MISCIBILITY STUDIES AND CHEMICAL MODIFICATION OF FUNCTIONALISED LOW MOLECULAR WEIGHT POLYETHYLENE FOR USE AS TOUGHENING AGENTS IN EPOXY RESINS

by

MARIAENRICA FRIGIONE

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Supervisor: Dr. L. Mascia

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TABLE OF CONTENTS

Page No

1. INTRODUCTION

1.1) Structure and Properties of Epoxy Resins.

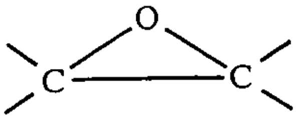
Epoxy resins are used extensively in composite materials for a variety of structural and electronics applications. They are the most versatile resins among the commercially available matrix systems. Their relatively low cost, combined with a broad range of attractive physical properties, mechanical strength and processing capabilities make them invaluable materials as thermoset matrices.

The uncured resins are available in a variety of physical forms, ranging from low-viscosity liquids to solids. Combined with a large selection of curing agents available, epoxy resins enable the composite fabricator to use a wide range of processing methods.

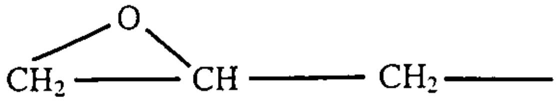
Commercial epoxy resins may contain aliphatic, cycloaliphatic or aromatic backbone chains. The crosslinking agents used are organic materials containing active hydrogen, the most common of them being polyamines, polycarboxylic acids and anhydrides The latter, however, require the addition of a tertiary amine to produce the active hydrogen.

Depending on the chemical structure of the resin and the curing agent it is possible to upgrade toughness, chemical and solvent resistance by the addition of modifying oligomers No by-products are formed during curing and the resulting shrinkage is low (1).

The chemistry involved in the use and application of epoxy resins is the key to their outstanding performance All epoxy resins contain epoxide (also known as oxirane or ethoxylene) groups, represented by the formula:



The epoxide function is usually a 1,2- or α-epoxide, i e.:



called the glycidyl group , which is attached to the remainder of the molecule by an oxygen, nitrogen or carboxyl linkage, hence the terms glycidyl ether, glycidyl amine or glycidyl ester are normally used to describe these resins

Curing of the resin results from the reaction of the oxirane group with compounds (hardeners or catalyst) that contain reactive hydrogen atoms, such as amines, carboxylic acids, mercaptans and polyphenols. The time taken for the resin to set (cure) is determined by the reactivity of the hardener chosen as well as by the temperature of the mixture. Cold and hot-setting processes differ in "gelation" time, being of a few minutes in the case of a hot-setting systems and rising to several hours in the other. However, cold-setting curing leads to lower mechanical properties (e.g. strength) than hot-setting curing.

The most common epoxy resins used commercially are the diepoxides produced by reacting bisphenol A with epichlorohydrin The components are co-reacted under alkaline conditions (1) to an epoxy equivalent weight of about 190 and a viscosity in the range of 12 to 16 Pa•s. (The epoxy equivalent weight is the weight of resin in grammes containing one gram equivalent of epoxy groups.) The diglycidyl ether of bisphenol A (DGEBA) and its higher homologues are characterised by excellent adhesion properties, which are due in part to the secondary hydroxy group located along the molecular chain In addition, when cured they have good mechanical and electrical properties, dimensional stability and good resistance to heat and chemical attack These properties are derived mainly from the aromatic nature of bisphenol A portion of the molecule and the excellent chemical and thermal stability of the phenolic-ether linkage. Since no small molecule, such as water, is liberated during the curing of epoxy resins, they exhibit unusually low shrinkage and they can be formed and cured under contact or low pressure Flame retardant versions of the bisphenol A-epichlorohydrin resins are also available. These resins acquire their fire retardant characteristics through bromine substitution in the phenyl ring of the bisphenol A (2).

Modification to the base resin usually consists of varying the epoxy equivalent weight and hydroxyl content, which results in an increase in viscosity.

The glycidyl ethers of various “novolac” resins are the second most important class of epoxy resins. They are manufactured by reacting epichlorohydrin with phenolic novolacs. These glycidyl novolacs are characterised by a multifunctionality in their chains (the functionality ranging from 2 5 to 6.0), which produces a tightly crosslinked system with better elevated-temperature performance, chemical resistance and adhesion but they have a higher viscosity than the bisphenol A based resins Because of the greater chemical resistance and high temperature properties, the epoxy novolac resins have found use in structural and electrical laminates, filament wound pipes, laboratory countertops, high temperature adhesives and electrical encapsulation by transfer and compression moulding (3). By using other reactive ingredients, however, a wide range of different epoxy resins can be manufactured with different properties and consequently different application fields

The triglycidyl ether of triphenyl methane (TGETMP) gives high Tg's, thermal oxidative stability and excellent moisture resistance (4). Resorcinol diglycidyl ethers (RDE) have good high-temperature performances but they have limited use because of their toxicity. The two last resins give products with low moisture absorption, good hot/wet strength and improved fracture toughness (5-7).

Cycloaliphatic epoxy resins are characterised by excellent electrical properties even at high temperatures (150°C), low viscosity and arc-track resistance at high voltages, but they cannot be cured easily at room temperatures. They are mainly used as high voltage insulators, encapsulations for transformers, motors and coils, filament wound pipe, missile cases, rocket motors, electrical and structural laminates

It has been already explained that to convert a liquid epoxy resin into a tough, hard solid a curing agent has to be added This curing agent may be a true catalyst which induces a self-polymerisation in the epoxy resin or a crosslinking agent which participates directly in the reaction and becomes chemically bound within the resin network Other reactive chemicals may be used to accelerate, promote or retard these crosslinking reactions.

It could be said that three chemical reactions are of greatest importance in the curing of epoxy composite matrices. the amine/epoxide reaction, the anhydride/epoxide reaction and the Lewis acid-catalysed epoxide homopolymerisation.

The most common curing agents are the amines, each of the amino hydrogens being capable of reacting with one epoxide group.

Aliphatic amines and their compounds are recommended for ambient-temperature curing. Typical applications include wet lay-up laminating operations such as tank linings, wet filament winding, patching (repairs), tooling, certain air frames and radomes and electrical insulations. The use of simple compounds, such as diethylenetriamine (DTA) and triethylenetetramine (TETA), gives products which, when properly post-cured, retain high strength at temperatures greater than 100°C Although compounds of this type are cheap and exhibit low viscosity, they are toxic, have high vapour pressures and can cause surface "blushing" on a laminate when exposed to the atmosphere. To overcome these disadvantages, they are often used in the form of epoxy resin adducts, at the expense of higher viscosity.

In the case of the polyamide condensation products, elevated-temperature performance, chemical resistance and viscosity are sacrificed in order to increase toughness, moisture resistance, pot life and to achieve lower toxicity.

Cycloaliphatic amines offer a compromise between the room-temperature curing agents and the higher-temperature curing aromatic amines Systems cured with these amines require lower curing temperatures than systems cured with aromatic amines. On the other hand, their elevated-temperature performance, solvent resistance and chemical resistance are generally superior to those obtained when the systems are cured at room temperature with aliphatic amines.

Aromatic amines are widely used in composite fabrication in both wet and dry lay-up applications for filament winding, electrical applications, piping, tooling and whenever maximum chemical resistance is needed. They provide moderate viscosity at room temperature with the liquid resin, long pot life, excellent chemical resistance and electrical properties and good elevated-temperature performance. Higher-temperature cures and longer cure times are required to achieve these advantages.

The curing chemistry of anhydride systems is very complex. It was initially proposed that the anhydride reacts with hydroxy groups to form a half-acid ester, which in turn reacts with the epoxide group to form a second ester linkage, producing a new hydroxyl group. The reaction continues in this manner until all of the reactive groups are consumed. More recently it has been suggested that the reaction with anhydrides, often catalysed by tertiary amine, proceeds through the activation of the anhydride groups by the amine, followed by a subsequent attack of this "salt" on the epoxy groups (8,9). It should be noted that in anhydride curing, one anhydride group reacts with each epoxide group. This is important in calculating resin/curing agent ratios for anhydride systems, bearing in mind also the possibility of reactions with hydroxyl groups, particularly during post-curing Consequently, larger amounts that the "nominal" calculated stoichiometric quantities can be used producing a higher network

Acid anhydrides are characterised by a long pot life, better heat ageing in air at elevated temperatures, and better electrical properties. Their applications in composites are generally the same as for aromatic amines, and they are chosen to impart specific properties to the laminating system A large part of the reason why acid anhydrides can produce higher heat distortion temperatures than aromatic amines is that they are so much more efficient in causing epoxy polymerisation as well as crosslinking through the reactive acid groups. Curing normally involves the addition of an accelerator, such as benzyldimethylamine (BDMA) Because anhydrides are hygroscopic materials, extended exposure to moist atmosphere results in hydrolysis of the anhydride to the parent acid. This can drastically reduce the elevated-temperature performance of the cured resin. The dibasic acid anhydrides with cycloaliphatic ring structures, such as hexahydrophthalic anhydride (HHPA) and methyltetrahydrophthalic anhydride (MTHPA), perform equally well at elevated temperatures, giving a heat distortion temperature in the region of ≈130 to 140°C, with the exception of methyl nadic anhydride (MNA), which gives a somewhat higher "heat distortion temperature", HDT (*) , due to additional crosslinks produced by free radical reactions at the double bond of MNA. All three anhydrides afford low viscosity in the laminating resin system. Hexahydrophthalic anhydride has excellent electrical properties and gives almost colourless laminates with superior weathering and anti-yellowing properties. The anhydride MTHPA also has excellent electrical properties, while providing low viscosity at a moderate cost.

Chlorendic anhydride (CA) imparts fire retardancy, but is difficult to use it alone because of its high reactivity, giving a limited pot life. Anhydrides of higher functionality cause handling problems because of their solid nature and lower solubility, but higher heat distortion temperatures are attainable with their use even as partial replacement of more common anhydrides.

The third curing process to consider is epoxide homopolymerisation through polyether formation by means of Lewis acids as catalysts, which proceeds by a cationic mechanism The most common Lewis acid used in epoxy composites is boron trifluoride in the form of its monoethylamine complex (BF_3-MEA). This curing agent is characterised by a long pot life and imparts high Tg values.

Dicyanamide (DICY), on the other hand, is a true "latent" catalyst for epoxy resin curing, and in mixtures with some epoxy resins it has shown a room-temperature storage life in excess of 4 years with little or no change in viscosity. This curing agent is used primarily for dry lay-up laminating, finding their major

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(*) The HDT is an empirical parameter which is closely related to the glass transition temperature, Tg use as circuit board materials requiring good electrical properties, water resistance and retention of strength at elevated temperatures (10).

For specific applications liquid modifiers can be use to reduce the resin viscosity (diluents) or to raise impact strength (flexibilisers and plasticisers), or just to make the system cheaper (extenders).

When primarily required to lower the viscosity of an epoxy resin, diluents can be divided in two classes. a) reactive diluents (some glycidyl ethers, such as allyl, butyl, phenyl) are compounds that become permanently bound into the network and thus have the least degrading effect on properties. As implied from the examples given reactive diluents are normally monofunctional and, therefore, will reduce the crosslinking density of the network b) non-reactive diluents (dibutyl phthalate, dibutyl sebacate, dioctyl phthalate, chlorinate biphenyl) do not react chemically with either the epoxy resin or the curing agent and therefore could migrate to the surface with time

Flexibilisers and plasticisers, on the other hand, consist of flexible long-chain molecules which are added to the mixture either as non-reactive (plasticisers) or sparsely reactive (flexibilisers) The reactive long chains provide internal molecular chain flexibility, while the non-reactive plasticisers reduce the interactions between groups within the network. The function of a flexibiliser or plasticiser is a) to impart some degree of resilience or toughness, b) to improve peel and cleavage strength, c) to reduce internal stresses, d) to decrease the exotherm and shrinkage, and e) to produce a generally better system for low-temperature applications, particularly for adhesives (11) It should be noted that some curing agents can also act as flexibilisers A typical flexibiliser for epoxy resins is polypropylene glycol diglycidyl ether

1.2) Toughness Enhancement and Morphology of Epoxy Resins by the Addition of CTBN Oligomers.

1 2.1) Toughening Mechanism.

Although cured epoxy resins exhibit good engineering properties, such as high stiffness and strength, creep resistance and chemical resistance, they are intrinsically brittle. 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 before curing and allowing the precipitation of crosslinked rubbery particles during curing (12). It is essential that the toughening agent is a low molecular weight oligomer to ensure that the viscosity of the resin is not increased excessively in order not to impair the processability of the system (13)

For the effective toughening of these resin systems, the rubber-epoxy interfacial bond plays an important role In fact a weakly bonded rubber particle is almost mechanically equivalent to a void, therefore they are completely ineffective in toughening brittle epoxy resins, particularly if they are fairly large in diameter

A theory to explain rubber toughening of brittle materials is due to Bucknall and Smith (14). The basis of this theory is that rubber particles both initiate and control craze growth (15). Under tensile stress, crazes are initiated at points of maximum principal strain, which are usually near the equators of rubber particles, and propagate outwards following the planes of maximum principal strain. Craze growth is terminated when the stress concentration at the tip falls below the critical level for propagation, or when a large particle or other obstacle is encountered. This results in a large number of small crazes, which is in contrast with the small number of large crazes formed in the same polymer in the absence of rubber particles It can be deduced the importance of good adhesion between the matrix and the rubber particles. The craze termination mechanism cannot operate when the bond between the rubber and the resin is weak. Instead of stabilising the craze, a weakly bonded rubber particle is pulled away from the matrix, leaving a hole from which the craze can propagate further to form a crack

This mechanism is unlikely to operate in the case of highly cross-linked systems, such as epoxides, since the chain length between cross-links is too short to produce effectively the fibrils of oriented chains which act as bridges between the two main surfaces of the craze (16).

More recent theories (17-19) for the toughening of cross-linked polymers by rubber inclusions involve the concept of shear yielding of the matrix around the particles as a mechanism for increasing toughness. This is basically achieved by changing locally the fracture mode from a crack opening type to micro-yielding. For this reason the adhesion between matrix and rubber particles is still a crucial factor in improving toughness by the shear yielding mechanism. The greater deformability of the particles relative to the matrix provides, in fact, the mechanism for the onset of shear deformations in the matrix. Without interfacial adhesion stresses cannot be transferred to the dispersed particles and, therefore, the matrix remains under a state of tensile stressing. When the particles are extremely small, on the other hand, the large interfacial area may be sufficient to achieve stress transfer across the interfaces even if the intrinsic chemical bonds are weak (i e not covalent). This mechanism, however, relies on the ability of the matrix around the particles to undergo a "degree" of yielding or a highly non-linear deformational behaviour. For this reason it is unlikely to operate when the crosslinking density of the matrix is very high. For the latter case the only possibility to toughen the resin is by energy absorption through deformations within the rubber particle itself, particularly through volumetric dilatations (e g. microvoiding)

The way to obtain a good bond between rubber particles and matrix is primarily a matter concerning miscibility between the two phases. In fact it is known that a mixture of two completely miscible polymers has properties intermediate between those of its constituents, and is in many respects similar to a random copolymer of the same composition. Full miscibility between a rubber and a resin does not produce effective toughening, but merely serves to plasticise the matrix. Total immiscibility is equally undesirable, since a completely immiscible rubber of reasonably high molecular weight (which would be required to achieve an adequate level of mechanical properties) will not form a fine dispersion in the resin (due to large differences in interfacial energy between dispersed particles and matrix), nor will it produce a strong bond at the rubber-matrix interface The ideal rubber for the purposes of toughening is one which is semi-miscible, i.e. it exhibits either lower critical solution temperature (LCST) or upper critical solution temperature (UCST) behaviour within the curing temperature range.

It is then possible to improve the adhesion between the epoxy matrix and the toughening phase by allowing the particle to precipitate through a spinodal decomposition so that they will contain not only the rubbery material but also the epoxy resin and possibly a catalyst to promote reactions between the two The demixing via spinodal decomposition (SD) is important for the morphology design of polymer blends, since the characteristic morphology can be fixed or frozen by quenching the demixed system below Tg after an appropriate time of phase decomposition. For the materials design, however, more interesting is the SD induced by chemical reaction (20) In particular for epoxy systems the SD is expected to take place in the curing process. It has been found that various reactive end groups in the structure of a liquid rubber modifier, e g. carboxyl, hydroxyl, epoxy, mercaptan, phenol, methylol and amine, may be used (21,22), to induce particle precipitation through reactions with the resin and to achieve a good interfacial bond.

McGarry and Willner (23) showed that low molecular weight carboxy terminated butadiene-acrylonitrile copolymers (CTBN) are one of the most effective agents for improving the fracture toughness of epoxy resins. CTBN used in epoxy resins has a molecular weight in the region of 2000-10000 and the acrylonitrile content which allows the highest toughness of the resin is between 12 and 18 % by weight (21). It has been found that triphenylphosphine (TPP) is a very effective catalyst to promote the reaction between carboxyl and epoxy groups (24), which assist the nucleation of the particles from the original solution.

Having a relatively low viscosity the addition of CTBN does not impair appreciably the processability of the resin.

The presence of fine rubbery precipitated particles (1-5 μm) imparts an enhanced resistance to crack propagation and impact strengths to the multiphase material (25). By inducing the rubbery phase to precipitate the epoxy network remains essentially unchanged, thereby preserving its main properties (26). However, the use of large amounts of CTBN produces a simultaneous decrease in the glass transition temperature and modulus of the resin (27) through plasticisation effects Both these effects are highly undesirable because the main use of epoxy resin is for structural applications for which a high glass transition is usually required.

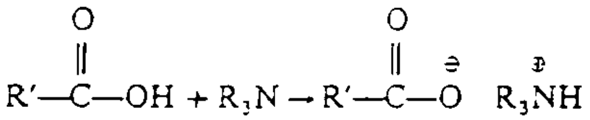
The choice of rubber is determined by two factors. Firstly, there is a miscibility requirement, i.e. the rubber must dissolve and become dispersed in the resin, but it has also to precipitate before the occurrence of gelation. Secondly, there is a chemical requirement, i e the rubber must react with the epoxide groups. Both requirements are met with the use of CTBN rubbers. The difference in solubility parameters between CTBN and DGEBA, for example, is sufficiently small to allow the rubber to dissolve in the resin, but not so small that the polymers will not undergo phase separation during curing However, phase separation is driven by the reactions between the two before adding the hardener, which forces the gelation of the resin to start at the activated sites, i.e. the junctions between the epoxy groups and the acid groups of CTBN.

1 2.2) Curing Mechanism

The following is a typical formulation for an epoxy resin toughened with CTBN:

	wt
DGEBA epoxy resin	100
CTBN rubber	10
Piperidine $(CH_2)_5NH$	5

Because of molecular weight differences, there are about 100 epoxy groups and 10 amine groups for every carboxyl group in this formulation. Infrared studies have shown that the carboxylic acid forms first a salt with the amine [(28)] (i e. the activated sites leading to particle precipitation):

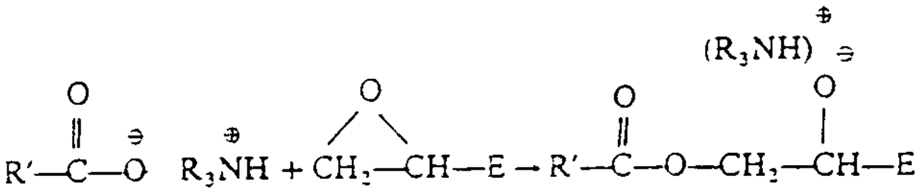


$$R'-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R_3N \rightarrow R'-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus}{O}\quad \overset{\oplus}{R_3NH}$$

(1)

where: R = H or/and alkyl

The carboxylate salt then reacts quite rapidly with the epoxy group:



(2)

The resulting rubber adduct is probably similar in structure to an ABA block copolymer, where in this case A is composed of DGEBA resin units and hardener, and B is the poly(butadiene-co-acrylonitrile) chain of a single CTBN molecule Phase separation takes place as the epoxy resin begins to cure, and the molecular weight starts to rise However, in addition to causing phase separation, the curing reactions lead to an increase in viscosity, and eventually to gelation.

The resulting reduction in molecular mobility lowers the rate of reactions. It appears that phase separation is confined to the early stages of curing, and stops well before the matrix resin reaches the gel point.

Although the improvement in toughness of rubber-toughened epoxies can be quite large, not all thermosets can be toughened by the above technique, as they may not allow the precipitation of the toughening particles. In general the high stiffness and strength of thermoset resins are, to some extent, reduced by the presence of low stiffness elastomer particles and through plasticisation effects, as it has already been pointed out.

To avoid a reduction in the inherent stiffness and strength and a reduction in the Tg of the resin some engineering thermoplastics, e g. polyethersulphone (PES) and polyetherimide (PEI) have been used (29) to produce ductile particles dispersed in the epoxy matrix. These are dissolved in a solvent and then mixed with the epoxy resin. The solvent is allowed to evaporate and then the curing agents are added. During curing the engineering thermoplastic component precipitates to produce small spherical particles Furthermore the viscosity of the mixture is considerably higher than that of the parent resin and the adhesion between the two phases is also rather poor, unless these are functionalised to react with the resin (see later).

The search for alternative toughening particles to CTBN is also driven by the necessity to overcome their poor thermoxidative resistance resulting from the unsaturation in the polymer chains, even though the epoxy resins themselves are intrinsically fairly resistant to oxidation It is the presence of double bonds in the chains that can cause chain scission reactions and/or further crosslinking with the loss of elastomeric or ductile properties of the precipitated particles which, ultimately, become rigid and brittle, though such a degradative process requires exposing the elastomer to severe conditions

One of the main problems of cured epoxy resins is their capability to absorb and retain water. The great affinity with water is explained by the presence of highly polar groups in the epoxy network. It has been proposed, in fact, that the diffusion of penetrant molecules into polymers depends on two factors (30): the forces of attraction between the polymer and the penetrant molecules, and the availability of appropriate molecular size holes in the polymer network The first factor concerns the chemical nature of the penetrant versus that of the polymer. The relatively high water absorption capacity of epoxy resin derives from the presence of hydroxyl (OH) groups in the epoxy chains, which attract the polar water molecules through hydrogen-bond formation (31,32) . The second factor, on the other hand, involves the presence of holes determined by the polymer structure and morphology, which in turn depends on the fluctuations in crosslink density, and molecular chain stiffness, which determines their ability to pack closely in an amorphous system The formation of an appropriate hole also depends on the cohesive energy density of the polymer and on the size of the penetrating molecules Water molecules, for example, are hydrogen-bonded and can form clusters within the polymer (33). Thus this particular factor affecting diffusion is essentially a geometrical one, i e. the free volumes available within the polymer for occupation by the penetrant molecules.

1.3) Aims of the Work.

The idea behind this research project is to use a low molecular weight crystalline thermoplastic polymer to toughen the epoxy matrix, using the same approach as in the CTBN technology To this end the work has been focused on to the compatibilisation of a thermoplastic low molecular weight polyethylene with epoxy resins through telechelic extensions brought about by reactions with functional groups.

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

Low molecular weight functionalised polyethylenes as the toughening agent have been chosen, for the following reasons:

a) there are no double bonds and, therefore, are more thermally stable;

b) it may be possible to lower the curing temperature to facilitate the precipitation of the toughening phase through crystallisation, albeit it may still be possible 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 as for CTBN,

c) it is possible to reduce the water absorption of the epoxy resin by introducing in its structure polyolefinic chains which are intrinsically hydrophobic.

The main objective of the present research, therefore, is to evaluate the miscibility of functionalised low molecular weight polyethylenes in epoxy resins cured with anhydride hardeners and to introduce suitable telechelic extensions via the functional groups in order to enhance their miscibility without adversely affecting their reactivity with the oxirane groups of the resin

2. LITERATURE SURVEY

2.1) Miscibility of Reactive Modifiers in Epoxy Resins.

It is recognised that the miscibility of polymers is determined by a balance between enthalpic and entropic contributions to the free energy of mixing, ΔGm (34). Thus, the condition of negative change in ΔGm for complete miscibility, is always satisfied for exothermic mixtures, while mixing is unlikely to lead to miscibility owing to the very small increase in entropy The miscibility of polymers, however, can be further enhanced by introducing functional groups in the components capable of undergoing chemical reactions which would result in a higher reduction in enthalpy than is possible with physical interactions.

Under specific conditions, a characteristic interpenetrating structure is formed (35-37). The domain size of the dispersed phase is mainly dependent on the interfacial tension, i.e. the size usually decreases as the interfacial tension diminishes

2.2) Toughness Enhancement of Epoxy Resin.

The principal objective of rubber modification is the improvement of fracture properties commensurate with the smallest possible decrease in modulus and strength. The CTBN and ATBN (carboxyl and amine-terminated butadiene acrylonitrile) copolymers have contributed considerably to achieving this objective but these two elastomers possess some drawbacks, e g. their glass transition temperature is relatively high (38), which limits their use at very low temperatures (19 39), and their highly unsaturated structure provides sites for degradation reaction in oxidative and high temperature environments (40)

Several attempts have been made in the last two decades to find alternative polymeric systems to CTBN and ATBN for the toughening of epoxy resins. The aim of the researchers in this field has been to impart better properties to the epoxy matrix, especially in terms of toughness and water absorption, while avoiding the drawbacks associated with the use of CTBN and exploiting other beneficial characteristics of new systems.

Attempts to introduce fluorine atoms in the network of crosslinked epoxy formulations have been made through the addition of specially functionalised fluoroelastomers with the aim of enhancing simultaneously the toughness and thermal stability characteristics (41) The elastomer and the resin/hardener components were mixed from solutions to obtain an initially monophase system which would subsequently allow the precipitation of the elastomer, after the evaporation of the solvent, into fine particles through post-curing heat treatments. Mijovic et al. (42) have grafted functional groups on a fluorocarbon elastomer to render them compatible and reactive with epoxy resins. A large increase in fracture energy was observed with the addition of 15% elastomer in the resin, though this was accompanied by a decrease in Tg, probably due to the solubilisation of some elastomer molecules within the epoxy network. However, in both previous cases the dissolution of high molecular weight polymers into a thermosetting resin requires the use of solvents which have to be removed by vacuum extraction prior the curing. This limitation makes such formulations usable only in thin layer systems, such as adhesives or fibre impregnations, in so far as there is a large increase in viscosity which impairs the processing characteristics, particularly in low pressure applications. It is for this reason, therefore, that functionalised oligomeric modifiers are preferred.

One approach that has been explored to enhance the toughness of brittle thermosetting systems is to prepare a thermoplastic/thermoset blend consisting of one linear polymer and one highly crosslinked polymer. Such a system is called semi-IPN.

An interpenetrating polymer network (IPN) is defined as a combination of two polymers both in network form, at least one of which is synthesised and/or crosslinked in the immediate presence of the other (43). They are held together by permanent entanglements formed by crosslinking of the component networks. Therefore, unlike co-crosslinked resin mixtures, there is no covalent bond between the two polymers, i e. monomer A reacts only with itself.

It is possible to obtain three types of IPN: simultaneous, sequential and semi-IPN. In a simultaneous IPN, the crosslinkable monomers are mixed together and then polymerised separately through different mechanisms In the case of a sequential IPN, first one type of monomer is crosslinked, then a second type of monomer is added and polymerised within the network of the first. In a semi-IPN only one of the polymers forms crosslinks. In other words, it consists of a molecular mixture of a thermoset and a thermoplastic polymer. The thermoset polymer gives high-temperature and chemical resistance, while the thermoplastic provides toughness and resistance to impact (44). But not all polymers can be combined to form IPNs, the two polymers must be miscible in order to avoid phase separation and to achieve a greater improvement in mechanical properties.

Selfton and co-workers (45) have incorporated high performance polyaromatic thermoplastics into epoxy resin systems again in the attempt to carry over the very high toughness of thermoplastics into the epoxy resin system. The results have shown that it is possible to control the semi-IPN morphology by modifying the thermoplastic backbone The different morphologies so obtained give rise to different degrees of toughening by involving different energy absorbing mechanisms.

Another approach to the formation of IPN molecular structures has been reported by Sperling et al. (46) and Touhsaent et al (47) These workers have synthesised two polymer networks by simultaneous independent reactions in the same container They have indicated that inter-crosslinking reactions are eliminated in these simultaneous interpenetrating networks (SINs) by combining free radical (acrylate) and condensation (epoxy) polymerisation. By this method they modified epoxy resin with poly(n-butyl acrylate) polymer. They have found that a two-phase morphology emerged (consisting of co-continuous dispersed rubber domains, their diameters being about 0.1-0 5 μm) within the epoxy resin which constituted the major phase The dimension of the dispersed rubber phase domains and the extent of molecular mixing between the two components were found to depend on the relative reaction rates (or gel times) in relation to the rate of phase separation. Better mechanical properties resulted when the extent of molecular mixing was minimised and heterophase IPN's were produced.

Other reports (48,49) have shown that the combination of various chemical types of polymeric networks often results in different controlled morphologies. These produced IPNs with synergistic properties such as improved adhesion, higher shock absorption and enhanced stress-strain properties.

Banthia et al. (50) have used various carboxy terminated elastomeric acrylate oligomers to toughen a diglycidyl ether of bisphenol A They have found that acrylate monomers exhibit extremely good miscibility with the conventional epoxy resin, but precipitate as a distinct phase during network formation. A two phase morphology was obtained and, in the case of inclusion of ethylhexyl acrylate oligomers (4-10% by weight), the cured castings were found to exhibit enhancements in impact strength comparable to traditional toughened epoxy systems. In conclusion the above authors have found that carboxyl-terminated telechelic ethylhexyl acrylate oligomers are potentially effective elastomeric toughening agents, exhibiting better oxidative and thermal stability with respect to CTBN toughening systems.

Wang et al. (22) used as modifiers to toughen epoxy resins novel polyfunctional elastomers with medium molecular weight. The polyfunctional poly(n-butylacrylates) reported in their study were epoxy functionalised poly(n-butylacrylate) (ETPnBA) and carboxy functionalised poly(n-butylacrylate) (CTPnBA), both obtained by photopolymerisation The effect of the functionality and kind of functional group in the elastomers used as toughening agents was investigated by tensile and impact tests and electron microscopy. It was found that there exists an optimum functionality of elastomers for maximum impact resistance in epoxy group (ETPnBA) and carboxyl groups (CTPnBA) copolymer-modified systems. Studies on morphology of the modified epoxy resin system indicated that the better toughening effects of epoxy groups ETPnBA in an epoxy resin matrix can be attributed to the existence of a multiple distribution of particle sizes. The aggregation of rubber particles occurring with the use of carboxy functionalised CTPnBA modified epoxy resin was believed to be the cause of the observed reduction in toughness.

Lee and co-workers (51) obtained similar results by using a family of n-butyl-acrylate/acrylic acid (nBA/AA) copolymers with a broad functionality range (1.62-9.93). They reported, in fact, that improvements of adhesive strength could be achieved by incorporating the nBA/AA copolymer in a DGEBA epoxy matrix and that an optimum functionality for matrix adhesion strength existed.

The search for functionalised oligomers for the production of toughened epoxy resins suitable for high temperature applications has also been the focus of attention of other research workers in this area.

For example Takahashi et al (52) have examined several amine terminated silicone oligomers as toughening agents for epoxidised novolac resins for use as encapsulants for semiconductor integrated circuit devices, i.e low electrical stress applications In such cases siloxane oligomers offer the advantage of a) lower Tg values for the dispersed rubbery particles than conventional elastomers, b) very good thermal stability and c) a reduction in thermal expansion coefficient of the cured moulding compound The miscibility of the silicone oligomers with epoxy resin was found to increase with increasing the ratio of phenyl methyl siloxane units relative to dimethyl siloxane units in statistical copolymers. Total solubility in the epoxy resin was achieved, however, only in the case of phenyl methyl siloxane homopolymers which produced transparent, monophase, cured products. For other siloxane oligomers a two-phase morphology was observed in every case, but the dispersed particles became extremely small (i.e. about 0.01 µm) when the silicone oligomers were added to the resin as solutions in toluene.

Siloxane elastomers have been chosen also by other workers as an attractive alternative to traditional toughening systems, although some of these oligomers are quite expensive. Beside the advantages already mentioned, they exhibit good weatherability, oxidative stability, high flexibility and moisture resistance, having hydrophobic characteristics (53). Moreover, the non-polar nature and low surface energy of siloxanes constitute a thermodynamic driving force for them to migrate to the air-polymer interface, provided the chains are sufficiently mobile This migration can occur with simple physical blends as well as with systems containing chemically linked microphase-separated segments. During the early stages of cure of a siloxane-modified epoxy, i e. before extensive crosslinking begins to impair the diffusion characteristics, such migration is considered possible and is believed to lead to the formation of a very hydrophobic and chemically bound surface coating (54). Evidence suggests that such a surface layer reduced friction and improves the wear properties of the epoxy substrate (55).

Yorkgitis and co-workers (56) have chemically modified epoxy resins with functionally terminated poly(dimethylsiloxane), poly(dimethyl-co-methyltrifluoropropyl siloxane) and poly(dimethyl-co-diphenyl siloxane) oligomers and have analysed the morphology, solid-state properties and friction and wear properties of the systems. They have found that the miscibility of siloxane modifiers in epoxy resins can be enhanced by increasing the percentage of methyltrifluoropropyl (TFP) siloxane or diphenyl (DP) siloxane relative to dimethyl siloxane

It is known that the solubility parameter is a good indicator of the miscibility of one substance with another and, together with molecular weight and temperature, can adequately predict the possible occurrence of phase separation of the elastomer from the resin during cure. Through copolymerisation of dimethyl siloxane with partially aromatic diphenyl siloxane or polar methyltrifluoropropyl siloxane, it is possible to raise the solubility parameter of the siloxane elastomer from $3\ 7 \bullet 10^{-3}$ $(J/m^3)^{1/2}$ close to that of the epoxy resin, approximately $4\ 5 \bullet 10^{-3}$ $(J/m^3)^{1/2}$ (12). This is analogous to the manner in which the solubility parameter of ATBN and CTBN elastomers are controlled by adjusting the acrylonitrile content. In this way the level of miscibility of the siloxane modifier in the epoxy resin controls the size and make-up of the phase-separated elastomeric domains, i.e. the morphology and the resulting modulus and fracture toughness of the modified resin. The authors have reported that, while unmodified polydimethylsiloxane, due to the large difference in solubility parameter, phase separates from the epoxy resin into large domains which do not increase the fracture strength, the fracture toughness of the epoxy resin can be improved by modification with siloxanes containing 40% or higher methyltrifluoropropyl content, or 20 and 40% diphenyl content.

Cecere et al. (57) concentrated their efforts to the optimisation of both molecular weight and diphenyl contents of the poly(diphenyl-dimethyl) siloxane oligomers in order to obtain the maximum impact strength in the modified epoxy networks without sacrificing the flexural modulus They have found that siloxane copolymers when used as impact modifiers are not very effective in increasing fracture toughness over that of an unmodified system. It appears that a system incorporating 15% by weight of a 40% diphenyl/60% dimethyl-copolymer with a molecular weight of approximately 5000 g/mole yields the highest impact strength with a small decrease in flexural modulus This system phase-separates into evenly dispersed particles with an average diameter of 1 μm.

More recently other workers (58) have studied the rubber-modification of bifunctional and tetrafunctional epoxy matrices by means of a block copolymer of polydimethylsiloxane and polyoxyethylene (PDMSO-co-PEO) elastomer or an anhydride-grafted polybutene (PB-g-SA) The choice of these types of liquid reactive elastomers was determined by their higher thermal and photo-oxidative resistance compared with classical unsaturated elastomers The results showed that the mechanism of fracture of bifunctional resins can be positively influenced by the addition of the above mentioned rubbery systems, while for a tetrafunctional epoxy resin, like TGDDM, the same elastomers do not produce any improvement in impact properties. The above authors have tried to give an explanation on the basis of the different networks obtained in the two matrix systems. In particular, in the case of TGDDM the resin has a very high crosslink density and, therefore, its capacity to deform by shear yielding is highly reduced. Hence the contribution of the rubbery particles to enhance fracture toughness by promoting localised shear yielding in the matrix is rather small. The authors have finally concluded that conventional rubber-toughening procedure cannot achieve the desired results owing to the lack of ductility of the TGDDM.

The constant search for thermally stable systems to use as toughening agents for epoxy resin, has induced some researchers to investigate several alternatives

By reacting in solution an acid fluoride functionalised perfluoroligomer with a diglycidyl ether of bisphenol A, Rosser et al (59) have produced a prepolymer which was subsequently used to modify an epoxy/diaminodiphenylsulphone resin matrix for a glass cloth composite. They have demonstrated that this immiscible elastomeric prepolymer exhibits sufficient chemical reactivity with the epoxy resin to give rise to improvements in flexural ductility and impact resistance, without loss of strength and modulus or lowering the glass transition temperature It was suggested that an interpenetrating polymer network was formed, which is responsible for the improvements in the mechanical properties of the composite

The use of modified perfluoropolyether oligomers in an epoxy resin was also found by Mascia et al. (60) to produce both IPN and particulate two phase systems, the morphology depending on procedure details Hydroxy-terminated fluoroalkene oxide oligomers were reacted with chlorendic anhydride and subsequently with ε-caprolactone to produce carboxy-terminated perfluoroether prepolymers that were totally miscible with diglycidylether of bisphenol A. Curing the epoxy resin mixtures with hexahydrophthalic anhydride hardener and benzyl dimethylamine catalyst produced transparent products exhibiting a heterogeneous IPN morphology. Pre-reacting the fluoroalkenoxide prepolymers with an excess of epoxy resin, prior to the addition of hardener and catalyst, resulted in opaque products displaying a two-phase dispersed particles morphology Analysis of mechanical properties showed for both systems remarkable improvements in fracture energy (450-600%), flexural strength (24-75%) and strain at break (300-500%), even with the use of only small amounts of perfluoropolyethers, i.e. 3 5-5 0%. However, these were achieved at the expense of a small decrease in modulus (20-30%) and Tg (10-25°C). It must be noted that these effects were much more pronounced for products exhibiting a two-phase, dispersed particles morphology, than for IPN systems. The above authors (61) also found that both IPN and particulate two-phase formulations showed a reduction in flexural strength after 21 days ageing at 200°C, but the measured values were always much greater then for the non-aged control samples. The strain at break for IPN systems, however, increased considerably with ageing in proportion to the concentration of prepolymer used, this being a very unusual occurrence in the field of thermosets.

High performance thermoplastics, such as polyetherimide (PEI) and polyethersulphone (PES), have been also used to improve the fracture toughness of highly crosslinked thermosetting resins, leading to the additional advantage of causing no reduction of glass transition temperature and mechanical properties.

When a tetrafunctional epoxy resin is toughened with PEI, improved fracture toughness is obtained, i e the K_c value has been found to increase from 0.5 to 1 42 MPa $(m)^{1/2}$ with the addition 25 phr of PEI, without any appreciable decrease in Young's modulus (62). Similar results have been also found with a trifunctional epoxy resin (63). The analysis of the morphology, in the latter case, has shown the occurrence of phase inversion with a PEI content of about 15 wt % or greater, as it begins to form a continuous phase The interfacial adhesion between the PEI dispersed phase and a tetrafunctional epoxy resin can be enhanced by using a modified polyetherimide, obtained through hydrolysis of PEI with NaOH solution (64 65) The results have confirmed that improved toughening effect can be achieved in high performance epoxy resins by the incorporation of the modified PEI. For this system a fracture toughness value 40% higher than for the unhydrolysed PEI/epoxy resin system with equal PEI content, i e. 5 wt %. The hydrolysis time has been found to play an important role in controlling morphology of the cured system: the more hydrolysed the PEI, the more miscible it becomes with epoxy resin. Thus, the number and size of dispersed PEI particles is reduced with increasing hydrolysis time of PEI. Subsequently, an optimum hydrolysis time can be determined

Raghava (66) has blended a low molecular weight polyethersulphone (PES) containing hydroxyl end groups with a tetrafunctional epoxy. He expected that the reactive end groups of PES would participate in the chemical reactions during curing of the epoxy resin For this reason the modified cured epoxy was expected to possess enhanced fracture toughness Analysis of fracture toughness of modified epoxy compared to that of unmodified system showed, however, that the increase in toughness of epoxy-polyethersulphone system was only marginal.

Bucknall and Partridge (67,68) have confirmed the results reported by Raghava. They have found only a small increase in fracture toughness of blends of PES with tetrafunctional and trifunctional epoxy resins, separately cured with diaminodiphenyl-sulphone (DDS) and dicyandiamide (DICY). They also reported that the PES-toughened tetrafunctional epoxy resin cured with both type of hardeners did not show phase separation, while in the case of a trifunctional resin phase separation was observed

Diamont and Moulton (69) have also investigated the toughening of a tetrafunctional epoxy resin using various ductile and tough thermoplastic polymers possessing a high glass transition temperature They observed that a mixture of epoxy and PES did not possess a two-phase structure and that the fracture toughness of the modified system was not markedly different from the values measured for unmodified epoxy. The lack of toughening effects in a tetrafunctional epoxy resin by simply mixing it with a PES may be due to the high crosslink density of the resin. Polyethersulphone, perhaps, decreases the crosslink density by shielding the reaction sites of epoxy resin. This is obviously not sufficient to increase the ductility of the modified system by promoting shear banding in the matrix. Also, polyethersulphone is notch-sensitive and its impact properties are dependent upon specimen thickness (70). These factors reduce PES ductility and hence its ability to toughen an epoxy is reduced. In addition Bucknall (68) suggested that PES is a polar material and actually has a higher solubility parameter than the epoxy network, which could limit the interfacial adhesion between resin and PES and consequently reducing the fracture toughness. More importantly, the polysulphone modifier was simply physically blended into the epoxy resin and did not chemically react thereby giving poor interfacial adhesion.

The miscibility of a polyethersulphone and a tetrafunctional epoxy, cured with an aromatic anhydride, was studied by Raghava (29) using scanning electron microscopy and dynamic mechanical spectroscopy. The influence of the morphology of the epoxy/PES blend on its fracture toughness and toughening mechanism were also analysed by the above author The modified system exhibited a two-phase bimodal particle distribution morphology. Dynamic mechanical spectroscopy results did not show an intermediate glass transition temperature, but this was attributed to the Tg of the phases not being sufficiently different. As in other studies, the same author found a lack of enhancement in low temperature fracture toughness values for PES modified epoxy resin. This was again attributed to the very high crosslink density of the cured tetrafunctional epoxy. The inclusion of low concentrations of PES is not sufficient to produce formation of shear bands The Young's modulus of the modified system was found to be slightly smaller than the values for the neat epoxy resin.

This suggests that PES acts as a non-reactive diluent for the highly crosslinked epoxy, provided it does not precipitate out

From the last examples, it emerges that the incorporation of ductile polymeric modifiers as a method to enhance the fracture toughness of epoxy resins not always yields satisfactory results in the case of highly crosslinked epoxies (tri- and tetra-functional resins).

As an alternative approach to toughen a highly crosslinked epoxy resin, Martuscelli and co-workers (71) have used as modifier an engineering ductile thermoplastic polymer, namely the bisphenol-A based polycarbonate (PC). A critical step towards the preparation of successful thermosetting blends is to start from a single-phase, homogeneous reactants mixture, prior to the curing process. This was achieved by a reactive blending process in which the PC was dissolved at high temperature (220°C) in the uncured epoxy resin, giving a clear, homogeneous solution. After the addition of the curing agent and the accelerator at lower temperatures (80°C), the temperature was increased again for curing and for post-curing purposes. According to this procedure, blends containing 0 to 20% in weight of PC were prepared. The FTIR analysis performed on the uncured epoxy/PC mixtures demonstrated the occurrence of physical and chemical interactions among the blend components In particular, it was found that PC chains with epoxide end groups were formed during the dissolution process. These functionalities take part in the subsequent crosslinking reactions, thus incorporating PC backbones within the epoxy network. Dynamic mechanical measurements and scanning electron microscopy (SEM) analysis of the epoxy/PC blends did not show any evidence of phase separation of the minor component during the curing process The fracture behaviour of this blend system studied at low and high strain rate gave rise to a marked increase in toughness with increasing the amount of PC in the blend In particular, for low speed tests the addition of 20% by weight of PC increases the toughness of the epoxy matrix by a factor of about 7, while for the high speed tests the increase is about 5.

Moreover, this toughening effect with the use of PC was achieved without significantly reducing other desirable properties of the matrix such as the elastic modulus. The modulus decreased by less than 10% for a content of 25% of PC. From SEM analysis it was found that localised yielding at the crack-tip and the consequent crack-tip blunting is the mechanism controlling the degree of plastic deformation during the fracture process

The utilisation of functionalised thermoplastic modifiers has been a major research focus in several laboratories

Hedrick et al (72) used phenolic hydroxyl and aromatic amine end functionalities in poly(arylene ether sulphone) oligomers to modify chemically epoxy networks. The oligomers were reacted with a large molar excess of epoxy resin and then cured into crosslinked networks with a stoichiometric quantity of 4,4'-diaminodiphenylsulphone (DDS). The aryl ether sulphone was found to be molecularly miscible with the epoxy precursor over the entire range of compositions and molecular weights investigated, developing a two phase structure during curing, in which polysulphone formed discrete particles evenly dispersed in the epoxy matrix. Despite the existence of a two-phase structure, the crosslinked systems were nearly transparent, due to a similarity in refractive index of the two components. The fracture toughness of these modified networks under plane strain conditions was improved significantly with minimal deterioration in the flexural modulus The authors attributed this result to the presence of polysulphone particles in the epoxy matrix, which deformed plastically during fracture and induced shear yielding in the epoxy matrix.

More recently Yoon and co-workers (73) used aminophenyl terminated polyethersulphone to impart better properties to a difunctional epoxy resin. These authors showed that the aminophenyl functionality in polysulphone remarkably improved the fracture toughness and adhesive bond strengths of epoxy resins. In contrast to commercial PES modified epoxy systems, the improved properties by using reactive PES modifications were mainly attributed to the reactive end groups which provided chemical linkages with the epoxy matrix. Moreover, it was found that the samples used for tensile tests, fracture toughness measurements and adhesion tests exhibited different phase separation behaviours, but a similar trend of properties was observed.

Kemp et al. (74) reported their attempts to incorporate several types of linear polysulphide rubber (10 to 20 phr) in a diglycidyl ether of bisphenol A. Their study covered the physical microstructure of the toughened epoxide and its mechanical and dynamic-mechanical properties. The results showed that most of the cured materials featured disperse rubber particles with diameters of <1μm. It was also found that addition of polysulphide rubbers to the epoxy nearly always led to improvements in properties, notably the development of ductility. However, it was not clear whether these improvements were necessarily due to the presence of the rubber as a discrete particles or dispersed as IPN's in the matrix.

Silicone rubber toughened epoxy resins seem to be an attractive alternative to CTBN and ATBN systems, exhibiting stable physical properties over a broad range of temperatures. Because epoxy and silicone rubber are completely immiscible, the addition of a compatibiliser is necessary to obtain a satisfactory dispersion of the rubber in the resin

The main objective of Kasemura and co-workers (75) was to find an appropriate surface active agent to reduce the interfacial tension between the resin and the rubber in order to compatibilise the two components. These authors achieved compatibility with the epoxy resin with the use of a polyether modified silicone oil (EtMPS) to disperse a RTV (room temperature vulcanising) silicone rubber or silicone diamine The results showed that the impact fracture energy of the resin was increased by the addition of the RTV silicone rubber up to two times that of the unmodified resin, while the addition of silicone diamine had almost no effect, possibly because the molecular weight was too low. Moreover, T-peel strengths of aluminium plates bonded by epoxy resin filled with RTV silicone rubber and with silicone diamine effectively increased with the silicone content, showing a maximum at 10-20 phr. By a scanning electron microscope, many particles of silicone rubber, 1-20 μm, were observed across the whole of the fracture surface.

Finally Frischinger et al. reported (76) an attempt to introduce epoxidized vegetable oils in a DGEBA epoxy. It was possible to obtain two-phase structures with rubbery particles by using epoxidized soya bean liquid rubber (ESR), based on epoxidized soya bean oil and DDM, which exhibited a high toughness, similar to that of other rubber-modified (CTBN) epoxies, as well as a low water absorption. They exhibited, however, slightly lower Tg values and Young's modulus in comparison to the unmodified resins, whereas the dielectric properties remained unchanged.

2.3) Toughening of Thermoset Polymers by Rigid Crystalline Particles.

The question of how to improve best the toughness of highly crosslinked epoxy resins without deteriorating other desirable properties has led to the search of alternative systems. Engineering thermoplastics although can provide a high modulus and temperature resistance, have been found to be effective only in a few cases. In fact, a relatively high fracture toughness was obtained only when the morphology became a two-phase co-continuous microstructure, in absence of any interactions between the components This can lead to poor high temperature creep resistance and/or reduced solvent resistance. When a crystalline second phase is successfully incorporated into an epoxy matrix, the crystalline phase is expected to act as a toughening agent, without other drawbacks, such as reduction in modulus and glass transition temperature of the toughened resin.

One possible toughening mechanism in such systems is phase transformation toughening, which is well known in ceramic materials (77). An example is represented by zirconia-containing ceramics (78-83). The metastable tetragonal phase of zirconia is incorporated into the ceramic, and under the influence of the stress field ahead of a crack tip, this phase transforms to the stable monoclinic phase. Because the monoclinic phase is less dense than the tetragonal phase, compressive stresses are set up on one of the phases, which superimposes on the tensile stress field ahead of the crack tip producing shear deformations, which have the effect of increasing the critical fracture energy.

Such a toughening mechanism might be applicable to brittle polymers if a stress-transformable crystalline polymer were used as the rigid second phase. However, only few studies have been carried out to verify this hypothesis for polymeric materials (84). For dispersed crystalline polymers to be effective for toughening by phase transformation, several properties similar to those of the metastable tetragonal phase of zirconia are required First, the polymers should have a variety of crystalline phases and transformations from one to another can be induced by an applied stress. The desired phase transformation is one in which volume dilatation and distortion both occur in response to the stress field ahead of a crack tip Second, the desired stress-free crystalline phases should be stable or stabilisable in the temperature and pressure ranges under which the brittle matrix resins are processed Third, these polymers should form strong interfacial bonds with the matrix

Kim and Robertson (13) studied the toughening of an aromatic amine-cured diglycidyl ether of bisphenol A epoxy with particles of crystalline polymers. The crystalline polymers chosen were poly(butylene terephthalate) (PBT), nylon 6 and poly(vinylidene fluoride) (PVDF). Each of these was found to be capable of undergoing phase transformation as the result of the application of a stress field, and each of these polymers could be bonded to epoxies For the case of PVDF, however, an amine curing agent is necessary to achieve a good bond with the epoxy resin. The authors reported that nylon 6 and PVDF were found to toughen epoxy resins to an extent similar to what is achievable with an equivalent amount of CTBN rubber. Fracture toughness, on the other hand, was increased two-fold by the inclusion of PBT over that achieved with nylon 6 and PVDF. From microscopy studies the above authors found that the toughness of PBT-epoxy systems was independent of particle size, for particles in the range of tens of micrometers, while the toughness of nylon 6-epoxy systems decreased with increasing particle size, for particles smaller than about 40 μm. There was no reduction in either modulus or yield strength of the epoxy resin with the inclusion of either nylon 6 or PBT and a lower reduction of such properties was observed with the inclusion of PVDF than with the inclusion of rubber

In a recent work, Kubotera and Yee (85) investigated the possibility of using a crystalline block copolymer, containing amorphous end chains, as a modifier to improve the fracture toughness of highly crosslinked epoxy resins. They reported that both polyetheretherketone (PEEK) and PBT units can form crystals when they are combined to form triblock copolymers with amorphous PES. The DSC curves and the micrographs showed that even a short chain length of the PBT and PEEK units, having only 3 and 4 repeating units, can form a crystalline phase. The main reason for using copolymers rather than crystalline homopolymers was that the copolymers were expected to have better solubility with epoxy prepolymers, owing to the solubility of the amorphous blocks. All copolymers, in fact, gave homogeneous epoxy mixtures with loadings up to 15-20% in weight, resulting in multiphase structures. The morphology of the cured blends was found to depend on the structure of the copolymer. From the micrographs it was recognised a second phase dispersed in the epoxy phase. This second phase was not the result of spontaneous liquid-liquid phase separation, but that of crystallisation and agglomeration Finally, the fracture toughness of each system was evaluated The results showed that, although each blend presented some improvement in toughness, the average behaviour was not very different from that of unmodified systems. The most effective modifier, in terms of toughness, appeared to be the triblock PEEK-PES-PEEK system, which gave almost a single phase structure from optical microscope observations

The study of miscibility of polymer blends where one component is crystallisable and another is highly crosslinked has received relatively little attention.

Noshay and Robeson (86) maintained that the curing of epoxy resins with anhydrides in the presence of dihydroxy-terminated polyester or polyether modifiers produces block copolymer structures in which one block forms the crosslinked epoxy/anhydride network, while the other segment acts as a non-crosslinked diluent. The morphology of the cured system was found to be dependent upon the modifier molecular weight. Subsequently the above authors examined the miscibility of a range of anhydride-cured epoxy resins with poly(ε-caprolactone) (PCL) and poly(propylene oxide) of various molecular weights and with different end-groups. They concluded that above a critical molecular weight value in the region of 3000-5000 for the two modifiers, the mixtures had a two-phase structure and that the PCL end-groups reacted with the anhydride-curing agent to produce a type of block copolymer Below this level, however, single phase systems were obtained The results showed that two-phase systems displayed a superior balance of heat distortion temperature and impact strength, thus providing tough systems with better elevated temperature capabilities than were obtained with single-phase systems.

