# Miscibilization of Low Molecular Weight Functionalized Polyethylenes in Epoxy Resins. I. Effects of Composition and Modifications Chemistry

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**ABSTRACT:** Toughening of epoxy resins is traditionally carried out by adding small proportions of a low  $T_g$  oligomer containing reactive end groups. These induce the precipitation of crosslinked rubbery particles during curing. In this study, an investigation was carried out to examine the possibility of using randomly functionalized low molecular weight polyethylene for the same purpose. In the first part of the work we examined the miscibility of binary and ternary blends of several low molecular weight polyethylenes, containing either hydroxyl or acid functional groups, with two types of epoxy resins and two anhydrides, respectively. Various chemical reactions were performed on some of the polyethylenes, as well as on a bisphenol epoxy resin, with the view to increase the miscibility between the components prior to the curing. From these experiments it was established that by modifying the polyethylene component with a monofunctional epoxy resin it is possible to substantially improve their miscibility with both types of difunctional epoxy resins, but to a lesser extent in the presence of anhydride hardeners. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1457–1470, 1999

**Key words:** miscibilization; low molecular weight functionalized polyethylenes; epoxy resins; composition; modifications chemistry

## INTRODUCTION

Epoxy resins are used extensively in composite materials for a variety of structural and electronics applications. Their relatively low cost, combined with a broad range of attractive physical properties, mechanical strength, and processing capabilities, make them invaluable materials as thermoset matrices. Although cured epoxy resins exhibit good engineering properties, such as high stiffness and strength, creep resistance, and chemical resistance, they are intrinsically brittle, due to their high crosslinking density. For this reason they are frequently toughened by dissolving a small proportion (10-20%) of a liquid rubber containing reactive end groups in the liquid epoxy system and inducing the precipitation of crosslinked rubbery particles during curing.<sup>1</sup> It is essential that the toughening agent is a low molecular weight polymer to ensure that the viscosity of the resin is not increased excessively so that the processability of the system is not impaired.<sup>2</sup>

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If the modifiers remain fully miscible with the resin, after curing they will act as plasticisers. Total immiscibility, however, is equally undesirable, as this will not produce a strong bond at the rubber-matrix interface. The ideal rubber for toughening purposes is one that is "semimiscible," i.e., a mixture near the critical solution conditions at the cure temperature that will, therefore, desolubilize as a result of the increase in molecular weight, resulting from the chemical reactions between constituents.<sup>3</sup> Hence, the toughening effect of the modifier can be controlled by the "level" of miscibility with the epoxy resin. An improved adhesion between the epoxy matrix and the toughening phase is obtained when particles precipitate from a homogeneous mixture. The dispersed particles so formed contain not only the rubbery material but also the epoxy resin in proportions determined by compositional factors and thermal history. The miscibility of the two components of the resin system is enhanced by the presence of functional groups capable of undergoing chemical reactions prior to gelation due to a higher reduction in enthalpy than is possible with physical interactions.

These requirements are met with the use of CTBN and ATBN (carboxyl and amine-terminated butadiene acrylonitrile) rubbers as toughening agents for difunctional epoxy resins.<sup>4-8</sup> The difference in solubility parameters between these oligomers and a diglycidyl ether of bisphenol A epoxy resin (DGEBA), for example, is sufficiently small to allow them to dissolve completely in the resin, but still large enough to allow phase separation after an increase in molecular weight before gelation.

Studies performed on binary mixtures of a DGEBA resin with either CTBN or ATBN showed that these systems exhibit an upper critical solution temperature (UCST) phase behavior.<sup>6,9</sup> During curing the UCST is elevated by the increase in the molecular weight of the epoxy, which brings the mixture into a two-phase region. This implies that one can control the two-phase morphology by manipulating the kinetics of phase separation and curing reactions.

The principal objective of rubber modification is the improvement of fracture properties commensurated with the smallest possible decrease in modulus and strength. CTBN and ATBN copolymers can be effective for this purpose but present a few drawbacks. First, their glass transition temperature is relatively high, and second, their highly unsaturated structure provides sites for degradation reaction in oxidative and high temperature environments.  $^{10-12,13}$ 

Several attempts have been made over the last 2 decades to find alternative polymeric systems to CTBN and ATBN for the toughening of epoxy resins.<sup>3</sup> In the present study, the use a low molecular weight crystalline thermoplastic polymer, using the same approach as in the CTBN technology, is being explored.

The selection of a thermoplastic crystalline phase is based on the hypothesis that a less detrimental effect would result on the stiffness and strength of the cured epoxy resins than by using rubbery particles. Mixtures of crosslinked epoxy resin and crystalline polymers have received relatively little attention in the past.<sup>2,14–18</sup> Low molecular weight functionalized polyethylenes are particularly appropriated as a toughening agent, being more thermally stable than traditional rubber modifiers, and are also expected to reduce the water absorption of the epoxy resin. For these systems it may be possible to lower the curing temperature to facilitate the precipitation of the toughening phase through crystallization. It would still be possible, however, to induce the precipitation of the polyethylene phase in the epoxy matrix even above its melting point, simply through chemical reactions at the functional groups, similar to CTBN and ATBN systems.

The miscibilization of oligomers through telechelic end-of-chain extensions is likely to constitute the most efficient mechanism for the nucleation of particle precipitation during curing of the resin. The use of such oligomers is also likely to minimize the reduction in the  $T_g$  of the matrix through plasticization by nonprecipitated oligomeric species, as they cannot form true solutions in the resins but only highly swollen molecular aggregates. Consequently, with these systems phase separation by particle nucleation and growth during curing is expected to occur very readily and completely.

