

Contents lists available at ScienceDirect

Applied Materials Today



journal homepage: www.elsevier.com/locate/apmt

Magnetocuring of temperature failsafe epoxy adhesives

Richa Chaudhary, Varun Chaudhary, Raju V. Ramanujan, Terry W.J. Steele*

School of Materials Science and Engineering (MSE), Division of Materials Technology, Nanyang Technological University (NTU), Singapore639798, Singapore

ARTICLE INFO

Article history: Received 2 July 2020 Revised 2 September 2020 Accepted 5 September 2020

Keywords: Adhesives Alternating magnetic field Curie nanoparticles Epoxy Ferrites Magnetocuring

ABSTRACT

Adhesive technology is of high and increasing interest in a wide variety of conventional and emerging applications. One-component adhesives typically cure using moisture, heat and light. These approaches limit applications to specific substrates, inefficient handling in manufacturing, and can only be indirectly activated. Hence, we developed a method for remote, wireless, contactless curing of adhesives using alternating magnetic fields (AMF). This approach ("magnetocuring") offers energy efficient, on-demand adhesion. Exposure of $Mn_xZn_{1-x}Fe_2O_4$ Curie temperature tuned magnetic nanoparticles (CNP) additives within commercial epoxy adhesives to an AMF cured thermoset resins within min with minimal rise in substrate temperature. The heating of the CNP "switches off" above its Curie temperature offering failsafe heating. The *in-situ* heating of the CNP can be controlled by CNP composition, CNP loading, and AMF strength. Internal temperatures of 160 °C could be reached in 5 min, allowing curing of most commercial epoxy adhesives without resin scorching. The maximum lap shear adhesion strength exceeded 6.5 MPa. Magnetocuring is demonstrated on wood, ceramics, and plastics, which is of considerable interest in sports, automotive, and aerospace industries.

© 2020 Elsevier Ltd. All rights reserved.

1. Introduction

Chemical curing adhesives (CCA) are preferred over mechanical fixation due to their light weight and stress distributed bonding which is free of substrate damage. The global market of instant curing adhesive is expected to be more than \$ 3 billion USD [1] by 2023 and is dominated by two-part, thermosetting structural adhesives. [2] Structural adhesives require mixing of epoxy/hardener resins or thermal activation of one-pot epoxy/hardener blends (thermocuring), which leads to energy losses and stress/strain mismatches due to non-uniform temperature cycling of the substrates and resin. Attempts to overcome these impediments have led to alternative methods such as snap-cure epoxy [3-5], photocuring [6,7], electron beam curing [8], and electrocuring [9-12].

Snap-cure thermosets are one pot adhesives that rapidly cure within min. However, the rapid curing nature is of limited benefit to insulating or heat-sensitive materials (e.g., wood, ceramics, or plastics) [13]. Photocuring offers non-contact activation, but is dependent on UV transparent materials and free radical initiators, which contribute to manufacturing problems of dermal sensitivity [14]. Electron beam curing works by impinging high speed electrons that initiate free radicals within the polymerinitiator. The high energy of the electron beams/ radiation pen-

* Corresponding author. E-mail address: wjsteele@ntu.edu.sg (T.W.J. Steele).

https://doi.org/10.1016/j.apmt.2020.100824 2352-9407/© 2020 Elsevier Ltd. All rights reserved. etrates offers uniform curing, but requires high capital and infrastructure investments. All parts must be electron irradiated, which requires shielded rooms and advanced technical personnel [15,16]. Surface-curing adhesive is methyl/ethyl-cyanoacrylate, also known as 'Superglue'. It has the unique property of either forming strong substrate bonds or not bonding at all. The inability to bond rough/acidic surfaces, the difficulty in handling brittle materials, and unsatisfactory temperature stability (cured bonds must be kept < 70 °C) limits surface curing to do-it-yourself home repairs [17].

Alternating magnetic field (AMF) mediated adhesive curing ('magnetocuring') occurs by in situ activation of thermoset adhesives. It is a non-contact method of bonding non-metal materials. Previous studies have investigated magnetocuring based on FeCo epoxy composties [18]. Induction curing of thiol-acrylate and thiolene composite systems using cobalt and nickel particles has been demonstrated [19]. Polymerization of cyanate ester using Fe₃O₄ as an internal heat source through induction heating was studied [20]. Induction curing was also studied with nickel nanoparticles for bonding of composites [21] and polymerization using iron oxide nanochains [22]. However these formulations were never successfully commercialized due to the follwing limitations: (i) absence of surface functionalization leads to poor colloidal stability of the magnetic nanoparticles. This would prevent adequate shelf stability due to the formation of large aggregates (ii) nanoparticle aggregates lead to thermal hotspots and localized resin/epoxy pyrolysis [18], (iii) high power input (3–32 kW) [19] paired with inefficient metallic Co (2 μ m) and Ni (3 μ m) particles[20] or Fe₃O₄ particles [22], (iv) use of high frequency (>2 MHz) and broad particle size distribution (70 nm – 22 μ m) [21].

To overcome these limitations, colloidal stability and aggregate induced hotspots needs to be addressed. Herein, it is hypothesized that surface functionalized magnetic nanoparticles (CNP) will serve as magnetocuring additives within thermoset resins. This allows one-pot adhesive formulations that activate substrate bonding and adhesive crosslinking upon exposure to AMF. The bonding initiation can be precisely tuned to the Curie nanoparticle cutoff temperature with optimized heating, allowing bonding to heat-sensitive substrates while eliminating scorching. In order to support the hypothesis, following steps were carried out: (1) $Mn_xZn_{1-x}Fe_2O_4$ CNP will be synthesized by a facile hydrothermal method with controlled particle size (< 20 nm) and Curie temperature (Tc). The Curie temperature of Mn_xZn_{1-x}Fe₂O₄ ferrites can be tuned by changing the ratio of Mn to Zn content. (2) Organic coatings and surface functionalization on CNP with oleic acid and bisphenol A diglycidyl ether was used to overcome previous laboratory failures with long term CNP colloidal stability in liquid epoxy/adhesives. (3) Incorporation of CNP into adhesives and optimal AMF induction (low power system) that allows snap-curing formulations while preventing substrate hotspots and scorching. (4) Lastly, the loading of CNP, thermal and physical properties of adhesives, selection of substrates will allow tuning of mechanical properties and shear adhesion strength.

CNP offers a prime advantage over other magnetic nanoparticles due to its failsafe temperature limits. This is the major rationale for choosing them for magnetically induced heating and activation of thermoset epoxy adhesives. For the first time, CNP have been employed to cure one component epoxy adhesives through a non-contact modifier methodology. The modifier methodology allows its incorporation into already commercialized thermoset adhesive formulations. Magnetocuring offers a more cost-effective activation method, since the adhesive is heated directly without substrate thermal conduction. Here, curing of one-component epoxy adhesives through AMF activation or 'magnetocuring' is demonstrated on wood, ceramics, and plastics, which is of significant interest in sports, automotive, and aerospace industries.

The novelty of the present work includes i) development of several temperature fail safe magnetoadhesives using commercial one component adhesives, ii) proof of concept to join a range of materials using magnetoadhesive under AMF, these materials are close to impossible to join using a conventional oven method, iii) Our approach of curing is remotely controlled, rapid and localized heating, reduced processing cost and energy and absence of scorching.

2. Materials and methods

2.1. Materials

One component epoxy adhesives (ES558 Permabond and TIM-813HTC-1HP) are purchased from Permabond, USA and TIMTRON-ICS, USA, respectively. The divalent manganese (II) chloride tetrahydrate (MnCl₂. 4H₂O, 99%), zinc chloride, anhydrous (ZnCl₂, 98%) and trivalent iron (III) chloride hexahydrate (FeCl₃. 6H₂O), oleic acid (OA), bisphenol A diglycidyl ether (BADGE) and dicyanamide (DICY) are purchased from Sigma Aldrich and used as received. Wood popsicle sticks and polymethyl methacrylate (PMMA) sheets are purchased from Art Friend, Singapore. Acrylonitrile butadiene styrene (ABS-100) used for 3D printing is purchased from Additive 3D Asia, Singapore. Microscope slides, borosilicate (25.4 mm x 76.2 mm, thickness 1–1.2 mm) are purchased from Newton 101 PTE. LTD. Singapore.

2.2. Methods

2.2.1. Synthesis of magnetocuring adhesive modifier Curie nanoparticles (CNP)

Magnetocuring additives, CNP of composition Mn_xZn_{1-x}Fe₂O₄ (x = 0.4, 0.5, 0.6 and 0.7) are synthesized using a modified hydrothermal method [23,24]. Briefly, for the synthesis of a 4 g batch Mn_{0.7}Zn_{0.3}Fe₂O₄ particles, 10 mL solutions of 70 mmol MnCl₂•4H₂O (2.22 g) and 30 mmol ZnCl₂ (0.654 g) are prepared separately in distilled water (DI water). 200 mmol of FeCl₃•6H₂O (8.64 g) is dissolved in 40 mL DI water and NaOH (4 M) solution is added dropwise until the pH value reached at 8. The resulting brown precipitate is centrifuged and washed three times with DI water, and transferred to a beaker equipped with a mechanical stirrer. The separately prepared Mn and Zn salt solutions are then added together into the beaker and the mixed solution is stirred vigorously while adding NaOH solution dropwise until the pH value of the reaction mixture reached 12. This resulting slurry is decanted into a Teflon-lined stainless-steel autoclave (4748A Parr, USA) and placed in an oven at 190 °C for 2 h. The resulting nanoparticles is washed three times with DI water and two times with ethanol (96%), followed by vacuum drying for 48 h. 95% yield of vacuum dried particles is obtained. All other CNP (Mn_{0.4}, $Mn_{0.5}$ and $Mn_{0.6}$) are also synthesized in a similar fashion with 95-97% yield and stored under vacuum. Prior to further modification, all the synthesized CNP are characterized for their structural, functional and magnetic properties using XRD, ICP-MS, TGA, FTIR, and PPMS.

