Infrared thermography characterization of smart multi-functional materials for the aeronautical industry

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Abstract (Arial, 9pt, bold)

The use of multi-material structures, the ability to join different materials and keep them together for the lifetime of the structure, or to separate them for repair or recycling at the end of their useful life, are fundamental aspects to enable a smart industry aligned with sustainable development objectives. However, conventional joining technologies do not meet these conditions. The aim of this study is to take advantage of the effects associated with the presence of magnetic nanoparticles (MNPs), such as hyperthermia, to develop reversible adhesives and characterize them using non-contact infrared thermography technology.

1. Introduction

Conventional joining technologies, such as welding, mechanical fastening, or adhesive bonding, do not meet the conditions necessary to enable a smart industry aligned with sustainable development goals. Welding, for example, provides a strong but permanent joint and is not applicable to all types of materials, such as thermosets. Mechanical fastening allows for component repair and reuse; however, in some materials, this type of joint is not possible due to stress concentration at certain points or aesthetic concerns. Adhesive bonds (generally with thermosetting polymers) are strong but flexible, can dampen noise, are insensitive to many corrosive environments, preserve surface aesthetics, and allow for uniform stress distribution across the entire contact area, without significantly increasing the structure's weight. However, adhesive bonds are often permanent, making the removal of components for repair or replacement impractical.

In recent years, significant efforts have been made in the development of dynamic covalent networks [1], which are networks crosslinked covalently like thermosetting polymers, offering notable recyclability based on exchange reactions of the bonds. Current stimuli to induce these exchange reactions mainly include heat and light. The use of light has the disadvantage of relatively poor penetration into a piece, making heat an advantageous option for achieving these changes. The possible heating through a magnetic field of these networks has been previously demonstrated [2], although it has not been related to the adhesive properties of the network itself, making the development of reversible adhesives based on dynamic networks and the use of hyperthermia induced by the inclusion of magnetically active nanoparticles inside a novel technology.

The aim of this study is to harness the effects associated with the presence of magnetic nanoparticles (MNPs) such as hyperthermia, solar adsorption, controlled activation, etc., to develop new intelligent multifunctional materials for the industry. More specifically, the proposal is to create a reversible adhesive based on the presence of dynamic covalent networks and the incorporation of magnetic nanoparticles and hyperthermia generated by an electromagnet. The incorporation of nanoparticles into various types of thermoplastic adhesives or thermosetting adhesives with reversible bonds is studied. The effect of nanoparticle concentration on the mechanical and adhesive properties of the materials, curing or heating time, as well as the speed at which the bond disappears and regenerates, and the behavior of the bond after several cycles of bonding/unbonding are analyzed.

To optimize the properties of the adhesive, the magneto-active behavior of different compositions is characterized, investigating the modeling of magneto-thermal behavior, evaluating the functionality of the new materials and developed systems, and assessing the effect of nanoparticles. For this purpose, different models representing the thermomagnetic effects of the new materials based on their composition are developed. The data used to build these models are obtained from the controlled magnetic stimulation of adhesives using variable frequency inductors, and the acquisition of thermal evolution during the magnetic stimulation process is carried out using infrared sensors to avoid any interaction with the system under study [3,4].

Table 1. *Composition of the adhesives under study.*

Sample ID	Resin	Resin ratio	Hardener	Resin / Hardener ratio	Magnetic particles
1	ESO	100	VSB	1:1	Nano
2	ESO	100	VSB	1:1	Micro
3	ESO / TGDDM	75:25	VSB	1:1	Nano
4	ESO / TGDDM	75:25	VSB	1:1	Micro