## **EXPERIMENTAL**

#### Materials

Several low molecular weight functionalized polyethylenes (supplied by Allied Signals Inc.) were used as a precursor for the production of modifiers for epoxy resins. These were: (a) an oxidized homopolymer (AC 6702), with an acid functionality of 0.26; (b) two ethylene acrylic acid copolymers

	Acid	Hydroxyl			$T_m$			
	No.	f	No.	f'	(°C)	$M_w$	$M_n$	$M_w/M_n$
AC 6702	15	0.26		0	63	2140	970	2.2
AC 540	40	1.2	_	0	105	4560	1710	2.6
AC 5120	120	2.1	_	0	89	3325	1005	3.3
AC 1450	35	2.0	_	0	88		а	
AC 80	42 - 46	1	75 - 115	1	55		а	

Table I Chemical and Physical Properties of Low Molecular Weight Functionalized Polyethylenes

Acid No. = acid number (= mg of KOH required to neutralize all the acid groups contained in 1 g of the polymer); Hydroxyl No. = hydroxyl number (= mg of KOH equivalent to the hydroxyl content of 1 g of the polymer); f = acid functionality, calculated from  $M_n$ ; f' = OH functionality;  $T_m$  = melting point;  $M_w$  = weight average molecular weight;  $M_n$  = number average molecular weight;  $M_w/M_n$  = polydispersity.

<sup>a</sup> Number-average molecular weight  $(M_n)$  is expected to be in the region of 2000–4000 for AC 1450 and 1000–2000 for AC 80.

(AC 540 and AC 5120), with functionalities approximately 1.2 and 2.0, respectively. The chemical structure of the above oligomers is shown schematically below

$$\begin{array}{c} (\mathrm{CH}_2 \mathrm{\longrightarrow} \mathrm{CH}_2)_n \mathrm{\longrightarrow} (\mathrm{CH}_2 \mathrm{\longrightarrow} \mathrm{CH})_m \\ | \\ \mathrm{COOH} \end{array}$$

#### Scheme 1

Estimated acrylic acid content (mol %): 0.8 for AC6702, 2 for AC540, and 7 for AC5120. (c) An ethylene acrylic acid-vinyl acetate terpolymer (AC 1450), having an acid functionality of approximately 2 and an equivalent weight of carboxylic groups equal to 1200 (the equivalent weight is the weight of the polymer in grams containing 1 g equivalent of the carboxylic groups).

The chemical structure of the above oligomers is shown schematically below

$$\begin{array}{c} \operatorname{COOCH_3} \\ | \\ (\operatorname{CH_2-CH_2})_n - (\operatorname{CH_2-CH})_m - (\operatorname{CH-CH_2})_p \\ | \\ \operatorname{COOH} \end{array}$$

Estimated acrylic acid content = 4% molar

#### Scheme 2

(d) An ethylene acrylic acid–vinyl acetate–vinyl alcohol terpolymer (AC80), containing both hydroxyl and carboxyl groups with an average acid functionality equal to the average OH functionality, both approximately equal to 1. The equivalent weight of OH groups is 485–750, while the equivalent weight of COOH is 1194. The chemical

$$\begin{array}{c} \operatorname{COOCH_3} \\ (\operatorname{CH-CH_2}) - (\operatorname{CH_2-CH_2})_n - (\operatorname{CH_2-CH})_m - (\operatorname{CH-CH_2})_p \\ \\ | \\ \operatorname{OH} \\ \end{array} \\ \begin{array}{c} \operatorname{COOH} \\ \end{array} \\ \end{array}$$

Estimated acrylic acid content = 4% molar

#### Scheme 3

The main properties of the oligomers used are shown in Table I.

Two epoxy resins were evaluated: Epikote 828, which is a liquid DGEBA resin, having an epoxide equivalent of 184–190 (the epoxide equivalent is the weight of the resin in grams containing 1 g equivalent epoxide group) (supplied by Shell Chemicals) and a cycloaliphatic resin, Araldite CY 179, with an epoxide equivalent approximately equal to 135 (supplied by Ciba-Geigy).

## **Miscibility of Original Oligomers**

To determine the miscibility of the oligomers with the stated epoxy resins, binary mixtures were prepared by manually mixing the two components in different ratios. The mixtures were heated in an oven for different periods of time, varying from 10 min to 24 h, at 115°C, i.e., a temperature higher than the melting point of the olefin oligomers.

Binary mixtures of two different hardeners, hexahydrophthalic anhydride (HHPA) and methyl nadic anhydride (MNA) (both supplied by Aldrich Chemical Co. Ltd.), with each of the stated oligomers and with both epoxy resins, were also prepared. Finally ternary mixtures were prepared by adding different amounts of hardener to binary mixtures of the epoxy resins containing various amounts of each oligomer, and subsequently heating the resulting mixtures in an oven at 115°C for 10 min.

The miscibility of the systems was subsequently studied using a Reichert optical microscope equipped with an hot-stage device and a Mettler FP52 temperature controller. The premixed samples were first melted on a hot plate at about 115°C, and a droplet of the melted mixture was then squeezed between glass slides. These were placed in a polarizing hot-stage microscope to determine the approximate temperature at which miscibility occurred when the sample was heated above the melting point of the crystalline phase. The samples were heated at 10°C per minute up to 250°C, and then cooled at 3°C per minute to monitor phase separation and recrystallization phenomena. Micrographs were taken at different temperatures during both heating and cooling stages to record the events associated with the stated phase transitions. The solubilization temperatures recorded from the hot-stage microscope analysis were used to construct ternary phase diagrams. In a few cases the miscibilization of the components of the mixtures was also studied under isothermal conditions by monitoring the decrease in the dimensions of the dispersed particles with time.