In another paper by Clark et al (87), PCL blends with amine-cured epoxy resins were examined and attention was paid to the opportunity that existed to produce hydrogen bonds with amine-cured epoxy resin/PCL blends. They found that PCL with average molecular weight about 20000 was partially miscible with amine-cured epoxy resins although it was largely immiscible with the anhydride-cured epoxy resins reported by Noshay and Robeson The different miscibility with PCL between amine-cured and anhydride-cured systems was considered to be due to the presence of groups in the amine-cured system, which offer an excellent potential for hydrogen-bonding interaction with the ester groups of PCL in blends.

Qipeng and co-workers (88) have described the results of a study on epoxy resin/poly(ethylene oxide) (PEO) blends and, in particular, the role of the degree of crosslinking with respect to the miscibility of the epoxy resin with PEO and the phase structure of the resulting blends. The preparation of such blends was realised first by mixing resin and PEO at a temperature above the melting point of PEO, then cooling the mixture at room temperature Finally the curing agents were added and the mixture, after being stirred at higher temperature, was cured at 110°C for 4 hours (i.e. above the melting point of PEO). From the results, the authors concluded that PEO with Mn=20000 was miscible with the uncured epoxy resin, but became immiscible when an amine hardener was added. It was concluded that PEO may be miscible with partially cured epoxy resin or partially miscible with an epoxy resin advanced to a higher degree of cure. The miscibility of epoxy resin /PEO blends was also studied more recently by Luo and co-workers (89). It was confirmed that all the uncured DGEBA/PEO blends were miscible in the molten state. Moreover, in this case the system cured with phthalic anhydride (PA) resulted in a completely miscible cross-linked product. The presence of dissolved PEO, however, caused incomplete curing of the epoxy resin and gave rise to a less perfect network. The presence of DGEBA in the blends, on the other hand, hindered the crystallisation of PEO, depressing the melting point and elevating the crystallisation temperature The addition of DGEBA results, in fact, in an increased Tg (before and after curing) of the miscible blend, and thus reduces the molecular chain mobility of the crystalline component and the perfection of crystals. The melting point also decreases with increasing the amount of curing agent (PA); on the other hand, the crystallisation temperatures increase because the increase in the hardener, that corresponds in an increase in crosslinking density, causes PEO crystallisation to be difficult and reduces the perfection of PEO crystals.

2.4) Water Absorption in Epoxy Resins.

Under service conditions epoxy resins are often subjected to varying degrees of humidity and temperatures. Moisture has a detrimental effect, especially at elevated temperature, on the mechanical properties of cured epoxy resins, which is particularly important for composites (90,91). The degradation of properties is evidently caused by water-induced plasticisation and the concomitant lowering of the glass transition temperature of the matrix resin (92), resulting in structure degradation by hydrolysis, matrix-fibre separation and crack formation (93,94)

In the last decade many attempts have been made to improve the hydrophobicity of epoxy resins For instance, the incorporation of halogens in the network structure of epoxies will improve the resin durability in moist environments and lowers its moisture sorption.

According to Diamant et al. (95) the diffusion coefficient of water into an epoxy resin depends on four main factors: (i) the polymer network structure; (ii) the polymer polarity, determining polymer-water affinity; (iii) the physical morphology of the polymer (e.g , a two-phase structure); and (iv) the development of microdamage under severe humidity conditions. In his study, however, he concludes that it is difficult to predict which of these factors, or combination of them, dominates in moisture diffusion processes.

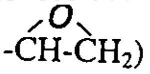
The sorbed water can cause degradation of properties of cured epoxies, although it does not seriously affect the cohesive properties of the resin. Moisture can easily penetrate and plasticise most epoxies, thus lowering the glass transition temperature (Tg) (96,97) and deteriorating the mechanical properties (e.g. strength and modulus) (98,99). Moisture can also hydrolyse ester groups and cause chemical decomposition, as previously mentioned.

Moreover, absorbed water may create serious interfacial problems especially if there is an adherent metallic surface in contact. Primers which contain vinyls or elastomers are sometimes used as interfacial water barriers to prevent corrosion of metal surfaces. The use of primers usually reduces the bond strength and their use is justified only in special cases (11), i.e. when a strong protection against corrosion is required. In this case it is preferred to have a bond with a slightly lower strength but with a much longer durability.

It should be pointed out that problems associated with moisture absorption in epoxy systems are more apparent when the epoxy is cured and used at elevated temperatures. Fisher and al. (100) have studied the Tg and moisture absorption of a tetraglycidyl epoxy cured with an aromatic amine agent as a function of cure conditions. These authors have found that the amount of moisture absorption increases with extent of cure due to the increase in number of hydroxyl groups formed. This is very surprising, however, since a more dense network would have a lower amount of free volumes to accommodate the small water molecules. The data have confirmed that the absorbed moisture interacts primarily with the hydroxyl sites created during curing, i.e. in the vicinity of the amine groups which have reacted with the epoxy groups.

Eckstein (101) used a chlorinated diaminodiphenyl methane to cure a diglycidyl ether of bisphenol A epoxy and found the absorption of moisture to be 15% lower than the halogen-free counterparts.

Barrie et al. (102) studied the effect of halogen containing substituents on the sorption and transport of water in cured epoxy resins, such as tetraglycidyl 4,4' diaminodiphenyl methane/diaminodiphenyl sulfoxide (TGDDM/DDS) systems. The results indicate that the introduction of halogen containing groups reduces the sorption over the whole activity range. However, the effect is greatest for the fluorine containing systems. The mechanism by which the presence of halogen reduces moisture absorption is still unclear.

Fisher et al. (100) and Hu et al. (103) demonstrated that the water absorption of epoxy TGDDM/DDS can decrease significantly by reacting the residual functional groups (i.e. hydroxyl -OH, amine $-NH_2$, and epoxide  $-\overset{O}{CH-CH_2}$) with appropriate blocking reagents. About 75% reduction in moisture absorption was obtained when the residual functional groups were blocked by silylation, cyanoethylation, or carboxylation. The optimum results were obtained when the blocking reagents contained fluorine. The treated epoxy resin, in fact, was found to be stable to hydrolysis even after long exposure to moisture at room temperature.

Fluorinated epoxy resins were found to possess very low water absorption properties compared to pure unmodified epoxy resins (104), setting, in fact, the lower limit for water absorption and water vapour permeability. The works of Griffith et al. (105,106) on the synthesis of epoxy resins containing fluoro substituents in the oligomeric chains has demonstrated that a substantial reductions in water absorption can be achieved even with the use of conventional curatives, such as amines and anhydrides. It has been reported that an anhydride cured fluoroepoxy absorbs only 0.35% by weight of water, whereas a conventional epoxy absorbs 3.5% or more by weight for an immersion period of six months (107). Other investigators (108) have achieved similar results by using perfluoro-butenyloxyphthalic anhydride as curing agents for a diglycidylether bisphenol A resin. They found a reduction of water absorption of 75% compared with the methylnadic anhydride cured systems.

It has been earlier mentioned the attempt of Rosser et al. (59) to use reactive perfluoroether oligomers in epoxy resin. An appreciable reduction in water uptake was obtained, which was attributed to the formation of solubilised fluorinated oligomeric species in the matrix layers surrounding the dispersed particles

2.5) Chemical Criteria and Modification of Toughening Agents for Epoxy Resins.

There is general agreement regarding the necessity to have full compatibility between liquid rubber and uncured epoxy resin until the crosslinking reactions take place.

Drake and Siebert (109) indicated that in any rubber-modified epoxy system, the compatibility between the rubber and the epoxy resin before and during cure is a critical chemical criterion for toughening the matrix

Riew and co-workers (110), on the other hand, suggested that the liquid polymer modifiers should have at least "some degree" of solubility in the epoxy resin without phase separation or agglomeration before gelation, while Sultan and McGarry (111) and Bucknall and Yoshii (112) proposed that initially the rubber should be completely soluble in the epoxy resin They also suggested that the solubility depends upon the initial molecular weight of the rubber, the chemical composition of the functional groups and the solubility parameters of the rubber and the epoxy.

Gazit and Bell (113) indicated that the rubber does not contribute to the improvement of impact strength without good initial rubber dissolution. He used poly(n-butyl acrylate) modified, methylene dianiline (MDA), cured epoxy systems in his work. Others have suggested that the overall matrix toughness is probably significant, but that poor elastomer-resin compatibility during the initial phase of crosslinking prevents development of suitable particle size (17). Some workers have concluded that the improved toughness was related to the particle size and the distribution of rubber domains (114), whereas others have indicated that the resin-rubber compatibility determined the toughness (115).

Another important chemical criterion for toughening the epoxy matrix is the reactivity of functional groups of the liquid polymers Riew and co-workers (110) demonstrated that the terminal reactive groups are more effective than pendant groups in toughening epoxy resins Furthermore, they concluded that the liquid modifier should have at least two functional end-groups Moreover, they pointed out that the selectivity of the functional groups is also very important. They indicated, in fact, that the acid functional end groups such as phenolic and carboxylic are highly selective in forming anions with amine catalysts The order of selectivity, which is the reverse of that for reactivity, is as follows. carboxyl>phenol>hydroxyl>mercaptan (116) In other words, oligomers with mercaptan end groups are the most reactive but give the least improvement in toughness

Earlier was reported the attempt of Mijovic and co-workers (42) to improve the toughness of epoxy matrices with fluorocarbon elastomers, which were initially incompatible with the resin They introduced polar groups into the fluorocarbon backbone exploiting the hypothesis that a chemical modification of the elastomer would result in miscibility with the partially cured resin through various intermolecular interactions. The latter, however, would be disrupted at high temperature (post-cure) leading to the separation of the rubbery phase. They finally concluded that, through a careful control of post-cure conditions (time and temperature) it may be possible to produce "tailor-made" morphology and to improve the resulting physical and mechanical properties.

It was mentioned earlier that in order to improve the properties of epoxy resin (toughness, water absorption and heat ageing resistance) small amounts of perfluoropolyether oligomers were incorporated in the resin (117). Mascia et al. have found, in fact, that chemical modification of the perfluoropolyether was necessary to impart miscibility with epoxy resin (61) This modification involved reactions with acid anhydrides, followed by further chain extension with ε-caprolactone to produce carboxy terminated prepolymers In this way it was demonstrated, by viscosity measurements and infra-red spectroscopy, that not only end capping but also chain extension reactions occur during the modification of perfluoropolyether The prepolymer obtained through the introduction of non-fluorinated segments at the chain ends was miscible with epoxy resin at all concentrations Furthermore, changing the pre-reaction time and temperature of the epoxy-extended pre-polymer it was possible to modify its molecular weight before curing. This in turn was found to affect the morphological and mechanical properties of the modified cured system

3. EXPERIMENTAL

3.1) Materials.

The following low molecular weight functionalised polyethylenes were selected as potential modifiers for epoxy resins:

a) Oxidised homopolymer (AC 6702),
b) Ethylene acrylic acid Copolymer (AC 540),
c) Ethylene acrylic acid Copolymer (AC 5120)

All the three materials were supplied by Allied Signals Inc.. The first is in a waxy form, while the last two are supplied in solid granules. The main physical properties of these materials are summarised in the Table I.

TABLE I: Main physical properties of the three low molecular weight functionalised polyethylenes under investigation.

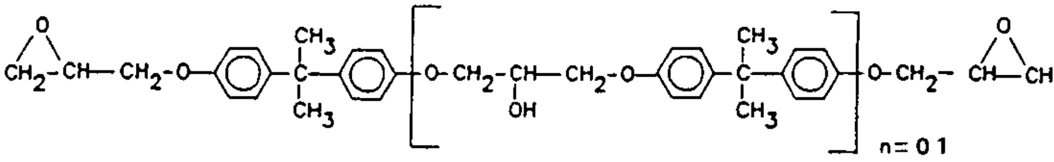
	Acid No.	f	T_m (°C)	DP (°C)	$\overline{Mw}$	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$	Dens. (g/cc)	Visc. (cps)
AC 6702	15	0.26	63	88	2140	970	2.2	0.85	35
AC 540	40	1.22	105	105	4560	1710	2.6	0.93	575
AC 5120	120	2.15	89	92	3325	1005	3.3	0.94	650

Acid No = acid number, DP = drop point, Dens = density, Visc = viscosity at 140°C, all from the Data Sheets provided by Allied Chemicals f = functionality, calculated from $\overline{Mn}$ Tm = melting point, from DSC analysis $\overline{Mw}$ = weight average molecular weight, $\overline{Mn}$ = number average molecular weight, $\overline{Mw}/\overline{Mn}$ = polydispersity, all measured at RAPRA Technology LTD

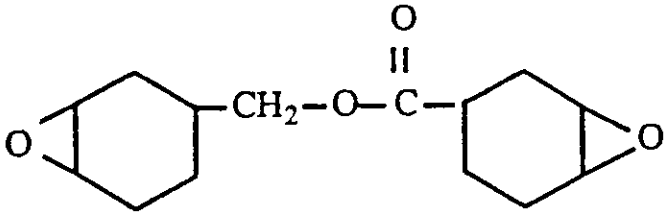
The following epoxy resins were selected for evaluations:

a) Epikote 828,
b) Araldite CY 179.

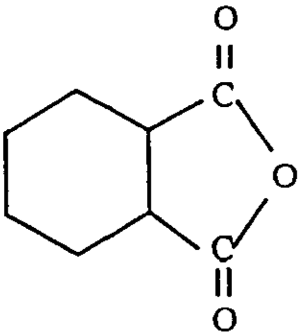
The first is an unmodified liquid bisphenol A - epichlorohydrin epoxide resin (DGEBA) of medium viscosity (12-14 Pa•s at 25°C), combining reasonable ease of handling with high chemical and mechanical performance. It is the standard liquid resin in many industrial applications. The resin has an epoxide equivalent of 184-190 (i e 184-190 g of resin contain 1.0 g equivalent of epoxide). It was supplied by Shell Chemicals. The chemical structure of Epikote 828 is shown below:

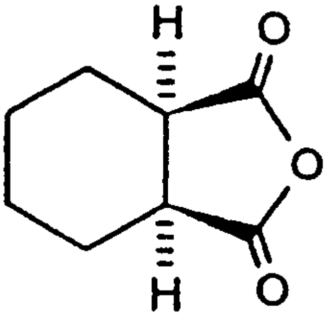


The second resin used, Araldite CY 179, is a cycloaliphatic liquid epoxy resin. It has a lower viscosity than Epikote 828 (0 35 Pa•s at 25°C) and it is usually employed in electrical applications or when a low viscosity is required. It was supplied by Ciba-Geigy. The chemical structure of Araldite CY 179 is shown below:



The first hardener chosen was hexahydrophthalic anhydride (HHPA), supplied by Aldrich Chemical Co Ltd., corresponding to cis-1,2-cyclohexanedicarboxylic anhydride, i e

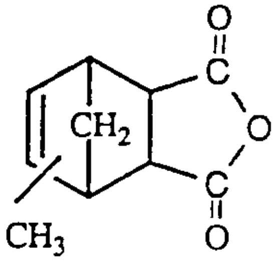




cis-form

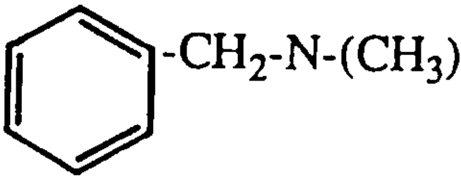
It has a molecular weight of 154 Note that the melting point for the cis-form of HHPA is 32-34°C, whereas the trans- form has a melting point of 145-147°C. (Other characteristics and the main applications of HHPA are reported in the Introduction).

A second hardener was also chosen for evaluation, the methyl nadic anhydride (MNA), supplied by Aldrich Chemical Co Ltd.. It is a methyl-5-norborene-2,3-dicarboxylic anhydride, with a molecular weight of 179. The chemical structure is shown below:

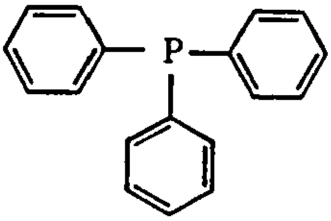


It is the preferred curing agent for elevated-temperature applications.

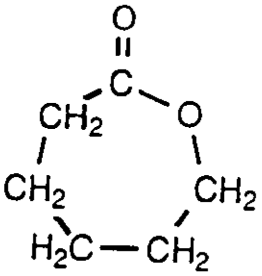
The first catalyst used was a benzyldimethylamine (BDMA). It is a N,N-dimethylbenzylamine with a melting point of -75°C and a boiling point of 183-184°C. As reported in literature, it is often used to accelerate the curing rate when an acid anhydride is used as hardener (normally 1 part by weight of BDMA per hundred part of resin (phr) at 100°C). It was supplied by Aldrich Chemical Co. Ltd.. The chemical structure is shown below·



Another catalyst was used, triphenylphosphine (TPP). It has a melting point of 79-81°C and a boiling point of 377°C. Again it was supplied by Aldrich Chemical Co Ltd.. Its chemical structure is

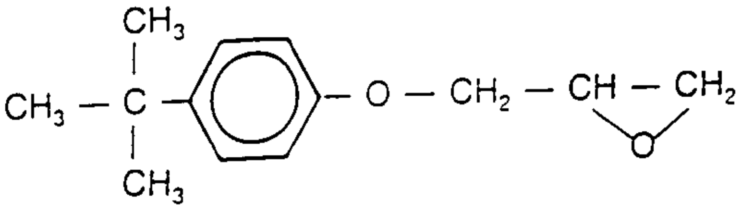


As a modifier of the acrylic acid copolymer AC 5120 was chosen ε-caprolactone (supplied by Aldrich Chemical Co. Ltd.) It is an internal ester of ε-hydroxy caproic acid (6-hexanolactone, 2-oxepanone). It is a liquid with a boiling point of 96-97°C. The chemical structure is shown below



The most important property of ε-caprolactone is the readiness with which its ring is opened by a variety of chemicals; it can react with hydroxyl and carboxylic acid compounds and polymerises readily to polycaprolactone.

The second modifier for the acrylic acid copolymer AC 5120 was Eurepox RVP (p-t-butylphenol-glycidyl ether) It is an aromatic monofunctional resin, normally used as reactive diluent for epoxy systems. It has an epoxy equivalent of 213-233 and was supplied by Witco Corporation UK Limited The chemical structure of Eurepox RVP is shown below·



Finally montanic acid was chosen to modify Epikote 828. It is an octacosanoic acid ($C_{28}H_{56}O_2$) with a molecular weight of 424 and a melting point of 92-94°C. It was supplied by Hoechst. Technical grades are mainly obtained by acid oxidation of deresinified crude wax and are generally used, in the form of acids or esters, as internal and external lubricant for plastics. The structure of montanic acid is shown below:

$$CH_3\,(CH_2)_{26}\,COOH$$

3 1 1) Preparation of Binary and Ternary Mixtures

Binary mixtures were prepared by mixing each of the functionalised polyethylenes in different ratios with the epoxy resins The compositions used, generally, were 10, 25, 50, 75 and 90 wt % of polyethylene in the epoxy resin. The pre-weighed mixtures were heated in an oven for different periods of time at a fixed temperature, chosen on the basis that it should be higher than the melting point of the polyethylene modifiers, but it should be also suitable for mixing the hardener and the catalyst within reasonable time without incurring the risk of premature curing On the basis of these considerations the temperature of 115°C was chosen. The heating time in the oven was varied in steps until an apparent miscibility between the polyethylene and the epoxy resin was achieved (i.e. a transparent mixture was obtained) The heating time was varied from 10 minutes to 24 hours

Binary mixtures of the hardener HHPA with each of the two polyethylenes, AC 540 and AC 5120, and each of the two epoxy resins, were also prepared. The amounts of HHPA used in the binary blends with the polyethylenes were 25, 50 and 75 wt %, while the ratio of anhydride to epoxy resin was 50/50. The preparation technique was the same that in the previous case, i.e. the mixing temperature was again 115°C and the heating time 1 hour.

Ternary mixtures, over a wide range of compositions, were prepared by adding different amount of hardener HHPA to binary mixtures of the epoxy resins with polyethylene modifiers AC 540 or AC 5120, and subsequently heating in an oven at 115°C for different times. The heating time for preparing the binary mixtures polyethylene-epoxy resin was varied from 10 minutes to 24 hours, while the mixtures containing the hardener were heated for only 10 minutes at 115°C

To obtain a comparison with a well known system and to test the efficacy of the method used, binary and ternary mixtures consisting of a carboxylterminated butadiene acrylonitrile oligomer (CTBN, i e. Hycar 1300x8, by BFGoodrich Chemicals), Epikote 828 and HHPA were also prepared, using the same procedure and compositions described earlier.

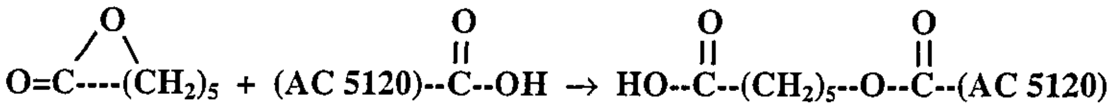
3.2) Modifications of AC 5120 Polymer.

From the given acid number, which was also checked by titrations (see later), and the measured molecular weight, the functionalised polyethylene AC 5120 was found to have the highest functionality value (see Appendix 7.1), i.e. approximately 2.0 . Complete miscibility between this polymer and each of the two epoxy resins, however, was never achieved. For this reason chemical modifications of AC 5120 were performed to extend the polymer chains with soluble telechelic segments and in turn to increase the level of solubilisation in mixtures with epoxy resins.

3.2.1) Reactions with ε-Caprolactone.

ε-Caprolactone was first chosen to modify the functionalised polyethylene AC 5120. A characteristic of caprolactones is the readiness with which the ring can be opened, e.g. with compounds containing hydroxyl and carboxylic acid groups. This reaction has already been successfully used to modify chemically perfluoropolyether oligomers in order to render them miscible with epoxy resins (60, 117).

Following the same principle, mixtures of ε-caprolactone and AC 5120 were prepared. The reaction occurring between ε-caprolactone and the polymer is shown below:



$$O{=}\overset{\diagup O \diagdown}{C{-}{-}{-}{-}(CH_2)_5} + (AC\ 5120){-}{-}\overset{\overset{O}{\|}}{C}{-}{-}OH \rightarrow HO{-}{-}\overset{\overset{O}{\|}}{C}{-}{-}(CH_2)_5{-}{-}O{-}{-}\overset{\overset{O}{\|}}{C}{-}{-}(AC\ 5120)$$

The two reactants were added in a glass flask, placed in an oil heated bath and continuously stirred. To prevent oxidising reactions, a flux of nitrogen was passed over the surface of the sample and a water condenser was used to reflux caprolactone, being the temperatures used well above its boiling temperature (96-97°C). To follow the progress of the reaction, samples were taken every hour and subsequently analysed by a hot stage microscope (see 3.6). These were also weighed before and after a 1 hour treatment in a vacuum oven at 120°C in order to evaporate the unreacted caprolactone. The results were used to determine the time required to reach a constant degree of conversion. Finally, titrations (see 3.5.1) were performed on final products to determine the reaction yield.

Mixtures with two different compositions were prepared, taking into account the molecular weight difference of the two components, to achieve respectively 25 and 100 % reaction of the acid groups

The first composition was a 50/5 weight ratio of AC 5120/caprolactone, giving a molar ratio 1/0 6. As the functionality of AC 5120 is equal to 2.1, about a quarter of the total acid groups of the functionalised polyethylene were expected to react with ε-caprolactone. The reactants were first heated and stirred at 115°C for 7 hours and 40 minutes. Then the temperature was raised to 160°C, the condenser removed to evaporate the unreacted caprolactone and the mixture was stirred for 2 hours and 30 minutes.

A second composition, 50/20 AC 5120/caprolactone, was chosen in order to increase the extent of reaction of the acid groups react with caprolactone. In this case every acid group has the possibility to react with more than 1 molecule of caprolactone, being the molar ratio AC 5120 to caprolactone equal to 1/2.4 . The mixture was heated at 115°C and continuously stirred for 6 hours and 30 minutes. Then the temperature was risen to 160°C and the sample stirred for 8 hours without the condenser to remove the excess caprolactone. The loss of weight was again 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 (see 3.5.3).

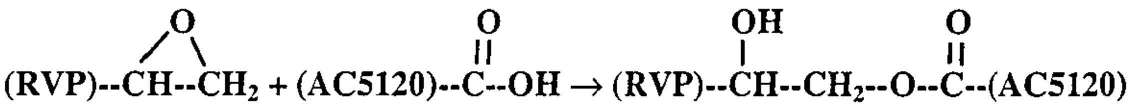
The miscibility of caprolactone with Epikote 828 was verified by producing 50/50 mixture at room temperature This was to establish that the chain extension carried out on the polyethylene is able to enhance its solubility in the epoxy resin.

Mixtures with the two caprolactone modifications of AC 5120 and Epikote 828 at 50/50 weight ratio, were prepared and placed in an oven at 115°C for 10 minutes and 2 hours for the case of AC 5120-caprolactone (50/5)/Epikote 828, and only for 10 minutes for the case of AC 5120-caprolactone (50/20)/Epikote 828.

The hardener HHPA was added to two mixtures of AC 5120-caprolactone/Epikote 828 previously prepared as described above. The resulting mixtures, with composition AC 5120-caprolactone/Epikote 828/HHPA 10/70/20, were heated at 115°C for 10 minutes.

3.2.2) Reactions with Monofunctional Epoxy Modifier

The functionalised polyethylene AC 5120 was also modified with a monofunctional epoxy resin, Eurepox RVP. The chemical reaction occurring between RVP and AC 5120 is shown below:



$$\text{(RVP)--}\overset{\overset{\displaystyle O}{/\ \backslash}}{\text{CH--CH}_2} + \text{(AC5120)--}\overset{\overset{\displaystyle O}{||}}{\text{C}}\text{--OH} \rightarrow \text{(RVP)--}\overset{\overset{\displaystyle OH}{|}}{\text{C}}\text{H--CH}_2\text{--O--}\overset{\overset{\displaystyle O}{||}}{\text{C}}\text{--(AC5120)}$$

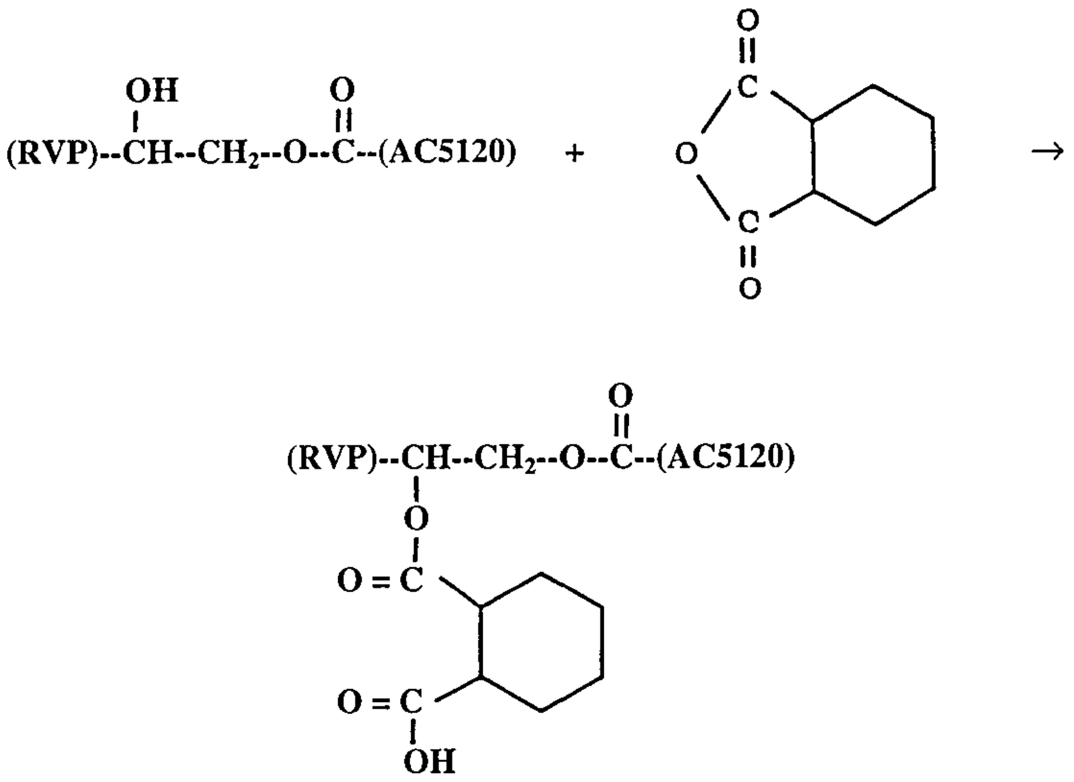
i.e. each carboxylic acid group from AC 5120 produces a hydroxyl group, through chemical reaction with RVP.

The composition chosen was 69 8/30 2 weight ratio for AC 5120/RVP, corresponding to the calculated stoichiometric amounts with 5% in excess of RVP, to ensure that each acid group in the polyethylene had the possibility to react with one molecule of RVP.

The two components, pre-weighed in a glass flask, were placed in an oil bath and heated at 140°C for 9 hours with continuous stirring A flow of nitrogen was passed on the surface of the sample to prevent oxidation, while a water condenser was used to avoid any evaporation of the components from the flask. Again, the progress of the reaction was followed by taking small amounts of mixture every hour and subsequently examined them in hot stage microscope (see 3.6). To complete the reaction, the sample sealed in the flask, was placed in a oven at 90°C for 12 hours

Mixtures of AC 5120 modified with RVP, at 25, 50 and 75 wt %, and the two epoxy resins, Epikote 828 and CY 179, were prepared and heated at 115°C for 10 minutes and 3 hours.

To increase the solubility of modified AC 5120 in the epoxy resins, further reactions were carried out to transform the hydroxyl groups into carboxylic acid groups, being these more reactive with epoxy end groups At the same time the telechelic extensions were expected to increase further the miscibility. To achieve this, the AC 5120 modified with RVP was allowed to react with HHPA at molar ratio of 1:1 (+ 10% excess), corresponding to a composition of 80 wt % AC 5120-RVP and 20 wt % HHPA. The reaction is expected to follow the scheme below:



Another advantage that arises from this type of modification is the elimination of the need to remove any residual (unreacted) anhydride from the mixture, as it would subsequently act as a hardener for the epoxy resin.

To produce the above modification, the components were again pre-weighed in a flask and placed in an oil bath at 140°C for 6 hours. During this time, they were stirred frequently by hand and samples were taken to be examined in the hot stage microscope (see 3 6). A flow of nitrogen on the surface of the sample and a water condenser were used as in the previous experiments.

To this mixture was added at 115°C Epikote 828, both alone and with HHPA. For comparative studies with ternary mixtures previously examined, were also prepared mixtures of anhydride extended AC 5120-RVP with CY 179 and HHPA. The heating time used to prepare the mixtures was 10 minutes in all cases.

To accelerate the chemical reaction between AC 5120 and RVP, 1.0 and 1.5 wt % triphenylphosphine (TPP) catalyst was added to each mixture 69 8/30.2 AC 5120/RVP. The reaction was carried out in the same conditions described above. To the final mixture was added a quantity of HHPA as in the previous case. To determine the time required to reach the maximum conversion of all the reactions described, a titration procedure was again employed Binary and ternary mixtures were realised at 115°C with the addition of Epikote 828 and or HHPA.

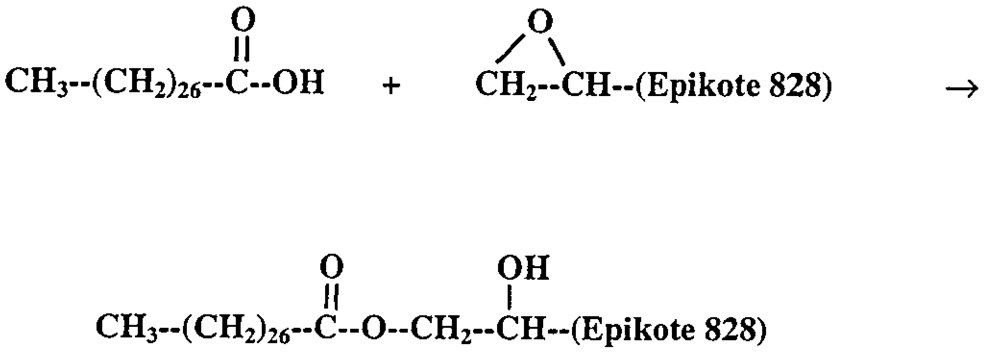
Finally, the adduct of AC 5120 with RVP was mixed at 140°C with the hardener MNA using the same procedure as for HHPA. The composition used, (AC 5120/RVP 69 8/30.2)/MNA 77.9/22.1, was chosen in order to permit the reaction of each OH group of modified AC 5120 with a molecule of MNA with a 10% excess of MNA Titrations were again employed to follow the progress of the reaction. Binary and ternary mixtures of AC 5120-RVP with MNA were produced at 115°C to be compared with similar mixtures with HHPA

3.3) Modifications of Epoxy Resin Epikote 828 with Montanic Acid.

The possibility of reacting montanic acid with an epoxy resin to improve its miscibility with polyolefins, has previously been explored at IPTME (118). The reaction of montanic acid with epoxy resin was used to produce a chain extension at the two ends of the resin. In this way it was possible to obtain an ABA oligomer, having the two ends miscible with the polyolefin.

In the present study it was thought to use the same chain extension with montanic acid using the resin Epikote 828, as it was expected that the montanate chains would solubilise into the ethylene acrylic acid copolymers used as modifiers. A further increase in level of solubilisation would be achieved using AC 5120 modified with caprolactone, monomeric and oligomeric units being totally miscible with Epikote 828

The reaction between Epikote 828 and montanic acid was carried out in a flask, placed in an oil bath, heated at 150°C for 9 hours and continuously stirred. The reaction between montanic acid and Epikote 828 is expected to follow the scheme below:



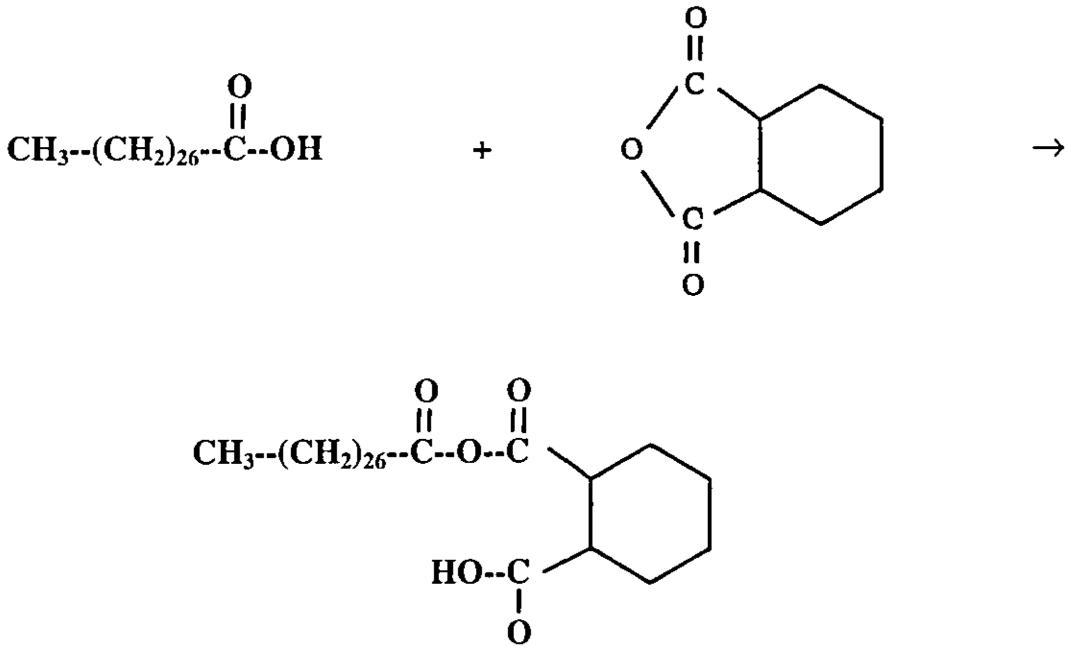
The composition was 6.6/1 weight ratio of Epikote 828/montanic acid, equivalent to 1 mole montanic acid for every 8 moles of Epikote 828, i.e. the maximum of 1 in 16 epoxy groups of Epikote 828 is expected to react with montanic acid. In this way the solubility of AC 5120 in Epikote 828, could be increased without decreasing appreciably the number of epoxy groups necessary to carry on the curing process. The progress of the reaction was again monitored by a titration procedure.

A 75/25 mixture of AC 5120/montanic acid was also prepared by heating the components at 115°C for 10 minutes, in order to verify the miscibility between the components.

Finally the Epikote 828 modified with montanic acid was mixed in composition 50/50 with AC 5120, both by itself and in the modified forms with caprolactone.

3.4) Reaction of HHPA with Montanic Acid.

Examinations in the hot stage microscope suggested that HHPA by itself or in mixtures with epoxy resins or acrylic acid copolymers could be transformed from the cis-form to the trans-form. The possibility to overcome this transformation was envisaged by forming a eutectic mixture with montanic acid. It was thought that the two could form strong physical interactions or could even chemically react to form a mixed acid/anhydride system, as shown below:



HHPA/montanic acid mixtures, at 90/10, 80/20, 70/30, 60/40 and 50/50 weight ratios, were heated together in an oven at 115°C for 10 minutes and 1 hour.

The wide range of compositions were chosen to determine the lowest content of montanic acid at which the transformation of HHPA from the cis- to the trans-form could be prevented. From molecular weight calculations, in the case of the mixture with only 10% w/w montanic acid, only 1 molecule of HHPA in 25 could react with montanic acid. On the other hand, 1 molecule of HHPA in 11 can react in the mixture with 20% of montanic acid and 1 in 3 of the same when the montanic acid content is 50 %.

The introduction of montanic acid, especially at low concentrations, was expected to increase also the miscibility of Epikote 828 with acrylic acid functionalised polyethylene in the presence of HHPA as hardener. For this reason, binary mixtures of HHPA with AC 5120, unmodified or modified with RVP, and with Epikote 828, and ternary mixtures with both unmodified, or modified, AC 5120 and Epikote 828, were prepared in different compositions using a heating time of 1 hour for binary blends and 10 minutes for ternary mixtures.

3.5) Characterisations of Pure Materials and Reaction Products.

The mixtures produced were characterised by a series of tests to follow the progress of modification reactions and, whenever possible, also to determine the level of miscibility between components. For comparison the same tests were performed also on the pure materials used.

3.5.1) Acid Titration.

In order to calculate the residual acid groups in the products of the reactions and, therefore, to follow the progress of the reactions, acid number measurements were made on the different modifications of AC 5120 and on Epikote 828 reacted with montanic acid. The samples were analysed at the beginning of each reaction and at intermediate times in order to calculate the time necessary to reach the maximum degree of conversion. Titration experiments were performed also on the pure materials, i.e. AC 5120, Epikote 828, RVP and montanic acid as controls.

Once verified that all the samples were soluble in a mixture of 50/50 by volume of xylene/DMF, the samples were dissolved in this solvent mixture at about 85°C, and kept at this temperature to prevent precipitation during titration. Acid number determinations were then made using alcoholic KOH at two different concentrations to check the reproducibility of the test; 0.01M and 0.05M, using phenolphtalein as indicator, whose colour changes from colourless (acid) to pink (alkali). During the titration the pH values and temperatures of the solutions were recorded by an electrode, immersed in each solution, connected to a digital pHmeter. Two measurements were made for each sample using the two alcoholic solutions of KOH, and the results with each solution averaged and compared.

3.5.2) Molecular Weight of the Modified Copolymers.

The molecular weight distributions of the three polyethylenes were determined using high temperature GPC procedure in the laboratories of RAPRA Technology Ltd. The procedure of the analysis was as follows:

Solutions were prepared by adding 50 ml of boiling solvent to 50 mg of sample and gently boiling for 20 minutes. A part of each solution was filtered through a glass fibre pad at 160°C and the filtered solutions were re-heated to near boiling immediately prior to injection.

The chromatographic conditions were:

Columns : Pl gel 2 x mixed gel-B, 30 cm, 10 μm
Solvent 1,2 dichlorobenzene, with antioxidant
Flow-rate : 1.0 ml/min (nominal)
Temperature : 140°C (nominal)
Detector : refractive index measuring device

Each solution was run in duplicate The GPC system used for this work was calibrated with polystyrene and a nominal correction was used to allow for the diference in molecular weight of the monomeric units between styrene and ethylene.

For the sample AC 5120 the analysis was repeated on a different occasion to check the reproducibility of the GPC technique

In the case of AC 5120 modified with caprolactone, the determination of the molecular weight distribution was performed to obtain an indication of the type of reactions occurring between the components It is possible, in fact, that instead of the more desirable unitary grafting, in which one molecule of caprolactone reacts with one acid group of AC 5120, polymerisation reactions may occur, with caprolactone molecules reacting together to form oligomeric chains.

3.5.3) Differential Scanning Calorimetry of Uncured Mixtures

Differential Scanning Calorimetry (DSC) was used to determine and compare thermal properties of the materials used and of the mixtures prepared. A

Du Pont 910 DSC and a Mettler TA 4000 DSC were used, both operating in nitrogen atmosphere, to avoid oxidative degradation of the specimens, and both equipped with a controlled cooling system. The specimens prepared were of about 10 mg in weight and were enclosed in aluminium pans, closed by lids but not sealed. All the experiments were performed by heating the samples from -20°C to 200°C (i e. well above the melting point of the materials) at a heating rate of 20°C/min and kept for 3 minutes at the maximum temperature before they were cooled also at 20°C/min down to room temperature. The DSC instrument was connected to a computer and the analysis data elaborated by a software which printed directly all the required parameters, such as transition temperature and peak areas

3.6) Miscibility Studies by Hot Stage Microscope.

The miscibilisation of the epoxy resins and the ethylene acrylic acid copolymers was the first hurdle to overcome in order to assure an effective toughening of the resin. The mixtures prepared with only Epikote 828 and each of the three polyethylenes were immiscible, i e. gave a cloudy appearance even at temperatures well above the melting point of the polyethylenes The miscibility was consequently studied using a Reichert optical microscope equipped with an hot stage device and a Mettler FP52 temperature controller This apparatus enables microstructural changes to be observed as a function of temperature and time Any sample to be examined was first melted on a hot plate at about 115°C and a droplet of the melted mixture was then squeezed between glass slides.

The hot stage microscope was then used to determine both the approximate melting point of the samples and the temperature at which miscibility took place, i.e. above the melting point of the crystalline phase. For the latter experiments all the samples analysed were heated at 10°C/min up to

250°C or until miscibility had been reached The samples were then cooled at a cooling rate of 3°C/min to room temperature. Polarised light was used both in the heating and in the cooling cycles to determine the melting and the crystallisation temperatures. Micrographs were also taken at different temperatures in both the heating and cooling stage to record the thermal transition events

In a few cases the miscibilisation 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 (see section 3.7 for details).

3.6 1) Phase Diagrams of Unmodified and Modified Mixtures.

In the hot stage microscope analyses were recorded the temperature at which the disappearance of dispersed droplets took place during the heating stage, and then the temperature at which precipitation of one of the phases occurred on subsequent cooling. The magnitude of the temperature difference between solubilisation in the heating stage and subsequent precipitation in the cooling stage provided an indication of the diffusion rate of the two components. Micrographs were also taken to record the events; from them ternary diagrams were constructed to identify the miscibility region. The maximum temperature for the observations was 250°C, as this was considered to be the maximum practical temperature at which curing of the systems could be carried out

3.7) Particle Size Analysis of Uncured Mixtures.

To analyse better the effect of the chemical modifications on mixtures of AC 5120/Epikote 828 50/50, a study of dimensions and shapes of the second phase droplets was carried out.

Four 50/50 mixtures were studied: AC 5120/Epikote 828; [AC 5120-graft-caprolactone (50/20)]/Epikote 828; AC 5120/[Epikote 828-graft-montanic acid (6.6/1)]; and [AC 5120-graft-caprolactone (50/20)]/[Epikote 828-graft-montanic acid (6 6/1)]. The samples were placed in the oil bath at 130°C and stirred at a constant rate for 1 minute Then a droplet of sample was quickly taken, poured on a glass slide, placed on a hot plate at 140°C, and covered with a glass slip. Analysis in the hot stage microscope was carried out, heating each sample at 10°C/min up to 120°C and holding it at this temperature for 5 minutes. Micrographs were taken before and after the isothermal step to record any change in droplets' shape and dimensions. The samples, then, were allowed to cool to room temperature at 3°C/min

Using the hot stage microscope the kinetics of the solubilisation of the components of the mixtures were also studied 50/50 mixtures of Epikote 828 with AC 540 and AC 5120 respectively were used for this purpose. The two mixtures were first heated in an oven at 115°C for 24 hours, for the case of AC 540, and 6 hours, for the case of AC 5120. These thermal treatments were carried out to ensure that all chemical reactions were completed prior to being examined for miscibility. The samples were then placed in the hot stage at different constant temperatures, above the melting point of the polyethylene component. Photographs were taken at different time intervals to monitor the decrease of the dimensions of the dispersed droplets as function of time

Two temperatures were chosen in the case of the AC 540/Epikote 828 50/50 mixture, respectively 110°C and 160°C. The first was considered to be probably too low for complete solubilisation of the dispersed phase even after long time; while the second temperature was considered to be high enough to achieve a fairly rapid solubilisation. For the mixture AC 5120/Epikote 828 50/50 the temperatures chosen were 110°, 130° and 160°C.

3.8) Cured Mixtures of Unmodified and Modified Systems.

To analyse the possible differences in crosslinked systems due to the introduction of ethylene acrylic acid copolymers and their chemically modified products, a series of formulations were cured according to the conditions and procedures described below The thermal and morphological properties of the cured systems were then determined.

3.8.1) Formulations and Curing Procedures.

In Appendix 7.2, Tables 1 to 5, are reported the details of the formulations of the cured systems examined.

Different control samples were first produced to analyse the effect of a) type of hardeners (HHPA and MNA); b) amount of hardener, c) concentration of catalyst; and d) curing and post-curing temperature. The same effects were also examined on the modified samples, obtained by dissolving in the liquid resin Epikote 828 different contents of the three unmodified polyethylenes or the modified AC 5120, i.e. previously reacted with RVP (with or without TPP) and HHPA In some formulations (all those reported in Tables 1, 2, 4 plus M1, M3, R1 and R3) the quantity of the hardener was chosen to give a total amount of acid from HHPA (or MNA) and the olefin oligomer, equal to the amount of acid present in the hardener used in the control formulations, i e 80 parts per hundred of epoxy, which is the amount typically used in commercial products Additional formulations (M'2, M'3, R'2 and R'3) were also produced with a constant amount of HHPA (i e. 80 parts per hundred) to monitor possible reductions in Tg through plasticisation due to the presence of dissolved olefinic phase. In other formulations (K1, K2 and K3) the effects of introducing small amounts of the catalyst TPP in the mixtures during the curing process was studied and compared to systems with similar composition.

Two curing temperatures were selected, respectively 115°C and 60°C. The first is above the melting temperature of the functionalised polyethylene (Tm≈ 90°C); while the second temperature was expected to induce the precipitation of oligomeric modifier through crystallisation prior to curing ensuring the formation of two-phase cured products

The schedule of the curing cycle was·

a) Epikote 828 was mixed with different amounts of ethylene acrylic acid copolymers or modified AC 5120 and placed in an oven at 115°C for 30 minutes, to ensure that physical solubilisation took place

b) For the case of mixtures K1, K2 and K3, to ensure that the reactions between modifier and epoxy resins were completed, TPP was also added and the mixtures were placed in the oven at 115°C for 5 hours.

c) The hardener was added to all the mixtures at 115°C, stirred to dissolve the components and then placed in a vacuum oven at 115°C for 30 minutes, in order to remove air bubbles.

d) The catalyst BDMA was added to the mixtures and quickly stirred. This was the crucial point of the process, because the mixtures had to remain in the melt state and to avoid crystallisation and separation of ethylene acrylic acid copolymers from the mixtures and at the same time to prevent crosslinking during mixing

e) Each mixture was cast in Teflon moulds (60 x 12 x 2.5mm, to produce specimens used in dynamic mechanical analysis and flexural tests; 80 x 10 x 4mm for fracture toughness and Charpy impact tests) and cured in an oven at 115°C for 6 hours and at 60°C for 40 hours, respectively, except for the samples containing a larger amount of BDMA (5 parts) which were cured at 60°C for 24 hours and subsequently at 115°C for 4 hours

f) Finally post-curing was carried out in an oven at 150°C for 3 hours followed, in some cases, by 1 hour post-curing stage at 180°C.

The cured samples were allowed to cool to room temperature and then removed from the moulds

In Table 5 is also reported the composition of a sample containing 10 parts of CTBN liquid rubber, prepared, cured and post-cured as previously described. It was used as reference in order to assess the efficiency of a traditional toughening agent in the systems analysed

Additional samples containing an amount of RVP equal to that present unreacted in some of the previous samples containing modified AC 5120 and calculated from the conversion degree of the reaction between AC 5120 and RVP, with or without TPP, were also prepared and cured following the same procedure as before. The compositions are reported in Tables 6 and 7

3 8 2) DSC Analysis on Cured Samples

Thermal analysis was carried out on the cured systems produced using a Du Pont 910 DSC or a Mettler TA 4000 DSC The procedure was the same as that reported in section 3 5 4 A first heating cycle from -20°C to 200°C at 20°C/min was followed by a cooling cycle at 20°C/min to room temperature, after a 3 minutes isotherm at 180°C. Since phase separation occurred in most of the systems containing ethylene acrylic acid copolymers, causing the polyethylene phase to migrate to the surface, the thermal analysis in such cases was carried out in different zones of the samples, i e. at the surface and in the middle

3.8.3) SEM Examinations of Cured Samples.

Morphological studies were performed on the cured systems using scanning electron microscope (Cambridge Stereoscan 360 SEM).

The samples to be analysed were obtained by cooling the cured specimens of different formulations keeping them in liquid nitrogen (-196°C) for about 5 minutes. They were then quickly removed and broken to produce a brittle fracture. The samples were fixed on the appropriate stubs and the fracture surface of each sample was coated with a gold-palladium alloy, using vacuum coating techniques, in order to produce a conductive surface suitable for SEM examination.

The SEM micrographs were subsequently used to analyse morphology, fracture characteristics, particle size and volume fraction of the dispersed phase.

3.9) Evaluation of Mechanical Properties.

3.9.1) Dynamic Mechanical Analysis.

Dynamic mechanical tests were carried out on some of the control cured samples as well as on modified systems, using a Du Pont 983 DMA System instrument. In it a sample is clamped and subjected to flexural deformations while a sensor detects its response to the applied forces. From this, the machine is able to calculate the viscoelastic properties of the material: storage modulus (G'), loss modulus (G'') and tan δ.

To determine the dynamic moduli (G' and G'') at room temperature, first isothermal tests at 25°C were performed at a frequency of 1 Hz and at an amplitude of oscillation of 0 25 mm for 5 minutes. Dynamic tests were then performed in the temperature range 25°C to 160°C at a frequency test of 1 Hz, with an amplitude of 0 30 mm and at an heating rate of 3°C/min.

3.9.2) Flexural Tests on Cured Samples.

Flexural strength, modulus and strain at break of some of the cured specimens were measured at room temperature using an Instron tensile testing machine equipped with a 5 kN load cell A three-point bending system was used and the crosshead speed was 10 mm/min. At least five specimens were tested for each formulation chosen.

The specimens used for the flexural tests had the geometry shown in Figure 3.1; the span (S) to thickness (d) ratio used was 16:1, according to ASTM D 790-92 Flexural strength, flexural modulus and strain at break were calculated directly by the software of the Instron system.

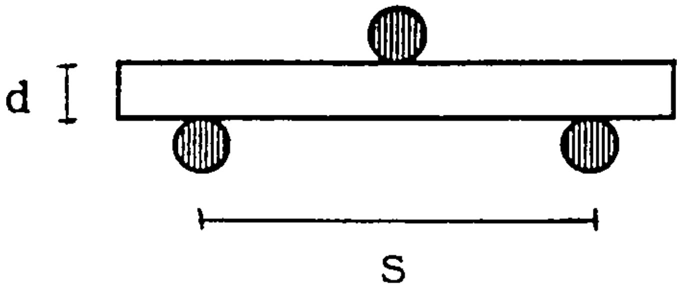


Figure 3.1: Flexural test, 3-point bending specimen geometry.

3.9 3) Fracture Toughness Tests

The same procedure was used as for the flexural tests (see 3.9.2) except that the specimen used for the fracture toughness tests was a single edge notched specimen and the specimens were loaded edge-wise rather than flat-wise. The geometry of the specimen is shown in Figure 3 2 A 1 kN load cell was chosen, while the span (S) to width (W) ratio used was 4·1, according to ASTM D 5045-93.

