RESEARCH ARTICLE

Adhesives Based on Poly(glycidyl methacrylate-*co*-butyl acrylate) with Controlled Structure: Curing Behavior and Adhesion Properties on Metal Substrates

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The adhesion properties of poly(glycidyl methacrylate (GMA)-*co*-butyl acrylate (BA)) statistical copolymers, synthesized by atom transfer radical polymerization (ATRP), are investigated employing three different curing agents or hardeners, such as diethanolamine (DEA), dicyandiamide (DICY), and 2-cyanoacetamide (2-CA) on copper, iron, brass, aluminum, and titanium metal surfaces. This work describes the treatment of the different surfaces, establishes the optimal curing conditions from differential scanning calorimetry (DSC) analysis of these novel adhesive systems, and evaluates the results of the single-lap shear test for metal joints. Thus, by dynamic DSC measurements of the mixtures, a low curing temperature of 90 °C is defined when DEA is used as a curative; while systems based on DICY and 2-CA require temperatures of 150 °C and 160 °C, respectively. In addition, the curing process of this controlled acrylic copolymer with DICY exhibits a singular behavior, possibly due to the curing reaction mechanism, where multiple epoxy-amine ring-opening polyaddition reactions take place between DICY's active hydrogens and epoxy groups of poly(GMA-*co*-BA). This latter curing system shows the highest adhesion features with lap-shear strength at room temperature of 15.5 MPa, using copper as metallic substrate; however, the best results are obtained using 2-CA as curing agent with aluminum and iron.

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1. Introduction

Adhesives are products that have achieved great acceptance over time due, in large part, to the constant improvements in their behavior and properties. Thus, in the decade of the 50s of the last century, adhesives with extraordinary formulations for general purposes left room for the development of those with specific properties and applications. Currently, it is possible to prepare a large number of adhesive formulations as a result of an extensive research in polymer chemistry, associated lately with safety of use and environmental impact.[1] In line with the above, epoxy adhesives have shown great popularity among consumers, who soon perceived the advantages offered by these products; being easily applicable and not requiring high temperatures or high curing pressures, and offering in return extraordinary resistance to separation. With an optimal substrate wetting capacity and unbeatable mechanical behavior, based on he low shrinkage experienced during curing and the absence of structural stresses, epoxy adhesives have been used significantly in fields such as construction,[2] naval,[3] automotive,[4] and aeronautics.[5]

Precisely, in this last industrial sector, polymers have been used in the manufacture, repair, and assembly of components, both internal and external. Nevertheless, adhesives have not succeeded in replacing rivets in primary structures. Its use is particularly focused on the elaboration of metallic structures such as honeycomb, predestined to serve as elevators, ailerons, and spoilers, in whose manufacture epoxy adhesives are used exclusively in secondary and tertiary structures. [6] Thus, the success of adhesives based on epoxy resins lies in the high reactivity of the epoxy groups with a large number of hardeners, offering a multitude of formulations and curing conditions, improving not only the mechanical, physical, and chemical properties of common formulations, but also those based on new renewable resources.[7–9]

Regarding the molecular structure, most of the epoxy adhesives used are linear prepolymers that produce a three-dimensional network when cure with hardeners of different functionalities. In adition, it is well known that most epoxy adhesive references are related to diglycidyl ether of bisphenol A (DGEBA) type resins because they have been widely used as

linear bifunctional epoxy resins, where epichlorohydrin provides an epoxy group and the ability to enlarge the resin backbone chain. On the contrary, high-performance nonlinear multifunctional epoxy adhesives have been developed to provide new structural advanced products, showing lower viscosity, better flowability, and processability than linear DGEBA, and offering new information about the cure reaction mechanism.[10,11] In addition to epoxy prepolymers, acrylic monomers have also been used in the preparation of epoxy adhesives. As is the case, the methacrylic monomer glycidyl methacrylate (GMA or 2,3-epoxypropyl-1-methacrylate) has two functional groups: a methacrylic double bond and a glycidyl group, which is capable of reacting as well. Therefore, its nature makes GMA an interesting monomer to be studied for adhesive applications. In fact, in the past and regarding DGEBA, GMA has been used in DGEBA adhesives as a plasticizer, thinner, or termination agent to reduce the reactivity and cross-linking density too. It affects its physical and chemical properties, increasing flexibility, impact, tensile strength, or flame resistance due to the oxirane ring modification capacity.[12,13]

In particular, the GMA surface modification treatments of low-polarity materials with poor adhesive behavior have been studied. An example is the polymerization of GMA through plasma pretreatment under different glow discharge conditions, causing local disorders on the surface of inert materials with low surface energy, achieving polar reactive interfaces, which will be cured or modified later.[14,15] This method was employed introducing epoxy groups onto the polyethylene surface to improve the adhesion to epoxy resins, using amines as coupling agents.[16] Similarly, high-density polyethylene surface was modified by argon plasma polymerization of GMA, improving its adhesive properties.[17] In parallel, the surface modification for adhesion improvement by GMA polymerization has been also developed by combining plasma activation and photopolymerization with ultraviolet radiation, to increase the adhesion strength on the interface.[18,19]

