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An Epoxy Adhesive Crosslinked through Radical-Induced Cationic Frontal Polymerization

*Matteo Turani, Andrea Baggio, Valentina Casalegno, Milena Salvo, and Marco Sangermano**

UV-initiated cationic frontal polymerization is exploited as a solvent-free, extremely fast, and low-temperature technique to obtain epoxy-based adhesives. Epoxy formulations are prepared by blending commercial resins at different weight ratios and adding photo and thermal initiators at different percentages. In addition, the influence of other critical parameters, including the joint thickness, the nature of the adherends, and the temperature, is studied. As the reaction front is thermally sustained, the boundary conditions play a key role during the curing process and heat dissipation through the adherends in particular. The thermal properties of the epoxy formulation are studied through differential scanning calorimetry analysis, and the joint strengths are investigated by carrying out single lap off-set shear tests under compression. The results demonstrate the feasibility of obtaining joints by means of the radical induced cationic frontal polymerization of the epoxy adhesives, which exhibit comparable epoxy group conversion and mechanical performances to the ones cured by traditional energy-intensive techniques.

1. Introduction

Epoxy resins are widely used as high-performance adhesives and coatings in various fields, including the automotive, aerospace, and naval industries.[1–3] Traditionally, epoxy-based adhesives are thermally cured in the presence of hardeners, generally, amines or polyfunctional anhydrides,[4] to produce crosslinked thermoset structures characterized by good mechanical properties, good adhesion to the adherends, as well as thermal and chemical resistance.[5] However, thermal curing is a slow process and therefore requires a large amount of energy to maintain appropriate temperatures for the whole processing time.[6]

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As an alternative, epoxy resins can be crosslinked by means of UV-light in the presence of onium salts (diaryliodonium or triarylsulfonium); these salts, under irradiation, are able to photogenerate a strong Bronsted acid, which starts the cationic ring-opening polymerization of epoxy monomers.[7–11]

The cationic UV-curing of epoxy resins takes place very quickly, compared to the thermal crosslinking process. The main limitation of epoxy UV-curing is the low penetration depth of UV light.[12] In recent years, different authors have reported the feasibility of proceeding with the light-induced curing of epoxy resins to fabricate thick-bulk materials.[13–15] This is possible by exploiting radical induced cationic frontal polymerization (RICFP).

Frontal polymerization (FP) is a process whereby a monomer is converted into polymer by exploiting the exothermicity of the polymerization reaction.[16–24] The effect is a localized thermal reaction front that propagates through the photocurable formulation as a thermal wave.

In 2004, Mariani et al. reported, for the first time, the combination of cationic photopolymerization of epoxy resins with frontal polymerization.[25] In this process, the exothermal cationic ring-opening polymerization of epoxy resin is exploited to activate a thermal-radical initiator that generates a carbon-centered radical. Subsequently, the radicals are oxidized to carbocations, because of the presence of iodonium salts (**Figure 1**). Radical-induced cationic ring-opening polymerization occurs toward the thickness of the samples, as long as the thermal front is able to propagate.

In 2007, Crivello reported that the RICFP of epoxy resins was able to achieve curing for an elevated thickness.[26] More recently, a RICFP has been reported for curing epoxy composites.[27–30]

The same process can also be exploited to induce the epoxy curing of adhesives triggered by light. Moreover, RICFP can be used to mitigate the main drawback of the UV-curing process: adherends that are opaque to UV radiation are very difficult to bond using the UV curing process, and the RICFP of epoxy adhesives can be an interesting alternative joining process for such materials.

Only a few papers have reported the exploitation of this process for thin layers, coatings, and adhesives.[20,31–33] Moreover, to