The notch was produced by means of a saw at the centre of each specimen across the width to depths approximately of 3 to 5 mm. At least 3 specimens were prepared for each notch length A small cut at the tip of the slits was made with the aid of a sharp razor blade The total length of the notch (a) was measured with the aid of an optical microscope and a graduated ocular.

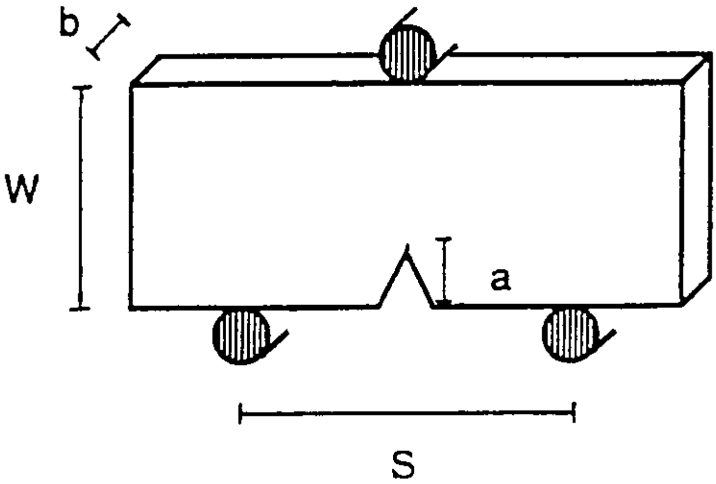


Figure 3.2: Fracture test, 3-point bending specimen geometry.

The critical stress intensity factor, K_c, was calculated as the slope of the straight line obtained by plotting P against $(BW^{1/2})/Y$, where P is the load at fracture, B the thickness of each sample, W the width and Y is the compliance calibration factor, which is a function of the crack length to width ratio (a/W) and can be obtained from appropriate tables (119). The intercept of the straight line must be zero, i.e. the line passing through the axes origin.

The critical strain energy release rate, G_c, on the other hand, was calculated using the formula:

$$G_c = \frac{K_c^{\ 2}}{E'}$$

where E' is the effective modulus, corresponding to the Young's modulus under plane stress conditions, i.e. for very thick specimens. (It was obtained for each formulation from flexural tests, as reported in 3.9.2).

The impact strength of unnotched specimens was also determined by Charpy impact test, according to ISO 179-1992 E. Rectangular specimens of control sample CL as well as sample with modified AC 5120, i.e. M1 and M'2, all cured at 115°C, were analysed using a span to width ratio of 4:1. The Charpy impact strength (a_{cU}) was calculated as the ratio between the impact energy effectively absorbed in breaking the specimen, i e. the energy consumed to propel the sample was measured and subtracted from the total energy recorded, and the original cross-sectional area of the same specimen:

$$a_{cU} = U/A$$

At least 5 samples of each formulation were tested and the results averaged.

4. RESULTS

4.1) Miscibility of Uncured Epoxy Systems.

The results of the hot stage microscope analyses performed on pure materials and on all the mixtures prepared are reported below.

4.1.1) Binary Mixtures.

In Table 8 (Appendix 7.2) are summarised the results of the miscibility studies for the binary mixtures AC 6702/Epikote 828 subjected to two different heating treatments carried out in oven. For each mixture, as well as for pure AC 6702, at least two experiments were performed to check the reproducibility of the results. In Table 8 are reported the average values obtained from the different experiments.

The first point to note is that the melting and crystallisation temperatures of the polyethylene phase seem to have not been affected very much by the presence of the epoxy resin, even in the mixtures heated for 24 hours in the oven.

Regarding the miscibilisation and phase precipitation temperatures, it is noted that the mixtures heated for only 10 minutes at 115°C are completely immiscible, at least up to the maximum temperature of 250°C used in the experiments. This means that at this high temperature it was still possible to discern the presence of droplets of the dispersed phase. In the case of mixtures heated for 24 hours at 115°C, on the other hand, in some cases it was possible to observe the occurrence of solubilisation, albeit this may have occurred at temperatures well above 200°C. The mixtures with the lower solubility temperatures are those with intermediate polyethylene content, i.e. 25% and 50%. The phase separation temperature on cooling is also very high and not very different from the corresponding solubilisation temperature It has been noted the tendency of the small droplets to coalesce in the heating stage at temperatures higher than 130°C, remaining segregated from the mixture, and to separate again in small particles on cooling.

These results show clearly the difficulty to reach complete miscibility of oxidised polyethylene and Epikote 828. This result is in accordance with the low functionality value (~ 0.26) for the AC 6702 (see Table I and Appendix 7.1). This means that on average only one chain in four contains an acid group capable of reacting with the epoxy resin.

Because of the difficulty to solubilise such a type of system, it was decided not to consider it for curable epoxy formulations, as it would be impossible to reach very high temperatures, necessary for the miscibilisation, when the hardener and the catalyst have to be added to cure the system.

The results of miscibility studies on mixtures with the ethylene acrylic acid copolymer AC 540 and the two epoxy resins, Epikote 828 and CY 179, are summarised in the Table 9 and 10 (Appendix 7.2), respectively, showing the average values of at least two experiments for each sample. The behaviour of the mixtures heated in an oven at two different heating times is compared with that of AC 540 by itself.

The melting and crystallisation temperatures of the mixtures were slightly lower than those of the pure AC 540, especially for the mixtures heated for 24 hours.

For the mixtures of AC 540 with Epikote 828, solubilisation of the two phases occurred much more easily than for the case of AC 6702. In fact even only 10 minutes heating in the oven at 115°C was found to be sufficient to solubilise the two components The critical solution temperature decreases when these mixtures are heated for longer times at 115°C, but never become lower than 200°C. The most miscible compositions are those containing 25, 50 and 75% of AC 540 On the other hand, those containing 90% AC 540 were immiscible up to

250°C. Furthermore the temperature of phase separation on cooling is lower in the case of the mixtures heated for 24 hours in the oven. In a few cases when the temperature is lowered, the mixtures remain homogeneous until crystallisation of the polyolefin occurs.

Solubilisation seems to be even easier for AC 540 mixtures with the cycloaliphatic epoxy CY 179. The 50/50 mixture is soluble at just above the melting point even when the mixture is heated for only 10 minutes in the oven. For the other compositions it was possible to reach complete solubilisation at temperatures not much higher than 200°C Again the effect of increasing the heating time in the oven was to improve the solubility between the two phases. For almost all the mixtures based on AC 540 and CY 179, when complete solubilisation was achieved, the system remained soluble even when the temperature was decreased, until crystallisation of the ethylene copolymer occurred. The mixtures with AC 540 were also found to show a tendency for the small droplets to coalesce together just above the melt temperature

The results are in accordance with what was expected from the higher functionality of AC 540, which was estimated to be about 1.2 (see Appendix 7.1). A higher functionality means a greater ability for the ethylene copolymer chains to react with the epoxy resin

In Tables 11 and 12 are reported the hot stage microscope results for mixtures of the other ethylene acrylic acid copolymer, AC 5120, with Epikote 828 and CY 179, respectively

In the first case mixtures heated for different periods of time in the oven at 115°C were analysed, while in the second the mixtures were heated only for 10 minutes at 115°C

Analysing first the melting and crystallisation behaviour, in both cases the melting temperatures of the mixtures seem to be not very different from that of the ethylene copolymer

The tests to determine the critical solution temperature of the mixtures with Epikote 828 showed that solubilisation occurs quite easily and the upper critical solution temperature appears to be always around 200°C, but once solubilised most of the mixture remains soluble on subsequent cooling until crystallisation of the ethylene copolymer takes place. This time the heating pre-treatments in the oven seem to have no influence on the miscibilisation temperatures of the mixtures. At temperatures above the melting point, again droplets showed the tendency to coalesce and to segregate from the mixture. In these mixtures gelation was observed after about 21 hours at 115°C for composition with 25% AC 540, increasing to 23 hours for 50/50 mixtures and 24 hours for 75/25 mixtures.

The mixtures with AC 5120 and CY 179 were found to be totally miscible at temperatures just above the melting temperature On cooling, phase separation occurred only through the crystallisation of AC 5120

The results are again in accordance with the high functionality of AC 5120, estimated to be about 2.0 (see Appendix 7 1), which allows the copolymer to react readily with epoxy resins

A confirmation of the occurrence of a greater solubility with Epikote 828 with increasing the content of acid groups in the polyethylene chains is obtained from an inspection of the optical micrographs in Figures 1, 2 and 3 (Appendix 7.3). It is known that in a binary liquid mixture, under static conditions, the dimensions of the droplets of the dispersed phase depend mainly on the difference between the interfacial tensions of the two components The lower the difference the smaller the dimensions of the droplets In accordance with this, Figures 1, 2 and 3 reveal the droplet dimensions in the order: AC 6702 > AC 540 > AC 5120, i.e. the increase of the functionality in the olefin oligomer reduces the interfacial tension between the two components and brings about a reduction in the size of the dispersed particles Since the viscosity of the three functionalised polyolefins is approximately the same, the controlling factor is the interfacial tension.

Passing to analyse the miscibility results for the mixtures of the hardener HHPA with AC 540 and AC 5120, in Tables 13 and 14 are reported the data from the hot stage microscope. For comparison the results for pure ethylene acrylic acid copolymers and HHPA, respectively, are also shown.

An unexpected behaviour of HHPA was found from the hot stage microscopy analysis. Although the disappearance of some crystals was observed to start at 40°C, the hardener seemed to reach complete melting at much higher temperatures, i.e. in the range 108-136°C. These values compare with a melting point of 32-34°C for the cis-form and 145-147°C for the trans-form. It can be hypothesised that a partial transformation of HHPA from the cis- to the trans-form takes place and that the lower melting point of the trans form could be due to the formation of a eutectic with the cis form. The poor reproducibility of the upper Tm could be due to variabilities in such eutectics.

In the mixtures with the two acrylic acid copolymers, AC 540 and AC 5120, the peculiar behaviour of HHPA that was observed in tests as a single component, seemed to become more pronounced. In all cases the melting and crystallisation temperatures of the ethylene copolymer rich phase did not differ from those of pure polymers, AC 540 and AC 5120. Few crystals, probably of HHPA, remained unmelted up to temperatures even higher than for pure HHPA. In the case of mixtures with AC 540, a first crystallisation was observed on cooling at a temperature similar to that of melting. No crystallisation of the HHPA rich phase was observed, on the other hand, in mixtures with AC 5120. For all mixtures the crystallisation of the ethylene copolymer rich phase seemed to occur at temperatures very similar to crystallisation temperature of the pure polymers, AC 540 and AC 5120

In Tables 13 and 14 are reported as solubilisation temperatures the melting temperatures of the HHPA rich phase because the mixture appeared to be completely miscible above this temperature There are also reported in brackets the temperature at which the mixture became a single phase, except for the presence of residual HHPA crystals.

On cooling, the mixtures with AC 540 seemed not to phase separate and the crystallisation temperature of HHPA phase could be considered the demiscibilisation temperature. The mixtures with AC 5120, on the contrary, did not show crystallisation of the HHPA component but phase separation was observed at temperatures not very different from those at which miscibility occurred on heating.

The mixtures of HHPA with Epikote 828 and CY 179, respectively, were also analysed with the aid of hot stage microscope; the results are listed in Table 15. The two mixtures appeared to be completely miscible above the melting point of HHPA, which in both cases was about 100°C. Moreover, no crystallisation occurred in the cooling stage, even at room temperature after long time.

4.1.2) Ternary Mixtures.

The results of the hot stage microscope analysis for the ternary mixtures of AC 540, Epikote 828 and HHPA, are summarised in Table 16.

As in the case of binary mixtures, the melting and crystallisation temperatures of the ethylene copolymer phase, are almost unaffected by the presence of the other components. Melting and crystallisation of the HHPA component, on the other hand, did not take place at all, i.e. the hardener was always found to remain dissolved in the epoxy resin.

The most striking result is the immiscibility of most mixtures; only the mixtures containing a large amount of epoxy resin were found to be semi-miscible. This means that, even if the binary mixtures with individual pairs of the three components were miscible, though only at high temperatures, the simultaneous presence of the three components reduces the miscibility of the system.

In Figures 4, 5 and 6 (Appendix 7.3) are shown the ternary mixtures of AC 540/Epikote 828/HHPA of compositions 10/70/20, 14/62/24 and 16.7/50/33.3, respectively, at 250°C It is clear that decreasing the epoxy resin content leads to a deterioration in miscibility between the different phases.

The results of the hot stage analysis for the ternary mixtures with AC 540, CY 179 and HHPA, are summarised in Table 17.

Again the melting and crystallisation temperatures of the ethylene copolymer phase are only slightly affected by the presence of the other two components and the melting and crystallisation temperatures of the HHPA component was not observed

As for the previous ternary mixtures, partial miscibility is achieved only with respect to compositions containing large amounts of epoxy resin. Miscibility in this case seems to be more difficult, in contrast to the easier miscibility observed for the binary mixtures with AC 540 and CY 179 On the mixture 33.3/33 3/33 3 was also performed an additional test to investigate the possible influence of HHPA transformation, from the cis- to the trans-form, on the miscibility of the system The mixture was heated at 145°C (around the temperature at which the HHPA transformation is expected to take place) and it was kept at this temperature for about 30 minutes Microscope observations did not show any change in dimensions and shapes of the dispersed droplets, i.e. the mixture remaining completely immiscible

In Table 18 are reported the results from hot stage microscope analysis for the ternary mixtures with AC 5120, Epikote 828 and HHPA.

The melting temperature of the AC 5120 phase was not affected by the presence of the other components Furthermore, the crystallisation temperature was found to be similar to that of the pure acrylic acid copolymer only in the case of mixtures with larger amounts of AC 5120 Melting and crystallisation of HHPA was again not observed in hot stage microscope tests

The greater propensity of AC 5120 to become miscible in Epikote 828, observed in their binary mixtures, was again revealed in ternary mixtures. In the latter, it was possible to reach total miscibility at temperatures even lower than those observed for binary mixtures of AC 5120/Epikote 828, except for the case of a low amount of acrylic acid copolymer (5% by weight). In this last case, in fact, the mixture never reaches total miscibility at reasonable temperatures even if heated at 115°C for more than 2 hours. Once solubilised, the ternary mixtures remained miscible with decreasing the temperature, until crystallisation took place.

In Figures 7 and 8 (Appendix 7.3) are shown the micrographs taken at 200°C on the systems AC 5120/Epikote 828/HHPA of compositions 5/60/35 and 33.3/33.3/33 3, respectively. In the first mixture was evident the presence of two phases, while the other system was found to be completely miscible at this temperature.

Finally, the results of the hot stage analysis for the ternary mixtures with AC 5120, CY 179 and HHPA are reported in Table 19

In this case is evident a decrease in the crystallisation temperature of the mixtures with respect to the acrylic acid copolymer by itself. It must be said, however, that on cooling only very few and small crystals were observed in the samples. An explanation for the lower crystallisation temperatures could be that it was not possible to detect the occurrence of crystallisation due to the small size of the crystallites formed.

The effect of introducing HHPA in binary mixtures with acrylic acid copolymer and CY 179 seems again to lead to a decrease of miscibility of the system The temperature at which miscibilisation takes place is always higher than that for the binary mixtures of AC 5120 with CY 179 and only partial miscibility is possible to reach for the case of mixtures containing lower amounts of AC 5120 (5% by weight) Also these systems did not show any phase separation in cooling stage before crystallisation took place.

4 1.3) Binary and Ternary Mixtures based on Modified AC 5120

The first microscopic analysis was carried out on mixtures of AC 5120 grafted with ε-caprolactone.

From the difference in weights of the samples of the two mixtures before and after the thermal treatment in the vacuum oven, it has been possible to calculate the percentage of caprolactone unreacted and in turn to have an estimate of the progress of each reaction. It was found that the mixture AC 5120-graft-caprolactone 50/5, reacted for 2 hours at 115°C under reflux conditions, reached the maximum conversion of about 75% and approached a 90% conversion when the reaction temperature was raised at 160°C and the reflux removed. For the mixture AC 5120-graft-caprolactone 50/20 it was estimated that, after a 2 hours reaction at 115°C under reflux conditions, a constant conversion of caprolactone of about 65% was reached. With increasing the reaction temperature to 160°C and removing the reflux, the conversion of caprolactone increased to about 95%. The unreacted caprolactone was completely removed by vacuum extraction of all the samples of AC 5120-graft-caprolactone before mixing with other components. Because of the incomplete reactions, the compositions of such mixtures should be considered only nominal

The results of hot stage analyses performed on some of the mixtures of AC 5120-graft-caprolactone are reported in Table 20. The two different compositions used were analysed after stirring in an oil bath at 115°C for 5 hours.

In both cases the melting and crystallisation temperatures of the mixtures were very similar to those recorded for the acrylic acid copolymer by itself, though for the mixture with the lower amount of caprolactone a first melting was also observed at a lower temperature. At about 47°C, in fact, was noted the disappearance of few and brighter crystals, with different shape from those of AC 5120.

The behaviour with respect to miscibilisation was found to be different for the two mixtures. While the mixture containing AC 5120 grafted with the lower amount of caprolactone became soluble at a high temperature and phase separated at a similar temperature on cooling, the mixture containing the higher amount of caprolactone, appeared to become soluble just above its melting point and did not phase separate on subsequent cooling until crystallisation took place.

Mixtures of AC 5120 modified with ε-caprolactone at two levels with Epikote 828 were subsequently analysed. The results are reported in Tables 21 and 22. Tests were performed on samples of AC 5120 with caprolactone reacted for different times at high temperatures, i.e 115° and 160°C. The influence of the heating time for the mixtures with Epikote 828 was also analysed. (For a better understanding compare with Table 11, keeping in mind that the effective amounts of AC 5120 in the mixtures with caprolactone are different from that in 50/50 mixture AC 5120/Epikote 828, owing to the presence of caprolactone which reduces the amount of AC 5120)

In all cases a decrease in melting and crystallisation temperatures relative to those of AC 5120 by itself was observed, an effect which was even more marked than that observed for 50/50 mixture AC 5120/Epikote 828.

For all mixtures, miscibilisation was found to be strongly affected by the reaction time, i e the miscibilisation temperature seemed to increase with increasing the reaction time, which in turn corresponds to a greater extent of reaction of the acrylic acid copolymer with caprolactone. For the mixtures containing the AC 5120 grafted with lower amount of caprolactone, the heating time used in adding Epikote 828 seemed to have had no influence on miscibilisation temperatures These mixtures appeared to become more easily dissolved than those with higher amount of caprolactone, for equal reaction time at 115°C. Finally, for almost all the mixtures phase separation was not observed on cooling Furthermore an additional test was performed on the sample AC 5120-graft-caprolactone 50/20 heated for longer time at 115°C first and then at

160°C (last row of Table 22). The mixture was allowed to reach 160°C in the hot stage device and it was kept at that temperature for 18 hours, during this time observations were made. Even after 18 hours the sample did not show miscibility but two well separate phases were always present.

In Table 23 are reported the results of the hot stage analysis on ternary mixtures obtained with AC 5120 modified with caprolactone (two compositions). The results can be compared with those in Table 18, even though there is not a perfect equivalence of compositions due to the presence of caprolactone.

Again it is observed a strong influence of the modification with caprolactone on the behaviour of the mixtures. The comparison shows that melting and crystallisation temperatures are lower than those found for the similar mixture without the modification, and crystallisation appears not to have occurred at all in the mixture with larger amount of caprolactone However, neither mixtures seem to have reached complete miscibilisation.

In conclusion, the grafting of the acrylic acid copolymer AC 5120 with ε-caprolactone does not lead to an appreciable increase in miscibility neither in binary mixtures with Epikote 828 nor in ternary mixtures with HHPA. That is to say that this modification only changes the melting and crystallisation characteristics but not miscibility.

The results of the second modification process obtained by grafting AC 5120 with a monofunctional epoxy reactant, RVP, are shown in Table 24. It reports the data obtained in the hot stage analysis for reaction products, at 140°C, of AC 5120 with RVP, in the presence or not of TPP

Melting and crystallisation temperatures were found to be slightly lower than those of the acrylic acid copolymer alone. Moreover, the most striking result is the occurrence of complete miscibility for all the mixtures just above their melting point No phase separation was observed in the mixtures on cooling until crystallisation occurred The results appear to be independent of the heating conditions and irrespective of whether TPP was used to catalyse the grafting reaction.

In Tables 25 and 26 are shown the results of the hot stage analysis for the mixtures of AC 5120, grafted with RVP, and the two epoxy resins, Epikote 828 and CY 179. These results can be compared with those in Tables 11 and 12, though the compositions are not exactly the same owing to the presence of RVP.

While there is no effect on melting and crystallisation temperature values, the modification of AC 5120 with RVP was found to have a very large effect on the miscibility characteristics. The solubility temperatures appeared to be considerably lower than those of unmodified systems, especially in the case of the mixtures with Epikote 828. Phase separation on cooling almost always took place before crystallisation and at temperatures generally lower than those at which miscibilisation had occurred on heating stage. In these experiments was also noted a delay in the occurrence of solubilisation of about 10°C in the edges of the samples with respect to the centre. In the same way, on cooling phase separation appeared to take place first in the edges and then in the centre of the samples. (The values of temperature reported in Tables 25 and 26 refers to the centre of samples).

In Table 27 are shown the results of analysis performed on mixtures of AC 5120-graft-RVP with HHPA. A comparison can be made with results in Table 14, although (due to the presence of RVP) the compositions in the two tables are not exactly the same.

Both melting and crystallisation temperatures seem to be slightly lower than those for pure AC 5120 and for mixtures AC 5120/HHPA reported in Table 14. Furthermore, the high temperatures of melting and crystallisation of the HHPA component were not observed in mixtures with AC 5120-graft-RVP.

Solubilisation was reached just above the melting point of the ethylene copolymer and no phase separation before crystallisation was observed on cooling. The heating times of the two mixtures did not seem to influence their miscibility and crystallisation behaviour.

In Tables 28 and 29 are reported the results from the hot stage analysis on mixtures of AC 5120-graft-RVP with HHPA and Epikote 828 and also with CY 179, respectively. (A qualitative comparison can be made with the data in Tables 18 and 19, respectively).

As in previous cases, a small decrease in melting and crystallisation temperatures was observed and, in certain instances, crystallisation did not take place in the cooling cycle.

With respect to the miscibilisation of the mixtures, there appeared to be no distinctly clear trends. The reaction of HHPA with AC 5120-graft-RVP seems to be effective in increasing the solubility with Epikote 828.

It appears that the modification of AC 5120 with the monofunctional epoxy resin, RVP, leads to an enhancement in miscibility of mixtures with Epikote 828 and the hardener HHPA only when HHPA has been previously reacted with AC 5120-graft-RVP, i.e. the acid groups appear to be more effective in miscibilising the epoxy resin than hydroxyl groups.

In Tables 30 and 31 are reported the results of the hot stage measurements for mixtures of AC 5120, grafted with RVP in presence of 1 part of TPP (catalyst), and Epikote 828

Comparing these results with those of Tables 11 and 25, again the melting and crystallisation temperatures appear to have not been affected by the grafting of RVP in presence of TPP. On the other hand, the presence of TPP in the reaction between AC 5120 and RVP produces a further increase in miscibility with Epikote 828. This clearly results from the higher yield of grafted RVP when the TPP catalyst is used. The heating time in the modification reaction, on the other hand, has only a small influence on solubilisation temperatures. It is to be noted, finally, that phase separation never occurred before crystallisation took place.

No mixtures of Epikote 828 and AC 5120 modified with RVP in presence of 1.5 parts of TPP were prepared since the presence of a larger amount of TPP did not produce any increase of conversion in the reaction with AC 5120 and RVP (see 4.3.1).

In Table 32 are presented the hot stage results of mixtures of AC 5120, modified with RVP in presence of 1 part of TPP, and HHPA heated at 140°C for different times. They can be compared with Tables 14 and 27

The behaviour of all mixtures, on heating as well as on cooling, is similar to that reported in Table 27, i.e. when the catalyst TPP is absent. In grafting RVP on AC 5120, the use of reaction times no longer than those required to obtain the maximum conversion can improve miscibilisation between the phases.

In Tables 33 and 34 are reported the results of hot stage analysis performed on mixtures of AC 5120, modified with RVP in presence of 1 part of TPP and, then reacted with HHPA for different heating times, with Epikote 828 and HHPA.

Due to the absence of crystals, it was not always possible to record the melting and crystallisation temperatures In few cases, melting points similar to those observed in Table 14 for HHPA rich phase were found (see Table 34).

A comparison with data in Tables 18 and 28 suggests that a certain increase in miscibility in ternary blends can be obtained only when the heating times used were those strictly necessary to obtain the maximum conversion in both reactions, i e AC 5120+RVP+TPP and (AC 5120-graft-RVP/TPP)+HHPA. At long reaction times the solubilisation with epoxy resin became always more difficult, possibly due to undesirable reactions of unreacted catalyst TPP with Epikote 828 and or HHPA, when longer heating times were employed, or possibly because the reaction with HHPA was not complete at short times. As observed for other ternary mixtures, the miscibilisation temperature decreased with increasing the content of Epikote 828. It is noted that in these cases phase separation took place almost always as a result of crystallisation.

In conclusion, the modification of AC 5120 with RVP appears to have been effective in solubilising Epikote 828 at lower temperatures, especially when the modification was carried out in presence of TPP. On the other hand, the addition of HHPA in mixtures of grafted AC 5120 with Epikote 828 leads, in some cases, to an increase of solubilisation temperatures, even with respect to the mixtures containing not modified AC 5120. It is also important to note that an appropriate heating time was required to prepare the mixtures, i.e. sufficiently long to reach a final maximum conversion.

An indication of the effect of the nature of the hardener on the solubility in (AC 5120-graft-RVP/TPP 69.8/30 2/1)/Epikote 828 blends can be obtained from an analysis of the data in Table 35, where are reported the results from hot stage tests performed on mixtures of MNA hardener with modified AC 5120 and/or Epikote 828.

The 50/50 mixture Epikote 828/MNA is completely miscible at room temperature.

Comparing the melting and crystallisation temperatures of a (AC 5120-graft-RVP)/MNA mixture with those of the analogous mixtures with HHPA, Table 32, it can be seen that all the transition temperatures are similar, although always slightly higher, than those of mixtures with HHPA.

A similar behaviour for the two mixtures is also observed with respect to miscibilisation, which always occurs just above the melting point, and phase separation, which does not take place before crystallisation.

The ternary mixtures of Table 35 can be compared with those of Table 33.

Melting temperatures are again similar to those of mixtures containing HHPA. It was often difficult to record these temperatures due to the small dimensions of the crystals, which could probably also explain the apparent absence of crystals on cooling

All the mixtures with MNA were completely immiscible, even at very high temperatures.

In conclusion, the use of MNA hardener in modified AC 5120/Epikote 828 blends does not improve miscibilisation. On the contrary, it leads to a more difficult solubilisation process.

In Table 36 are shown the data from the hot stage analysis of mixtures montanic acid/AC 5120 and montanic acid/Epikote 828, together with respective controls.

Montanic acid appears to be completely miscible with AC 5120 just above its melting point and with Epikote 828 at a slightly higher temperature, however phase separation on cooling takes place only for the mixture with Epikote 828

In Table 37 are shown the results of the analysis for the mixtures of AC 5120 with montanic acid modified Epikote 828

A comparison with Table 11 (keeping in mind the difference of composition due to the presence of montanic acid) shows that the crystallisation and melting temperatures are closer to those of pure AC 5120 than to the 50/50 mixture of AC 5120/Epikote 828 The solubilisation occurs at temperatures always lower than those observed for the mixture without montanic acid, and phase separation on cooling does not take place until crystallisation occurs. During the heating stage again was noted a delay of the edges of each sample in reaching completely solubility relative to the centre This is probably due to the thermal lag, i e the temperature in middle is always higher than at edge. The heating time seems to have only a small influence on the behaviour of mixtures.

In Table 38 are shown the data obtained from the hot stage analysis performed on mixtures of AC 5120, modified with ε-caprolactone at two concentrations, and Epikote 828 modified with montanic acid.

It appears clear that the modification of AC 5120 with caprolactone leads to a decrease of miscibility of the mixtures, reaching complete solubility at temperatures even higher than those for 50/50 mixture AC 5120/Epikote 828 (Table 11).

A comparison of miscibility data of all the 50/50 mixtures AC 5120/Epikote 828, modified or not, is presented in Table 39. Here are reported the values of the solubilisation and phase separation temperatures, taken from Tables 11, 21, 22, 25, 30, 37 and 38, for mixtures kept at high temperatures for the time required to assure the completion of all the chemical reactions.

The grafting of caprolactone to AC 5120 leads, in all cases, to a decrease in miscibility, even when montanic acid is used as modifier for Epikote 828. The most effective modification appears to be the reaction of AC 5120 with RVP in presence of TPP, although by modifying Epikote 828 with montanic acid some improvements in the solubility of acrylic acid copolymer in epoxy resin are also obtained.

In Table 40 are reported the results of the analysis performed on mixtures of HHPA with montanic acid.

It appears that the introduction of small amounts of montanic acid is able to prevent the undesirable transformation of HHPA from the cis- to the trans-form. All the mixtures containing amounts of montanic acid equal to or higher than 20% did not show a second melting temperature. Furthermore, these mixtures become soluble at about 100°C on heating and phase separate at similar temperatures on cooling. Since a reduction of melting and crystallisation temperatures of mixtures with respect to those of pure constituents is observed, HHPA and montanic acid could probably form an eutectic. (Therefore, their mixtures will be indicated as HHPA-e-montanic acid.)

In Table 41 are shown the results of the hot stage analysis performed on blends of AC 5120 (both modified and unmodified with RVP) with HHPA premixed with montanic acid (i e. HHPA-e-montanic acid).

A qualitative comparison with Tables 14 and 27 shows melting and crystallisation temperatures slightly lower than those measured in mixtures in which HHPA is added alone, i.e. in the absence of montanic acid

In binary mixtures with unmodified AC 5120 the addition of montanic acid to HHPA avoids the transformation of the latter from the cis to the trans-form, i.e. higher melting points are not observed (Table 14). For the mixture with AC 5120 modified with RVP, miscibilisation is reached just above the melting point, as for pure HHPA. It is noted that phase separation, on cooling, always occurs before crystallisation.

In Table 42 it can be observed that the melting and crystallisation temperatures of blends of Epikote 828 with HHPA-e-montanic acid correspond to those of montanic acid, reported in Table 40. On the other hand, a comparison with Table 15 reveals higher solubilisation and phase separation temperatures than those observed for the straight mixture Epikote 828/HHPA.

In Tables 43 and 44 are presented the hot stage results found for ternary mixtures of unmodified or modified AC 5120, Epikote 828 and HHPA-e-montanic acid, respectively. They can be compared with those in Tables 18 and 28.

While similar, or slightly lower, melting and crystallisation temperatures are observed in all cases, solubilisation seems to occur always at higher temperatures when montanic acid is added to HHPA. It is noted that phase separation takes place before crystallisation.

In conclusion, even if it is possible to overcome the transformation of HHPA to the trans-form by forming an eutectic solution with montanic acid (>20%), this modification is not effective in avoiding the demiscibilisation effect that HHPA has when added to binary blends of the acrylic acid copolymer with the epoxy resin.

4.1.4) Phase Diagrams of Ternary Mixtures.

The miscibility data of most of the mixtures studied by hot stage microscope analysis are reported as ternary phase diagrams to show clearly the location of the solubility areas.

In Figures 4.1 and 4.2 are shown the ternary diagrams for the systems with AC 540, HHPA and Epikote 828 and with AC 540, HHPA and CY 179, respectively. (The number adjacent to each composition corresponds to its solubilisation temperature.)

In both cases the trend is the same, i.e. only the mixtures with large amount of epoxy resin are semi-miscible and it is not possible to reach complete miscibility for any composition tested, though the binary mixtures are always miscible. The mixtures with CY 179 are less miscible than those with Epikote 828, even though the binary mixtures with AC 540 become miscible at lower temperatures. It can be hypothesised that miscibility of AC 540 and each of the two epoxy resins is chemically induced. When HHPA is present, this reacts preferentially with the epoxy resin and, therefore, decreases the extent of reaction of the latter with AC 540, thereby reducing miscibility.

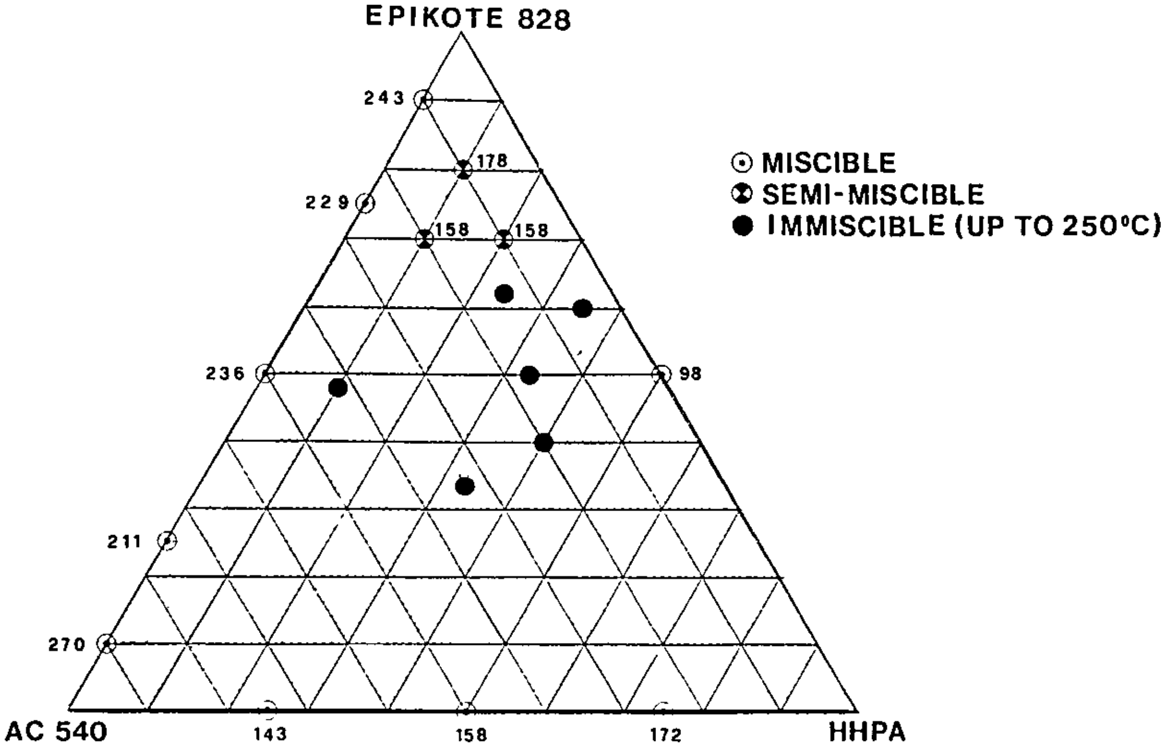


Figure 4.1: Phase diagram for the mixtures of AC 540, Epikote 828 and HHPA.

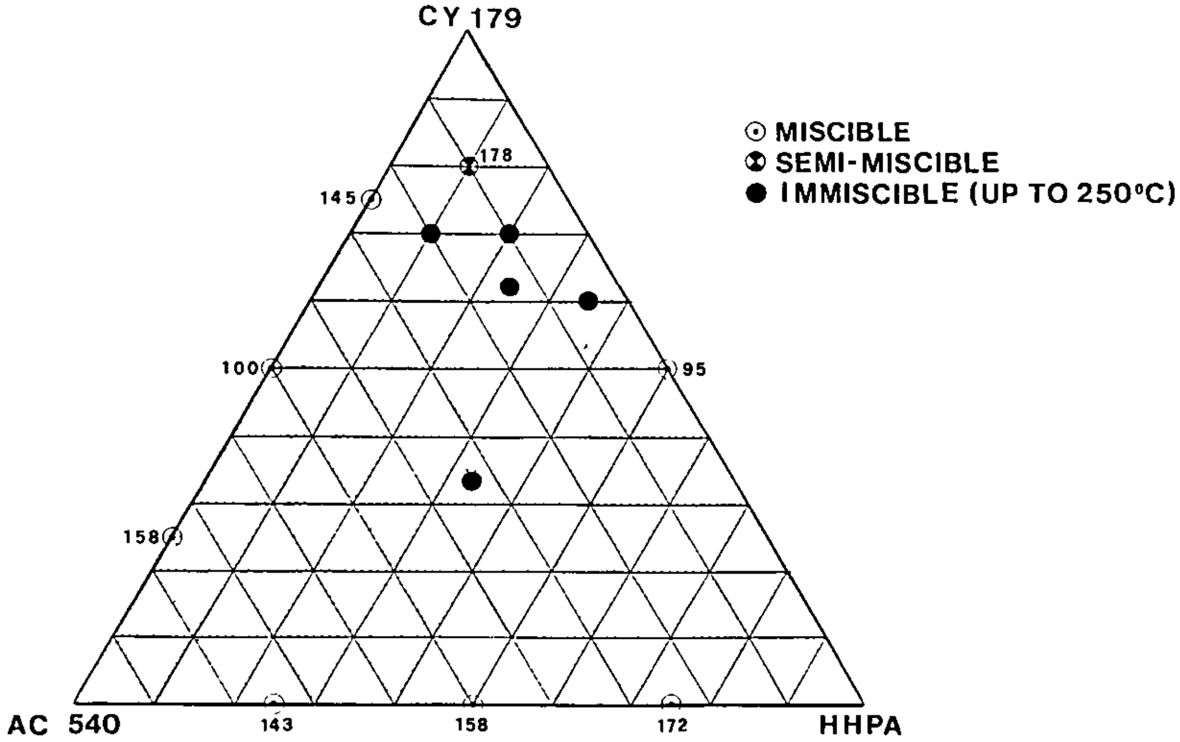


Figure 4.2: Phase diagram for the mixtures of AC 540, CY 179 and HHPA.

In Figures 4 3 and 4.4 are shown the ternary diagrams for the mixtures AC 5120 with HHPA and Epikote 828 and AC 5120 with HHPA and CY 179, respectively.

These mixtures appear to be more miscible at all compositions than those with AC 540. Almost always it is possible to reach complete solubility in both systems. This time the mixtures with CY 179 seem to be even more miscible than those with Epikote 828 showing lower solubility temperatures. In both cases, the mixture with lowest content of AC 5120, i e. 5%, is the least miscible

The diagrams in Figures 4 1 and 4.3 can be compared with that of Figure 4.5 for the system CTBN/HHPA/Epikote 828.

All the mixtures appear to be completely miscible at room temperatures or at temperatures always lower than 100°C. These results show clearly the possibility in such systems to reach solubility, i.e. the presence of HHPA does not hinder the miscibilisation between the epoxy resin and the liquid rubber.

In Figures 4.6 and 4 7 are reported the ternary diagrams for the systems containing AC 5120, grafted with ε-caprolactone at two levels, HHPA and Epikote 828. As already reported, the conversion of the reactions with caprolactone was calculated from the difference in weight as: 90% and 95% for 50/5 and 50/20 compositions, respectively.

Even with very few points in the diagrams, it is possible to have a clear indication of the influence of ε-caprolactone on solubility Comparisons with the diagram in Figure 4.3 show that the grafting with caprolactone has resulted in a large decrease in miscibility of the systems, not reaching complete solubility even with a high content of Epikote 828 Furthermore, it is noted that the decrease in solubility becomes even more pronounced when higher amounts of caprolactone have been used to modify the acrylic acid copolymer

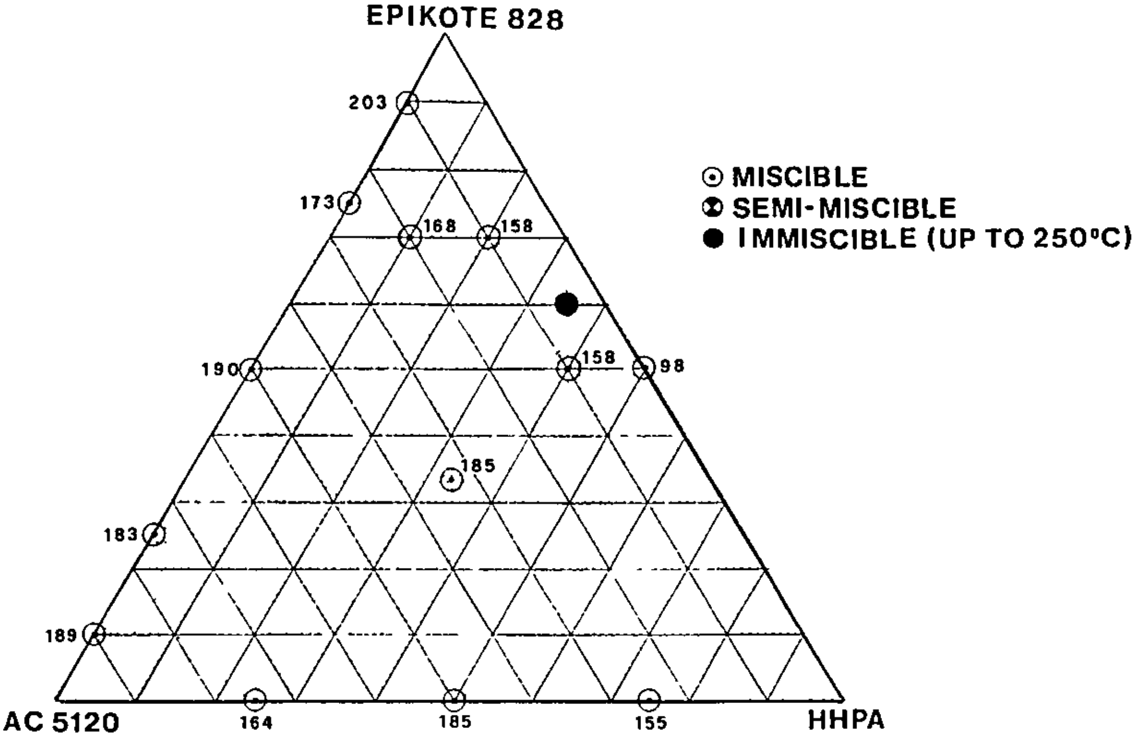


Figure 4.3: Phase diagram for the mixtures of AC 5120, Epikote 828 and HHPA.

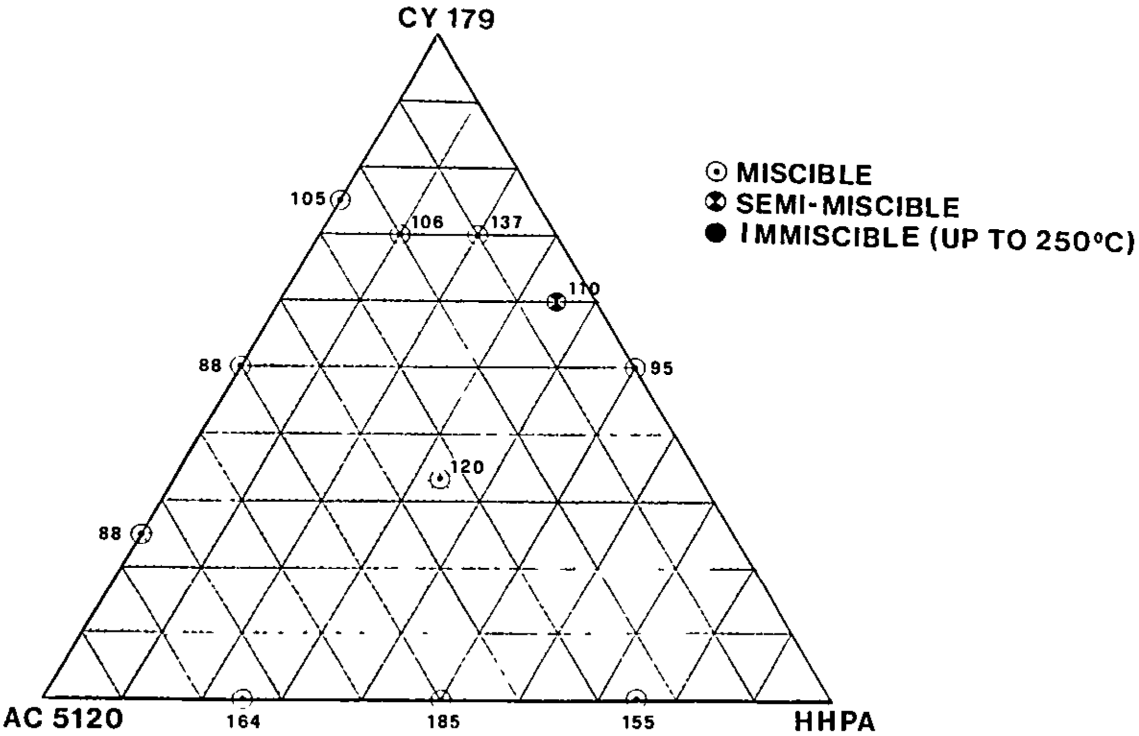


Figure 4.4: Phase diagram for the mixtures of AC 5120, CY 179 and HHPA.

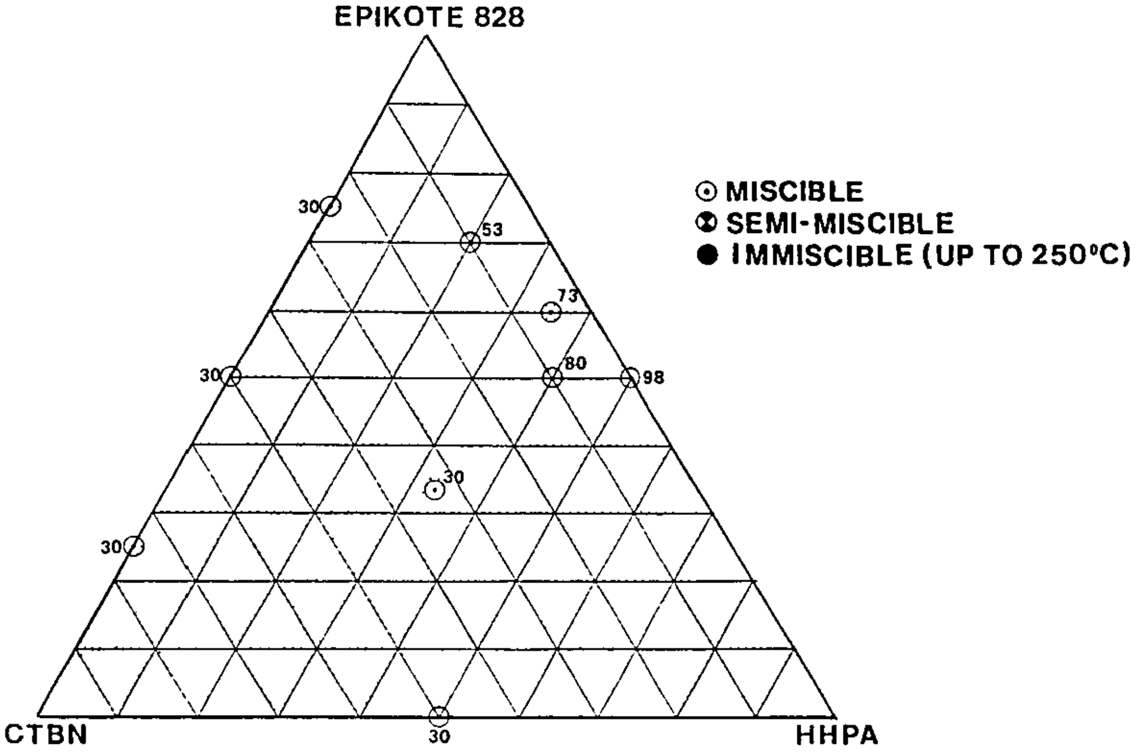


Figure 4.5: Phase diagram for the mixtures of CTBN, Epikote 828 and HHPA.

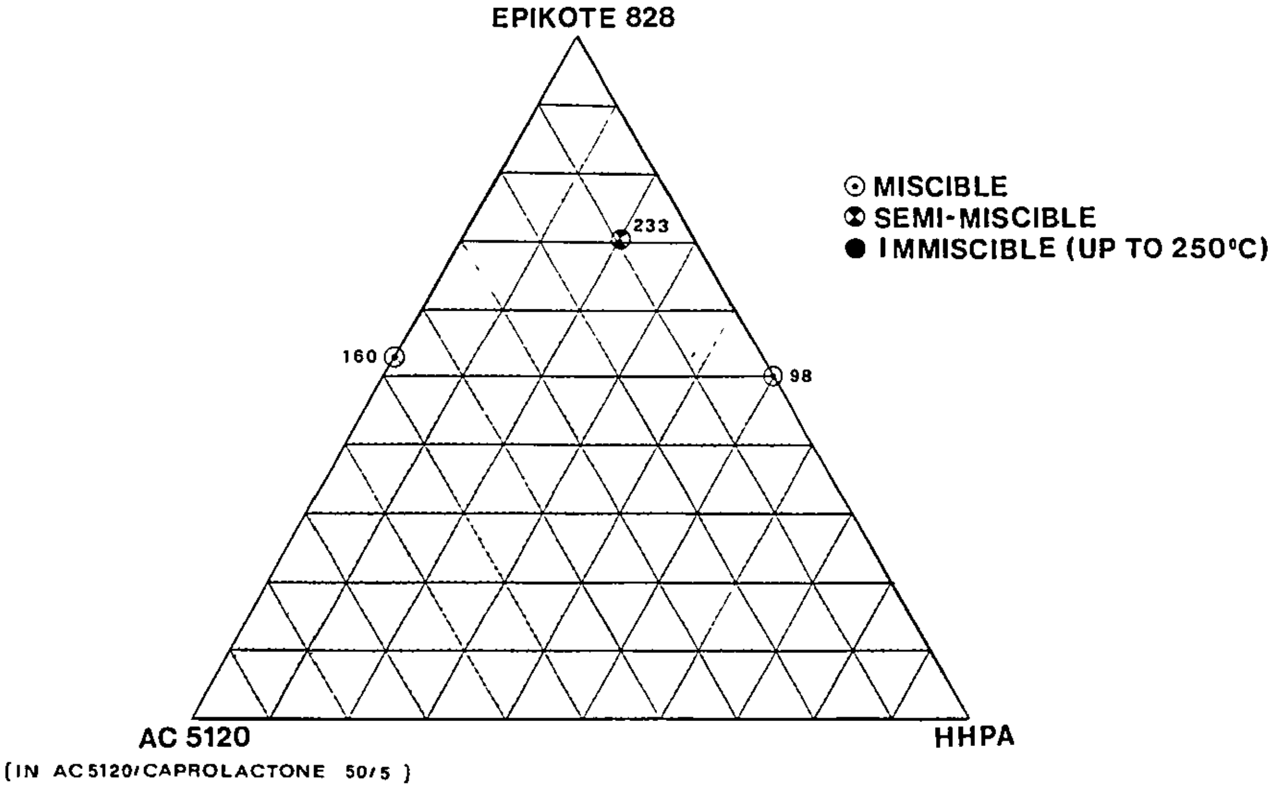


Figure 4.6: Phase diagram for the mixtures of AC 5120 grafted with ε-Caprolactone, at weight ratio 50/5, Epikote 828 and HHPA.

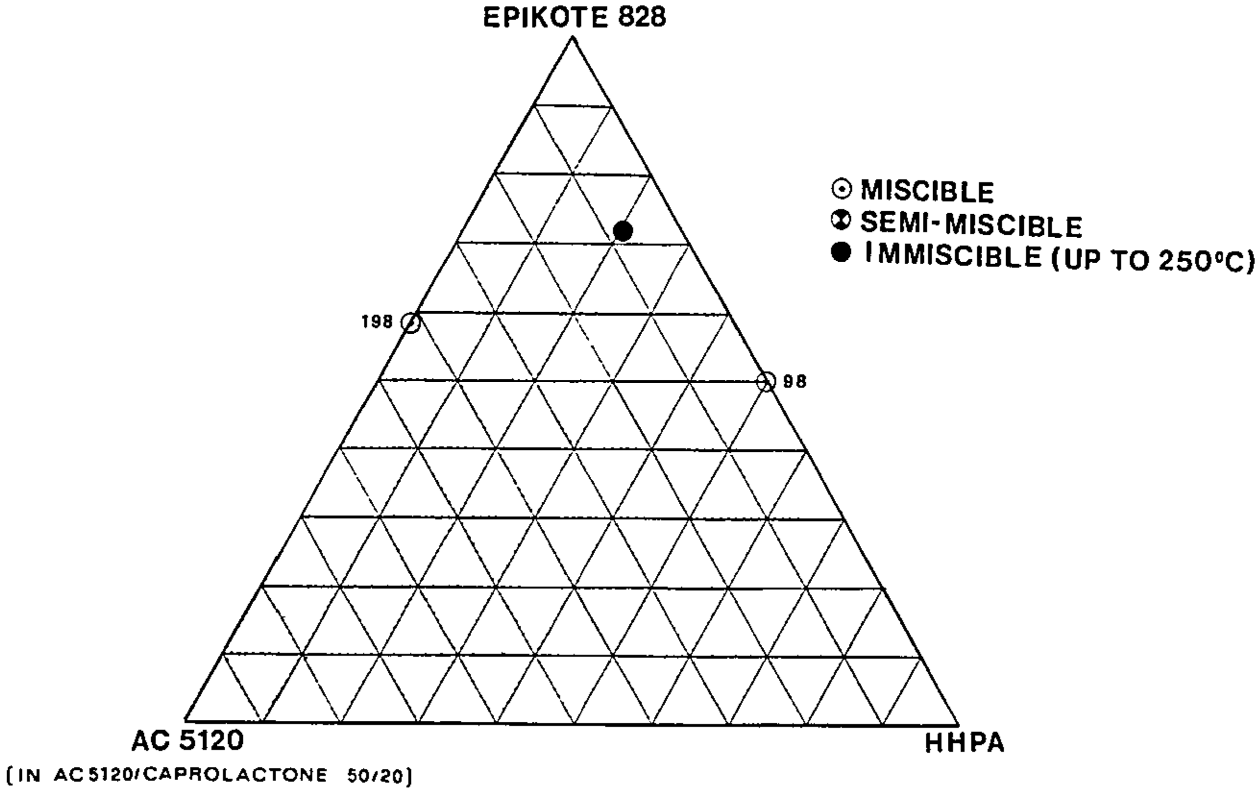


Figure 4.7: Phase diagram for the mixtures of AC 5120 grafted with ε-Caprolactone, at weight ratio 50/20, Epikote 828 and HHPA.

