Self-Toughening Liquid Crystalline Vinyl Ester Adhesives

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Summary: Vinyl ester resins are widely used as thermosetting matrices for production of advanced composite and structural adhesives. They are obtained by end-capping unsaturated vinyl groups on a large variety of suitable oligomeric precursor, resulting in thermosetting resin with a good processability and outstanding end-use properties. In this paper we describe the shynthesis of a new methacrylated derivative of p-(2,3-epoxypropoxy)-α-methylstilbene exhibiting liquid crystalline phases, referred to as MD3A2. For the sake of comparison, a model compound has been synthesized with very similar chemical backbone. The model compound, referred to as MEP3A2, features isotropic phase and is derived form the commercially available Epon 825® epoxy resin (Shell Oil Company). Fracture resistance of samples has been tested according to ASTM D1002-72 (Strength Properties of Adhesives in Shear by Tension Loading) on aluminum supports and related to the presence of isotropic or liquid crystalline phases.

Keywords

Structural adhesive, liquid crystalline thermoset, vinyl ester resin, fracture resistance.

Introduction

Vinyl esters are thermosetting resins prepared by reacting acrylic or methacrylic acid with a suitable oligomeric precursors, including urethane, novolac, bisphenol and alogenated bisphenol resins [1-3]. They exhibit end-use properties and raw material costs which are intermediate between the high performance epoxy and the cheap unsaturated polyester resins (UPE).

The end-use properties of vinyl ester resins are strongly influenced by the chemical nature of starting precursors, while the presence of unsaturated vinyl end-groups affects the crosslinking reaction and the processability of the resin.

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The most widely used vinyl esters are the epoxy based ones, which find useful application as matrices for advanced composites [4-10].

Introducing unsaturated terminations, the curing process changes from the step reaction mechanism to the free radical polymerization, similar to that occurring with unsaturated polyesters. In the case of radical crosslinking reaction, gelation occurs at a much lower fractional conversion with respect to step reaction mechanism (i.e. epoxy resins). This leads to sensible processing advantages, enabling the production of large manufacts cured at room temperature. It has been found that vinyl ester resins cured at room temperature can achieve up to 80-90% of their optimal mechanical properties. Moreover, the epoxy backbone confers better toughness, elongation and chemical resistance to vinyl ester resins compared to unsaturated polyesters. These features are mostly due to the presence of ether groups along the molecular chain, unlike polyesters in which ester linkages are present. Ester groups are more sensitive to hydrolysis than ether groups, especially in the presence of strong bases and acids. In vinyl ester resins the ester linkages are produced by the addition reaction of unsaturated acids to epoxy end-groups. In the case of methacrylated resins, the steric hindrance of large methyl groups next to each ester linkage largely improves the hydrolytic resistance of material.

The adhesion of vinyl esters to solid substrates strongly benefits from the presence of secondary –OH groups in β–position to the C=O groups, resulting from the addition reaction of the carboxylic acid to the epoxy ring. As a result, vinyl ester resins wet effectively and strongly bond to solid substrates and reinforcing fibers. Long-term durability, resistance to thermal, oxidative and hydrolytic degradations, and bond retention after extended exposure to moisture are essential requirements of both structural adhesives (which must be highly crosslinked, hence harder and more brittle) and protective coatings (for which moisture impermeability and corrosion protection are required).

Processability of vinyl ester resins can be further improved by the addition of a co-reactive solvent, usually styrene, which drops the viscosity down to 100-500 mPa*s at room temperatures, thus allowing a rapid and effective wet-out of the glass fiber. The co-reactive solvent is incorporated into the polymeric backbone during crosslinking reaction. Depending on their specific properties [11-13], which are related to solvent content, the epoxide backbone, and the kind of termination, vinyl esters find useful applications as glass fiber composites, adhesives, bulk molding and sheet molding compounds for

appliance housings and automotive components. In particular, due to the high reactivity of the double bonds, acrylated vinyl ester resins are widely used for UV curable inks and coatings.

In this paper, the synthesis and properties of a liquid crystalline vinyl ester resin are presented and compared to a suitable isotropic model compound. The liquid crystalline and the isotropic resins have been tested as adhesive for aluminum substrates, in order to evaluate their use as adhesives for strong metal-to-metal structural joints and durable protective coatings. In fact, structural adhesives offer a significant alternative to conventional metal joining techniques, with lower prices, higher durability, faster application and better resistance.