### **Chemical Modifications of the Oligomers**

The second stage of the work was concerned with the chemical modification of the higher functionality oligomers, AC 5120, AC 1450, and AC 80, with the view to enhance their miscibility with the epoxy resins and hardeners.

The first attempt to reduce the critical solution temperature of the epoxy resin/oligomer mixtures was made by reacting the acrylic acid copolymer, AC 5120, with  $\varepsilon$ -caprolactone (supplied by Aldrich Chemical Co. Ltd.). This reaction produces side group extensions while maintaining the original acid functionality, as shown schematically below:



### Scheme 4

Mixtures of  $\varepsilon$ -caprolactone and oligomer AC 5120 were stirred in a glass flask, heated in an oil bath

at 115°C under refluxing conditions. A flux of nitrogen was passed over the surface of the sample to minimize oxidation reactions.

Two different mixtures were prepared to achieve, respectively, 25 and 100% reaction of the acid groups, i.e., 50/5 and 50/20 weight ratios AC 5120/caprolactone, corresponding to molar ratios of 1/0.6 and 1/2.4, based on the average numberaverage molecular weight of the AC 5120 oligomer. The latter corresponds to approximately 10% excess caprolactone, based on the functionality value for AC 5120 equal to 2.

The reactants were first heated and stirred at 115°C for 7 h, and then the temperature was raised to 160°C. The unreacted caprolactone was allowed to evaporate by heating the mixture at 80°C for 3 h under vacuum. The loss of weight was used to estimate the extent of reaction, while the possible formation of telemeric chain branches was examined by measuring the molecular weight distribution by gel permeation chromatography (GPC). The latter was carried out by RAPRA Technology Ltd, using 0.1% solutions in 1,2 dichlorobenzene at 140°C. Because the GPC data were calibrated for polystyrene, a nominal correction was used to allow for the difference in molecular weight of the monomeric units between styrene and ethylene. The effects of comonomer or termonomer units were ignored.

The second modification of the acrylic acid copolymer AC 5120 was made by reacting the acid groups with *p*-*t*-butylphenol-glycidyl ether (Eurepox RVP, supplied by Witco Corporation, (UK). This reaction produces hydroxyl groups in the  $\beta$ position adjacent to the ester groups at the junctions with the ethylene oligomer chains, according to the scheme shown below:



#### Scheme 5

The composition chosen was 69.8/30.2 weight ratio AC 5120/RVP, corresponding to a 5% molar excess RVP of the calculated stoichiometric amount.

The two components were heated in an oil bath at 140°C under reflux conditions for 9 h with continuous stirring and with a flux of nitrogen passed on the surface of the reaction mixture. To bring the reaction to completion, the sealed flask was subsequently placed in a oven at  $90^{\circ}$ C for 12 h.

To increase the reactivity of the oligomer AC 5120 modified with RVP towards the epoxy resin, the hydroxyl groups produced in the above step were converted again to acid groups by reaction with a 1:1 molar ratio (plus a 10 mol % excess) of hexahydrophthalic anhydride (HHPA), corresponding to *cis*-1,2-cyclohexanedicarboxylic anhydride, at 140°C under reflux conditions for 6 h



#### Scheme 6

The progress of both reactions was monitored by titrating the acid groups at different time intervals. Each sample was dissolved in a 1:1 mixture of xylene/DMF and kept at  $85^{\circ}$ C to prevent precipitation, and the acid titration was performed using an alcoholic KOH solution (0.01 and 0.05 *M*) and a digital pH meter to detect the end point. A 1.0 wt % triphenylphosphine (TPP) catalyst (supplied by Aldrich Chemical Co. Ltd.) was also added to accelerate the chemical reaction between AC 5120 and RVP.

The glycidoxy modifier, Eurepox RVP, was used to enhance the solubility of functionalized terpolymers, AC 1450 and AC 80, by reacting RVP, respectively, with AC 1450 at a molar ratio of 2 : 1, and with AC 80 at a molar ratio of 1 : 1 (see Scheme 5). The weight ratios, estimated for a 10% excess RVP, were 83/17 wt % for both AC 1450/RVP and AC 80/RVP (because the equivalent weight of COOH groups for both is 1200). The reactions were carried out, with the addition of 1% of the catalyst TPP, in an oven at 140°C with frequent stirring.

In a second step, the adducts of AC 1450 and AC 80 with RVP were reacted further with chlorendic anhydride (CA), which is 1,4,5,6,7,7-hexachloro-5-norborene-2,3-dicarboxylic anhydride (supplied by Aldrich Chemical Co. Ltd.). Chlorendic anhydride was chosen in view of its high reactivity, which would ensure a high level of conversion of the hydroxyl groups of the modified oligomers in carboxylic acid groups (Scheme 6). This reaction was carried out in oven at 150°C, until the mixtures became transparent. A further step in the modification of the oligomers to enhance their miscibility with epoxy resins was the subsequent reaction with  $\varepsilon$ -caprolactone, to produce AC 80-RVP-CA-CP and AC 1450-RVP-CA-CP (see Scheme 4). The latter reactions were carried out under a flux of nitrogen at 150°C in an oil bath.