On the other hand, the syntheses of several GMA copolymers have been studied as adhesives too. In this way, it has been reported the achieving of GMA and butyl acrylate (BA) copolymers by emulsion, and their behaviour as adhesion additives.[20] Similarly, GMA was copolymerized by free radical polymerization with 2,5-dichlorophenyl acrylate, to be used as adhesives employing diethanolamine (DEA), and tested for the adhesive properties on leather at different temperatures.[21] In the same way, for metal automotive applications, epoxy acrylate copolymers of acrylic resins are produced in solution with specific proportions of co-monomer GMA. So depending on the desired properties, such as glass transition temperature (T_g), melt viscosity, leveling, gelling time, and cross-linking density, the monomers are selected; and the acrylic resin with the desired molecular weight is produced. For example, a highly reactive GMA acrylic resin with good leveling can be used for automotive clearcoats, while a medium-reactive GMA resin is applied for clearcoats on aluminum alloy wheels.[22] In the particular case of GMA copolymers used as adhesives on metals, it is worth noting the incorporation of particular monomers, such as vinyl catechol, to reinforce the adhesion phenomenon,[23] inspired in adhesive materials that mimic the adhesive proteins secreted by a mussel's foot.[24]
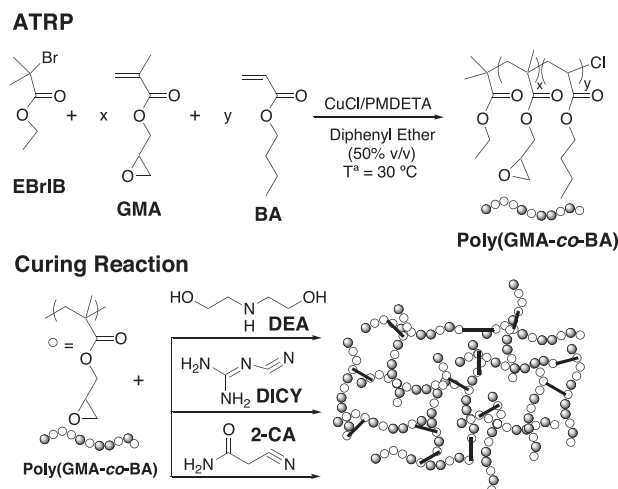
Scheme 1. Synthesis of the poly(GMA-*co*-BA) copolymer by ATRP and of the curing reaction in the production of the corresponding adhesives.

As can be seen, GMA has been used several times for adhesive applications before. Thus, in previous works, our group has studied the homopolymerization reaction of GMA by a reversible-deactivation radical polymerization, such as atom transfer radical polymerization (ATRP); a synthesis technique that allows the control of the monomer composition inside the polymer backbone chain with very low polydispersities, employing mild conditions at room temperatures.[25] The study was completed with the synthesis of statistical copolymers based on GMA and BA by ATRP.[26,27] Finally, its cure reaction with a commercial linear diamine, Jeffamine D-230, was monitored using differential scanning calorimetry (DSC) and rheology techniques, to find out the complete time-temperature-transformation cure diagram of this polyfunctional epoxy acrylic resin with controlled microstructure.[28–30] With these previous works, the aim of the present article, is the study of the reaction of this epoxy reactive copolymer with three different hardeners by calorimetry, achieving the best cure reaction settings, and applying it in metal–metal single-lap joints to study its adhesive behavior on iron, brass, aluminum, titanium, and copper surfaces.

2. Results and Discussion

This section is divided into two main parts. The first part describes and compares the curing reactions monitored by DSC to define the best conditions to apply each new adhesive under study. From these results, the second part focuses on their adhesion behaviors on five metal substrates.

2.1. DSC Cure Reactions

A copolymer obtained with a 75:25 GMA/BA composition in the feed was chosen to investigate the curing behavior of the system under study, as is shown in **Scheme 1**. The molecular characteristics of this copolymer were as follows: GMA copolymer composition = 0.850 was obtained by ^{1}H nuclear magnetic resonance (NMR) spectroscopy (see Figure 3 in this reference).[26] The

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number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size exclusion chromatography (SEC), giving $M_{n,\,SEC} = 16800$ g mol^{-1}, $M_w/M_n = 1.33$; and a $T_g = 46.4$ °C. The epoxy equivalent weight (EEW) of the copolymer was determined by titration, which gave 171 g eq^{-1}. This value was in agreement with that estimated from the copolymer composition determined by ^{1}H NMR (EEW = 167 g eq^{-1}). The curing reaction of poly(GMA-*co*-BA) statistical copolymer with stoichiometric commercial DEA, dicyandiamide (DICY), and 2-cyanoacetamide (2-CA) has been carried out using DSC to determine the specific cure temperature of adhesion reaction onto metal–metal surface probes. It is important to note that DSC operating in dynamic or nonisothermal mode is a useful tool to characterize the curing kinetics of epoxy resins. It is the most widely used method for monitoring the curing process as the rate of heat released is directly proportional to the rate of reaction.[31] Moreover, it is found that the physical properties of the cured epoxy resins depend on their structure, the extent of curing, and the conditions of the time of temperature of the reaction. In particular the curing agent plays a crucial part in determining the fundamental curing mechanism, curing conditions, processability, pot life, cured network structure, end-use properties, and ultimate practical application fields of the final epoxy materials.

2.1.1. Poly(GMA-co-BA)/DEA System

Regarding the employment of this hardener with epoxy resins, usually DGEBA, it must be taken into account that DEA has three reactive groups: a secondary amine hydrogen, and two hydroxyls, as it is shown in Scheme 1. The secondary amine reacts quickly, forming an adduct containing tertiary amines, epoxides, and hydroxyls. Then, the epoxides react in the presence of the amines to cross-link and vitrify the resin through the gelation reaction. The gelation reaction is not a simple change, exhibiting unusual dependencies on both temperature and degree of cure, according to recent studies where both DSC and isothermal microcalorimetry have been used to determine the characteristic procceses and times associated with the reaction.[32,33]

In the reaction of the copolymer with DEA, dynamic scans were initially performed to determine the total curing reaction enthalpy, ΔH_T. A single exothermic peak, in the temperature range from approximately 75 °C to 130 °C, is observed for this curing reaction using a heating rate of 10 °C min^{-1}, as can be seen in **Figure 1**a. From these DSC runs, a T_g for the uncured system of $T_{g0} = 21$ °C was estimated, and a $\Delta H_T = 280$ J g^{-1} can be determined. These results and curing behavior are consistent with those obtained previously when this copolymer was cured with the cross-linker Jeffamine D-230.[28] It is important to note that the curing reaction is uniform, according to the DSC profile, which could be not expected since a multifunctional random copolymer is used. However, its synthesis from ATRP allows to obtain a well-controlled macromolecular system, with low polydispersity and a homogeneous composition, as it has been adequately described previously.[26,27]