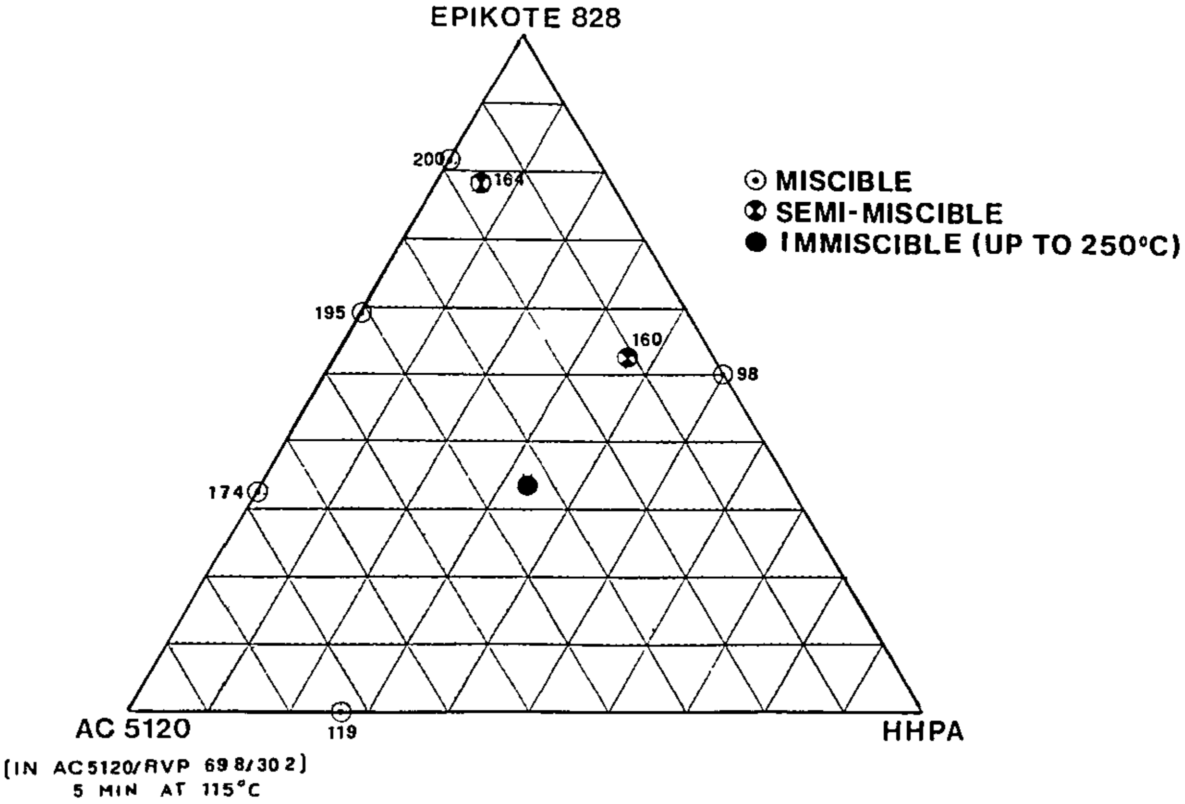


Figure 4.8: Phase diagram for the mixtures of AC 5120 grafted with RVP for 5 minutes, Epikote 828 and HHPA.

In Figures 4.8 and 4 9 are shown the ternary diagrams for the mixtures AC 5120, grafted with RVP at two conversion levels, i.e. 7% and 21%, respectively (see 4.3.1), HHPA and Epikote 828 These can be compared with the diagram of Figure 4.3.

The conversion level in all cases seems to play an important role in solubility of systems, i.e. the binary and ternary mixtures containing the product of grafting reaction at high conversion are more easily to solubilise than those containing the product of reaction at low level of conversion.

The comparison of phase diagrams of Figures 4 3 and 4 9, suggests that the final product of the grafting reaction gives higher solubility in binary mixtures with epoxy resin than similar mixtures containing unmodified AC 5120. In ternary mixtures, on the other hand, the grafting with RVP does not give large improvements in miscibility. In some cases the solubility temperatures are even higher than those reported for unmodified systems, but always lower than those observed for the systems modified with caprolactone

Similar conclusions can be derived from the data of the diagram reported in Figure 4.10, for the system (AC 5120-graft-RVP 69.8/30.2)/HHPA/CY 179, when compared with the analogous system of Figure 4 4

The final conclusion is that the modification of AC 5120 with RVP is not effective in increasing the solubility of mixtures with any of the two epoxy resins and HHPA, possibly due to the low conversion that are obtained, even at very long reaction times.

In Figures 4.11 and 4.12 are shown the phase diagrams for the mixtures of AC 5120-graft-RVP/TPP 69.8/30 2/1, with a conversion of the modification reaction equal to 82% (see 4 3.1), Epikote 828 and HHPA or MNA, respectively

While the modification of AC 5120 with RVP in presence of TPP catalyst leads to an increase in miscibility for binary blends with Epikote 828, it seems to be less efficient in ternary blends, i e when a hardener is also present, even if it

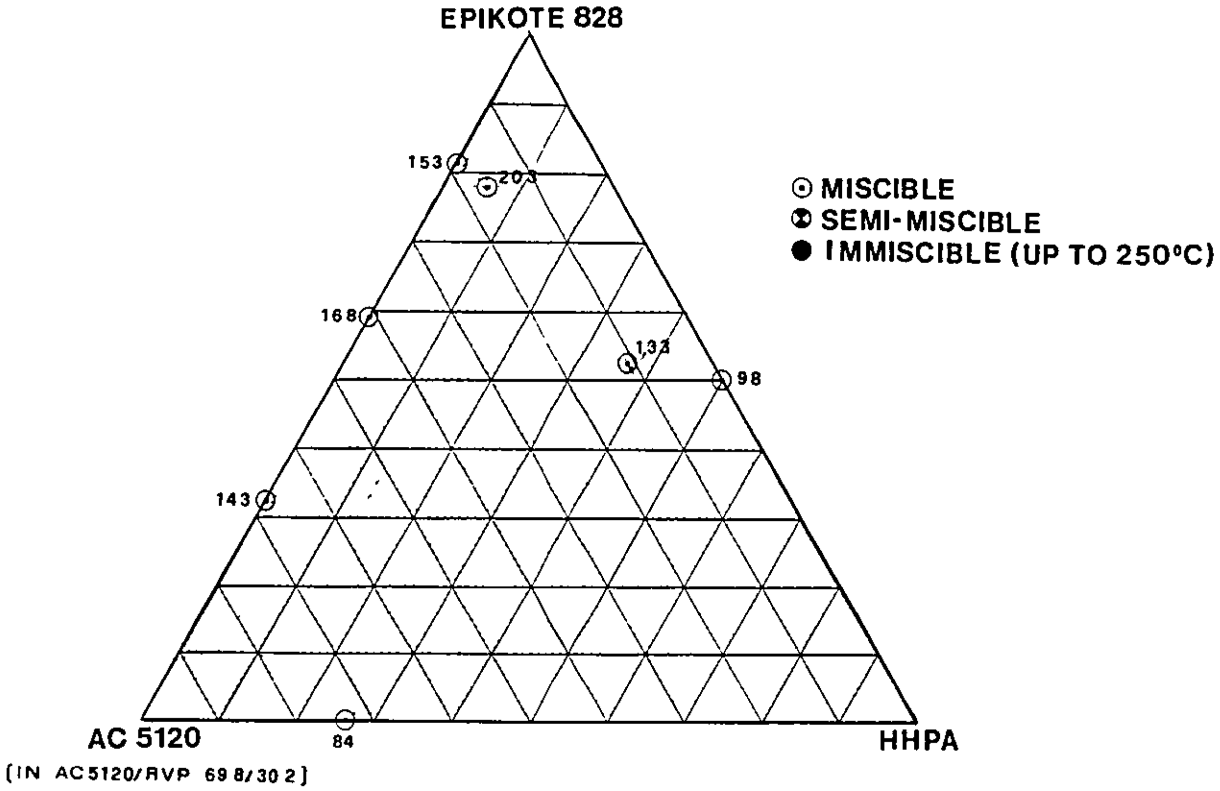


Figure 4.9: Phase diagram for the mixtures of AC 5120 grafted with RVP, Epikote 828 and HHPA.

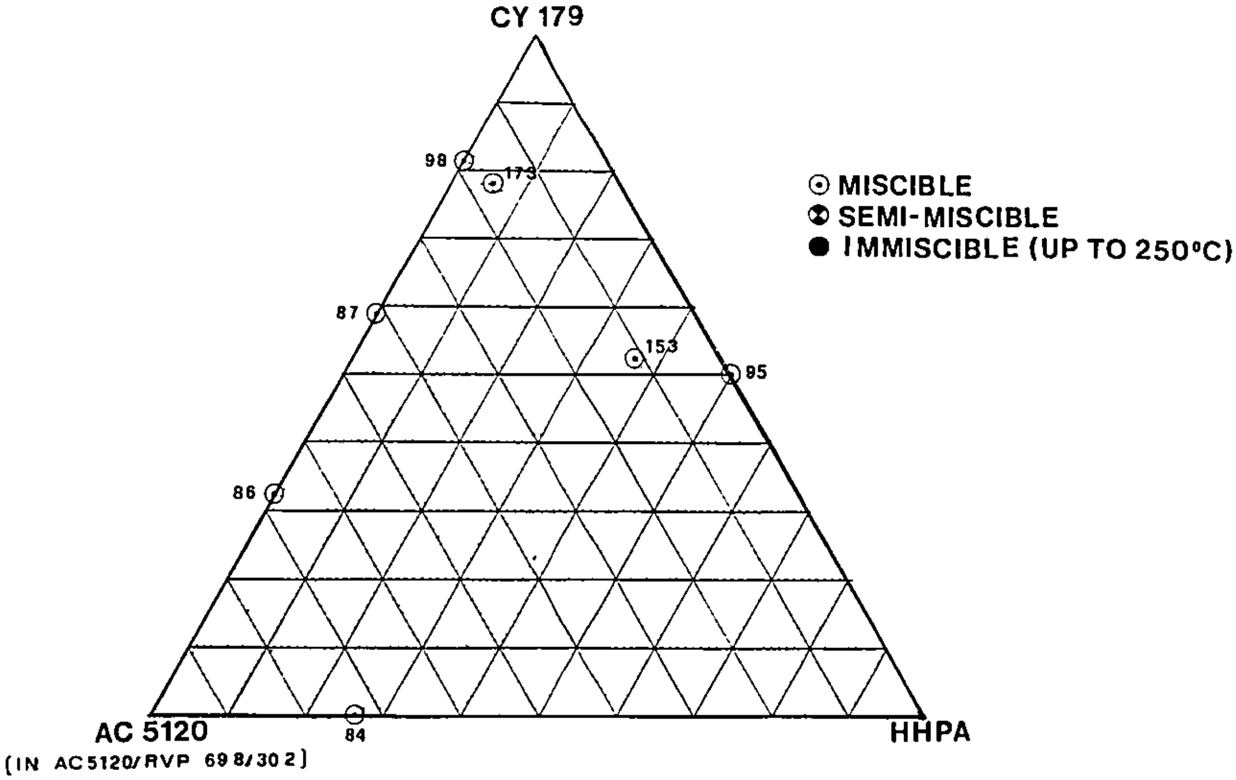


Figure 4.10: Phase diagram for the mixtures of AC 5120 grafted with RVP, CY 179 and HHPA.

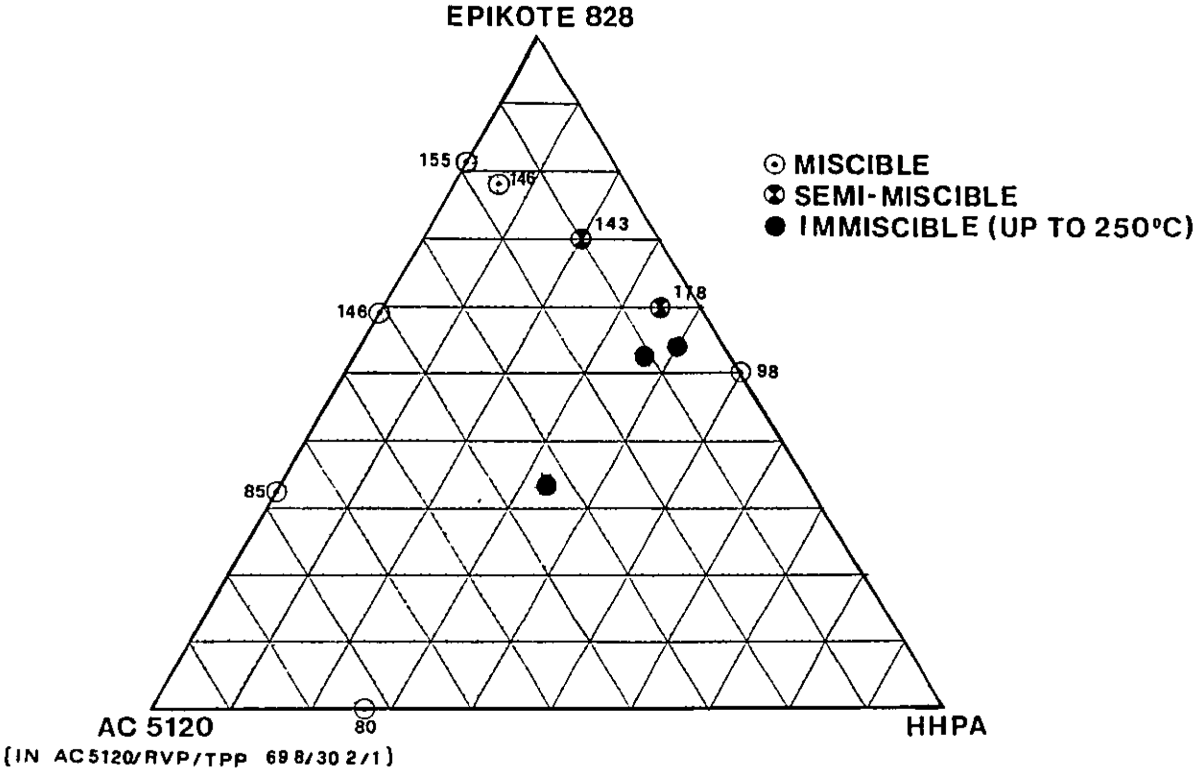


Figure 4.11: Phase diagram for the mixtures of AC 5120 grafted with RVP, in presence of TPP, Epikote 828 and HHPA.

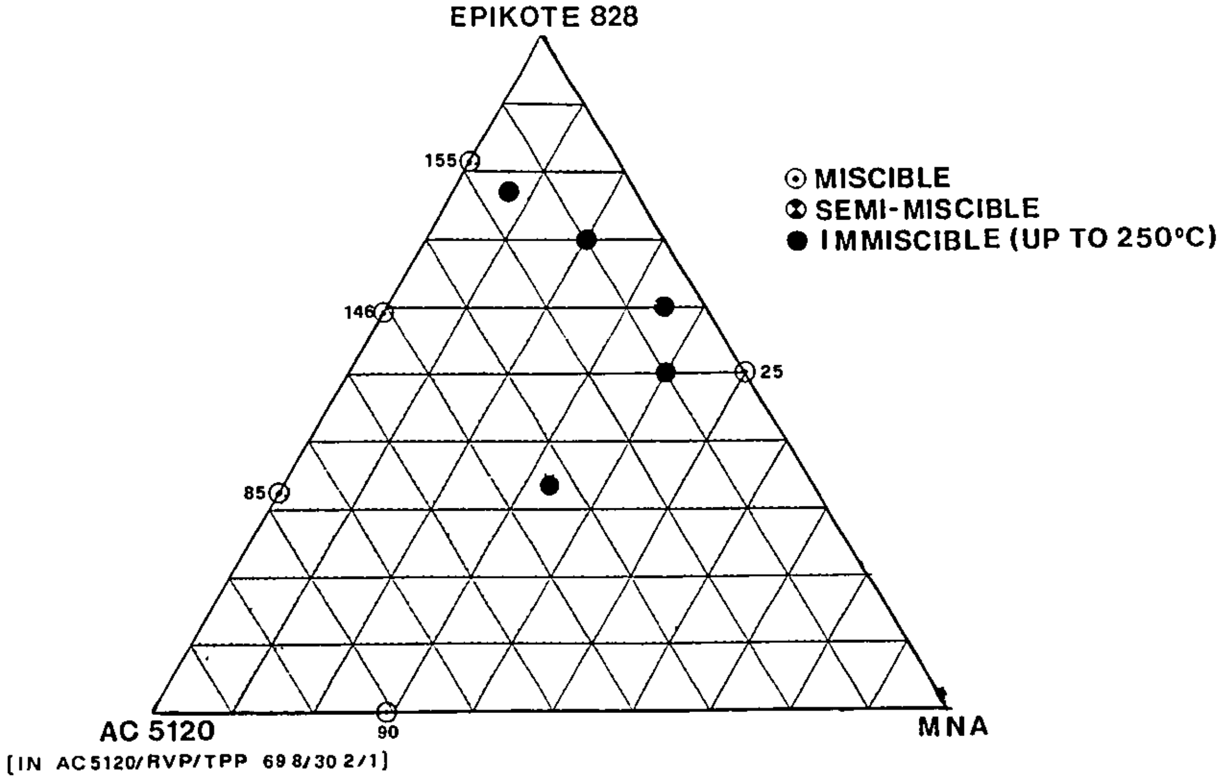


Figure 4.12: Phase diagram for the mixtures of AC 5120 grafted with RVP, in presence of TPP, Epikote 828 and MNA.

is pre-reacted at high temperature (140°C) with the respective hardener. With respect to the chemical modifications performed on AC 5120 with caprolactone, that performed with RVP seems to give better results in terms of miscibility. However, the ternary mixtures are not completely miscible at low temperatures in any composition. The use of a different hardener, i e MNA instead of HHPA, lowers the level of solubilisation of ternary mixtures.

Finally, in Figures 4.13 and 4.14 are reported the ternary diagrams of mixtures based on unmodified and grafted AC 5120, HHPA-e-montanic acid and Epikote 828, respectively

In both cases the mixing of the montanic acid in the hardener to produce an eutectic does not produce any appreciable increase in solubility of ternary mixtures.

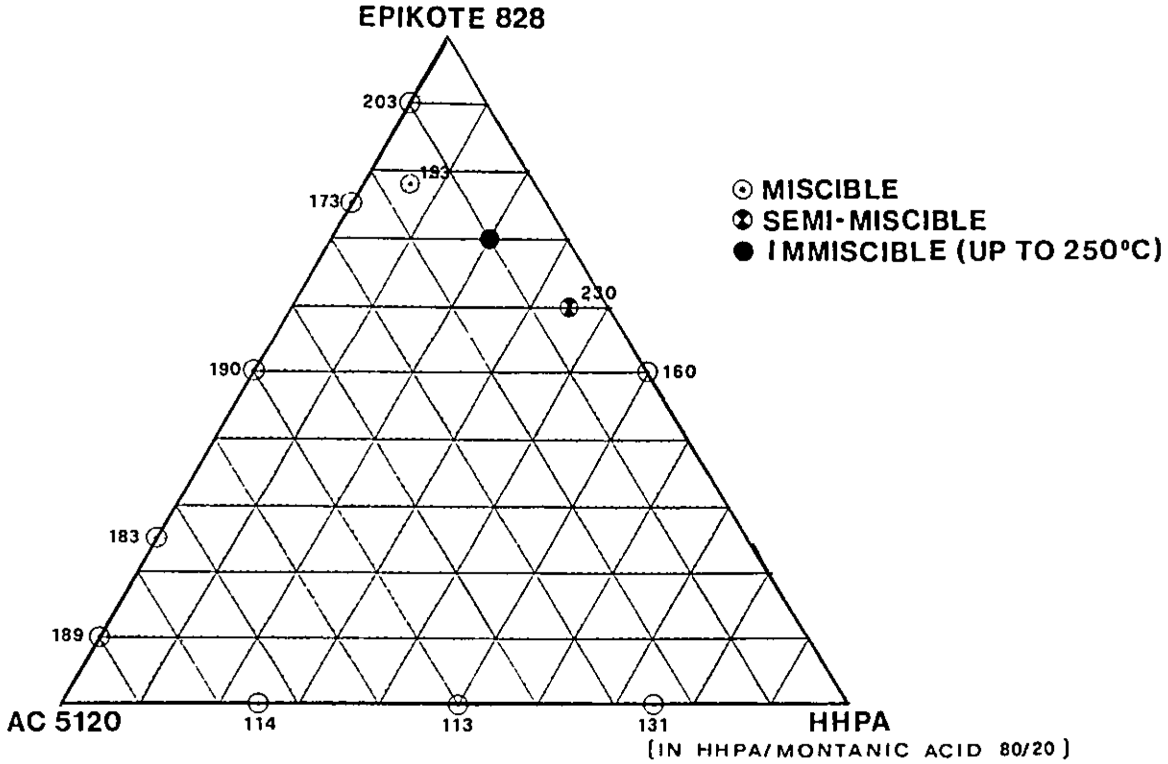


Figure 4.13: Phase diagram for the mixtures of AC 5120, Epikote 828 and HHPA-e-Montanic Acid.

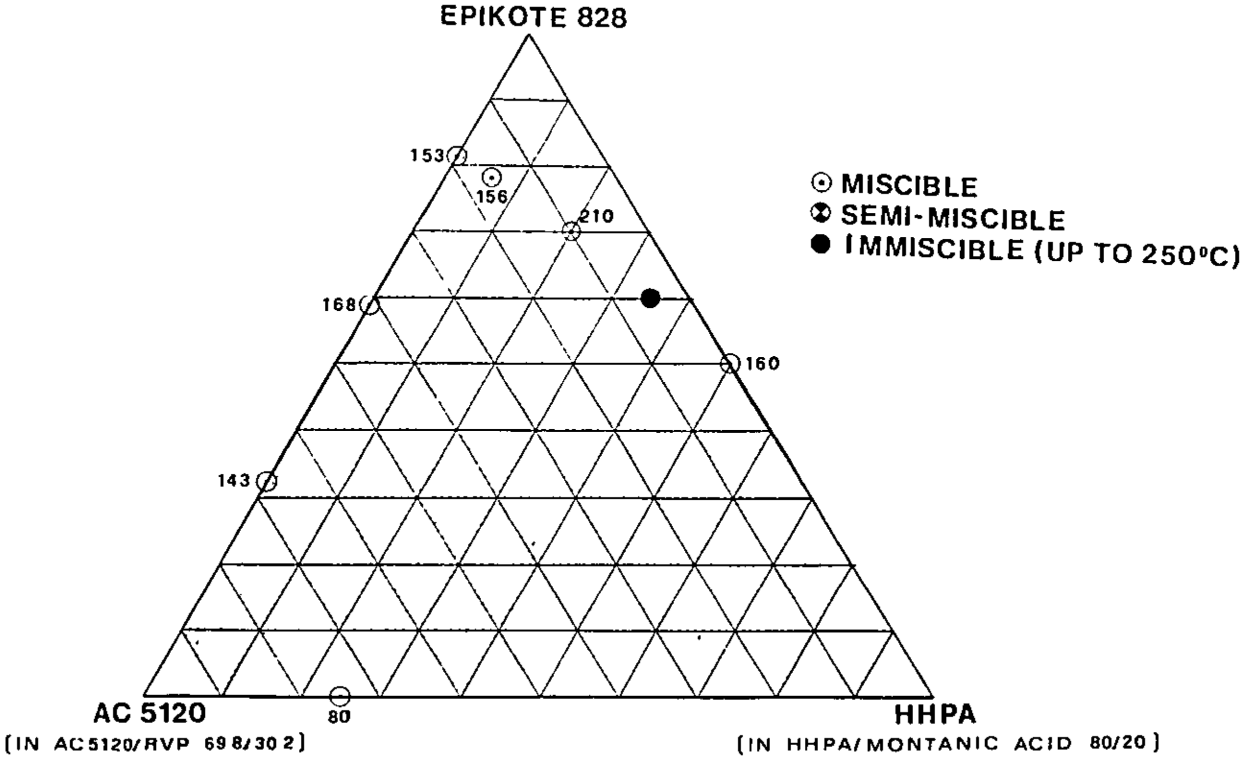


Figure 4.14: Phase diagram for the mixtures of AC 5120 grafted with RVP, Epikote 828 and HHPA-e-Montanic Acid.

4.2) Particle Size Analysis of Uncured Mixtures.

In Appendix 7.3 are reported some micrographs (Figures 9 to 16), taken on the hot stage microscope, for four 50/50 mixtures of modified and unmodified AC 5120/Epikote 828, as described in 3.7 .

For the case of the unmodified 50/50 mixture and that where Epikote 828 was grafted with montanic acid, (Figures 9, 10, 11 and 12) is noted the presence of a number of large and small particles which do not seem to change dimension and shape during the entire heating period at 120°C In the other micrographs, (Figures 13, 14, 15 and 16), are shown the comparison between the mixtures in which only AC 5120 has been modified with ε-caprolactone with those where AC 5120 has been modified with caprolactone and the Epikote 828 has been modified with montanic acid. This time the majority of particles of both systems seems to be very small, even if some large, two-phase regions are also observed, especially in the case of grafted AC 5120/grafted Epikote 828 mixtures. The duration of the treatment at 120°C does not seem to affect dimensions and shapes of the droplets in the mixture (AC 5120-g-caprolactone)/Epikote 828, while the size of the two-phase regions observed for the other mixture appear to be reduced after the 5 minutes. The comparison of data in Figure 9 with those in Figure 3 reveals that the heating time used to prepare the mixture has an effect on the dimensions of the dispersed particles, the dimensions, in fact, appear generally smaller when a longer heating time is used

In Figures 4.15 and 4 16 are illustrated how the dimensions of the dispersed droplets change with time under isothermal conditions at various temperatures, relative to mixtures 50/50 of AC 540/Epikote 828 and AC 5120/Epikote 828, respectively.

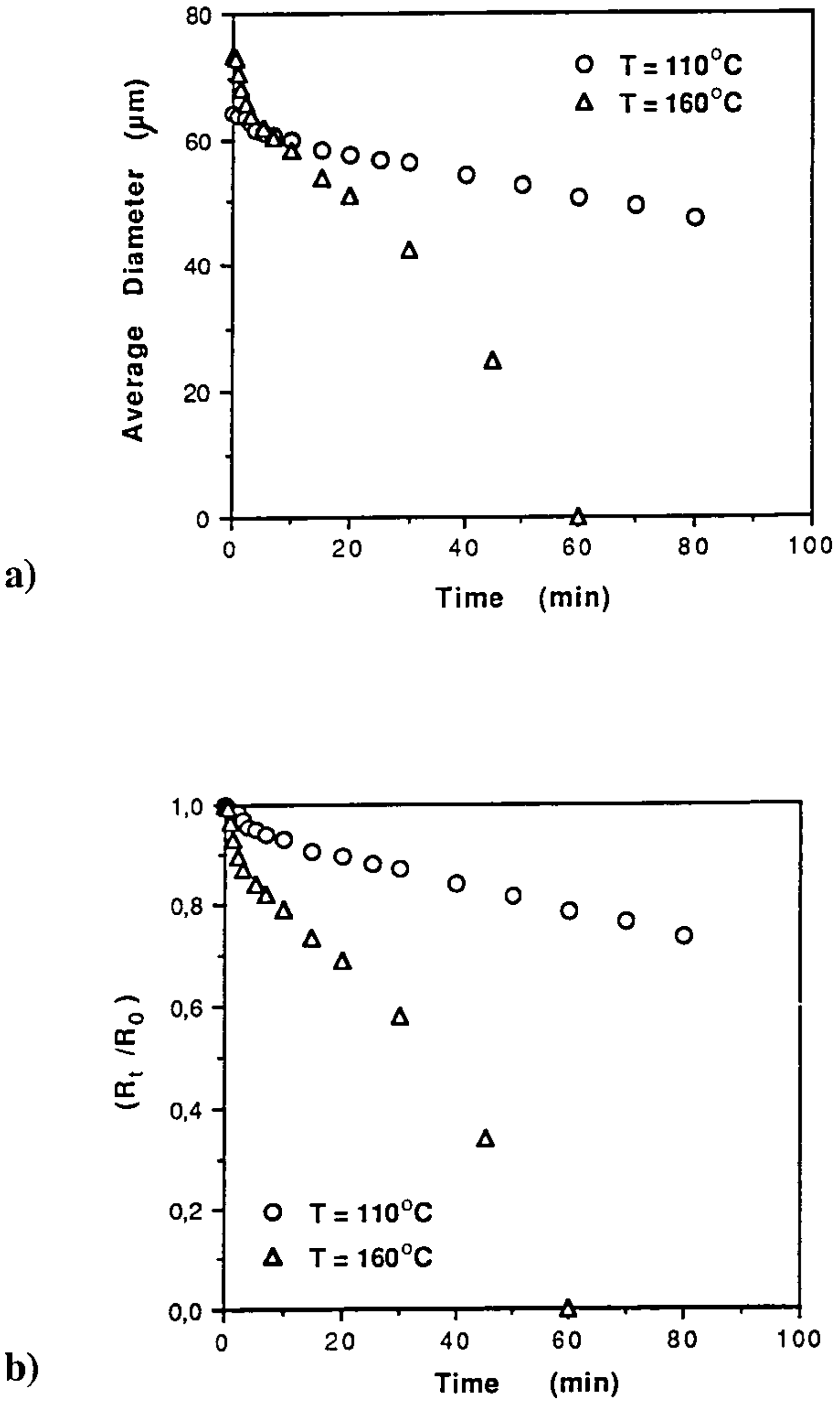


Figure 4.15: Solubilisation kinetics of dispersed particles for the system AC 540/Epikote 828 50/50. (R_o = initial radius and R_t = radius of the particle at time, t.)

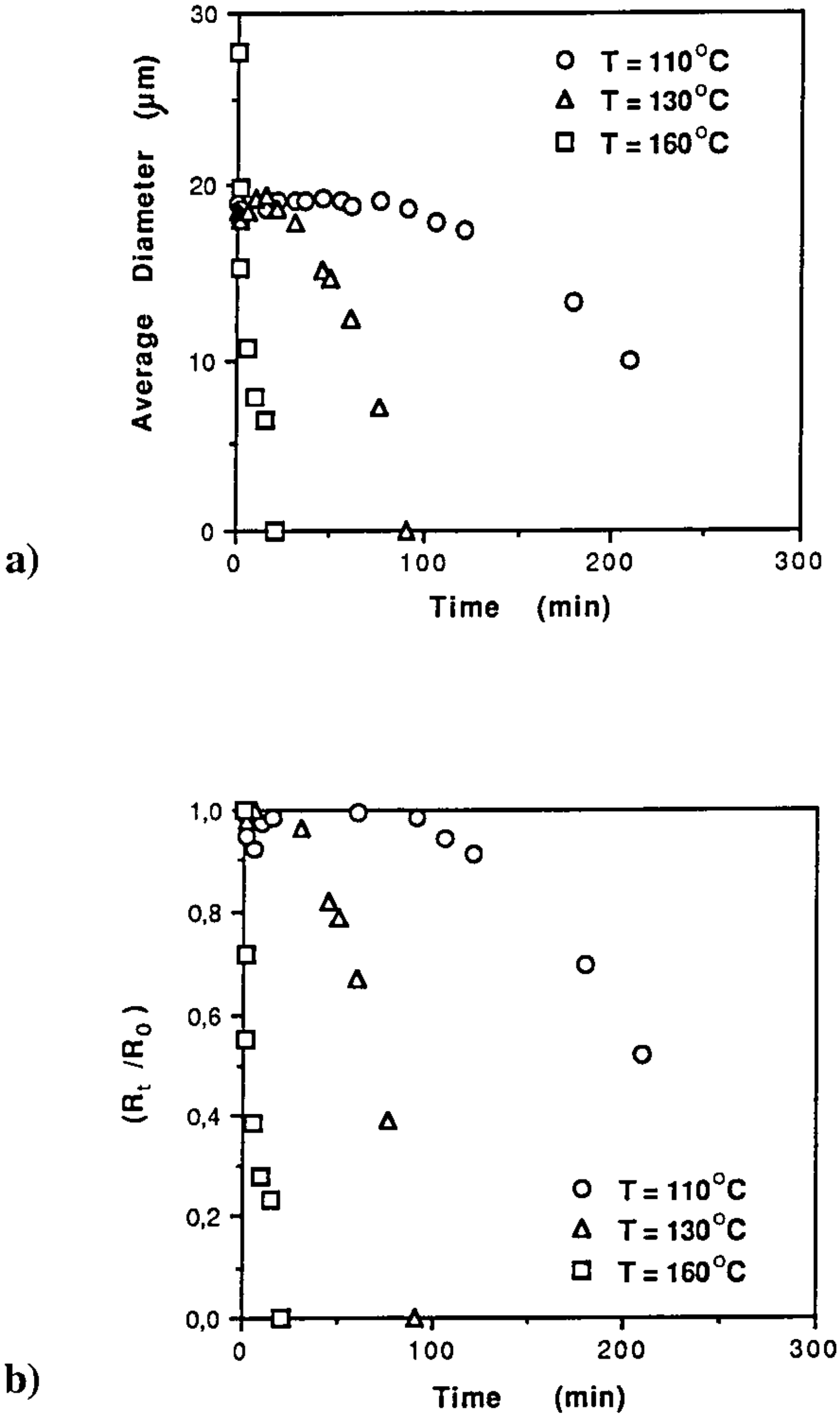


Figure 4.16: Solubilisation kinetics of dispersed particles for the system AC 5120/Epikote 828 50/50. (R_o = initial radius and R_t = radius of the particle at time, t.)

In Figures 4.15a and 4.16a it is shown how the test temperature affects the average dimensions of the particles. For the 50/50 mixture of AC 540/Epikote 828 at 110°C a rather long time is required to achieve complete solubility between the phases. In fact after one hour and 20 minutes, only 30% of the droplets with the original dimensions remained. At 160°C, on the other hand, complete miscibility of the system is reached within one hour. For the system AC 5120/Epikote 828, the disappearance of the particles of the second phase takes place more easily, taking about 25 minutes at 160°C and requiring about 4 hours at 110°C This result confirms the greater ability of AC 5120 to solubilise in Epikote 828 relative to AC 540, owing to its higher functionality

In mixtures with AC 540 the average diameter of the droplets is almost always larger than those for mixtures with AC 5120. Since the viscosity of the two oligomers is approximately the same (see 3.1), the difference in behaviour must be attributed to a difference in interfacial tension. In Figures 17 and 18 (Appendix 7.3) are reported the micrographs relative to the system AC 540/Epikote 828 50/50 at 110°C. The micrographs show the system at the beginning of the experiment and after 1 hour and 20 minutes at 110°C. For the micrographs in Figures 19 and 20 the test temperature is again 110°C but the system is the mixture 50/50 AC 5120/Epikote 828 From a comparison of Figures 17 and 18 with 19 and 20, it is clear that AC 5120 is more soluble than AC 540 in the epoxy resin.

In Figures 4 15b and 4 16b the process is analysed kinetically. In these figures the normalised dimension, i e the ratio between the radius of each particle at time, t, and the initial radius of the same particle, is plotted as a function of time for the two mixtures considered At lower temperatures two regions are noted: an horizontal part of the curve and a second, almost linear, descending part, related to the different processes that take place during the solubilisation. At 160°C, on the other hand, 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. This phenomenon can be related to differences in interfacial tension between the phases present in the mixtures. It is interesting to note that the aggregation occurs over only for a short time for the AC 540/Epikote 828 mixture for both test temperatures, whereas it is strongly dependent on test temperature for the case of AC 5120/Epikote 828 mixtures, being almost absent at 160°C. The second part of the curve shows a linear decrease of the dimensions of the particles with time and can be related to the diffusion process It can be hypothesised, in fact, that the diffusion process is Fickian and that the slope of the curve is related to the diffusion coefficient. This slope depends on the test temperatures and on the functionality of the polyethylene, i.e the higher the test temperature or the functionality value the faster the disappearance of the second phase droplets.

From all these observations, it can be concluded that both phenomena that take place in the solubilisation process depend on the polyethylene used and on test temperature 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 Using high temperatures, on the other hand, the process of coalescence becomes more difficult to occur while the diffusion takes place easily.

4.2.1) Analysis of the Diffusion Process Taking Place in two Phases Systems during Solubilisation

The diffusion process taking place from the precipitated particles into the surrounding liquid system, containing mainly the epoxy resin, can be examined analytically The following scheme is hypothesised:

a) If the gap between the glass slides is very small with respect to the surface area of the system, each particle can be considered to be a cylinder with a height, δ, equal to the distance between the slides.

b) Each particle has a concentration (with respect to the bulk) of polyethylene mixed with a small amount of epoxy resin, cp, which remains constant with time, since it seems reasonable to assume that the two components diffuse together from the particle into the bulk of the system during the miscibilisation process.

c) On the other hand, the effective number of moles of polyethylene, mixed with low amounts of epoxy resin, contained in each particle changes with time, i.e. decreasing as the miscibilisation proceeds,

d) The radius of the particle, indicated as R, decreases with time again as a result of the solubilisation process,

e) Outside each particle the concentration of polyethylene, indicated as c, decreases from the border of the particle to the bulk of the system. The gradient of concentration changes with time A fast change in concentration at the beginning of the process is expected and it becomes constant at longer times

For a single particle, therefore, the removal of polyolefin from the particle with time can be written as.

$$\frac{d(\text{moles})}{dt} = \text{concentration}\ \frac{d(\text{volume})}{dt} = cp\ \frac{d(\pi\ R^2\ \delta)}{dt} =$$

$$= \left[cp\ \pi\ \delta\ (2\ R)\right] \frac{dR}{dt} \qquad (1)$$

From a molar balance on a ideal system taken outside the second phase particle, the opposite of the variation with time of the moles is equal to the molar flow, i e. Jr, which is to be multiplied by the surface through which the process takes place, i e. the lateral surface of the cylindrical particle If the process follows the Fickian law of diffusion, the molar diffusion flow from the particle can be expressed as.

$$Jr = -\mathcal{D}\left.\frac{dc}{dR}\right|_{\overline{R}}$$

where: - $\mathcal{D}$ 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). It is generally time dependent

Substituting this last expression for Jr in eq. (1), gives:

$$-\left[cp\ \pi\ \delta\ (2\ R)\right]\frac{dR}{dt} = -\mathcal{D}\left.\frac{dc}{dR}\right|_{\overline{R}}\left[2\ \pi\ R\ \delta\right]$$

The last equation becomes:

$$cp\frac{dR}{dt} = \mathcal{D}\left.\frac{dc}{dR}\right|_{\overline{R}} \qquad (2)$$

If now we consider the process far from its initial stage and for short periods of time, the gradient of concentration outside the particle can be supposed constant with time. In this hypothesis, equation (2) can be integrated in time, giving:

$$cp\ R = \mathcal{D}\left.\frac{dc}{dR}\right|_{\overline{R}}\ t + Const \qquad (3)$$

where the constant could be calculated considering that at the initial time for the diffusion process (t = 0) the radius must be equal to R_0. Then, Const. = cp • R_0. Dividing equation (3) by (cp • R_0), the variation of normalised radius is obtained as a function of the time, i e

$$\frac{R(t)}{R_0} = \left(\frac{\mathcal{D}}{cp \; R_0} \left. \frac{dc}{dR} \right|_{\overline{R}} \cdot t \right) + 1$$

The previous equation can be written also as:

$$\frac{R(t)}{R_0} = (C \; t) + 1 \qquad (4)$$

In the hypothesis made, the constant C is negative, being proportional to the variation of concentration with the radius that must be negative, since the concentration decreases going away from the borders of the particle.

The equation (4) correlates well the experimental data of the final part of the curves in Figures 4.15b and 4.16b, confirming that the hypothesis made can be considered correct. Moreover, the slope of the linear part of each curve could be used to calculate the diffusion coefficient of each system at different temperatures from the dimension of the initial radius of the particles, if the concentration in each particle, cp, and the gradient of concentration at the border of the same particle are known

4.3) Data from Physical and Chemical Evaluations of Uncured Mixtures.

The results of the physical and chemical tests performed on some of the uncured, modified and unmodified, mixtures prepared, are reported below.

4.3.1) Acid Titration.

In Table II are reported the results of the acid number measurements performed on final samples of each reaction carried out, as well as on pure materials. The acid number values, defined as the number of mg of KOH required to neutralise all the acid groups contained in 1 g of resin, are compared with those either reported in literature or given in data sheets, or those calculated theoretically (see Appendix 7.1). The two different alcoholic solutions of KOH used were found to give approximately the same results for each sample.

TABLE II: Results from titration tests performed on pure components and on the products of their reactions.

Sample	Acid No.$^{(1)}$	Acid No.$^{(2)}$	Degree Conv.
AC 5120	119.5	120	
ε-Caprolactone		0	
RVP	0.9	0	
HHPA		0	
MNA		0	
Epikote 828	0.2	0	
Montanic Acid	148.3	132	
AC 5120-g-Caprolactone 50/5	109.1	113.5	n.a.
AC 5120-g-Caprolactone 50/20	99.6	97.7	n.a.
AC 5120-g-RVP 69.8/30.2	65.9		21
AC 5120-g-RVP/TPP 69.8/30.2/1	15.2		82
AC 5120-g-RVP/TPP 69.8/30.2/1.5	15.9		81
(AC 5120-g-RVP 69.8/30.2)/HHPA 80/20	143.0	125.4	
(AC 5120-g-RVP/TPP 69.8/30.2/1)/HHPA 80/20	87.1	84.9	
(AC 5120-g-RVP/TPP 69.8/30.2/1)/MNA 77.9/22.1	78.0	81.0	
Epikote 828-g-Montanic Acid 6.6/1	1.1		94

Acid No.$^{(1)}$ (mg KOH/g resin) = acid number calculated from titration tests, Acid No.$^{(2)}$ (mg KOH/g resin) = acid number reported on data sheets or calculated theoretically, Degree Conv (%) = degree of conversion of acid groups. n.a. = not applicable

The acid number found for almost all the pure materials are in accordance with those reported in data sheets or obtained by theoretical calculations, except for montanic acid, whose values of acid number differ by about 10%. Montanic acid used is a technical grade and it is not expected to be pure. Moreover, there can be also experimental errors associated with some possible precipitation during titration tests.

Except for reactions with ε-caprolactone, the conversion for the reactions were calculated as the ratio between the acid groups consumed during each reaction and the initial acid groups. The reaction of AC 5120 with ε-caprolactone, in fact, leads to an extent of chains without the disappearance of the acid group at the chain end, i e each acid group produces another acid group. The calculation of the degree of conversion of acid groups gives null values, i.e. the same number of acid groups are present before and after the reaction, even if the true conversion is almost 100% In this case, the time required to reach a constant degree of conversion for the reaction was calculated by monitoring the residual amount of caprolactone, as already explained in 4.1.3. Moreover, since the experimental acid numbers found for both the final mixtures of AC 5120 with caprolactone are similar to those calculated theoretically (Appendix 7.1) with the hypothesis that AC 5120 reacted stoichiometrically with caprolactone, the occurrence of competition of this reaction with that for the homopolymerisation of caprolactone can be excluded In the latter case, in fact, an increase in molecular weight would occur in the final mixtures, due to the formation of polycaprolactone, with a reduction of acid numbers relative to the values calculated in Appendix 7 1 .

For the reaction of AC 5120 with the monofunctional epoxy resin RVP, it can be observed in Table 45 (Appendix 7 2)

Conversion after 5 min at 115°C = 7%

Final Conversion = 21%.

Allowing for experimental errors, it can be stated that even after 9 hours at 140°C with a continuous stirring followed by 12 hours in the oven at 90°C, it is never possible to reach a conversion higher than 21%, even if for the composition chosen a 100% conversion should have been possible.

As expected, the inclusion of low percentages of the catalyst TPP extends further the reaction between AC 5120 and RVP Table II reports conversions higher than 80% for compositions containing 1 and 1.5 parts of TPP. From Table 45 (Appendix 7 2), on the other hand, it can be seen that it is possible to reach the final conversion of the reaction after 1 hour and 30 minutes, with 1 part TPP, and only after 30 minutes by increasing the TPP concentration to 1.5 parts. Since the only advantage in using a larger amount of TPP resides in reducing the reaction time, as no increase in final conversion is observed, the use of 1.5 parts of TPP was precluded, as an excess of catalyst with a longer reaction time than that required to reach the complete conversion, could lead to undesirable reactions with HHPA and/or Epikote 828 in the final mixture.

The experimental results of titration tests performed on the products of reaction of modified AC 5120, with or without TPP, with HHPA and MNA are in good accordance with the theoretical values, also reported in Table II, especially in the case of the reactions in which TPP was present. For the latter case, it can be said that an almost complete conversion of the alcoholic groups to acid groups was obtained. When TPP was absent, on the other hand, there was an initial lower amount of alcoholic groups in AC 5120-graft-RVP mixture, due to the incomplete reaction between AC 5120 and RVP, which gives a final acid content different from that expected theoretically on the assumption that each molecule of HHPA had reacted with an alcoholic group.

It can be also noted, Table 45, that both the reactions of AC 5120-graft-RVP with HHPA or MNA reach completion in about 2 hours.

For the reaction between Epikote 828 and montanic acid the final conversion was 94%, i e an almost total conversion was obtained. This, therefore, reflects the importance of having miscible components. It is possible, however, that the uneven distribution of the functionality in the AC 5120 is responsible for the low solubility and the incomplete conversion in any reaction. It is possible that there could be large amounts of chains with functionality less than 2.

4 3 2) Molecular Weight of Unmodified and Modified Copolymers.

In Table 46 are reported the results of molecular weight measurements performed by GPC on the three functionalised polyethylenes and on the products of the modification of AC 5120 with ε-caprolactone at two different ratios and two different reaction times.

The lack of reproducibility between the tests performed at different times was commented by RAPRA as follows: "It should be noted that the long term reproducibility of GPC is not particularly good. It is best to treat the results in a simple comparative manner " (24th June 1992) "Whatever the problems of long term reproducibility and poor low molecular mass resolution, the short term comparison of samples is usually very good " (1st March 1993) In Figure 4.17a are reported the two curves of molecular weight distributions obtained at different times for AC 5120. They appear to be very different even in the shape.

In Figure 4.17b the curves of molecular weight distributions for the three functionalised polyethylenes are reported Finally, in Figure 4.17c the curves of molecular weight distributions for AC 5120 and its modifications with ε-caprolactone are shown From this figure and from Table 46 it appears clear that the presence of caprolactone has only a very small influence on the apparent molecular masses, the differences becoming larger with increasing the content of ε-caprolactone. This result confirms that the reaction of the acrylic acid copolymer with caprolactone has produced a unitary grafting, i.e. most of the acid groups of polyethylene have reacted with caprolactone without the formation of polycaprolactone. If the latter case had occurred, the curve of molecular weight distribution would have become broader or shifted to higher values of molecular weights.

Finally, a comparison between the molecular weights found from GPC measurements on both mixtures with ε-caprolactone (Table 46) and those calculated in Appendix 7.1, used to evaluate the acid numbers, shows an appreciable difference between these values only in the case of the 50/20 mixture It must be stressed again, however, the poor reliability of the GPC technique for these systems.

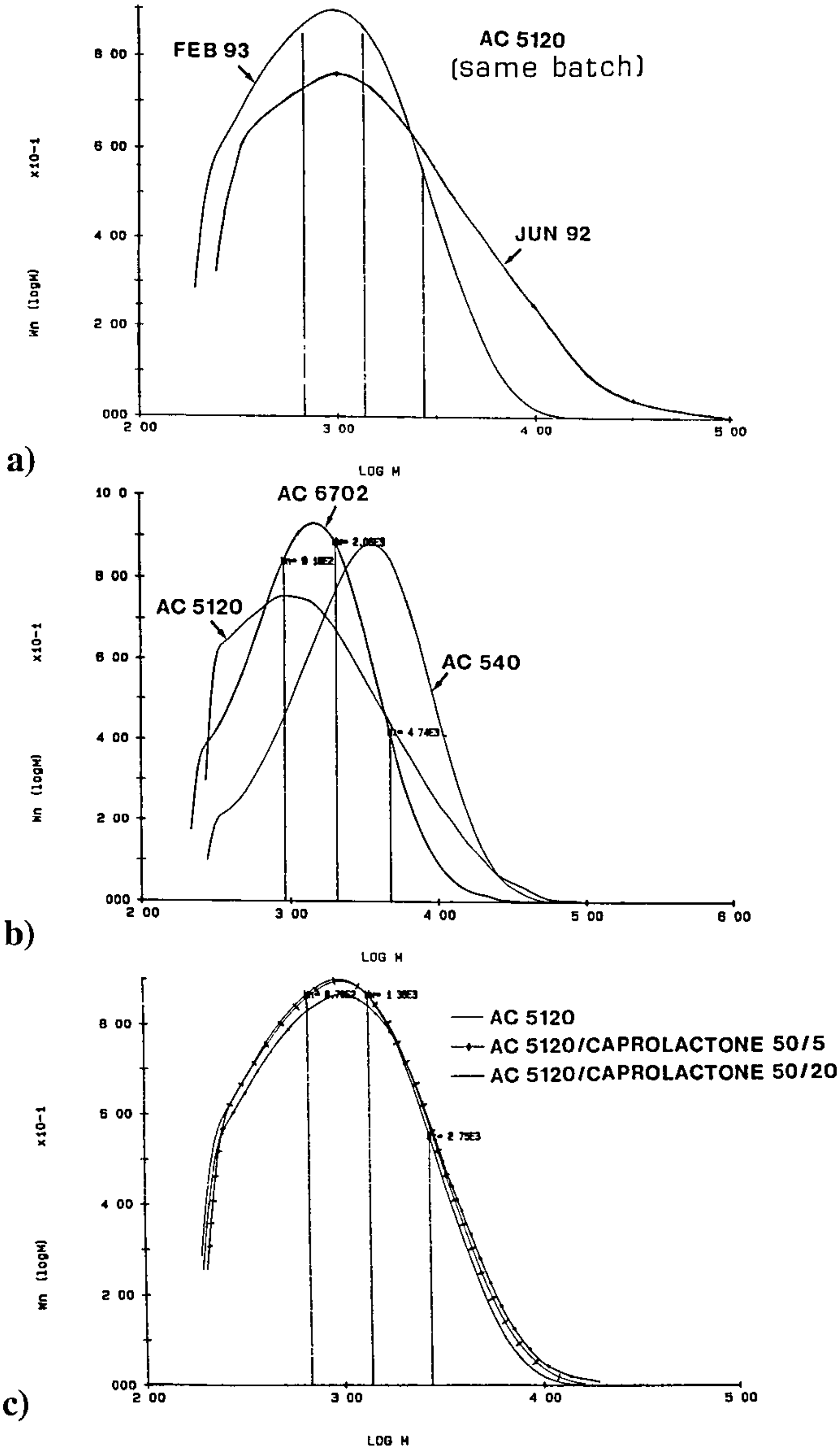


Figure 4.17: Molecular weight measurements performed at GPC on the three functionalised polyethylenes and on AC 5120 grafted with ε-Caprolactone in two compositions.

4.3.3) DSC Analysis of Uncured Mixtures

The thermal properties of the three functionalised polyethylenes, determined by DSC with scans from room temperature to 200°C, are reported in Table 47, Appendix 7.2 .

The results of the thermal analysis can be summarised as follows:

a) all three ethylene acrylic acid copolymers show a broad melting peak;

b) the crystallisation peak is narrower and the heat of crystallisation is lower than the heat of fusion recorded in the first heating cycle

The fact that all three polyethylenes have broad melting peaks is probably due to a wide dispersity of molecular structure. That is, the melting of the less perfect crystals takes place at lower temperatures, while a higher temperature is required to melt the more perfect crystals

The data of the analysis by DSC tests for some of the binary mixtures investigated, are reported in Tables 48, 49 and 50 (Appendix 7 2). In these are compared the thermal data of the mixtures with the corresponding functionalised polyethylene For greater clarity, the DSC results of the controls are also reported

From the data in Table 48, related to mixtures of AC 6702 with Epikote 828, it is noted that the melting peak temperatures of the mixtures are 16-18°C higher than that of the pure AC 6702 and that melting starts at a lower temperature. The melting enthalpies of the mixtures, normalised to polyethylene content, however, are approximately the same as that of the pure AC 6702. Furthermore, it is noted that in the crystallisation process the peak temperature of the mixtures is not very different from that of pure AC 6702 and that the initial and final crystallisation temperatures are slightly lower than for the corresponding temperatures of the pure polyethylenes The most striking result in this study is the higher heat of crystallisation for the mixtures with respect to that of pure AC 6702, being about double for the case of mixtures with the higher polyethylene content, i.e. 75%, and even higher at 50% polyethylene content. An explanation for these observations could be that, in the case of the oxidised polyethylene, crystallisation is slow, since it consists of a mixture of chains containing terminal acid groups and non-functionalised chains. When the polymer is mixed with the epoxy resin and reacts with it, by heating the mixture for a long period of time at high temperature, fractionation takes place and allows the non-reactive homopolymer chains to crystallise more freely.

