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Polydopamine-Mediated Silver and Nickel Metallization of Phase Change Microcapsules for Multifunctional Flexible Epoxy Composites

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ABSTRACT

This work reports an environmentally friendly method to metallize phase change material (PCM) microcapsules with thin silver or nickel coatings, using polydopamine (PDA) as a bioinspired adhesion promoter, and their incorporation into flexible epoxy matrices to produce composites with enhanced thermomechanical properties. Commercial paraffin microcapsules were first coated with an ultrathin PDA film via a simple wet chemical process, followed by electroless metallization. Silver treatment produces a discontinuous, cluster-like coating with minimal mass addition (2 wt%), preserving 98% of the original phase change enthalpy (222 J/g vs. 225 J/g for neat PCMs) while maintaining excellent interfacial adhesion with the epoxy matrix. Nickel treatments create more uniform, continuous coatings with progressively higher mass addition (15 and 28 wt% for 2- and 8-min treatments, respectively), resulting in remarkable thermal diffusivity enhancement (from 0.22 to 0.42 mm²/s for powder beds at room temperature) but reduced matrix adhesion due to shielding of the chemically active PDA layer. The phase change capability is successfully preserved across all treatments, with melting/crystallization temperatures remaining stable around 45°C/32°C. When incorporated into flexible epoxy, metallized PCMs provide increased diffusivity and heat storage, retaining mechanical strength and deformability, with strain at break values of 20%–60%. These results establish the considerable potential of metallized PCM microcapsules as multifunctional fillers for advanced thermal management applications in electronics, thermal interface materials, and smart thermoregulating packaging.

1 | Introduction

Phase change materials (PCMs) have emerged as an important technology for thermal energy storage (TES) and management, thanks to their ability to absorb, store, and release large amounts of latent heat during phase change at nearly constant temperature [1, 2]. Among the various classes of PCMs, organic solid–liquid PCMs (paraffins, poly(ethylene glycol)s, fatty acids/alcohols, etc.) are interesting for applications in the low-medium temperature range (0°C–100°C), thanks to their relatively high phase change enthalpy per unit mass, congruent melting, minimal

supercooling, high chemical stability, non-corrosiveness, and cost-effectiveness [3, 4]. However, their two main limitations are their low thermal conductivity [5, 6] and the need to be confined to prevent leakage in the melted state [7–9].

One of the most effective strategies to address these challenges, and especially the leakage issue, is microencapsulation, which consists in the inclusion of PCM within micrometric polymeric or inorganic shells, stable in the working temperature interval [10, 11]. Other than preventing the PCM leakage, this approach also inhibits undesired reactions with the surrounding

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environment, accommodates volume changes during phase transitions, and increases the specific surface area of the storage medium, thereby enhancing the thermal exchange efficiency [12]. Moreover, the resulting microencapsulated PCMs can be readily dispersed in various matrices, facilitating their integration into structural and functional materials [13]. In this case, the encapsulant material can be designed to be compatible with the surrounding matrix and reach optimal interfacial adhesion. This can be done either through in situ modifications during encapsulation or as a subsequent step after the shell is formed.

The incorporation of microencapsulated PCMs into flexible polymer composites has enabled the production of multifunctional materials that combine interesting mechanical properties with thermal management capabilities. These composites show particular promise for applications in food and electronics packaging [14–16], thermal interface materials [17, 18], smart textiles [19–21], building envelope systems [22, 23], and adhesive formulations, where both structural integrity and temperature regulation are required [24]. Flexible epoxy matrices are especially attractive for such applications due to their excellent processability, chemical resistance, damping, and adhesive properties [25, 26].

A key factor determining the performance of composites containing PCMs is the quality of the filler-matrix interface [27]. It is well known that, in composites in general, a suboptimal interfacial adhesion can lead to a decrease in thermal conductivity and mechanical properties. This is especially true with PCM-containing composites designed to operate under thermal cycling conditions, which induce volume expansion and contractions in the PCM and further deteriorate the mechanical and thermal continuity [28, 29]. The most commonly used shell materials for commercial PCM microcapsules are melamine-formaldehyde (MF) and melamine-urea-formaldehyde (MUF) resins, which, despite their thermal stability and cost-effectiveness, exhibit limited surface reactivity due to the lack of functional groups [30]. This chemical inertness poses challenges for achieving strong interfacial bonding with polymer matrices [31, 32].

To address this limitation, our research group has extensively investigated the use of polydopamine (PDA), a bioinspired synthetic polymer, as an adhesion promoter between PCM microcapsules and epoxy matrices [30, 33, 34]. PDA, formed through the oxidative self-polymerization of dopamine, mimics the adhesive proteins found in mussels and demonstrates remarkable versatility in binding to a wide variety of surfaces, including chemically inert substrates [35–39]. Its versatile functional properties have made PDA an interesting material to combine with PCMs in various forms for many applications, including water desalination [40], solar thermal conversion and storage [7, 41], and personal cooling suits [42]. The unique chemistry of PDA, featuring catechol and amine functional groups, enables both covalent and non-covalent interactions with epoxy resins, significantly enhancing interfacial adhesion. Our previous work demonstrated that PDA coating not only improves mechanical interlocking through increased surface roughness but also enables covalent bonding with oxirane groups during epoxy curing, resulting in substantial improvements in the mechanical properties of the final composites while preserving the TES capability of the PCM [30, 33].

Although PDA modification successfully addresses interfacial adhesion challenges, the inherently low thermal conductivity of organic PCMs remains a limiting factor for many thermal management applications. Metallization of PCM microcapsules represents a promising approach to enhance thermal conductivity while potentially introducing additional functionalities, such as electrical conductivity and electromagnetic responsiveness. Our recent work demonstrated that PDA-coated microcapsules can serve as an excellent platform for electroless metallization, with the PDA layer acting as both an adhesion promoter and a reducing agent for metal deposition. Specifically, we showed that nickel metallization of PDA-coated paraffin microcapsules significantly enhanced thermal diffusivity while preserving phase change functionality and enabled rapid heating through microwave radiation [34].

Building upon these studies, the present work aims to expand the metallization approach beyond nickel to include silver coatings and to systematically evaluate the performance of both Ag- and Ni-metallized microcapsules as multifunctional fillers in flexible epoxy composites. The specific objectives include (i) investigating the morphological characteristics of Ag-metallized PDA-coated microcapsules and comparing them with Ni treatments of varying durations, (ii) characterizing the metallized microcapsules in terms of TES properties and thermal transport behavior, and (iii) preparing flexible epoxy composites containing these advanced fillers at various loadings and evaluating the thermal, mechanical, and processing characteristics.

The methodology involves the surface modification of commercial microencapsulated PCMs through ultrathin PDA deposition, followed by electroless metallization with either silver or nickel under different processing conditions. The resulting metallized microcapsules were then incorporated into a flexible epoxy matrix to produce composites with enhanced thermal and mechanical performance. This integrated approach aims to demonstrate the potential of metallized PCM microcapsules as next-generation multifunctional fillers for advanced heat management applications.

2 | Materials and Methods

2.1 | Materials

Paraffin microcapsules Microtek MPCM43D (MCs) were purchased from Microtek Laboratories (Dayton, OH, USA). They are made of a paraffin wax core, the PCM phase, and a melamine-formaldehyde resin shell (average diameter 17–20 μm , melting temperature 43°C, melting enthalpy 190–200 J/g). The bi-component epoxy system Elan-tech EC251/W242 NF was kindly provided by Elantas Europe S.r.l. (Collecchio, Italy). Dopamine hydrochloride (99%, DA) was purchased from Thermo Fisher GmbH, Germany. For the TRIS buffer, 2-amino-2 (hydroxymethyl) propane-1,3-diol (99.9%, Sigma-Aldrich, St. Louis, MI, USA) was first dissolved in deionized water (0.055 $\mu\text{S}/\text{cm}$) and then adjusted to pH 8.5 with hydrochloric acid (37%, VWR International, France). For the production of the metallization bath series, the baths UDIQUE 879 W, UDIQUE accelerator 8810, UDIQUE 891 nickel, and UDIQUE 893 stabilizer from MacDermid Enthone GmbH (Germany) were employed in accordance with their usage instructions.

TABLE 1 | List of the prepared samples with nominal compositions and duration of the Ni treatment (short = 2 min; long = 8 min).