From this well-defined curing behavior, different samples were cured isothermally for 60 min at five curing temperatures (T_Cs) between 50 °C and 90 °C. After these thermal treatments, dy-
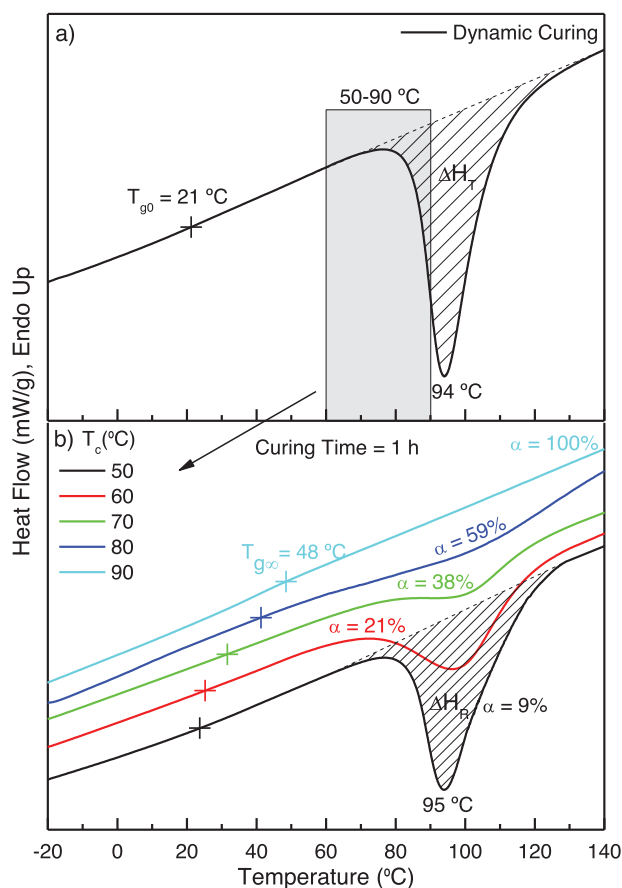

Figure 1. a) DSC curing reaction of the adhesive system based on poly(GMA-*co*-BA) and DEA. b) DSC analysis after the corresponding isothermal curing reactions at different temperatures for a reaction time of 1 h. Heating rate 10 °C min^{-1} and nitrogen flow.

namic DSC experiments were performed to determine the degree of curing achieved, from the estimate of the residual enthalpy, ΔH_R, which were compared with the total enthalpy previously calculated according to a dynamic curing (Figure 1a). Thus, the fractional conversion α can be described as $\alpha = 1 - (\Delta H_R/\Delta H_T)$. These DSC-grams are shown in Figure 1b as an example of the methodology in this study, where it is possible to find out that the samples cured for 1 h at the highest temperature of 90 °C have fully reacted, showing no remaining heat of reaction. However, when lower temperatures are applied, ΔH_Rs can be determined, as is clearly observed in this figure, where fractional conversions are indicated. Furthermore, because of the increase of the cross-linking density in the network, the T_g is shifted to higher temperatures and the residual reaction heat diminishes as the curing temperature rises. Thus, for example, after 60 min of curing reaction, the samples cured at 70 °C exhibit a T_g of 32 °C, having reached a curing degree of 38%, while the samples completely cured at 90 °C show a $T_{g\infty} = 48$ °C.

2.1.2. Poly(GMA-co-BA)/DICY System

The same calorimetric methodology was applied in the following system under study, in this case, focused on the DICY, which

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is a solid powder with limited solubility in habitual solvents and epoxides at room temperatures; nonetheless, it has been widely used as latent curing agent epoxy resins elaboration and adhesives formulation.[11] However, there are still controversies about its curing mechanism, since a clear understanding of it has not yet been achieved. According to the literature studies, the following reactions were proposed in the curing process of epoxy/DICY system: (1) The ring-opening addition reaction of epoxy ring and primary amine for producing chain growth and secondary amine for building chain branches, (2) the etherification of epoxy ring with pendant hydroxyl group, and (3) the homopolymerization of unreacted epoxy group at higher temperature in the absence of active N–H functionality. It should be considered the addition reaction between the nitrile group in DICY and the resultant hydroxyl group or excess epoxy group to generate imine and further rearrangement reaction to yield amide. In theory, the above-mentioned reactions may occur, either simultaneously or at different stages of the curing process, depending on the relative reactivity of the components and the process temperature.[34–39]

In the case of GMA-BA copolymer reaction with DICY, the dynamic curing reactions were performed using the same heating rate of 10 °C min^{-1}, as it is illustrated in the **Figure 2**a. DSC curves obtained present a first exothermic peak centered at 171 °C, and with a reaction heat associated with 42 J g^{-1}. Immediately after is observed a sharp endothermic peak around 200 °C, which was assigned with the melting point of DICY, as discussed below; and then a new exothermic process occurs that extends up to approximately 270 °C. In this case, a T_{g0} of 40 °C was determined for the uncured system, as it is indicated in this figure.

In order to identify the origin of these thermal processes found, the analysis of pure DICY is represented under identical experimental conditions in the same graph. The DICY calorimetric analysis by DSC shows a narrow endotherm corresponding to its melting peak, and immediately after, an exothermic zone appears covering a temperature range from 210 °C to 278 °C, where a first peak is located at 230 °C, and another one with different profile is observed at 242 °C. This process has been studied by Grenier-Loustalot et al.,[40] who postulate that DICY reacts with itself once it reaches melting point temperature, studying the disappearance of the bands belonging to the vibrational strain of the nitrile group by infrared (IR) spectroscopy, confirming the appearance of the new ones owing to melamine structure. They propose that once the diamine melts, one of its tautomeric forms decomposes into two cyanamide molecules, which react once more time with DICY to form two molecules of melamine.[40]