The direct modification of AC 80 with chlorendic anhydride was also investigated at a 1 : 1 molar ratio, using a 1 wt % TPP catalyst to transform all the hydroxyl groups to carboxylic acid groups (see Scheme 6). The adduct AC 80-CA was further modified with  $\varepsilon$ -caprolactone, following the procedure described before (Scheme 4).

Two Differential Scanning Calorimeters, respectively a Du Pont 910 DSC and a Mettler TA 3000 DSC, were used for the thermal analysis. All the experiments were performed by heating the samples in a nitrogen atmosphere from -20 to 200°C, at a heating rate of 20°C per minute, and kept for 3 min at the maximum temperature before they were cooled at 20°C per minute down to room temperature.

#### **Chemical Modifications of the Epoxy Resin**

Another approach used to increase the miscibility of the components of the resin mixtures was to react the epoxy resin with minor amount of montanic acid, i.e., octacosanoic acid ( $C_{28}H_{56}O_2$ ) (supplied by Hoechst). The possibility of reacting montanic acid with an epoxy resin to improve its miscibility with polyolefins has previously been explored by Mascia and Moggi.<sup>19</sup> This reaction produces telechelic extensions at the two chain ends of the resin to obtain an ABA oligomer that contains two outer segments that are miscible with the polyolefin component (see Scheme 5).

The reaction between DGEBA (Epikote 828) and montanic acid was carried out at a molar ratio of 16:1 in a flask, heated in an oil bath at  $150^{\circ}$ C for 9 h, and continuously stirred. The progress of the reaction was monitored by titrating the acid groups with an alcoholic KOH solution, as described earlier.

To assess the level of miscibilization achieved with each modification, several binary and ternary mixtures were prepared and examined in a hot-stage microscope.

Finally, a comparison was made with a wellknown system, i.e., a carboxyl-terminated butadiene acrylonitrile oligomer (CTBN, Hycar 1300x8, BF Goodrich Chemicals), using binary and ternary mixtures of Epikote 828 and HHPA.

Table II Solubilization Temperature on Heating ( $T_s$ ) and Phase Separation
Temperature on Cooling $(T_p)$ for 50/50 Mixtures of AC 6702, AC 540,
Unmodified, and Modified AC 5120, AC 1450, and AC 80, with Unmodified
and Modified DGEBA Resin (Epikote 828) or Cycloaliphatic Resin
(Araldite CY 179)

Formulations	$\begin{array}{c} T_s \\ (^{\circ}\mathrm{C}) \end{array}$	
AC 6702/Epikote 828	273	246
AC 540/Epikote 828	236	188
AC 5120/Epikote 828	190	$74^{\mathrm{a}}$
(AC 5120-g-Caprolactone 50/5)/Epikote 828	160	$78^{\rm a}$
(AC 5120-g-Caprolactone 50/20)/Epikote 828	198	$72^{\rm a}$
(AC 5120-g-RVP 69.8/30.2)/Epikote 828	168	$82^{\rm a}$
(AC 5120-g-RVP/TPP 69.8/30.2/1)/Epikote 828	146	$86^{\mathrm{a}}$
AC 5120/(Epikote 828-g-Montanic Acid 6.6/1)	158	$80^{\mathrm{a}}$
(AC 5120-g-Caprolactone 50/5)/(Epikote 828-g-Montanic Acid 6.6/1)	213	$74^{\mathrm{a}}$
(AC 5120-g-Caprolactone 50/20)/(Epikote 828-g-Montanic Acid 6.6/1)	238	205
AC 540/Araldite CY 179	100	$95^{\mathrm{a}}$
AC 5120/Araldite CY 179	88	$79^{\mathrm{a}}$
(AC 5120-g-RVP/TPP 69.8/30.2/1)/Araldite CY 179	87	76
AC 1450/Epikote 828	211	110
(AC 1450-g-RVP/TPP 83/17/1)/Epikote 828	160	102
AC 80/Epikote 828	167	$70^{\mathrm{a}}$
(AC 80-g-RVP/TPP 83/17/1)/Epikote 828	151	70
[(AC 80-g-RVP/TPP)-g-CA 70/30]/Epikote 828	142	112
[(AC 80-g-RVP/TPP-g-CA)-g-Caprolactone 76/24]/Epikote 828	90	72
(AC 80-g-CA/TPP 63/37/1)/Epikote 828	128	$67^{\mathrm{a}}$

<sup>a</sup> Phase separation occurs concomitantly with crystallization.

The effects of the morphological features of such systems on mechanical properties are reported elsewhere.<sup>20</sup>

# Eutectics of Hexahydrophthalic Anhydride (HHPA) with Montanic Acid

Earlier examinations with the hot-stage microscope suggested that HHPA, both alone and in mixtures with either epoxy resins or acrylic acid copolymers, could be transformed to the corresponding acid by heating. The possibility of preventing this transformation was explored by attempting to produce a eutectic mixture of the anhydride with montanic acid.

A wide range of compositions was chosen, varying from 90/10 to 50/50 weight ratios HHPA/montanic acid, in order to determine the lowest amount of montanic acid that may be necessary to prevent the above-stated transformation of HHPA. The mixtures were heated together in an oven at  $115^{\circ}$ C for 10 min and 1 h, respectively.