2.2.2. Surface modification of Curie nanoparticles with oleic acid (OA)

CNP are coated with oleic acid to prevent agglomeration. 2 g of CNP are dispersed in 80 mL of deionized water and placed in a sonicating water bath (Elmasonic S 60 H, Germany) for 20 min. to break up the aggregates. 4 mL of OA is added to the solution and sonicated for 10 min. This solution is heated at 80 °C for 1 h under mechanical stirring at 400 rpm. The resultant solution is washed 3–4 times with ethanol, the OA coated CNP are separated using a permanent magnet. The oleic acid coated particles are modified with bisphenol A diglycidyl ether.

2.2.3. Surface modification of $Mn_xZn_{1-x}Fe_2O_4/OA$ with bisphenol A diglycidyl ether (BADGE)

 $Mn_xZn_{1-x}Fe_2O_4/OA$ particles from the first step are dispersed into 10 mL of tetrahydrofuran (THF) and sonicated for 30 min. A solution of 10 g bisphenol A diglycidyl ether (BADGE) in 20 mL THF is added to the above solution and sonicated again for 30 min. This solution is kept for 16 h until the surface of nanoparticles is completely wetted with BADGE. This consequent solution is washed by tetrahydrofuran and acetone and the $Mn_xZn_{1-x}Fe_2O_4/OA/epoxy$ nanocomposites are separated using a permanent magnet followed by vacuum drying for 24 h. On the basis of the dried particles weight, 1.94 g yield for the surface functionalization is observed. The amount of OA and BADGE anchored on the surface of the functionalized particles is determined by thermogravimetric analysis.

2.2.4. Alternating magnetic field heating of functionalized Curie nanoparticles

The alternating magnetic field (AMF) generator of D5 series (640 W mono frequency F1 driver) from nB nanoScale Biomagnetics, Spain is used by incorporating a solenoid coil (S^{56}) at a fixed frequency of 400 kHz. AMF heating of the CNP dispersed in BADGE for different concentrations (5–30 *wt.%*) are determined at applied magnetic fields ranging from 50 to 140 Oe. The temperature under AMF is measured using a fibre optic temperature sensor (Neoptix T1S-01-PT15, USA). All the samples are freshly prepared by dispers-

Table 1

Dimensions of ABS coupons and parameters used for 3D printing.

Dimensions	Values	
Length	90 mm	
Width	20 mm	
Thickness	3 mm	
Printing parameters		
Extruder temperature	240 °C	
Bed temperature	115 °C	
Chamber temperature	45 °C	
Layer Height	0.25 mm	
Wall thickness	0.8 mm	
Infill	20%	

ing the appropriate amount of CNP into BADGE and treated with ultrasound sonication for 60 min.

2.2.5. Specimen preparation by 3D printing

All the ABS coupons are printed using a Cubicon 3DP-110F printer. The T-shaped geometry of ABS coupons is created using Solidworks and saved as stereolithographic (STL) file. This STL file is opened in 3D printer software and the Gcode is exported to the printer. The dimensions of ABS coupons and printing parameters are listed in Table 1.

2.2.6. Adhesive curing by AC magnetic field

Commercially procured Permabond ES558 and TIMTRONICS 813-HTC and a mixture of BADGE and dicyanamide (100:12) are used for magnetocuring of one-component epoxy adhesives. A range of CNP loading (15–30 *wt.*%) with respect to the adhesive/BADGE is used for magnetocuring of wood, glass, PMMA and ABS coupons. Samples are cured at a magnetic field strength of 140 Oe and frequency of 400 kHz.

2.2.7. Structural and magnetic characterizations of CNP

X-ray diffraction (XRD) is carried out with a Bruker D8 Advance powder diffractometer, using Cu-K α radiation operated at 40 kV and 40 mA, in the range from $2\theta = 20^{\circ}$ to 70°, at a scan rate of 5°min⁻¹. Phase identification is performed by matching diffraction peak positions and relative intensities to reference JCPDS files. The crystallite size is calculated using the Scherrer formula D = 0.9 $\lambda/(\beta \cos \theta)$, where λ is the wavelength of the X-rays (1.54 Å), β is the full width at half maximum (FWHM) of the 311 diffraction peak and θ is the Bragg angle.

2.2.8. Elemental composition of CNP

Elemental composition of the CNP is measured by Inductively coupled plasma mass spectrometry (ICP-MS) Agilent 7700, Japan. Samples are prepared by dissolving the particles in a mixture of hydrochloric acid (HCl) and nitric acid (HNO₃) at a ratio of 3:1 followed by the dilution with millipore water. Prior to the analysis, the sample solution is filtered using 0.2 μ m pore sized syringe filter (Agilent).

2.2.9. Physical property measurement of CNP

The magnetic properties of CNP are measured using a physical property measurement system (PPMS) (EverCool-II, Quantum Design, USA), equipped with a vibrating sample magnetometer and an oven (model P527). The room temperature hysteresis curves of the CNP are recorded up to an applied field of 2 T. The magnetization versus temperature curves are measured in the temperature range of room temperature to 600 °C at different applied magnetic fields ranging from 50 Oe to 140 Oe.

2.2.10. Quantification of coating on the CNP

Thermal degradation of the bare nanoparticles and the amount of OA and BADGE coated on the nanoparticles are measured using thermogravimetric analysis (TGA). TGA is carried out using a TA Instruments TGA Q500 over a temperature range from 30 to 900 °C at a ramp rate of 10° Cmin⁻¹ under nitrogen atmosphere.

2.2.11. Colloidal stability of CNP

The stability of the CNP are examined by a Zetasizer (Zetasizer Nano, Malvern Instruments, UK) using a 173° backscatter measurement. The colloidal stability of the functionalized nanoparticles dispersed in ethanol is investigated by measuring the mean count rate (kilo count per second, kcps) versus time. 5 mg of CNP ($Mn_xZn_{1-x}Fe_2O_4/OA/BADGE$) are dispersed in 5 mL of ethanol and sonicated for 1 h. For all the samples, ten measurements with ten repeated runs were recorded.

2.2.12. Particle size of CNP

The particle size and morphology of the synthesized and functionalized Curie nanoparticles are characterized using a JEOL 2010 transmission electron microscope operating at 200 kV. Samples are prepared by ultrasonically dispersing a small amount of powder in ethanol placing a drop of the suspension on a holey carbon-coated copper grid. Prior to analysis, samples are dried in vacuum oven overnight. ImageJ image processing software is used to analysed the particle size.

2.2.13. Curing temperature from differential scanning calorimetry

DSC analysis is performed using a simultaneous DSC/TGA system, TA Instrument, SDT Q600. Analysis is carried out from 30 to 600 °C at a ramp rate of 10 °Cmin⁻¹.

2.2.14. Confirmation of Curie nanoparticle functionalization and percentage crosslinking

FTIR (Perkin Elmer Frontier) measurements of functionalized CNP are performed using a universal Zn-Se ATR (attenuated total reflection) accessory in the 500–4000 cm⁻¹ region. The FTIR spectra of CNP and functionalized CNP is recorded by the KBr pellet method. 3–4 mg of CNP are added into 20 mg of potassium bromide (KBr) and mixed with a mortar pestle. This mixture is used to prepare the pellet with a 13 mm KBr die set by applying 10 tons of pressure via a KBr hydraulic press (Specac, UK). The FTIR measurements of adhesives and cured adhesive are performed with a Universal ATR fixture of a ZnSe crystal. Each measurement is an accumulation of 32 scans with a resolution of 4 cm⁻¹.

2.2.15. Lap shear adhesion

Magnetocuring is demonstrated on different substrates: glass, wood, ABS and PMMA. 125 mg of adhesives are applied onto the substrate/adherent section area of $1 \times 1 \text{ cm}^2$. The thickness of the samples is ~ 0.45 mm (±0.05) on all the substrates. The adherents are tightly gripped together with cello-tape. The Lap shear adhesion tests of the magnetocured samples are performed on a Static Mechanical Tester (Criterion MTS C43, USA) with a 2.5 kN load cell and a testing speed of 3 mm/min.

2.2.16. Statistical analysis

All the experiments are performed in triplicate and data presented here as mean \pm SD (n = 3). Significance is determined by one-way ANOVA with Tukey correction, carried out using Origin-Pro 2018b 64-bit Software, where p < 0.05. (*) is considered to be statistically significant.