If these results are compared with the data from the hot stage microscope analysis (Table 8) it is noted that in all cases the melting and the crystallisation temperature obtained from the DSC are lower then those obtained from the hot stage. It must be remembered that in the hot stage analyses are recorded only the temperatures at which the crystals disappear or are formed during cooling, and not the initial melting. Furthermore the heating and cooling rates in the two experiments were different

The thermal data for the mixtures containing one of the two acrylic acid copolymers and Epikote 828, can be discussed together, since they show similar trends. In all cases the melting peaks are less sharp and occur at lower temperatures than the corresponding polyethylene in isolation. In the case of the mixtures of AC 540 with Epikote 828, the shape of the melting areas are closer to those of pure AC 540, while for the case of the mixtures of AC 5120 the shape of the trace is quite different, exhibiting a larger decrease in the melting peak temperatures (about 15°C). As these systems are random copolymers and there is a high probability that all the chains contain acid groups, it could be hypothesised that in all three cases the reaction with the epoxy resin takes place primarily with the polyethylene chains of higher molecular weights, as these are expected to have more acid groups in the chain A support for this hypothesis can be found in the observation that the final melting temperatures are always slightly lower than those of the pure polyethylenes, i e about 5-7°C

The comparison of the heats of fusion shows that, in the majority of the cases, these values are lower than those of the corresponding acrylic acid polyethylenes, probably indicating that only those chains that have not reacted with the epoxy resin or have produced only mono-esters, are capable of crystallising. Moreover, it must be remembered that the samples have been subject to different thermal histories, and this could be a major source of variations.

If now are compared the results of the crystallisation process (i e. the cooling cycle of the DSC analysis), it is observed that in all cases the peak temperatures of the mixtures are higher than those of the pure polyethylenes. The onset temperature for the crystallisation process is not very different to that of the pure polyethylene, especially for the mixtures with AC 540, while the temperature for completion of the crystallisation is higher, especially for the mixtures with AC 540 and those of AC 5120 with CY 179

In all the mixtures with Epikote 828 the differences in heats of crystallisation are very small from the pure acrylic acid copolymer, while in mixtures with CY 179 the polyethylene phase shows always a higher heats of crystallisation with respect to the corresponding polyethylene in isolation.

The comparison of DSC results for the binary mixtures with AC 540 with those obtained from the tests on the hot stage microscope, Tables 9 and 10, shows that the melting temperatures obtained from the two techniques are quite similar; while the crystallisation temperatures obtained in the DSC are at least 10°C lower than those obtained from the hot stage

For AC 5120, the melting point measured in the hot stage microscope is exactly the same as that measured by DSC (Tables 11 and 12), while the values for the crystallisation temperature are very different For its mixtures both melting and crystallisation temperatures measured in the hot stage microscope are higher (15-20°C) than the values obtained on the DSC tests.

The data from DSC analysis for the hardener HHPA and some of its mixtures with AC 540 and AC 5120 are reported in Table 51 For pure HHPA it can be noted that after the expected melting temperature of 31°C there is another endothermic peak at 173°C. It can be hypothesised that it represents the evaporation of HHPA, (the reported boiling point of the cis-form is 158°C). This explanation is supported by the observation that the DSC trace for HHPA in the cooling stage do not present any crystallisation and that the sample pan appears to be empty at the end of the DSC test.

For the mixtures with the two acrylic acid copolymers it seems that only the 50/50 mixture of HHPA with AC 540 shows the melting of HHPA at 32°C, as this does not appear in the case of the 50/50 mixture of HHPA with AC 5120. In the first case the melting peak is narrow in relation to that of pure HHPA and the heat of fusion is smaller

From the comparison of DSC data for AC 540 and AC 5120 and those for the mixtures with HHPA are noted the narrow melting peaks of the mixtures and lower values of heats of fusion. The heats of crystallisation are closer to those of the pure acrylic acid polyethylenes and have similar values of the melting enthalpy of the heating stage. Also for these mixtures it has been noted that after the melting of the polyethylene phase an endothermic peak appears, which is probably due to the evaporation of all or part of the HHPA. For this reason it seems correct to normalise the heats of crystallisation to the initial weight of acrylic acid polyethylene in the mixtures.

Comparing the results of HHPA from DSC with those from the hot stage analysis, Tables 13 and 14, a notable difference is observed The DSC results appear to be closer to those reported in literature and no melting at higher temperatures is observed.

Similarly for the mixtures of HHPA with the two acrylic acid copolymers, in the DSC trace there was no melting peak after the melting of polyethylene phase, nor any crystallisation at temperatures higher than those of AC 540 and AC 5120, which are observed in the hot stage However, it must be remembered the different conditions of samples in the two tests. The HHPA entrapped between the glassy slides could be not able to evaporate and this makes possible its transformation to the trans-form.

In Tables 52 and 53 are reported the ternary mixtures of the two acrylic acid copolymers, respectively, with the two epoxy resins used and the hardener HHPA

In all the mixtures there is only one melting peak and one crystallisation peak, in all cases similar to those of the respective pure polyethylenes The peak temperatures are slightly lower in the melting process and higher in the crystallisation process.

The theoretical values of the heats of fusion, reported in brackets and calculated with the rule of mixtures applied to each polyethylene and HHPA, are in most cases higher than the experimental values The heats of crystallisation, normalised for polyethylene content, are similar to those of the pure polyethylenes.

Finally the results from DSC tests appear this time similar to those by hot stage analysis, Tables 16, 17, 18 and 19, except for the crystallisation temperatures that are lower for the DSC tests

In Table 54 are reported the data from DSC tests for the 50/5 and 50/20 mixtures of AC 5120 grafted with caprolactone.

In Figure 4.18a, b and c are shown the DSC curves for pure AC 5120 and for the mixtures 50/5 and 50/20 of AC 5120-graft-caprolactone, kept for longer time at 160°C. A broader melting peak is observed for all the mixtures with respect to the pure AC 5120, beginning the melting process at lower temperatures (about 15°C). Moreover, the peak temperatures are progressively shifted to lower values with increasing the content of caprolactone and the reaction time. The explanation for this behaviour has to be connected to the occurrence of reactions with the functional groups in AC 5120 chains

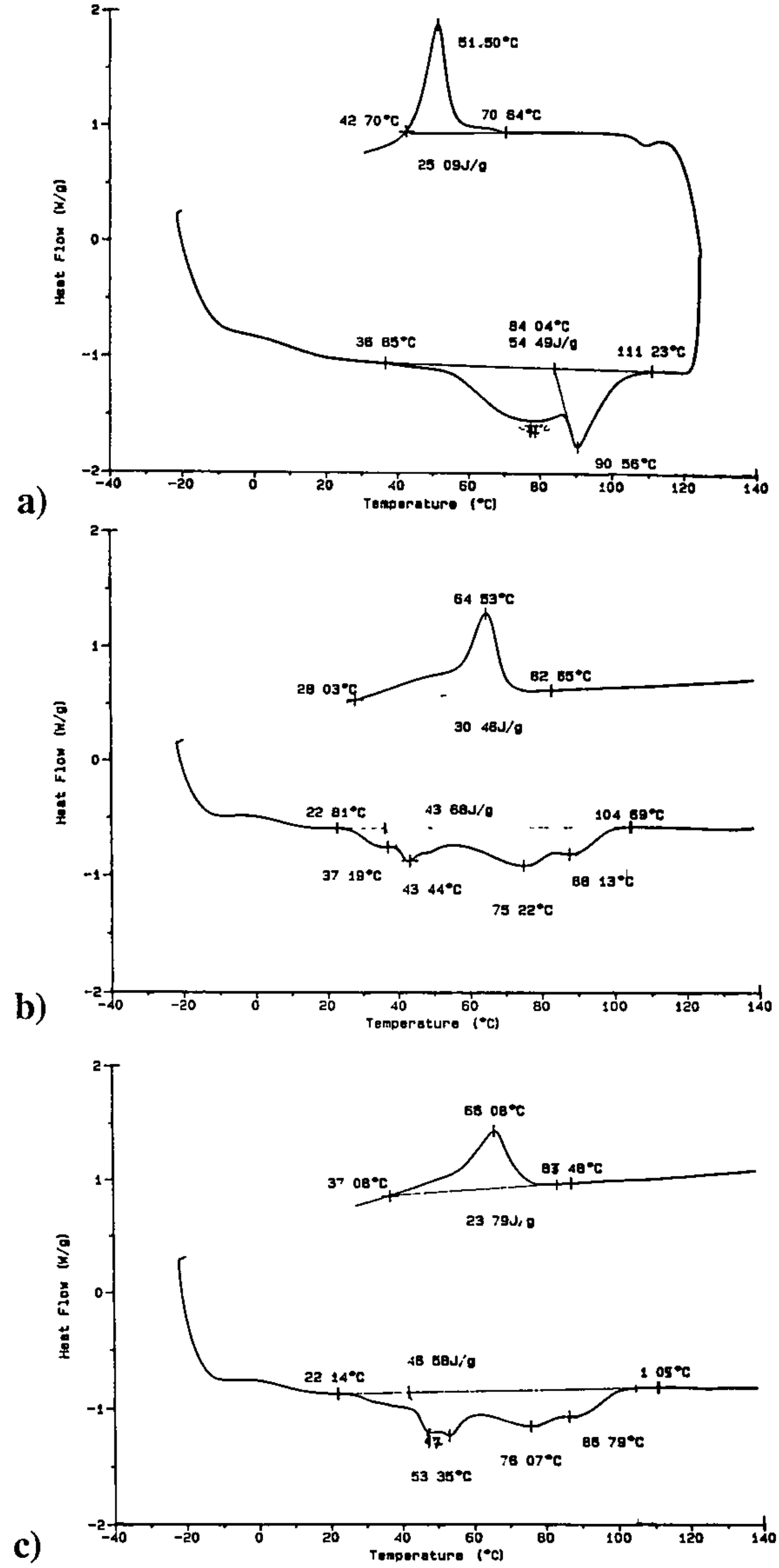


Figure 4.18: DSC scans performed on: a) AC 5120; b) AC 5120-g-Caprolactone 50/5, c) AC 5120-g-Caprolactone 50/20.

In Table 54 are reported the total heats of fusion, even though a direct comparison with pure AC 5120 is not possible owing to the presence of caprolactone Regarding the crystallisation process on cooling, the peak crystallisation temperature of the mixtures is higher than that of pure AC 5120 and the peaks appear to be wider in relation to that of pure polyethylene.

In Table 55 are reported the DSC results for the mixtures of the two different AC 5120-graft-caprolactone systems with Epikote 828

A comparison of these results with those in Table 54 shows very similar temperature values for the melting and crystallisation processes. The melting and crystallisation enthalpies, normalised to polyethylene plus caprolactone content, are also very similar to those for the mixtures of AC 5120-graft-caprolactone. Moreover, from a comparison with Table 50 it is noted that the temperatures and the enthalpy values for both melting and crystallisation processes are very similar to those of binary mixtures 50/50 of unmodified AC 5120 with Epikote 828. From a direct observation of the DSC traces for 50/50 mixtures of AC 5120, unmodified or ε-caprolactone modified, with Epikote 828, it is noted the coincidence of the curves which becomes exact in the case of mixtures AC 5120/Epikote 828 and (AC 5120-graft-caprolactone 50/5)/Epikote 828.

In Table 56 are reported the DSC data for the mixtures of AC 5120-graft-RVP 69.8/30.2 subjected to different heating conditions, and in Figure 4.19 is shown the DSC trace for the reaction product AC 5120-graft-RVP, which can be compared with that in Figure 4 18a (control sample).

From these traces and the data in Table 56 it is noted a similar trend for AC 5120-graft-RVP systems relative to the systems grafted with caprolactone. In both cases, in fact, the modification of AC 5120 leads to an widening of the melting and crystallisation peaks, to lower melting peak and higher crystallisation peak temperatures. The explanation could be the same that for the modification with caprolactone. This time the enthalpy values, normalised to AC 5120 content, are very similar to those of pure AC 5120.

In Table 57 are reported the DSC results for the mixtures of AC 5120-graft-RVP with Epikote 828 and CY 179

The shapes of the melting and crystallisation peaks of the mixtures with the two epoxy resins are very similar to those of AC 5120-graft-caprolactone and Epikote 828, and in turn with those of 50/50 mixtures of unmodified AC 5120 with Epikote 828 and CY 179, respectively. The peaks are again very broad and the transition temperatures are very similar to those of AC 5120-graft-RVP in isolation.

In Table 58 are reported the results of the DSC analysis for the mixtures of AC 5120-graft-RVP reacted with HHPA for different periods of time at 140°C. The DSC trace of the mixture heated for 6 hours at 140°C is shown in Figure 4.20 .

From the comparison with Table 56 and Figure 4.19 it is noted that the crystallisation peaks are very similar to those relative to AC 5120 grafted with RVP, while the melting temperatures of the mixtures with HHPA are slightly higher than those of AC 5120-gratt-RVP. In no case it is observed the presence of the HHPA melting peak (normally at 31°C). The melting and crystallisation enthalpies of the reaction product with HHPA, normalised to AC 5120-graft-RVP content, are very similar to those of AC 5120-graft-RVP by itself. From all these observations it seems that the addition of HHPA has no effect on the thermal behaviour of these mixtures From Figure 4 20 it is noted, however, the beginning of a new endothermic peak at temperatures higher than 120-130°C, similar to the peak observed for pure HHPA, albeit for the latter it occurs at higher temperatures This kind of phenomenon has not been observed, however, for AC 5120-graft-RVP (Figure 4.19)

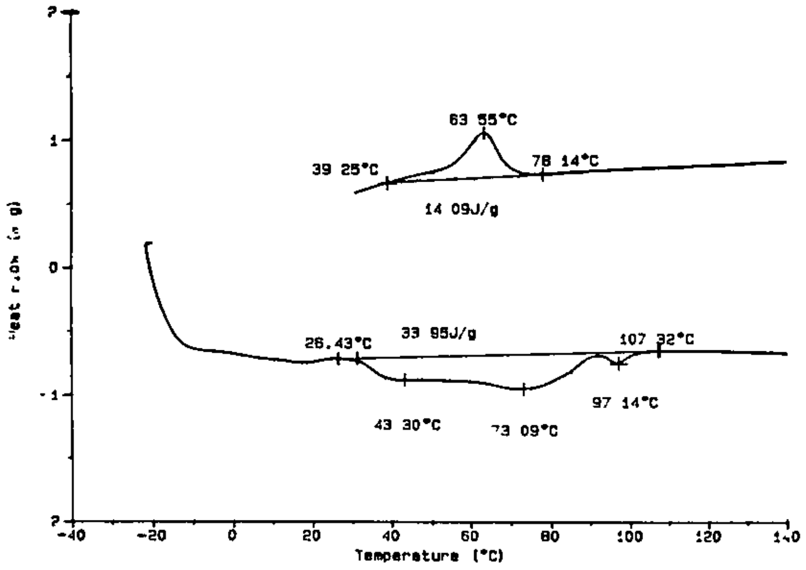


Figure 4.19: DSC scan performed on AC 5120 grafted with RVP.

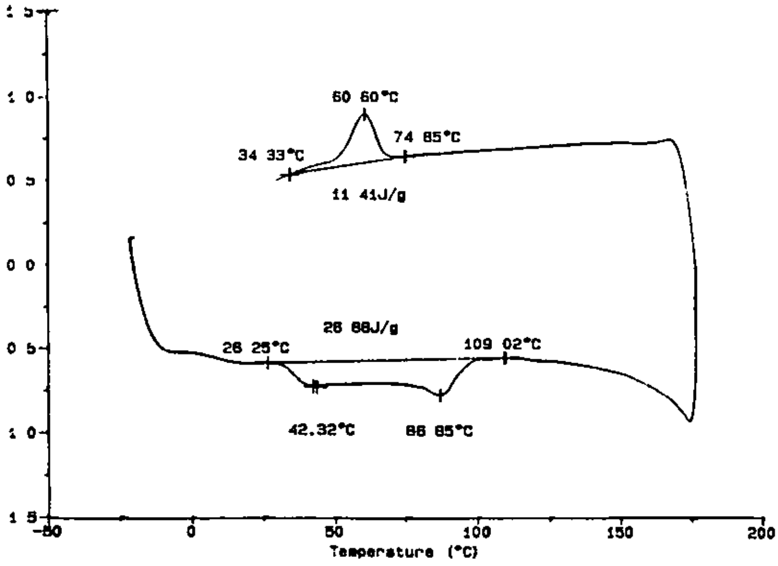


Figure 4.20: DSC scan performed on AC 5120 grafted with RVP and then reacted with HHPA.

In Table 59 are reported the DSC results for the ternary mixtures of AC 5120-graft-RVP, HHPA and Epikote 828 and CY 179, respectively. These results can be compared with those of Table 53 for ternary mixtures with unmodified AC 5120

The results are in all cases very similar to those of the mixtures with unmodified AC 5120 with respect to peak temperatures and also for the shapes of melting and crystallisation peaks. The enthalpy values are in all the cases very different from the theoretical values and also from those of similar ternary mixtures containing unmodified AC 5120.

In Tables 60 and 61 are reported the results from DSC analysis performed on AC 5120 grafted with RVP in presence of TPP as catalyst at two compositions. In the tables can also be observed the influence of the reaction time on thermal behaviour of these mixtures.

From a comparison with Table 56 it can be deduced that the introduction of the catalyst TPP in the reaction of AC 5120 with RVP has an influence only on the fusion and crystallisation enthalpies, which have been reduced considerably with respect to those reported in Table 56 This can be explained by the higher degree of conversion of the reaction with RVP when TPP is present, i e. a larger number of polyethylene chains are not able to crystallise having reacted with RVP.

From a comparison between the data in Tables 60 and 61, it can be concluded that, as in the case of systems grafted without TPP, the reaction time does not have an appreciable effect on the thermal characteristics of these mixtures.

The influence of each modification on the thermal characteristics, expressed in terms of peak crystallisation temperature (Tc) and heat of crystallisation (ΔHc) in the cooling cycle, is summarised in Table 62.

The thermal treatment alone can have a substantial effect on the crystallisation behaviour of AC 5120, particularly the crystallisation temperature. With respect to this sample, the data reveal a slight increase in crystallisation 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 reduction in heat of crystallisation, denoting a lowering of the level of crystallinity, which is particularly significant for systems modified with RVP at high levels of conversions. The residual RVP in systems at low levels of modification probably has a solvent effect on the crystallisation of the oligomer.

In Table 63 are reported the data from DSC tests performed on montanic acid and on its mixtures with AC 5120 and Epikote 828. For comparison the DSC results for pure AC 5120 are also shown.

The mixture of montanic acid with AC 5120 shows melting peaks similar to those of both pure components. This is because the two components melt at similar temperatures Furthermore, the heat of fusion of the mixture has a value similar to that calculated from the rule of mixture, reported in brackets. Similar results are observed for crystallisation process, with an enthalpy very similar to the theoretical value. This time, however, the crystallisation peaks of the two single components, found in DSC experiments, are very different (by about 20°C) and for this reason on cooling stage a crystallisation area has been found characterised by two different peak temperatures This could be explained by the presence of two single crystalline phases with no interaction between them.

The DSC trace of Epikote 828 grafted with montanic acid appears very different from that of pure montanic acid. The melting peak temperature is shifted to a lower value, though another small peak during melting is observed at 81°C. The heat of fusion normalised to montanic acid content is similar to that of pure montanic acid. The crystallisation peak of the mixture is also very similar to that of pure montanic acid, even though the shape of the curve is very different and shows another peak value at 50°C, which was not observed during crystallisation of pure montanic acid This time the normalised heat of crystallisation is lower than that of pure montanic acid.

The results from the DSC analysis of the mixtures with AC 5120, pure or grafted with caprolactone, and Epikote 828 grafted with montanic acid, are reported in Table 64

From a comparison with the DSC data of the other 50/50 mixtures of AC 5120, unmodified or modified, with Epikote 828 (Tables 50, 55 and 57) it is observed that the melting and crystallisation temperatures are very similar in all cases. It must be said, however, that the mixtures with Epikote 828 grafted with montanic acid present melting and crystallisation shapes different from those of the 50/50 mixtures of unmodified or modified AC 5120 with non-grafted Epikote 828.

Finally, the DSC data of the mixtures HHPA-e-montanic acid are reported in Table 65. For greater clarity are also reported the DSC results for pure HHPA and montanic acid

In all the mixtures it is noted the presence of melting and crystallisation peaks relative to the montanic acid rich phase with slightly lower values for the peak temperature respect to those of pure montanic acid. At the same time only for mixtures with high HHPA contents (higher than 70%) is observed the presence of a first melting peak relative to the HHPA rich phase.

The normalised heats of fusion and crystallisation appear, in most cases, to be lower than those of the pure components, except in the case of the mixtures that show only a single melting peak. Moreover, all the mixtures analysed exhibit in the heating stage the beginning of a new peak after the melting of the montanic acid rich phase, at temperatures lower than that observed for pure HHPA. As for the hardener by itself, it is thought that this peak could be related to the evaporation of HHPA phase

Comparing Tables 65 and 40 similar values of melting and crystallisation temperatures pertaining to the montanic acid rich phase are observed for the DSC and hot stage microscope experiments.

4.4) Characteristics of Cured Systems.

From the results of the miscibility studies performed on ternary mixtures of unmodified or modified polyethylenes with Epikote 828 and HHPA or MNA (see 4.1.4), it is possible to obtain an indication of the solubilisation temperature of each of the mixtures in relation to the curing and post-curing procedure to be used. (For details of formulations of cured mixtures refer to section 3.8.1 and Appendix 7.2, Tables 1 to 5)

Regarding the mixtures with each of the three unmodified polyethylenes with Epikote 828 and MNA, i e. J1, J2, J3, K1, K2 and K3, it has been found that AC 5120-graft-RVP is completely immiscible with Epikote 828 and MNA hardener. Hence, these mixtures have to be deemed to be insoluble before curing.

The mixtures containing AC 5120, Epikote 828 and HHPA, i e S1, S3, U1 and U3, are probably miscible at temperatures close to 158°C, as can be implied from Figure 4.3 (see 4.1 4)

The solubilisation temperatures are much lower for mixtures containing AC 5120-graft-RVP, Epikote 828 and HHPA. The data in Figure 4.9 show that the solubilisation temperature is around 133°C for I3, P3, L3, Q3, FHA and FHZ, and somewhat lower for I1, P1, L1 and Q1.

Partial miscibility is expected for mixtures containing AC 5120-graft-RVP, prepared in presence of TPP catalyst and then reacted with HHPA, i.e. M1, R1, M'2 and R'2, from the data observed in Figure 4 11; a lower degree of miscibility, on the other hand, is expected for the compositions M'3, R'3, M3 and R3 (i.e mixtures containing 20 parts of AC 5120-graft-RVP/TPP).

Complete miscibility at temperatures between 80-100°C results in mixtures, RU, containing CTBN liquid rubber, i e a non-crystallisable oligomer.

4 4.1) DSC Analysis of Cured Systems

As previously explained, DSC tests were performed on samples taken from different parts of the cured bars, the surface of which being richer in acrylic acid copolymer component. The samples containing one of the three unmodified polyethylenes, for instance, show a melting peak only in the upper part of the specimen; while the analysis of the lower part of these samples shows only the Tg of the epoxy resin. The samples containing AC 5120-graft-RVP, on the other hand, show in both the parts of each specimen both the Tg of the epoxy resin and a melting peak, even if the enthalpy of specimens at the surface is often higher than that measured in the lower part of the sample The Tg values, finally, are independent of the part of the specimen analysed. From these observations it can be concluded that, when there is a low level of miscibility between the polyethylene, the epoxy resin and the hardener, as for unmodified polyethylenes with Epikote 828 and MNA, phase separation takes place before gelation of the system and the phase richer in polyethylene migrates towards the surface of the sample, due to the lower density of the polyethylene modifier relative to the epoxy phase Microscopic observations on these samples confirm the existence of non-transparent isolated zones on their top. The samples containing AC 5120 grafted with RVP, on the other hand, appear more uniform and homogeneous, with the presence of only few separated zones, confirming the higher solubility of these systems. A final observation is related to the appearance of the samples in relation to the curing temperature employed The modified samples cured at a temperature higher than the melting point of the polyethylene phase (Tc = 115°C) appear to be more transparent than those cured at lower temperatures (Tc = 60°C).

In Appendix 7.2 (Tables 66 to 72) are reported the DSC results for all the cured systems produced. The analysis of the thermal data reported in these tables prompts the following comments.

* For samples with identical compositions, the Tg is not affected by the curing temperature (115 or 60°C), nor by the post-curing cycle employed (3 hrs at 150°C or 3 hrs at 150°C plus 1 hr at 180°C).

* MNA and HHPA hardeners give the same Tg value for control samples.

* The reduction of 10 parts of hardener content produces a decrease of about 10°C in Tg.

* The Tg value decreases as the content of the catalyst (BDMA and/or TPP) increases For instance, a 5 fold increase in BDMA content leads to a decrease in the glass transition temperature by about 15°C This could be explained by the presence of an excess of catalyst which may act as diluent for the system, or it could be due to a reduction in degree of crosslinking through a decrease in amount of anhydride available for curing, as a result of the formation of a quaternary salt with the BDMA

* The introduction of an unmodified or modified polyethylene leads in any case to a lowering of the Tg with respect to control samples The plasticisation effect of the polyolefin phase becomes more evident at higher contents of polyethylenes and for RVP modified systems, i e at a higher level of solubilisation of the AC 5120 component in the epoxy matrix. It must be observed, however, that some of the samples containing larger amounts of polyethylenes were prepared with a reduced quantity of the hardener (70 parts), in the belief that part of the acid groups necessary for the crosslinking reaction of the epoxy resin could be derived from the functionalised polyethylenes The reduction in Tg in these cases can also be due, therefore, to the lower content of hardener

* The presence of larger amounts of unreacted RVP also produces an appreciable reduction in Tg values.

* All the samples containing the ethylene oligomers, unmodified as well as modified, show a melting transition with a peak temperature lower than that found for the corresponding polyethylene, unmodified or modified, in isolation

* It is not possible to make any comment on melting enthalpies of cured systems being unknown the exact content of the polyethylene component in the specimens analysed, as it changes from zone to zone.

In conclusion, the analysis of the thermal properties suggests that the presence of a polyolefin modifier reduces the density of the epoxy network. The softening of the epoxy matrix could be attributed in part to the dilution effect of the polyethylene phase, solubilised in the liquid resin before its hardening, and in part to the plasticisation effect by the unreacted monofunctional epoxy modifier.

4.4 2) SEM Observations on Cured Systems.

The results of the SEM analysis performed on cured systems are presented in Figures 21 to 38 (Appendix 7 3), where are shown some of the micrographs taken on the surface of samples fractured at low temperatures

For comparison purposes, the microstructure of the control sample (CL) cured at 115°C is shown first in Figure 21.

A feature similar to that observed in the control (CL) sample, i.e distinct fracture lines characteristic of brittle resins, is found in sample J3 (Figures 22 and 23). Like the other cured systems prepared with unmodified functionalised polyethylene, J3 presents on surface a layer rich in polyethylene component, while no dispersed particles are observed in the bulk of the sample. It is, therefore, confirmed that for all the systems prepared with unmodified functionalised polyethylenes the second phase introduced in the epoxy system separates and migrates to the top of the sample, and is not available, therefore, to act as a toughening agent in the bulk of the sample.

The effectiveness of the acrylic acid copolymer AC 5120 as toughening agent begins to be revealed, on the other hand, when it is modified with the monofunctional epoxy resin RVP (Figures 24 to 27). Although a part of polyethylene phase again accumulates on the surface of the cured sample, as shown in Figure 24, some particles are present in the bulk, as shown in Figures 25 and 26, for the system cured below the melting point of AC 5120 (FHZ), and in Figure 27, for the system cured at 115°C (FHA). In Figure 25, in particular, it is possible to observe the well dispersed particles at the edge of the advancing fracture planes, acting as crack stoppers The spherical particles range in size from 5.0 to 25 μm. In Figure 26 is shown in detail one of the larger particles. It is noted the different feature of the fracture surface inside the particle relative to the brittle fracture of the epoxy matrix, i e the particle appears to be fractured in a ductile manner. The ability to slow down the propagation of the brittle fracture through the matrix is also demonstrated by the ductile failure of the particles of the system FHA, as shown in Figure 27. Finally, the adhesion between these particles and the matrix in both systems appears to be very good, suggesting that the particles could contain also a certain amount of epoxy resin. Similar considerations can be made for the systems containing lower amount of AC 5120-graft-RVP, shown in Figures 28 to 31. It is again possible to observe in these systems the presence of small spherical particles, potentially capable of arresting the fracture propagation in the matrix. The feature of the fracture surface through the particles, moreover, is characteristic of aggregated particles. The thickness of the separated layer on surface, on the other hand, diminishes with decreasing the content of modified AC 5120

When the functionalised polyethylene is modified with RVP in presence of TPP (i.e. at high extent of conversion), the spherical particles are able to precipitate in a more uniform way and display a reduced migration effect to the surface, as shown in Figures 32 to 38. For systems cured at higher temperatures, these particles appear at the end of brittle fracture planes, acting as crack stoppers, independently of their composition (Figures 32 to 34) When the curing temperature used is lower, on the other hand, it seems that a higher content of modified AC 5120 is necessary to arrest the propagation of the fracture inside each particle (Figures 35 to 38). For the samples cured at 60°C, the particles appear to fracture in a more ductile way (Figures 36 and 38) than those present in systems cured at 115°C (Figures 33 and 34) which are more smooth and regular. In other words, at 60°C the system is below the melting point of the polyethylene phase and, therefore, it retains much of the original ductility of this phase. The particles that precipitate from the high temperature curing schedule, on the other hand, contain epoxy resin and hardener and are likely to be crosslinked

In Figure 39 is shown the system containing CTBN liquid rubber as modifier. Even if not very clear, the presence of numerous very small particles (0.5-0.7 μm) is noted also in this case. The size distribution of these particles, however, is very uniform relative to those observed in the systems containing the modified AC 5120.

In Table III are reported the values of the volume fraction of the particles of some cured systems, V_P, calculated measuring the dimensions of the particles on SEM micrographs, assuming that they have broken exactly in the middle, relative to the volume of the matrix, corresponding to the total area of the photograph, i.e.

$$V_P = \frac{\text{Total Area of Particles in the Photograph}}{\text{Area of the Photograph}}$$

In Table III is also shown the theoretical volume fraction, i.e. V_M , expected in each system for the polyethylene modifier, calculated using the following formula:

$$V_M = \frac{W_M / \rho_M}{W_M / \rho_M + W_E / \rho_E}$$

where: W_M is the weight fraction of the polyolefin modifier,

W_I is the weight fraction of the epoxy resin;

ρ_M is the density of the polyolefin modifier ($\cong$ 0.85 g/cm^3);

ρ_E is the density of the epoxy resin ($\cong$ 1.15 g/cm^3)

TABLE III: Volume fraction values calculated on some of the cured system.

Sample	W_M	V_M	V_P
R1	5	6.6	3.7
R3	17	21.7	8.3
M3	17	21.7	4.6

W_M (%) = weight fraction of the polyethylene modifier, i.e. AC 5120-graft-RVP/TPP, V_M (%) = volume fraction of the polyethylene modifier, V_P (%) = volume fraction of the precipitated particles (Formulations for R1, R3 and M3 are shown in Table 5, Appendix 7.2)

The volume fraction of the precipitated particles calculated through the observation of the SEM micrographs are always much lower than those calculated theoretically from the content of the polyethylene in each sample. Although the theoretical volume fraction values are subjected to some errors, since the density of the modifier is considered to be the same as of the polyolefin, the values in Table III show clearly that only a fraction of polyethylene phase is precipitated as spherical particles. Especially for the sample cured at high temperature, i.e. M3, it was difficult, however, to measure accurately the dimensions of the particles, hence the results may, again, not be very accurate.

Bearing in mind these limitations, the most impressive result is the diminishing of the effective (precipitated) volume fraction with increasing the curing temperature used.

In conclusion, the different curing temperatures employed seem to have an appreciable effect on the nature and the characteristics of the precipitated particles that form inside the epoxy matrix. The systems cured at temperatures lower than the melting point of the polyethylene, in fact, should contain particles formed by additional polyethylene phase precipitating out as primary particles separated through chemical reactions When the curing temperature is higher than the melting point, on the other hand, the only mechanism acting is that of nucleation and growth. In the first case, the curing process produces particles very rich in the crystallisable component, explaining the very ductile surface of the particles. In the second, the precipitation involves a mixture of modified polyethylene with epoxy resin giving rise to amorphous particles not too different from the surrounding brittle matrix, but still able to act as crack stoppers. Both systems, however, show a very good adhesion between the matrix and the particles The dimensions and the number of the precipitated particles, finally, seem to be influenced by the curing temperature and by the amount of modified polyethylene. The dimensions of the particles, in fact, increase with the content of AC 5120-graft-RVP/TPP and using a lower curing temperature (60°C) Their number decreases when using a higher curing temperature.

4 4 3) Mechanical Characteristics of Cured Systems.

4 4 3.1) Dynamic Mechanical Analysis

The results of the DMA tests performed on some of the samples, cured at 115 or 60°C and always post-cured at 150 and 180°C, are shown in Figures 4 21, 4.22 and in Table 73 (Appendix 7 2)

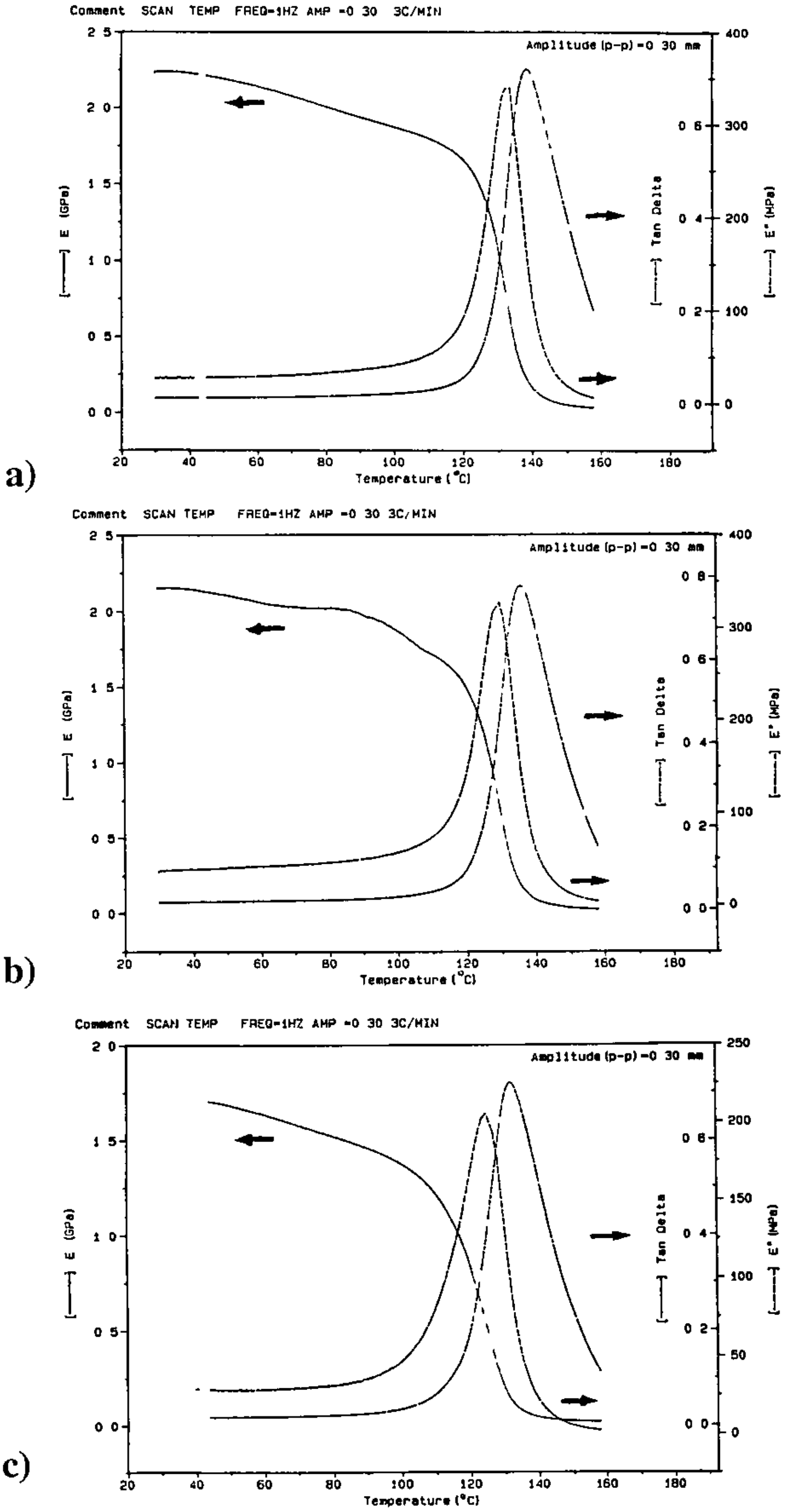


Figure 4.21: DMA scans performed on a) control sample, CL; b) sample with 5 parts of grafted AC 5120, M1; and c) sample with 20 parts of grafted AC 5120, M'3.

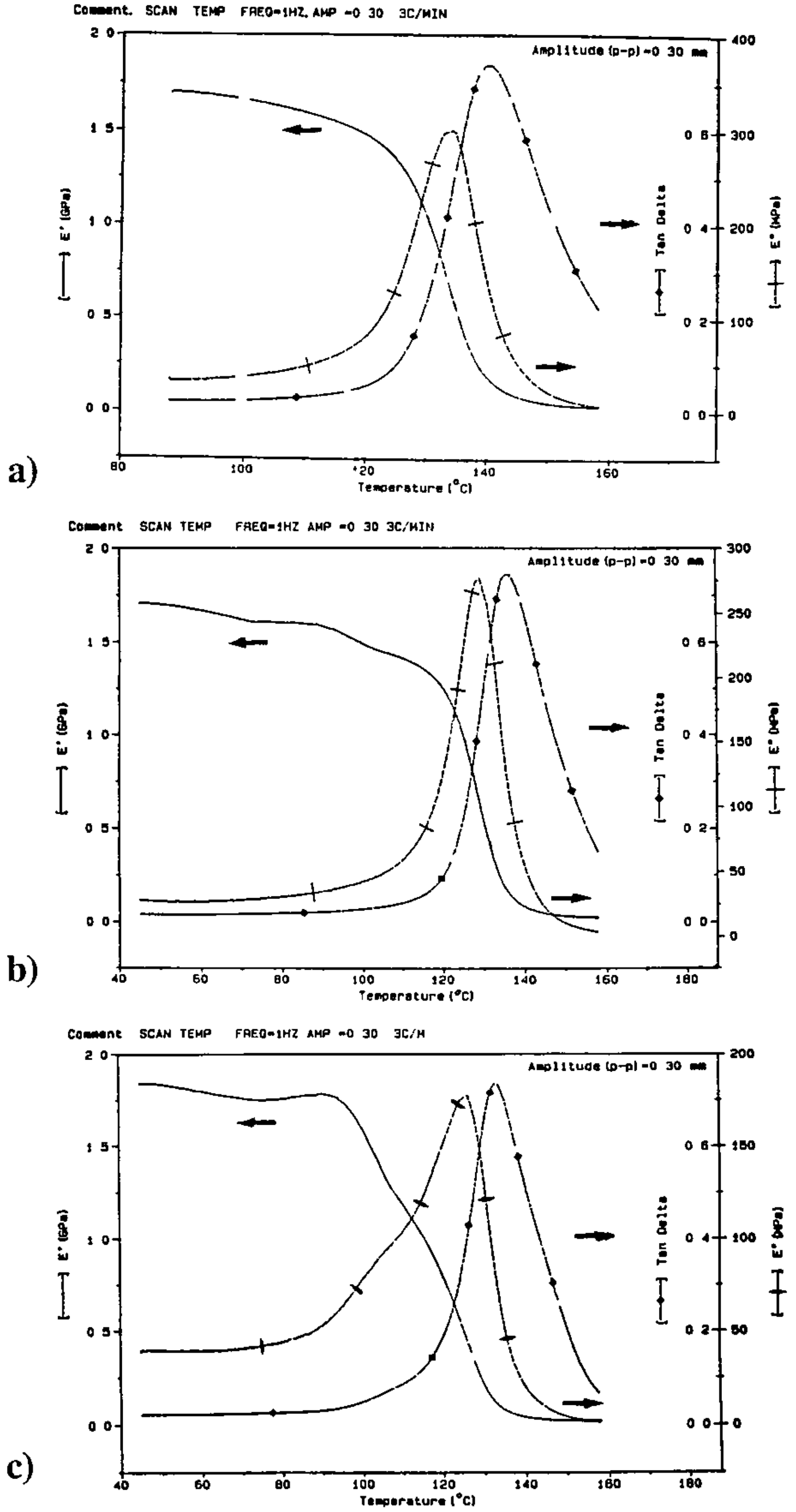


Figure 4.22: DMA scans performed on a) control sample, CR; b) sample with 5 parts of grafted AC 5120, R1; and c) sample with 20 parts of grafted AC 5120, R'3.

It can be first noted that the curing temperature used seems to have a certain influence on both dynamic moduli, i e. a lower curing temperature produces a general decrease (~ 15-20%) of these moduli In examining the influence of the addition of modified polyethylene on dynamic moduli at room temperature, it is revealed that for lower contents of AC 5120 grafted with RVP (M1 and R1 samples) the storage modulus is slightly lowered (5-10%), while the loss modulus shows an increase of about 25%. Less clear is the trend when the content of modified AC 5120 is increased to 20 parts. The storage modulus appears to decrease by different amount and the loss modulus has values similar to or twice as large as to the control samples, both depending on the curing temperature employed. In conclusion, it can be said that the inclusion of low percentages of the modified polyethylene AC 5120 has only a small effect on the dynamic-mechanical properties of the cured samples. Increasing the amount used, the decrease in storage modulus becomes more pronounced

Some comments can also be made from the observation of the curves relative to dynamic parameters measured in temperature scans for control and modified samples, reported in Figures 4 21 and 4.22. The presence of large peaks in G' curves found for almost all the modified samples at about 90°C, temperature close to the melting point of the crystalline phase, suggests that the melting process has a certain effect on the storage modulus. For the sample containing 20 parts of grafted AC 5120 and cured at 60°C (R'3) it can be also noted a peak in G'' curve at a higher temperature, i e at about 105°C. It is thought that this peak could be a consequence of the presence of a dispersed phase, even if is not clear the effect of this phase on the loss modulus.

From a comparison of Table 73 with Tables 68 and 70, finally, it can be observed that the Tg values, calculated in temperature scan tests as the temperature at which the maximum of the G'' curve is reached, are in good agreement with those measured by DSC technique (i.e. they are about 2°C higher than those found by the DSC analysis)

4 4.3.2) Flexural Tests

In Tables 74 to 76 (Appendix 7 2) are reported the results of Flexural Tests performed on some of the cured samples produced. The values of flexural modulus, strength at break and strain at break can be compared at different curing and post-curing temperatures with respect to the content of modified AC 5120.

Comparing first the control samples, all the mechanical properties measured seem do not seem to be affected by the curing and post-curing cycles used, although some anomalous results are observed (for instance the properties found for the control cured at 60°C with 5 parts of the catalyst BDMA (CQ) are higher than those found for the control cured at the same temperature with only 1 part of BDMA, i e. CR. This behaviour is not found for the other control cured at 60°C with 5 parts of catalyst but post-cured only at 150°C (CP)

The inclusion of a low percentage of RVP grafted AC 5120, irrespective of whether the catalyst TPP was used or not, has no influence on the flexural characteristics with respect to the control samples On the other hand, when the content of modified polyethylene is increased, the modulus and strength measured in flexural tests are reduced by more than 15-20% It must be remembered that all the samples analysed with 20 parts of modified AC 5120 contain only 70 parts of the hardener HHPA. Therefore, the true cause of the decrease of the mechanical properties could be associated with the low degree of crosslinking of these systems, as already verified by the Tg values measured in the DSC tests No clear trend is found for the results of elongation at break.

In conclusion, the presence of limited percentage (5 parts) of polyolefin leaves almost unaffected the flexural properties found for the control samples. These properties seem to be very slightly influenced by the level of modification of the polyethylene added to the epoxy resin.

4.4.3 3) Fracture Toughness Tests.

In Table 77 are reported the results from Fracture Toughness Tests in 3 point bending performed on some of the cured samples realised.

For both the toughness parameters measured, i e. K_c and G_c, the results depend on the curing cycle used. Samples cured at 60°C present values of both K_c and G_c lower by about 10% with respect to analogous samples cured at 115°C.

The addition of a polyethylene phase produces an increase (about 10%) in the critical stress intensity factor, K_c, only at a low percentage of modified AC 5120 (5%), while K_c remains almost unaffected when the percentage reaches 10%. Low contents of the polyolefin lead to an even more remarkable enhancement in the critical strain energy release rate G_c , i e about 20%. These increases are recorded independently from the curing temperatures employed. It must be mentioned, however, the not very good reproducibility of the tests, especially for small lengths of notches (< 50% of the total width). In Figures 4 23 and 4 24 are shown the results of the tests performed on a control (CL) and a modified (M'2) cured sample, respectively. In these figures P is plotted against $(BW^{1/2})/Y$ in order to calculate K_c as the slope of the straight line fitting the experimental data

In Table 77 is also reported the K_c value found for the system containing CTBN rubber An increase of about 17% is observed for this system with respect to the control, i.e. CL

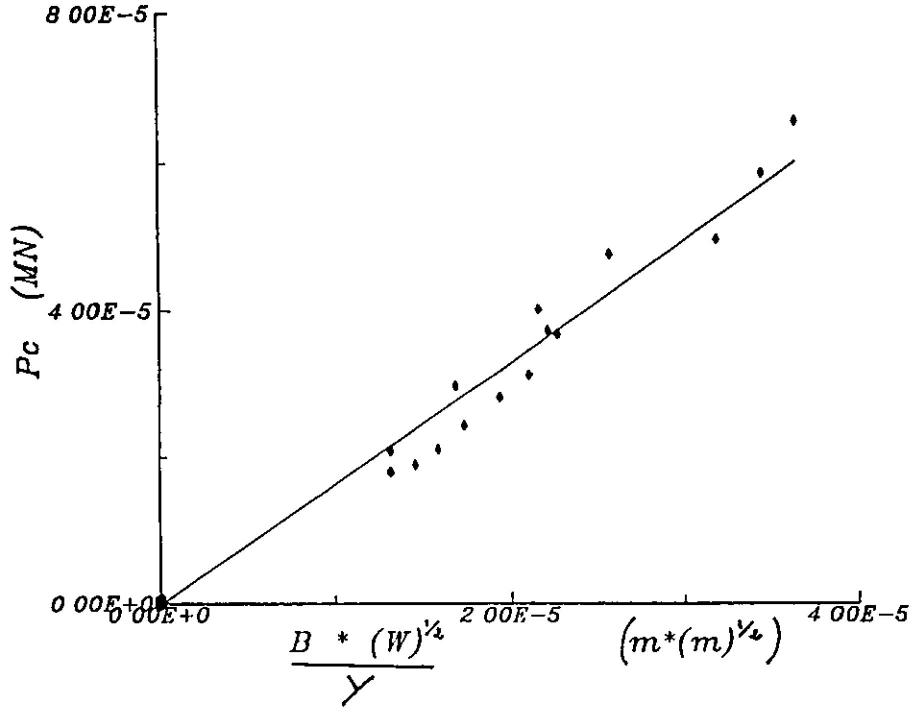


Figure 4.23: Plot for critical stress intensity factor (K_c) of control sample, CL. K_c = 1.65 MPa*m$^{1/2}$.

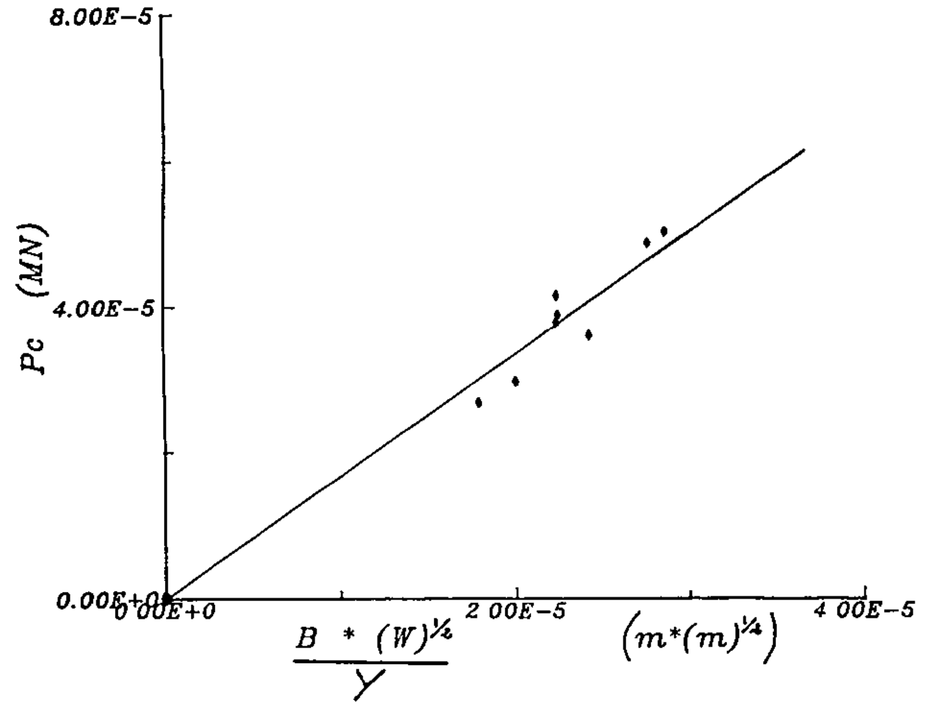


Figure 4.24: Plot for critical stress intensity factor (K_c) of sample with 10 parts of grafted AC 5120, M'2: K_c = 1.67 MPa*m$^{1/2}$.

The results of Charpy Impact Strength for the unnotched samples analysed are reported in Table 78, Appendix 7 2 It is noted that the inclusion of low percentages (5 and 10 %) of modified AC 5120 produces an increase in impact strength values of about 10 and 15%, respectively, with respect to the control sample It seems, therefore, that by increasing the content of modified polyethylene it is possible to obtain a certain increase in the toughness of the cured samples. It must be said, however, that all the modified samples showed a wide variability of results, i.e larger than in the case of the control samples. This is probably due to the fact that it is not possible to obtain completely homogeneous cured samples, as already observed, without zones with the modified AC 5120 demixed from the system.

In conclusion, the addition of low percentages of the modified AC 5120 produces a limited increase in all the parameters related to the toughness

5. DISCUSSION

5.1) Effects of the Functionality of Low Molecular Weight Polyethylenes on their Miscibility with Epoxy Resins.

The miscibility of the binary mixtures of the two epoxy resins with any of the three functionalised polyethylenes under investigation has been found to be strongly dependent on the functionality of the polyethylene

An aid to the solubilisation process was found in the prolonged heating of the mixtures at temperatures higher than the melting point of the polyethylenes. Nevertheless, to achieve complete miscibility between the different phases, it is necessary to heat the mixtures at high temperatures, even higher than 200°C for the polyethylenes with lower values of functionality (i.e $f = 0.26$ and 1.22). It is thought that for these systems the solubilisation process takes place through chemical reactions of the acid groups of the functionalised polyethylenes with the epoxy resin, often resulting in crosslinked products before achieving complete miscibilisation. In support of this hypothesis there is the observation that most of the mixtures of the acrylic acid copolymers with higher functionality values, once solubilised, did not show the precipitation of particles of the second phase in the cooling stage. This is also confirmed by the strong adhesion between the glass covers at temperatures higher than the melting point of the polyethylene

The inducement of miscibilisation of different phases is related to the diffusion processes between these phases The studies on diffusion in the mixtures of functionalised polyethylenes with epoxy resins gave a confirmation of the influence of functionality, i.e. an increase in the diffusion rate from the particles into the resin was found with increasing the functionality of the polyethylene component. Moreover, from the observations of the solubilisation and precipitation temperatures in hot stage experiments, and bearing in mind that a wide gap between these temperatures indicates a slow diffusion process and a narrow temperature gap indicates a fast diffusion, it is possible to arrive to the same conclusion. The acrylic acid copolymer AC 540, having a functionality of 1 2 and showing a wide temperature gap, is characterised by a slow diffusion rate. The opposite is the case for AC 5120 which has a functionality of about 2

The functionality of the acrylic acid copolymers plays an important role also for the solubility of their ternary mixtures with an epoxy resin and a hardener

Again the mixtures with the polyethylene having lower functionality, AC 540, turn out to be less miscible than those with AC 5120. It is also noted that the addition of the hardener HHPA decreases the solubility of the ternary mixtures, which is probably due to an isomorphic transformation of the hardener when heated or simply to a change of the solubility parameters Most of the ternary mixtures, in fact, show a solubilisation temperature higher than that of the correspondent binary mixture Larger amounts of epoxy resin seem to make easier the solubilisation process with the polyethylene and the hardener.

