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# Reversible graphene-based adhesives for automotive applications

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ARTICLE INFO	A B S T R A C T
Keywords: Adhesive Graphene Automotive Mechanical properties	This study introduces a reversible graphene-based adhesive activated by microwaves. Single-lap joint tests reveal a 20 % increase in stiffness with no compromise in load-bearing capacity compared to unmodified adhesives. The adhesive enables clean joint separation within 70 s using only 1 wt% graphene, significantly reducing the use of nanoparticles and power requirements compared to conventional nanoparticle-based methods presented in the literature. This approach demonstrates improved energy efficiency and potential for recycling and reusability of components in automotive manufacturing.

## 1. Introduction

The industrial use of adhesive bonding has steadily increased over the past 10 years [1]. Adhesive joints can significantly reduce vehicle weight, e.g., by substituting welding and bolts [2]. Their ease of application and better stress distribution than traditional mechanical fasteners make them suitable for replacing fasteners that introduce holes, thus, additional operations during the joining procedure [3,4].

However, some issues can limit their application. 1) In the case of thermoplastic adhesives, the open time can be short compared to the part-work time (e.g. ~30s for polyolefin-based adhesives [1]). The open time is the maximum amount of time between applying the adhesive and juxtaposing the surfaces to obtain a proper adhesive joint with acceptable mechanical properties, allowing handling of the parts for further operations [1]. Part-work time is the time needed to produce an adhesively bonded assembly (applying the adhesive and coupling the parts to apply the pressure required to complete the assembly). Thus, at room temperature, the open time limits the time to couple two components [1]. 2) The complexity of joint dismantling without damaging substrates or components [5]. Dismantling plastic components is very important, e. g. for maintenance during vehicle operative life [5], reuse and recycling of components at the vehicle end-of-life [5], and avoiding waste during joining processes [5]. In Europe, the end-of-life vehicles Directive 2000/53/EC [6] and Directive 2005/64/EC [7] set targets aiming to increase reusability, recoverability (i.e. separation and processing of waste products to reclaim useable materials [7]) and recyclability of vehicle materials and components to a minimum of 95 % of the average weight per vehicle. Meeting such targets is key for the automotive industry, where the lightweight trend is leading to multi-material joining and the use of composites [8]. Adhesive joining is the only way to bond heterogeneous materials since composites are very sensitive to discontinuities (such as holes) that can result in premature failure, given the nonuniform stress distribution introduced by them [9,10]. Disassembling technologies could provide the automotive industry with a new approach to reuse and recycling instead of shredding. The following list provides the abbreviations and acronyms used throughout this paper for clarity and ease of reference. These abbreviations are introduced where first mentioned in the text, but a consolidated list is provided here for convenience in Table 1.

Hot-melt adhesives (HMA) are thermoplastic polymers (i.e. polymers that can be submitted to repeated temperature cycling: melt when the temperature reaches a specific value and solidify upon cooling [11]). They are used in the automotive industry to bond plastic or thermoplastic-based composites. Usually, they are applied with a hot-melt gun that heats the adhesive to its melting point. Then, they are spread on the substrates so that the adhesives can cover the joining area [1]. HMA joints can be separated by 1) warming the adhesive up to its melting temperature [5], 2) by mechanically cutting the adhesive layer, or 3) by using solvents. However, in process 1), the melting temperature can be close to that of the plastic substrates, and the disassembly can

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Abbreviation	Full name		
EM	Electro-magnetic		
HMA	Hot Melt Adhesive		
MLGF	Multi-Layer Graphene Flake		
MW	Microwave		
NP	Nanoparticle		
SAR	Specific Absorption Rate		
SEM	Scanning Electron Microscope		
SLJ	Single lap Joint		
Т	Temperature		
TEP	Thermally Expandable Particle		
TGA	Thermogravimetric a		

cause severe damage [5]. In process 2), damage to the components can happen due to the nonuniform shape of the bondline, i.e. the main path of the bonding area [5]. In some cases, the bondline is not visible since it is integrated into the structures, and the only way to separate the components is to destroy at least one of them [5]. A typical automotive application where the bondline is in the inner part is the rear plastic bumper [1]. Process 3) can only be used on rare occasions since many components are not resistant to solvents. Environmental concerns also need to be considered (solvent disposal).