Because the introduction of montanic acid was expected to increase the miscibility of Epikote 828

with the ethylene acrylic acid copolymer in the presence of HHPA, a series of binary mixtures were prepared. These were mixtures of HHPA with AC 5120, both unmodified and modified with RVP, and with Epikote 828, and also ternary mixtures with both unmodified and modified AC 5120 and Epikote 828.

# **RESULTS AND DISCUSSION**

### **Miscibility of Uncured Epoxy Systems**

In Table II the solubilization temperature on heating and phase separation temperature on cooling, obtained by hot-stage microscopy examinations, for 50/50 mixtures of AC 6702, AC 540, or unmodified and modified AC 5120 with unmodified and modified Epikote 828 are reported.

It is noted that the olefin oligomers with lower functionality values, AC 6702 and AC 540, are much less soluble with the epoxy resin, i.e., they require higher temperatures to reach homogeneity. They also require longer miscibilization times

(b)





(c)

Figure 1 50/50 Mixtures of Epikote 828: (a) AC6702, (b) AC540, and (c) AC5120. Heating conditions: 24 hours at  $115^{\circ}$ C; observation temperature =  $100^{\circ}$ C; Scale = 1/400.

to become soluble (i.e., up to 24 h), and undergo phase separation at higher temperatures in the cooling stage. The 50/50 mixture based on AC 5120 shows the lowest solubilization temperature. The mixtures containing Epikote 828 and each of the acrylic acid copolymers are presumed to exhibit the typical UCST behavior of oligomeric mixtures, but the large gap between solubilization and precipitation temperatures is an indication that solubilization occurs as a result of chemical reactions between the components. In support of this hypothesis, there is the observation that most of the mixtures of the acrylic acid copolymers with higher functionality values, AC 5120, did not show the precipitation of particles of the minor phase during cooling before the onset crystallization.

Another indication of reaction-induced solubilization is the observation that, when the samples are reheated after a first cycle in the hot stage, the solubilization temperature is appreciably reduced, and sometimes the mixtures become homogeneous after melting of the crystals. It has been also found that the extent of heating at 115°C prior to examination has an influence on miscibility only in the case of the mixtures with AC 6702, which become increasingly more soluble at lower temperatures with increasing mixing time.

Higher solubilization temperatures are observed, on the other hand, if chemical modifications are made on the epoxy resin, as a result of the decreased functionality that reduces the extent of reaction with the olefin oligomer. Conversely, the grafting reaction of AC 5120 with RVP, using TPP as a catalyst, is conclusively the most effective modification to enhance its miscibility with the epoxy resin Epikote 828.

The evidence of the improvement in miscibility achieved with increasing the acid functionality in the polyethylene chains as a result of the increased extent of reaction between the two components can be obtained from an inspection of the optical micrographs in Figure 1(a)-(c). These dis-

Formulations	$T_m$ (°C)	$T_c$ (°C)	$T_s$ (°C)	$T_p$ (°C)	$T'_m$ (°C)
ННРА					120
HHPA-e-Montanic Acid 90/10	79	72	101	95	101
HHPA-e-Montanic Acid 80/20	80	75	107	104	
HHPA-e-Montanic Acid 70/30	80	74	102	100	
HHPA-e-Montanic Acid 60/40	79	74	97	94	
HHPA-e-Montanic Acid 50/50	78	73	91	88	
Montanic Acid	82	76			

Table III Transition Temperatures for Mixtures of HHPA and Montanic Acid Obtained by Hot Stage Microscope Experiments: Melting  $(T_m)$  and Crystallization  $(T_c)$  of Montanic Acid Phase, Solubilization  $(T_s)$ , Phase Separation  $(T_p)$ , and Melting  $(T'_m)$  of HHPA Phase

play a reduction in particle dimension in the order AC 6702, AC 540, AC 5120.

In Table II the miscibilization temperature on heating and the phase separation temperature on cooling for the 50/50 mixtures with the cycloaliphatic resin CY 179 for both unmodified and modified polyethylenes are also reported. The data show that: (a) the solubilization temperature is always lower than the value found for the corresponding mixtures with Epikote 828. and (b) phase separation always occurs as a result of the crystallization of the polyolefinic component.

In Table II the results from the hot-stage microscope analysis performed on the ethylene acrylic acid vinyl acetate terpolymer, AC 1450, and on its modification with RVP are also illustrated. These show, once more, that the chemical modification aids the solubilization of the oligomer with the epoxy resin.

The same conclusion can be reached from the data in Table II, on the miscibilization and phase separation temperatures for the 50/50 mixtures of AC 80, both unmodified and modified with Epikote 828. The chemical modification of AC 80 by the reaction of its OH groups with chlorendic anhydride seems to be even more effective than the reaction of its COOH groups with RVP in enhancing its miscibility in epoxy resins.

It is worth noting that binary mixtures of the hardener HHPA with either the acrylic acid copolymers, unmodified and modified, or epoxy resins DGEBA and cycloaliphatic are all miscible. Solubilization appears to take place at temperatures just above the melting point of the olefinic component.

An unexpected behavior for HHPA was found, however, upon heating the sample in the hotstage microscope, both in isolation and in binary mixtures with the two acrylic acid copolymers, AC 540 and AC 5120. The hardener seemed to reach complete melting at temperatures in the region of  $108-136^{\circ}$ C, which is higher than the melting point (32–34°C) reported for the *cis*-form. The above melting range is close to that found for eutectic mixtures of HHPA and 1,3-cyclohex-anedicarboxylic acid, indicating that a partial transformation of the anhydride to the corresponding acid takes place.