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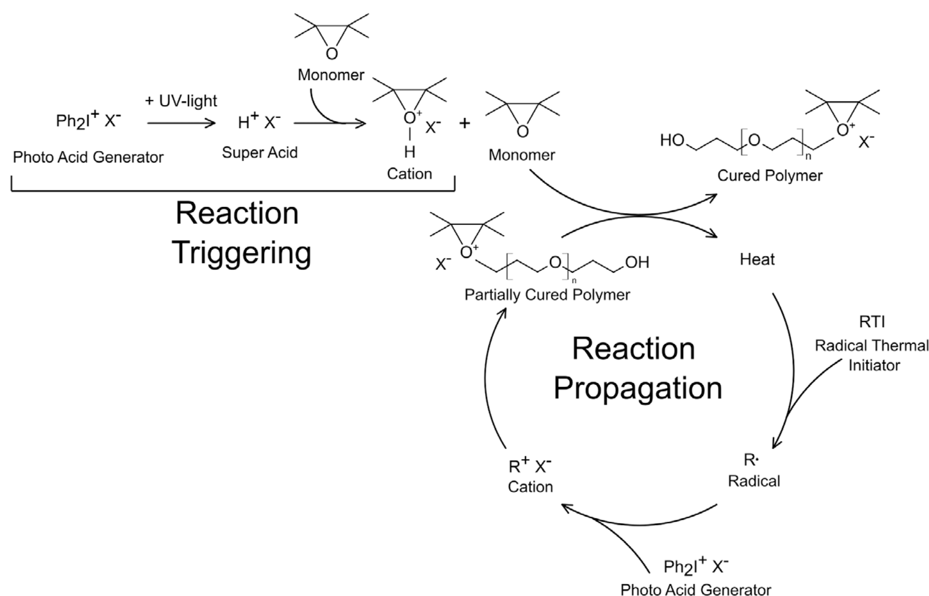

Figure 1. Radical induced cationic frontal polymerization (RICFP) reaction scheme.

the best of our knowledge, none of the previous studies attained a RICFP cured epoxy adhesive on metal adherends. Therefore, in this paper, we have investigated the possibility of using commercial epoxy resins to join an Al alloy through RICFP and have compared this technique with a thermal-curing process. To study the effects of the thermal conductivity of the adherend, the same RICFP process was used to bond a thermal insulating material (Foamglas).

The aim of this work has been to demonstrate the use of epoxy-based resins that are capable of sustaining the propagation of polymerization fronts between metallic substrates, thereby resulting in satisfactory adhesion levels. The findings of this activity may be exploited in several applications to avoid the thermal process involved in the curing of traditional, i.e., in the case of components that cannot sustain thermal stresses for a long time or in the case of the repairing and maintenance of damaged joints or components that cannot be removed or placed in an oven.

2. Results and Discussion

The investigated epoxy-adhesive formulation was the result of the mixing of two different epoxy resins: a bisphenol-based resin, bisphenol-A diglycidyl ether (DGEBA), to ensure better mechanical properties and adhesion to the adherends, and 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CE), which can be exploited to decrease the viscosity of the formulation and to increase exothermicity to ensure the propagation of the thermal front during curing.[34] Another important consideration for the RICFP process is the maintenance of exothermicity, which allows the propagation of the front for the entire thickness of the coated formulation.

The main challenges of the entire process are closely related to the thickness of the joint.[35] Indeed, if the adhesive thickness decreases, its impact on the weight and volume of the resulting structure is reduced, but, at the same time, the surface available for lateral UV-light irradiation is reduced to a great extent, and thus the triggering of the reaction is limited. A joining configuration is characterized by a high surface-to-volume ratio, thus the formulation is exposed to high and undesirable heat losses; furthermore, since the volume of the formulation is small, the exothermal heat associated with the epoxy ring opening reaction is reduced. Therefore, when the heat dissipation at resin-adherend interfaces is not properly balanced by the heat generated by the ring opening reaction, the thermal front stops, and the resin does not achieve complete curing.

The influence of different joining thicknesses, that is, of 250, 500, and 750 µm, has been studied by evaluating RICFP propagation. A satisfactory front propagation only occurred at 250 µm in a few cases, thus making RICFP an unreliable curing technique. On the other hand, 500 µm was found to be the minimum thickness for the adhesive that resulted in reproducible and totally propagated fronts for all the tested samples. Therefore, 500 µm was set as the adhesive thickness for all the joints on both the Al alloy and Foamglas substrates.

Experiments with different initiator (photoinitiator, PhI, and radical thermal initiator, RTI) concentrations were carried out for each resin ratio. However, it was found that the best performances, in terms of the reaction starting time, thermal front propagation, and monomer conversion, were reached with PhI and RTI concentrations of 2 phr (weight per hundred resin) and 4 phr, respectively. In particular, the reaction was triggered within an illumination time of 7–8 s, and it was completed in less than 10 s for the Al alloy joints and in 25–30 s for the Foamglas joints.