Fig. 1. Characterizations of Curie nanoparticles (CNP). **A**) XRD analysis revealing spinel phase formation in $Mn_{0.4}Zn_{0.6}Fe_2O_4$ to $Mn_{0.7}Zn_{0.3}Fe_2O_4$. **B**) Scherrer equation estimated crystallite size of CNP. **C**) The actual composition of CNP measured by ICP-MS with standard deviation (SD) of < 1%. **D**) Magnetic hysteresis loops and cohesivity measured at room temperature using PPMS.**E**) Normalized magnetization as a function of temperature for $Mn_xZn_{1-x}Fe_2O_4$ CNP in the range from room temperature to 400 °C at a magnetic field of 140 Oe. **F**) Temperature dependence of magnetization for $Mn_{0.7}Zn_{0.3}Fe_2O_4$ CNP at applied magnetic fields of 50 Oe, 80 Oe, 100 Oe and 140 Oe.

3. Results

A one-pot adhesive platform is designed for non-contact magnetocuring through exposure to AMF. On applying alternating magnetic field, CNP dissipate the applied magnetic energy into heat mainly by relaxation loss processes (Brown and Neel). The heating ability of these CNP exposed to AMF are quantified by specific absorption rate (SAR) parameter, which is calculated by the heat released in unit time by the unit mass of the CNP. The CNP have the advantage of a upper limit of temperature which is controlled by the Mn/Zn ratio. This temperature control prevents scorchinga detrimental property of other magnetic nanoparticles. The Mn/Zn ratio is tuned through the hydrothermal synthesis feedstock determined. Composition in the range of $Mn_{0.4}Zn_{0.6}$ to $Mn_{0.7}Zn_{0.3}$ are chosen as they span cutoff temperatures of 100-250 °C, relevant to most thermoset resins [25,26]. To prevent aggregation and maximise shelf stability, the bare CNP are surface functionalized with oleic acid and BADGE. Oleic acid (OA) is widely used in nanoparticle synthesis because it can form a dense protective layer on the nanoparticle surface, which stabilizes nanoparticles [27]. A surface coating of BADGE aims to interface with the resin upon thermoset initiation. The effect of CNP elemental ratio, additive loading, and magnetic field strength on the properties are determined. Lap shear adhesion tests on industrially relevant substrates is performed. Substrate and resin temperature during AMF exposure are independently determined through fiber optic probes. Resin activation and propagation are characterized with thermogravimetric analysis (TGA), dynamic scanning calorimetry (DSC), and infrared spectroscopy before and after magnetocuring.

3.1. XRD confirms the spinel structure and nanocrystalline size of CNP

The structural determination of $Mn_xZn_{1-x}Fe_2O_4$, Curie nanoparticles are analyzed by the X-ray diffraction patterns (**Fig. 1A**), confirming the formation of cubic spinel structure for all the samples. The experimental peaks are matched with JSPDS files and hkl planes are computed with Topas software. The intense crystalline peaks observed at 2θ (hkl) value of 29.9 (220), 35.08 (311), 42.6 (400), 52.9 (422), 56.3 (511), and 61.9° (440) match the experimental data for the franklinite spinel structure (JCPDS no. 10-0467), indicating the presence of $Mn_xZn_{1-x}Fe_2O_4$ in all the samples. The small diffraction peak at 2θ of 33.61° is due to a small fraction of hematite (α -Fe₂O₃) phase present in samples. The crystallite size of the particles was calculated using the Scherrer formula $(D = 0.9 \ \lambda / (\beta \cos \theta))$, the most intense diffraction peak at 2θ of 35.08° corresponds to the plane 311. An increase in the Mn content results in an increase in crystallite size of the particles. The crystallite size of Mn_{0.4}, Mn_{0.5}, Mn_{0.6} and Mn_{0.7} samples is found to be 9.5, 13.5, 13.7 and 13.8 nm, respectively (Fig. 1B).

3.2. The actual Mn to Zn ratio differs by 9% to 18% from feed stock ratio

ICP-MS is employed to determine the Mn/Zn ratio of the four different $Mn_xZn_{1-x}Fe_2O_4$ compositions. In **Fig. 1C**, the measured mol% ratios of manganese (Mn) and zinc (Zn) are presented as determined by ICP-MS and the results are compared to the nominal values. The ICP-MS results indicate that the actual mol fraction of $Mn_{0.4}$, $Mn_{0.5}$, $Mn_{0.6}$ and $Mn_{0.7}$ differ from the nominal compositions by 18%, 15%, 12% and 9%, respectively. Generally, the Zn cation gets uniformly distributed among the tetrahedral and octahedral sites [28-30]. Hence, it is expected that Mn^{+2} has a higher probability to get absorbed by a nucleus than Zn^{2+} . The smaller radius of Zn^{2+} (0.74 Å) compared to Mn^{2+} (0.83 Å) might be the reason for an increased absorption of Zn^{2+} into the lattice. The results also indicate that on increasing the Mn content, the difference between the nominal and experimental values decreases. Incorporation of

Table 2
Magnetic characteristics of CNP ($Mn_xZn_{1-x}Fe_2O_4$).

Sample	H_c (Oe)	M_r (emu/g)	M _s (emu/g)	M_r/M_s	$K^* (10^3 J/m^3)$	T_B (K)	$T_{irr}(\mathbf{K})$
Mn _{0.4}	27.6	0.534	33	0.01618	3.2	84	-
Mn _{0.5}	13.4	0.717	40	0.01793	4.7	125	-
Mn _{0.6}	2.8	0.156	46	0.00339	8.6	229	278
Mn _{0.7}	2.4	0.231	60	0.00385	9.8	260	300

* The effective anisotropy constant was calculated using the relation: $T_B = KV/25k_B$, where $T_B =$ blocking temperature, K = anisotropy constant, V = particles volume, $k_B =$ Boltzmann constant.

more Zn^{2+} ions is observed for the lower Mn content particles (Mn_{0.4}).

3.3. Magnetization and Curie temperature (Tc) increases with increasing Mn content

The magnetic properties in ferrimagnetic spinels is mainly due to the super exchange interaction mechanism between the metal ions in the A and B sublattices. The substitution of non-magnetic ${\rm Zn}^{2+}$ ion, which prefers to occupy the A site, reduces the exchange interaction between A and B sites. Hence, by varying the Mn/Zn ratio the magnetic properties of the CNP can be tuned. Fig. 1D presents the magnetization versus applied magnetic field curves measured at room temperature. The saturation magnetization (M_s) of $Mn_{0.4}$, $Mn_{0.5}$, $Mn_{0.6}$ and $Mn_{0.7}$ CNP is found to be 33 emu/g, 40 emu/g, 46 emu/g and 60 emu/g, respectively. All the particles exhibit superparamagnetic behaviour with negligible hysteresis. The room temperature coercivity (H_c) of all the samples are represented in the inset of Fig. 1D and Table 2. The H_c decreases with increasing Mn^{2+} content, down to a value of 2.4 Oe for $Mn_{0.7}$ particles. An increase of the Mn concentration in Mn_xZn_{1-x}Fe₂O₄ CNP leads to higher M_s . This increase in M_s is due to the compositional change, the magnetic moments of Mn²⁺ (5 $\mu_{\rm B}$) ions is higher than those of Fe²⁺(4 $\mu_{\rm B}$) and Zn²⁺ (0 $\mu_{\rm B}$) ions. For the Curie temperature measurements, the normalized temperature dependence of magnetization of CNP under an applied magnetic field of 140 Oe is recorded in the temperature range from room temperature to 400 °C (Fig. 1E). The CNP does not exhibit sharp transition at Curie temperature. Such broad distribution of Curie temperature in fine magnetic nanoparticles is often observed. In such cases, the spontaneous magnetization (*M*) scales as $(Tc-T)^{\beta}$ with a critical exponent, $\beta = 1/3$ [23,31-33]. Therefore, the M³ is plotted with respect to temperature and Tc is determined by extrapolating M^3 to zero [31]. The $\mathit{T_c}$ of $Mn_{0.4},$ $Mn_{0.5},$ $Mn_{0.6}$ and $Mn_{0.7}$ is found to be 61 °C, 115 °C, 138 °C and 237 °C, respectively (Fig. 1E). This increase in T_c with increasing Mn% in Mn_xZn_{1-x}Fe₂O₄ CNP is due to the enhanced total magnetic interactions within the unit cell [34]. The temperature dependence of magnetization (M-T) for Mn_{0.7}Zn_{0.3}Fe₂O₄ is also measured at different magnetic fields of 50 Oe, 80 Oe, 100 Oe and 140 Oe (Fig. 1F). The magnetization at room temperature increases with increasing the magnetic field, consistent with the higher AMF heating of these CNP at 140 Oe (more details will be discussed later). The change in nature of M-T curves with applied magnetic field is because more thermal energy is required to randomize the magnetic spin at high applied field.