The data in Table III suggest that the addition of quantities of montanic acid greater than 20% can prevent the transformation of HHPA to its acid form. Furthermore, these mixtures became miscible at about 100°C upon heating, and underwent phase separation at similar temperatures upon cooling. From the observed reduction in both melting and crystallization temperatures of these mixtures, relative to those of the pure constituents, it can be deduced that HHPA and montanic acid form a eutectic mixture that prevents the above-stated transformation to the anhydride to the corresponding dicarboxylic acid.

The miscibility data for the ternary mixtures examined in the hot stage microscope are reported in the form of ternary phase diagrams to identify the solubility composition areas. Typical examples are shown in Figures 2 and 3.

In Figure 2(a) is shown the ternary diagram for mixtures based on AC 540, HHPA, and Epikote 828. Complete miscibility is not observed for any composition examined, and only the mixtures with large amounts of epoxy resin can be considered to be semimiscible, i.e., a few droplets remain visible after heating at the stated temperature.

In Figure 2(b) is shown the ternary diagram for mixtures of AC 5120 with HHPA and Epikote 828. These mixtures appear to be more miscible at all composition ratios than those containing AC



**Figure 2** Miscibility diagrams for the following mixtures: (a) Epikote 828/HHPA, (b) AC5120/Epikote 828/HHPA, and (c) CTBN/Epikote 828/HHPA.

540. The diagram shows that it is possible to reach almost complete solubility for these systems at temperatures higher than 150°C.



**Figure 3** Miscibility diagrams for the following mixtures: (a) AC5120 grafted with RVP(5-min heating, i.e., 7% yield)/Epikote 828/HHPA, and (b) AC5120 grafted with RVP(27% yield)/Epikote 828/HHPA.

For mixtures of AC 1450 with HHPA and Epikote 828, despite the expected closer match of solubility parameters, both binary and ternary mixtures of AC 1450 with the epoxy resin appear to be less miscible than similar mixtures containing AC 5120. This observation, once more, highlights the reliance on chemical reactions between the oligomer and the epoxy resin for miscibility.

Binary and ternary mixtures based on AC 80 are more miscible with Epikote 828 relative to those based on AC 1450, possibly due to the lower  $M_n$  value. However, the acrylic acid copolymer AC 5120 produces the most miscible binary and ternary blends with Epikote 828, owing to its higher acid content.

In Figure 2(c) is reported the phase diagram for mixtures CTBN/HHPA/Epikote 828, which appear to be completely miscible even at room temperatures or at other temperatures but always lower than 100°C. Furthermore, in this case, the presence of HHPA does not hinder the miscibilization of the liquid rubber in the epoxy resin. As in the case of montanic acid, it is possible that the terminal acid groups in the liquid CTBN rubbers are easily accessible, owing to its intrinsically higher physical miscibility.

The ternary diagrams for systems containing AC 5120 modified through reaction with  $\varepsilon$ -caprolactone at two concentrations reveal that the grafting of caprolactone on the chains, despite the constancy of the acid content, results in a large reduction in miscibility of the systems, and that the effect becomes more pronounced with increasing the amount of caprolactone used to modify the acrylic acid copolymer.

In Figure 3(a) and (b) ternary diagrams for mixtures containing AC 5120 modified with RVP at two conversion levels, i.e., 7% (5-min heating) and 27% are shown. The conversion level seems to play an important role in the solubilization of these systems, i.e., the binary and ternary mixtures containing the product of the grafting reaction become increasingly more easy to solubilize with increasing the level of conversion. However, the ternary mixtures of AC 5120 grafted with RVP, Epikote 828, and HHPA are not much different in miscibility to similar systems based on unmodified AC 5120. It would seem, therefore, that the HHPA hardener causes the demixing of the modified polyethylene from the epoxy resin.

The pattern of reduced miscibility for ternary systems containing the anhydride hardner appears to repeat itself in all other cases examined. In fact, for some compositions containing HHPA the temperature required for full solubilization can be even higher than that reported for the unmodified AC 5120. It is worth noting that the addition of montanic acid to the hardener (even if it prevents the transformation of anhydride to acid) does not produce any appreciable increase in solubility of ternary mixtures. Consequently, the transformation of HHPA to the corresponding acid may be regarded as a consequence of the lack of miscibility and not the cause.

## **Diffusion Kinetics**

The greater capacity of oligomer AC 5120 relative to AC 540 to solubilise in Epikote 828, due to its higher functionality, can be inferred also from observations in Figure 4(a) and (b). Moreover, these show how the test temperature affects the average normalized dimensions of the particles (i.e., the ratio of the radius of each particle at time, t, to the initial radius of the same particle).



**Figure 4** Solubilization kinetics of dispersed particles for 50/50 mixtures of Epikote 828 with (a) AC540, and (b) AC5120. ( $R_o$  = initial particle radius and  $R_t$  = radius at time t.)

For the 50/50 mixture of AC 540/Epikote 828 at 110°C, a rather long time (about 6 h) is required to solubilize the two phases, whereas at 160°C complete miscibility is reached within 1 h. For the system AC 5120/Epikote 828, the disappearance of the particles of the second phase occurs faster, taking about 25 min at 160°C and requiring about 4 h at 110°C.