The dynamic differential scanning calorimetry (DSC) analyses were initially performed to evaluate the onset temperature of curing and the heat release for a complete epoxy group conversion of epoxy formulations containing 2 phr of PhI and 4 phr of RTI (the curves are reported in **Figure 2**a). Isothermal analyses were then performed, at 80 and 110 °C (the curves are reported in Figure 2b), to evaluate the conversion of the epoxy group during thermal curing. The conversion data are collected in **Table 1**. First, the

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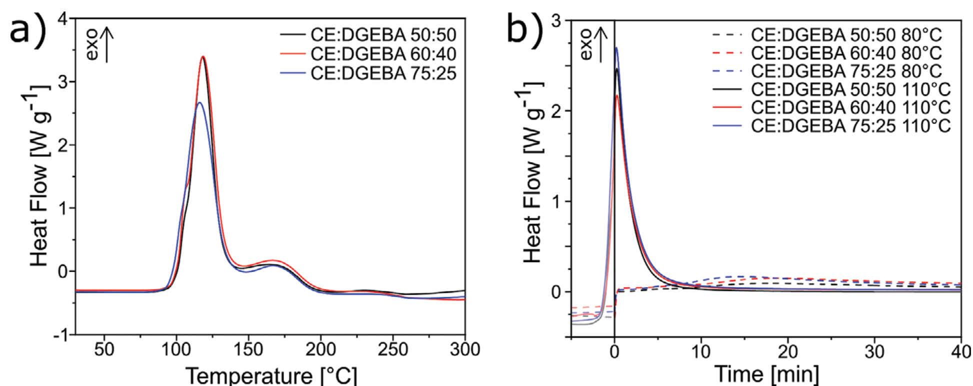

Figure 2. a) Dynamic and b) isothermal DSC plots of formulations for different CE:DGEBA ratios. The PhI and RTI concentrations were kept fixed at 2 and 4 phr, respectively.

Table 1. Thermal properties, monomer conversion, and apparent lap shear strength values are summarized for each formulation.

Formulations	T_{onset} [a)]	Conversion at 80 °C [b)]	Conversion at 110 °C [b)]	Conversion of RICFP [c)]	T_g [d)]	Apparent single lap shear strength [e)]	
						RICFP	Thermal
[CE:DGEBA]	[°C]	[%]	[%]	[%]	[°C]	[MPa]	[MPa]
50:50	104	10.4	83.0	83.3	130	13.1 ± 0.5	19.1 ± 5.5
60:40	100	12.6	72.7	91.5	125	19.9 ± 2.6	20.0 ± 1.7
75:25	99	19.6	94.3	91.4	109	18.3 ± 1.9	13.3 ± 3.0

[a)] Measured by means of dynamic DSC analysis; [b)] Evaluated on thermal cured adhesives by means of DSC analysis, as reported in the Experimental Section; [c)] Evaluated on UV-induced crosslinked adhesives by means of DSC, as reported in the Experimental Section; [d)] Evaluated on UV-induced crosslinked adhesives by means of DSC; [e)] Evaluated through a single lap offset shear test under compression, as reported in the Experimental Section.

extremely low reactivity of all the epoxy formulations at 80 °C is evident. On the other hand, a fast thermal reaction is activated at 110 °C. This clearly evidences the thermal stability of all the investigated formulations below 110 °C.

The monomer conversion percentages of the epoxy formulation, cured via RICFP, are summarized in Table 1 (the evaluation method is reported in the Experimental Section), where it can be observed that these values are satisfactory for all the formulations. Moreover, the conversion percentage is slightly higher than 83%, with a lower CE content, and reaches peaks of 91.5% and 91.4% for CE:DGEBA ratios of 60:40 and 75:25, respectively.

From the data collected in Table 1, it is also evident that when the CE content in the epoxy blend is increased, there is a decrease in the onset temperature and an increase in the epoxy group conversion. This is attributable to the higher exothermicity of the ring-opening polymerization of the cycloaliphatic ring than that of the glycidylepoxy group.

After evaluating the conversion and thermal properties of the epoxy formulations, the thermal boundary conditions need to be discussed detail to ensure frontal propagation of the curing reaction.

