 100% equivalent of carboxyl content before mixing with curing agent), it can be seen from the third column of *Table 7* that there is still some reticulation. This means that some of the carboxylic side groups have entered into a reticulated network despite the absence of any anionic reticulation. Note that the ER-20 shows a higher degree of reticulation in the presence of NH_4OH than does ERa-20 because of the partial grafting of the epoxy resin that took place during the polymerization reaction

Furthermore, when the acrylic acid (AA) monomer is replaced by an equivalent quantity of methyl methacrylate (MMA) in the polymer formulation, there are no longer any COOH side groups, and it was found that no reticulation takes place between the acrylic and epoxy resins. This can be seen in *Table 8*, where the two latex contain 20 ml% of epoxy resin. In the case of the ERNAa-20 resin, the observed degree of reticulation of 18.9% explained by the presence of epoxy resin at 20% w/w that was added after the polymerization process and that can be reticulated by the amine. This is also true for the ERNA-20 resin, but the overall degree of reticulation was slightly higher, possibly due to some grafting or other mechanism taking place between the epoxy resin and growing polymer chains during the polymerization. We can therefore conclude that COOH plays an important role in the reticulation process, and that reaction R3 is therefore not only important, but also present in cases where latex films show any significant degree of reticulation.

Despite the fact that we can demonstrate that reaction R3 takes place and results in the reticulation of the acrylic and epoxy resins, this still does not tell us just how the actual reticulation takes place. Since the ratio carboxyl/amine/epoxy (groups) was approximately 1/1.6/1.85 before reticulation, most of the amine present in the reticulating system forms amine salts. It is therefore indispensable to study the influence of the carboxylation of the amines on the reticulation. Furthermore, water evaporates from the reticulating film as it dries, and it is therefore equally important to study the influence of the presence of water on the reticulation process.

An *FT*i.r. spectrum of the model system ER/AA/BM (epoxy resin/acrylic acid/*n*-butylamine) both before and after three days of reticulation is shown in *Figure 7a* for a molar ratio of ER/AA/BM = 1/1/1. From *Figure 7a* it can be seen that the peak at 915 cm^{-1}, which corresponds to the epoxy group, disappeared after 3 days of curing, and that the amine (=NH, $-NH_2$) peaks in the neighbourhoods of 600–900 cm^{-1} and 1490–1640 cm^{-1} respectively are strongly diminished. These peaks give an indication of the reaction of the epoxy resin and the amine. However, it is interesting to note that a small peak appears at approximately 1725 cm^{-1}, which corresponds to an ester linkage, after reticulation. There has therefore been a small amount of reaction between the carboxyl and epoxy groups, but the principle reaction in this case appears to be R2 (amine plus epoxy). If we alter the relative concentrations of the three components by decreasing the carboxyl concentration and increasing the relative number of amine groups such that the molar ratio of the different groups becomes ER/AA/BM = 1/0.4/1.6, we obtain the *FT*i.r. spectrum shown in *Figure 7b*. From this pair of curves it can be seen that when the concentration of AA drops and that of amine increases the ester linkages are no longer formed, and there is little to no reaction between the epoxy and amine groups.

However, if the relative concentration of the amine groups is decreased, we obtain the spectra shown in *Figure 7c*. Here it can be seen that with a molar ratio of ER/AA/BM = 1./0.5/0.5 a peak corresponding to the ester group appears once again at 1732 cm^{-1}, and the amount of ester groups thus formed increases with a decreasing concentration of amine. These results suggest that both the amine and carboxyl groups can react with the epoxy resin at room temperature. The former reacts more quickly when there is a relatively high concentration of amine groups, and leaves little chance for the reaction between the carboxyl and epoxy to take place. However, when the equivalent number of amine groups is less than or equal to that of the epoxy, the reaction carboxyl plus epoxy is competitive.

Figure 7d shows the spectra obtained for the system ER/AA/DMBA (1/0.25/0.25), in which the amine does not contain the active hydrogen. In this case the epoxy group is diminished and a peak corresponding to an ester group appears. This may be an indication that the reaction between the carboxyl and epoxy groups can indeed take place at ambient temperature.

D.s.c. scans of ERE cured with either TEPA or T_{31} (1/1 by equivalent groups for both systems) both with and without water (water content was 15% of mass of amine plus epoxy) are shown in *Figure 8a*. The results suggest that the curing agent T_{31} is more efficient than TEPA in reticulating the epoxy resin, and that the presence of water has almost no effect on the behaviour