Recently, it has been shown that mechanical properties of epoxy resins can be strongly improved if a liquid crystalline structure is induced to the network [14-23]. The resulting materials are characterized by high toughness, high chemical resistance, high resistance to water permeability and, mainly, by the possibility of being oriented by magnetic or electric fields before or during curing [24-25]. This class of materials offers significant improvements over conventional resins for advanced applications.

Experimental Part

Synthesis

The p-(2,3-epoxypropoxy)-α-methylstilbene (DOMS) was synthesized according to procedures reported in the literature [26]. The synthesis of MD3A2 was carried out starting from the epoxy monomer DOMS, whose liquid crystalline properties in thermosets have been extensively studied and previously reported [27-31].

The chemical structure of MD3A2 is shown in figure 1.

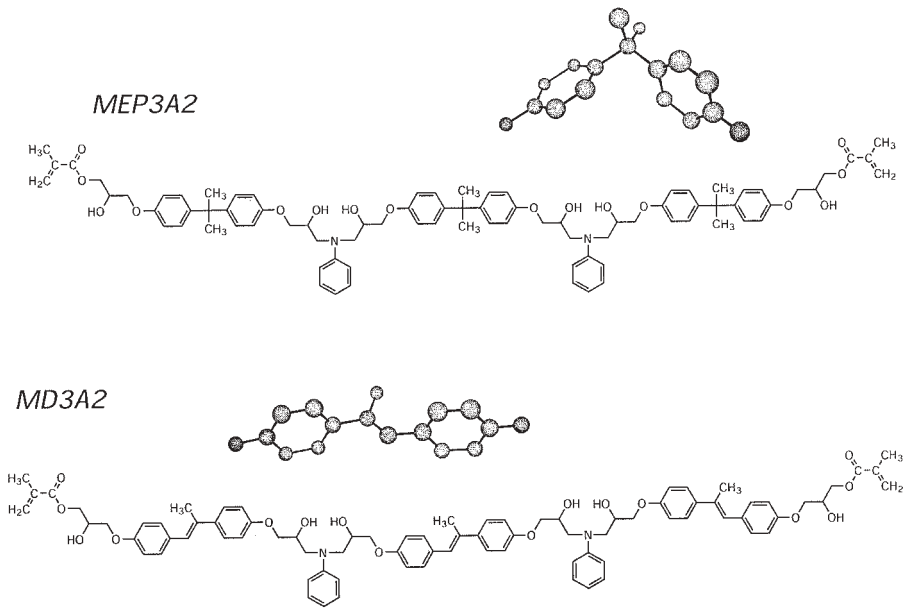


Fig. 1. Structural formulae of MD3A2 and MEP3A2; pictorial view of molecular moieties

In a typical procedure, DOMS (10 grams) was reacted with aniline (1.83 g) in a molar ratio of 3 to 2, using glacial acetic acid (5-7 drops) as catalyst and dioxane (20 ml) as solvent, at reflux temperature for 3 hours. In the second reaction step, 1.86 g of methacrylic acid (10% molar excess) were added, together with 1 mg of hydroquinone, to prevent the polymerization of methacrylic acid, and a few drops of N,N-benzyldimethylamine, as catalyst. The progress of the reaction between DOMS and methacrylic acid was followed by FT-IR. One droplet of reaction mixture was collected on KBr crystals every 30 minutes and analyzed, monitoring the decrease of the peak at 914 cm^{-1}, characteristic of the epoxy group. After 2 hours the product was precipitated into 1 liter of cold hexane. It was then filtered and washed with isopropanol (200 ml), filtered and washed with hexane (300 ml), filtered and vacuum dried at room temperature.

The final product was a white solid.

Yield: 67%. T_m=45°C (ΔH=29 J/g) T_i=94°C (ΔH=1.6 J/g). The melting and the isotropization temperatures, indicated with T_m and T_i respectively, are reported as the onsets of the calorimetric trace.

MEP3A2 is the methacrylic derivative of the epoxy monomer, synthesized from a commercial epoxy resin, Epon 825® and aniline in a molar ratio of 3 to 2, according to the same procedure followed for MD3A2.

Aniline was distilled before its use. All chemicals were purchased from Aldrich.

Sample preparation

MD3A2 and MEP3A2 were cured in the presence of benzoyl peroxide (1% wt.) as initiator and cobalt naphthenate (0.1% wt.) as catalyst at 150°C for 4 hours.