As previously mentioned, heat management plays a key role in the front reaction propagation and thus in a successful joining process. Theoretically speaking, if the heat generated by ring-epoxy opening is not sufficient to cleave a satisfactory amount of RTI, the formation of carbocations is hindered and, thus, the reaction stops. Therefore, if thermal insulating materials are used as adherends, the heat dissipation at the adherend/adhesive interface is reduced, a complete reaction occurs, and the adherends result to be fully joined.

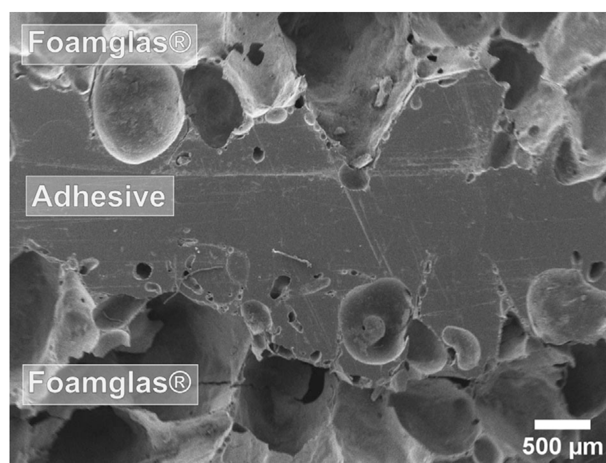

Figure 3. SEM image of a cross-section of Foamglas joined by RICFP using a CE:DGEBA weight ratio of 60:40 and PhI and RTI concentrations of 2 and 4 phr, respectively.

A test carried out using a porous glass (Foamglas) as an adherend proved that substrate materials with a thermal conductivity coefficient close to zero allow a stable thermal front propagation, which in turn leads to the complete curing of the epoxy adhesive. **Figure 3** shows a cross section of an RICFP joined Foamglas sample; the adhesive has penetrated as

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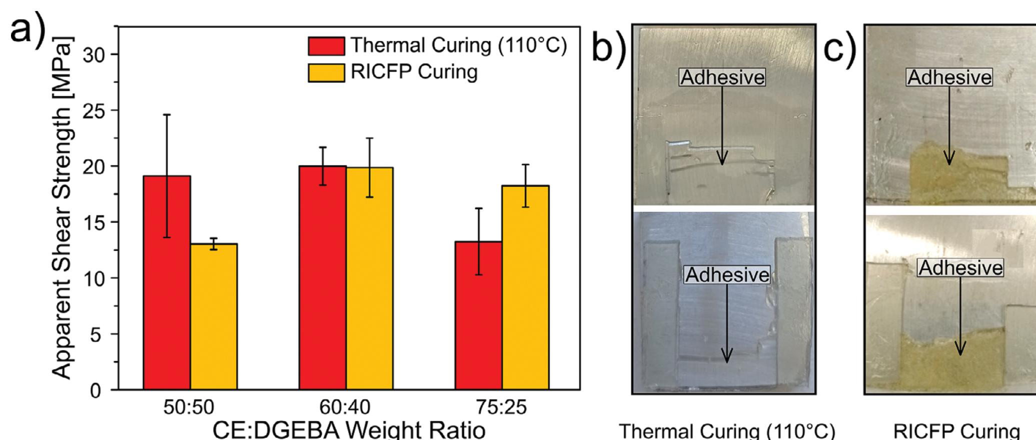

Figure 4. a) Apparent shear strength of joints attained for different CE:DGEBA weight ratios and curing techniques. Digital image, after a mechanical test, of the fracture surface of joints produced by b) thermal and c) RICFP curing. Both samples were produced using the CE:DGEBA formulation weight ratio of 60:40 and PhI and RTI concentrations of 2 and 4 phr, respectively.

a result of the porosity of the foam glass, thereby resulting in a homogeneous joint with a continuous and interpenetratable foam glass/adhesive interface.

On the other hand, when Al alloy adherends are used, a great heat dissipation occurs at the interface and, to balance this loss, the substrates need to be heated. For this reason, the light-induced curing reaction was performed on a heating plate at 80 °C, a high enough temperature to sustain the thermal front, but sufficiently low to avoid pure thermal initiation. It is clear, from a DSC analysis (Figure 2), that the system is unstable at 110 °C and a thermally initiated reaction occurs quickly. On the other hand, the thermal analysis shows that the temperature that ensures that thermal front propagation is maintained, without activating a pure thermal curing reaction, is 80 °C.