In view of these results, isothermal curing reactions between 110 °C and 150 °C were planned at a constant reaction time of 1 h. After these thermal polymerizations, the degree of cure was evaluated by DSC analyses, following the above procedure. These DSC-grams are very illustrative and they are collected in Figure 2b. Thus, the profiles of the curves show a clear evolution, which consists of a progressive decrease of the first exothermic process, which must be related to the curing reaction between the acrylic copolymer and DICY from the solid state. This DSC signal practically disappears in those samples cured at the higher curing temperatures, around 130–150 °C. However, even at these temperatures, the peak corresponding to the melting of the DICY that did not participate in the curing process is still observed. At higher temperatures, the curves showed practically the
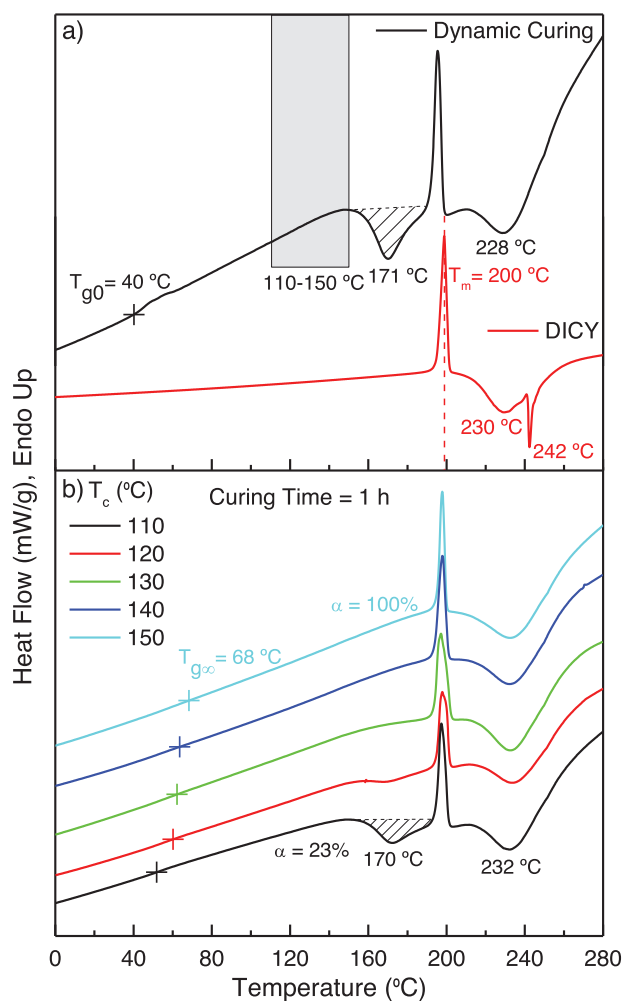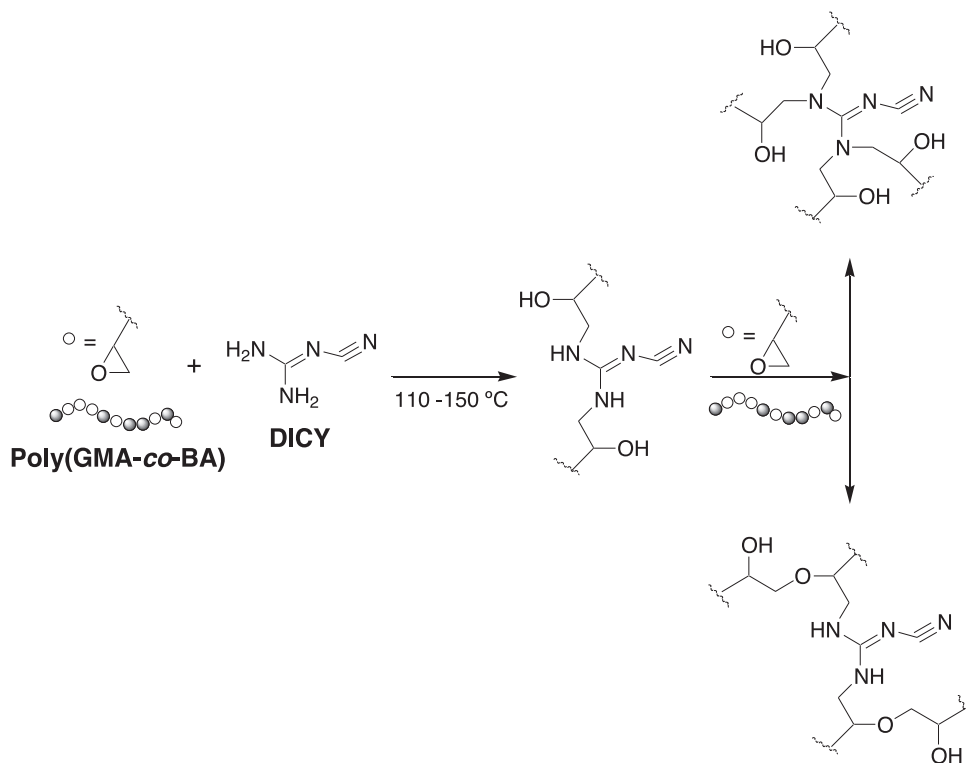

Figure 2. a) DSC curing reaction of the adhesive system based on poly(GMA-*co*-BA) and DICY, and thermogram of this curative; b) DSC analysis after the corresponding isothermal curing reactions at different temperatures for a reaction time of 1 h. Heating rate 10 °C min^{-1} and nitrogen flow.

same thermal behavior as that related to the melamine formation through the thermal decomposition of the DICY. In this case, a subsequence shift of the T_g toward higher temperatures is also detected, from a T_g of 52 °C, for the samples cured at 110 °C, up to a $T_{g\infty} = 68$ °C, for the samples prepared under isothermal conditions at 150 °C.

Regarding the curing mechanism and the formation of a three-dimensional network, DICY-based resins do not present a predominant reaction mechanism, which is influenced by various parameters such as temperature, the epoxy/amine ratio, the solvents, and/or the accelerators employed, as it was previously argued. Saunder et al. performed the first study on the curing mechanism of epoxy resins with DICY, where the use of NMR and IR spectroscopy techniques for the elucidation of the corresponding mechanism is described, even below its melting temperature.[39] Despite the high melting point of this curing agent, it has been found that the cure initiation with liquid resins occurs at lower temperatures, since DICY undergoes

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Scheme 2. Proposed curing reactions of poly(GMA-co-BA)/DICY adhesive system according to recent studies.[11]

diffusion in them, generating different types of reaction. Although in this sense, it is known that the particle size of DICY crystals is essential to achieve the reaction; in commercial adhesives and resins, accelerators based on tertiary amines or dimethylurea compounds are used to accelerate the reaction and achieve curing at lower temperatures. These results seem to indicate that the ring-opening reaction of epoxy rings of the GMA and primary amine takes place initially, and then the reactions between secondary amine and/or pendant hydroxyl groups and epoxy ring take place later (**Scheme 2**). In any case, the reaction mechanism between the epoxide ring with DICY is quite complex, as demonstrated by the numerous studies focused on this system,[11] and future works will be proposed to try to respond to the singular curing behavior described by DSC.