Lu et al. list several techniques to disassemble adhesive joints, comparing automotive applicability, complexity, capital costs, and disbonding efficiency. An overall rating is given through a score from one to four stars. The list includes both mechanical and chemical techniques. Typically, the former relies on cutting an adhesive layer that can be between 0.1 and 1.5 mm [3,4] and with no straight geometry. Thus, this is a craft job that can damage the components, making them unreusable. The latter uses solvents or chemical scission processes, therefore requiring caution for plants and workers.

The techniques reported in Ref. [5] have two drawbacks. i) The separated surfaces are not clean at the end of the process. Residues are detectable and constitute an obstacle for substrate material recycling or subsequent re-bonding (repair case). ii) The substrates can be damaged during separation [5,8–11]. For these reasons, a technique adaptable to the current components, automatable in operation, and not damaging

must be developed.

One option is the modification of thermoplastic HMA by adding particles that can be activated by electro-magnetic (EM) induction systems [12-28]. In Refs. [12,19,22,24,25], magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles (NPs) that can heat up when exposed to EM fields were embedded into HMA to separate adhesive joints by using an EM inductor (EM field generator) to increase the NPs temperature, T, and reach the melting temperature, Table 2. The operating principle is similar to that of an electric transformer [29]. A varying current produces a varying magnetic flux, which induces a varying electromotive force in the secondary circuit. Thus, the electrical energy is transferred from the primary to the secondary without a direct metallic connection. This produces heat in the secondary, due to hysteresis losses and eddy currents [29]. The primary is the inductor that generates an alternating EM field, while the secondary is the modified adhesive [12]. Since the inductor, under alternating current, acts as excitation and generates an alternating magnetic field, there is a T increase in the Fe3O4 NPs, thus, by thermal conduction in the adhesive. The T increase in Fe<sub>3</sub>O<sub>4</sub> NPs is mainly due to 3 concurrent effects: a) hysteresis losses [12], b) Neel [30], and c) Brown [31] relaxation. b) is related to the NP magnetic moment that, when NPs undergo EM excitation, tends to align their magnetic axes according to the magnetic field [12]. The cyclic rotation of the magnetic axis gives place to a magnetic viscosity that dissipates energy into heat [12,31]. c) is related to NP motion in the adhesive, which is trying to align the axis to the EM field direction. This also gives rise to a magnetic viscosity that dissipates energy into heat [31-33]. This dissipative effect depends on NP dimensions [32]. Fe<sub>3</sub>O<sub>4</sub> NPs, as well as all ferromagnetic NPs with dimension <50 nm, exhibit superparamagnetic behaviour that leads to a more rapid T increase with respect to other types of NPs, since the Néel relaxation effect exhibits larger magnetic viscosity [34,35]. The superparamagnetic behaviour is the ability of the particles to flip the orientation of their magnetic moment when they are exposed to an electro-magnetic field [36].

In superparamagnetic NPs, the heating is totally ascribed to Néel relaxation [38]. As a result of these concurrent effects, the NP T increases rapidly and leads the adhesive layer to the melting point. Thus, bonding or disassembling the adhesive joint is possible. Severijns et al. [39] used NPs for curing epoxy adhesives, taking advantage of Néel and

#### Table 2

Summary of the	e techniques	used for	disassemblya
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Technique	Type of particles	Particle size	Filler percentage wt %	Applied power (AP) and frequency (F)	Best $\tau_S$	Mechanical properties	Ref.
Microwave and MLGF	MLGF	15 µm	0.1, 0.5 and 1 %	AP: 300 W F: 2.45 GHz	70 s (bonded area: 20x12.5)	Toughness +23 %; Strength no change.	This work
Metal particles with EM	Iron particles	1-6, 60 and 450 μm	5 %	AP: 7 kW F: 100–400 kHz	190 s (bonded area: 20x25)	Toughness no change; Strength no change.	[15]
Iron NP with EM	Iron NP	<50 nm	3 %,5 % and 10 %	AP: 5.9 kW F: 315 kHz	13s (bonded area: 20x25)	Toughness +10 %; Strength +10 %	[12]
Iron NP with EM	Iron NP	<50 nm	5 % and 10 %	AP: 7.4 kW F: 270 kHz	24 s (bonded area: 20x15)	Toughness –3%; Strength –2%	[19]
Iron NP with EM	Iron NP	<50 nm	5 % and 10 %	AP: 300 W F: 2.45 GHz	32 s (bonded area: 20x15)	Toughness –3%; Strength –2%	[19]
Iron NP with EM	Iron NP + MLGF	NP <50 nm MLGF <15 μm	10.1 %, 10.5, 11 %	AP: 6 kW F: 326 kHz	11s (bonded area: 20x15)	Toughness +10 %; Strength +10 %	[25]
Iron NP with EM	Iron NP	50 and 100 nm	12 %, 16 % and 20 %	AP: 6.6 kW F: 200 kHz	60 s (bonded area: 25x25)	Toughness +13 %; Strength +7 %.	[22]
TEP particles with EM or oven heating	Polyvinylidene chloride and acrylonitrile copolymer	6–9 μm and 10–16 μm	5 %, 10 %, 15 %, 20 % and 25 %	AP: 10 kW F: n/a	60 s (bonded area: 20x25)	Toughness –30 %; Strength –40 %.	[13, 37]