Single lap offset (SLO) shear tests were carried out to evaluate the strength of RICFP cured joints, and the results were compared with those of thermally cured ones (110 °C for 60 min) for the same formulations. The apparent shear strength values are collected in Table 1 and shown in **Figure 4**a.

The RICFP joints show an increase in the apparent shear strength from 13.1 MPa, for the 50:50 CE:DGEBA formulation, to 19.9 MPa for the 60:40 CE:DGEBA formulation. This enhancement is probably related to the expected higher conversion achieved for the latter formulation. A slight decrease in the mechanical strength is evident for a further increase in the CE content (75:25 CE:DGEBA). This could be due to the lower rigidity of the CE units, with respect to the DGEBA units in the crosslinked network, as evinced by the glass temperature transition reported in Table 1. A similar trend can be observed for the thermally cured formulations with an apparent shear strength of about 20 MPa for the 50:50 and 60:40 CE:DGEBA formulations and 13.3 MPa for the 75:25 CE:DGEBA formulation, which is definitely lower than that obtained with the RICRP method.

Furthermore, it is worth mentioning that joints produced with the CE:DGEBA 60:40 formulation show identical mechanical properties for both RICFP and thermal processes, but RICFP curing ensures a remarkable saving in terms of time (only a few seconds for RICFP and several minutes for thermal curing), thus significantly reducing the process costs and energy consumption related to the bonding process.

Figure 4b,c shows fracture surfaces of joints produced on Al alloys; digital images of joints cured via thermal process (Figure 4b) and RICFP (Figure 4c) are reported. Both of the joints failed in an adhesive way, and no preferable adhesion on the upper or lower adherend was reported. Furthermore, in the most common cases, the adhesives failed in two clearly distinguishable parts, one attached to the upper adherend and the other to the lower one (fracture jumping from one interface to the other).

These results show that the epoxy adhesives with apparent shear strengths in the 13–20 MPa range were produced by bonding aluminum alloy substrates via RICFP; the obtained values satisfy the expectations for petroleum-based adhesives and comparable with the joint strengths obtained from the thermal curing of pristine CE or DGEBA resins, which show strengths of 7.5 and 19.0 MPa, respectively.[36–38] RICFP, with a maximum value of about 20.0 MPa, has proved to be a suitable and ultrafast curing method to obtain adhesives with a strength close to the one requested for the automotive and aerospace industries (20–35 MPa[36,39]). Furthermore, thermal insulating materials (e.g. building ceramics, glass and wood) are expected to be suitable for joining through RICFP at room temperature, without the use of heating devices, as is necessary for the foam glass used in this work.

Further work will be carried out to study the effect of the thickness of the adherends on heat dissipation at the resin-substrate and effective surface treatments on the Al alloy to increase the adhesion at the adhesive/adherend interface and to obtain cohesive failure of bonded samples.

3. Conclusions

The feasibility of obtaining joints by means of RICFP of epoxy adhesives has been investigated in this work. The adhesive formulation was prepared by mixing two different epoxy resins: DGEBA, to ensure better mechanical properties and adhesion to the adherends, and CE, which can be exploited to decrease the

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viscosity of the formulation and to increase exothermicity so as to ensure thermal front propagation during curing. The influence of different joining thicknesses was studied by evaluating the RICFP propagation for joint thicknesses of 250, 500, and 750 µm, and 500 µm was found to be the minimum thickness necessary for the adhesive to ensure reproducible and totally propagating fronts for all the tested substrates. The best ratio of all the considered thermal initiator/photoinitiators was assessed by means of DSC analysis. The importance of the sustainability of the heat front during curing was evidenced in this work by using porous glass (Foamglas) as an adherend and proving that substrate materials with a thermal expansion coefficient close to zero allow a stable thermal front propagation to take place, thus leading to a complete curing of the epoxy adhesive. When joints are prepared with an Al alloy, heat dissipation occurs at the interface. For this reason, the light-induced curing reaction was performed on a heating plate with a high enough temperature to sustain the thermal front, but sufficiently low to avoid pure thermal initiation. The light-induced crosslinked joint adhesive was tested and compared with thermal cured ones. The RICFP cross-linked adhesives showed a good performance that was comparable with the thermal-cured adhesives. The best compromise between heat release and joint strength was observed for the CE:DGEBA 60:40 formulation. In short, this work clearly demonstrates the feasibility of crosslinking epoxy adhesives through radical-induced cationic frontal polymerization, by means of a very fast curing method, to yield adhesives with a strength close to that requested for the automotive and aerospace industries.