Aluminum substrates were pretreated according to the ASTM standard 2651-90 (Standard Guide for Preparation of Metal Surfaces for Adhesive Bonding).

Degreasing was accomplished by wiping with a cloth dipped in 1,1,1,trichloethane. In addition to solvent degreasing, a chromic acid etching technique was carried out on the substrates. A solution of distilled water, sulfuric acid, and sodium dichromate dihydrate in a weight ratio of 100:30:6, respectively was used, commonly referred to as FPL solution. After degreasing and drying, the substrates were immersed in the FPL solution at T=70°C for 12 minutes, washed with cold running tap water and dried at 60°C for 30 minutes.

Characterization

Seiko differential scanning calorimeter (DSC) mod. 220C, was used to evaluate the melting and the isotropization temperatures, and the heat flows involved in the transition of monomers. The experiments were run at 10°C/min heating rate under nitrogen flow.

Morphological features of starting monomers and cured resins were observed in transmitted light with an optical microscope Reichert-Jung (mod. Polyvar) equipped with crossed polarizers. The temperature was controlled by means of a Linkam mod. TH 600 hot stage.

X-Ray diffraction patterns were recorded with a flat camera equipped with a modified Linkam THMS 600 hot stage, with a sample to camera distance of 8.0 cm (Ni-filtered Cu-Kα radiation). The Fujifilm MS 2025 imaging plate and a Fuji Bio-imaging Analyzer System, mod. BAS-1800, were used for digitizing the diffraction patterns.

Fourier Transform Infrared spectrometer (FTIR) Nicolet mod. 5PC at a resolution of 2 cm^{-1} was used for spectroscopic analysis.

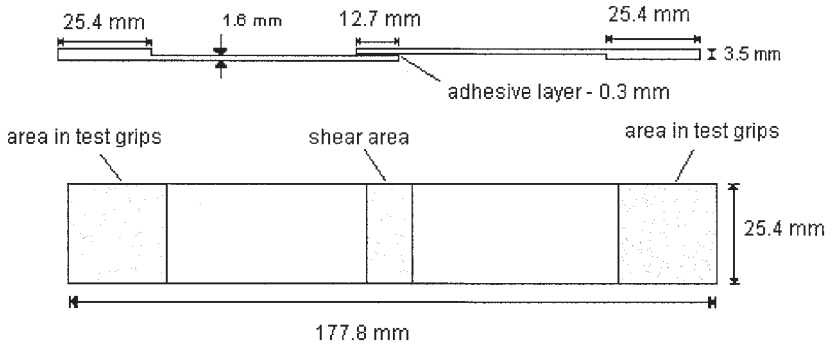


Fig. 2. Dimensions of substrates according to ASTM D1002-72

Strength of adhesive bonding was tested according to ASTM standard D 1002-72 (Strength Properties of Adhesives in Shear by Tension Loading). The shape and dimensions of the test specimens are shown in figure 2.

An electro-mechanical dynamometer INSTRON 4204 was used for mechanical testing, with a 5 kN load cell. Deformation rate was 1.3 mm/min. The specimens were fitted in such a way that their long axis coincided with the direction of applied deformation.

Dynamical Mechanical characterization has been carried out by means of TA Instruments DMA 2980, at a frequency of 1 Hz in tensile mode. Glass transition has been associated to loss modulus maximum.

Results and Discussion

Thermal analysis has been performed on MD3A2 by DSC. The first heating scan shows a solid-to-liquid crystalline phase transition centered at T=55°C (Tonset=45°C, ΔH=29 J/g) and a liquid crystalline-to-isotropic phase transition at T=101°C (Tonset=94°C, ΔH=1.6 J/g). The X-rays diffraction pattern obtained on the sample at T=75°C and the analysis of textures with optical microscope indicate the formation of a nematic phase in the temperature range between the melting and the clearing temperatures. The crosslinking reaction takes place after isotropization, as indicated by the exothermic peak centered at T= 140°C (Tonset=124°C, ΔH=74 J/g).