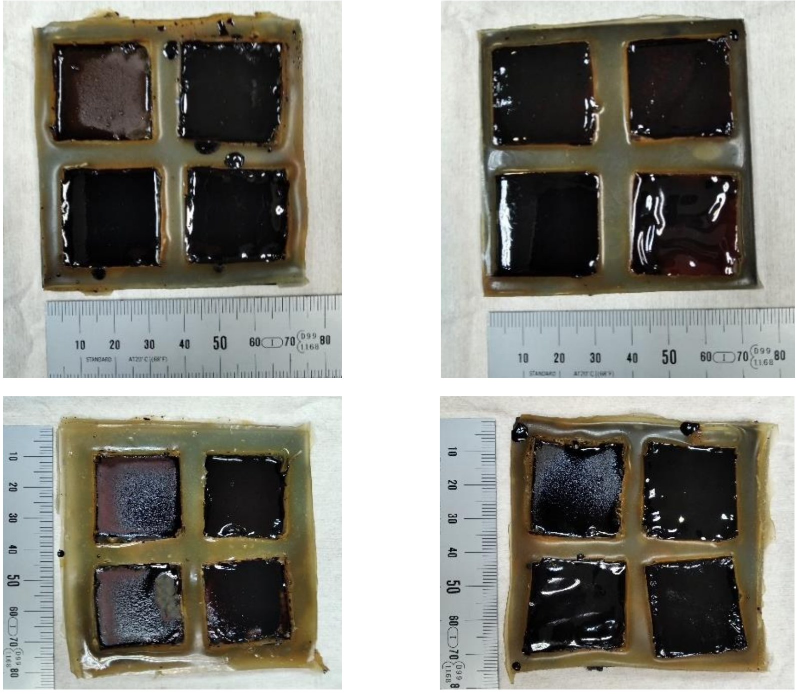


Fig. 1. *Samples used in the thermo-magnetic characterization of the adhesives.*

2. Materials and procedures

2.1. Test samples

The materials analyzed have been synthesized from resins with epoxy-type dynamic covalent bonds. For this purpose, a commercial epoxidized oil (soybean oil, ESO) has been selected and mixed with tetrafunctional epoxy resins to increase the glass transition temperature (Tg) values, while maintaining the recyclability and reprocessability of the dynamic resin or glassimero. Specifically, a tetraglycidyldiaminodiphenylmethane (TGDDM) resin has been used. As a hardener, a Schiff's base (VSB) derived from vanillin has been selected, due to the rigid structure of benzene and its natural origin.

Different ratios of epoxidized soybean oil and tetrafunctional epoxy resin have been used, maintaining in all cases a stoichiometric ratio (1:1) between the resin and the dynamic hardener for the preparation of the vitrimers. Magnetic Fe_2O_3 particles of two different sizes, nanoparticles (NPs) and microparticles (MPs), have been incorporated to these compositions in concentrations of 1, 5 and 10% by weight with respect to the glass-ceramic formulation (table 1). On a 7.5 x 7.5 cm and 2 mm thick carbon fiber composite substrate, a silicone is deposited to divide the substrate into holes of approximately 2.5 x 2.5 cm, which are then filled with the prepared formulations (figure 1).

2.2. Equipment

The tests were carried out in the photothermal techniques laboratory of the CTA, where specific tools were used to adjust the position of the specimens in a repetitive manner for each of the tests performed. The infrared (IR) camera used in this study was a Xenics Gobi-640-GigE model (Xenics NV, Leuven Belgium) with a spatial resolution of 640 x 480 pixels that works in the 8 μm to 14 μm spectral band. The induction equipment was a model AXIO 5/450, from Trumpf Hüttinger GmbH + Co. KG with a maximum power of 11 kW and maximum current of 35 A.

Table 2. *Parameter values used in the test campaigns.*

TEST ID	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
CURRENT [A]	5	5	5	10	10	10	15	15	15	20	20	20	25	25	25
DURATION [s]	30	60	120	20	30	60	15	20	40	10	15	20	5	7	10