2.1.3. P(GMA-co-BA)/2-CA System

The use of 2-CA as a curing agent for epoxy resins has not been described as much as in the case of DICY, however the number of related patents is very high. 2-CA has some features common to DICY. It is a white crystalline solid also and represents an example of a latent cross-linker, which requires the use of accelerators, where the cure can be carried out at temperatures lower than usual. On the contrary, it is soluble in liquid epoxy resins and in a wider range of solvents than DICY, which represents a great advantage, being able to be used in adhesives, powder coatings, and laminates. Regarding the curing of epoxy resins using cyanoacetamides, Renner et al.[41] have investigated the products result-

ing from this reaction, determining cyclic urethanes, spirodilactones, cyclo-oxa-1-hepten-4-one, pyrimidones, aminocrotonitrile, and tertiary amine. Far from presenting a mechanism capable of explaining the formation of this catalog of products, these authors point to the presence of a T_g during the curing of a DGEBA at approximately 200 °C, in addition to a high adhesion to metal surfaces.[41]

With this background, the curing dynamic study of the GMA-BA copolymer and 2-CA by DSC is displayed in **Figure 3**a. This DSC-gram shows a T_{g0} of our system at 45 °C, and then two endothermic peaks, the first one with low intensity at 86 °C, and the second one at a higher temperature close to 109 °C. The first peak is related to a solid–solid transition of this amide, which appears at 87 °C, and the second one with its melted form, at 114 °C, according to previous data in the literature,[42] as it is shown in this figure, where its DSC analysis is collected. Subsequently, a well-defined exothermic curing curve begins, which includes a temperature range of approximately 150 °C to 230 °C; and a ΔH_T = 370 J g^{-1} was determined, being this value higher than that obtained when DEA was used as hardener. These dynamic curing properties are very conclusive when choosing the range of temperatures to design the curing under isothermal conditions, in this case between 110 °C and 160 °C, for the same reaction time of 60 min.

These isothermal curing temperatures are very similar to those applied with the DICY, however, the DSC-grams after the curing are different, Figure 3b. In this case, endothermic peak associated with the melting process of the 2-CA is not observed, and a gradual decrease in the ΔH_R of polymerization is clearly found. In addition, the habitual shift on the T_g of the adhesive
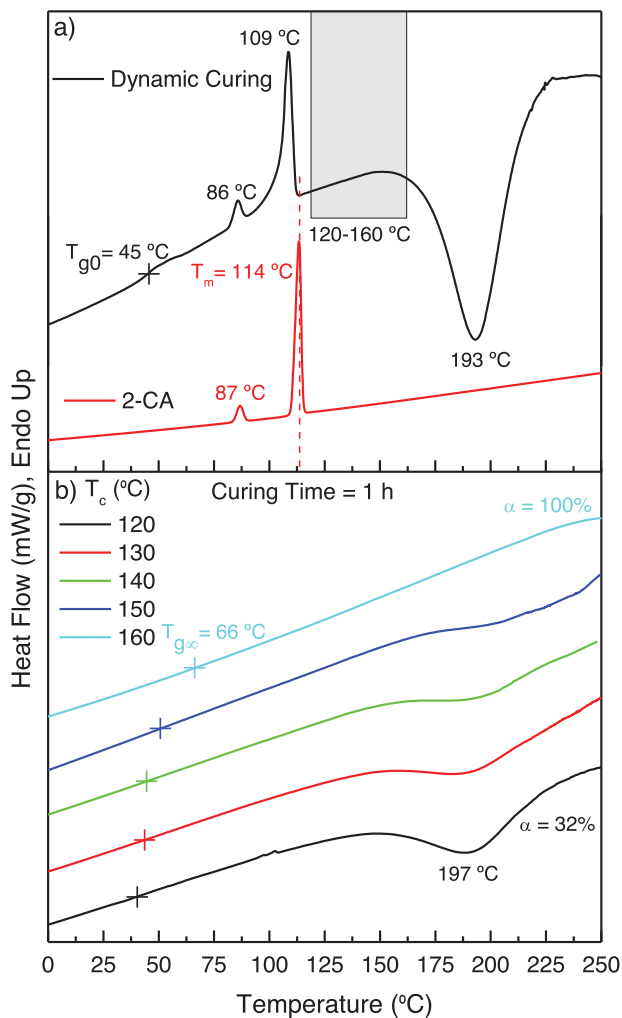
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Figure 3. a) DSC curing reaction of the adhesive system based on poly(GMA-*co*-BA) and 2-CA, and thermogram of this curative. b) DSC analysis after the corresponding isothermal curing reactions at different temperatures for a reaction time of 1 h. Heating rate 10 °C min⁻¹ and nitrogen flow.

Figure 4. a) Modules and b) lap shear strengths obtained from single-lap shear tests from metal–metal samples of iron, copper, brass, titanium, and aluminum joined with P(GMA-*co*-BA) and DEA, DICY, and 2-CA adhesive systems.

system is observed, and a $T_{g\infty}$ of 66 °C is determined of the samples totally cured when a cure temperature of 160 °C was applied.