Sample	Epoxy resin (B + H) (wt%)	Microcapsules (wt%)	Coating
MC	0	100	As received
MC-Ag	0	100	PDA + Ag
MC-NiS	0	100	PDA + Ni (short treatment)
MC-NiL	0	100	PDA + Ni (long treatment)
EP	100	0	n.a.
EP-Ag-10	90	10	PDA + Ag
EP-Ag-20	80	20	PDA + Ag
EP-Ag-40	60	40	PDA + Ag
EP-NiS-10	90	10	PDA + Ni (short treatment)
EP-NiS-20	80	20	PDA + Ni (short treatment)
EP-NiS-40	60	40	PDA + Ni (short treatment)
EP-NiL-10	90	10	PDA + Ni (long treatment)
EP-NiL-20	80	20	PDA + Ni (long treatment)
EP-NiL-40	60	40	PDA + Ni (long treatment)

Ammonium hydroxide (28–30 wt% solution of ammonia in water [NH₃-H₂O], Acros Organics B.V.B.A., Belgium) was used to adjust the pH of the metallization solutions. Silver nitrate, ACS reagent, ≥ 99.0%, was purchased from Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany. Ammonium hydroxide, for analysis, 28–30 wt% solution of NH₃ in water was used from Acros Organics, Geel, Belgium. Deionized water was used for the metallization procedure.

2.2 | Sample Preparation

2.2.1 | PDA Deposition on MCs

A total of 0.1 g of MCs were immersed in a bath stirred at 500 rpm containing aqueous solutions of 2 g/L DA and 10 mM TRIS buffer at pH 8.5 for 10 min. These treatment parameters were chosen to obtain a smooth and uniform PDA coating on the MC shells suitable for subsequent metallization, as reported in our previous studies [33, 34]. Then, polydopamine (PDA)-coated MCs were separated with a glass frit (porosity G3, DWK Life Sciences GmbH Germany), rinsed with deionized water, and dried under vacuum at 25°C.

2.2.2 | Metallization of PDA-Modified Microcapsules

The PDA-modified MCs were electroless metallized with nickel in a bath series, i.e., (i) in a palladium activator bath (UDIQUE 879W) at 30°C for 3 min, and then washed in a glass frit (G3) with deionized water, (ii) in an activator bath (UDIQUE accelerator 8810) for 2.5 min at 50°C, then filtered and washed in a glass frit, and (iii) in a nickel electrolyte bath (UDIQUE 891 nickel and UDIQUE 893 stabilizer) for 2 or 8 min at 30°C at a pH of approx. 9, then washed with deionized water and dried under vacuum at 25°C. For silver metallization, a solution of 0.1 mol/L silver nitrate in 450 mL of water and 50 mL ammonia was stirred

at 70°C. After adding the microcapsules, the metallization time was set to 30 min. After silver reduction, the microcapsules were vacuum-filtered and dried for 3 h under reduced pressure.

2.2.3 | Preparation of Epoxy Composites

The epoxy base and hardener were poured into a glass beaker at a weight ratio of 100:40, as suggested by the manufacturer. Modified MCs were sieved with a 100-μm sieve and added to the beaker in different weight fractions. The mixture was vigorously stirred with a magnetic stirrer at 300 rpm for 10 min, degassed with a vacuum pump, cast in silicon molds, cured at room temperature for 24 h, and post-cured at 60°C for 15 h. The prepared samples with nominal weight compositions are listed in Table 1.

2.3 | Characterization

The microstructure of the prepared samples was studied by acquiring SEM micrographs of the neat and modified microcapsules and the tensile fracture surfaces of the composites with an FE-SEM Zeiss Supra 40 (Carl Zeiss AG, Oberkochen, Germany) after Pt-Pd sputtering. The surface composition was investigated with a JEOL IT300 (JEOL, Japan) SEM equipped with an energy dispersive x-ray Spectroscopy (EDXS; Bruker, USA) system.

Differential scanning calorimetry (DSC) was performed on neat and modified microcapsules and on the cured composites with a Mettler DSC 30 calorimeter (Mettler Toledo Inc., Columbus, OH, USA), at 10°C/min, under a heating/cooling/heating cycle in the range −30/80°C under a nitrogen flow of 100 mL/min. The test allowed the measurement of the melting and crystallization temperatures (T_m , T_c) and enthalpy values (ΔH_m , ΔH_c) of the microcapsules and the glass transition temperature (T_g) of the epoxy resin. To study the thermal stability of the PCMs,

cyclic DSC tests were performed at 20°C/min between −10°C and 80°C. 100 heating–cooling cycles were performed on all the modified PCMs. One specimen per sample was tested.

Thermogravimetric analysis (TGA) was carried out with a Q5000IR thermobalance (TA Instruments Inc., New Castle, DE, USA) for the modified PCM microcapsules and with a Mettler TG 50 on the prepared composites. Specimens of approx. 5 mg (for the encapsulated PCMs) or 20 mg (for the prepared composites) were tested at a heating rate of 10°C/min up to 700°C, under a nitrogen flow of 10 mL/min. The test allowed the measurement of the temperatures corresponding to a mass loss of 1 and 5 wt% ($T_{1\%}$, $T_{5\%}$), the degradation temperature (T_d), intended as the peak of the mass loss derivative (DTG), and the residual mass after the test (m_r).

The thermal diffusivity of the MC powder beds was measured at 20°C, 40°C, and 60°C with a light flash apparatus LFA 467 Hyperflash (Netzsch-Gerätebau GmbH, Selb, Germany) equipped with a “pressure” sample holder, which allows the measurement of the thermal diffusivity of a powder bed sandwiched between two thin aluminum layers. Specimens were prepared by sieving the PCM powders with a 63- μ m metallic sieve, filling the sample holder with approx. 20 mg PCM powder, and applying a torque of 15 cN·m. One specimen was tested per composition, and five pulses were performed per specimen. Thermal diffusivity (α) was determined using the software Proteus (Netzsch) provided with the instrument, by applying the three-layer model with linear baseline and numerical pulse correction. The calculation of the diffusivity with this specific sample holder is possible only by providing the specific heat of the material (c_p) and the density of the prepared specimen (ρ). The c_p was determined with the DSC equipment described before, by using weight matched aluminum crucibles and sapphire as the reference material, as described by the standard ASTM E1269. The thermal diffusivity of the prepared bulk composites was measured at 20°C, 40°C, and 60°C with the same LFA apparatus described above. For the composites, the test was performed on round discs with a diameter of 12.7 mm, die-cut from the prepared as-cast composites. One specimen was tested per composition, and five pulses were performed per specimen. The thermal diffusivity was determined using the software Proteus by applying the penetration model with linear baseline and numerical pulse correction.

Dynamic mechanical thermal analysis (DMTA) was performed on the prepared composites with the TA Instruments DMA Q800 on as-cast specimens with nominal dimensions of 30×10×5 mm³. Tests were performed in single cantilever mode in the range −30/80°C at 3°C/min with a strain amplitude of 0.05% applied at 1 Hz. The distance between the grips was fixed at 17.5 mm. One specimen was tested per composition.

Tensile tests were performed on the prepared composites at room temperature with an electromechanical dynamometer Instron 5969 equipped with a 100 N load cell on as cast ISO 527-2-1BA specimens. For each composition, five specimens were tested at a crosshead speed of 0.25 mm/min for the measurement of the elastic modulus using a resistance extensometer Instron 2620 with a gauge length of 12.5 mm. According to ISO 527, the elastic modulus (E) was measured as the secant modulus on the

stress–strain curve between strain values of 0.05% and 0.25%. Five additional specimens were tested at 10 mm/min until failure. The test allowed determination of the ultimate tensile stress (UTS) and the strain at break (ϵ_b).