Brown effects, Table 2. Ciardiello et al. [12] showed that this technology can separate joints of two plastic substrates by using 10, 5, 3 wt% Fe<sub>3</sub>O<sub>4</sub> NPs, achieving 13, 55, 110s separation time,  $\tau_s$ , respectively, by using~5.9 kW to generate an alternating EM field~317 kHz, Table 2. The same technology has been used in Refs. [22-24] for Acrylonitrile Butadiene Styrene (ABS)-Fe<sub>3</sub>O<sub>4</sub> adhesives.  $\tau_{S_1}$  is defined as the time between the application of the EM field and the separation of the adhesive joints. Although  $\tau_{\rm S}$  for the adhesive with 10 wt% Fe<sub>3</sub>O<sub>4</sub> NPs [12] is short enough for a disassembly plant process, the required power is high (6 kW [12]) and the NP wt% is relatively large when considering increments of cost and weight of the adhesive, with respect to the cost of the pristine adhesive. Another technology to separate adhesive joints exploits Thermally Expandable Particles (TEP) [18], which are able to increase their volume when heated [13], thus reducing the adhesive volume. This uses a polyurethane adhesive prepared with from 5 to 25 wt% polyvinylidene chloride - acrylonitrile copolymer [40] polymer-based TEP particles, Table 2. In Ref. [19], both Multi-Layer Graphene Flakes (MLGF) and iron oxide particles (respectively 1 % and 10 %) were used to separate SLJs. The separation was obtained in 14s and 11s using microwaves and an induction heating system, respectively.

Banea et al. [13] used induction to heat the steel substrates of the adhesive joints up a T that induces NP expansion (90–140 °C). This resulted in  $\tau_S$ ~60s for adhesive joints prepared with 25 wt% of TEP particles and~100s for 5 wt%. However, the use of TEPs leads to a decrease of 40 % of the maximum sustained load compared to the pristine adhesive, ~14 % and 33 % for ~5 and 25 wt%, respectively. However, a clean separation surface was not achieved; thus, the substrates had to manually be cleaned in order to re-bond them.

Another way to heat NPs is by utilising microwave (MW) irradiation at 2.45 GHz [19], which is the typical frequency of MW ovens [41–43], Table 2. These pass MW radiation through materials, causing dielectric heating primarily by absorption of energy through polar bonds [44,45]. The advantage of MW over induction heating is the requirement of lower power [46]. Indeed, here we use a 300W MW oven, while [12,16]uses a 6 kW inductor. MWs interact with all materials with polar bonds because the molecules experience a torque when exposed to EM radiations, such as MWs, due to the presence of both positive and negative atoms [45–47]. This torque causes polar molecule rotation, resulting in T increase due to field oscillations [45–47].

Here, we combine the impedance of MLGF dispersed into a polyolefin HMA adhesive matrix with an MW process to melt the adhesive, leading to joint separation. The presence of MLGF in HMA has a beneficial effect on adhesive joint stiffness. We find that the adhesive joints have  $\sim 20$  % higher stiffness and no significant change of the maximum sustained load compared to joints prepared with pristine adhesives. MW heating tests show adhesive joints prepared with 0.5 % and 1 % wt. MLGF reach the melting temperature, thus separating joints. Our approach needs a power 20 times lower than that required for induction heating and leaves a clean surface at the end of the separation process since the adhesives can be removed entirely when in the liquid state. Further, the required MLGF wt% (maximum 1 %) is low compared with that of NPs reported in the literature ( $\sim$ 5–23 % [12,13,22]).