3.4. Low temperature magnetic measurements confirm the superparamagnetic nature of CNP

Zero field cooled (ZFC) and field cooled (FC) experiments are known to determine the blocking temperature (T_B) of magnetic nanoparticles. In the ZFC measurements, the CNP are cooled from 400 to 5 K in the absence of an applied magnetic field. After reaching 5 K, the magnetization is determined as a function of increasing temperature under an external magnetic field. For the FC measurements, the CNP are cooled from 400 to 5 K under an applied magnetic field of 140 Oe. Subsequently, the magnetization is recorded in two modes; with increasing temperature from 5 to 400 K which is known as field cooled warming (FCW) and with decreasing temperature from 400 to 5 K referred as field cooled cooling (FCC).

Fig. 2A depicts the ZFC, FCC and FCW magnetizations of all the CNP in the temperature range of 5–400 K at an external magnetic field of 140 Oe. For all the samples, the ZFC magnetization increases with the rising temperature and exhibits a broad maximum centred at the blocking temperature (T_B) . Such a peak temperature in the ZFC curves indicates the transition from a magnetically blocked state at low temperatures to a superparamagnetic state at higher temperatures. The T_B of Mn_{0.4}, Mn_{0.5}, Mn_{0.6} and Mn_{0.7} are found to 84, 125, 229 and 260 K, respectively, at magnetic field of 140 Oe, indicated by black vertical arrows in Fig. 2A. The shifting of T_B towards higher temperatures with increasing Mn content Mn_xZn_{1-x}Fe₂O₄ is because of the strong magnetocrystalline anisotropy of Mn²⁺ ion.

When CNP are cooled to 5 K without an external applied magnetic field, the net magnetic moments of CNP align along their easy axis to obtain a local minimum of potential energy [35]. The magnetic anisotropy of nanoparticles behaves as an energy barrier to keep the magnetization direction in the easy axis. When the temperature increases from 5 K, the CNP are thermally activated and starts to align along the external magnetic field which results in an increase in magnetization with rising temperature. The magnetic anisotropy energy barrier overcome by thermal energy at blocking temperature (T_B) , leading to a superparamagnetic state. Both FCW and FCC magnetization follow the same path and decrease with rising temperature, they merge with the ZFC magnetization at the irreversible temperature (T_{ir}) . T_{irr} is related to the blocking of the larger (or agglomerated) particles in the system. Therefore, the particle size distribution and degree of inhomogeneity can be qualitatively estimated from the T_{irr} - T_B and the Mr/Ms[36]. Higher values of T_{irr} - T_B and the Mr/Ms can lead higher inhomogeneity. The magnetic characteristics of CNP are summarized in **Table 2.** The T_{irr} of Mn_{0.6} and Mn_{0.7} are found to be 278 K and 300 K, respectively. Fig. 2B shows the ZFC, FCC and FCW magnetizations of coated Mn_{0.7} for a range of external magnetic fields from 100 Oe to 500 Oe, and in the temperature range of 5-400 K. At applied magnetic field of 140 Oe, the T_B , T_{irr} , and their difference $(T_{irr}-T_B)$ of coated Mn_{0.7} CNP exhibit lower values than those of the corresponding uncoated particles, which can be associated with decreased attractive forces between the coated CNP. It can also be noticed that both T_B and T_{irr} shift towards lower temperature with an increase in applied magnetic field, which is characteristic of superparamagnetic particles [36].

3.5. Infrared spectroscopy confirms oleic acid and epoxy surface functionalization

The functional groups present on CNP, oleic acid, BADGE and surface modifies CNP are presented in **Fig. 3A-3C**. The FT-IR spectra of bare $Mn_xZn_{1-x}Fe_2O_4$ (x = 0.5, 0.6 and 0.7) CNP have a sharp peak at 560 cm⁻¹, which corresponds to the characteristic features of ferrites (Fe-O-Fe). Broad peaks at 3400 cm⁻¹ and 1642 cm⁻¹



Fig. 2. Low temperature magnetic characterizations of CNP **(A)** Zero field cooled (ZFC), field cooled cooling (FCC) and field cooled warmed (FCW) magnetization curves of Mn_{0.4}, Mn_{0.5}, Mn_{0.6} and Mn_{0.7} nanoparticles measured at an applied magnetic field of 140 Oe and temperature range of 5 K to 400 K. **(B)** ZFC, FCC and FCW magnetization curves of coated Mn_{0.7} in the temperature range of 5 K to 400 K at an applied magnetic field of 100 Oe, 140 Oe, 250 Oe and 500 Oe. Gray lines, red lines and the blue lines indicate the ZFC, FCC and FCW, respectively.



Fig. 3. Functionalization, surface modification and stability of curie nanoparticles.

A) FT-IR spectra endorses the ferrite phase formation of Mn_{0.5}Zn_{0.5}Fe₂O₄, Mn_{0.6}Zn_{0.4}Fe₂O₄ and Mn_{0.7}Zn_{0.3}Fe₂O₄. B) Functional group representation of OA (oleic acid), BADGE (bisphenol A diglycidyl ether) and OA+BADGE. C) FT-IR spectra of OA and BADGE modified CNP

(* represents the presence of OA and BADGE). **D**) Weight percent coating analyzed from the change in weight with temperature measured using TGA. **E**) Representation of thermal degradation pattern of clean OA, BADGE and OA+BADGE. **F**) DLS reveals the particle size stability with time of functionalized CNP in ethanol.



Fig. 4. Transmission electron micrograph (TEM) and particle size distribution of (A-B) Mn_{0.7}Zn_{0.3}Fe₂O₄ and (C-D) Mn_{0.7}Zn_{0.3}Fe₂O₄/OA/BADGE.

also observed for the stretching vibrations and H–O-H scissoring from free or absorbed hydroxide groups (**Fig. 3A**) [37,38]. **Fig. 3B** &**C** indicates the FT-IR spectra of clean OA, BADGE, mixture of OA+BADGE and $Mn_xZn_{1-x}Fe_2O_4/Oleic acid/BADGE$ (x = 0.5, 0.6 and 0.7). Peaks for the presence of OA and BADGE are observed to be very close and overlapped. The presence of oleic acid is confirmed by the two sharp peaks at 2852 cm⁻¹ and 2924 cm⁻¹ for the symmetric and asymmetric stretching vibrations of -CH₂ and -CH₃(**Fig. 3C**). The peaks at 1720 cm⁻¹ and 1295 cm⁻¹ are due to the C = O and C–O stretching of the carboxylic group in oleic acid. Bending vibrations of C–H in the methylene at 2962 cm⁻¹ and 2927 cm⁻¹ with the appearance of oxirane ring peaks at 830 cm⁻¹ and 725 cm⁻¹ confirms the BADGE functionalization [39,40].

3.6. OA and BADGE surface functionalization accounts for 20 wt.% CNP mass

The amount of oleic acid and BADGE coated on the nanoparticles is determined by thermogravimetric analysis. **Fig. 3D and E** illustrates the TGA pattern of bare CNP and $Mn_xZn_{1-x}Fe_2O_4$ /Oleic acid/BADGE, BADGE, OA and mixture of OA+BADGE, respectively. A slight weight loss temperature below 150 °C in samples with and without coating could be associated with water content (**Fig. 3D**). Oleic acid exhibits complete weight loss at 400 °C while BADGE and mixture of OA + BADGE remains with some percentage of residue (**Fig. 3E**). The functionalized CNP exhibit two main weight loss stages between 150 and 500 °C and one weight loss at higher temperature (> 500 °C). The first weight loss is associated with the removal of physically absorbed OA and BADGE molecules from the surface of the CNP. The second weight loss at 460 °C due to the strong binding force between CNP, OA and BADGE. The third weight loss at ~750 °C is probably due to the complete decomposition of surfactant. The total amount of OA+BADGE coating onto the CNP is found to be 23, 21 and 16% (starting weight% at room temperature - end weight% at 800 °C) for $Mn_{0.5}$, $Mn_{0.6}$ and $Mn_{0.7}$, respectively.

3.7. Colloidal stability of surface modified CNP

The colloidal stability of CNP is analyzed using dynamic light scattering (DLS). Generally, an equilibrium between attractive forces (magnetic dipole-dipole and Vander Waals) and repulsive forces (electrostatic and steric) results in stability of nanoparticles [41]. Hence, bare CNP are less stable due to the low electrostatic repulsive forces between them (**Figure S1, ESI**). The colloidal stability of the functionalized CNP is determined by monitoring hydrodynamic size (**Fig. 3F**). An optimum size of 200–400 nm and count rate between ~300 to ~500 kcps is observed, confirming the stability of CNP in ethanol.

3.8. Transmission electron micrograph endorses the particle size of surface functionalized $Mn_{0.7}$ from 9 to 25 nm

The particles size and morphology of bare and coated Mn_{0.7} particles are studied by TEM. **Fig. 4** represents the TEM micrographs of bare and coated CNP and corresponding particle size dis-



Fig. 5. Alternating magnetic field (AMF) heating curves for 5 - 30 wt% loading of functionalized CNP into bisphenol A diglycidyl ether (BADGE) at 140 Oe. A) Mn_{0.5}Zn_{0.5}Fe₂O₄/OA/BADGE. B) Mn_{0.6}Zn_{0.4}Fe₂O₄/OA/BADGE. C) Mn_{0.7}Zn_{0.3}Fe₂O₄/OA/BADGE. D) 15 wt% Mn_{0.5}Zn_{0.5}Fe₂O₄/OA/BADGE at AMF of 50, 80, 100 and 140 Oe.

tribution histograms. TEM images shows equiaxed individual particles with some agglomeration. The particle size of bare particles is in the range of 8 to 60 nm with an average particle size of 26 nm. The observed aggregation is due to magnetic interactions between the particles and the absence of a surfactant layer. The particle size of the coated particles is in the range of 9 to 25 nm, with an average particle size of 16 nm, reasonably close to the value obtained from the XRD data (13.5 nm).