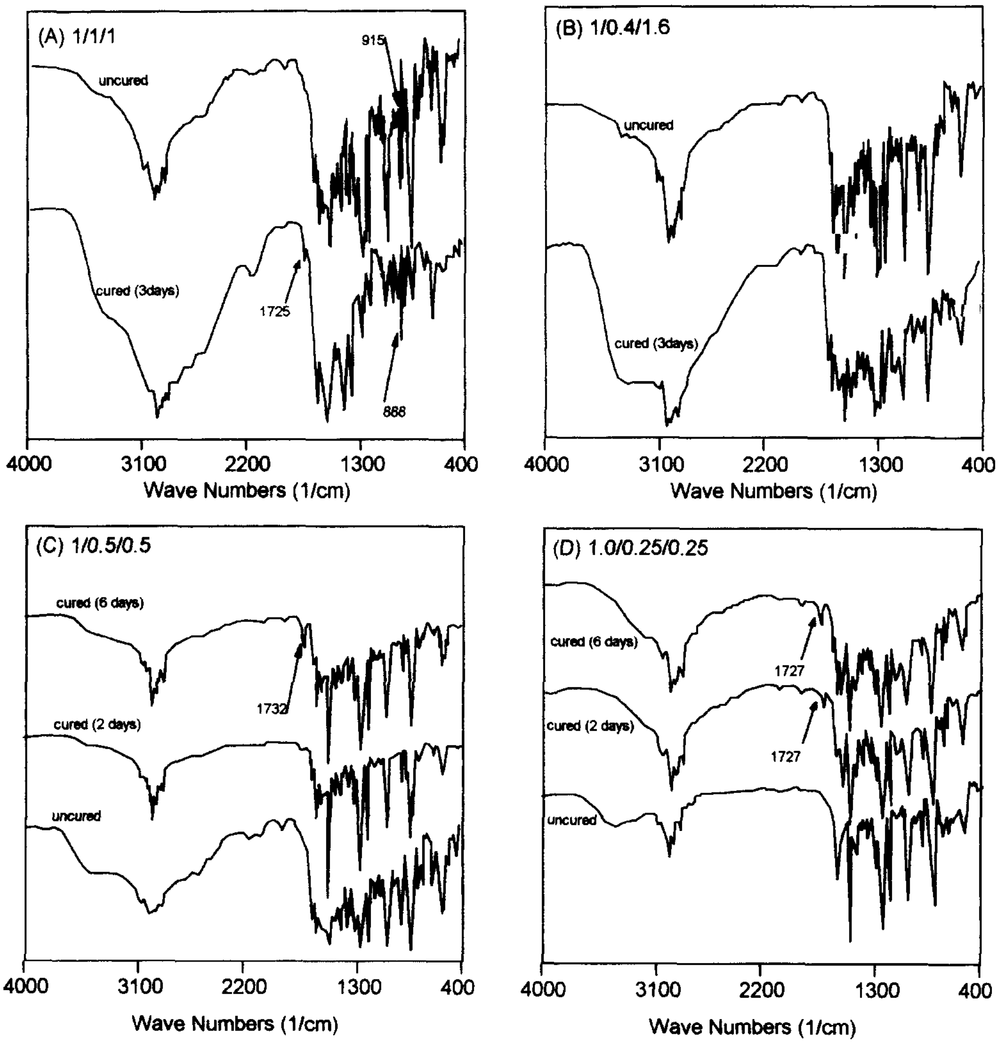


Figure 7 *FT*i.r. spectra of the system ER/AA/BM (A, B, C) and ER/AA/DMBA (D) before and after curing. Reaction temperature = 15°C. Molar ratios shown in upper left-hand corner of each graph

of the curing reaction. When acrylic acid is added to the epoxy/amine system (at molar ratios of functional groups of either 1/1/0.5 or 1/1/0.75 ER/T_{31}AA), two peaks are observed in the d.s.c. curves (*Figure 8b*). If one compares the curves in *Figures 8a* and *b*, it can be concluded that the first peak corresponds to the reaction of the epoxy resin and the amine, and the second peak to the reaction of the epoxy resin and the carboxylated amines (this might even include a slight reaction between the epoxy and carboxyl groups). Increasing the relative concentration of AA causes the first peak to diminish and the second to increase. Furthermore, the effect of the carboxylation is more pronounced in the case where TEPA is used than when the curing agent is T_{31}. The effect of adding water (15% of mass of ER plus amine plus AA) on the cure behaviour of the system is shown in *Figure 8c*. It can be seen that water has no effect on either of the peaks in the system where the amine used was T_{31}, and the first peak in the TEPA system. This would suggest that water does not influence the reaction between the epoxy resin and the T_{31}, nor that between the epoxy and the carboxylated T_{31}, nor that between the epoxy and the TEPA, but that it does have an impact on the reaction between the epoxy and the carboxylated TEPA. This might explain why the curing reaction is more rapid and efficient with T_{31} than with TEPA.

It is possible to propose a mechanism for the reticulation of the latex examined in this work using these results. When the latex is mixed with the amine, most of the amine is carboxylated by the carboxyl groups in the acrylic latex. Although the reaction between the epoxy and carboxyl groups is much slower than that between the epoxy resin and the amine, the carboxylation of the amine groups reduces the rate of the latter reaction, and allows the former to become competitive. The reaction of the carboxyl groups and the epoxy resin contributes to the crosslinking of the acrylic latex (although ionic reticulation can take place at the same time).