A summary of the experimental workflow is presented in Fig. 1. This flowchart outlines the sequential steps of the study, including adhesive preparation, graphene incorporation, mechanical testing, microwavebased separation, and evaluation of results. Real images corresponding to each step are also provided.

## 2. Materials and methods

## 2.1. Materials

#### 2.1.1. Multi-layer graphene flakes

MLGF, provided by Nanesa (Italy), are produced using liquid-phase exfoliation (LPE) of graphite as described in the technical datasheet and provided by the producer [48]. The main characteristics of the particles are reported in Table 3.

## 2.1.2. Adhesive and substrates

The adherents are made of a polypropylene copolymer with 10 wt% talc, (Hostacom CR 1171 G1A G14008, by Lyondell-Basell) used in automotive applications, such as plastic bumper fascia, dashboards, air ducts, and mouldings [1]. Rectangular adherents, 100 mm long with cross-section  $20 \times 3 \text{ mm}^2$ , are used as substrates. These dimensions are large enough to avoid failure and plastic deformations up to an overlap of 25 mm [12].

The substrates are bonded with Prodas, a polyolefin-based HMA

#### Table 3

Physical properties of the graphene particles used in this study [48].

Parameter	Value	Determination Method
Average lateral size	$\sim \! 15  \mu m$	Particle size analysis (sieving and d50 percentile)
Thickness	~9 nm	Scherrer equation (X-Ray diffraction, 002 peak)
Aspect ratio	1000	Ratio of lateral size to thickness
C:O atomic ratio	30:1	Energy Dispersive Spectroscopy (EDS)
Density	~2 g/	Weighting a known volume of powder over 5
	cm <sup>3</sup>	different batches



Fig. 1. Flow chart of the activity.

adheisve (Beardow Adams), a copolymer of polypropylene and polyethylene typically used in the automotive industry for bonding plastic components [12]. The substrate surfaces were cleaned with Isopropyl alcohol before the adhesive was applied. Table 4 summarises the mechanical properties of the substrates and adhesives.

#### 2.1.3. Preparation of the adhesive with MLGF particles

The modified adhesive is prepared by adding 0.1, 0.5, 1 wt% MLGF. The compound is prepared by dissolving HMA in toluene. MLGFs are then added and sonicated using a Fisherbrand<sup>TM</sup> Elmasonic S 300 Ultrasonic Cleaning for 3h at a power of 900 W, then left overnight at 100 °C for toluene evaporation. Henceforth we use S0.1, S0.5, S1 to refer to the adhesives modified with 0.1, 0.5, 1 wt% MLGF.

## 2.2. Methodology

#### 2.2.1. Preparation of the single lap joints and mechanical tests

Lap shear tests are then carried out on Single Lap Joints (SLJ) with geometry as in Fig. 2. The overlap length and thickness of the adhesive are selected to avoid permanent deformation of the substrate and to obtain cohesive failure of the adhesive joints. Cohesive failure means that the failure propagates within the adhesive and not in the substrates. In this way, the adhesive influence on the mechanical behaviour of the joint is maximised and can be studied, i.e. the SLJ curves do not include plastic deformation.

The SLJs are prepared following the procedure of [15,19,25]. An adhesive-thickness controller screw is used to fix the thickness of the adhesive layer at the desired value of 1 mm. First, an adherent is placed on the lower base (right substrate in Fig. 2) of the assembly device. Then, HMA is uniformly spread over the lower substrate with a hot melt gun equipped with a chamber able to heat the adhesive up to 190 °C, then extruded by using compressed air. The adhesive is spread within the 12.5 mm overlap in Fig. 2. An amount of adhesive larger than the joint area is used to ensure that the overlap of the lower substrate is completely covered. Then, the upper adherent (left substrate in Fig. 2) is placed on the molten adhesive. A 3.5 kg weight is put on the support of the upper adherend to eliminate the excess adhesive by squeezing it out until the required adhesive thickness of 1 mm is reached. Finally, the excess adhesive is removed from the bonded area by using a cutter. Two tabs of the same substrate material are applied in order to compensate for the adherend misalignment in Fig. 2. All SLJ tests are conducted at a constant displacement rate of ~100 mm/min, according to the Stellantis standard for HMA tests [12], using an Instron 8801 servo-hydraulic machine. SLJs are tested with both pristine and modified adhesives at a relative humidity of 50 % and a room temperature of 27  $^\circ$ C.