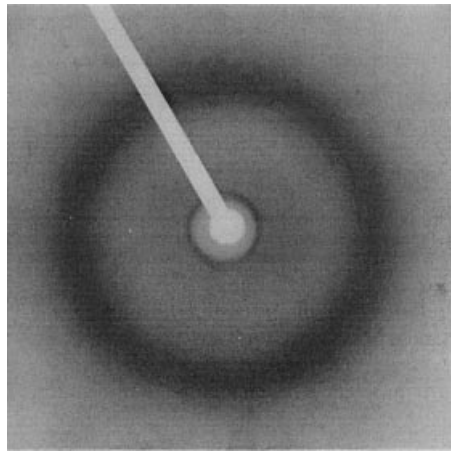


Fig. 3. X-ray diffraction pattern of cured MD3A2 recorded at room temperature

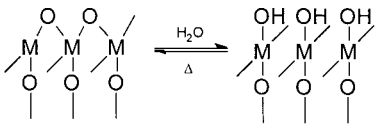
In the second heating scan the curve shows a glass transition at T=60°C and an endothermic peak centered at T=137°C (Tonset=123°C, ΔH=2.7 J/g), this latter corresponding to the isotropization of the resin. Upon curing, a LC polymeric network forms in which chains are still free of moving giving rise to the reversible LC-to-isotropic transition above T=123°C. The X-ray pattern obtained on the cured sample at room temperature indicates the formation of a smectic structure, with a sharp reflection at low

angle corresponding to a spacing d=20.5Å, which is typical of a smectic phase (see figure 3).

MD3A2 has been used as adhesive for aluminum joints. Its features have been compared to those of MEP3A2, chosen for the comparison. The chemical structures of the two monomers are very similar. However, due to the presence of an unsatured group between the two aromatic rings, MD3A2 exhibits a rigid structure, which is responsible for the formation of the LC phase. Differently, MEP3A2 has a more flexible chain, and thus exhibits isotropic properties (see figure 1).

To study the adhesion properties on aluminum joints of liquid crystalline resin in comparison with an isotropic one, a three-step procedure, consisting in the pre-treatment of aluminum supports, application of the resin, mechanical characterization of joints has been carried out.

Like any other metal, aluminum exhibits a very high surface energy (E>500 mJ/m2) and hence it reacts easily with the oxygen in the atmosphere giving rise to the formation of the corresponding oxide [32-34]. The oxide layer formed can isolate the underneath metal layer, thus reducing the interaction between the metal and the polymer used as adhesive. Furthermore, the oxygen atoms on the surface can easily hydrate in the presence of humidity in the atmosphere, according to the reaction (1):



(1)

The presence of hydroxyl groups can damage the joint by favoring the adsorption of water and polar contaminant. In particular, water can be strongly detrimental because hydrated aluminum oxides adhere weakly to the metal.

A solvent degreasing pre-treatment is required to remove surface contamination, such as machine oils, grease, release agents. It is usually followed by a strong acid etching. This latter provides a very rough metallic surface which favors the *mechanical interlocking* between the resin and the metallic substrate, and in the case of resin with quite low viscosity, a good penetration of the adhesive inside the small cavities and inhomogeneities formed [35]. The procedure followed for pre-treatment of joints is explained on the ASTM

standard D2651-90 (Standard Guide for Preparation of Metal Surfaces for Adhesive Bonding). Efficient removal of weak boundary layers, improved interfacial contact (better wetting and a greater area for interfacial contact) and the enhancement of energy dissipative mechanisms in the adhesive are obtained [36]. All these mechanisms contribute to improve the resin/metal adhesion and thus to increase the joint strength. To prevent the formation of new detrimental hydrated layers, the resin had to be applied as soon as the substrates were ready.