3 | Results and Discussion

3.1 | Characterization of the Surface-Modified PCM Microcapsules

Figure 1 shows the SEM micrographs of the neat and metallized microcapsules. The neat MCs (Figure 1a–c) exhibit their characteristic spherical morphology, with smooth surfaces displaying minimal features at all magnification levels examined, in good agreement with previous observations [30, 33, 34]. After metallization, distinct morphological differences can be observed between the silver and nickel coatings. The silver-metallized microcapsules (Figure 1d–f) display a highly heterogeneous surface characterized by the formation of discrete metallic clusters and nanoparticles distributed across the capsule surface. At higher magnifications, these silver deposits appear as agglomerated structures creating a rough, particulate coating rather than a continuous film. This cluster-like morphology is characteristic of silver deposition processes where nucleation occurs at discrete sites on the PDA-modified surface [43]. In contrast, the nickel-metallized microcapsules demonstrate markedly different surface characteristics. The short (2 min) nickel treatment (Figure 1g–i) produces a more uniform coating with a finer, more evenly distributed surface texture. The surface appears considerably more homogeneous compared to the silver coating, suggesting better wetting and film formation properties of nickel on the PDA layer. The extended (8 min) nickel treatment (Figure 1j–l) results in an even more continuous coating, with a similar surface roughness as the short treatment, although there are some areas in which the coating seems to have detached from the MC surface (Figure 1k). The EDX spectra and Ag and Ni elemental maps (see Figures S1 and S2) confirm the distribution of these two elements. In any case, the progression from discrete particle formation (silver) to increasingly uniform film formation (nickel treatments) demonstrates the superior metallization characteristics achieved with nickel compared to silver on PDA-modified microcapsule surfaces.

The thermal properties of the neat and metallized microcapsules were evaluated using DSC, and the results are presented in Figure 2. The DSC thermograms (Figure 2a) show that all samples exhibit characteristic endothermic peaks during the first heating scan at approximately 43°C–47°C, corresponding to the melting of the paraffinic core. Similarly, the cooling scans reveal exothermic crystallization peaks at around 28°C–35°C, confirming that the phase change capability of the PCM core is preserved following surface modification. The melting and crystallization temperatures (Figure 2b) remain relatively stable across all sample types, with only minor variations observed. The melting temperatures minimally vary from approximately 43°C for the neat microcapsules to 47°C for the MC-NiL samples, while crystallization temperatures show minimal deviation from the baseline values. This consistency indicates that, as expected, the metallization treatments do not significantly alter the fundamental phase change characteristics of the encapsulated paraffin.

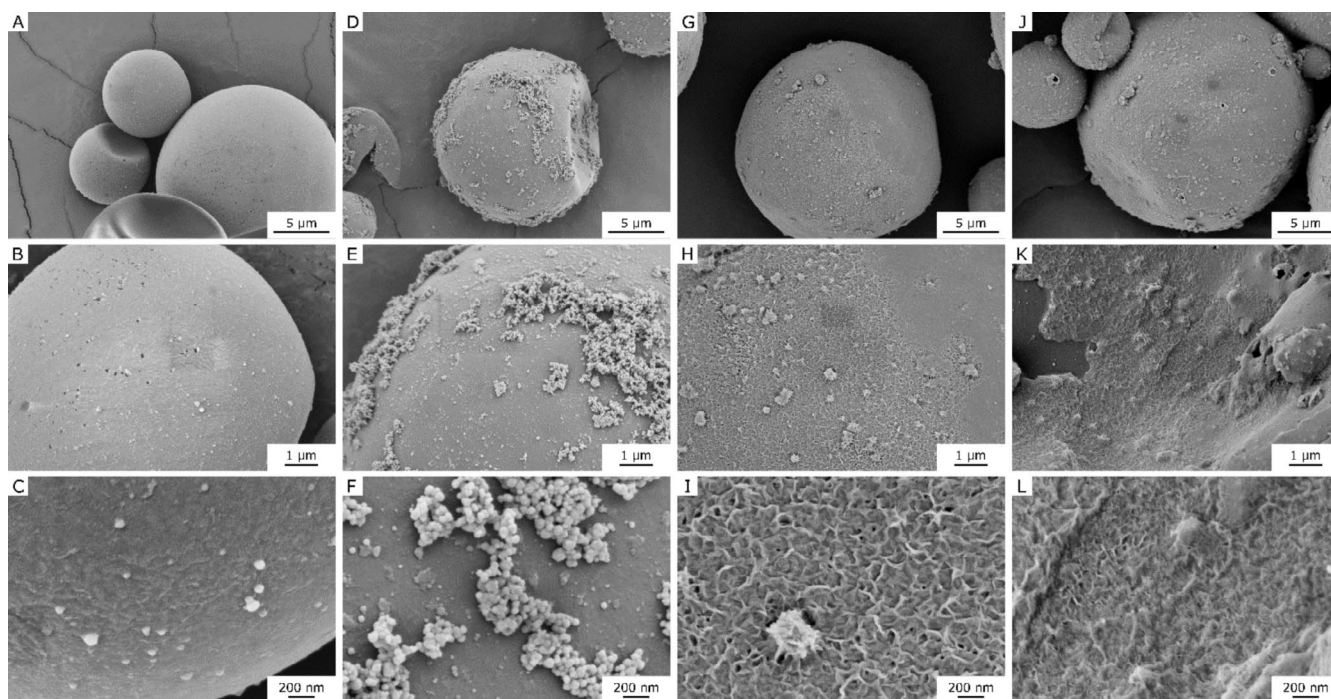


FIGURE 1 | SEM micrographs of neat and modified microcapsules. (A–C) neat MC; (D–F) MC-Ag; (G–I) MC-NiS; (J–L) MC-NiL.

However, the phase change enthalpies (Figure 2c) show a clear decreasing trend with surface modification. The melting enthalpy decreases from approximately 225 J/g for neat MCs to around 222 J/g for MC-Ag and further to 150–190 J/g for nickel-coated MCs. This reduction is directly attributable to the additional mass of the coating layers, which do not contribute to the phase change process. These enthalpy values were used to calculate the relative phase change enthalpies (Figure 2d), which provide insight into the proportion of active PCM remaining after modification. The values decrease progressively from 100% for neat microcapsules to approximately 98% for MC-Ag, 85% for MC-NiS, and 70% for MC-NiL samples. These reductions allowed the calculation of the mass of added coating material (Figure 2e), which increases from approx. 2 wt% for silver coatings to 15 wt% and 28 wt% for MC-NiS and MC-NiL samples, respectively. The higher mass addition for Ni-treated samples, particularly with extended treatment time, reflects the formation of thicker, more continuous metallic layers as observed in the SEM analysis. Cyclic DSC tests confirm the thermal stability of the coated PCMs, with the measured temperatures and enthalpy values remaining constant for up to 100 cycles (see Figure S3).

The thermal degradation behavior of the neat and metallized microcapsules was investigated using TGA, with results presented in Figure 3 and summarized in Table 2. As reported in previous studies [34], the thermal degradation of neat MCs begins with small steps in the temperature interval 100°C–250°C, attributable to the degradation of free (non-encapsulated) paraffin and low-molecular-weight compounds from the capsule synthesis. The main degradation event occurs in a remarkably narrow temperature interval around 420°C, with the spike in the DTG thermogram indicating rapid and abrupt degradation of both the capsule core and shell.

Metallization treatments produce distinct effects on degradation behavior. Silver-coated microcapsules show improved initial thermal stability, with $T_{1\%}$ increasing from 118.4°C to 129.2°C and $T_{5\%}$ from 241.2°C to 252.0°C. However, the degradation temperature (T_d) slightly decreases from 421.2°C to 410.6°C. In contrast, nickel-coated samples exhibit significantly lower initial degradation temperatures ($T_{1\%} = 70.0^\circ\text{C}$ for MC-NiS and 45.5°C for MC-NiL), consistent with previous observations on PDA-Ni coated microcapsules [34]. This early degradation is attributed to the thermal decomposition of the PDA layer and release of low-molecular-weight compounds from the metallization process, present especially after the NiL treatment. This difference is also reflected in the residual mass. While the residual masses for MC-Ag and MC-NiS align well with the coating masses calculated from DSC data, MC-NiL shows a slightly lower residual mass than expected based on DSC calculations. This discrepancy suggests the presence of volatile compounds associated with the extended nickel treatment, which is consistent with the irreversible thermal events observed in the DSC first heating scan for MC-NiL (Figure 2a). These findings indicate that optimization of the metallization parameters or the addition of a postprocessing treatment may be beneficial to minimize the incorporation of volatile residues. This is true especially for MC-NiL, in which $T_{1\%}$ is very close to the service temperature (i.e., the PCM melting temperature), which may influence the performance and the reliability in the first few thermal cycles. Hence, further post-treatments (e.g., extended washing or mild thermal conditioning) are needed that could fully remove these residues.

Notably, both Ni treatments result in enhanced thermal resistance at high temperatures, with T_d values of 442.2°C and 442.7°C representing approximately 20°C improvement over neat microcapsules, similar to previous findings [34].