Solubilisation between different phases can carry on through purely physical diffusion, driven primarily by entropy, or through both physical and chemical processes, which will be characterised by both entropy and enthalpy terms If the latter is the case of the mixtures with HHPA, i.e. the solubilisation in these mixtures is chemically induced, the endothermic heats recorded in DSC experiments on heating must be related to the enthalpy of mixing On the other hand, the total enthalpy recorded in the heating cycle of the DSC experiments take into account also the melting of the crystalline phases (AC 5120 and HHPA), and it is not easy to separate the single contributions, due to the fact that is not well understood in which form (cis- or trans-) is present HHPA Finally, a confirmation of the occurrence of solubilisation through chemical reactions for these mixtures can be derived from the observation under the optical microscope that phase separation not always occurs in the cooling stage. The irreversibility of chemical reactions, in fact, hinders the reformations of the second phase particles on cooling.

5.2) Effects of Chemical Modifications of the Polyolefin Component on its Miscibility with Epoxy Resins.

The modifications performed on the acrylic acid copolymer with the higher functionality, AC 5120, have not always led to an increased miscibility of its mixtures with the epoxy resins used

The reaction of AC 5120 with ε-caprolactone gave rise to modified systems that show a definite deterioration in miscibility with epoxy resins for both binary and ternary mixtures. Increasing the content of caprolactone and/or its reaction time with AC 5120, the mixtures become even less miscible. As the molecular weight of AC 5120 remains approximately constant after the reaction with caprolactone (see paragraph 4.3.2, Figure 4 17c, and data in Table 46 in Appendix 7 2) and the melting and crystallisation temperatures of AC 5120-graft-caprolactone decrease with respect to unmodified AC 5120 (see DSC data in Table 54, Appendix 7.2), it can be concluded that the reaction between AC 5120 and caprolactone leads to an effective unitary grafting of AC 5120 and that the formation of side branches hinders crystallisation. The explanation for the reduced miscibility of AC 5120-graft-caprolactone with Epikote 828 and/or HHPA must related, therefore, to intrinsic chemical factors For example, the branches produced through the grafting reactions could reduce the diffusion rate in the solubilisation process

On the other hand, by modifying AC 5120 with a monofunctional epoxy resin it is possible to achieve a substantial improvement in miscibility with epoxy resins. Moreover, almost all the binary mixtures, once solubilised in the heating stage, phase separate on cooling A further increase in miscibility is promoted by the use of a catalyst capable of producing a higher conversion for the acid groups of AC 5120. This time, however, no phase separation on cooling stage is recorded and, therefore, it shows that the UCST curve has moved to much lower temperatures.

The ternary mixtures of AC 5120 grafted with RVP, Epikote 828 and HHPA, however, are not much more miscible relative to similar systems based on unmodified AC 5120. The HHPA hardener, in fact, causes again the demixing of the modified polyethylene from the epoxy resin. The stoichiometric chemical reaction of HHPA with AC 5120-graft-RVP, in presence of the catalyst, leads to a certain improvement in the solubility of the total mixtures, especially relative to the modification with caprolactone (see Figures 4 3, 4 6, 4 7, 4.11) As already stressed in the presentation of the results, the reaction time for all the chemical reactions employed to produce modified systems is very important A better miscibility is achieved heating the mixture only long enough to obtain the maximum conversion in each reaction.

Various attempts have also been made to achieve better miscibility between the components A different hardener, MNA for istance, added to binary mixtures of RVP grafted AC 5120 with Epikote 828 gives rise to completely immiscible mixtures.

Also the attempt to modify the epoxy resin Epikote 828 with montanic acid has not been very successful. The montanic acid seems not to affect the diffusion processes occurring between the different components in a mixture, processes that are responsible of the solubilisation of the components. The studies on the hot stage microscope have shown similar solubilisation temperatures for systems differing only for the presence of montanic acid. Again, the addition of caprolactone in these systems produces a decrease in solubility

The montanic acid has been also used to prevent any isomorphic transformation of the hardener HHPA that could cause the low miscibility in mixtures of functionalised polyethylenes and epoxy resins Even if this experiment succeeded, i e the use of small amounts of montanic acid prevents the transformation of HHPA to the trans-form, this modification is not effective in enhancing the miscibility of ternary mixtures However, these experiments have been useful since they revealed the peculiar behaviour of HHPA, i e its high sensitivity to moisture, which could more readily promote the isomorphic transformation, even in presence of montanic acid

Finally, miscibilisation studies performed on mixtures of Epikote 828/HHPA in which a CTBN based liquid rubber was added, have revealed that these systems form totally miscible mixtures This proves that the initial system, resin plus hardener, is miscible even at room temperatures with traditional oligomeric systems used as toughening agents It can be inferred, therefore, that the miscibilisation of the polyethylene based modifiers must have resulted from chemical reactions with the epoxy resin, unlike the case of CTBN which is physically miscible with the epoxy resin .

5.3) Effect of Chemical Modifications of the Polyolefin Component on its Crystallinity.

All the chemical modifications performed on AC 5120 produced some effects on the crystallinity of the polyethylene

The modification reactions, leading to an extension of the chain length of the polyethylene, gave rise to a decrease in the crystallisation enthalpy. This decrease is more marked for the products of the reactions with a higher level of conversion and is accompanied by an increase in the peak crystallisation temperatures

The occurrence of a further decrease in heats of crystallisation, produced by the thermo-mechanical treatments (i.e. the stirring of the materials in the melting state), remains less clear to explain. The effect of the crystallisable component on crystallisation should be considered, therefore, as the net effect of both the difficulty to crystallise the longer chains and the treatment employed

5.4) Phase Separation Phenomenon during Curing of Epoxy Resins Containing a Functionalised Low Molecular Weight Polyethylene.

As already discussed, the modification of the acrylic acid copolymer AC 5120 with the monofunctional epoxy resin RVP, in the presence of a catalyst, was found to be the most effective in increasing the miscibility with the epoxy resin and to produce a two-phase system in a cured epoxy matrix, shown in SEM micrographs (see Figures from 32 to 38 in Appendix 7.3).

The use of AC 5120 without any modification to prepare cured epoxy systems was found to be ineffective, leading only to a migration of polyolefin component to the surface of the sample The centre of the sample, in fact, appeared to be transparent, not containing any particles Moreover, in comparing the Tg values of systems containing a functionalised polyethylene with that of a control sample, cured with the same amounts of hardener and catalyst, a small decrease in the Tg was observed (up to 4°C for a content of 20 parts of AC 5120) with respect to the corresponding control samples. This could suggest that the polyethylene present in the centre of each sample acts as a plasticiser only for samples with higher contents of AC 5120. On the other hand, a notable decrease in Tg values was found for the systems prepared with modified AC 5120, which becomes more pronounced with increasing the content of AC 5120. This time, both the more soluble polyethylene phase and the unreacted RVP could act as plasticisers It must be stressed, however, that even in these systems a completely stable and homogeneous system is never reached, since a part of polyethylene still migrates to the surface of the samples, as shown by the DSC analysis, which revealed the presence of a melting peak only in the upper part of the specimens

It can be concluded that the modification of AC 5120 with RVP, in the presence of TPP, improves the miscibility in mixtures with the epoxy resin and provides cured systems in which the polyethylene phase separates to give rise to a precipitated particles morphology. Since the modification reaction when the catalyst TPP is present goes to a high conversion, in the cured samples there must be only a low amount of unreacted RVP as potential plasticiser for the matrix On the other hand, in the same samples the plasticisation effect of the more soluble modified AC 5120 is stronger Therefore, the best results in terms of lowest reduction in glass transition temperature and greatest uniformity of particles distribution in precipitated systems, are achieved at low contents (5-10 parts) of AC 5120 grafted with RVP in presence of TPP.

The lower values of the volume fraction of the precipitated particles calculated from the SEM micrographs, with respect to those obtained theoretically from the precise amount of grafted AC 5120 added to the systems indicate that a large part of the polyolefin modifier does not precipitate as particles and, therefore, remains dissolved in the epoxy matrix and acts as plasticiser

The effect of the curing temperature on the precipitation of second phase particles, though not detected in the DSC analysis, was revealed from SEM observations. Systems cured at different temperatures are subjected to different precipitation mechanisms, as observed from the different features of the fractured surfaces and the characteristics (dimensions, numbers and volume fraction values) of the spherical particles precipitated in the epoxy system. On the other hand, the matrix consisting of epoxy resin mixed with a certain amount of modified AC 5120 shows the same morphology and Tg values, irrespective of the curing temperature

5.5) Mechanical Properties of Modified Cured Samples.

Both the content of modified AC 5120 and the curing temperature have an appreciable effect on mechanical properties

The introduction of 5 parts of the polyethylene, previously grafted with RVP in the presence of TPP, leads to an increase in the toughness properties from about 10% , for K_c and a_{cU} , to 20% , for G_c At the same time, the flexural and dynamic-mechanical moduli of these samples remained unaffected or slightly lowered with respect to the control samples Lower enhancements in toughness properties are found for samples containing 10 parts of modified AC 5120 Only the a_{cU} data for these samples show an increase of about 15% When the content of modified polyethylene is increased to 20 parts, on the other hand, the modulus showed, generally, a significant decrease (up to 25%) Only a slightly higher enhancement in toughness, as measured by K_c , was found for the system containing 10 parts of CTBN liquid rubber, i.e an increase of about 15% with respect the control CL.

From these observations it is concluded that the addition of either a polyolefin or a liquid rubber modifier, due to their ability to produce precipitated particles inside the cured systems, leads to better toughness properties, though these increases are lower than those expected, owing to the low yield of precipitated particles. Moreover, in the case of the modified polyethylene, the low enhancement in properties could also be attributed to the precipitated particles being too soft and not able to give rise to shear deformations in the matrix, the required condition for an effective toughening The precipitation of ductile particles, therefore, may not be a sufficient requirement to impart the desired properties to the system, even if a good adhesion between particles and matrix is assured.

From a comparison of the results found in this study with those reported by other authors on toughened systems, however, some discrepancies are observed.

It is reported that neat DGEBA resins cured with different agents (i.e. piperidine, diaminodiphenyl sulphone (DDS), diaminodiphenyl methane (DDM), anhydrides) generally present lower values of storage modulus, G', from 0.9 GPa

(120,121) to 1 4 (122) and 2 GPa (123), than those found for the systems examined in this study (i e. 2.4 GPa for CL and 1 95 GPa for CR) On the other hand, the above authors too have found that the inclusion of a toughening agent produces a slight decrease in G', i e 20% (122), while a very strong increase was found for G'', i e. up to 12-fold (60)

The experimental data found for the flexural modulus and the strength at break are more in line with those reported in the literature Several studies, in fact, have reported for standard DGEBA resins a value for the flexural modulus of 2 25-2 5 GPa (56,72) or slightly higher, i e 2 96-3 37 GPa (60 71 124 125) All the researchers reported a decrease in flexural modulus from 10% to 30% when introducing a toughening agent, not always a rubber, depending on the nature and the amount of this modifier The flexural strength reported in the literature (60,126) is, however, lower, i e. varying from 78 6 and 76.1 MPa, than those found in this work, in the range of 99 1-97 0 MPa Also for the other researchers the addition of low amounts of modifier leads to an increase in flexural strength, but at higher levels of addition it decreases to values even lower than those found for the control samples However, it must be said that these systems are probably more likely to give complete precipitation with respect to the systems of this study.

While no authors performed fracture toughness tests employing a Charpy pendulum on unnotched samples, many studies were concerned with toughness properties in slow speed 3 point-bending tests Also the K_c and G_c values obtained in this study are different to some extent to those reported by other authors. They have reported, for a standard DGEBA resin cured with HHPA hardener, values of G_c ranging from 0.136 to 0 153 kJ/m^2 (127), which are much lower than those found in this research for control systems, i e. 1 15 and 1 01 kJ/m^2. Similar values have been found for a DGEBA resin by other authors (61 71,76,122,124 128-130), i e G_c = 0.09-0.39 kJ/m^2, with increases up to 600% when a rubber modifier is added (124,128); while the increases in G_c are more limited (10-170%) when a thermoplastic toughening agent is employed, PC, PES, PI (71,122,128). The higher toughness of unmodified systems studied with respect to similar systems reported by others could explain the limited effect of the toughening agents found in this study.

The values reported for K_c using similar resins are again lower than those found in this study, corresponding to 1.65 and 1.52 MPa(m)$^{1/2}$. The disagreement in this case, however, is less significant, i.e. K_c values range from 0.6 to 1.1 MPa(m)$^{1/2}$ (56,72,73,76,122,124,128-132). Moreover, the Tg values found for most of the DGEBA cured systems are much higher (from about 150°C (13,56,60,122) to around 200°C (72,73,76,128)) than those found for the control systems in this study (~132°C). Therefore, the system analysed in this research could be intrinsically more ductile than those reported by the above authors, which is confirmed also from the lower values of flexural modulus. Again, the more remarkable increases in K_c are recorded with the addition of a rubbery modifier, i.e. from 80 up to 210% (124,128,131,132), while increases ranging from 15 to 75% only are found with about 10% of thermoplastic modifiers (72,73,122,128).

The enhancement in toughness of brittle resins is strictly related to the volume fraction of the dispersed particles, i.e. on increasing the volume fraction the toughness generally increases up to a level reaching a plateau or a maximum. In rubber toughened epoxy systems, moreover, the volume fraction of the precipitated particles is always higher than the volume fraction of the modifier added (60,61,124), suggesting that the particles are formed by a mixture of modifier and resin. This last observation may constitute the main explanation for the lower enhancement in toughness reached in the systems modified with grafted AC 5120, i.e. only a fraction of polyolefin modifier is capable of precipitating and forming dispersed particles. On the other hand, for the system in which the toughening agent is the rubber oligomer CTBN the lower increase in toughness with respect to the control (CL) can be explained by the use of a crosslinking agent different from those usually employed, i.e. generally amines (56,124,128) or piperidine (131,132) which are capable of inducing effectively the precipitation of particles. However, comparing the K_c value found in this study for the sample containing 10% of CTBN and cured with anhydride (K_c = 1.93 MPa(m)$^{1/2}$) with those reported in literature, i e. from 2.0 to 2 20 MPa$(m)^{1/2}$, for samples containing similar amounts of CTBN or ATBN rubbers cured at similar temperatures (~120°C) with different hardeners (124,131 132), the results are very similar.

The effect of lowering the curing temperature from 115°C to 60°C on mechanical properties is to decrease the dynamic modulus, by about 15-20% , and toughness properties, i e K_c and G_c by about 10% . Since these deteriorations of properties are also observed for control samples, they cannot be attributed to the different nature of particles precipitated through different mechanisms and/or different values of volume fraction for the two curing temperatures. Therefore, they are intrinsically related to the crosslinking network of the matrix

It is known that the properties of a neat resin depend markedly upon the curing temperature, even if an identical post-curing cycle is subsequently employed (133,134). Curing at different temperatures can lead to diverse network topologies and, in turn, to different mechanical characteristics of the matrix, also in toughened systems (134,135). The development of good mechanical properties requires the attainment of a sufficiently high degree of crosslinking This condition is typically obtained by curing or post-curing at high temperatures, but it does not necessarily result in better mechanical properties (136) Networks obtained at high temperatures, in fact, show a progressive increase of the fracture toughness and a corresponding reduction of the glass transition temperature and elastic modulus in the rubbery plateau (133).

The curing temperature can influence properties in several ways. Morgan and O'Neal showed that DGEBA can crystallise when the resin is cured at low temperature (137). On subsequent heating for post-curing the small crystals melt and diffuse into the surrounding matrix, thus leaving numerous holes, which exert a weakening action On the other hand, Gillham has demonstrated that during the cure of epoxy resins two phenomena take place, i e gelation and vitrification (138). Gelation results from an increase in the viscosity of the medium subsequent to branching reactions, whereas vitrification begins when the glass transition temperature reachs the curing temperature Since the mobility of the unreacted functional groups at this stage is appreciably reduced, further curing in the glassy state is controlled by diffusion The degree of polymerisation at vitrification increases with increasing the curing temperature. When the materials are post-cured, particularly above the Tg, the crosslink reactions start anew and eventually go to completion. In this step cycle, different network structures can result due to different extent of conversion attained at vitrification. A further complication is due to a possible volatilisation of the hardener, particularly at high curing temperatures (139,140), though some researchers did not observe any weight loss during the polymerisation at 120°C (141) Oxidation of the hardener also occurs as indicated by the progressive darkening of castings as the curing temperature is increased. Both phenomena can lead to less dense networks and then explain the decrease in Tg at high cure temperatures (135) It has frequently been observed, finally, that glasses obtained at low temperature have higher moduli, in spite of their lower crosslink density (136,142-144). This effect has been attributed to the higher free-volume content in glasses cured at high temperature

In another study (145) the variation of the molecular weight between crosslinks of a DGEBA resin, i.e Mc, was related to the curing temperature It was found that Mc is strongly dependent on the curing cycle, as already suggested by other researchers (146), and that the network structure can develop more effectively giving a lower Mc value at low temperatures An increase in Mc has a remarkable influence on properties, i.e the glass transition temperature decreased while ductility and fracture toughness were found to increase (147) The correlation found between Mc, tensile bulk properties and fracture toughness reflect the effect of the microstructure on bulk properties of DGEBA cured resins

The above discussion may in part explain the effect of the curing temperature on some properties of cured samples found in this study The resin of this study, however, did not show any variation in Tg or flexural modulus values with the curing temperature, which is in contrast with the results reported in the above mentioned papers

In conclusion, a general consideration of the mechanical characteristics of all the cured samples analysed suggests that better toughness properties with lower losses in moduli are achievable in samples containing 5-10 parts of modified AC 5120 and cured at 115°C The results for modified systems, however, are characterised by a certain scatter, probably due to the fact that these systems are not completely homogeneous. The results are in good agreement with those obtained from DSC analysis and SEM observations.

5.6) Additional Studies.

Having ascertained the possibility to improve the toughness of an epoxy resin through the addition of a low molecular weight polyolefin, previously chemically modified in order to reach a better miscibility with the uncured resin, many routes can be taken to continue the present work to optimise the enhancement in properties.

Some attempts have already been made in order to find alternative polyolefin components able to promote a better miscibility with the epoxy resins used. Following the same approach of the present work, it was first thought to use again a low molecular weight polyolefin possibly having a different type of functionality and, to this end, the influence of hydroxyl groups on miscibility in binary and ternary mixtures within the main chains of the copolymer was analysed

In a first attempt, work carried out by an ERASMUS student (148), an ethylene acrylic acid vinyl acetate terpolymer (AC 1450, from Allied Signals Inc.), having an acid number of 35 and an acid functionality of 2, and an ethylene acrylic acid vinyl acetate - vinyl alcohol polymer terpolymer (AC 80, from Allied Signals Inc), containing both hydroxyl and carboxyl groups with an average acid functionality equal to the average OH functionality, both equal to 1, were examined Chemical modifications were again performed to improve the miscibility of the polyethylenes with the epoxy resin (Epikote 828) and/or the hardener (HHPA) used The modifications that were foud effective in enhancing the solubility were those performed on AC 80, which was intrinsically more miscible than AC 1450 with epoxy resin and hardener It was found that successive reactions of AC 80 with RVP, chlorendic anhydride (CA) and ε-caprolactone give rise to a large decrease in solubilisation temperatures of binary systems, lowering these below the 100°C

In another experimental work (149) a low molecular weight hydroxyl functionalised polyethylene (ethylene vinyl alcohol copolymer or EVOH) was studied as a potential toughening agent for Epikote 828 using again HHPA A EVOH with functionality of 2 was chosen, i e. having an average of 2 hydroxyl groups at the end of each chain EVOH not being completely soluble with the epoxy resin in binary mixtures, telechelic extensions of EVOH were made through reactions with chlorendic anhydride and subsequently with ε-caprolactone It was found that the modification with CA in the ratio 1 0.75 EVOH/CA leads to an improvement of miscibility in binary mixtures with Epikote 828 The further chain extension with caprolactone improved the miscibility of ternary mixtures of compositions close to those used for cured formulations (solubilisation temperature estimated close to the melting point of the polyethylene phase) The cured epoxy resin modified by 3% of EVOH/CA + caprolactone appeared to offer the best potential as modifier agents for the resin, since the Tg of these cured systems was unaffected No mechanical tests or SEM observations have been performed on these cured samples, therefore, it is not known the effectiveness of these systems as toughening agents

In conclusion, these parallel studies confirmed the validity of the research leaving open many possibilities in order to continue and find the best modified polyethylene system able to modify effectively an epoxy resin

6. SUMMARY, CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1) Summary.

The major results obtained from this study concerning three different low molecular weight functionalised polyethylenes used as potential toughening agents for epoxy resins, using the same approach as in the CTBN technology, are as follows.

* <u>Miscibility of Functionalised Ethylene Acrylic Acid Copolymers with Epoxy Resins.</u>

Miscibilisation of the functionalised ethylene acrylic acid copolymers with a DGEBA epoxy resin, which is the essential requirement in order to assure an effective toughening of the resin, is strictly related to the functionality of the copolymer.

* <u>Miscibility of Grafted Modifications of Ethylene Acrylic Acid Copolymers with Epoxy Resins</u>

In order to increase further the miscibility between the ethylene copolymer having the highest functionality (AC 5120) and the DGEBA epoxy resin, several chemical modifications have been performed on the polyethylene phase by reactions through functional groups. The modifications have been realised by grafting on the ethylene copolymer different polymers. In this way the chain length of the polyethylene was increased while maintaining the same reactive functionality, i.e. acid, at the end of each chain In all grafting reactions, the employment of reaction times strictly necessary to obtain the maximum conversion is the crucial requirement to increase effectively the miscibility between the product of the grafting reaction and the epoxy resin.

* Miscibility of Functionalised Ethylene Acrylic Acid Copolymers with a DGEBA Epoxy Resin Partially Esterified with Montanic Acid

A second route to enhance the miscibility between the ethylene copolymer with the highest functionality, AC 5120, and the epoxy resin comprised a grafting reaction of montanic acid on the DGEBA resin While this attempt succeeded in binary mixtures of AC 5120 copolymer with the epoxy resin, when the epoxy resin grafted with montanic acid was mixed with AC 5120-graft-caprolactone, solubilisation temperatures higher than 200°C were found. Finally, the solubilisation temperatures recorded for the system AC 5120/Epikote 828-graft-montanic acid were always higher than those found for the binary systems of Epikote 828 with AC 5120-graft-RVP.

* Miscibility of Ternary Mixtures of Functionalised Ethylene Acrylic Acid Copolymers, a DGEBA Epoxy Resin and an Anhydride Hardener

The introduction of an anhydride hardener in a binary mixture of an ethylene acrylic acid copolymer with an epoxy resin leads always to a considerable increase of the solubilisation temperature, even when one of the two components of the binary system has been chemically modified to enhance the miscibility in the final system. The reaction performed on HHPA with montanic acid, in order to obtain an eutectic between the two reactants, even if capable of avoiding the transformation of HHPA from the cis- to the trans-form, was ineffective in reducing the demiscibilising action of HHPA in binary mixtures of ethylene copolymer and epoxy resin

* Phase Separation and Morphology Development during Curing of Epoxy Resins Containing Modified Ethylene Acrylic Acid Copolymers

The reaction of grafting of the monofunctional epoxy resin, RVP, on the polyethylene having highest functionality, AC 5120, has been found an essential step in order to obtain almost homogeneous systems after a thermal curing with an anhydride hardener The SEM analysis revealed, in fact, the precipitation in these systems of small spherical particles (via nucleation and growth) able to arrest the fractures that propagate easily inside the brittle matrix. The high solubility between grafted AC 5120 and the DGEBA epoxy resin involved, on the other hand, a decrease in the glass transition temperature (Tg) of the cured system, brought about by the plasticisation effect of both polyethylene and unreacted RVP in the epoxy matrix, ascertained also by a lower value of the volume fraction of the particles measured on SEM micrographs than that obtained from theoretical calculations.

* Mechanical Properties of Cured of Epoxy Resins Containing Modified Ethylene Acrylic Acid Copolymers.

The analysis of mechanical properties, measured both in static and dynamic conditions, performed on epoxy cured systems modified with the grafted ethylene acrylic acid copolymer have shown that better characteristics in terms of higher enhancements in toughness properties and lower decreases in moduli, as well as in the glass transition temperature, are achieved with the addition in the resin of low contents (5-10%) of grafted polyethylene It has been also found that the use of high curing and post-curing temperatures leads to higher dynamic moduli and toughness properties.

A comparison between the data found in this study and those reported by different authors revealed that the enhancements in toughening achievable by adding the grafted polyolefin to the epoxy resin are considerably lower than those attained using traditional toughening agents

6.2) Conclusions.

The conclusions that can be derived from this study are

a) only the low molecular weight functionalised polyethylene with the highest functionality value (i.e. 2.0) reaches complete miscibility with the DGEBA epoxy resin;

b) the most effective polymer used to modify this polyethylene in enhancing its miscibility with the epoxy resin, has been found to be the monofunctional epoxy resin (RVP),

c) neither the modification of epoxy resin with montanic acid nor the reaction performed on HHPA with montanic acid, were effective to enhance the miscibility with the low molecular weight functionalised polyethylene,

d) the addition of the RVP-grafted polyethylene to the DGEBA epoxy resin cured with HHPA, resulted in the precipitation of small spherical particles together with a decrease in the glass transition temperature of the cured system;

e) some limited enhancements in toughness properties of the cured materials are achievable with the addition in the epoxy resin of low contents of grafted polyethylene.

The main conclusion is that the procedure employed to modify the polyethylene and/or the same polyolefin are unlikely to represent the best conditions, since completely homogeneous cured systems have not been attained.

6.3) Suggestions for Further Work.

This present study has shown that is possible to miscibilise ethylene acrylic acid oligomers with an epoxy resin through telechelic extension reactions with appropriate chain modifiers The anhydride cured systems, however, did not allow the development of an efficient particle precipitation mechanism to achieve the full benefit of the modifications in terms of enhancement in mechanical properties. Since conventional CTBN showed a similar behaviour, it can be inferred that an amine or a Lewis acid curing catalyst, known to be effective for CTBN, should be more favourable for the precipitation of the olefinic phase during curing of the resin

It is recommended, therefore, that the experiments concerned with the effect of curing conditions will be repeated using either a BF_3 complex or an imidazole catalyst. It is suggested also that attempts should be made to measure the microhardeness of precipitated particles for systems cured at temperatures below and above the melting point of the oligomeric modifier. This could be related to the modulus of the precipitated particles to develop favourable mechanical conditions for the shear yielding of the surrounding matrix.

Capitalising on the success of Mascia et al. (60,61) to achieve an efficient particle precipitation mechanism with modified perfluoroether oligomers, even with anhydride cured systems, it is suggested to use the following curing schedule using the HHPA adduct of the RVP modified AC 5120 oligomer, i e. the same schedule used by the above researchers

a) Prereact branched carboxy functionalised oligomer with a large excess of epoxy resin in the presence of TPP, as selective catalyst, for different times.

b) Follow the viscosity of the reaction mixture until precipitation of some crosslinked species takes place

c) Select systems reacted for periods shorter than the time for incipient particle precipitation

d) Add the required amount of anhydride (HHPA) for curing and then the BDMA catalyst.

e) Gel at 120°C, cure at 180°C and post cure at 180°C.

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7. APPENDIX

7.1) Determination of Acid Number and Functionality of Pure Materials and Products of their Reactions.

Functionality is defined as the number of reactive functional groups present in each polymer molecule.

Referring to the montanic acid, which has the following chemical formula:

$$CH_3\,(CH_2)_{26}\,COOH$$

and a molecular weight of 424, it is obvious that its functionality is exactly equal to 1. This means that 424 g of polymer contain 1 acid equivalent, i e. 1 mole of acid groups; or that 1 g of polymer contains $1/424 = 2.36*10^{-3}$ acid equivalent.

By definition, the "Acid Number" of a polymer represents the mg of KOH required to neutralise all the acid groups contained in 1 g of the polymer. Since the functionality of montanic acid is equal to 1, it is necessary to have one mole of KOH, that is 56 g of KOH (being 56 the molecular weight of KOH), to neutralise one mole of acid groups, i.e. one mole of acid equivalent. Dividing for 1000:

i.e. 10^{-3} Acid Equivalent $\equiv$ 56 mg KOH .

From simple proportionality: $56 : 10^{-3} = x : 2.36*10^{-3}$

where x represents the acid number, because $2\,36*10^{-3}$ are the acid equivalent contained in 1 g of polymer. From the calculation, the acid number of the montanic acid results to be 132. Hence, for analogy with a system with twice its molecular weight (i.e. 848) the acid number would be half, i.e. 66; with a triple molecular weight (i.e. 1272) the acid number would be one third, i.e. 44; and so forth.

It is possible to calculate, therefore, the acid number of three polymers with functionality of 1, as before, but with molecular weights equal to those of the three polyethylenes:

- A molecular weight of 970 ($\bar{M}n$ of the oxidised polyethylene AC 6702) is equal to 2.29 times 424. Therefore, the acid number of this polymer would be 132 / 2.29 = 57.70 .

- A molecular weight of 1710 ($\bar{M}n$ of AC 540) is equal to 4.03 times 424. Therefore, the acid number would be 132 / 4.03 = 32.73 .

- Finally, a molecular weight of 1005 ($\bar{M}n$ of AC 5120) is equal to 2.37 times 424. Therefore, the acid number would be 132 / 2.37 = 55.69 .

For the polyethylene AC 6702, having an acid number of 15, form a simple proportion

$$f = 15 / 57\ 70 = 0.26 .$$

In the same way, for AC 540, which has an acid number equal to 40, the functionality is:

$$f = 40 / 32.73 = 1\ 22 .$$

Finally, the functionality of AC 5120, having an acid number of 120, is calculated as:

$$f = 120 / 55.69 = 2.15 .$$

These values can be considered an estimate of the true values of the functionalities of the three polyethylenes.

Following a similar procedure, it is possible calculate the theoretical acid number of the final mixtures of AC 5120 with ε-caprolactone.

The first composition employed, 50/5 AC 5120/caprolactone, was chosen with the view of reacting 25% of the acid groups of AC 5120 with caprolactone Hence, the molecular weight of the grafted product is:

$$1000 + [114 * (2 / 4)] = 1057$$

i.e.: Molecular weight of AC 5120 ≅ 1000

Molecular weight of ε-caprolactone = 114

Number of moles of caprolactone reacting with one mole of AC 5120 = 2/4 .

The acid groups contained in the final mixture must be equal to those initially contained in AC 5120 calculated respect to the final molecular weight:

$(1000 / 1057) * 120 = 113\ 5$

i e.: Acid number of AC 5120 = 120 .

Therefore, the acid number of the final mixture is 113.5 .

For the mixture AC 5120/caprolactone 50/20, the values can be calculated in the same way:

Molecular weight: $1000 + (114 * 2) = 1228$

Acid number: $(1000 / 1228) * 120 = 97.7$.

On the other hand, using for AC 5120 a molecular weight of 675 (the second value measured by GPC, see 4.3.2) the values for AC 5120/caprolactone 50/5 are:

Molecular weight: $675 + [114 * (2 / 4)] = 732$

Acid Number: $(675 / 732) * 120 = 110.7$

and for AC 5120/caprolactone 50/20:

Molecular Weight: $675 + (114 * 2) = 903$

Acid Number: $(675 / 903) * 120 = 89.7$.

The acid number of HHPA is equal to zero, provided it is not reacted with water to form phthalic acid. The reaction of the hardener HHPA with AC 5120-graft-RVP 69.8/30.2 gives rise to a total number of acid groups equal to the sum of the residual acid groups initially present in AC 5120-graft-RVP, corresponding to an acid number of 65.9, plus the acid groups formed through the reaction with HHPA. The latter can be calculated considering 1 g of final mixture that contains 0.2 g of HHPA, i e. 0.2/154 moles of HHPA, being 154 the molecular weight of HHPA.

Following the stoichiometry of the reaction, each mole of HHPA gives rise to one mole of acid groups (provided that no crosslinks are found) From its definition, the acid number of the final mixture is equal to:

(0.2 / 154) * 56 * 1000 = 72.7 mg KOH .

The total acid number will be then:

(65.9 * 0.8) + 72.7 = 125.4 .

In the same way, the total acid number for the final mixture (AC 5120-graft-RVP/TPP 69.8/30.2/1) / HHPA 80/20 can be calculated as:

(15.2 * 0.8) + 72.7 = 84.9 .

The product of the reaction AC 5120-graft-RVP/TPP (69.8/30.2/1) + MNA, being the composition 77.9% AC 5120-g-RVP/TPP and 22.1% MNA, has a final acid number equal to:

[(0.221 / 179) * 56 * 1000] + (15.2 * 0.779) = 81 0

being 175 the molecular weight of MNA.

7.2 Additional Tables

List of Symbols

For Tables 8 to 44:

T_m	Melting temperature (heating stage).
T_c	Crystallisation temperature (cooling stage).
T'_m	Melting temperature for HHPA phase (heating stage).
T'_c	Crystallisation temperature for HHPA phase (cooling stage).
T_s	Solubilisation temperature (heating stage). Solubilisation temperatures with (*) correspond to semi-miscible mixtures. Can be also reported, in brackets, the temperatures at which the mixtures, though not completely melted, become a single phase (see text 4.4.1).
T_p	Phase separation temperature (cooling stage).

For Table 46:

$\bar{M}w$	Weight Average Molecular Weight (kindly measured by Steve Holding at RAPRA Technology LTD).
$\bar{M}n$	Number Average Molecular Weight (kindly measured by Steve Holding at RAPRA Technology LTD).
$\bar{M}w/\bar{M}n$	Polydispersity.

For Tables 47 to 65:

T_{mp}	Melting temperature peak.
T_{mi}	Initial melting temperature.
T_{mf}	Final melting temperature.
ΔH_m	Heat of fusion (normalised to polyethylene content). Can be also reported, in brackets, the theoretical value.
T'_{mp}	Melting temperature peak for the HHPA rich phase.
T'_{mi}	Initial melting temperature for the HHPA rich phase.

T'_{mf}	Final melting temperature for the HHPA rich phase.
$\Delta H'_{m}$	Heat of fusion (normalised to HHPA content).
T_{ei}	Initial evaporation temperature for the HHPA rich phase.
T_{cp}	Crystallisation temperature peak.
T_{ci}	Initial crystallisation temperature.
T_{cf}	Final crystallisation temperature.
ΔH_{c}	Heat of crystallisation (normalised to polyethylene content).

For Tables 66 to 72:

T_{g}	Glass transition temperature.
T_{m}	Melting temperature peak.

For Table 73:

G'	Storage modulus.
G''	Loss modulus.
T_{g}	Glass transition temperature (from G'' peak).

For Tables 74 to 76.

E	Modulus.
σ_{b}	Strength at break.
ε_{b}	Strain at break.

For Table 77:

K_{c}	Critical stress intensity factor.
G_{c}	Critical strain energy release rate.

For Table 78:

a_{cU}	Charpy impact strength.

TABLE 1: Compositions (parts by weight) of samples post-cured at 150°C.

	CI	I1	I3	FHA	CP	P1	P3	FHZ
Epikote 828	100	100	100	100	100	100	100	100
HHPA	80	78	70	70	80	78	70	70
AC 5120-g-RVP (69.8/30.2)	---	5	20	30	---	5	20	30
BDMA	1	1	1	2	5	5	5	3
Curing Temperature (°C)	115	115	115	115	60	60	60	60

TABLE 2: Compositions (parts by weight) of samples cured with MNA hardener and post-cured at 150°C.

	C1	J1	J2	J3	K1	K2	K3
Epikote 828	100	100	100	100	100	100	100
MNA	80	78	75	64	78	75	64
AC 6702	---	10	---	---	10	---	---
AC 540	---	---	10	---	---	10	---
AC 5120	---	---	---	10	---	---	
BDMA	1	1	1	1	1	1	1
TPP	---	---	---	---	1	1	1
Curing Temperature (°C)	115	115	115	115	115	115	115

TABLE 3: Compositions (parts by weight) of control samples post-cured at 150°C and 180°C.

	CL	CS	CR	CT	CQ
Epikote 828	100	100	100	100	100
HHPA	80	70	80	70	80
BDMA	1	1	1	1	5
Curing Temperature (°C)	115	115	60	60	60

TABLE 4: Compositions (parts by weight) of samples post-cured at 150°C and 180°C.

	S1	S3	L1	L3	U1	U3	Q1	Q3
Epikote 828	100	100	100	100	100	100	100	100
HHPA	78	70	78	70	78	70	78	70
AC 5120	5	20	---	---	5	20	---	---
AC 5120-g-RVP (69.8/30.2)	---	---	5	20	---	---	5	20
BDMA	1	1	1	1	1	1	5	5
Curing Temperature (°C)	115	115	115	115	60	60	60	60

TABLE 5: Compositions (parts by weight) of samples post-cured at 150°C and 180°C.

	M1	M'2	M'3	M3	R1	R'2	R'3	R3	RU
Epikote 828	100	100	100	100	100	100	100	100	100
HHPA	78	80	80	70	78	80	80	70	80
AC 5120-g-RVP/TPP (69.8/30.2/1)	5	10	20	20	5	10	20	20	---
CTBN	---	---	---	---	---	---	---	---	10
BDMA	1	1	1	1	1	1	1	1	1
Curing Temperature (°C)	115	115	115	115	60	60	60	60	115

TABLE 6: Compositions (parts by weight) of samples containing free RVP and post-cured at 150°C and 180°C.

	T'M1	TM1	TL1	TM'3	TM3	TL3
Epikote 828	100	100	100	100	100	100
HHPA	80	78	78	80	70	70
RVP	0.327	0.327	1.208	1.310	1.310	4.832
BDMA	1	1	1	1	1	1
Curing Temperature (°C)	115	115	115	115	115	115

TABLE 7: Compositions (parts by weight) of samples containing free RVP and post-cured at 150°C and 180°C.

	T'R1	TR1	TQ1	TR'3	TR3	TQ3
Epikote 828	100	100	100	100	100	100
HHPA	80	78	78	80	70	70
RVP	0.327	0.327	1.208	1 310	1.310	4.832
BDMA	1	1	5	1	1	5
Curing Temperature (°C)	60	60	60	60	60	60

TABLE 8: Melting, crystallisation, solubilisation and phase separation temperatures of binary mixtures AC 6702/Epikote 828 obtained from hot stage microscope experiments

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 6702/Epikote 828 10/90	88	77	> 250	> 250	88	80	248	244
AC 6702/Epikote 828 25/75	86	76	> 250	> 250	89	76	233	228
AC 6702/Epikote 828 50/50	88	79	> 250	> 250	87	81	237	246
AC 6702/Epikote 828 75/25	85	77	> 250	> 250	89	78	257	255
AC 6702/Epikote 828 90/10	88	78	> 250	> 250	87	79	> 250	>250
AC 6702	89	76						
Heating Time at 115°C	10 min				24 h			

TABLE 9: Melting, crystallisation, solubilisation and phase separation temperatures of binary mixtures AC 540/Epikote 828 obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 540/Epikote 828 10/90	103	93	238	243	98	92	243	128
AC 540/Epikote 828 25/75					98	93	229	198
AC 540/Epikote 828 50/50	102	89	247	---	99	94	236	188
AC 540/Epikote 828 75/25					99	86	211	---
AC 540/Epikote 828 90/10	101	90	> 250	> 250	98	87	> 250	>250
AC 540	102	93						
Heating Time at 115°C	10 min				24 h			

TABLE 10: Melting, crystallisation, solubilisation and phase separation temperatures of binary mixtures AC 540/CY 179 obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 540/CY 179 25/75	98	95	198	---	99	95	145	123
AC 540/CY 179 50/50	100	95	100	---				
AC 540/CY 179 75/25	99	95	160	---	99	94	158	---
AC 540	102	93						
Heating Time at 115°C	10 min				2 h			

TABLE 11: Melting, crystallisation, solubilisation and phase separation temperatures of binary mixtures AC 5120/Epikote 828 obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)	
AC 5120/ Epikote828 10/90	80	68	203	---									Gel
AC 5120/ Epikote828 25/75					84	66	173	196	Gel	Gel	Gel	Gel	Gel
AC 5120/ Epikote828 50/50	81	71	212	198	84	72	199	198	78	74	190	---	Gel
AC 5120/ Epikote828 75/25					86	56	198	---	87	74	183	---	Gel
AC 5120/ Epikote828 90/10	85	77	189	198									Gel
AC 5120	87	86											
Heating Time at 115°C	10 min				6 h				21 h				24h

TABLE 12: Melting, crystallisation, solubilisation and phase separation temperatures of binary mixtures AC 5120/CY 179 obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120/CY 179 25/75	86	85	105	---
AC 5120/CY 179 50/50	88	79	88	---
AC 5120/CY 179 75/25	88	85	88	---
AC 5120	87	86		

All the mixtures were heated at 115°C for 10 minutes.

TABLE 13: Melting, crystallisation, solubilisation and phase separation temperatures of binary mixtures AC 540/HHPA obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)	T'_m (°C)	T'_c (°C)
HHPA					120	---
AC 540/HHPA 25/75	100	95	172 (100)	168	172	168
AC 540/HHPA 50/50	100	96	158 (100)	---	158	---
AC 540/HHPA 75/25	100	94	143 (100)	143	143	143
AC 540	102	93				

All the mixtures were heated at 115°C for 1 hour.

TABLE 14: Melting, crystallisation, solubilisation and phase separation temperatures of binary mixtures AC 5120/HHPA obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)	T'_m (°C)	T'_c (°C)
HHPA					120	---
AC 5120/HHPA 25/75	87	86	155 (123)	113	155	---
AC 5120/HHPA 50/50	87	85	185 (88)	118	185	---
AC 5120/HHPA 75/25	88	85	164 (118)	116	164	---
AC 5120	87	86				

All the mixtures were heated at 115°C for 1 hour

TABLE 15: Melting, crystallisation, solubilisation and phase separation temperatures of binary mixtures Epikote 828/HHPA and CY 179/HHPA obtained from hot stage microscope experiments.

	T'_m (°C)	T'_c (°C)	T_s (°C)	T_p (°C)
HHPA	120	---		
Epikote 828/HHPA 50/50	98	---	98	---
CY 179/HHPA 50/50	95	---	95	---

All the mixtures were heated at 115°C for 10 minutes.

TABLE 16: Melting, crystallisation, solubilisation and phase separation temperatures of ternary mixtures AC 540/Epikote 828/HHPA obtained from hot stage microscope experiments.

	Heating Time at 115°C	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 540/Epikote 828/HHPA 5/60/35	2 h + 10 min	100	93	> 250	> 250
AC 540/Epikote 828/HHPA 10/70/20	2 h + 10 min	100	92	158*	---
AC 540/Epikote 828/HHPA 10/80/10	2 h + 10 min	101	90	178*	---
AC 540/Epikote 828/HHPA 14/62/24	1 h + 10 min	101	94	> 250	> 250
AC 540/Epikote 828/HHPA 16.7/50/33.3	24 h + 10 min	98	87	> 250	> 250
AC 540/Epikote 828/HHPA 20/40/40	10 min	101	96	> 250	> 250
AC 540/Epikote 828/HHPA 20/70/10	2 h + 10 min	101	89	158*	---
AC 540/Epikote 828/HHPA 33.3/33.3/33.3	10 min	101	96	> 250	> 250
AC 540/Epikote 828/HHPA 42/48/10	1 h + 10 min	101	92	> 250	> 250

TABLE 17: Melting, crystallisation, solubilisation and phase separation temperatures of ternary mixtures AC 540/CY 179/HHPA obtained from hot stage microscope experiments.

	Heating Time at 115°C	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 540/CY 179/HHPA 5/60/35	2 h + 10 min	98	86	> 250	> 250
AC 540/CY 179/HHPA 10/70/20	2 h + 10 min	99	92	> 250	> 250
AC 540/CY 179/HHPA 10/80/10	2 h + 10 min	100	94	178*	165
AC 540/CY 179/HHPA 14/62/24	2 h + 10 min	98	89	> 250	> 250
AC 540/CY 179/HHPA 20/70/10	2 h + 10 min	98	94	> 250	> 250
AC 540/CY 179/HHPA 33.3/33.3/33.3	10 min	100	92	> 250	> 250

TABLE 18: Melting, crystallisation, solubilisation and phase separation temperatures of ternary mixtures AC 5120/Epikote 828/HHPA obtained from hot stage microscope experiments.

	Heating Time at 115°C	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120/Epikote 828/HHPA 5/60/35	2 h + 10 min	86	76	> 250	> 250
AC 5120/Epikote 828/HHPA 5/60/35	12 h + 10 min	87	73	> 200	> 200
AC 5120/Epikote 828/HHPA 10/50/40	1 h + 10 min	88	85	158	---
AC 5120/Epikote 828/HHPA 10/70/20	2 h + 10 min	87	86	158	---
AC 5120/Epikote 828/HHPA 20/70/10	2 h + 10 min	88	85	168	---
AC 5120/Epikote 828/HHPA 33.3/33.3/33.3	2 h + 10 min	86	85	185	---

TABLE 19: Melting, crystallisation, solubilisation and phase separation temperatures of ternary mixtures AC 5120/CY 179/HHPA obtained from hot stage microscope experiments

	Heating Time at 115°C	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120/CY 179/HHPA 5/60/35	30 min + 10 min	95	48	150*	---
AC 5120/CY 179/HHPA 5/60/35	3 h + 10 min	81	76	110*	---
AC 5120/CY 179/HHPA 10/70/20	30 min + 10 min	85	73	137	---
AC 5120/CY 179/HHPA 20/70/10	30 min + 10 min	85	77	106	---
AC 5120/CY 179/HHPA 33.3/33.3/33.3	30 min + 10 min	85	49	120	---

TABLE 20: Melting, crystallisation, solubilisation and phase separation temperatures for the mixtures of AC 5120 grafted with ε-Caprolactone obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120-g-Caprolactone 50/5 *(5 h at 115°C)*	86	86	178	168
AC 5120-g-Caprolactone 50/20 *(5 h at 115°C)*	85	84	85	---

TABLE 21: Melting, crystallisation, solubilisation and phase separation temperatures of the 50/50 mixtures of AC 5120 grafted with ε-Caprolactone and Epikote 828 obtained from hot stage microscope experiments.

		T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120-g-Caprolactone 50/5 *(1 h at 115°C)*	**+ Epikote 828** *(10 min at 115°C)*	85	84	161	---
	+ Epikote 828 *(2 h at 115°C)*	82	78	158	---
AC 5120-g-Caprolactone 50/5 *(2 h at 115°C)*	**+ Epikote 828** *(10 min at 115°C)*	83	84	183	108
	+ Epikote 828 *(2 h at 115°C)*	81	79	188	---
AC 5120-g-Caprolactone 50/5 *(7 h 40 min at 115°C + 2 h 30 min at 160°C)*	**+ Epikote 828** *(10 min at 115°C)*	81	69	218	---
	+ Epikote 828 *(2 h at 115°C)*	82	69	213	---

TABLE 22: Melting, crystallisation, solubilisation and phase separation temperatures for the 50/50 mixtures of AC 5120 grafted with ε-Caprolactone and Epikote 828 obtained from hot stage microscope experiments.

		T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120-g-Caprolactone 50/20 *(1 h at 115°C)*	**+ Epikote 828** *(10 min 115°C)*	83	72	198	---
AC 5120-g-Caprolactone 50/20 *(6 h at 115°C)*	**+ Epikote 828** *(10 min 115°C)*	83	74	213	---
AC 5120-g-Caprolactone 50/20 *(6h 30min 115°C + 2h 15min 160°C)*	**+ Epikote 828** *(10 min 115°C)*	83	69	233	---
AC 5120-g-Caprolactone 50/20 *(6 h 30 min at 115°C + 8 h at 160°C)*	**+ Epikote 828** *(10 min 115°C)*	83	78	238	138

TABLE 23: Melting, crystallisation, solubilisation and phase separation temperatures for ternary mixtures of AC 5120 grafted with ε-Caprolactone, Epikote 828 and HHPA obtained from hot stage microscope experiments.

	Heating Time at 115°C	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
(AC 5120-g-Caprolactone 50/5)/ Epikote 828/HHPA 10/70/20	2 h + 10 min	80	73	233*	---
(AC 5120-g-Caprolactone 50/20)/ Epikote 828/HHPA 10/70/20	2 h + 10 min	76	---	>250	---

Heating conditions refer to mixtures of AC 5120, grafted with ε-Caprolactone, Epikote 828 and HHPA.

TABLE 24: Melting, crystallisation, solubilisation and phase separation temperatures for the mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP), with or without TPP, obtained from hot stage microscope experiments.

	T_m (°C)	**T_c (°C)**	**T_s (°C)**	**T_p (°C)**
AC 5120-g-RVP 69.8/30.2 ***(10 min at 140°C)***	85	79	85	---
AC 5120-g-RVP 69.8/30.2 ***(1 h at 140°C)***	82	81	82	---
AC 5120-g-RVP 69.8/30.2 ***(3 h at 140°C)***	83	80	83	---
AC 5120-g-RVP/TPP 69.8/30.2/1 ***(1 h 30 min at 140°C)***	78	75	78	80

TABLE 25: Melting, crystallisation, solubilisation and phase separation temperatures for the mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP) and Epikote 828 obtained from hot stage microscope experiments.

	Heating Time at 115°C	**T_m (°C)**	**T_c (°C)**	**T_s (°C)**	**T_p (°C)**
(AC 5120-g-RVP 69.8/30.2)/ Epikote 828 25/75	10 min	75	83	153	89
	3 h	83	82	163	146
(AC 5120-g-RVP 69.8/30.2)/ Epikote 828 50/50	10 min	81	82	168	---
	3 h	80	83	172	---
(AC 5120-g-RVP 69.8/30.2)/ Epikote 828 75/25	10 min	82	80	143	128
	3 h	83	82	155	86

Heating conditions refer to mixtures of AC 5120, grafted with RVP, and Epikote 828.

TABLE 26: Melting, crystallisation, solubilisation and phase separation temperatures for the mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP) and CY 179 obtained from hot stage microscope experiments.

	Heating Time at 115°C	**T_m (°C)**	**T_c (°C)**	**T_s (°C)**	**T_p (°C)**
(AC 5120-g-RVP 69.8/30.2)/CY 179 25/75	10 min	87	84	98	88
(AC 5120-g-RVP 69.8/30.2)/CY 179 50/50	10 min	87	74	87	76
(AC 5120-g-RVP 69.8/30.2)/CY 179 75/25	10 min	86	82	86	---

Heating conditions refer to mixtures of AC 5120, grafted with RVP, and CY 179.

TABLE 27: Melting, crystallisation, solubilisation and phase separation temperatures for the mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP) and HHPA obtained from hot stage microscope experiments.

	Heating Time at 140°C	**T_m (°C)**	**T_c (°C)**	**T_s (°C)**	**T_p (°C)**
(AC 5120-g-RVP 69.8/30.2)/HHPA 80/20	10 min	85	83	85	---
(AC 5120-g-RVP 69.8/30.2)/HHPA 80/20	3 h	84	82	84	---

Heating conditions refer to mixtures of AC 5120-graft-RVP with HHPA.

TABLE 28: Melting, crystallisation, solubilisation and phase separation temperatures for the mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP), Epikote 828 and HHPA obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
(AC 5120-g-RVP 69.8/30.2)/Epikote 828/HHPA 15/50/35 (*)	84	82	133	---
(AC 5120-g-RVP 69.8/30.2)/Epikote 828/HHPA 15/50/35 *(10 min at 115°C)*	81	---	> 250	> 250
(AC 5120-g-RVP 69.8/30.2)/Epikote 828/HHPA 21.8/72.8/5.4 (**)	79	71	203	158

Heating conditions:

(*) {(AC 5120-g-RVP 69.8/30.2)/HHPA 80/20 6 h at 140°C} + Epikote 828 + rest of HHPA 10 min at 115°C

(**) {(AC 5120-g-RVP 69.8/30 2)/HHPA 80/20 6 h at 140°C} + Epikote 828 10 min at 115°C.

TABLE 29: Melting, crystallisation, solubilisation and phase separation temperatures for the mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP), CY 179 and HHPA obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
(AC 5120-g-RVP 69.8/30.2)/CY 179/HHPA 15/50/35 *(10 min at 115°C)*	88	---	153	---
(AC 5120-g-RVP 69.8/30.2)/CY 179/HHPA 21.8/72.8/5.4 (*)	78	70	173	---

Heating conditions·

(*) {(AC 5120-g-RVP 69.8/30.2)/HHPA 80/20 6 h at 140°C} + CY 179 10 min at 115°C.