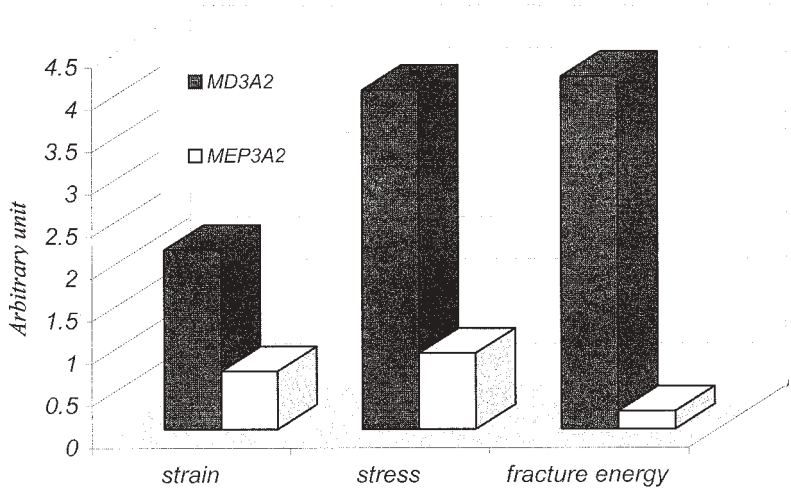


Fig. 4. Comparison between mechanical properties of MD3A2 and MEP3A2

After the pre-treatment, the resin has been readily applied on supports. Before being applied, the resin has been mixed with the benzoyl peroxide (1% wt.) used as radical initiator, and the cobalt naphtenate (0.1 % wt.) used as catalyst. The resin between joints was cured in oven at T=150°C for 4 hours.

The adhesion properties of joints have been tested according to the ASTM D1002-72 (Strength Properties of Adhesives in Shear by Tension Loading).

The characterization of liquid crystalline and isotropic resins is summarized in table 1. The glass transition temperature and elastic modulus of MD3A2 have been calculated by DMA

analysis. The elastic modulus value, calculated at 25°C, is in good agreement with the expected value for and amorphous glassy polymer. Even though the sample exhibits a liquid crystalline phase, the random domain orientation does not contribute to the modulus increase in the elongation direction. The value of single lap shear strength is in agreement with literature data.[37]

Table1. Physical chemical characterization and mechanical properties of MD3A2 and MEP3A2.

Nature of resin	sample	T_g (°C)	E (GPa)	Max. stress (MPa)	Max. strain	Energy
LC	**MD3A2**	62 *	2.5 *	4.0	2.7	19
ISO	**MEP3A2**	47 *	1.2 *	0.9	unity	unity

* result of DMA characerization.

The last two columns in table 1 report mechanical testing results. Due to the presence of defects in the resin bulk, and the absence of a suitable strain gauge for the accurate measure of sample deformation, the results are expressed as the ratio of the actual values of LC resin versus isotropic one.

Figure 4 shows the comparison between mechanical properties of MD3A2 and MEP3A2 used as adhesives.

A big contribution to the interpretation of mechanical test results is provided by SEM images of fractured surfaces. Figure 5 shows the fracture surface of MD3A2, which appears rough, with a microfibrillar structure. It is possible to hypothesize that the fracture mechanism is related to the peculiar structure of liquid crystalline thermosetting resins. The microstructure of LC thermosets is characterized by locally ordered regions, so that when the material starts deforming the crack is forced to deviate continuously along the differently oriented domains. This kind of fracture has been previously observed on other liquid crystalline thermosetting resins and composites [38-40]. The mechanism is comparable to that of rubber modified thermosets, which is typical ductile fracture.

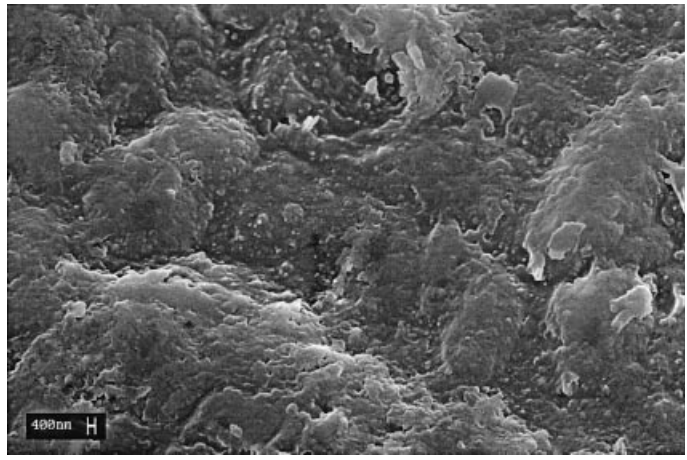


Fig. 5. SEM micrograph of fratcurated MD3A2

This feature can be explained taking into account the particular microstructure of cured liquid crystalline thermosets (LCTs) [41, 42]. An LC network is characterized by a polydomain morphology, in which portions of liquid crystalline domains are embedded in an isotropic matrix. LCTs tend to form a macroscopically disordered polydomain in the absence of external fields. The presence of such domains causes a ductile fracture: this inhomogeneity is responsible for the outstanding toughness of this class of materials.