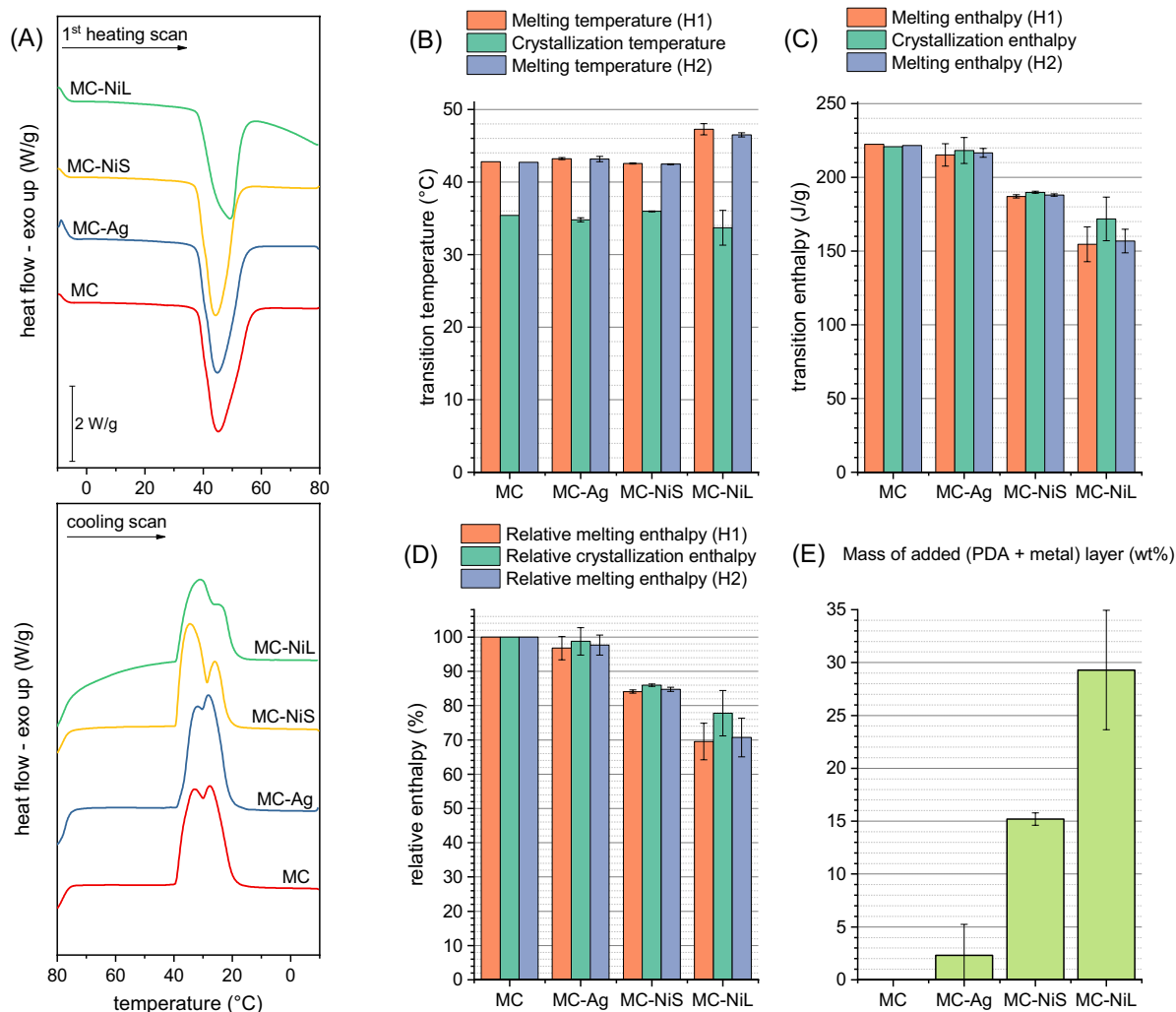


FIGURE 2 | Results of the DSC characterization on the neat and modified microcapsules. (A) Representative thermograms of the first heating and cooling scans; (B) melting and crystallization temperatures measured in the first heating, cooling, and second heating scans; (C) melting and crystallization enthalpies measured in the first heating, cooling, and second heating scans; (D) relative melting and crystallization enthalpies; (E) mass of added layer (PDA + Ag or PDA + Ni) calculated from the relative melting and crystallization enthalpies. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.70424)]

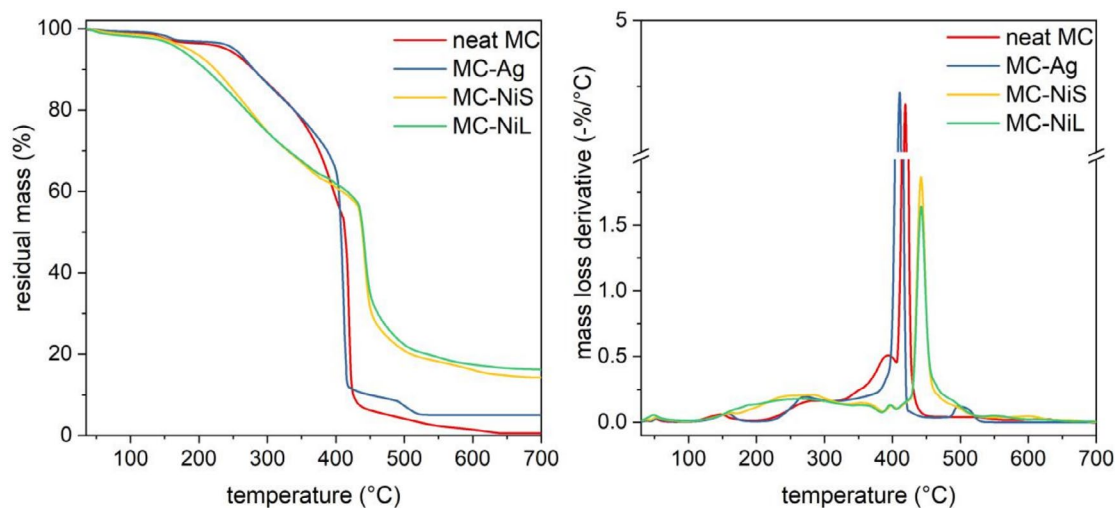


FIGURE 3 | Main results of the TGA tests on the neat and modified microcapsules. Residual mass and mass loss derivative (DTG) as a function of temperature. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.70424)]

The thermal diffusivity of the individual microcapsule powder beds was evaluated as a function of temperature, with results shown in Figure 4. The neat microcapsules exhibit thermal diffusivity values of approximately $0.22 \text{ mm}^2/\text{s}$ at 20°C , consistent with previous results [34].

Surprisingly, the MC-Ag and MC-NiS show comparable or in some cases slightly lower thermal conductivity values compared to neat MC. This counterintuitive behavior can be attributed to the increased surface roughness introduced by these coatings, which may impede efficient particle-to-particle contact and heat transfer within the powder bed structure. In contrast, the extended nickel treatment (MC-NiL) brings a substantial enhancement in thermal diffusivity, reaching approximately $0.42 \text{ mm}^2/\text{s}$ at 20°C —nearly doubling the performance of neat MC. This significant improvement is in agreement with the formation of a thick, continuous Ni

layer observed in SEM, which provides efficient thermal conduction pathways throughout the powder bed. All samples exhibit a clear temperature dependence, with thermal diffusivity decreasing as temperature increases from 20°C to 60°C . This trend is particularly evident around the PCM melting temperature ($\sim 45^\circ\text{C}$), where the phase change process affects the thermal transport properties of the powder bed.

3.2 | Characterization of the Epoxy Composites

Figure 5 shows representative SEM micrographs of the tensile fracture surfaces of the prepared composites containing different metallized microcapsules at varying loadings. The images compare composites containing MC-Ag (Figure 5a–c), MC-NiS (Figure 5d–f), and MC-NiL (Figure 5g–i) microcapsules at both 10 wt% (Figure 5a,d,g) and 40 wt% (Figure 5b,c,e,f,h,i) loadings.

At 10 wt% loading (Figure 5a,d,g), all composite types show homogeneous microcapsule distribution throughout the epoxy matrix without significant agglomeration. The microcapsules maintain their spherical morphology and appear well-integrated into the matrix structure. As the loading increases to 40 wt% (Figure 5b,e,h), the higher microcapsule concentration becomes evident, yet the distribution remains relatively uniform across all metallization types. However, during sample preparation, at 40 wt% the viscosity of the epoxy/hardener/PCM mixture became very viscous, which hindered proper degassing

TABLE 2 | Main results of the TGA tests on the neat and modified microcapsules.