## 2.2.2. Microwave heating

The MW sensitivity of the adhesives is analysed by using a Discover (CEM Corporation) MW oven, with a magnetron frequency~2450 MHz and a maximum power output~300 W. This can work with an open chamber, where T can be monitored with an infrared camera (IRtech Radiamatic Timage) with 80 mK sensitivity, and an image acquisition rate of 80Hz. MW can lead to a nonuniform field [45]. Thus, a square sample is first tested between the bottom (0 mm) and the top of the chamber (78 mm) until the point of most rapid T rise is determined. This is 63 mm from the chamber bottom. This value is then used for all measurements. The MW power is set to 300W to minimise heating time. These tests were carried out at a relative humidity of 50 % and a room

Table 4	
Summary of the mechanical properties of adherends and adhesive [	12,19].

Property	Adherend	Adhesive	Unit
Tensile modulus Maximum load	1550 20	10 1.5	MPa MPa
Elongation at break	28	60	%

#### temperature of 27 °C.

Two adhesive weights are tested:  $0.25 \pm 0.03$  and  $0.50 \pm 0.03$ g, corresponding to the adhesive quantity used for SLJs with 12.5 and 25 mm overlaps. Tests are carried out to assess whether there is a dependence on the mass of MW heating rate, finding no significant difference between the two samples. These are placed in the centre of the chamber on a Teflon stage. 4 tests are carried out for each sample to assure statistical consistency.

The separation tests are carried out by cutting the substrates in their transversal direction to fit the SLJ on the MW stage and chamber. The cut is necessary due to the 76 mm width of the MW chamber. Two procedures are used to separate the SLJs based on the melting temperature. The adhesive starts to melt at ~124 °C, and it is completely molten at 155 °C. Thus, we test the separation at 130 and 160 °C. The T-time curves obtained by exposing the adhesive to MW are used to establish the time needed to arrive at 130° and 160 °C. SLJs are then exposed to MWs at the same time. S1 requires 70s to reach 130 °C and 85s for 160 °C; S0.5 needs 260s and 340s, respectively; S0.1 does not surpass 100 °C, so the joint cannot be separated.

## 2.2.3. Scanning electron microscope analysis

SEM analysis was carried out with a Magellan XHR 400L FE-SEM – FEI. An electronic high tension of 1 kV was used together with secondary emission signal. The specimens were properly coated in order to have better images.

#### 2.2.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to evaluate the effective concentration of the particles in the adhesive matrix. TGA was performed using a Q50-TGA (TA Instruments) under an argon atmosphere (100 mL/min flow rate). Samples were heated from 25 °C to 100 °C at a rate of 10 °C/min and held isothermally for 60 min to remove any residual moisture/solvents before ramping to 1000 °C at a rate of 10 °C/min.

# 3. Results

# 3.1. SEM analysis

Fig. 3 presents scanning electron microscope (SEM) images of the different MLGF/adhesive compositions at magnifications of 1000X and 2500X. The micrographs present MLGFs as irregular and brighter lines within the darker adhesive matrix. Adhesive compounds prepared using the sonication process exhibit a homogeneous dispersion of MLGFs, with a significant reduction in agglomerates compared to conventional preparation methods. Similar results were obtained by using an extrusion process in Ref. [19]. In Fig. 3a and 2b, corresponding to the S1.0 sample at 1000X and  $2500 \times$  magnifications, the MLGF content is visibly higher, as expected, due to the greater filler concentration. The distribution appears uniform across most areas, with minimal signs of aggregation. This uniformity suggests that the sonication process effectively dispersed the fillers, promoting better integration within the matrix. Fig. 3c and d, showing the S0.5 sample at 1000X and  $2500 \times$ magnifications, reveal a lower density of MLGFs compared to S1. While the dispersion remains relatively similar to the S1.0 sample, some localised areas display a closer accumulation of MLGFs, which do not look agglomerated. Fig. 3e and f, corresponding to the S0.1 sample, depict a sparse distribution of MLGFs within the matrix. The absence of significant aggregation reflects the homogeneity achieved at lower filler concentrations. However, the reduced quantity of MLGFs may limit the adhesive ability to enhance mechanical properties and heat the adhesive when exposed to microwaves since they represent the heating source of the adhesive. Overall, no potential weak points have been identified since the particle distribution appears uniform for all the produced adhesive concentrations.