TABLE 30: Melting, crystallisation, solubilisation and phase separation temperatures for some of the mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP) in presence of TPP, and Epikote 828 obtained from hot stage microscope experiments.

		T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120-g-RVP/TPP **69.8/30.2/1** ***(1 h 30 min at 140°C)***	**+ Epikote 828 25/75** ***(10 min at 115°C)***	85	85	155	---
	+ Epikote 828 50/50 ***(10 min at 115°C)***	84	86	146	---
	+ Epikote 828 75/25 ***(10 min at 115°C)***	85	84	85	---

TABLE 31: Melting, crystallisation, solubilisation and phase separation temperatures for the last mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP) in presence of TPP, and Epikote 828 obtained from hot stage microscope experiments.

		T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120-g-RVP/TPP 69.8/30.2/1 ***(6 h at 140°C)***	**+ Epikote 828 50/50** ***(10 min at 115°C)***	81	83	142	---
AC 5120-g-RVP/TPP 69.8/30.2/1 ***(9 h at 140°C)***	**+ Epikote 828 50/50** ***(10 min at 115°C)***	79	85	133	---

TABLE 32: Melting, crystallisation, solubilisation and phase separation temperatures for the mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP) in presence of TPP, and HHPA obtained from hot stage microscope experiments.

		T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120-g-RVP/TPP 69.8/30.2/1 ***(1 h 30 min at 140°C)***	**+ HHPA 80/20** ***(2h 30 min at 140°C)***	80	77	80	81
AC 5120-g-RVP/TPP 69.8/30.2/1 ***(6 h at 140°C)***	**+ HHPA 80/20** ***(10 min at 140°C)***	83	84	83	---
AC 5120-g-RVP/TPP 69.8/30.2/1 ***(9 h at 140°C)***	**+ HHPA 80/20** ***(10 min at 140°C)***	84	85	84	---

TABLE 33: Melting, crystallisation, solubilisation and phase separation temperatures for some of the mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP) in presence of TPP, Epikote 828 and HHPA obtained from hot stage microscope experiments.

		T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120-g-RVP/TPP **69.8/30.2/1** ***(1 h 30 min at 140°C)***	**/Epikote 828/HHPA 7.1/58.7/34.2**	68	---	178*	---
	/Epikote 828/HHPA 8.5/52.6/38.9	---	---	> 250	> 250
	/Epikote 828/HHPA 13.9/67.0/19.1	83	58	143*	---
	/Epikote 828/HHPA 15.0/50.0/35.0	---	---	> 250	---
	/Epikote 828/HHPA 21.8/72.8/5.4	---	58	146	86
	/Epikote 828/HHPA 42.0/29.0/29.0	80	---	> 250	---

Heating conditions:
{(AC 5120-g-RVP 69.8/30.2)/HHPA 80/20 2 h 30 min at 140°C} + Epikote 828 + rest of HHPA 10 min at 115°C.

TABLE 34: Melting, crystallisation, solubilisation and phase separation temperatures for the last mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP) in presence of TPP, Epikote 828 and HHPA obtained from hot stage microscope experiments.

		T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120-g-RVP/TPP **69.8/30.2/1** ***(6 h at 140°C)***	**/Epikote 828/HHPA 15.0/50.0/35.0**	138	70	> 250	> 250
	/Epikote 828/HHPA 21.8/72.8/5.4	---	83	> 250	> 250
AC 5120-g-RVP/TPP **69.8/30.2/1** ***(9 h at 140°C)***	**/Epikote 828/HHPA 15.0/50.0/35.0**	153	72	> 250	> 250
	/Epikote 828/HHPA 21.8/72.8/5.4	---	84	153*	198

Heating conditions:
{(AC 5120-g-RVP 69.8/30.2)/HHPA 80/20 10 min at 140°C} + Epikote 828 + rest of HHPA 10 min at 115°C.

TABLE 35: Melting, crystallisation, solubilisation and phase separation temperatures for mixtures of MNA with AC 5120 grafted with the Monofunctional Epoxy Resin (RVP) in presence of TPP, and or Epikote 828 obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
Epikote 828/MNA 50/50 (*)	---	---	25	---
(AC 5120-g-RVP/TPP 69.8/30.2/1)/MNA 77.9/22.1 (**)	90	81	90	---
(AC 5120-g-RVP/TPP 69.8/30.2/1)/Epikote 828/MNA 7.0/58.7/34.3 (***)	78	---	> 250	> 250
(AC 5120-g-RVP/TPP 69.8/30.2/1)/Epikote 828/MNA 13.9/47.8/38.3 (***)	---	---	> 250	> 250
(AC 5120-g-RVP/TPP 69.8/30.2/1)/Epikote 828/MNA 13.9/67.0/19.1 (***)	78	---	> 250	> 250
(AC 5120-g-RVP/TPP 69.8/30.2/1)/Epikote 828/MNA 21.6/71.8/6.6 (***)	75	---	> 250	> 250
(AC 5120-g-RVP/TPP 69.8/30.2/1)/Epikote 828/MNA 42.0/29.0/29.0 (***)	---	---	> 250	> 250

Heating Conditions:
(*)10 min at 115°C
(**) 2 h 30 min at 140°C
(***) {(AC 5120-g-RVP/TPP 69.8/30.2/1)/MNA 77.9/22.1 2 h 30 min at 140°C} + Epikote 828 + rest of MNA 10 min at 115°C.

TABLE 36: Melting, crystallisation, solubilisation and phase separation temperatures for the mixtures of Montanic Acid with AC 5120 and Epikote 828 obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
Montanic Acid	82	76		
AC 5120	87	86		
Montanic Acid/AC 5120 25/75 ***(10 min at 115°C)***	86	83	86	---
Epikote 828-g-Montanic Acid 6.6/1 ***(9 h at 150°C)***	83	79	114	105

TABLE 37: Melting, crystallisation, solubilisation and phase separation temperatures for the 50/50 mixtures of AC 5120 and Epikote 828 grafted with Montanic Acid obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120/(Epikote 828-g-Montanic Acid 6.6/1) 50/50 ***(10 min at 115°C)***	85	84	163	---
AC 5120/(Epikote 828-g-Montanic Acid 6.6/1) 50/50 ***(1h at 115°C)***	86	80	158	---
AC 5120/(Epikote 828-g-Montanic Acid 6.6/1) 50/50 ***(3 h at 115°C)***	83	84	178	---

TABLE 38: Melting, crystallisation, solubilisation and phase separation temperatures for the mixtures of AC 5120 grafted with ε-Caprolactone and Epikote 828 grafted with Montanic Acid obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
(AC 5120-g-Caprolactone 50/5)/ (Epikote 828-g-Montanic Acid 6.6/1) 50/50 ***(10 min at 115°C)***	80	74	213	---
(AC 5120-g-Caprolactone 50/20)/ (Epikote 828-g-Montanic Acid 6.6/1) 50/50 ***(10 min at 115°C)***	83	75	238	205

TABLE 39: Solubilisation and phase separation temperatures for the 50/50 mixtures of unmodified and modified AC 5120 and unmodified and modified Epikote 828 obtained from hot stage microscope experiments.

	T_s (°C)	T_p (°C)
AC 5120/Epikote 828 50/50	193	---
(AC 5120-g-Caprolactone 50/5)/Epikote 828 50/50	213	---
(AC 5120-g-Caprolactone 50/20)/Epikote 828 50/50	238	---
(AC 5120-g-RVP 69.8/30.2)/Epikote 828 50/50	172	---
(AC 5120-g-RVP/TPP 69.8/30.2/1)/Epikote 828 50/50	146	---
AC 5120/(Epikote 828-g-Montanic Acid 6.6/1) 50/50	178	---
(AC 5120-g-Caprolactone 50/5)/(Epikote 828-g-Montanic Acid 6.6/1) 50/50	213	---
(AC 5120-g-Caprolactone 50/20)/(Epikote 828-g-Montanic Acid 6.6/1) 50/50	238	205

The mixtures were obtained with the final products of each modification reaction, i.e. using the heating time required for the maximum conversion.

TABLE 40: Melting, crystallisation, solubilisation and phase separation temperatures of binary mixtures HHPA-e-Montanic Acid obtained from hot stage microscope experiments.

	Heating Time at 140°C	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)	T'_m (°C)	T'_c (°C)
HHPA						120	---
HHPA-e-Montanic Acid 90/10	10 min	78	67	98	---	98	---
	1 h	79	72	101	95	101	---
HHPA-e-Montanic Acid 80/20	10 min	80	75	103	100	---	---
	1 h	80	75	107	104	---	---
HHPA-e-Montanic Acid 70/30	10 min	80	74	105	102	---	---
	1 h	80	74	102	100	---	---
HHPA-e-Montanic Acid 60/40	10 min	79	74	102	100	---	---
	1 h	79	74	97	94	---	---
HHPA-e-Montanic Acid 50/50	10 min	78	73	98	90	---	---
	1 h	78	73	91	88	---	---
Montanic Acid		82	76				

TABLE 41: Melting, crystallisation, solubilisation and phase separation temperatures for binary mixtures of AC 5120, unmodified and modified with RVP, and HHPA-e-Montanic Acid obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120/(HHPA-e-Montanic Acid 80/20) 21.1/78.9	86	80	131	130
AC 5120/(HHPA-e-Montanic Acid 80/20) 44.4/55.6	82	80	113	90
AC 5120/(HHPA-e-Montanic Acid 80/20) 70.6/29.4	82	81	114	83
(AC 5120-g-RVP 69.8/30.2)/ (HHPA-e-Montanic Acid 80/20) 77.5/22.5	80	76	80	82

All the mixtures were heated 1 h at 115°C.

TABLE 42: Melting, crystallisation, solubilisation and phase separation temperatures for binary mixtures of Epikote 828 and HHPA-e-Montanic Acid obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
Epikote 828/(HHPA-e-Montanic Acid 80/20) 44.4/55.6	82	76	160	140

The mixture was heated 10 min at 115°C.

TABLE 43: Melting, crystallisation, solubilisation and phase separation temperatures for ternary mixtures of AC 5120, Epikote 828 and HHPA-e-Montanic Acid obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
AC 5120/Epikote 828/(HHPA-e-Montanic Acid 80/20) 4.6/55.2/40.2	88	78	230*	81
AC 5120/Epikote 828/(HHPA-e-Montanic Acid 80/20) 9.5/66.7/23.8	76	74	>250	>250
AC 5120/Epikote 828/(HHPA-e-Montanic Acid 80/20) 15.8/76.8/7.4	83	77	193	80

All the mixtures were heated 10 min at 115°C.

TABLE 44: Melting, crystallisation, solubilisation and phase separation temperatures for ternary mixtures of AC 5120 grafted with RVP, Epikote 828 and HHPA-e-Montanic Acid obtained from hot stage microscope experiments.

	T_m (°C)	T_c (°C)	T_s (°C)	T_p (°C)
(AC 5120-g-RVP 69.8/30.2)/Epikote 828/ (HHPA-e-Montanic Acid 80/20) 6.5/54.1/39.4	86	73	>250	>250
(AC 5120-g-RVP 69.8/30.2)/Epikote 828/ (HHPA-e-Montanic Acid 80/20) 13.1/64.0/22.9	77	70	210	79
(AC 5120-g-RVP 69.8/30.2)/Epikote 828/ (HHPA-e-Montanic Acid 80/20) 21.1/72.0/6.9	85	83	156	108

All the mixtures were heated 10 min at 115°C.

TABLE 45: Results of tritation tests performed on AC 5120 grafted with RVP, with or without TPP (1 and 1.5 pbw), and HHPA or MNA.

	Heating Conditions	Acid Number (mg KOH/g resin)	Degree of Conversion
AC 5120-g-RVP **69.8/30.2**	5 min at 115°C	77.3	7
	9 h at 140°C + 12 h at 90°C	65.9	21
AC 5120-g-RVP/TPP **69.8/30.2/1**	0 h at 140°C	84.3	0
	1 h at 140°C	15.7	81
	1 h 30 min at 140°C	15.2	82
	3 h at 140°C	15.1	82
	9 h at 140°C	15.2	82
	9 h at 140°C + 12 h at 90°C	15.2	82
AC 5120-g-RVP/TPP **69.8/30.2/1.5**	0 h at 140°C	63.3	23
	30 min at 140°C	15.3	81
	3 h at 140°C	15.6	81
	9 h at 140°C	15.9	81
(AC 5120-g-RVP/TPP 69.8/30.2/1) / HHPA 80/20	0 h at 140°C	29.3	
	1 h at 140°C	85.9	
	2 h at 140°C	87.1	
	2 h 30 min at 140°C	87 1	
(AC 5120-g-RVP/TPP 69.8/30.2/1) / MNA 77.9/22.1	0 h at 140°C	22.9	
	1 h at 140°C	80.1	
	2 h at 140°C	78 3	
	2 h 30 min at 140°C	77.5	

TABLE 46: Molecular weight results, measured at RAPRA Technology LTD, for the three functionalised polyethylenes and for AC 5120 grafted with ε-Caprolactone.

	$\overline{Mw}$	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$
AC 6702	2140 (*)	970(*)	2.2(*)
AC 540	4560(*)	1710(*)	2.6(*)
AC 5120	3325(*)	1005(*)	3.3(*)
	1385(**)	675(**)	2.0(**)
AC 5120-g-Caprolactone 50/5 (at 90% conversion)	1490(**)	710(**)	2.1(**)
AC 5120-g-Caprolactone 50/20 (at 95% conversion)	1595(**)	725(**)	2.2(**)

(*) Refers to tests performed on June 1992

(**) Refers to tests performed on February 1993

TABLE 47: DSC results for the three low molecular weight functionalised polyethylenes.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
AC 6702	63	35	101	44	67	81	44	13
AC 540	105	28	123	101	78	93	32	76
AC 5120	89	37	110	54	51	71	43	25

TABLE 48: DSC results for some of the binary mixtures with AC 6702.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
AC 6702	63	35	101	44	67	81	44	13
AC 6702/Epikote 828 50/50	79	26	100	56	64	76	33	34
AC 6702/Epikote 828 75/25	81	26	99	44	64	74	33	27

TABLE 49: DSC results for some of the binary mixtures with AC 540.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
AC 540	105	28	123	101	78	93	32	76
AC 540/Epikote 828 10/90	94	23	115	242	79	89	42	197
AC 540/Epikote 828 50/50	101	23	118	91	83	92	53	64
AC 540/Epikote 828 75/25	100	22	117	92	84	92	50	62
AC 540/Epikote 828 90/10	101	21	121	91	82	90	41	70
AC 540/CY 179 25/75	96	22	114	159	83	92	41	131
AC 540/CY 179 75/25	99	27	115	87	81	91	41	72

TABLE 50: DSC results for some of the binary mixtures with AC 5120.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
AC 5120	89	37	110	54	51	71	43	25
AC 5120/Epikote 828 50/50	74	22	105	37	59	75	42	25
AC 5120/Epikote 828 75/25	74	23	104	43	59	78	46	26
AC 5120/CY 179 50/50	76	20	114	67	54	81	23	66
AC 5120/CY 179 75/25	75	21	113	46	51	82	24	44

TABLE 51: DSC results for HHPA and for 50/50 mixtures of HHPA with AC 540 and with AC 5120.

	T'_{mp} (°C)	T'_{mi} (°C)	T'_{mf} (°C)	$\Delta H'_m$ (J/g)	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{ei} (°C)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
HHPA	31	12	61	99					173				
AC 540					105	28	123	101		78	93	32	76
AC 5120					89	37	110	54		51	71	43	25
HHPA/AC 540 50/50	32	24	51	38	99	57	111	72	152	83	94	57	70
HHPA/AC 5120 50/50	---	---	---	---	85	28	108	44	169	61	75	29	50

TABLE 52: DSC results for some of the ternary mixtures with AC 540.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
AC 540/Epikote 828/HHPA 5/60/35	101	84	113	5 (98)	84	100	60	53
AC 540/Epikote 828/HHPA 33.3/33.3/33.3	99	20	114	88 (99)	85	92	38	101
AC 540/Epikote 828/HHPA 42/48/10	101	23	116	73 (100)	85	94	41	114
AC 540/CY 179/HHPA 20/70/10	102	21	122	124 (100)	79	98	57	85
AC 540/CY 179/HHPA 33.3/33.3/33.3	101	21	116	92 (99)	85	96	48	88

TABLE 53: DSC results for some of the ternary mixtures with AC 5120.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
AC 5120/Epikote 828/HHPA 5/60/35	---	---	---	---	---	---	---	---
AC 5120/Epikote 828/HHPA 10/70/20	74	23	97	3 (83)	65	77	54	10
AC 5120/Epikote 828/HHPA 33.3/33.3/33.3	74	22	106	33 (76)	66	76	51	21
AC 5120/CY 179/HHPA 20/70/10	80	20	111	66 (69)	56	66	42	26
AC 5120/CY 179/HHPA 33.3/33.3/33.3	79	21	111	19 (76)	52	72	41	12

TABLE 54: DSC results for the mixtures of AC 5120 grafted with ε-Caprolactone.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
AC 5120	89	37	110	54	51	71	43	25
AC 5120-g-Caprolactone 50/5 ***(5 h 115°C)***	76	22	106	43	66	91	26	38
AC 5120-g-Caprolactone 50/5 ***(7 h 40 min 115°C+3 h 160°C)***	75	23	105	44	65	83	28	30
AC 5120-g-Caprolactone 50/20 ***(5h 115°C)***	75	22	107	33	66	84	35	27
AC 5120-g-Caprolactone 50/20 ***(6 h 30 min 115°C+7 h 160°C)***	53	22	105	47	66	83	37	24

The heats of fusion and crystallisation, ΔH_m and ΔH_c, are the total heats measured.

TABLE 55: DSC results for the 50/50 mixtures of AC 5120 grafted with ε-Caprolactone and Epikote 828.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
(AC 5120-g-Caprolactone 50/5)/ Epikote 828 50/50	75	23	104	40	65	83	47	21
(AC 5120-g-Caprolactone 50/20)/ Epikote 828 50/50	76	24	104	36	67	79	47	17

The heats of fusion and crystallisation, ΔH_m and ΔH_c, are normalised to polyethylene plus ε-Caprolactone content.

TABLE 56: DSC results for the mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP).

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
AC 5120	89	37	110	54	51	71	43	25
AC 5120-g-RVP 69.8/30.2 ***(10 min 140°C)***	79	28	103	57	61	75	38	22
AC 5120-g-RVP 69.8/30.2 ***(9 h 140°C)***	82	27	102	52	60	74	39	23
AC 5120-g-RVP 69.8/30.2 ***(9 h 140°C + 12 h 90°C)***	73	26	107	49	64	78	39	20

TABLE 57: DSC results for the mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP) and Epikote 828 or CY 179.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
(AC 5120-g-RVP 69.8/30.2)/ Epikote 828 50/50	71	24	106	38	62	75	45	21
(AC 5120-g-RVP 69.8/30.2)/ Epikote 828 75/25	71	23	104	37	62	76	44	22
(AC 5120-g-RVP 69.8/30.2)/ CY 179 50/50	72	25	115	50	65	80	52	10
(AC 5120-g-RVP 69.8/30.2)/ CY 179 75/25	83	26	113	44	63	77	37	19

TABLE 58: DSC results for the 80/20 mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP) and HHPA.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
(AC 5120-g-RVP 69.8/30.2)/ HHPA 80/20 *(10 min at 140°C)*	85	27	107	23 (28)	62	75	37	12
(AC 5120-g-RVP 69.8/30.2)/ HHPA 80/20 *(6 h at 140°C)*	87	26	109	27 (34)	61	75	34	14

The heats of fusion are the total heats measured. Those reported in brackets are normalised to polyethylene plus RVP content.
The heats of crystallisation are normalised to polyethylene plus RVP content.

TABLE 59: DSC results for the mixtures of AC 5120 grafted with the Monofunctional Epoxy Resin (RVP), Epikote 828 or CY 179 and HHPA.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
(AC 5120-g-RVP 69.8/30.2)/ Epikote 828/HHPA 15/50/35 *(10 min at 115°C)*	72	25	101	25 (79)	62	73	48	41
(AC 5120-g-RVP 69.8/30.2)/ Epikote 828/HHPA 21.8/72.8/5.4 (*)	73	24	104	19 (47)	63	73	52	8
(AC 5120-g-RVP 69.8/30.2)/ CY 179/HHPA 15/50/35 *(10 min at 115°C)*	88	25	106	16 (79)	52	65	41	21
(AC 5120-g-RVP 69.8/30.2)/ CY 179/HHPA 21.8/72.8/5.4 (*)	80	27	104	34 (47)	51	64	37	17

(*){ (AC 5120-g-RVP 69.8/30.2)/HHPA 80/20 6 h at 140°C} + Epikote 828 (or CY 179) 10 min at 115°C.

The heats of fusion and are normalised to polyethylene-graft-RVP plus HHPA content. Those reported in brackets are the theoretical values.
The heats of crystallisation are normalised to polyethylene-graft-RVP content.

TABLE 60: DSC results for the mixtures AC 5120-g-RVP/TPP 69.8/30.2/1 at different reaction times.

Heating Conditions	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
0 h at 140°C	80	39	107	39	62	78	44	11
3 h at 140°C	79	32	114	43	58	73	42	9
6 h at 140°C	80	32	111	48	57	71	42	9
9 h at 140°C	84	31	106	42	57	73	40	12
9 h at 140°C + 12 h at 90°C	78	32	111	37	53	70	38	15

TABLE 61: DSC results for the mixtures AC 5120-g-RVP/TPP 69 8/30.2/1.5 at different reaction times.

Heating Conditions	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
0 h at 140°C	86	35	112	47	62	74	41	113
30 min at 140°C	81	35	108	41	54	71	41	12
1 h at 140°C	81	34	110	45	53	70	40	14
3 h at 140°C	81	33	109	40	57	71	40	11
9 h at 140°C	80	33	110	43	58	72	39	11

TABLE 62: Crystallisation temperatures and enthalpies from DSC tests for AC 5120 and its modifications.

	T_c (°C)	ΔH_c (J/g)
AC 5120	49	27
AC 5120 (thermally treated) (*)	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 5120-g-RVP/TPP 69.8/30.2/1.5 (at 81% conversion)	54	12

(*) Subjected to the same thermal history as that used in the chemical modified products.

TABLE 63: DSC results for Montanic Acid and its mixtures with AC 5120 and Epikote 828.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
AC 5120	89	37	110	54	51	71	43	25
Montanic Acid	83	30	104	188	71	80	28	165
AC 5120/Montanic Acid 75/25	80	24	106	75 (87)	54/66 (*)	77	31	63 (60)
Epikote 828-g-Montanic Acid 6.6/1	51	24	118	170 (**)	71	79	37	75 (**)

(*) The first crystallisation temperature is related to the polyethylene component, while the second to Montanic Acid.
The values (**) are normalised to Montanic Acid content.

TABLE 64: DSC results for the 50/50 mixtures of AC 5120 grafted with ε-Caprolactone and Epikote 828 grafted with Montanic Acid.

	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
AC 5120/ (Epikote 828-g-Montanic Acid 6.6/1) 50/50	74	23	102	30	66	78	35	21
(AC 5120-g-Caprolactone 50/5) / (Epikote 828-g-Montanic Acid 6.6/1) 50/50	75	23	103	28	66	78	37	18
(AC 5120-g-Caprolactone 50/20) / (Epikote 828-g-Montanic Acid 6.6/1) 50/50	75	24	101	25	64	83	37	16

The heats of fusion and crystallisation, ΔH_m and ΔH_c, are the total heats measured.

TABLE 65: DSC results for the mixtures of HHPA and Montanic Acid.

	T'_{mp} (°C)	T'_{mi} (°C)	T'_{mf} (°C)	$\Delta H'_m$ (J/g)	T_{mp} (°C)	T_{mi} (°C)	T_{mf} (°C)	ΔH_m (J/g)	T_{ei} (°C)	T_{cp} (°C)	T_{ci} (°C)	T_{cf} (°C)	ΔH_c (J/g)
HHPA	31	12	61	99					173				
HHPA-e-Montanic Acid 90/10	35	21	59	75 (84)	79	59	96	10 (104)	150	68	78	33	12 (117)
HHPA-e-Montanic Acid 80/20	32	18	51	48 (60)	77	56	99	22 (108)	169	67	77	20	26 (128)
HHPA-e-Montanic Acid 70/30	33	23	51	41 (59)	78	57	97	32 (107)	170	67	77	26	37 (123)
HHPA-e-Montanic Acid 60/40	---	---	---	---	78	28	97	74 (185)	137	60	69	26	59 (147)
HHPA-e-Montanic Acid 50/50	---	---	---	---	77	22	99	87 (174)	163	60	70	27	75 (150)
Montanic Acid					83	30	104	188		71	80	28	165

The heats of fusion and crystallisation, ΔH_m and ΔH_c, are the total heats relative to Montanic Acid phase. Those reported in brackets are normalised to Montanic Acid content.
The values of heats of fusion $\Delta H'_m$ are the total heats relative to HHPA phase. Those reported in brackets are normalised to HHPA content.

Details of Formulations reported in Tables 66 to 78 are reported in Tables 1 to 7.

TABLE 66: DSC results for samples cured at 115 or 60°C and post-cured at 150°C.

	CI	I1	I3	FHA	CP	P1	P3	FHZ
T_g (°C)	136	109	109	106	110	106	108	117
T_m (°C)	---	42	63	85	---	65	47	88

TABLE 67: DSC results for samples cured at 115°C and post-cured at 150°C.

	C1	J1	J2	J3	K1	K2	K3
T_g (°C)	133	---	---	109	129	122	106
T_m (°C)	---	90	100	89	57	92	54

TABLE 68: DSC results for control samples cured at 115 or 60°C and post-cured at 150°C and 180°C.

	CL	CS	CR	CT	CQ
T_g (°C)	132	122	132	119	116

TABLE 69: DSC results for samples cured at 115 or 60°C and post-cured at 150°C and 180°C.

	S1	S3	L1	L3	U1	U3	Q1	Q3
T_g (°C)	132	118	130	117	134	116	121	108
T_m (°C)	43	48	73	67	47	70	54	55

TABLE 70: DSC results for samples cured at 115 or 60°C and post-cured at 150°C and 180°C.

	M1	M'2	M'3	M3	R1	R'2	R'3	R3
T_g (°C)	127	123	122	109	129	122	122	111
T_m (°C)	49	46	46	47	45	47	46	45

TABLE 71: DSC results for samples containing free RVP cured at 115°C and post-cured at 150°C and 180°C.

	T'M1	TM1	TL1	TM'3	TM3	TL3
T_g (°C)	127	133	124	114	118	111

TABLE 72: DSC results for samples containing free RVP cured at 60°C and post-cured at 150°C and 180°C.

	T'R1	TR1	TQ1	TR'3	TR3	TQ3
T_g (°C)	130	135	117	112	118	105

TABLE 73: Results from DMA tests for samples cured at 115°C or 60°C and post-cured at 150°C and 180°C.

	G' (GPa)	**G'' (GPa)**	**T_g (°C)**
CL	2.24	27.0	132
M1	2.10	34.5	129
M'3	1.68	27.0	124
CR	1.95	20.0	134
R1	1.71	25.0	129
R'3	1.86	41.0	126

The moduli G' and G'' are calculated at room temperature.

TABLE 74: Results from Flexural tests for samples cured at 115°C or 60°C and post-cured at 150°C.

	E (GPa)	**σ_b (MPa)**	**ε_b (%)**
CI	2.37	92.7	6.7
I1	2.32	105.7	6.7
I3	1 81	90.1	6.6
CP	2 33	105.4	10.4
P1	2.35	101.3	7 0
P3	1.90	75.5	5.4

TABLE 75: Results from Flexural tests for samples cured at 115°C or 60°C and post-cured at 150°C and 180°C.

	E (GPa)	**σ_b (MPa)**	**ε_b (%)**
CL	2.37	99.1	8.4
CR	2.28	97.0	7.0
CQ	3.11	116.9	6.5
Q1	2.66	99.9	5.9
Q3	2.14	81.2	5.5

TABLE 76: Results from Flexural tests for samples containing AC 5120 grafted with RVP, in presence of TPP, cured at 115°C or 60°C and post-cured at 150°C and 180°C.

	E (GPa)	σ_b (MPa)	ε_b (%)
M1	2.36	111.4	7.7
M3	2.17	86.2	5.4
R1	2.21	96 3	5.7
R3	2.13	86 6	5 8

TABLE 77: Results from Fracture Toughness tests, in 3 point bending, for samples cured at 115 or 60°C and post-cured at 150°C and 180°C.

	K_c (MPa*m$^{1/2}$)	G_c (kJ/m^2)
CL	1.65	1.15
M1	1.81	1.39
M'2	1.67	
CR	1.52	1.01
R1	1.64	1.22
R'2	1.49	
RU	1.93	

TABLE 78: Results from Charpy Impact Strength tests for samples cured at 115°C and post-cured at 150°C and 180°C.

	a_{cU} (kJ/m^2)
CL	14.9
M1	16.2
M'2	17.1

7.3 Additional Figures

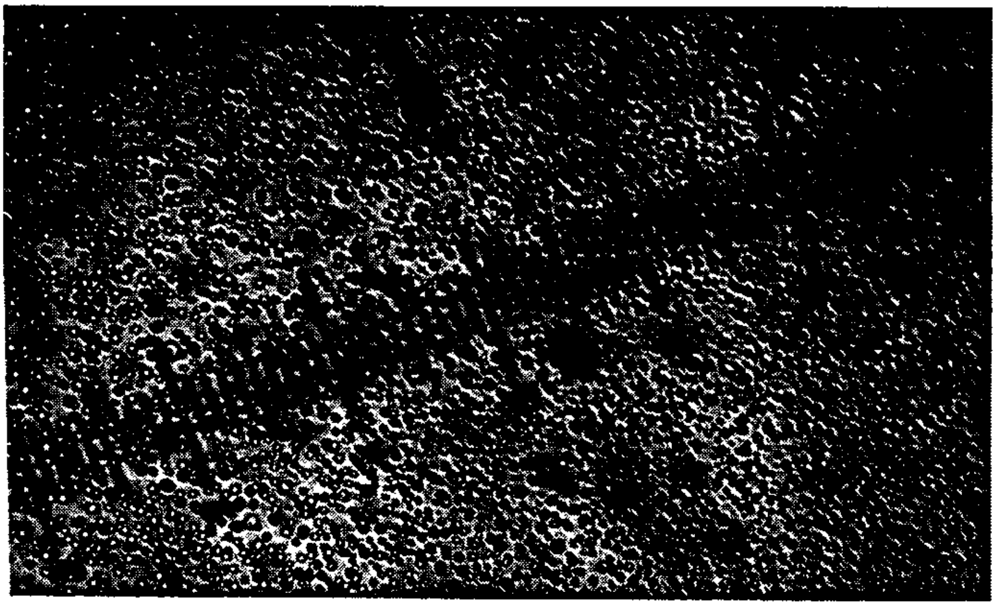

Figure 1: AC 6702/Epikote 828 50/50 (T = 100°C) (Heating time at 115°C = 24 hrs) Scale = 1/400

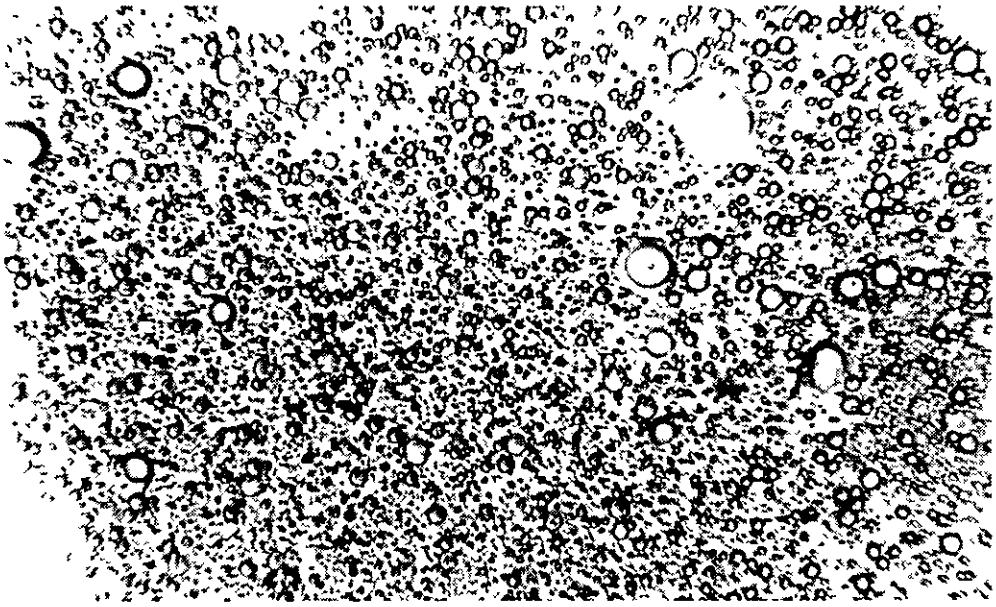

Figure 2: AC 540/Epikote 828 50/50 (T = 100°C) (Heating time at 115°C = 24 hrs) Scale = 1/400

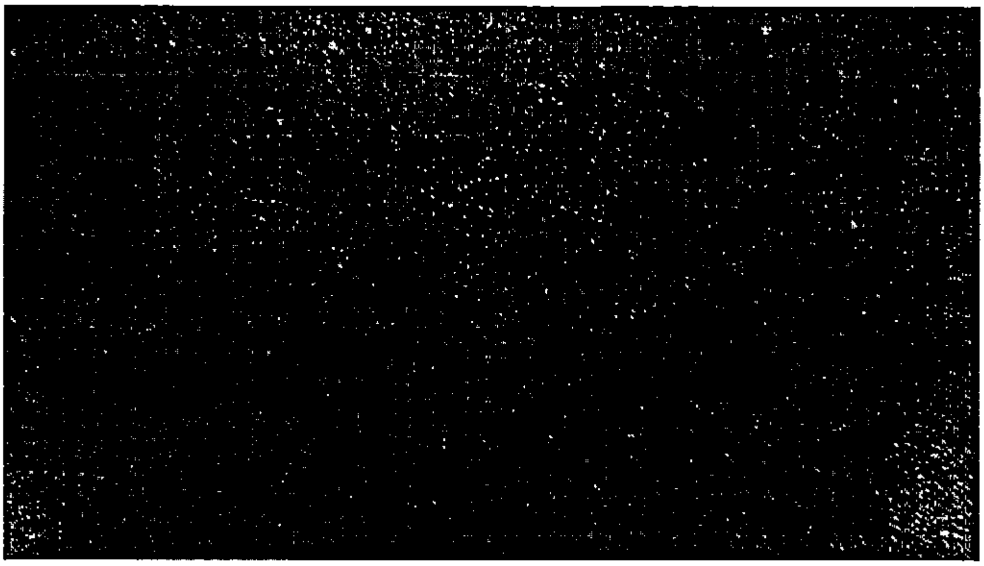

Figure 3: AC 5120/Epikote 828 50/50 (T = 100°C) (Heating time at 115°C = 21 hrs) Scale = 1/400

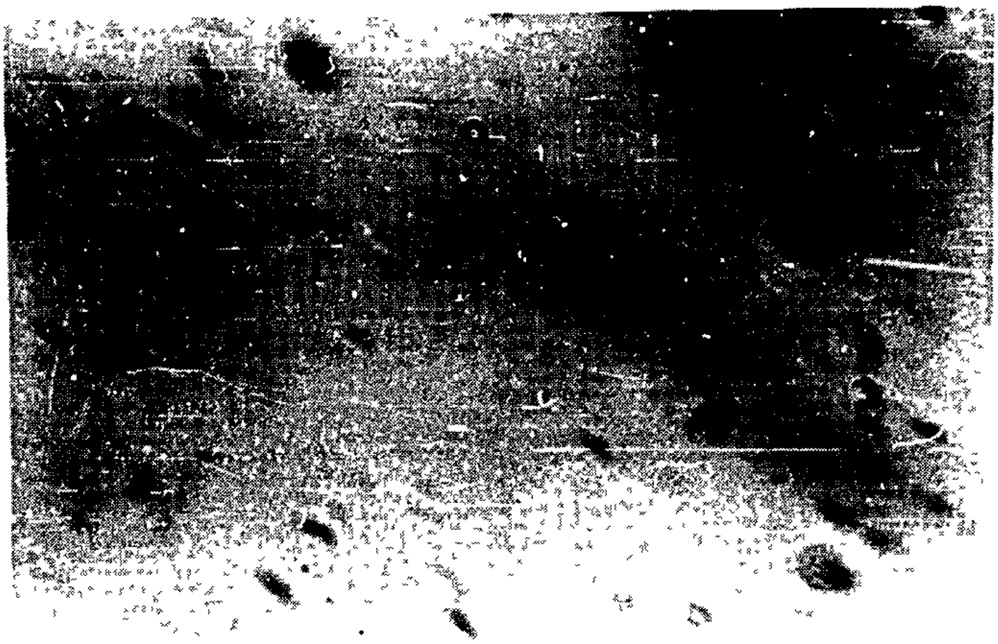

Figure 4: AC 540/Epikote 828/HHPA 10/70/20 (T = 250°C) (Heating time at 115°C = 10 min) Scale = 1/400

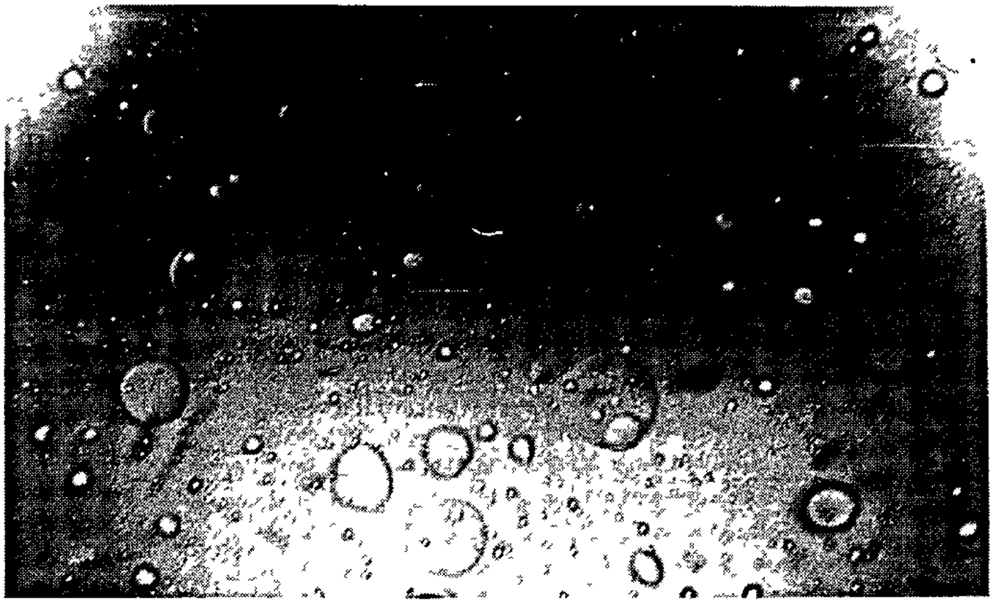

Figure 5: AC 540/Epikote 828/HHPA 14/62/24 (T = 250°C)

(Heating time at 115°C = 10 min) Scale = 1/400

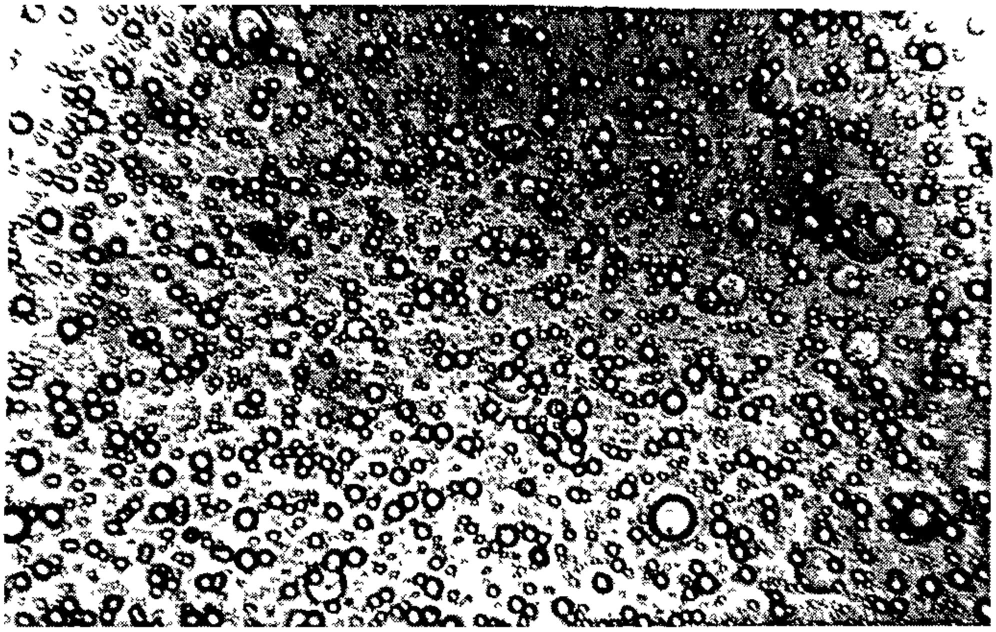

Figure 6: AC 540/Epikote 828/HHPA 16.7/50/33.3 (T = 250°C)

(Heating time at 115°C = 10 min) Scale = 1/400

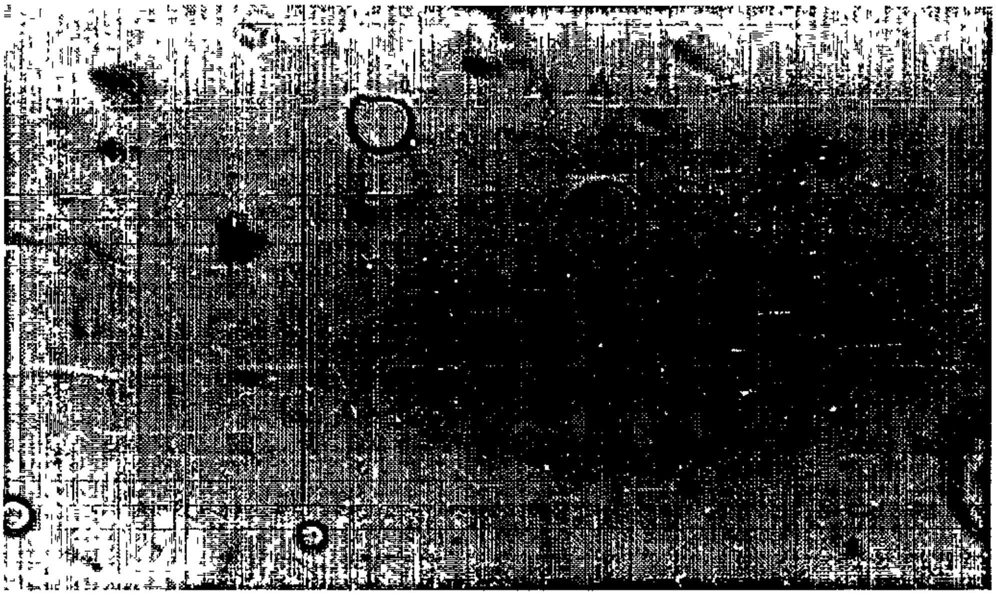

Figure 7: AC 5120/Epikote 828/HHPA 5/60/35 (T = 200°C)

(Heating time at 115°C = 10 min) Scale = 1/400

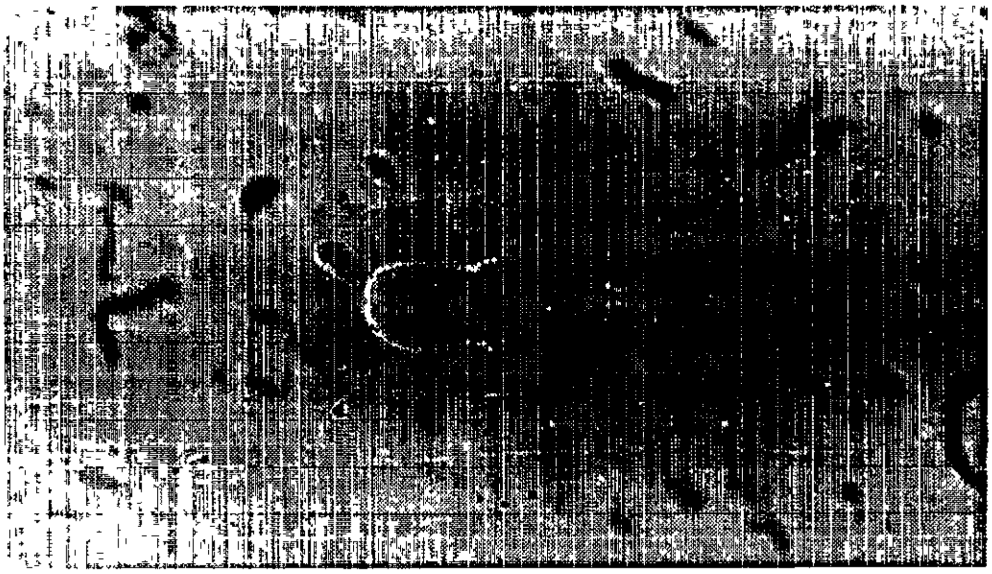

Figure 8: AC 5120/Epikote 828/HHPA 33.3/33.3/33.3 (T = 200°C)

(Heating time at 115°C = 10 min) Scale = 1/400

Figure 9: AC 5120/Epikote 828 50/50 (T = 120°C, 0 min)
(Heating time at 115°C = 6 hrs) Scale = 1/400

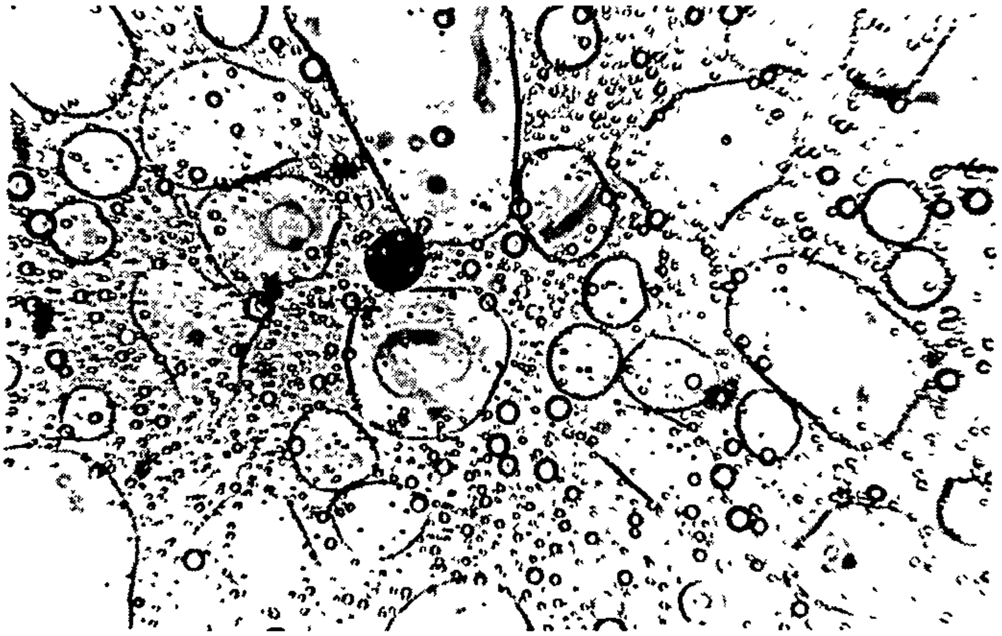

Figure 10: AC 5120/Epikote 828 50/50 (T = 120°C, 5 min)
(Heating time at 115°C = 6 hrs) Scale = 1/400

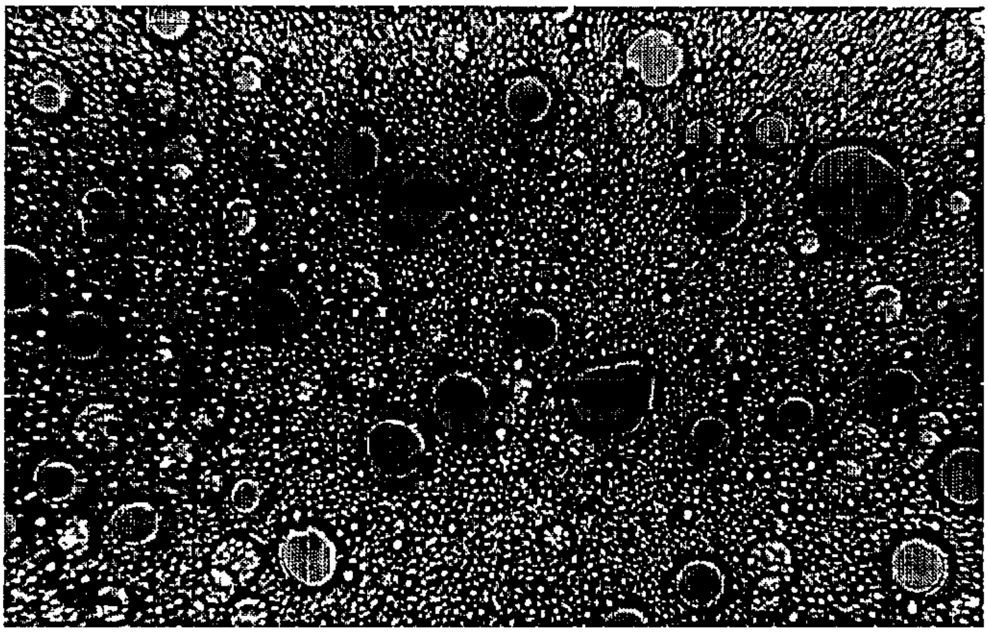

Figure 11: AC 5120/(Epikote 828-g-Montanic Acid 6.6/1) 50/50 (T = 120°C, 0 min) (Heating time at 115°C = 3 hrs) (Scale = 1/400)

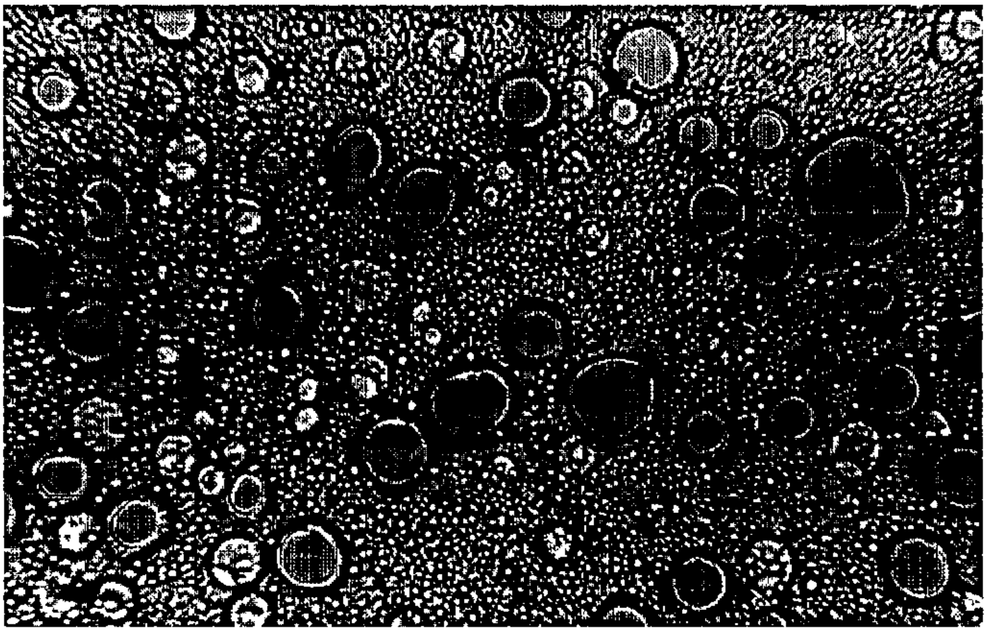

Figure 12: AC 5120/(Epikote 828-g-Montanic Acid 6.6/1) 50/50 (T = 120°C, 5 min) (Heating time at 115°C = 3 hrs) (Scale = 1/400)

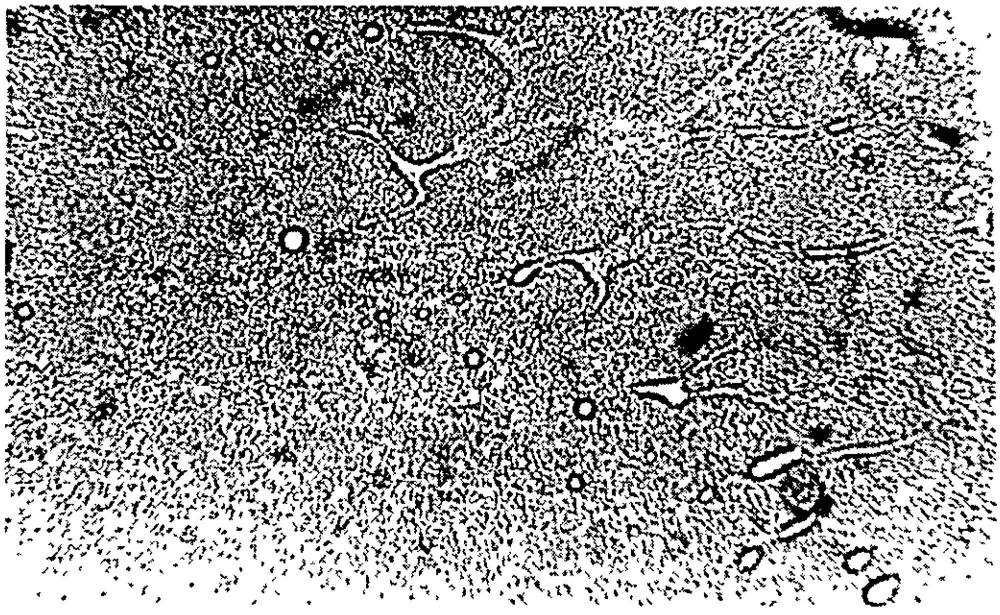

Figure 13: (AC 5120-g-Caprolactone 50/20)/Epikote 828 50/50 (T = 120°C, 0 min) (Heating time at 115°C = 10 min) Scale = 1/400