Sample	$T_{1\%}$ ($^\circ\text{C}$)	$T_{5\%}$ ($^\circ\text{C}$)	T_d ($^\circ\text{C}$)	m_r (%)
MC	118.4	241.2	421.2	0.3
MC-Ag	129.2	252.0	410.6	5.0
MC-NiS	70.0	185.5	442.2	14.2
MC-NiL	45.5	162.1	442.7	16.3

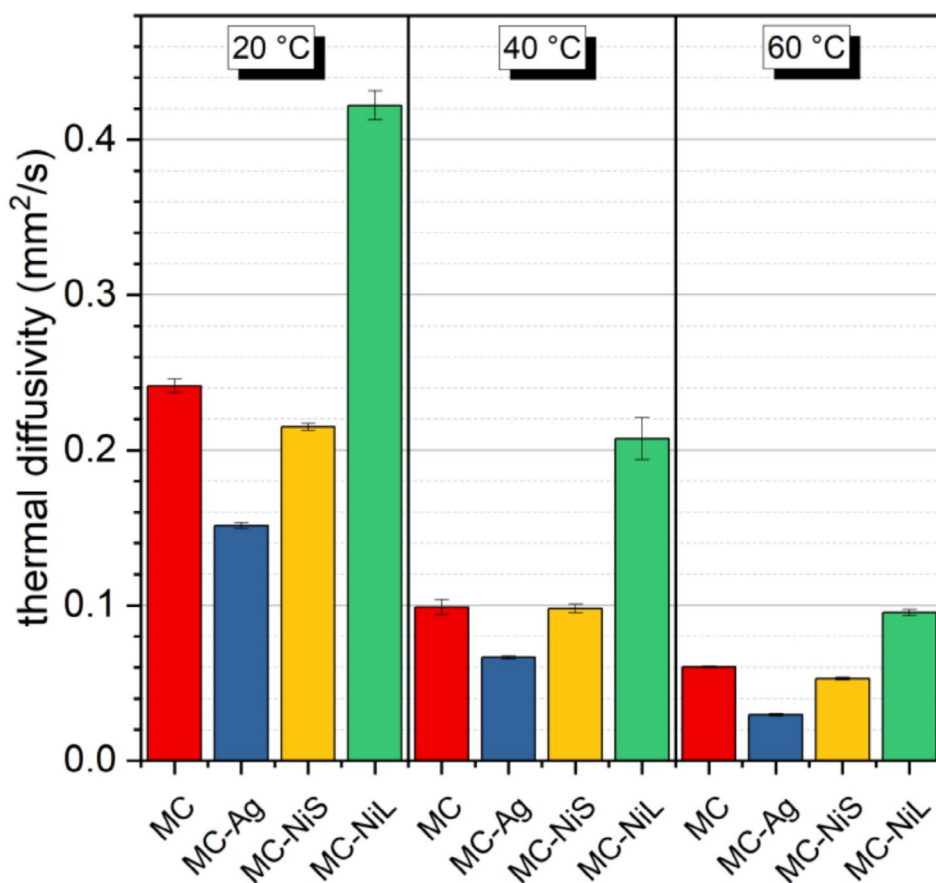


FIGURE 4 | Main results of the LFA tests on the neat and modified microcapsules. Thermal diffusivity of the microcapsule powder beds as a function of temperature. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

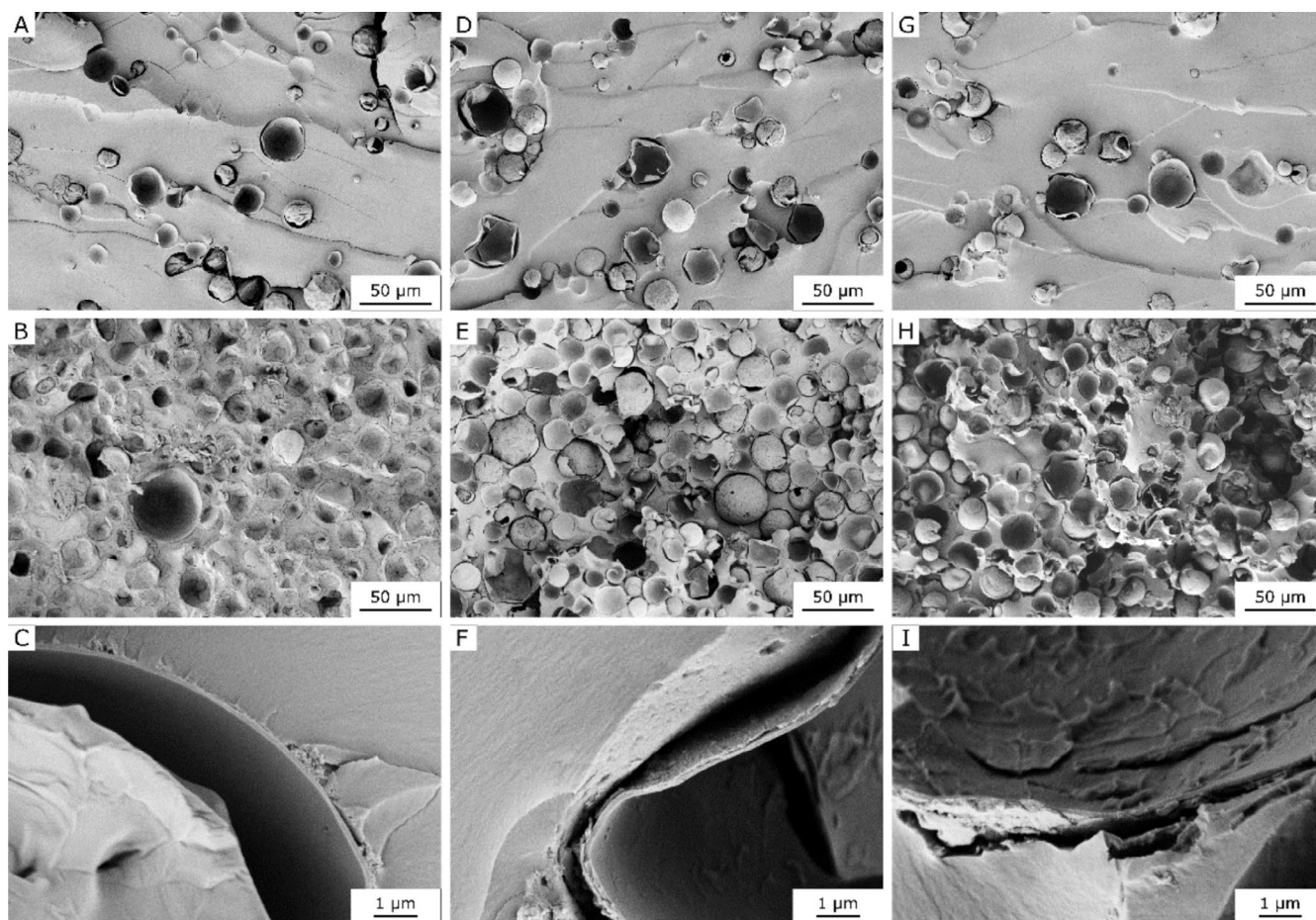


FIGURE 5 | SEM micrographs of the tensile fracture surface of the prepared composites. (A) EP-Ag10; (B) EP-Ag40; (C) EP-Ag40, higher magnification; (D) EP-NiS10; (E) EP-NiS40; (F) EP-NiS40, higher magnification; (G) EP-NiL10; (H) EP-NiL40; (I) EP-NiL40, higher magnification.

and decreased the chances of specimens free from macroscopic defects and bubbles after casting. This observation is in good agreement with the rheological behavior of epoxy/PCM mixtures before casting, performed in a previous study [31], which evidenced that the mixture viscosity of epoxy increases sharply and becomes highly shear-thinning with rising microcapsule content, severely reducing processability at high loadings and preventing reliable mixing or degassing above ~40–50 wt% MC. This could lead to a higher void concentration and thus reduced mechanical properties in the final composite. Hence, 40 wt% MC was set as the upper filler threshold in this work.