2.2. Adhesion Properties of Poly(GMA-*co*-BA) Adhesives

Once the time and temperature conditions necessary for optimal curing of the GMA-BA copolymer and the three chosen cross-linkers were determined by DSC, the simple-lap shear specimens were prepared. Thus, cure reactions were carried out for 60 min using temperatures of 90 °C for DEA, 150 °C for DICY, and 160 °C for 2-CA. Consequently, the specimens were subjected to single-lap shear tests, which are surely the most used experimental procedure to characterize adhesive behaviors, due to their simplicity. As it is well-known, this test is an effective screening and process control test for evaluating adhesives, surface preparations, and for in-process control.
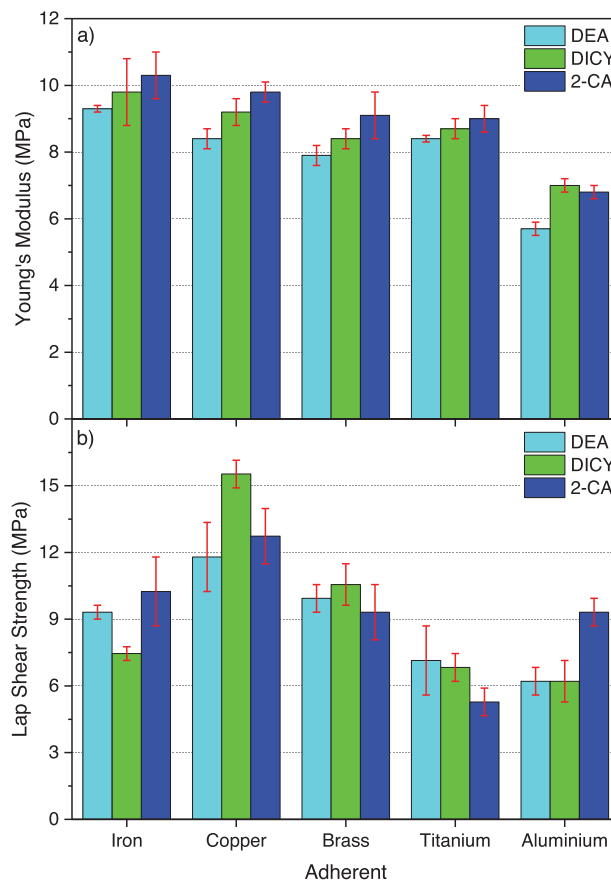
Figure 4a represents the modulus of elasticity or Young's modulus for the different metallic specimens adhered when curing the GMA-BA copolymer with DEA, DICY, and 2-CA. These values have been determined with 10 samples of each of the metals and cross-linkers. In general, Young's modulus values determined vary approximately between 6 and 10 MPa, being ordered according to the metal tested as follows: iron > copper > brass > titanium > aluminum. It should be noted that the highest results coincide with the metals that underwent a more aggressive surface treatment, and therefore, generated a greater specific surface area and a lower adhesion thickness. About the thickness of the adhesive, it has been verified that smaller values can provide higher data of tensile strength.

Concerning aluminum, results of a similar order have been found in the literature. Thus, the group led by Ureña, applying the test method corresponding to the UNE-EN-ISO 1465 standard, has determined in tensile tests on titanium specimens joined by a DGEBA-based adhesive, 4.4′-diaminodiphenylsulfone and poly(3-aminopropenylmethylsilane) values between 4 and 6 MPa.[43] On the other hand, Kinloch gives higher values of approximately 28 MPa for aluminum specimens, and 38 MPa for those prepared with steel.[44,45] Regarding the curing agents, a repetitive

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and independent behavior of the metal used during the test should be highlighted. As can be seen, the increase in modulus is a function of the cross-linker used, obtaining the lowest values for DEA, intermediate values for DICY, and the highest values for 2-CA, except when aluminum is the adherent. This fact may be related to the $T_{g\infty}$ of the adhesion systems discussed previously.

In the results obtained, an evident difference between the modules of the iron and aluminum specimens can be observed, with a difference of approximately 2 MPa. This difference may be due to the chemical attack carried out during the surface treatment, which is decisive when it comes to increasing the specific surface area and thus favoring the wetting process. During the treatment of the surfaces, it was possible to verify how the chemical attack produced a significant change in the iron sheets, while on the contrary, a phenomenon of equal intensity was not observed in the aluminum. The experimental section shows the surfaces of the adhesion zones after carrying out the tensile tests on specimens prepared from DICY.

In contrast, the estimated lap-shear strengths for each test do not reflect any repetitive variation, Figure 4b. On this occasion, the most representative values are obtained for copper specimens, where DICY stands out above the other two agents with an average strength of 15.5 MPa. For iron and brass, the results are similar and approximately 9 MPa was registered. The lowest values are offered by aluminum and titanium specimens with maximum failure strengths of ≈6 MPa, with important variations in the case of 2-CA. As can be seen, and despite its low solubility, the mixture was homogeneous for all the tested specimens, finding cohesive and adhesive-cohesive type fractures, as planned.

3. Conclusion

In this work, three novel acrylic epoxy copolymer adhesives based on GMA with stoichiometric conventional curing agents, such as DEA, DICY, and 2-CA, have been developed. The dynamic curing was monitored by the DSC technique, and from these corresponding thermograms, where only one exothermic peak attributed to the curing reactions was found, well-defined cure regimes in the temperature range of 50–90 °C and 120–160 °C were analyzed for subsequent isothermal curing for the blends with DEA and 2-CA, respectively. Although in both cases, only the isothermal curing procedure at the highest temperatures allows to achieve a complete curing in 1 h. On the other hand, when the latent curing agent DICY is used, the DSC-grams exhibit two apparent curing regimes on both sides of its melting point of around 200 °C. At the first regime to lower temperatures, takes place the curing reaction, and at the second regime above 210 °C occurs a thermal decomposition process of the DICY, with the formation of a melamine structure according to literature studies. This singular cure behavior was verified when isothermal curing, in the range of 110–150 °C was performed. In addition, these isothermal reactions confirm that at higher temperatures, above than 130 °C, a fully cured is produced in just 60 min, though a readjustment in the formulation must be carried out to guarantee the complete consumption of the DICY.

Once the curing conditions were adequately established through a detailed DSC analysis, the adhesion behavior was also investigated from the lap-shear tests. Thus, the failure strength at room temperature for copper–copper single-lap joint reached the maximum value of 15.5 MPa when DICY was the curing agent, and around 12 MPa was found for other curing agents. Moderate adhesion properties were observed with the rest of the metallic adherents, being particularly relevant to the results found in aluminum, where 2-CA presents the best behavior. The developed GMA adhesives are promising for application as the epoxy-adhesive-bonded metallic joints for various engineering applications.