For the same mixtures, Figure 4 illustrates the kinetics of the miscibilization process in the form of a plot of the normalized radius of each particle against time. In both graphs, two regions are noted at lower temperatures—one where there is no change in particle size, and a second where there is an almost linear decrease due to diffusion taking place during the solubilization process. At 160°C only the second linear descending part can be observed. In a first stage, corresponding to the

horizontal line, a strong aggregation phenomenon of the particles was observed, i.e., small droplets coalesce to form larger particles. At both test temperatures aggregation occurs over only a period of short time for the AC 540/Epikote 828 mixture, whereas it is strongly dependent on the ambient temperature for the case of AC 5120/Epikote 828 mixtures and is almost absent at 160°C.

The AC 5120 oligomer shows a strong aggregation at the beginning, due probably to a higher interfacial tension, and a faster diffusion process at longer times. At high temperatures, on the other hand, coalescence becomes more difficult while diffusion takes place readily.

# Analysis of the Diffusion Process for the Solubilization of Particles

The diffusion of the polyolefin particles into the surrounding liquid epoxy resin can be modeled analytically, making the following assumptions: (a) the gap between glass slides is very small with respect to the surface area, so that each particle can be considered to be a disc whose height  $\delta$  is equal to the distance between the slides; (b) each particle has a density  $\rho$ , which remains constant with time; (c) the total number of mol of polyolefin contained in each particle decreases as the miscibilization proceeds; (d) the radius R of the particle decreases with time as a result of the diffusion into the surrounding liquid; and (e) outside each particle the concentration c (expressed as mass/ volume) of polyolefin decreases with distance from the border of the particle to the surrounding liquid, and the concentration gradient changes with time. A fast change in concentration is expected at the beginning, and it becomes constant at longer times.

For a single particle, therefore, the rate of diffusion of polyolefin into the surrounding liquid can be written as:

$$\frac{d(\text{mass})}{dt} = \text{density} \cdot \frac{d(\text{volume})}{dt} 
= \rho \cdot \frac{d(\pi \cdot R^2 \cdot \delta)}{dt} = \left[\rho \cdot 2\pi \cdot R \cdot \delta\right] \cdot \frac{dR}{dt} \quad (1)$$

If the process follows the Fick's law of diffusion, the rate of diffusion J from the particle to the surrounding liquid can be expressed as:

$$J = -D \cdot \frac{dc}{dR} \Big|_{\bar{R}}$$

where D is the diffusion coefficient; dc/dR is the derivative of concentration with radius, and it is calculated at the border of the particle (i.e., at radius R).

Substituting the last expression for J in eq. (1), gives:

$$-\left[\rho \cdot 2\pi \cdot R \cdot \delta\right] \cdot \frac{dR}{dt} = -D \cdot \frac{dc}{dR} \Big|_{\bar{R}} \cdot \left[2\pi \cdot R \cdot \delta\right]$$
$$\rho \cdot \frac{dR}{dt} = D \cdot \frac{dc}{dR} \Big|_{\bar{R}}$$
(2)

Under steady-state conditions, the concentration gradient outside the particle can be presumed to remain constant with time. Hence, eq. (2) can be integrated in time:

$$\rho \cdot R = D \cdot \frac{dc}{dR} \Big|_{\bar{R}} \cdot t + \text{Const.}$$
(3)

The constant of integration (Const.) could be calculated considering that initially, i.e., at time t = 0, the radius is  $R_0$ , i.e., Const. =  $\rho \cdot R_0$ . Dividing eq. (3) by ( $\rho \cdot R_0$ ), the change in radius with time, R(t), can be obtained, i.e.:

$$\frac{R(t)}{R_0} = \left(\frac{D}{\rho \cdot R_0} \cdot \frac{dc}{dR}\Big|_{\bar{R}} \cdot t\right) + 1$$

which can be written also as:

$$\frac{R(t)}{R_0} = (C \cdot t) + 1 \tag{4}$$

where:

$$C = rac{D}{
ho \cdot R_0} \cdot rac{dc}{dR}\Big|_{ar{R}} = ext{constant}$$

The constant C is negative because the change in concentration with the radius is negative, i.e., the concentration decreases in moving away from the borders of the particle.

Equation (4) correlates well with the experimental data for the tail end of the curves in Figure 4(a) and (b), confirming the validity of the assumption on which this analysis is based. Because the concentration gradient at the border of the particle is primarily determined by the rate of reaction of the acid groups in the polyolefin with



**Figure 5** Molecular weight distribution by GPC for AC5120 and modifications  $\varepsilon$ -caprolactone.

the epoxy resin, the much higher slope for the system AC 5120 relative to AC 540 can be easily forecast, and the plots in Figure 4 provide a fundamental basis for comparison purposes.

## Physical and Chemical Characterizations of Modified Oligomers

The study of the progress of the reactions of AC 5120 with caprolactone has shown that the mixture 50/5 reaches the maximum conversion of about 75% after 2 h at 120°C and increases to 90% when the reaction temperature is raised at 160°C. For the 50/20 mixture AC 5120/caprolactone, the maximum conversion after 2 h is 65%, and increases to 95% when the temperature is increased to 160°C.

In Figure 5 are shown the GPC curves of molecular weight distributions for AC 5120 and its modifications with  $\varepsilon$ -caprolactone. The results are summarized in Table IV. These show that the grafting of caprolactone onto the chains has only a very small effect on the molar mass, from which it can be deduced that the reaction of the acrylic acid copolymer with caprolactone produces short grafts. The increase in the average molar mass corresponds approximately to the estimated value from the measured amount of grafted caprolactone. It can be concluded, therefore, that the reduced miscibility of AC 5120-graft-caprolactone with Epikote 828 and/or HHPA is related to intrinsic chemical factors. The branches produced through the grafting reactions, for instance, could reduce the diffusion rate, and the subsequent reaction rate with the epoxy resin, in the solubilization process.