The fracture morphology reveals predominantly cohesive failure, with most microcapsules fractured rather than debonded from the matrix, indicating reasonable interfacial adhesion for all metallized systems, as observed for other epoxy/MC systems [31]. However, at higher magnifications (Figure 5c,f,i), important differences in interfacial quality become apparent. The silver-coated microcapsules (Figure 5c) exhibit superior interfacial bonding with minimal gaps between the capsule shell and the matrix. This enhanced adhesion can be attributed to the discontinuous nature of the silver coating observed in surface characterization, which likely leaves portions of the underlying PDA layer exposed. Since PDA has demonstrated excellent chemical affinity with epoxy resins through covalent bonding mechanisms [30], these exposed areas facilitate strong interfacial interactions.

In contrast, the Ni-treated samples (Figure 5f,i) show progressively larger interfacial gaps and evidence of capsule-matrix debonding. This reduced adhesion may result from the poor chemical compatibility between the continuous nickel layer and the epoxy matrix. While the uniform and continuous nickel coating provides benefits for thermal and electrical properties, it appears to impede the interfacial bonding by shielding the chemically active PDA layer from direct contact with the epoxy resin, thereby reducing the effectiveness of the PDA-mediated adhesion mechanism.

The thermal behavior of the prepared composites was characterized using DSC and DMTA, with representative thermograms shown in Figures 6 and 7, respectively, and key results summarized in Table 3. Both techniques reveal that the epoxy matrix and encapsulated PCM retain their characteristic thermal transitions when combined in the composite structure.

The glass transition of the epoxy matrix occurs at approximately 8°C–11°C (DSC) and 20°C–27°C (DMTA) across all compositions, consistent with previous observations [33]. Both techniques show minimal variation in glass transition temperature with microcapsule loading or metallization type, indicating that the metallized microcapsules do not significantly alter the cross-linking density or molecular mobility of the epoxy network.

The PCM phase change behavior is clearly preserved in all composites, as evidenced by the distinct endothermic melting

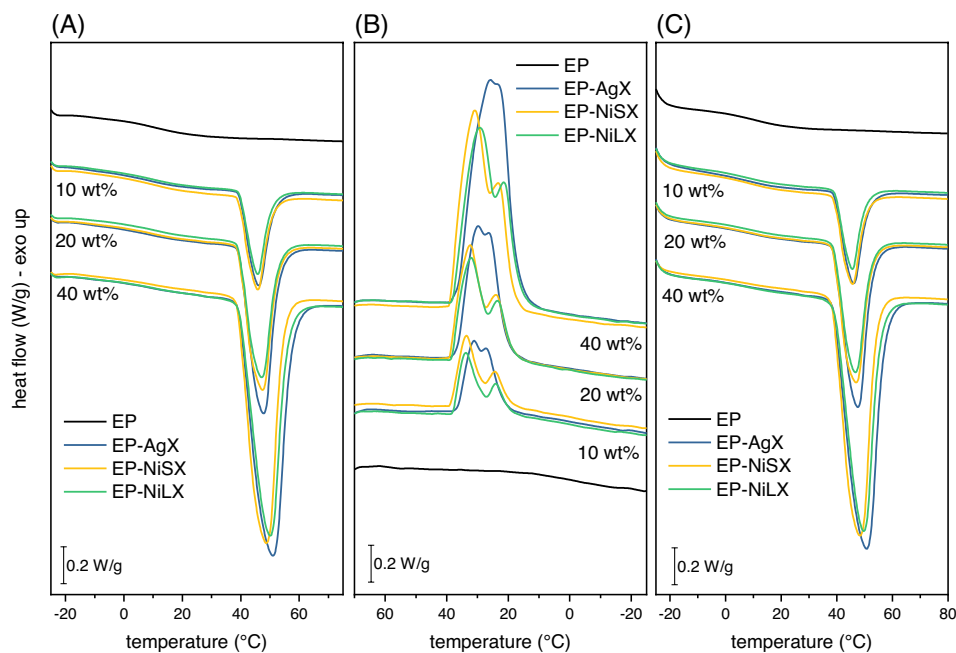


FIGURE 6 | Results of the DSC analysis on neat epoxy resin (EP) and the prepared composites. (A) First heating scan; (B) cooling scan; (C) second heating scan. Labels indicate the nominal weight percentage of PCM in the composites. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.70424)]

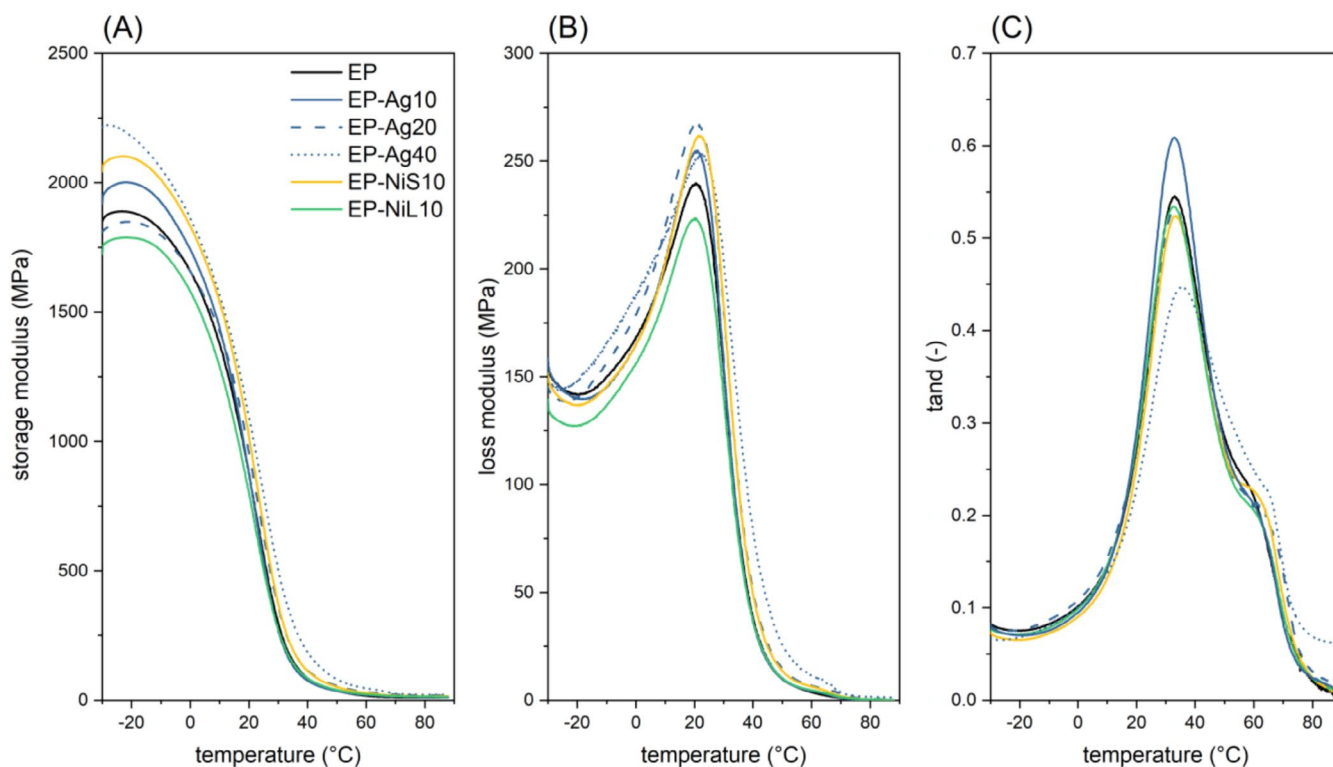


FIGURE 7 | Results of the DMA tests on the prepared composites. (A) Storage modulus, (B) loss modulus, and (C) $\tan \delta$ as a function of temperature. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.70424)]

peaks in the DSC heating scans (Figure 6a,c) at approximately 44°C–48°C and the corresponding exothermic crystallization peaks in the cooling scan (Figure 6b) at around 31°C–35°C. The melting and crystallization temperatures remain relatively stable across all compositions, indicating that the encapsulation and surface modification do not adversely affect the fundamental phase change characteristics of the paraffin core.

As expected, the phase change enthalpies increase proportionally with microcapsule loading, reaching values of approximately 19–24 J/g, 40–50 J/g, and 80–100 J/g for the 10, 20, and 40 wt% compositions, respectively. The different metallization treatments show differences in enthalpy values at equivalent loadings, which reflect the different coating masses determined from the MC characterization. EP-Ag samples generally exhibit

the highest enthalpies due to their lower coating mass, while the EP-NiL samples show the lowest values corresponding to their higher metallic content. These results confirm that the metallization process successfully preserves the thermal energy storage capability of the MC while maintaining the thermal stability of the epoxy matrix, demonstrating the viability of these materials for thermal management applications.