3.9. In situ heating of epoxy resins to 160 °C within 5 min

CNP serve as AMF-to-thermal transducers to initiate thermosetting. To determine heating efficiency, functionalized CNP are dispersed in BADGE using ultrasonication and the solution is then placed within the induction coil at a frequency of 400 kHz and magnetic field strength ranging from 50 Oe to 140 Oe. The heating efficiency depends strongly on AC magnetic field strength, Tc and CNP content in BADGE. The temperature required for thermoset activation can be achieved within 5 min by controlling the strength of the applied magnetic field. The temperature increases until a plateau is reached at ~ 300 s. When magnetic nanoparticles suspended in an adhesive are subjected to an AC magnetic field, losses from the cyclic reversal of magnetization results in a conversion of electromagnetic energy to heat. The plateau temperature is a function of the AC magnetic field strength and concentration of CNP in the adhesive. Fig. 5A-D depicts the temperature versus time plots as a function of Mn/Zn ratio, percent loading, and field strength. The maximum temperature (T_{max}) of Mn_{0.7}Zn_{0.3}Fe₂O₄/OA/BADGE is higher than the corresponding values of Mn_{0.5}Zn_{0.5}Fe₂O₄/OA/BADGE, Mn_{0.6}Zn_{0.4}Fe₂O₄/OA/BADGE. In all three cases, the high loading of CNP in BADGE results in a higher maximum temperature. This maximum temperature is controlled by the Tc of the particles. The Mn_{0.7} particles exhibit the highest Tc (237 °C) and Ms (60 emu/g). A maximum temperature of 90 °C and 105 °C is observed for $Mn_{0.5}$ and $Mn_{0.6}$ particles, respectively. The temperature can also be controlled by tuning the AC magnetic field and time. Fig. 5D depicts the AMF heating of Mn_{0.7}Zn_{0.3}Fe₂O₄/OA/BADGE (15 wt.%) particles at field strengths ranging from 50 -140 Oe. The temperature of 48 °C, 90 °C, 118 °C and 134 °C correspond to AC magnetic fields of 50 Oe, 80 Oe, 100 Oe and 140 Oe, is achieved respectively. The maximum temperature is reached within 10 min. A maximum temperature of 140 °C and 160 °C is observed for 20 and 30 wt.% loading of $Mn_{0.7}$ particles in BADGE, respectively, at an AC field strength of 140 Oe. The curing temperature of commercial thermoset adhesives (TIM 813-HTC and ES558) and mixture of BADGE:DICY (100:12) are also within the range of 140 °C to 160 °C [17,42,43]. Hence, Mn_{0.7}Zn_{0.3}Fe₂O₄/OA/BADGE formulation is selected. To prevent scorching/ hotspot formation during adhesive curing, temperature and cure time is crucial. The AC field strength and time can be selected to achieve the desired temperature.

3.10. Highest specific absorption rate (SAR) of 5 Wg^{-1} is achieved for $Mn_{0.7}Zn_{0.3}Fe_2O_4/OA/BADGE$ at 140 Oe

The heating efficiency of the magnetic nanoparticles under AC magnetic field is defined by specific absorption rate (SAR) or specific loss power (SLP), expressed in Wg^{-1} [44]. SAR is defined as the amount of heat generated per unit mass of magnetic materials per unit time. It is calculated as per the Equation 1:

$$SAR = C_{solvent} m_{solvent} (dT/dt) / m_{CNP}$$
(1)

where $C_{solvent}$ is specific heat capacity of BADGE (346 J/mol K), m is the total mass of the solvent, m_{CNP} is the mass of the CNP and dT/dt is the temperature increase per unit time, that is, the initial slope of the temperature versus time curve. The average



Fig. 6. Representation of specific adsorption rate (SAR) for $Mn_{0.5}Zn_{0.5}Fe_2O_4/OA/BADGE$ ($Mn_{0.42}$), $Mn_{0.6}Zn_{0.4}Fe_2O_4/OA/BADGE$ ($Mn_{0.53}$) and $Mn_{0.7}Zn_{0.3}Fe_2O_4/OA/BADGE$ ($Mn_{0.63}$) (**A**) temperature increase per second with mass of curie nanoparticles (m_{CNP}). (**B**) SAR with maximum AMF heating (T_{max}) for different formulations.

SAR value is calculated for a range of loading of surface modified CNP. The temperature increase per time as a function of CNP mass is represented in Fig. 6. The SAR increases linearly with the magnetic field amplitude and the highest SAR (5 Wg⁻¹) is observed for Mn_{0.7}Zn_{0.3}Fe₂O₄/OA/BADGE at 400 kHz frequency and 140 Oe amplitude because of the high M_s of these CNP. The SAR of $Mn_{0.8}Zn_{0.2}Fe_2O_4$ at a frequency of 100 kHz and amplitude of 72 Oe was reported as low as 0.13 Wg^{-1} [45]. High SAR (57 Wg^{-1} (Mn + Fe)) is reported for $Mn_{0.62}Zn_{0.41}Fe_{1.97}O_4$ at higher frequency of 970 kHz and field amplitude of 80 Oe [46]. SAR of ~ 7.5 to 10 Wg⁻¹ of Mn-Zn ferrite is also reported at different frequency and magnetic field strength of 520 kHz and 166 Oe [47]. It is concluded that SAR depends on several parameters, such as sample preparation method, structural and magnetic properties of the nanoparticles, amplitude and frequency of the applied magnetic field, shape and size of nanoparticles, etc [48-53].

3.11. Magnetocuring additive cure commercial epoxy adhesives

A study of magnetocuring of epoxy adhesives with loading of CNP (15, 20 and 30 *wt.%*) in Permabond ES558, TIM 813-HTC or BADGE-DICY system to join various adherent materials (PMMA, ABS, glass and wood) was performed. Mn_{0.7}Zn_{0.3}Fe₂O₄/OA/BADGE particles with an average size of 14 nm are use due to their greater heating temperature range. The incorporation of functionalized CNP into adhesives is done by hand mixing within the liquid thermoset resins. The manufacture's recommended oven cure cycle is as follows: Permabond ES558; 75 min@130 °C, 60 min@150 °C, or 40 min@170 °C [54]. TIM 813HTC; 1h@100 °C + 1h@150 °C (recommended) or 30 min@150 °C (alternate) [42]. Control experiments of oven curing are performed at 160 °C for 1 h with a heating ramp rate of 10 °C/min.

Neat adhesives (ES558, TIM 813HTC and BADGE-DICY) are applied between the ABS coupons (see Fig. 7A) and determined as a negative control. With no magnetic additives, there is no heating within the AMF coil. Next, epoxy/CNP magnetocuring additives samples are placed within the induction coil, a rapid increase in temperature is observed. As CNP are exposed to the AMF, heat dissipation takes place due to Neel and Brown relaxation losses [55-57].

3.12. Steady lap shear adhesion strength is optimized at 20–30% loading

After AMF exposure, the samples are cooled to room temperatures and determined on a tensile tester under lap-shear mode with a 500 N load cell. A typical profile is displayed in **Fig. 7B** with the following formulation; 20 *wt.*%CNP+ES558 resin on ABS substrates.As **Fig. 7C** shows, loading% will affect the final temperature, epoxy crosslinking kinetics and lap shear adhesion. ES558 thermoset with 15 and 20 *wt.*% magnetocuring additives displays a lap-shear strength of 0.83 MPa, and 2 MPa, respectively, as shown in **Fig. 7C**. Both thermosets TIM 813HTC and BADGE-DICY(100:12) also bond ABS coupons to varying degrees (**Fig. 7D**).

30 *wt.*% loading of CNP into ES558 is assessed against natural, plastic and glass substrates typically found in industry (**Fig. 7E**). The highest lap-shear strength is achieved for wood (6.7 MPa) followed by glass (3.5 MPa), and plastics (<3 MPa), which roughly correlates to surface roughness and porosity. This does not represent the maximum adhesive bond, as the samples of plastic and glass have substrate failure modes. Wood displays interfacial debonding at the resin/substrate interface. Oven curing of ES558, TIM 813HTC and BADGE-DICY when compared to magnetocured samples displays little variation in lap shear strength for each product when magnetocuring is used (**Fig. 7F**).

3.13. Curie nanoparticles provide precise temperature control with no scorching

Sample surface and thermoset resin temperatures are determined. Surface temperatures are determined in real-time through a fibre optic thermocouple, internal thermoset resin temperature is simultaneously determined with a fibre optic thermocouple and infrared camera. **Fig. 8A** show the surface temperature of four different substrates during magnetocuring of ES558 with 20 *wt.%* loading of CNP. Surface temperature never exceeds 60–65°C for the 1–3 mm thick specimens, despite internal resin temperatures of 140 °C (**Fig. 8B**). No overheating is observed. Images captured by the FL-IR camera during AMF curing of 20 *wt.%* loaded ES558, also confirms the local heating.