4. Experimental Section

Materials: GMA (98%, Merck), BA (98%, Merck), and *N, N,N´,N´´,N´´*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) were purified by vacuum distillation before use. Ethyl 2-bromoisobutyrate (EBrIB, 99%, Aldrich), copper chloride (CuCl, 99.99%, Aldrich), and diphenyl ether anhydrous (99.9%, Aldrich) were used as received. Titration reactants glacial acetic acid (99.5%, Panreac), tetraethylammonium bromide (anhydrous crystals, 99%, Panreac), perchloric acid (60%, Scharlau), acetic anhydride (98%, Panreac), methylene chloride (99.5%, Fluka), crystal violet indicator (Riedel de Haën), and potassium acid phthalate (98%, Aldrich) were used as received. The curing agents were commercial DEA (98%, Aldrich), DICY (99%, Aldrich), and 2-CA (99%, Aldrich), which were used as received. The reagents for surface oxidative treatment were nitric acid, HNO_3 (65%, Panreac), sulfuric acid, H_2SO_4 (98%, Panreac), and sodium dichromate, $NaCr_2O_7$, (99.5%, Aldrich) and they were used directly as received. The metallic probes for the performance of the substrate surfaces were machined from copper, brass, aluminum, iron, and titanium 1.6 mm thickness sheet plates.

ATRP and Copolymer Characterization: Statistical GMA-BA copolymerization at a feed monomer composition of 75:25 was carried out under ATRP conditions with EBrIB as an initiator, CuCl as a catalyst, and PMDETA as a ligand (both concerning the initiator), in 50% (v/v) diphenyl ether solution, at 30 °C ([GMA + BA]$_0$/[EBrIB]$_0$/[CuCl]$_0$/[PMDETA]$_0$ = 200:1:1:1), as it can be seen in Scheme 1. These experimental conditions, with an exchange halide technique, were chosen based on previous GMA homo and copolymerization results reported by our group.[25–27] In the typical procedure, the reaction mixture was introduced into a glass ampoule, degassed by three freeze–pump–thaw cycles, and then sealed under a high vacuum. The ampoule was placed in an oil bath with a pre-set temperature of 30 °C during 60 h, and a final conversion around 94% was obtained. The resulting polymer was isolated as follows. The polymer was dissolved in chloroform and passed through a neutral alumina column to remove the catalyst. The majority of the chloroform was removed by rotary evaporation, and the polymer, dissolved in a minimum amount of chloroform, was poured into a large excess of hexane. The precipitated product was filtered and dried in a vacuum oven at room temperature until a constant weight was reached. The total monomer conversion was measured gravimetrically, and M_n and M_w/M_n were determined by SEC with a chromatographic system (515, Waters Division Millipore) equipped with a Waters model 410 refractive-index detector. Tetrahydrofuran (THF, Scharlau) was used as the eluent at a flow rate of 1 mL min^{-1} at 35 °C. Styragel packed columns (HR1, HR3, HR4E, and HR5E) were used. Polystyrene standards (Waters Associates) between 3.5×10^6 and 1.3×10^3 g mol^{-1} were used to calibrate the columns. ^1H NMR spectroscopy was used to determine the copolymer composition and also molecular weight. Spectra were recorded at 50 °C in approximately 8% solution in deuterated chloroform with a Varian Oxford 300 spectrometer operating at 300 MHz. Typical parameters for the proton spectra were a 9-µ pulse width (45°), a pulse delay of 1 s, an acquisition time of 5 s, a 4000-Hz spectral width, and 254 scans. To determine the EEW of the copolymer, epoxy titration was performed per ASTM D1652.[46] The copolymer was dissolved in 10–15 mL of methylene chloride, and 10 mL of a tetraethyl ammonium bromide solution was then added to the mixture. The sample was titrated with a perchloric acid/peracetic
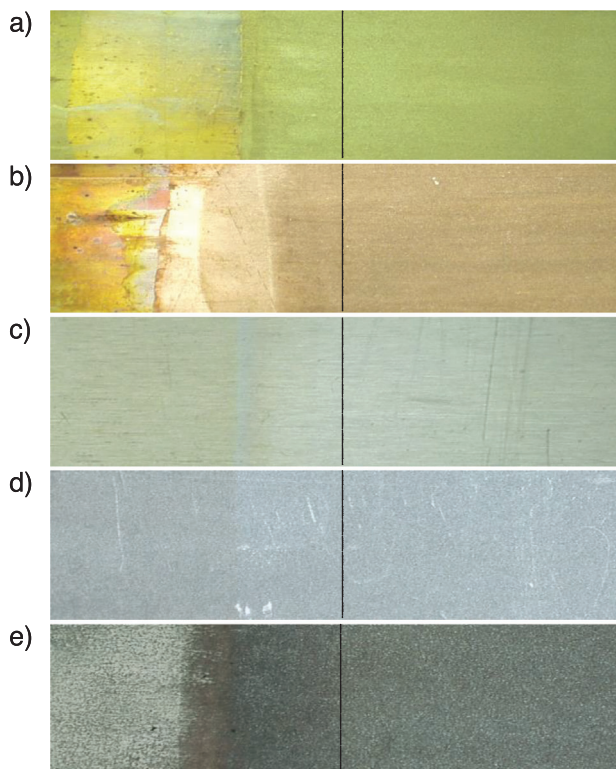
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Figure 5. Images of the surfaces of the brass (a), copper (b), aluminum (c), titanium (d), and iron (e) untreated (left) and treated (right) substrates, before the application of the adhesive.

acid solution until the indicator, crystal violet, changed color from blue to green. This test was performed several times to ensure the value.

Preparation of GMA Copolymer-Adhesives, Curing Reaction, and Lap-Shear Properties: Three types of adhesives based on GMA-BA copolymer with DEA, 2-CA, and DICY, (Figure 1), were prepared for use in single-overlap metal specimens, as follows:

Poly(GMA-co-BA)/DEA System: An amount of 50 mg (0.003 mmol) of GMA-BA copolymer, 31.5 mg (0.3 mmol) of DEA, and 1 mL of acetone were placed in a vial to dissolve the mixture. It was homogenized and then carefully pipetted onto the metal surface, allowing the acetone to evaporate from each layer that was created. Once the solvent was completely removed, the other sheet of metal, held with two clamps, was placed on the sides to prevent the entry of air, and the specimen was placed in an inert chamber at a specified temperature and the curing time was always 60 min.