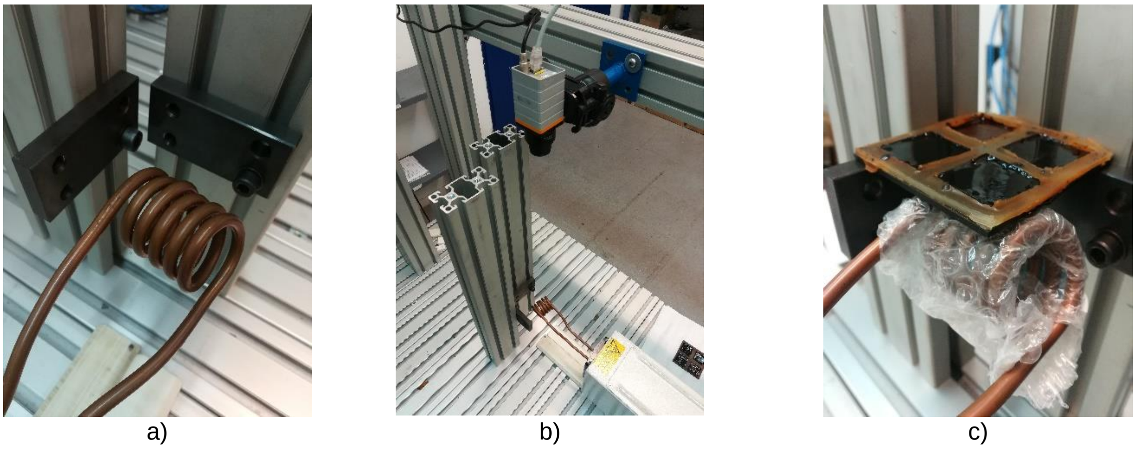

a) b) c)

Fig. 2. *Test setup: a) specimen holder and position of the induction coil, b) position of the infrared camera with respect to the specimen holder, and c) position of the coil and specimen during the tests.*

The camera was calibrated radiometrically to establish the relationship between the radiation detected and the temperature of the observed object. For this purpose, a small oven was used, inside which there were a series of thermocouples that measure the internal temperature and through a lateral hole in the oven the radiation inside the chamber is measured. The oven was brought to a series of defined temperature values and the process was repeated three times. The calibration parameters were calculated by applying the standard adjustment to the measured values [5,6].

2.3. Testing procedure

The synthesized materials have been subjected to a series of magnetic induction conditions to characterize their thermal behavior, and to determine to what degree the incorporated particles favor the temperature increase of the material to promote the debonding of parts. Thus, the measurement and analysis of the temperature increase that occurs in the samples, and the development of models of thermomagnetic behavior of the proposed adhesives, made it possible to optimize their composition and to define procedures for disassembly and repair of the materials in operation.

The test parameters used to characterize the materials and develop these models are shown in table 2. The current intensities and time intervals of field application have been defined to limit the power introduced on the samples to avoid damaging the CFRP base material. A possible limitation for the application of doped adhesives on composite materials is the limitation of the maximum temperature to which these materials can be subjected in order not to damage the polymer matrix. Validating that the glass transition temperature (Tg) of the proposed adhesives is lower than the allowable temperature of CFRP was one of the objectives of the study. Otherwise, their application would not be feasible.

The fabricated specimens were placed horizontally on the bench supports that held the specimens from two sides, leaving the specific area to be inspected isolated without contact, to reduce heat transfer by conduction. To generate the magnetic fields and induce currents in the analyzed material, an induction coil was used. This induction coil was specifically manufactured to apply a uniform field on the sample under study. The frequency of the currents in the inductor was set at 257 kHz. The size of the coil was 5 cm in length and 4 cm in diameter. The distance between the induction coil and the bottom face of the specimens was kept constant at 2 mm, and to avoid possible electrical contacts it was protected with bubble wrap (figure 2).

The thermographic camera was placed on the specimen perpendicular to its surface and at a distance of 45 cm to measure the temperature values reached by the samples during the tests. Prior to carrying out the proposed tests, the emissivity of the test material was determined using high emissivity coatings placed over the measurement area and adjusting the emissivity value of the material to measure the same temperature value as that recorded with a thermocouple attached to the specimen. The emissivity value determined for the material under study was 0.92.