Fig. 2. SLJ scheme and sizes. The light-yellow part is the adhesive layer, while the two grey parts are the polypropylene substrates.



Fig. 3. SEM images of MLGF/adhesives: (a,b) S1 at magnifications (a) 1000X and (b) 2500X (b). (c,d) S0.1 at magnifications (c) 1000X and (d) 2500X. (e,f) S0.1 at magnifications (e) 1000X and (f) 2500X.

## 3.2. Thermogravimetric analysis

TGA was performed to evaluate the concentration of multilayer graphene flakes (MLGF) incorporated into the polyolefin-based adhesive matrix end to assess a possible thermal effect related to the addition of the graphene filler. As shown in Fig. 4, the TGA curves for the three adhesive compositions (S1, S0.5, and S0.1) are nearly superimposed, indicating that the overall thermal degradation behaviour is not significantly influenced by the varying concentrations of MLGF. The adhesive matrix, composed of a polyolefin base, undergoes complete thermal decomposition at approximately 500 °C, consistent with the high thermal stability of polyolefins due to their saturated hydrocarbon chains [49]. The residual weight at the end of decomposition to the MLGF theoretical content in each formulation: S1.0, with the highest MLGF loading, shows a residual weight that exceeds the theoretical value. S0.5 and S0.1 exhibit lower residual weights in line with their reduced MLGF content, confirming that filler concentration do not affect the decomposition trend compared to the pristine adhesive.

Graphene-based fillers are known for their high thermal conductivity and stability, yet the low MLGF concentrations in these formulations appear insufficient to significantly alter the bulk thermal characteristics of the polyolefin matrix. These results align with the literature on polyolefin-graphene composites, where low graphene concentrations (<1 %) enhance mechanical properties without markedly affecting thermal stability [49]. In particular, all the analysed adhesive formulations present a 0, 0.15, 0.5 and 1.1 g for the pristine, S0.1, S0.5 and S1.0, respectively.

## 3.3. Mechanical and separation results

Fig. 5a plots representative load-displacement curves for SLJs. The initial slopes of the modified adhesives, representative of the stiffness of the adhesive joint, are higher than the pristine ones and increase with MLGF loading. The stiffness values are computed by building the linear



Fig. 4. TGA of HMA with and without MLGF.



Fig. 5. a) representative load-displacement curves of SLJ tests for pristine and MLGF modified adhesives. b) Shear strengths and stiffness of SLJ prepared with pristine and MLGF modified adhesives.

interpolation of the initial linear slope of the load-displacement experimental curves and reporting the value *m* of the linear equation (e.g. y=mx + c). The representative curves of the SLJs with modified HMA show lower ductility, i.e. they have a lower ability to absorb energy after the peak force in the plastic region, compared to pristine HMA, as can be observed by the shorter right parts in Fig. 5a, that is an index of the ductility of the material.

Fig. 5b collects two relevant characteristic values in a diagram: shear strength and stiffness of the SLJ specimen for pristine and 3 MLGF-modified adhesives. Fig. 5 bindicates that the stiffness of SLJ prepared with MLGF/adhesives are~15 %, 20 %, 23 % higher, respectively for S0.1, S.05, S1 when compared to SLJs prepared with the pristine adhesive.

This increase is due to a toughening effect of the adhesive thanks to the presence of MLGF [50,51]. The maximum loads sustained by the SLJ prepared with MLGF/HMAs do not change significantly with MLGF wt% and with respect to the pristine adhesive. The maximum load for S1 is only 1.3 % higher than pristine HMA, whereas S0.1 and S0.5 are 4.5 %, 3.8 % lower, respectively. However, the error bars in Fig. 5 simply that the increase/decrease is not significant.

Thus, the introduction of MLGF does not lead to a significant change in the maximum strength. Similar results were obtained in Refs. [19,49], where the same adhesive was modified with iron oxide NPs. The work [12] reported  $\tilde{a}10 \%$  increase in maximum shear strength compared to the pristine adhesive and  $\tilde{a}10$ –16 % increase of adhesive joint ductility for 10 wt% NPs. On the other hand, a detrimental effect on the mechanical properties of adhesive joints prepared with TEP NPs up to 33 % of the maximum shear strength was reported [13,37], Table 2.