This result was also found by Sue et al. who studied the fracture behavior of a liquid crystalline resin based on the diglycidyl ether of 4,4'-dihydroxy-a-methylstilbene cured with sulfanilamide [42]. In their paper, the authors observed crack segmentation, crack branching, crack bridging, and crack deflection.

The behavior of MEP3A2 is different, as confirmed by SEM image (figure 6). The fracture surface is smooth, which is typical of fragile materials: the crack propagates quickly and linearly, leaving the surface homogeneous and smooth.

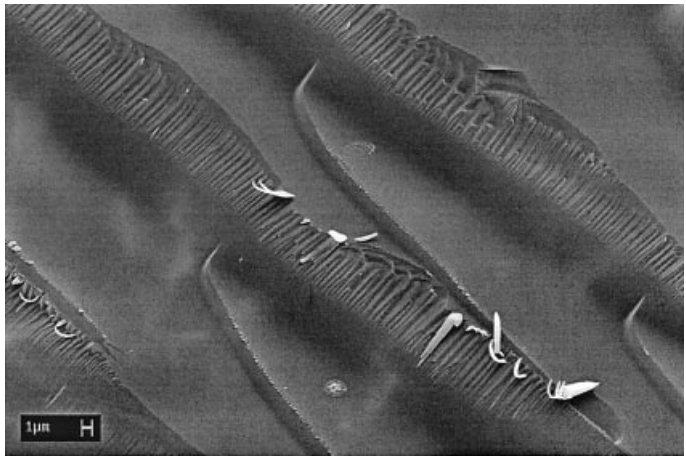


Fig. 6. SEM micrograph of fratcurated MEP3A2

From SEM analysis it is also evident that both in MD3A2 and MEP3A2 case, a cohesive rupture occurs, which is located in the bulk of the resin and not at the interface. This is related to several factors, the most significant of them are:

- Non-bonding interactions between the resin and metal oxides:

The adhesion between the resin and the substrate is mostly due to the presence of hydrogen bonds which form between the oxide layer and both the hydroxyl groups in β-position to the carboxylic group, and ether groups.

Furthermore, in a work carried out by Holubka et al. [44], according to theoretical studies based on semiempirical computational models, it has been shown that methacrylic monomers, as well as acrylic ones, can interact with aluminum oxides, both through the carbon-carbon double bond C=C, and the carbon-oxygen double bond C=O (figure 7). The basic idea is that the aluminum oxide and the unsatured material act as Lewis acid and Lewis base respectively. The reaction occurs through the formation of intermediates, which favor the adhesion of the resin to the oxide immediately before the curing reaction. The stability of these structures can affect the final features of adhesives.

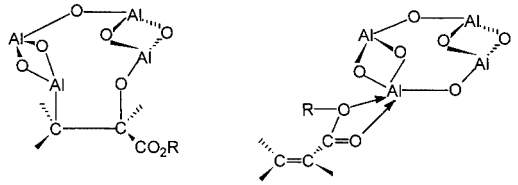


Fig. 7. Schematic representation of interactions between resin and aluminum oxide

- Pre-treatment of metallic substrates:

Another factor is related to the treatment performed on the metal substrate before the joint is prepared. The surface must be as rough and porous as possible to insure a good adhesion with the resin. When the resin melts during the cure, it can easily penetrate the cavities formed, so that when the adhesive is completely cured, it turns out to be embedded in the oxide structure. An interfacial layer with composite structure forms, that can better dissipate the energy when is deformed, thus improving the adhesion strength.

Conclusions

In the last decades, adhesive bonding has achieved rapid growth, due to the numerous advantages that structural adhesives offer over conventional joining methods.

In this work, it has been shown that high adhesion strength can be achieved by using liquid crystalline adhesives. The maximum strain and stress obtained was much higher for the joints with the liquid crystalline adhesive than with the isotropic one.

The different fracture behaviors have been related to the microstructures of the two cured resins.

The mechanical interlocking and the molecular interactions between the resin and the metallic substrates have given rise to the formation of a very strong and stable interface layer in which the adhesion forces are stronger compared with the internal cohesive forces in the bulk of the resin, so that the rupture under mechanical stress occurred within the resin and not at the interface with the metallic substrate, producing a cohesive rupture.

Moreover, due to the higher toughness observed in the case of liquid crystalline resin, the adhesion strength of this latter turns out to be higher compared to that of the isotropic resin.

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