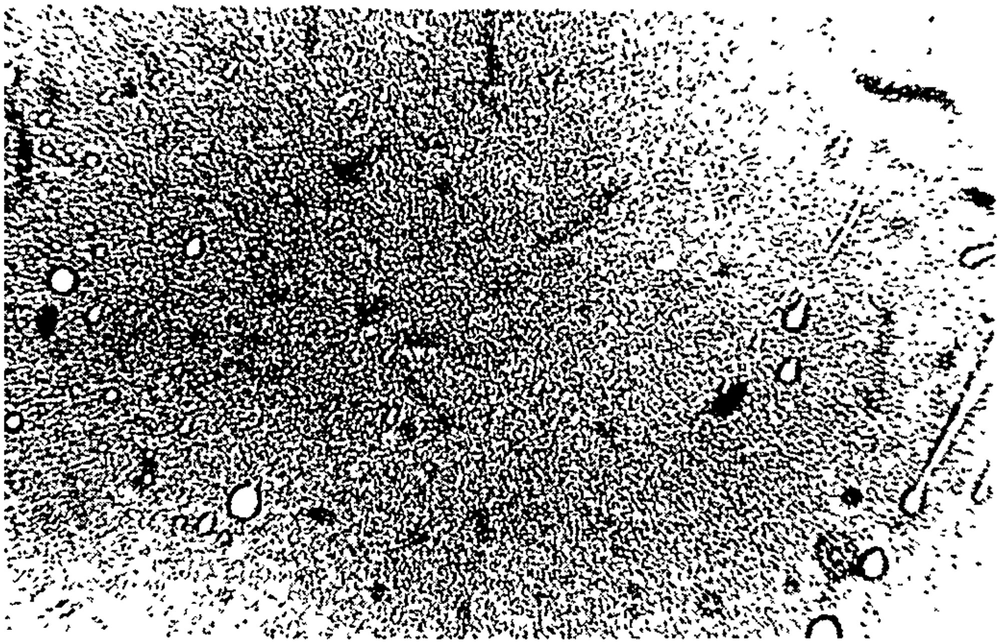

Figure 14: (AC 5120-g-Caprolactone 50/20)/Epikote 828 50/50 (T = 120°C, 5 min) (Heating time at 115°C = 10 min) Scale = 1/400

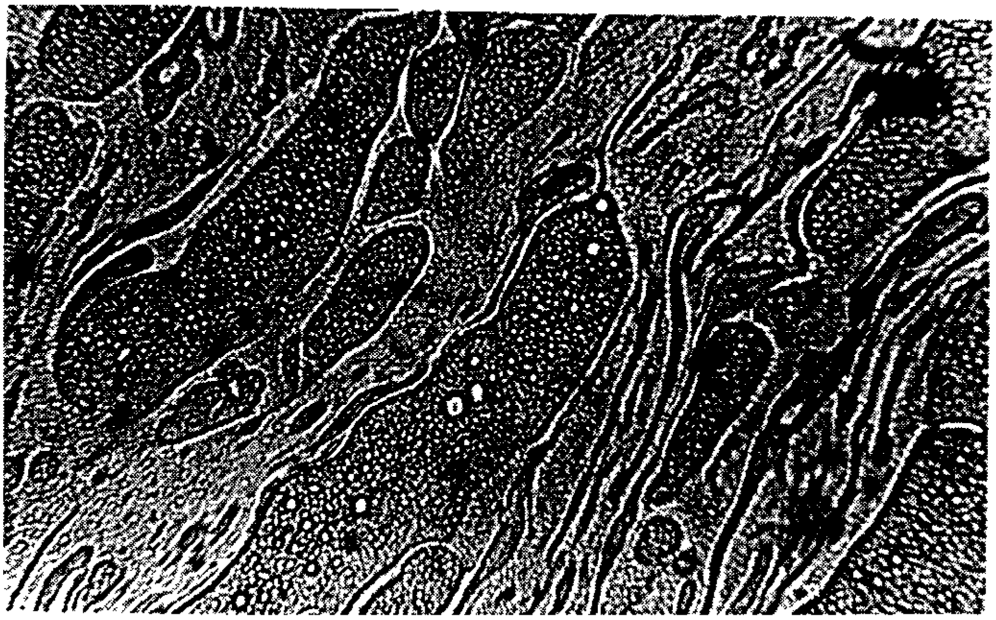

Figure 15: (AC 5120-g-Caprolactone 50/20)/(Epikote 828-g-Montanic Acid 6.6/1) 50/50 (T = 120°C, 0 min) (Heating time at 115°C = 10 min) Scale = 1/400

Figure 16: (AC 5120-g-Caprolactone 50/20)/(Epikote 828-g-Montanic Acid 6.6/1) 50/50 (T = 120°C, 5 min) (Heating time at 115°C = 10 min) Scale = 1/400

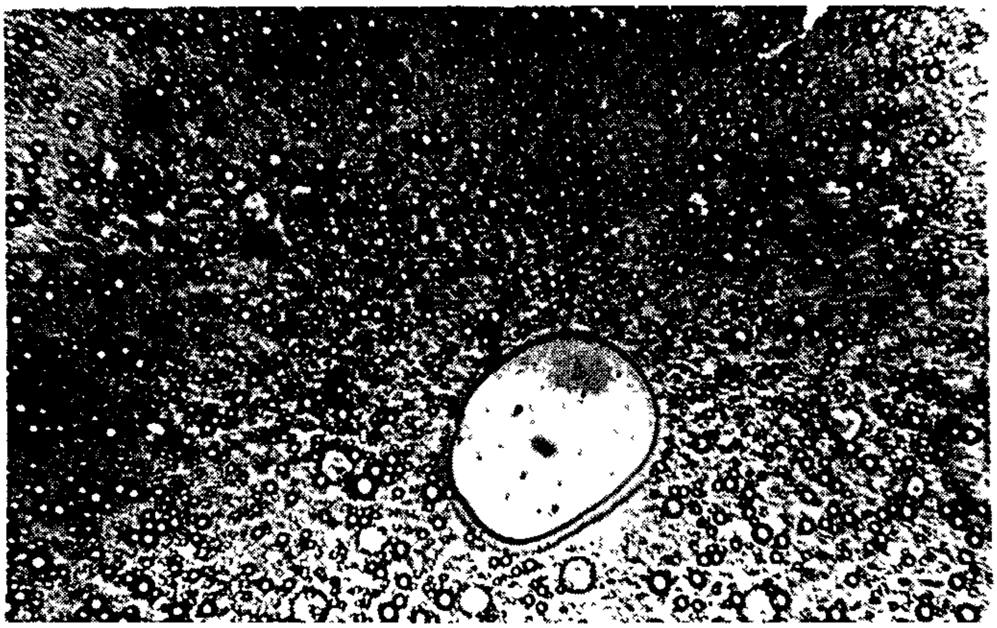

Figure 17: AC 540/Epikote 828 50/50 (T = 110°C, 0 min)
(Heating time at 115°C = 24 hrs) Scale = 1/400

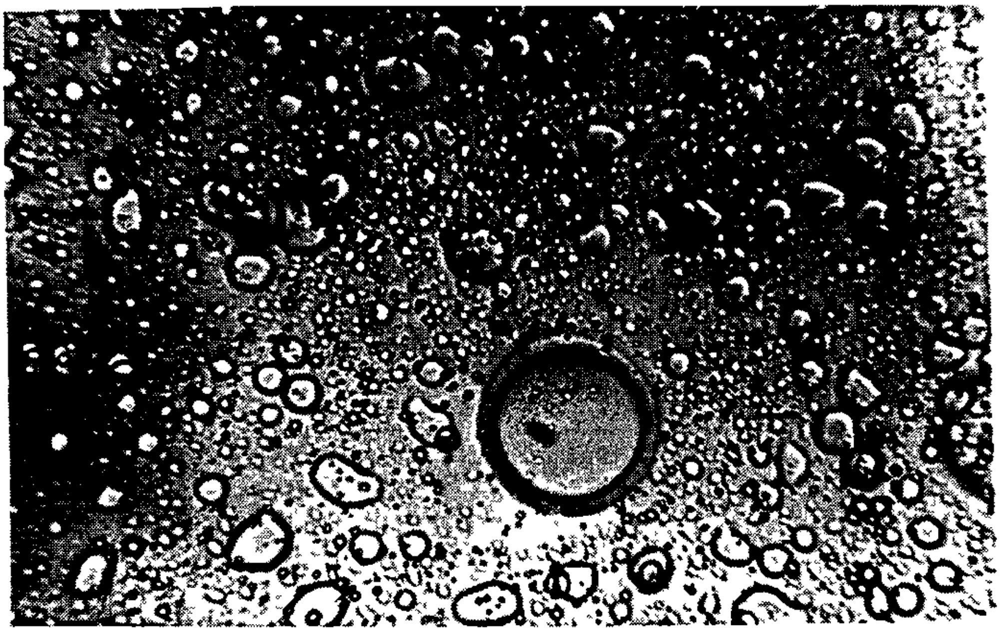

Figure 18: AC 540/Epikote 828 50/50 (T = 110°C, 1 hr 20 min)
(Heating time at 115°C = 24 hrs) Scale = 1/400

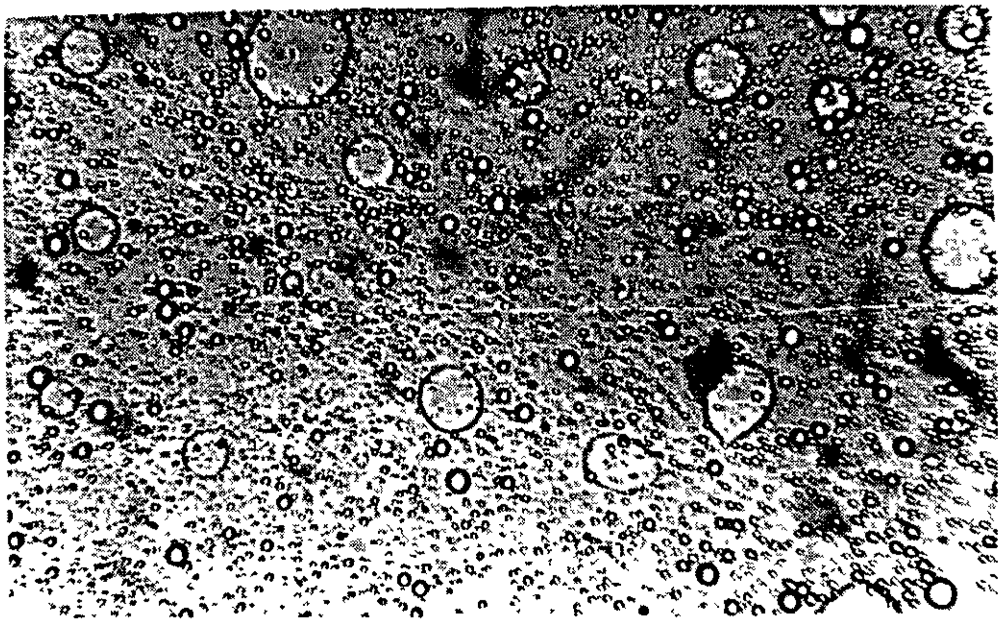

Figure 19: AC 5120/Epikote 828 50/50 (T = 110°C, 0 min)
(Heating time at 115°C = 6 hrs) Scale = 1/400

Figure 20: AC 5120/Epikote 828 50/50 (T = 110°C, 1 hr 30 min)
(Heating time at 115°C = 6 hrs) Scale = 1/400

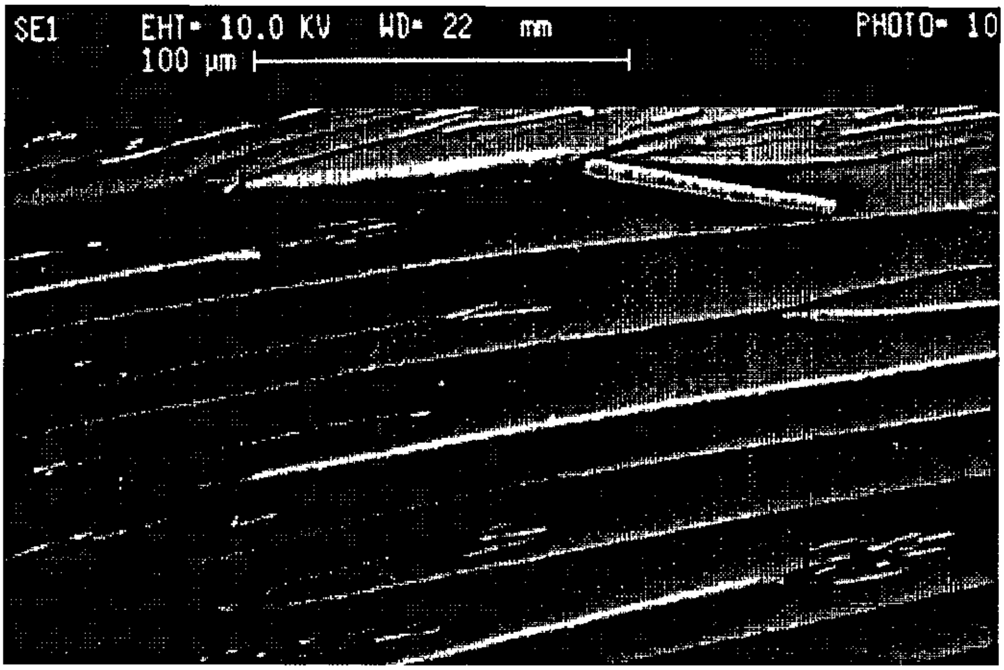

Figure 21: CL Cured System (Control Sample, T_{cure} = 115°C)

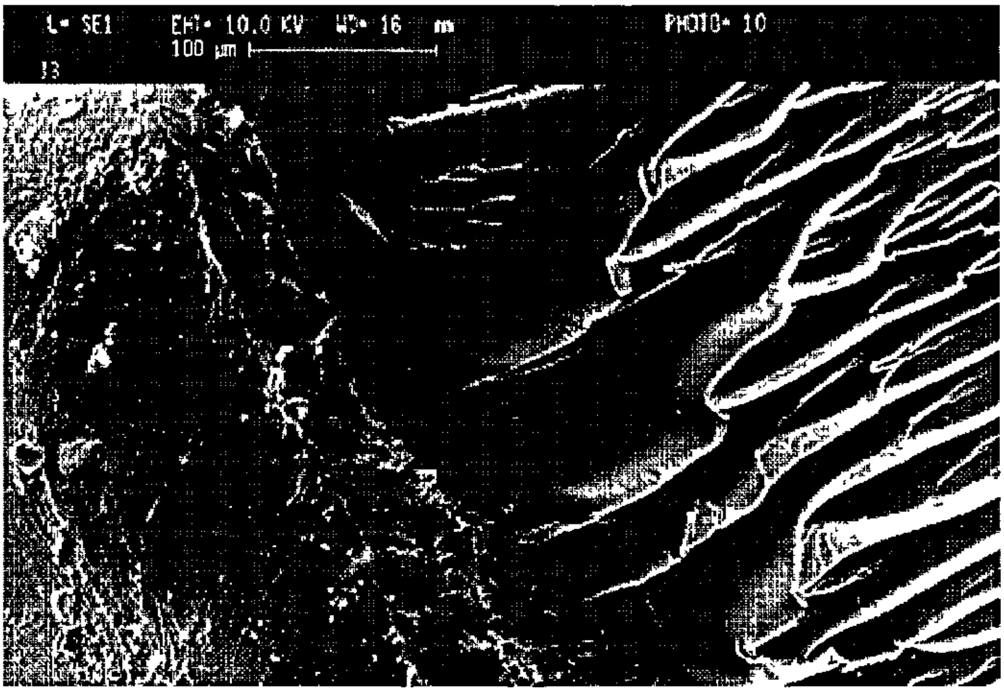

Figure 22: J3 Cured System (10 parts AC 5120, T_{cure} = 115°C)

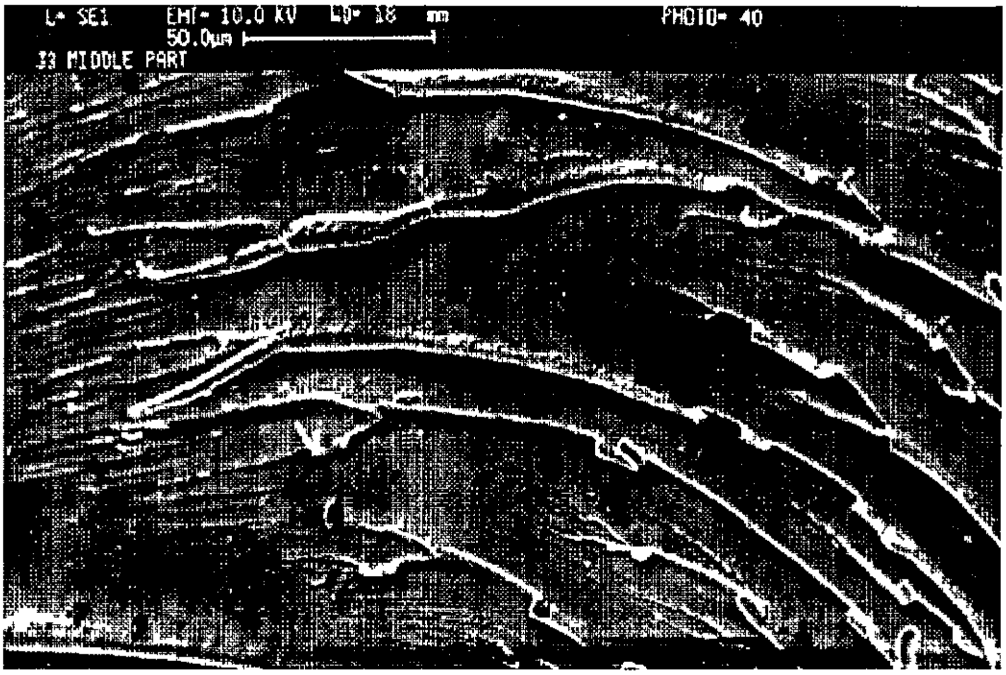

Figure 23: J3 Cured System (10 parts AC 5120, $T_{cure} = 115°C$)

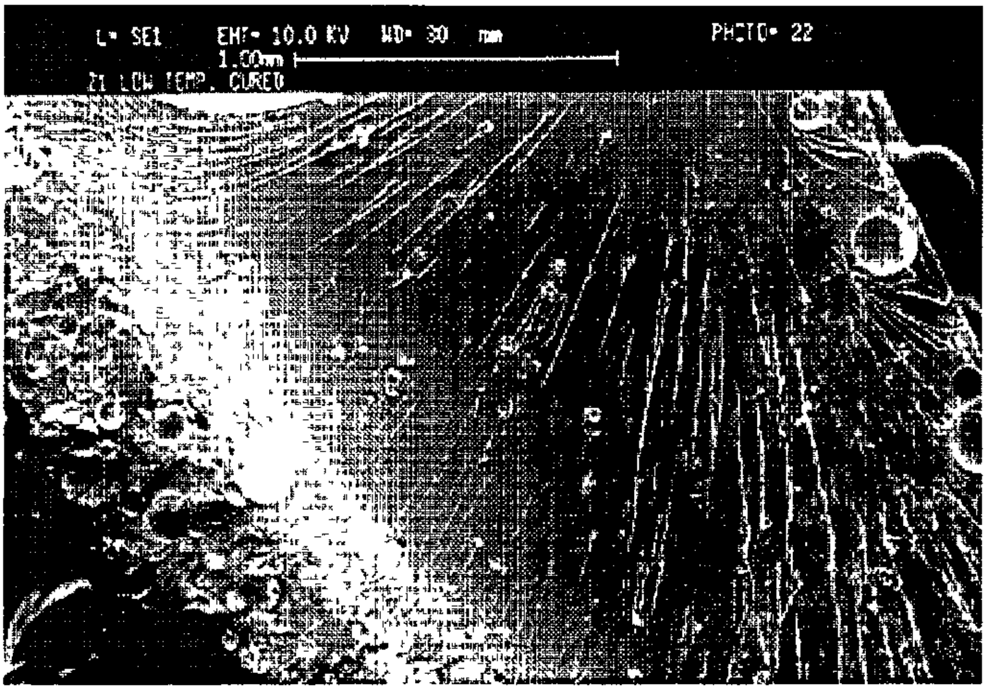

Figure 24: FHZ Cured System (30 parts (AC 5120-g-RVP 69.8/30.2), $T_{cure} = 60°C$)

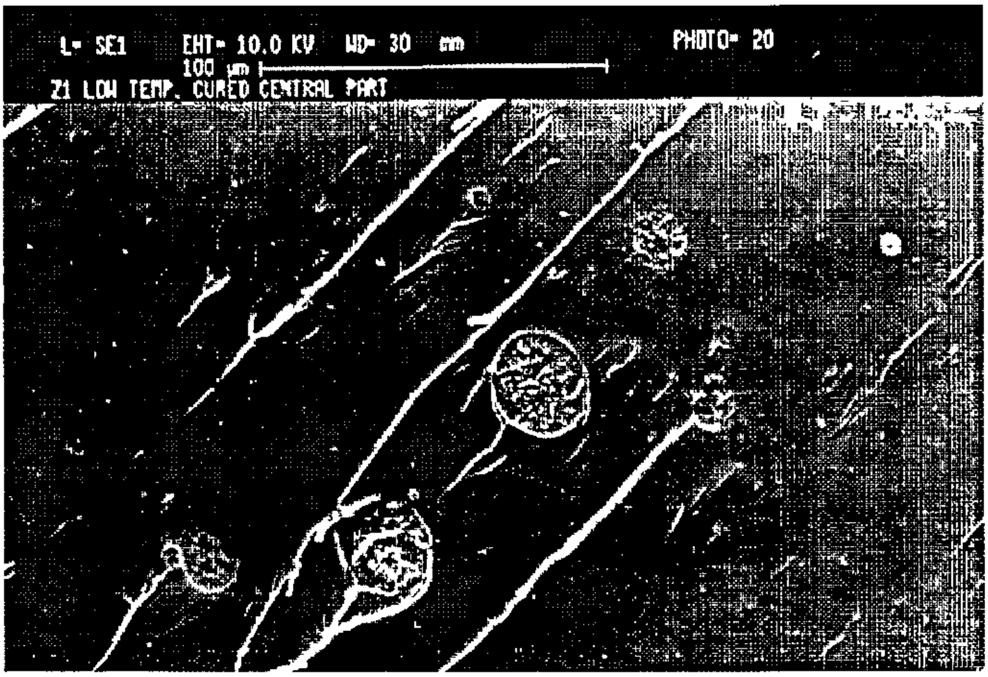

Figure 25: FHZ Cured System (30 parts (AC 5120-g-RVP 69.8/30.2), $T_{cure} = 60°C$)

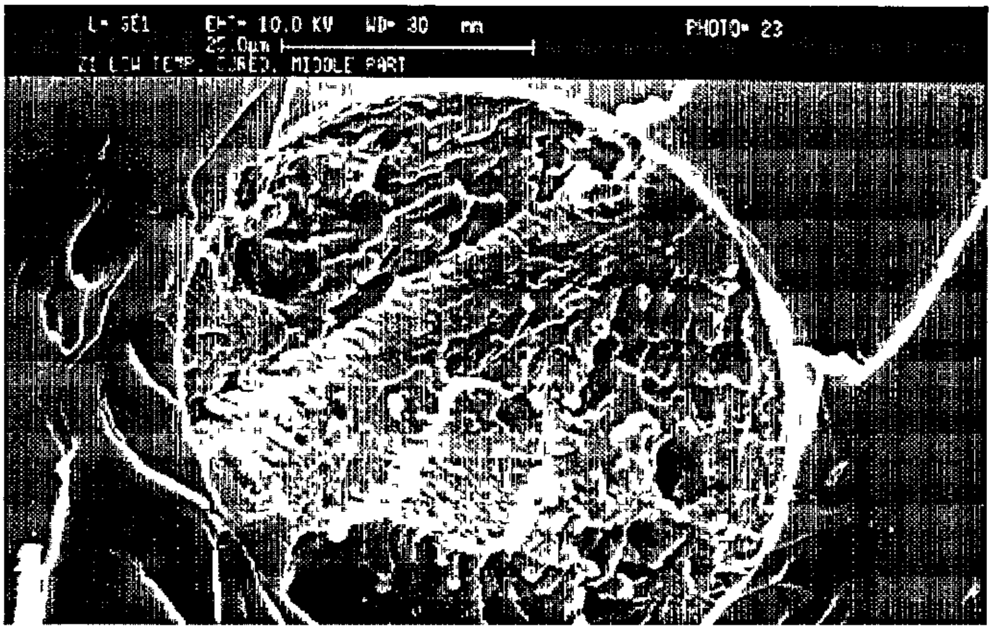

Figure 26: FHZ Cured System (30 parts (AC 5120-g-RVP 69.8/30.2), $T_{cure} = 60°C$)

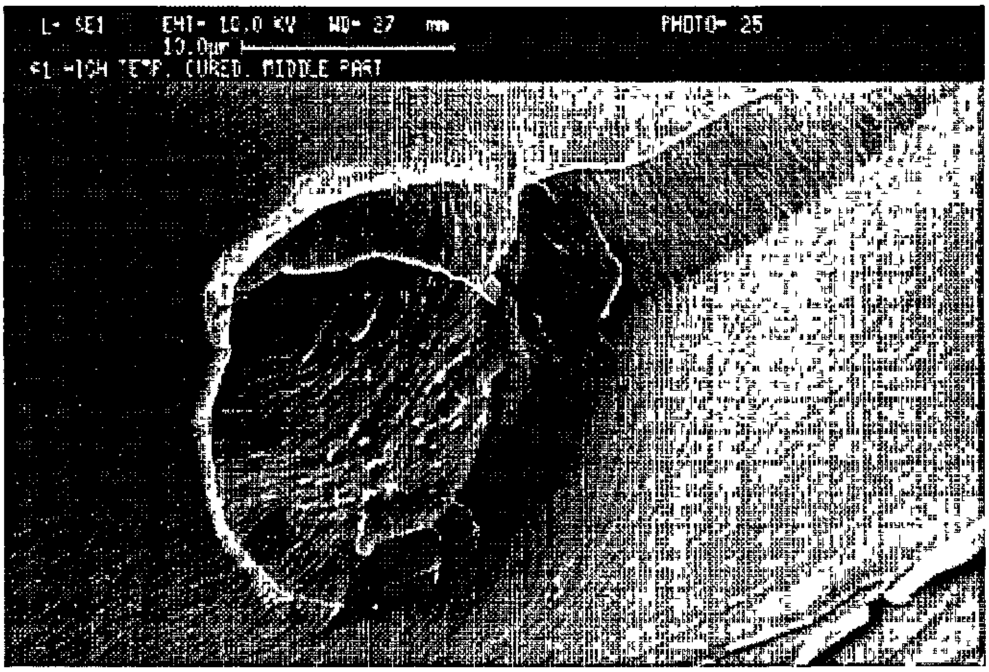

Figure 27: FHA Cured System (30 parts (AC 5120-g-RVP 69.8/30.2), $T_{cure} = 115°C$)

Figure 28: I3 Cured System (20 Parts (AC 5120-g-RVP 69.8/30.2), T_{cure} = 115°C)

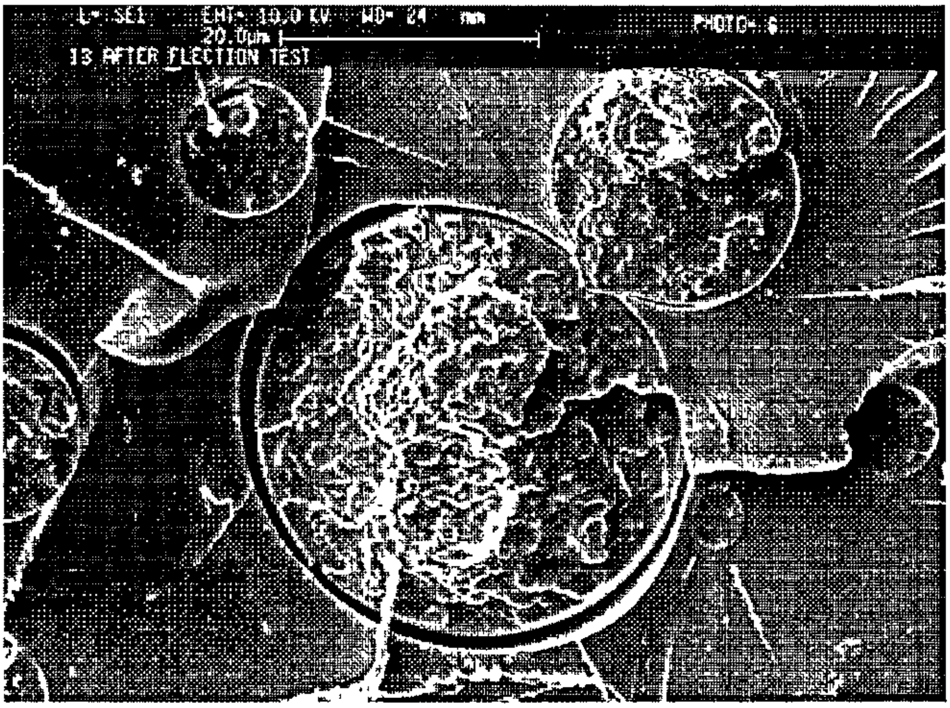

Figure 29: I3 Cured System (20 Parts (AC 5120-g-RVP 69.8/30.2), T_{cure} = 115°C)

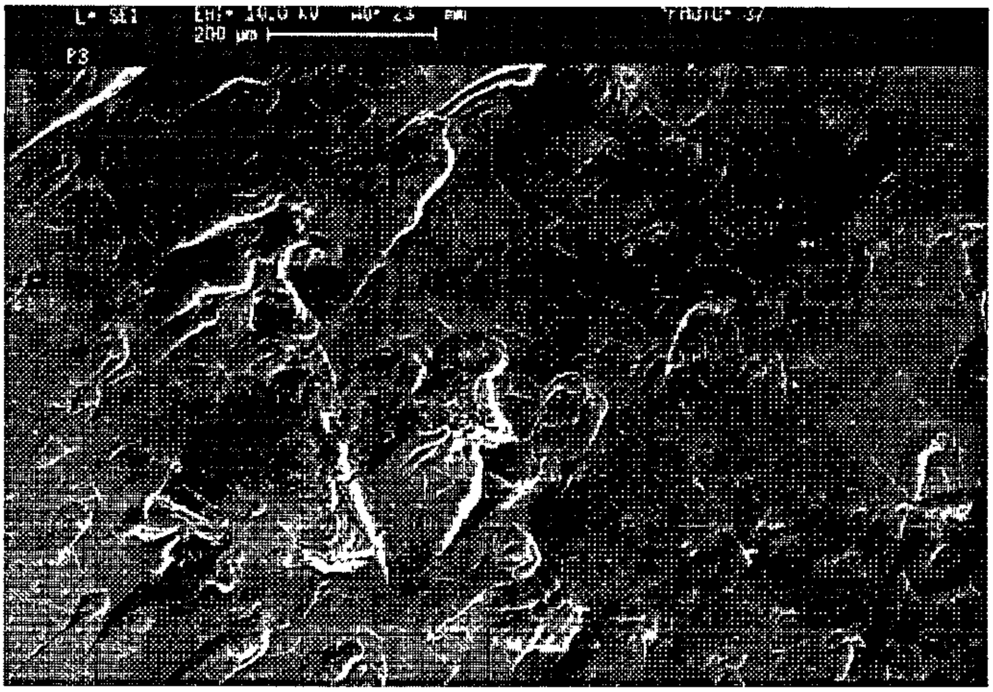

Figure 30: P3 Cured System (20 parts (AC 5120-g-RVP 69.8/30.2), T_{cure} = 60°C)

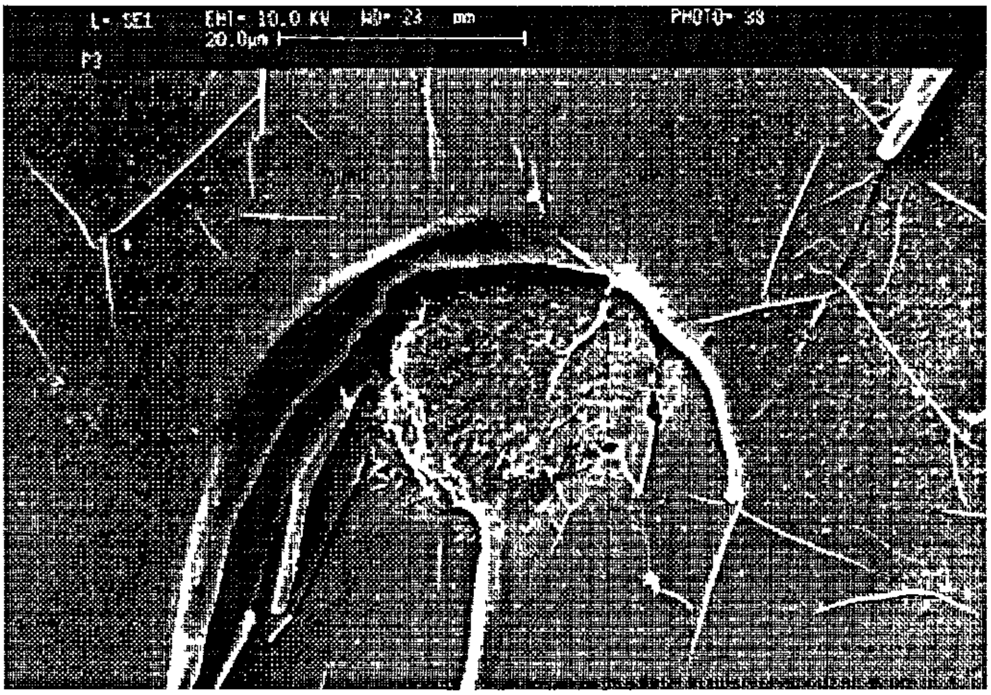

Figure 31: P3 Cured System (20 parts (AC 5120-g-RVP 69.8/30.2), T_{cure} = 60°C)

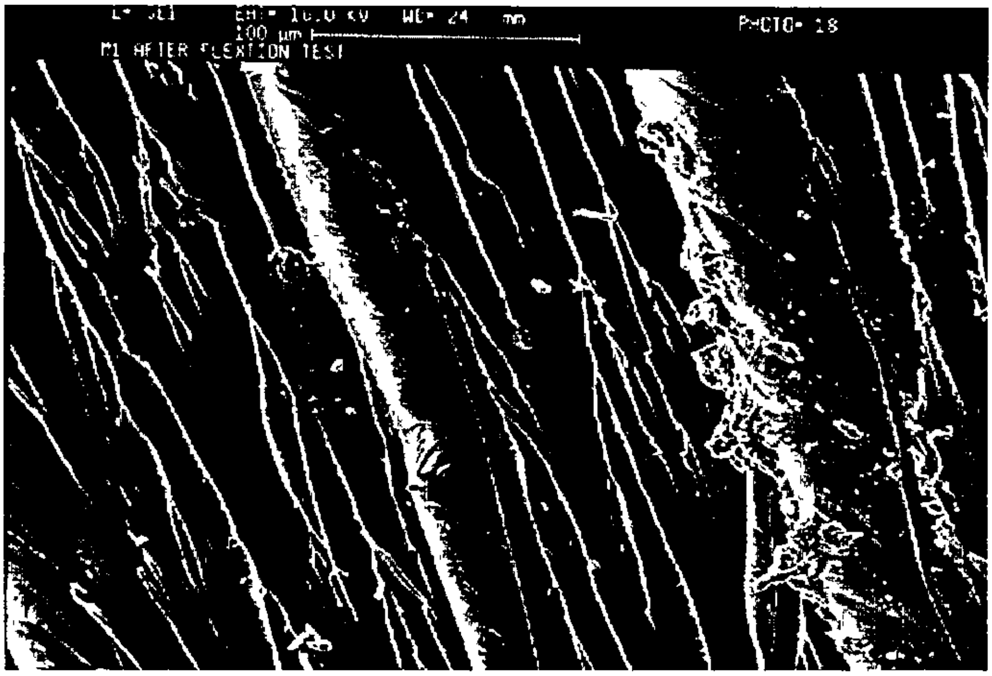

Figure 32: M1 Cured System (5 parts (AC 5120-g-RVP/TPP) T_{cure} = 115°C)

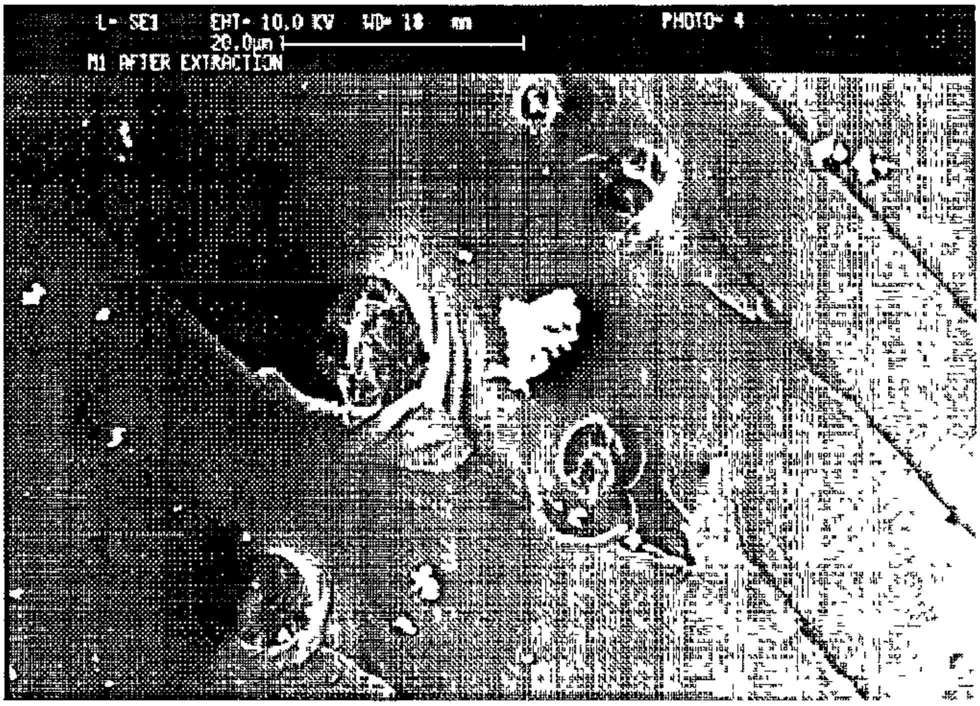

Figure 33: M1 Cured System (5 parts (AC 5120-g-RVP/TPP) T_{cure} = 115°C)

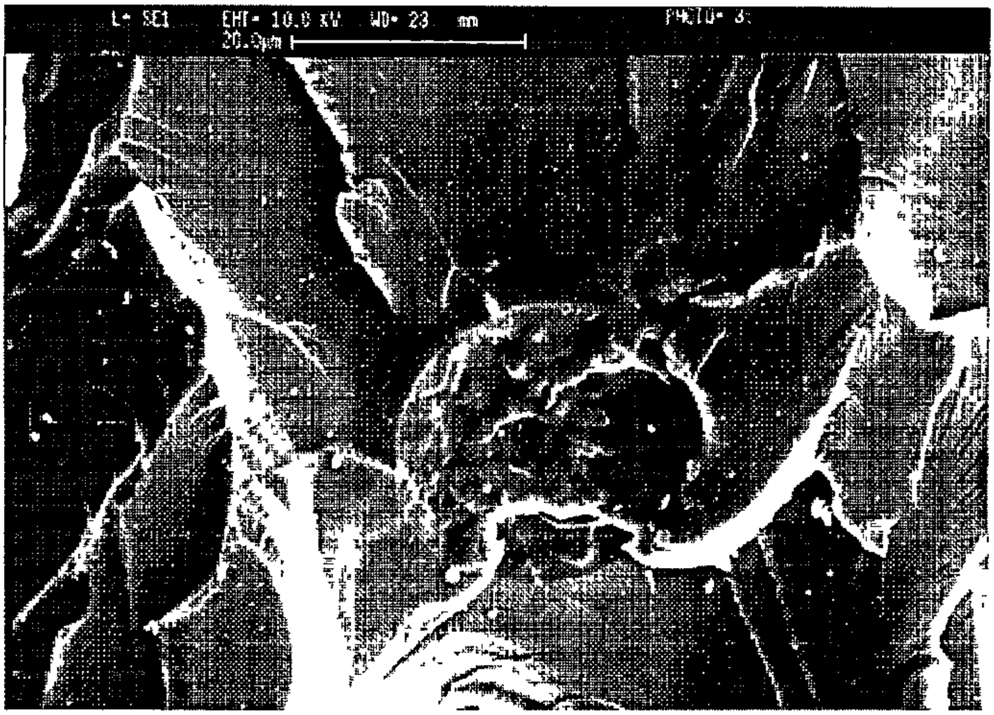

Figure 34: M3 Cured System (20 parts (AC 5120-g-RVP/TPP)

T_{cure} =115°C)

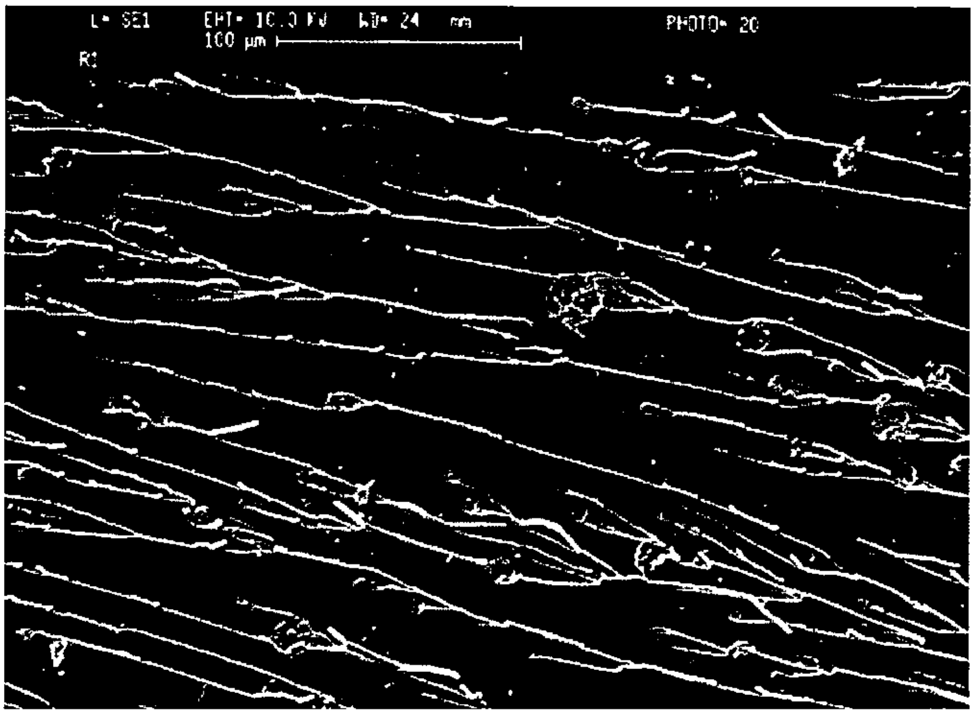

Figure 35: R1 Cured System (5 parts (AC 5120-g-RVP/TPP 69.8/30.2/1) $T_{cure} = 60°C$)

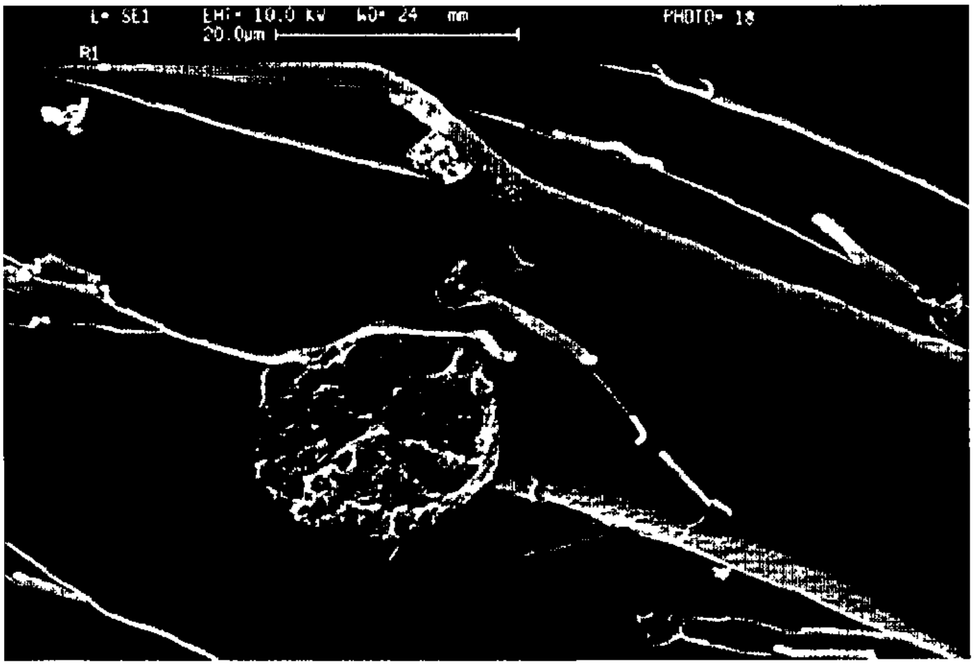

Figure 36: R1 Cured System (5 parts (AC 5120-g-RVP/TPP 69.8/30.2/1) $T_{cure} = 60°C$)

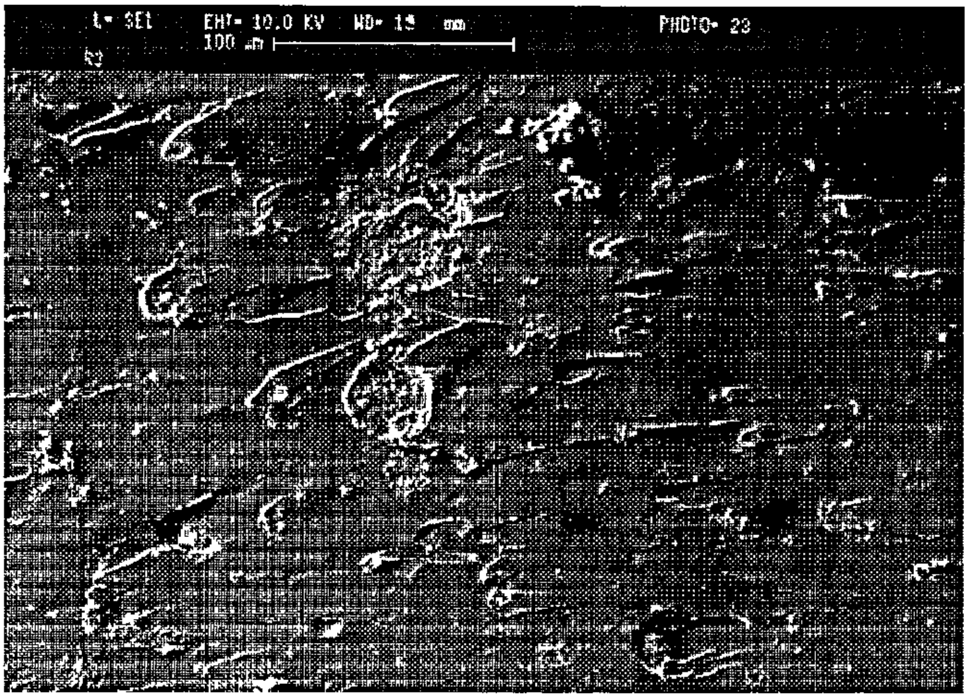

Figure 37: R3 Cured System (20 parts (AC 5120-g-RVP/TPP 69.8/30.2/1) T_{cure} = 60°C)

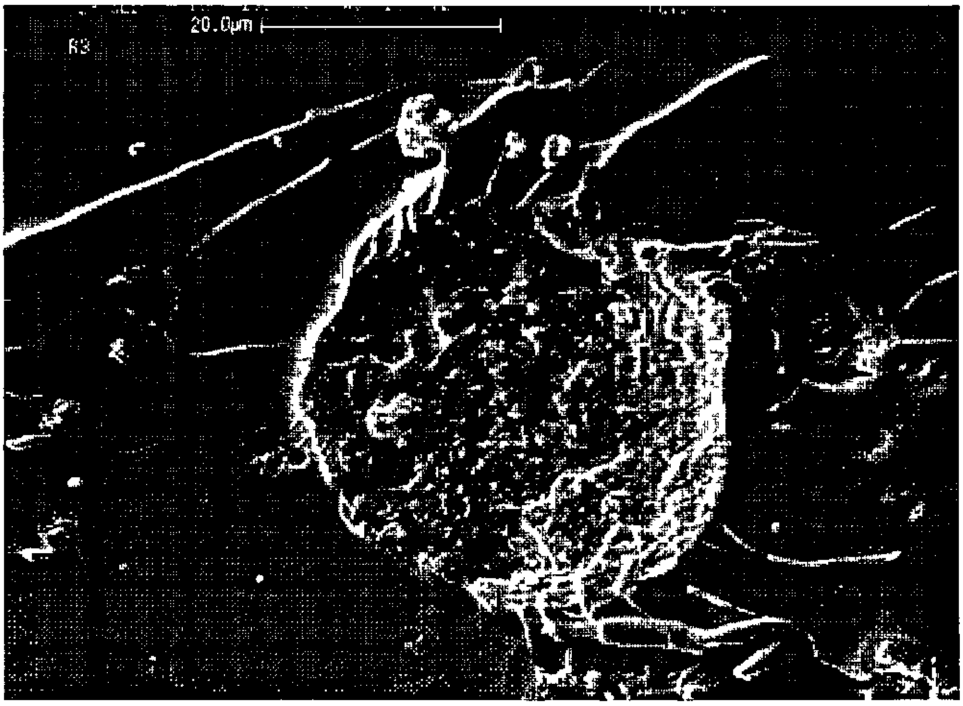

Figure 38: R3 Cured System (20 parts (AC 5120-g-RVP/TPP 69.8/30.2/1) T_{cure} = 60°C)

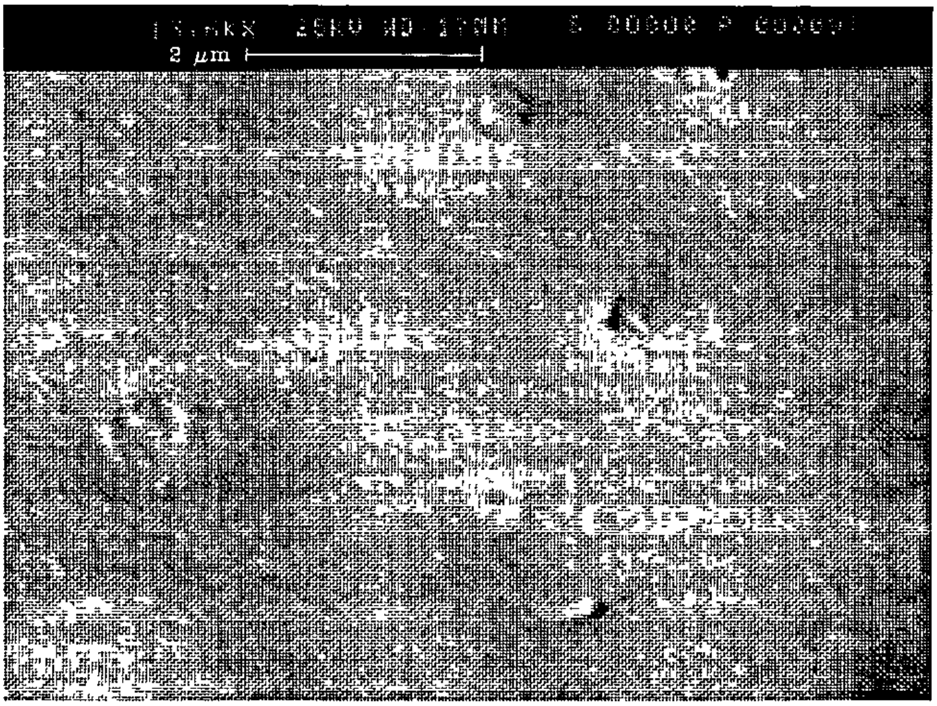

Figure 39: RU Cured System (10 parts CTBN $T_{cure} = 115°C$)