The thermal degradation behavior of the prepared composites was evaluated using TGA, with results presented in Figure 8 and Table 4. All composites exhibit similar degradation patterns, with thermal stability maintained up to approximately 130°C–150°C, followed by gradual mass loss and complete degradation by 500°C. The degradation profiles are dominated by the epoxy matrix behavior, with the relatively low microcapsule loadings having minimal impact on the thermal stability.

The main degradation peaks in the DTG curves occur around 340°C–400°C, corresponding primarily to the decomposition of the epoxy network and the PCM. The residual masses at 700°C reflect the metallic content, with nickel-containing composites showing higher residual values consistent with their higher metallic coating content. It can be concluded that neither metallization treatments compromise the thermal stability of the epoxy composites within their intended operating temperature range.

The thermal diffusivity of the prepared composites was measured using LFA at 20°C, 40°C, and 60°C, with results presented in Figure 9. The neat EP exhibits relatively low thermal diffusivity of approx. 0.08 mm²/s, characteristic of polymeric materials.

The incorporation of metallized microcapsules significantly enhances the thermal diffusivity of the composites, with all

TABLE 3 | Main results of the DSC and DMTA tests on the prepared composites.

Sample	T_{g1} (°C)	$T_{g_{EN}}$ (°C)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_c (°C)	ΔH_c (J/g)	T_{g2} (°C)	T_{m2} (°C)	ΔH_{m2} (J/g)
EP	8.9	20.2	—	—	—	—	10.8	—	—
EP-Ag-10	8.1	20.5	44.3	24.1	32.4	24.2	8.8	44.4	23.7
EP-Ag-20	8.4	20.7	45.9	49.2	31.4	50.8	10.6	45.6	48.4
EP-Ag-40	7.1	22.5	48.0	99.5	28.4	100.4	3.4	48.0	97.9
EP-NiS-10	11.1	21.7	44.4	22.9	34.6	25.1	8.6	44.4	22.6
EP-NiS-20	8.9	22.5	45.4	43.5	34.1	45.1	10.2	45.0	42.6
EP-NiS-40	10.3	22.8	46.9	83.7	32.3	85.1	1.5	46.6	82.8
EP-NiL-10	9.6	20.1	44.5	19.3	34.8	20.7	8.1	44.3	18.9
EP-NiL-20	9.7	24.0	45.0	40.2	33.7	41.5	9.3	44.7	38.4
EP-NiL-40	10.9	26.8	48.0	80.1	31.0	82.0	6.6	47.7	80.2

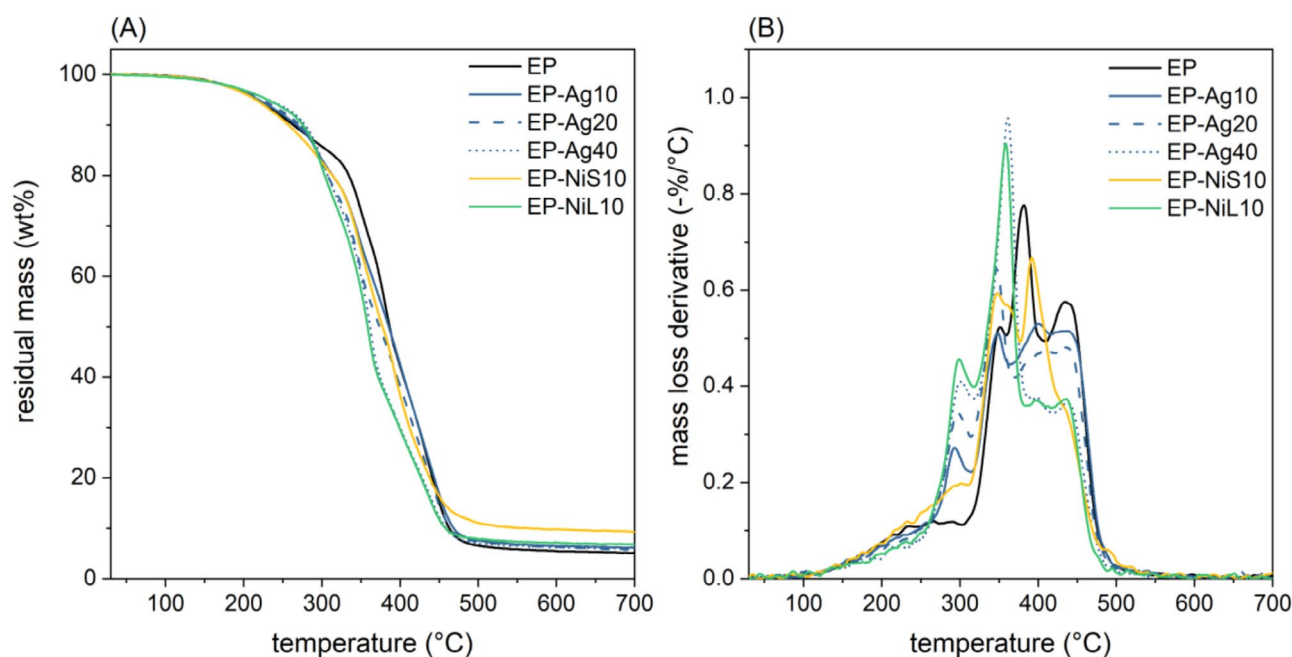


FIGURE 8 | Results of the TGA tests on the prepared composites. Representative thermograms of the residual mass (A) and mass loss derivative (B) as a function of temperature. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.70424)]

compositions showing progressive increases with increasing PCM loading. Interestingly, the different metallization treatments yield comparable thermal diffusivity values at equivalent loadings. This phenomenon can be attributed to the competing effects of intrinsic thermal properties and interfacial adhesion. While Ni-coated microcapsules possess superior intrinsic thermal diffusivity, as demonstrated by the LFA results of PCM powder beds (Figure 4), the Ag-coated PCMs demonstrate better interfacial adhesion with the epoxy matrix, as evidenced by SEM (Figure 5). Since interfacial thermal resistance is a critical factor governing heat transfer in composite materials, the enhanced adhesion in EP-Ag composites likely compensates for their lower intrinsic thermal properties (Figure 4), which may result in similar thermal diffusivity for the composites across the different metallization types. However, further studies are needed to fully clarify this point.

A notable temperature dependence is observed for all compositions, with thermal diffusivity generally decreasing as temperature increases from 20°C to 60°C. This behavior is particularly evident around the PCM melting temperature (~45°C), where the phase change process temporarily affects heat transport efficiency.

TABLE 4 | Main results of the TGA tests on the prepared composites.

Sample	$T_{1\%}$ (°C)	$T_{3\%}$ (°C)	T_d (°C)	R_c (wt%)
EP	148.3	191.3	382.5	5.1
EP-Ag-10	144.2	191.5	400.0	6.1
EP-Ag-20	144.2	194.0	346.8	5.7
EP-Ag-40	138.2	199.0	360.8	6.0
EP-NiS-10	144.3	189.8	392.3	9.3
EP-NiS-20	138.2	190.2	346.0	11.4
EP-NiS-40	135.0	188.9	340.5	13.2
EP-NiL-10	138.8	198.3	358.5	6.8
EP-NiL-20	133.0	183.3	349.7	9.9
EP-NiL-40	134.0	184.7	361.7	13.3

The mechanical behavior of the prepared composites was evaluated through tensile testing, with representative stress–strain curves and main results presented in Figure 10. The elastic modulus increases substantially with microcapsule loading for all metallization types, reaching values of approximately 140–150 MPa at 40wt% loading, representing a substantial enhancement over the 95–110 MPa reported for neat and PDA-coated microcapsules at equivalent loadings [33]. The Ni-coated microcapsules, particularly the extended treatment (EP-NiL), show the highest modulus values, likely due to the rigid and thicker metallic coating. It must be pointed out that increasing stiffness is not necessarily a desired outcome, and the optimal stiffness value must be selected as a function of the target application. Still, the introduction of metallized microcapsules expands the mechanical property range of these composites and, therefore, their applicability.