Resin curing is further analysed by thermogravimetric analysis and dynamic scanning calorimetry (DSC). Incomplete curing of the resin can be identified by the presence of a peak at the activation temperature. **Fig. 8C** displays the DSC spectra of uncured ES558 resin (positive control) and magnetocured CNP composites. A single peak for the thermoset activation temperature is observed at 150 °C for the positive control but is absent in the magnetocured composites. The overlapping TGA curves of thermocured vs. magnetocured sample ssuggests no scorching of the magnetocured samples. A late peak after 500 °C can be seen in both clean and cured adhesive, which is due to oxidation and pyrolysis.



Fig. 7. Mechanical and adhesion properties of commercial and homemade epoxy system. **A)** (i) Representation of digital model (CAD) used to print ABS coupons by 3D printer (ii) ABS coupons with magneto-adhesive cured under AMF (iii) Organised setup for mechanical test (iv) Bond/ABS breaking after mechanical test. **B)** Stress-strain curve of cured ES558@ABS with 20 *wt%* CNP. **C)** Lap shear adhesion strength of magneto-cured ES558@ABS with different loading of CNP. **D)** Lap shear adhesion strength of different magneto-cured adhesives@ABS with 30 *wt%* loading of CNP. **E)** Lap shear adhesion strength of magneto-cured ES558 @ different adherent materials with 30 *wt.%* loading of CNP. **F)** Lap shear adhesion strength of oven and AMF cured adhesives@Glass. Data presented as mean \pm SD, n = 3 and significance is determined by one-way ANOVA, at p < 0.05.

3.14. Infrared spectroscopy indicates epoxy ring opening and a rigid matrix

The degree of crosslinking in ES558 is qualitatively consistent with the infrared spectroscopy results. **Fig. 8D** compares uncured resin and the magnetocured CNP composites. Bending vibrations of C–H in methylene (2923 cm⁻¹) and stretching vibrations of C = C in aromatic ring (1602 and 1508 cm⁻¹) are both diminished, which is evidence of a rigid crosslinked resin. The disappearance of the peaks at 915, 812 and 752 cm⁻¹ indicates the opening of epoxy rings to form ether cross links.

4. Discussion

A platform magnetocuring technology is developed to cure commercial thermoset resins via exposure to alternating magnetic fields. The in situ thermal kinetics, particle loading, field strength, and nature of the resins can be used to optimize performance of this technology. Overheating prevention and colloidal stability in polar organic environments are advantages of this technology. Previous demonstrations of magnetocuring adhesives observed resin scorching due to runaway heating from a combination of particlesize dependent thermal kinetics and agglomeration of metal oxide particles organic resins [19-22,58]. The CNP designed in the present work "switch off" above the Curie temperature, no feedback electronics is required. The aggregation of high surface energy curie CNP, chemical reactivity and dispersibility in solution was controlled by coating the CNP with functional shells of resin based coatings for ease of dispersion. The coating is performed by post-synthesis grafting of oleic acid on CNP via covalent bonds. The oleic acid coated particles are grafted with epoxy monomers (BADGE) to improve thermoset initiation and like-dissolves-like particle miscibility in one-component epoxy adhesives. The interaction of Fe³⁺ ions and hydroxyl groups present at the surface of particles can interact with the polar groups of oleic acid and BADGE, providing colloidal stability in epoxy [59,60]. FT-IR spectra and TGA analysis reveals the proper coating with oleic acid and BADGE onto the surface of particles. This may be due to the interaction between oleic acid and BADGE (Fig. 3C). Long-term colloidal stability of functionalized CNP in BADGE was observed. Particles settled down after 1-2 h but dispersed well again after sonication/ vortex for few min.

Heating in CNP arise from relaxation effects, i) the Brownian mechanism of relaxation, in which the magnetic moment is locked to the crystal axis and therefore the entire particle rotates with the magnetic field, ii) the Neel relaxation mechanism, in which



Fig. 8. A) Surface temperature during AMF curing @ different adherents. B) The temperature of magnetoadhesive curing in AMF process measured by fiber optic thermocouple and FLIR camera (size bar: 10 mm). C) TGA-DSC analysis of clean, oven and AMF cured ES558. D) FTIR-ATR spectra of uncured ES558 and magnetocured CNP composite.

the magnetic moment rotates within the particle in an external magnetic field [60-63]. ZFC-FC measurements confirm that the majority of the particles exhibit superparamagnetic behavior at room temperature. Moreover, Mn_{0.7} particles, which were used for magnetocuring, possess a low H_c (2.4 Oe), low M_r/M_s (0.0038) and CNP embedded in a highly viscous/ solid matrix (adhesive). Therefore, the dominant heating mechanism should be the result of relaxation processes, preferably Neels relaxation. The presence of nonzero coercivity and nonzero M_r/M_s measured at room temperature can result in relatively small hysteresis losses. Furthermore, the heating ability also depends on the properties of the nanomaterials, such as particle size, magnetization and magnetic anisotropy, strength of applied magnetic field (H) and frequency (f) [64,65]. Owing to the high Curie temperature and magnetization of Mn_{0.7} particles, highest heating of CNP was observed for the Mn_{0.7}Zn_{0.3}Fe₂O₄/OA/BADGE particles. In addition to high Ms and Tc, Mn_{0.7} nanoparticles exhibit higher magnetic moment than those of Mn_{0.4}, Mn_{0.5} and Mn_{0.6}, revealed from magnetization versus temperature curves at applied field of 100 and 140 Oe (Figure S2, ESI). The SAR of these functionalized CNP dispersed in BADGE was found to be 5 Wg^{-1} . The variation in SAR with mol% of Mn in $Mn_xZn_{1-x}Fe_2O_4$ might be due to the change in *Ms* and therefore a notable change in the dipolar interparticle interactions. Further, the product of the frequency and the magnetic field amplitude $(H \times f)$ can decide whether the field/frequency is in safe zone of medical application or not. Brezovich criterion sets a safety threshold to use the AC magnetic field for human exposure by limiting the product of frequency and amplitude to 5×10^8 Am⁻¹s⁻¹[66]. The use of high-frequency and high-amplitude AMF produce eddy currents in conducting media which can results in nonspecific heating or damage the human body. Other literature suggests that Hf factor should not be more than 5 \times $10^9 \mbox{ Am}^{-1} \mbox{s}^{-1}$ for medical applications, considering that smaller field exposure must be better

tolerated by the patients. [67] The maximum *Hf* for our system is 4.4×10^9 Am⁻¹s⁻¹, which suggest that curing using the present approach can be applied for medical translation.

AMF heating of CNP results in crosslinking of one-component epoxy adhesives through in situ heating. Complete curing of ES558 magnetoadhesive was achieved by applying 140 Oe of magnetic field strength for 1 h at a fixed frequency of 400 kHz. The structure activity relationship were studied for different loading of CNP, adhesive systems, adherent and controlled with oven-curing. The increase in the loading of CNP increases the shear strength upto 3 MPa @ ABS. The increased shear strength was due to the interactions between the Curie nanoparticles and the adhesives. The interaction was facilitated by the presence of the BADGE coating on the surface of Curie nanoparticle. This results in greater stress transfer between the Curie nanoparticles and the matrix resulting in increased strength.

The strongest adhesion was observed for wood due to the pores on the wood surface. The Magnetoadhesive can easily penetrate into the porous structure of wood during magnetocuring process, which results in high lap shear strength. The maximum surface temperature was less than 65 °C irrespective of the type of adherent, magnetocuring can locally heat the joining part while preventing scorching.

A few of the limitations to scope and magnetocuring strategy should be noted. Undeniably, magnetic properties of CNP are strongly depend on the synthesis procedures and SAR values are mainly governed by the evaluating parameters like magnetic field amplitude, frequency and CNP concentration. Due to the limitation of current AMF instrument, maximum field of 140 Oe can be applied, which offers the SAR upto 5 Wg⁻¹. Although, high viscosity of the media can be an another important considerable parameter as it will affect the heat generation mechanism of CNP by Neel and Brown relaxations [68,69]. These properties are strongly speckled from one report to another. Furthermore, the current magnetocuring approach is limited to the non-metallic substrates. The described oleic acid and epoxy functionalized CNP are committed to the magnetocuring of one-component epoxy adhesives, but it can also be further functionalized or decorated with various functional materials as per the requirement. AMF heating results illustrates that the cap of magnetic field (140 Oe) and frequency (400 kHz) ceases the heating of CNP below Curie temperature. Increase in the magnetic field could leads to increase the AMF heating upto the Curie temperature control point. In order to resolve these limitations, further scrutinizes will be focused on the magnetic measurements of these CNP under AC magnetic field.

5. Conclusion

A series of $Mn_xZn_{1-x}Fe_2O_4$ nanoparticles were developed with a Curie temperature range from 80 to 239 °C. Oleic acid/BADGE functionalized CNP dispersed well in BADGE and provided colloidal stability in epoxy and one-component epoxy adhesives. 20 - 30 wt.% loading of $Mn_{0.7}Zn_{0.3}Fe_2O_4/OA/$ BADGE into ES558 was found to be suitable for magnetocuring of one-component epoxy adhesives without scorching. Mechanical testing results in a lap shear strength of upto 6.69 MPa for wood samples. The onecomponent magnetocuring adhesive allows us to develop or modify the existing formulations with CNP as filler/modifier. This technology is highly relevant to various applications in the field of sports, automotive and aerospace components and systems.