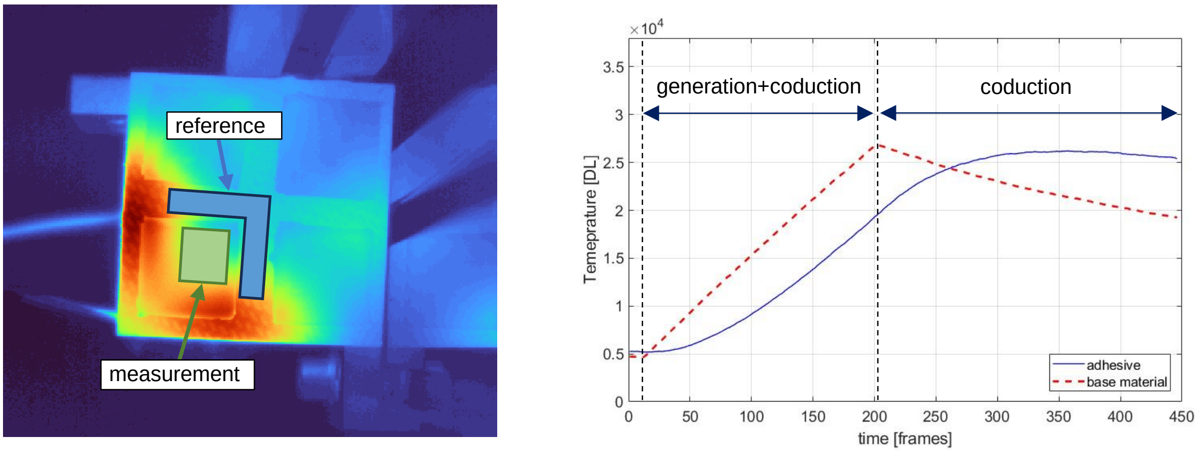


Fig. 3. *Thermographic data recorded during the induction process applied to the samples: raw thermogram (right), and mean thermographic signals in the reference and measurement areas (left).*

The temperature on the surface of the base material (CFRP) and on the surface of the adhesive was measured to determine the degree of additional heating that occurs due to the incorporation of the magnetic particles. The raw adhesive does not experience changes in its thermal conditions when subjected to magnetic fields because it is a dielectric material. Therefore, the only heating mode in the raw adhesive during the tests was through thermal conduction mechanisms due to the overtemperature reached by the base material on which it is deposited.

The base material was heated due to the action of the applied magnetic fields, so it was possible to determine an approximate value of the temperature of the surface in contact with the adhesive by measuring the area adjacent to the adhesive with the thermography camera. In this way, it was possible to experimentally know the heat source applied to the bottom surface of the adhesive. This was the thermal process that occurred in raw adhesives, without added particles, but in our case we had added magnetic particles that behaved, to some extent, as thermal sources inside the adhesive.

The development of behavioral models provides the opportunity to study various conditions that may be difficult or impossible to impose experimentally, investigating the impact of thermophysical and magnetic properties on their thermal and dynamic response. In addition, it allows to know the response of materials with different compositions without the need to manufacture or test them. Therefore, knowing the temperatures of the base material and adhesive, as well as the conditions of application of the magnetic fields and the thermo-physical properties of the materials, the thermal diffusion equation (1) was used the to estimate the power of the heat sources due to the added particles.