Poly(GMA-co-BA)/2-CA System: An amount of 50 mg (0.003 mmol) of GMA-BA copolymer, 12.6 mg (0.15 mmol) of 2-CA, and 1 mL of acetone were placed in a vial to dissolve the mixture. The rest of the procedure was identical to that described above, except for the temperature.

Poly(GMA-co-BA)/DICY System: An amount of 50 mg (0.003 mmol) of GMA-BA copolymer, 12.6 mg (0.15 mmol) of DICY, and 0.5 mL of dimethyl-formamide, DMF, were placed in a vial to dissolve the mixture. The rest of the procedure was identical to that described previously.

The curing profiles of these three specimens were studied using a DSC. Thus, the monitoring of the curing reactions by calorimetric measurements were made on a Perkin Elmer DSC/TA7DX PC series with an intracooler for low temperatures. The temperature scale was calibrated from the melting point of high-purity chemicals, lauric and stearic acids, and indium. Dynamic curing reactions were recorded in the calorimeter with copolymer samples of ≈20 mg, under dry nitrogen (20 mL min^{-1}), and the heating rate was always 10 °C min^{-1}. The poly(GMA-*co*-BA)/DEA samples scanned between −40 °C and 150 °C, and the other adhesive systems
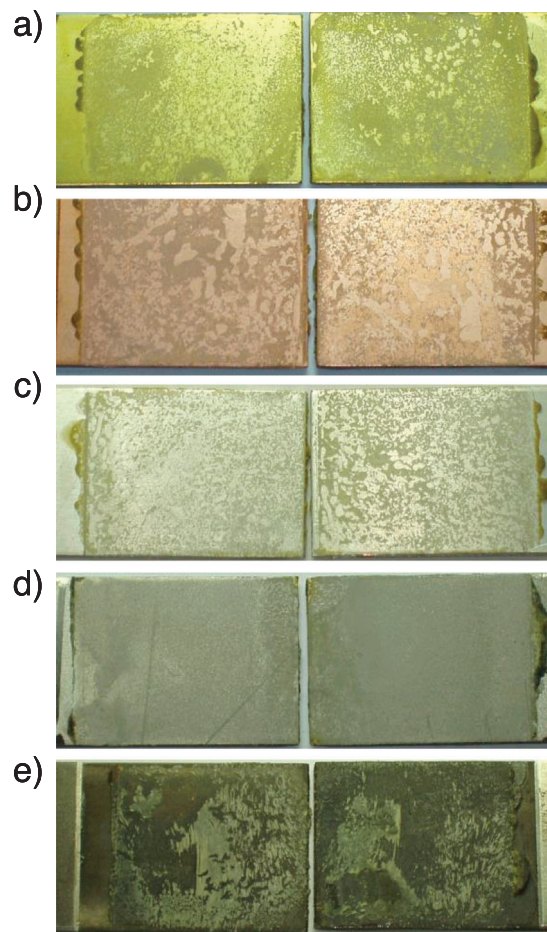

Figure 6. Images of the surfaces of the brass (a), copper (b), aluminum (c), titanium (d), and iron (e) adhesive metal–metal joints after the single-lap shear tests using an adhesive system poly(GMA-co-BA)/DICY (dicyandiamide).

were analyzed in the range −40–280 °C, and −40–250 °C for curing agents DICY and 2-CA, respectively. From these experiments, the isothermal T_Cs for each specimen were established. After the corresponding isothermal curing processes, dynamic DSC analyses were conducted with the same conditions above indicated. The total and residual heat of reaction were estimated by drawing a straight line connecting the baseline before and after the peak and integrating the areas under the peak. The actual values for the T_gs were estimated as the temperatures at the midpoint of the line drawn between the temperature of the intersection of the initial tangent with the tangent drawn through the point of inflection of the trace and the temperature of the intersection of the tangent drawn through the point of inflection with the final tangent. Each test was repeated at least twice to ensure a consistent result. The current value is the average for several measurements realized for each sample. Taking as reference the ASTM D-2651 and D-3165 standards for the surface treatment and the preparation of metallic specimens according to the test method for strength properties in shear by tension loading of single-lap joint laminated assemblies, respectively.[47,48] The single-overlap specimens were made using different metals, the adhesives mentioned above, and mechanical tensile tests were performed as explained below. From 1.6 mm copper, brass, aluminum, iron, and titanium plates, parts 177.8 mm long and 25.4 mm wide were machined. These pieces were then degreased by immersing them in a chloroform bath at 35 °C for 2 days and subsequently cleaned with a cloth soaked in the same solvent. After this common step for the five types of metal, chemical oxidation was carried out by acid attack. For copper and

brass treatment, the piece was introduced in 40% diluted nitric acid (a higher concentration can attack the piece in excess) for about 15 s, completely attacking the surface to be treated until the corrosion completely disappeared. Subsequently, the acid was removed by rinsing the piece in distilled water, it was carefully dried with a dry cloth or paper, and the adhesive was quickly applied. On the other hand, for aluminum, iron, and titanium, a solution was prepared with 100 parts of concentrated sulfuric acid and 30 parts of saturated sodium dichromate solution. The piece was introduced into the solution for about 12 or 15 min at a temperature of 70 °C. After that, the piece was rinsed and gently dried, immediately applying the adhesive.

In **Figure 5**a–e, pieces of brass, copper, aluminum, titanium, and iron are shown, where the difference between the area treated by the chemical attack (right) and the area that remains untreated can be distinguished. The overlap length recommended for all specimens was 12.7 ± 0.3 mm and the total shear area was 322 mm^2 (ASTM-D-3165).

The tensile tests of the adhesion specimens (5×) were carried out with an Instron model 3360 Series Standard equipment, operating at a test speed of 2 mm s^{-1} at room temperature and relative humidity of 50%. As an example in **Figure 6**a–e is shown the surfaces of the adhesion zones after carrying out the tensile tests on specimens prepared from DICY.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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