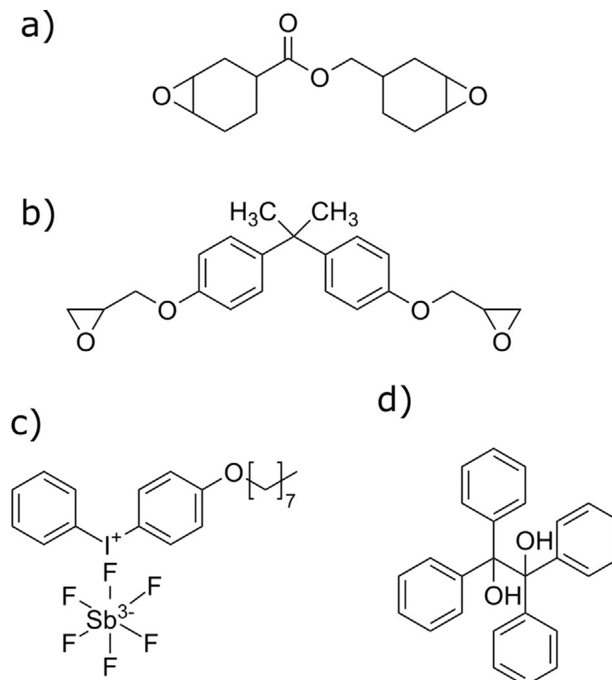

Figure 5. Chemical formula of the resins: a) 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CE) and b) bisphenol-A diglycidyl ether (DGEBA), and the initiators: c) *p*-(octyloxyphenyl) phenyliodonium hexafluoroantimonate (PhI or PAG) and d) 1,1,2,2-tetraphenyl-1,2-ethandiol or TPED (RTI).

4. Experimental Section

Materials: The cycloaliphatic epoxy resin, CE (viscosity 250–400 mPa s[34]) and the bisphenol-based resin, DGEBA (4000–6400 mPa s[34]) were purchased from Sigma Aldrich.

The (*p*-octyloxyphenyl) phenyliodonium hexafluoroantimonate, supplied by ABCR, was used as a cationic photoinitiator (PhI or PAG), while 1,1,2,2-tetraphenyl-1,2-ethandiol (TPED or benzopinacole), from Alpha Aesar, was used as a RTI. **Figure 5** shows the chemical formulas of the resins and initiators.

An aluminum alloy, EN AW 7075 (thermal conductivity coefficient, k_{th} = 130–160 W m^{-1} K^{-1}[40]) and Foamglas (T4), from Pittsburgh Corning (Pittsburgh, PA) (k_{th} = 0.042 W m^{-1} K^{-1}[41]), were used as the adherend materials.

Joint Preparation and Characterization: A typical adhesive formulation was prepared as follows: DGEBA was heated at 50 °C for 10 min to decrease its viscosity and prevent its intrinsic crystallinity, and the CE resin was then added at CE:DGEBA weight ratios of 75:25, 60:40, and 50:50.

The concentrations of the initiators were used in weight per hundred resin (phr) by the total of the epoxy formulation. The concentration of both initiators was varied between 2 and 4 phr.

Formulations were sonically mixed for 30 min at 35–45 °C and then magnetically stirred for at least 120 min at 50 °C. To prevent reactions from occurring accidentally during the mixing operations, the process was performed in the dark and paying attention to keep the formulation temperature way below the activation temperature (≈100 °C, see the onset temperature from the DSC results, Table 1). The formulations were stored in the dark and deposited at room temperature.

The formulations were tested before curing using a Mettler Toledo DSC instrument (Milan, Italy) in both dynamic configurations (from 25 to 300 °C with an increasing rate of 10 °C min^{-1}) and isothermal ones (at 80 and 110 °C, after a temperature increasing rate of 10 °C min^{-1}). Dynamic analyses were also carried out, for the same parameters, on cured epoxy resins after the joints had been broken. The onset temperature (T_{onset}), the percentage of monomer conversion, and the reaction kinetics were evaluated through a thermal analysis. Epoxy group conversion was estimated for samples cured at 80 °C, 110 °C, and via RICFP. This was calculated by dividing the integral of the DSC curve resulting from the thermal analysis on a residual crosslinked adhesive and the peak integral of the curve attained from the dynamic DSC analysis of the uncured formulation.