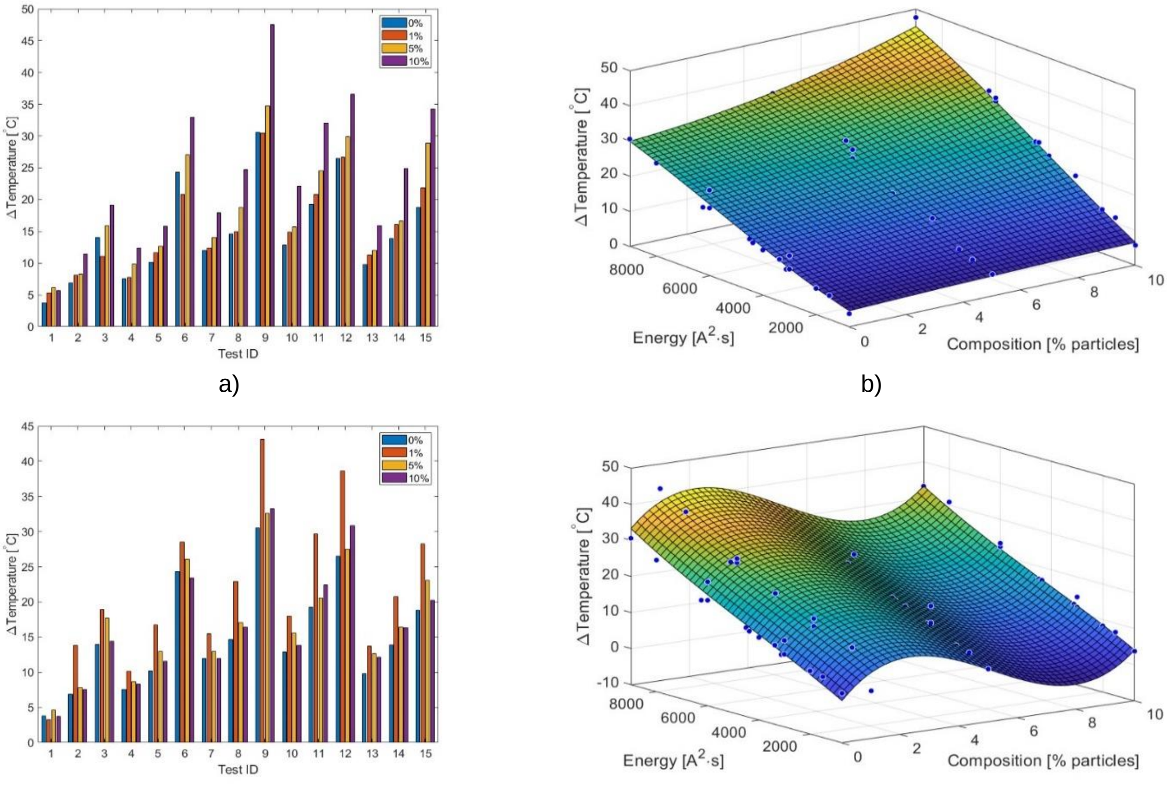
$$\frac{\partial T}{\partial t} = \alpha\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) + \frac{Q}{\rho c} \tag{1}$$

The temperature values T(x,y,x,t) were determined experimentally in the laboratory. The adhesive parameters were previously known, considering the variation produced by the incorporated particles negligible due to their small size and concentration (diffusivity α=0.1e-6 m2/s, density ρ=1.3e3 kg/m3, and specific heat c=1.1e3 J/(kgK)). Applying a finite difference discretization of the thermal model, a solver of this equation was programmed to estimate the Q values due to the added particles.

3. Results

After performing the tests under the conditions defined in table 2, the recorded data were processed to extract the necessary information to carry out the analysis. Adiabatic conditions were assumed during the thermal process; that is, there was no convective heat transfer with the surroundings. Under adiabatic conditions, all samples tested under the same conditions store the same amount of heat. If, in addition, the specimens have the same dimensions, they should reach the same final temperature. In case different specimens of the same dimensions and subjected to the same test conditions reach different final temperatures, this would indicate that the thermal properties of the specimens are different.

Analyzing the thermal process under study, it is deduced that the adhesive undergoes two distinct phases of heat transfer: a phase in which heat generation and conduction mechanisms coexist while the magnetic field is being applied, and another phase in which only heat conduction mechanisms are produced towards the colder zones. Among the samples tested, adhesives without added particles are also included. These samples are very convenient to verify there are thermal effects associated with the addition of particles. Moreover, these samples allow characterizing the base material and decoupling its effect on the thermomagnetic models developed.



a)
b)
c)
d)

Fig. 4. *Temperature increments reached by adhesives with different particle concentrations and corresponding regression models fitted with polynomial functions: a) and b) for nanoparticles, and c) and d) for microparticles.*

Observing the recorded thermograms, the edges of the specimens experienced a higher heating due to the geometry of the specimen and the edge effects produced by the induced currents (figure 3). In order not to penalize the measurements with the temperature values at the edges, the internal area of the specimen that does not contain adhesive was selected as the reference region, and the quarter square of the innermost adhesive area of the specimen was selected as the measurement region.