With our approach, we can separate adhesive joints without affecting the mechanical properties (in particular, the strength). This aspect is positive because, in the automotive industry, the adhesive bonding area of the component does not need to be redesigned with respect to that already used in production since this has similar mechanical performance.

Fig. 6a plots representative T-time curves for S0.1, S0.5, S1. T increases more rapidly with the increase of MLGF wt%. S0.1 reaches a maximum T~93 °C (Standard deviation 16.8 °C) after 10 min and does not melt. The maximum T achievable by S0.5 and S1 are above the 250 °C range of our IR camera. However, since the adhesive melts at 155 °C, the IR camera covers the whole T range of interest. The increase in T is constant within the samples.

The heat dissipation of the modified adhesives under MW is determined by evaluating the Specific Absorption Rate (SAR) [W/g] [52]. SAR measures the rate at which energy is absorbed per unit mass by the adhesive when exposed to MW or EM fields generated by induction heating. SAR can be evaluated as [52]:

$$SAR = C \frac{dT}{dt} \frac{m_{tot}}{m_p} \tag{1}$$

where C [J/(°C·g)] is the specific heat capacity of the adhesive,  $\frac{dT}{dt}$  is the



Fig. 6. a) T - time curves MLGF/adhesive under MW. b) SAR for different MLGF/adhesive compositions.

initial slope of the T– time curve of the type presented in Fig. 6a,  $m_{tot}$  is the total mass of the adhesive and  $m_p$  is the MLGF mass. The same value of C,  $1.85 \frac{J}{\circ C_g}$ , is used in the computation of SAR for both pristine and modified adhesives since Ajorloo et al. [53] did not report a significant change of the specific thermal conductivity by embedding 1%wt of MLGF, with sizes of 8 and 100 µm, in polypropylene polymer. The specific heat capacity is directly proportional to the thermal conductivity [54]:

$$C = \frac{k}{\alpha \bullet \rho} \tag{2}$$

where  $k \begin{bmatrix} \frac{W}{c C m} \end{bmatrix}$  is the thermal conductivity,  $\rho \begin{bmatrix} \frac{g}{m^3} \end{bmatrix}$  the density, and  $\alpha \begin{bmatrix} \frac{m^2}{s} \end{bmatrix}$  the diffusivity, defined as the rate of transfer of heat of a material from the hot to the cold end [55].

Further, the work [56] showed that a significant *k* change is obtained for PP modified with 5%wt. MLGF: it increased~10 % for 8 µm MLGFs and  $\sim 88$  % for 100 µm MLGFs. Thus, by considering that k is not changing for a small %wt., C can be assumed constant as well since the only parameter that is varying is the density due to the addition of MLGFs. However, for the %wt. of adhesive and MLGF used here, the adhesive density ranges from 0.98 to 0.99 g/cm<sup>3</sup> when 1%wt. MLGF is used, leading to a 0.1 % change in *C* from Eq. (2). For the two samples, 0.25 and 0.50g, the SAR in Fig. 6b does not differ much since the heating rates are similar. This is mainly due to the increase of the initial slopes, with the MLGF weight being compensated by the decrease of  $\frac{m_{tot}}{m_p}$ : 1000 (S0.1), 200 (S0.5), 100 (S1). The initial  $\frac{dT}{dt}$  are 0.18 (S0.1), 0.96 (S0.5),  $1.92 (S1) \frac{\circ C}{s}$  for 0.25g, and 0.18 (S0.1), 0.90 (S0.5), 1.89 (S1)  $\frac{\circ C}{s}$  for 0.50g. Ciardiello et al. [12] reported SAR  $\sim 308 \frac{W}{g}$  by using 5.9 kW induction power and ã10 wt% magnetite NP concentration. Thus, our MLGF/adhesive joints can be separated with a SAR~15 % higher than a preliminary work [12], with 10 times lower wt% and 20 times lower power, see Table 2

Fig. 7 a-d are representative fracture surfaces of SLJs prepared with pristine and MLGF/adhesives. A visual inspection shows no significant differences in the fracture surfaces. There are three possible failure surfaces [4]: 1) Adhesive fracture, when there is poor bonding between adhesive and substrate, so at the end of the test, the substrate looks clean in the bonding area without any adhesive residual. 2) Cohesive fracture when it occurs in the middle plane of the adhesive layer, so there is adhesive on both separated substrates. 3) Substrate failure occurs when the substrates fail, and no damage occurs within the adhesive. In our case, the fractures are cohesive and very similar.