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. The authors declare no conflict of interest.

CRediT authorship contribution statement

Richa Chaudhary: Methodology, Investigation, Formal analysis, Writing - original draft. **Varun Chaudhary:** Methodology, Formal analysis, Writing - review & editing. **Raju V. Ramanujan:** Supervision, Funding acquisition, Writing - review & editing. **Terry W.J. Steele:** Conceptualization, Supervision, Funding acquisition, Writing - review & editing.

Acknowledgements

This work was financially supported by the Agency for Science, Technology and Research (A*Star) IRG17283008 "Microprocessorbased methods of composite curing. The Facility for Analysis, Characterization, Testing is also acknowledged.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.apmt.2020.100824.

References

- https://www.marketwatch.com/press-release/instant-adhesive-market-2019global-industry-size-growth-segments-revenue-manufacturers-and-2024forecast-research-report-2019-09-03.
- A.M.G. Breifing, https://www.giiresearch.com/report/tbrc535848-traditionaladhesive-dressings-market-global.html, Business Research Company, (2017).
 S. Gillissen, E. Nelis, G.V. Wuytswinkel, M.D. Pater, C. Chih- Min, V. Buffa,
- [3] S. Gillissen, E. Nelis, G.V. Wuytswinkel, M.D. Pater, C. Chih- Min, V. Buffa, W.O. Hara, X. Bo, S. Jayesh, Low Temperature Snap Cure Thermoset Adhesives with Good Worklife, in: 5th International Conference on Polymers and Adhesives in Microelectronics and Photonics, IEEE, 2005 166-170.

- [4] C. Dispenza, S. Alessi, G. Spadaro, Carbon Fiber Composites Cured by γ -Radiation-Induced Polymerization of an Epoxy Resin Matrix, Adv. Polym. Technol. 27 (2008) 163–171.
- [5] X.K.D. Hillewaere, R.F.A. Teixeira, L.-T.T. Nguyen, J.A. Ramos, H. Rahier, F.E. Du Prez, Autonomous Self-Healing of Epoxy Thermosets with Thiol-Isocyanate Chemistry, Adv. Funct. Mater. 24 (2014) 5575–5583.
- [6] S. Rengasamy, V. Mannari, Development of Soy-Based UVCurable Acrylate ligomers and Study of Their Film Properties, Prog. Org. Coat. 76 (2013) 78–85.
- [7] S.C. Ligon-Auer, M. Schwentenwein, C. Gorsche, J. Stampfl, R. Liska, Toughening of Photo-Curable Polymer Networks: a Review, Polym. Chem. 7 (2016) 257–286.
- [8] R. Rizzolo, D. Walczyk, J. Kuppers, Rapid Consolidation and Curing of Advanced Composites with Electron Beam Irradiation, in: 30th Technical Conference of the American-Society-for-Composites, Destech Publications, Inc, Lancaster, 2015, pp. 25–38.
- [9] V. Mogal, V. Papper, A. Chaurasia, G. Feng, R. Marks, T.W.J Steele, Novel On-Demand Bioadhesion to Soft Tissue in Wet Environments, Macromol. Biosci. 4 (2014) 478–484.
- [10] J. Ping, F. Gao, J.L. Chen, R.D. Webster, T.W.J Steele, Adhesive curing through low-voltage activation, Nat. Commun. 6 (2015) 1–9.
- [11] V.T. Mogal, C.S. Yin, R. O'rorke, S. Boujday, C. Méthivier, S.S. Venkatraman, T.W.J. Steele, Tuning model drug release and soft-tissue bioadhesion of polyester films by plasma post-treatment, ACS Appl. Mater. Interfaces 8 (2014) 5749–5758.
- [12] M. Singh, C.S. Yin, S.J. Page, Y. Liu, G. Wicaksono, R. Pujar, S.K. Choudhary, G.U. Kulkarni, J. Chen, J.V. Hanna, R.D. Webster, Synergistic Voltaglue adhesive mechanisms with alternating electric fields, Chem. Mater. 32 (2020) 2440–2449.
- [13] J. Bauer, M. Bauer, Cyanate Ester Based Resin Systems for Snap Cure Applications, Microsyst. Tech.8 (2002) 58–62.
- [14] A. Vitale, G. Trusiano, R. Bongiovanni, UV-curing of adhesives: a critical review, Rev. Adhes. Adhes. 2 (2017) 105–161.
- [15] M. Laksin, Electron Beam Curing in Packaging-Challenges and Trends, RadTech. Rep.24 (2010) 2.
- [16] J.G. Drobny, Radiation Technology for Polymers, CRC press, 2010.
- [17] A. Pizzi, K.L. Mittal, Handbook of Adhesive Technology, Revised and Expanded, Taylor & Francis, 2003.
- [18] K.J. Miller, K.N. Collier, H.B. Soll-Morris, R. Swaminathan, M.E. McHenry, Induction heating of FeCo nanoparticles for rapid rf curing of epoxy composites, J. Appl. Phys. (2009) 105.
- [19] S. Ye, N.B. Cramer, B.E. Stevens, R.L. Sani, C.N. Bowman, Induction Curing of Thiol-Acrylate and Thiol-Ene Composite Systems, Macromolecules 44 (2011) 4988–4996.
- [20] J.W. Hubbard, F. Orange, M.J. Guinel, A.J. Guenthner, J.M. Mabry, C.M. Sahagun, C. Rinaldi, Curing of a bisphenol E based cyanate ester using magnetic nanoparticles as an internal heat source through induction heating, ACS Appl. Mater. Interfaces 5 (2013) 11329–11335.
- [21] W. Suwanwatana, S. Yarlagadda, J.W. Gillespie Jr., Hysteresis heating based induction bonding of thermoplastic composites, Compos. Sci. Tech. 11-12 (2006) 1713–1723.
- [22] M. Ma, Q. Zhang, J. Dou, H. Zhang, D. Yin, W.G. Zhou, Fabrication of one-dimensional Fe3O4/P (GMA–DVB) nanochains by magnetic-field-induced precipitation polymerization, J. Colloid Interface Sci. 1 (2012) 339–344.
- [23] A.S. Ahmed, R.V. Ramanujan, Curie temperature controlled self-healing magnet-polymer composites, J. Mater. Res. 30 (2015) 946–958.
- [24] V. Chaudhary, Z. Wang, A. Ray, I. Sridhar, R.V. Ramanujan, Self pumping magnetic cooling, J. Phys. D Appl. Phys. (2016) 50.
- [25] M.P. Edward, Epoxy Adhesive Formulations, McGrwa-Hill, New York, 2006.
- [26] R.A. Pethrick, Composite to metal bonding in aerospace and other applications, in: M.C Chaturvedi (Ed.), Welding and Joining of Aerospace Materials, Woodhead Publishing, 2012, pp. 288–319.
- [27] R. Hao, R. Xing, Z. Xu, Y. Hou, S. Gao, S Sun, Synthesis, Functionalization, and Biomedical Applications of Multifunctional Magnetic Nanoparticles, Adv. Mater. 22 (2010) 2729–2742.
- [28] A. Zapata, G. Herrera, Effect of zinc concentration on the microstructure and relaxation frequency of Mn–Zn ferrites synthesized by solid state reaction, Ceram. Int. 7 (2013) 7853–7860.
- [29] R. Gimenes, M.D. Baldissera, M.R.A.D. Silva, C.A.D. Silveira, D.A.W. Soares, L.A. Perazolli, M.R.D. Silva, M.A. Zaghete, Structural and magnetic characterization of MnxZn1- xFe2O4 (x= 0.2; 0.35; 0.65; 0.8; 1.0) ferrites obtained by the citrate precursor method, Ceram. Int, 1 (2012) 741-746.
- [30] I.C. Masthoff, A. Gutsche, H. Nirschl, G. Garnweitner, Oriented attachment of ultra-small Mn (1-x)ZnxFe2O4 nanoparticles during the non-aqueous sol-gel synthesis, CrystEngComm 12 (2015) 2464–2470.
- [31] K.L. McNerny, Y. Kim, D.E. Laughlin, M.E. McHenry, Chemical synthesis of monodisperse γ-Fe-Ni magnetic nanoparticles with tunable Curie temperatures for self-regulated hyperthermia, J. Appl. Phys. 107 (2010).
- [32] A. Belayachi, J.L. Dormann, M. Noguès, Critical analysis of magnetically semi-disordered systems: critical exponents at various transitions, J. Phys. 10 (1998) 1599-1619.
- [33] K. Fabian, V.P. Shcherbakov, S.A. McEnroe, Measuring the Curie temperature, Geochemistry, Geophysics, Geosystems 14 (2013) 947–961.
- [34] R. Arulmurugan, G. Vaidyanathan, S. Sendhilnathan, B. Jeyadevan, Mn–Zn ferrite nanoparticles for ferrofluid preparation: study on thermal-magnetic properties, J. Magn. Magn. Mater. 298 (2006) 83–94.