Analyzing the thermal evolution measured in the regions of analysis, the temperature value reached by the adhesive zone on its outermost surface is similar to the temperature reached by the CFRP material (figure 3). This indicates that indeed the adhesive generates heat, magnetic particles behaving as heat sources. However, the temperature increase of the adhesive does not occur immediately when the magnetic fields are applied, but starts sometime later, which leads to think that this heating is due only to the heat conduction generated in the CFRP. A deeper analysis of this physical interpretation was carried out by means of numerical simulations and comparison with experimental data.

The temperature evolution recorded with the thermography camera should show that the adhesive increases in temperature from the beginning of the induction. This effect would occur provided that the concentration of magnetic particles is homogeneously distributed in the adhesive volume. However, due to the sample preparation process, it is highly probable that the particles have decanted towards the base of the sample due to the effect of gravity and the low viscosity of the resin in the initial curing stage. In none of the tests performed, the instantaneous effect of the temperature increase of the adhesive sample has been observed, but there is always a delay with respect to the start of heating of the CFRP base material. The variance of the thermal signal recorded by the infrared sensor in the adhesive zone was also analyzed to estimate the concentration of particles, but the results obtained were inconclusive. These two facts reinforce the hypothesis of particle settling towards the base of the adhesive.

From the experimental results it was determined that there was indeed an increase in the maximum temperature reached in adhesives containing magnetic particles (figure 4). The maximum temperature values achieved include both the generative effects of the particles and the heat supplied by conduction from the CFRP material. The heat inputs to the adhesive by both mechanisms are valid to achieve the desired goal of reaching the Tg of the adhesive, therefore, it is correct to take them into account in the analysis of results.

As a key result of the analysis, it was concluded that the percentage of particles affects the heating of the adhesive, but there is no direct proportion relationship in all cases. Analyzing the behavioral models developed, it was deduced that the nanoparticles increase heat generation as their concentration in the sample increases, however, the microparticles produce a maximum temperature for a specific concentration, from which the efficiency decreases as their concentration continues to increase, showing a clear magneto-thermal saturation effect.

4. Conclusions and future actions

This study investigates reversible adhesives for aeronautical applications with CFRP materials, to separate joined parts for repair or recycling at the end of their service life, and to enable a smart industry aligned with sustainable development goals. The reversibility effect is based on the addition of magnetic particles to the adhesive to favor the temperature increase until reaching its temperature Tg, from which it is possible to separate the bonded elements.

Adhesives with different resin and particle compositions have been evaluated and subjected to inductive processes to analyze the thermal effects generated. Experimental data have been collected using a thermographic camera to avoid contact with the analyzed samples and to reduce external effects on the thermal process.

The analysis of results has been mainly experimental, relying on theoretical heat transfer models. The conclusions reached indicate that magnetic particles are suitable for producing reversible adhesives since they generate a temperature rise sufficient for their deconsolidation using relatively low magnetic fields.

A thermomagnetic saturation effect has been identified for the case of MPs. From a given particle concentration, heat generation does not increase with increasing concentration. This behavior has not been detected in the case of NPs, which have produced increasing values of generated heat for increasing particle concentrations in all cases.

The combination of resin and particles that has shown the best thermoinductive properties has been ESO/TGDDM for the 1% concentration of MPs. The final feasibility of this case will be decided by adhesive strength tests, since adhesives must not only meet the reversibility requirement, but also the condition of maintaining high adhesion capacity after successive consolidation cycles.

In the final phase of the study, proof-of-concept tests are planned to evaluate the effect of magnetic hyperthermia. A representative case will be designed for adhesive preparation, and the behavior of the magnetic material during the bonding phase will be monitored using infrared sensors. Specimens of materials typical in the aerospace sector, such as CFRP composites and metals, will be joined, and the quality of adhesion obtained will be evaluated by conducting standard mechanical tests.

ACKNOWEDGMENTS

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