This aspect implies a good interaction between adhesives and substrates [4]. No plastic deformations are observed in the substrates. Fig. 7e–h shows representative separation surfaces after MW process at 130 °C (e,f) and 160 °C (g, h) for adhesive joints prepared with S0.5 and S1, i.e. those that can reach the melting temperature under MW. Fig. 7e



Fig. 7. Fracture surfaces after SLJ tests for (a) pristine adhesive, (b) S0.1, (c) S0.5, (d) S1. SLJs prepared with (e) S0.5 and (f) S1.0 separated with MW at 130  $^{\circ}$ C. SLJs prepared with (g) S0.5, (h) S1.0 separated with MW at 160  $^{\circ}$ C.

and f shows the separation surface after 260s for S0.5 and 70s for S1, i.e. the time to reach 130  $^\circ\text{C}.$ 

 $\tau_S = 70s$  for S1 is an outstanding result, considering the MLGF wt% = 1 %, Table 2. In Ref. [12], similar adhesive joints were separated (polypropylene substrates with the same adhesive used here but modified with 10 wt% Fe<sub>3</sub>O<sub>4</sub> NPs) in 13s by using an induction heating system with 6 kW (470A) at 317 kHz, Table 2. Banea et al. [13] reported  $\tau_S \sim 60s$  with 25 wt% TEP particles [13,37] and by using an inductor with 30A at 360 kHz, Table 2. In Ref. [22], a separation time of 60s is reported for 20 wt% of iron oxide NPs by using an inductor at 200 kHz with 30A. Here, we can separate adhesive joints with 1 wt% MLGF and

300W, 25 times lower than the one obtained in Ref. [24].

The samples in Fig. 7e and f can be separated by applying a shear load, allowing for the relative sliding of the substrates. Fig. 7e, f shows that the adhesive is not completely molten. The separation surfaces do not look as expected after liquefaction. Fig. 7g and h report the separation surfaces after 340s and 85s for S0.5 and S1, i.e. the time to reach 160 °C. These look as expected after liquefaction. The adhesive starts to flow on the substrates when it is molten, making it easy to separate the joints. When the adhesive is completely molten, it can be removed, thus, it is possible to obtain a clean surface that can be easily reused. This is a limitation for other techniques for joint dismantling, where the separation surfaces cannot be easily cleaned. Thus, a cleaning process had to be designed and actuated to reuse the components. Our MLGF/adhesives can be easily removed when they are molten.

#### 4. Conclusions

This study presents a novel approach to developing reversible graphene-based adhesives for automotive applications. The incorporation of multi-layer graphene flakes into a polyolefin-based hot-melt adhesive matrix enables effective joint disassembly through microwave activation. The adhesive formulation demonstrates significant improvements in joint stiffness, achieving up to a 20 % increase without compromising load-bearing capacity. Furthermore, the separation process is highly efficient, with complete joint disassembly achieved within 70 s using minimal power (300 W) and only 1 wt% graphene loading.

Key advantages of this approach include the clean separation of adhesive joints, allowing substrate reusability, and the reduction in required material and energy compared to conventional nanoparticlebased systems. These features align with the automotive industry's goals of improving sustainability, recyclability, and reducing energy consumption, particularly in the context of lightweight design and multi-material joining.

The findings highlight the potential of graphene-based adhesives not only for mechanical properties but also for enabling more sustainable end-of-life management of automotive components. Future work could explore scaling up this process for industrial applications, investigating the performance with various substrate materials, and evaluating the long-term durability and environmental impact of the adhesives under real-world operating conditions.

#### CRediT authorship contribution statement

**R. Ciardiello:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **G. Belingardi:** Writing – review & editing, Supervision, Methodology, Conceptualization. **B. Martorana:** Conceptualization. **V. Brunella:** Validation. **S.A. Hodge:** Investigation, Formal analysis, Data curation. **D.T.L. Galhena:** Investigation. **Y. Lin:** Investigation. **A.C. Ferrari:** Writing – review & editing, Supervision, Resources, Project administration.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Data availability

Data will be made available on request.

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