The acid titration results for the products of the reaction between AC 5120 and the monofunctional epoxy resin RVP show that reaction at 115°C gives a conversion of 7% after 5 min, and that the conversion increases only to 21%, even after 9 h at 140°C, with a continuous stirring followed by 12 h in an oven at 90°C.

Table IV	Weight-Average Molecular Weight
$(M_w)$ , Nun	nber-Average Molecular Weight (M <sub>n</sub> ),
and Polyc	lispersity $(M_w/M_n)$ Calculated for AC
5120 both	Unmodified and Grafted with $\varepsilon$ -
Caprolact	one

Formulations	$M_w$	$M_n$	$M_w/M_n$
AC 5120	1385	675	2.0
AC 5120-g-Caprolactone 50/5 (at 90% conversion)	1490	710	2.1
(at 95% conversion)	1595	725	2.2

Formulations	$T_c$ (°C)	$\Delta H_c^{a}$ (J/g)
AC 5120	49	27
AC 5120 (thermally treated) <sup>b</sup>	61	20
AC 5120-g-Caprolactone 50/5 (at 90% conversion)	65	17
AC 5120-g-Caprolactone 50/20 (at 95% conversion)	66	16
AC 5120-g-RVP 69.8/30.2 (at 21% conversion)	60	24
AC 5120-g-RVP/TPP 69.8/30.2/1 (at 82% conversion)	58	9
AC 1450	74	22
AC 1450-g-RVP/TPP 83/17/1	76	18
(AC 1450-g-RVP/TPP)-g-CA 70/30	70	21
(AC 1450-g-RVP/TPP-g-CA)-g-Caprolactone 76/24	74	9
AC 80	57	8
AC 80-g-RVP/TPP 83/17/1	54	20
(AC 80-g-RVP/TPP)-g-CA 70/30	31	18
(AC 80-g-RVP/TPP-g-CA)-g-Caprolactone 76/24	37	23
AC 80-g-CA/TPP 63/37/1	44	15
(AC 80-g-CA/TPP)-g-Caprolactone 87/13	55	10

Table V Crystallization Temperature  $(T_c)$  and Enthalpy  $(\Delta H_c)$  from DSC Tests for AC 5120, AC 1450, AC 80, and Their Modifications

<sup>a</sup> Crystallization Enthalpy Values are normalized to 100% polyolefin content.

<sup>b</sup> Subjected to the same thermal history as for the chemical modified systems.

When the reaction between the AC 5120 oligomer and RVP was carried out, on the other hand, in the presence of the catalyst TPP, a final conversion of 82% was reached just after 1 h and 30 min at 140°C. From titration experiments it was also found that the time required to reach the maximum conversion in the subsequent reaction with HHPA was quite short, i.e., about 2 h, and that the disappearance of hydroxyl and the related formation of carboxyl groups was almost complete.

The influence of each modification on the thermal characteristics of the functionalized polyethylene AC 5120, expressed in terms of peak crystallization temperature  $(T_c)$  and heat of crystallization  $(\Delta H_c)$  in the cooling cycle, is illustrated in Table V. From these results is evident that a thermal treatment alone can have a substantial effect on the crystallization characteristics of AC 5120. The data also reveal a slight increase in the crystallization temperature for systems modified with caprolactone and a small reduction for systems modified with RVP. All modified samples, except those modified with RVP at low conversion levels, show a decrease in the heat of the crystallization associated with a reduction in the level of crystallinity, which is particularly significant for systems modified with RVP at high levels of conversions.

However, the influence of chemical modifications on the crystallization temperature and enthalpy for the terpolymer AC 1450 seems to be only marginal. The crystallization enthalpy of this polymer is substantially reduced only after the reaction with caprolactone.

The crystallization temperature peaks of AC 80 systems are reduced appreciably as a result of the chemical modifications, and the crystallization enthalpy is always higher than that of unmodified AC 80, particularly when the copolymer is reacted with RVP before being chain extended with chlorendic anhydride and caprolactone.

## **CONCLUSIONS**

From the analysis of the data obtained in this study it is possible to draw the following conclusions regarding the miscibility of acid functionalized crystallizable olefin oligomers in epoxy resins.

1. Crystallizable ethylene-based oligomers with number-average molecular weight in the region of 1000–2000 have limited miscibility in both DGEBA and cycloaliphatic epoxy resins. Miscibility in cycloaliphatic resins is higher than in DGEBA. In either case, the very low level of solubility results from chemical reactions between the two components, and is generally reduced when an anhydride hardener is also present. Predictably, the level of miscibility increases with increasing the acid functionality in the oligomer.

- 2. Grafting of  $\varepsilon$ -caprolactone units through the reaction with acid groups generally impairs the miscibility of the oligomer. Grafting reactions with *p*-*t*-butylphenol-glycidyl ether, on the other hand, increases the miscibility of the olefin oligomer with epoxy resins but to a much lesser extent in the presence of an anhydride hardener.
- 3. The observation that mixtures of Epikote 828/HHPA with a CTBN liquid oligomer produce totally miscible systems suggests that lower miscibility of functionalized olefin oligomers, even after chemical modification may be related to their crystallinity and to their branched nature, which prevents the formation of strong interactions with the polar groups of the epoxy oligomer.

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