- [35] C. Murugesan, G. Chandrasekaran, Structural and Magnetic Properties of Mn1-xZnxFe2O4 Ferrite Nanoparticles, J. Superconduct. Novel Magnet. 29 (2016) 2887–2897
- [36] S. Dey, R. Mondal, S.K. Dey, S. Majumder, P. Dasgupta, A. Poddar, V.R. Reddy, S Kumar, Tuning magnetization, blocking temperature, cation distribution of nanosized Co0.2Zn0.8Fe2O4 by mechanical activation, J. Appl. Phys. 118 (2015) 103905.
- [37] R.D. Waldron, Infrared spectra of ferrites, Phys. Rev. 99 (1955) 1727-1735.
- [38] M. Kaiser, Effect of preparation condition on nickel zinc ferrite nanoparticle: a comparison between sol-gel, J. Alloys Compd. 468 (2009) 15-21.
- [39] M.G. González, J.C. Cabanelas, J. Baselga, Applications of FTIR on epoxy resins-identification, monitoring the curing process, phase separation and water uptake, Infrared Spectroscopy-Materials Science, Eng. Tech. 2 (2012) 261 - 284
- [40] E.V. Barreiro, F.F. López, A. Jover, F. Meijide, E. Rodríguez, J.V. Tato, Paramagnetic epoxy resin, Express Polym. Lett. 11 (2017) 60.
- I. Sharifi, H. Shokrollahi, S. Amiri, Ferrite-based Magnetic Nanofluids Used in [41] Hyperthermia Applications, J. Magn. Magn. Mater. 324 (2012) 903–915. [42] TIMTRONICS 813HTC, https://timtronics.com/wp-content/uploads/2018/03/
- TIM-813HTC TDS.pdf.
- [43] Permabond ES558, https://www.permabond.com/wp-content/uploads/2016/ 04/ES558_TDS.pdf, (25 October 2019).
- [44] G. Cotin, F. Perton, C. Blanco-Andujar, B. Pichon, D. Mertz, S. Bégin-Colin, Design of Anisotropic Iron-Oxide-Based Nanoparticles for Magnetic Hyperthermia, Nanomaterials for Magnetic and Optical Hyperthermia Applications, Elsevier, 2019.
- [45] T.M. Elkhova, A.K. Yakushechkina, A.S. Semisalova, Y.K. Gun'ko, Y.I. Spichkin, A.P. Pyatakov, K.I. Kamilov, N.S. Perov, A.M. Tishin, Heating of Zn-substituted manganese ferrite magnetic nanoparticles in alternating magnetic field, Solid State Phenomena, Trans. Tech. Pub. Ltd. 233 (2015) 761-765.
- [46] J. Stergar, Z. Jirák, P. Veverka, L. Kubíčková, T. Vrba, J. Kuličková, K. Knížek, F. Porcher, J. Kohout, O. Kaman, Mn-Zn ferrite nanoparticles coated with mesoporous silica as core material for heat-triggered release of therapeutic agents, . Magn. Magn. Mater. 475 (2019) 429-435.
- [47] A. Jordan, P. Wust, H. Fählin, W. John, A. Hinz, R. Felix, Inductive heating of ferrimagnetic particles and magnetic fluids: physical evaluation of their potential for hyperthermia, Int. J. Hypertherm. 1 (1993) 51-68.
- [48] E. Kita, T. Oda, T. Kayano, S. Sato, M. Minagawa, H. Yanagihara, M. Kishimoto, C. Mitsumata, S. Hashimoto, K. Yamada, N. Ohkohchi, Ferromagnetic nanoparticles for magnetic hyperthermia and thermoablation therapy, J. Phys. D Appl. Phys. 43 (2010) 474011.
- [49] P. De la Presa, Y. Luengo, M. Multigner, R. Costo, M.P. Morales, G. Rivero, A. Hernando, Study of heating efficiency as a function of concentration, size, and applied field in γ -Fe2O3 nanoparticles, J. Phys. Chem. C 116 (2012) 25602-25610.
- [50] M.A. Gonzalez-Fernandez, T.E. Torres, M. Andrés-Vergés, R. Costo, P. De la Presa, C.J. Serna, M.P. Morales, C. Marquina, M.R. Ibarra, G.F. Goya, Magnetic nanoparticles for power absorption: optimizing size, shape and magnetic properties, J. Solid State Chem. 182 (2009) 2779-2784.
- [51] N.K. Prasad, K. Rathinasamy, D. Panda, D. Bahadur, Mechanism of cell death induced by magnetic hyperthermia with nanoparticles of γ -Mn x Fe 2-x O 3 synthesized by a single step process, J. Mater. Chem. 17 (2007) 5042-5051.

- [52] C. Martinez-Boubeta, K. Simeonidis, A. Makridis, M. Angelakeris, O. Iglesias, P. Guardia, A. Cabot, L. Yedra, S. Estradé, F. Peiró, Z. Saghi, Learning from nature to improve the heat generation of iron-oxide nanoparticles for magnetic hyperthermia applications, Sci. Rep. 3 (2013) 1652.
- [53] Y. Piñeiro-Redondo, M. Bañobre-López, I. Pardiñas-Blanco, G. Goya, M.A. López-Quintela, J. Rivas, The influence of colloidal parameters on the specific power absorption of PAA-coated magnetite nanoparticles, Nanoscale Res. Lett. 6 (2011) 383.
- [54] Permabond ES558, https://www.permabond.com/wp-content/uploads/2016/ 04/ES558_TDS.pdf, (25 October 2019).
- [55] L. Néel, Influence of thermal fluctuations on the magnetic after-effect of solid ferromagnetics in the Rayleigh region, J. Phys. Radium 11 (1950) 49-61.
- [56] W.F. Brown Jr, Thermal fluctuations of a single-domain particle, Phys. Rev. 130 (1963) 1677.
- [57] K.L. McNerny, Y. Kim, D.E. Laughlin, M.E. McHenry, Chemical synthesis of monodisperse γ -Fe–Ni magnetic nanoparticles with tunable Curie temperatures for self-regulated hyperthermia, J. Appl. Phys. 9 (2010) 09.
- [58] K.J. Miller, K.N. Collier, H.B. Soll-Morris, R. Swaminathan, M.E. McHenry, Induction heating of FeCo nanoparticles for rapid rf curing of epoxy composites, J. Appl. Phys. 105 (2009) 07e714.
- [59] W. Wang, C. Zang, Q. Jiao, Wear-resistant and electromagnetic absorbing behaviors of oleic acid post-modified ferrite-filled epoxy resin composite coating, J. Magn. Magn. Mater., 378261-266.
- [60] R.E. Rosensweig, Heating magnetic fluid with alternating magnetic field, J. Magn. Magn. Mater. 252 (2002) 370-374.
- [61] V. Chaudhary, Y. Zhong, H. Parmar, V. Sharma, X. Tan, R.V. Ramanujan, Mechanochemical synthesis of iron and cobalt magnetic metal nanoparticles and iron/calcium oxide and cobalt/calcium oxide nanocomposites, Chemistry-Open 8 (2018) 590-598.
- [62] P. Lemal, S. Balog, L. Ackermann-Hirschi, P. Taladriz-Blanco, A.M. Hirt, B. Rothen-Rutishauser, M. Lattuada, A. Petri-Fink, Simple and fast evaluation of relaxation parameters of magnetic nanoparticles, J. Magn. Magn. Mater. 499 (2020) 166176.
- [63] M.N. Halgamuge, T. Song, Optimizing Heating Efficiency of Hyperthermia: specific Loss Power of Magnetic Sphere Composed of Superparamagnetic Nanoparticles, Progr. Electromagn. Res. 87 (2020) 1-17.
- [64] C. Martinez-Boubeta, K. Simeonidis, A. Makridis, M. Angelakeris, O. Iglesias, P. Guardia, A. Cabot, L. Yedra, S. Estrade, F. Peiro, Z. Saghi, Learning from nature to improve the heat generation of iron-oxide nanoparticles for magnetic hyperthermia applications, Sci. Rep. 3 (2013) 1652.
- [65] R. Kappiyoor, M. Liangruksa, R. Ganguly, I.K. Puri, The effects of magnetic nanoparticle properties on magnetic fluid hyperthermia, J. Appl. Phys. 108 (2010) 094702
- [66] I.A. Brezovich, Low frequency hyperthermia: capacitive and ferromagnetic thermoseed methods, Med. Phys. Monogr. 16 (1988) 82-111.
- [67] R. Hergt, S. Dutz, Magnetic particle hyperthermia-biophysical limitations of a visionary tumour therapy, J. Magn. Magn. Mater. 311 (2007) 187-192
- [68] S. Bae, S.W. Lee, Y. Takemura, Applications of Ni Fe2O4 nanoparticles for a hyperthermia agent in biomedicine, Appl. Phys. Lett. 89 (2006) 252503.
- [69] E.Y.K. Ng, S.D. Kumar, Physical mechanism and modeling of heat generation and transfer in magnetic fluid hyperthermia through Néelian and Brownian relaxation: a review, Biomed. Eng. Online 16 (2017) 36.