CONCLUSIONS

The feasibility of an ambient temperature process for the reticulation of acrylic latex has been demonstrated in this work. Significant, irreversible gains in physical properties can be obtained using this two stage reticulation process with as little as 5 wt% of epoxy resin. After reticulation, the tensile strength, and the water and alkali resistance of the latex increase sharply, and their rate of elongation decreases significantly.

An examination of the mechanism of reticulation

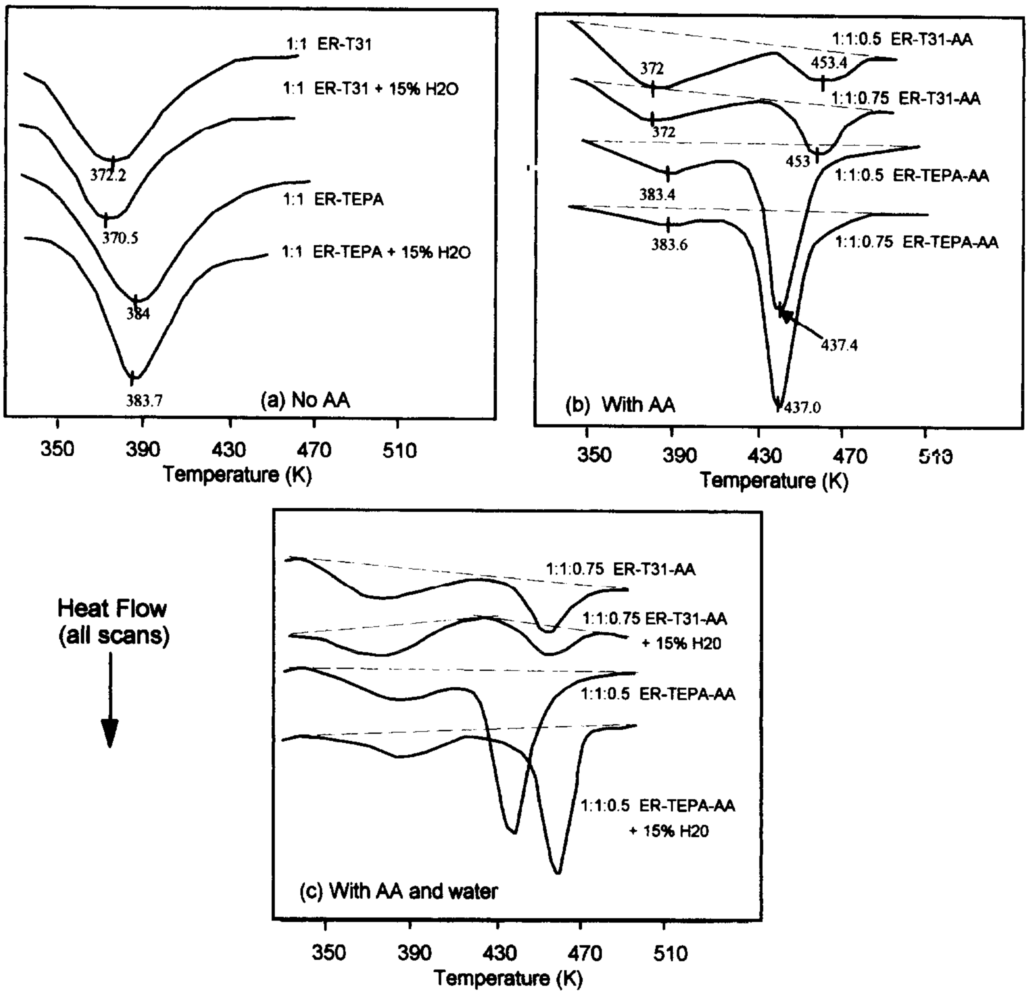


Figure 8 D.s.c. scans of an (a) epoxy resin/amine, (b) epoxy resin/amine/acrylic acid, and (c) epoxy resin/amine/acrylic acid plus water system

revealed that reticulation was the result of a reaction between epoxy and carboxyl groups, although a reversible ionic reticulation reaction might exist at the same time. Reticulation is favoured when the concentration of amine is low relative to that of the epoxy groups, and when the amine is carboxylated by the carboxyl groups of the acrylic polymer.

The curing behaviour of TEPA and T_{31} curing agents were evaluated, and the influence of the presence of water and carboxylating agents were examined. It was found that the reticulation was faster with T_{31} than with TEPA. The rate of reticulation was shown to decrease for both curing agents when they were carboxylated with AA, with TEPA showing a stronger reduction than T_{31}. Water had no effect on the curing rate in the presence of T_{31}, carboxylated T_{31}, and TEPA. It did, however, slow the rate of reticulation of carboxylated TEPA remarkably.

The process of the grafting of epoxy and acrylic resins during polymerization was also studied. It has been demonstrated that this reaction takes place by esterification of the carboxyl groups on the acrylic acid polymer chains, not via a free radical mechanism, and that the amount of grafting could be increased by adding a tertiary amine catalyst. The results of this work demonstrate the interest of this simple, effective and low cost reticulation procedure. It is thought that this could have interesting industrial applications.

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