A polishing machine, equipped with sandpaper (320 grit), was used to make the Al alloy surfaces uniform, and after the polishing treatment, substrates were sequentially rinsed in a sonic bath with acetone and ethanol for 10 min each. Polyethylene (PE) sheets (thickness 250 µm) were cut and placed on the substrate to establish the desired thickness of the joints; multiple layers of PE were used to obtain joint thicknesses of 500 and 750 µm. The aluminum alloy substrates were placed on a hot plate equipped with a thermocouple and heated at 80 °C. The Foamglas substrates were cut into slices, using a saw, and PE sheets were applied in the previously reported way, and then used at room temperature without any further operations.

Finally, the formulations were deposited onto the lower adherends, the upper ones were then placed in such a way as to form single overlap joints, and one side of the joints was irradiated with a UV-lamp for 7–8 s with a light intensity of 150 mW cm^{-2}. A Lightning Cure LC8, Hamamatsu (Milan, Italy), equipped with an optical fiber, was used to irradiate the samples. The steps followed to join the Al alloy substrates are shown in **Figure 6**.

For comparison purposes, the same epoxy formulations were used to join identically treated Al alloy substrates via thermal curing. The substrates were placed in an oven pre-heated at 110 °C for 1 h.

The morphology of the as-prepared joints was evaluated by observing cross-section images taken by a benchtop scanning electron microscope (SEM), JCM-6000 plus, Jeol (Peabody, MA), used under high vacuum conditions and at a voltage of 15 kV.

All the attained samples were tested through a SLO test under compression at room temperature, adapted from ASTM D905-08 (universal

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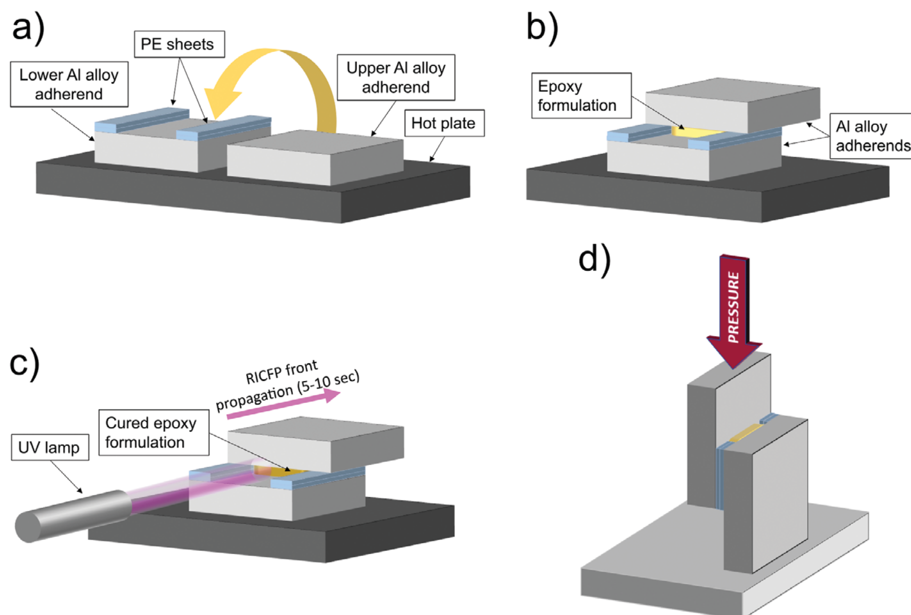

Figure 6. Schematic representation of the preparation of the joints. a) Substrates, with PE sheets, were placed on the hot plate, b) the epoxy formulation was deposited onto the lower substrate, and c) the formulation was irradiated with UV-light and then cured. d) Schematic representation of a single lap offset shear test under compression.

testing machine SINTEC D/10). Figure 6d shows the application direction of the load, which was applied at a load speed of 1 mm min^{-1}. The peak load obtained from the software was then divided by the nominal joint area to attain a reliable apparent shear strength value. At least three samples were tested for each joint. All the fracture surfaces were observed and macroscopically characterized.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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