Similarly, the ultimate tensile strength improves with increasing microcapsule content, with 40wt% composites achieving strengths of 3.5–4.5 MPa compared to ~3 MPa for neat epoxy. These values are comparable to the 4.2–4.8 MPa achieved with PDA-coated microcapsules [33]. While the strength improvements are less dramatic than the modulus gains, they demonstrate that the metallization process maintains the beneficial effects of the PDA interlayer while adding the stiffening benefits of the metallic coating. Interestingly, the Ag-coated microcapsules demonstrate competitive performance despite their lower coating mass, which can be attributed to their superior interfacial adhesion as observed in the fracture surface analysis.

Conversely, the strain at break of the composites is worse than that of the neat EP, especially at higher loading. However, fracture still occurs at relatively high strain values (20%–60%), similar to or higher than those reported for PDA-coated systems and higher than those measured on the composites with neat MC [33], indicating that the composites retain good ductility despite the addition of rigid filler particles. These results demonstrate that metallization represents a significant advancement over previous surface modifications, providing enhanced mechanical reinforcement while preserving the thermal energy storage functionality and interfacial adhesion benefits established in earlier work.

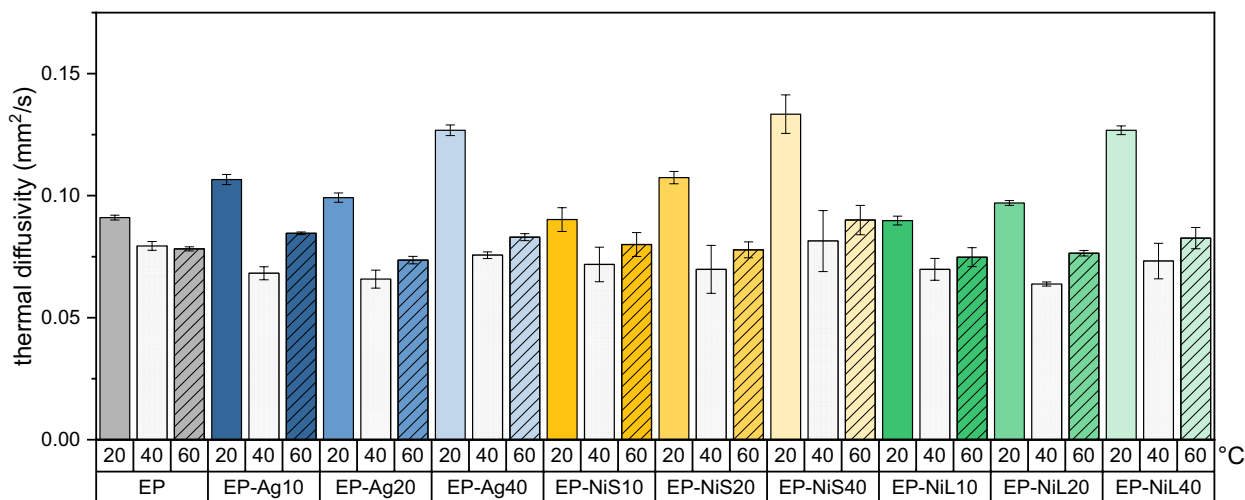


FIGURE 9 | Results of the LFA tests on the prepared composites. Thermal diffusivity as a function of temperature and composition. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

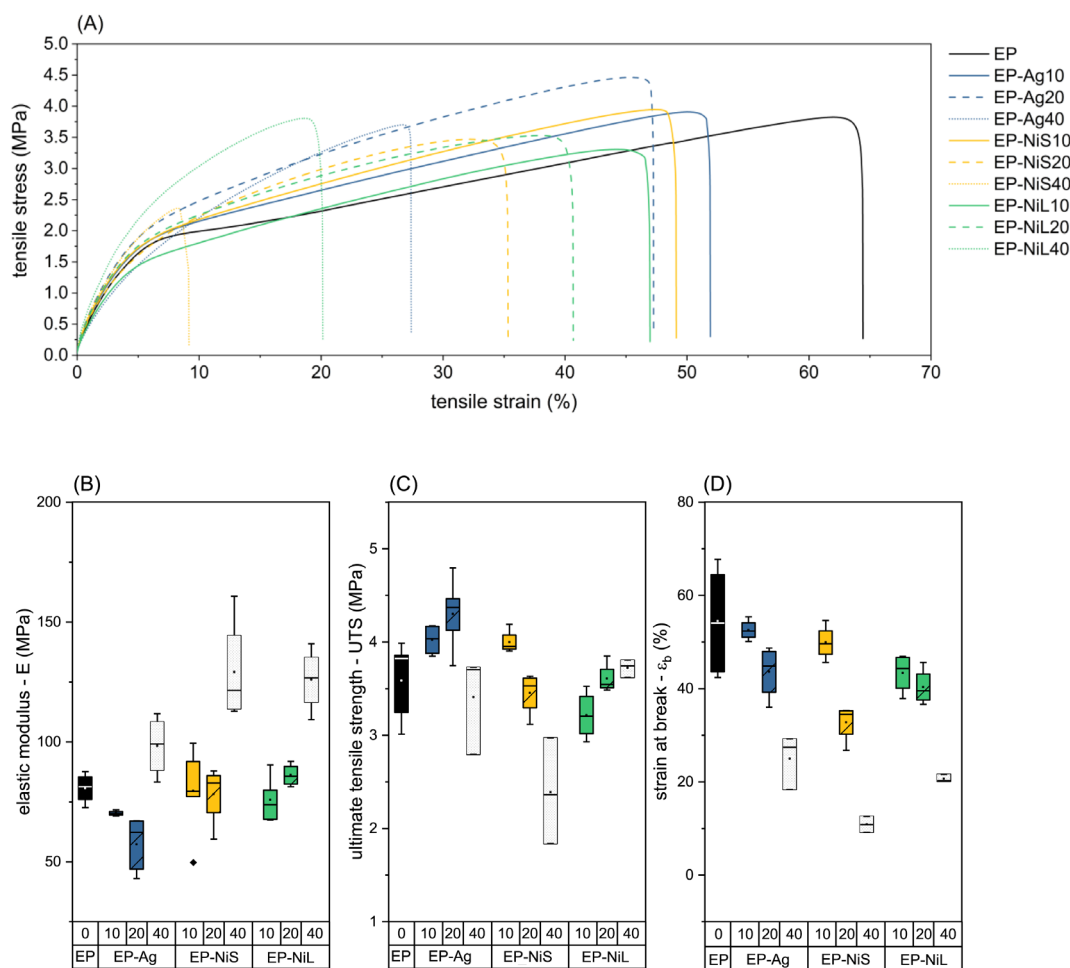


FIGURE 10 | Results of the tensile tests on the prepared composites. (A) Representative stress–strain curves; (B) elastic modulus as a function of the composition; (C) ultimate tensile strength as a function of the composition; (D) strain at break as a function of the composition. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

4 | Conclusions

This work demonstrates the silver and nickel metallization of PDA-coated PCM microcapsules and their integration in flexible epoxy resins, resulting in multifunctional composites that combine thermal energy storage, enhanced mechanical properties, and improved thermal transport characteristics. The bioinspired polydopamine interlayer proves to be an effective adhesion promoter for both silver and nickel deposition, enabling the formation of metallic coatings on otherwise chemically inert melamine-based MC surfaces.

The metallization treatments yield distinctly different coating morphologies and properties. Silver metallization produces discontinuous, cluster-like coatings with minimal mass addition (~2 wt%), preserving 98% of the original phase change enthalpy while maintaining excellent interfacial adhesion with the epoxy matrix. In contrast, nickel treatments create more continuous, uniform coatings with progressively increasing mass addition (15 and 28 wt% for 2-min and 8-min treatments, respectively), resulting in greater thermal diffusivity enhancements but reduced interfacial adhesion with the surrounding epoxy matrix, likely due to the shielding of the chemically active PDA layer.

The TES capability of the microcapsules is successfully preserved across all metallization treatments, with T_m and T_c remaining stable around 43°C–47°C and 28°C–35°C, respectively. While the phase change enthalpies decrease proportionally with coating mass, the metallized microcapsules retain substantial energy storage capacity, in the range 150–220 J/g depending on the treatment. Although the MC metallized with the extended nickel treatment (MC-NiL) demonstrate the lowest phase change enthalpy, they show particularly promising thermal transport properties, nearly doubling the thermal diffusivity of microcapsule powder beds compared to neat MC. This indicates that the MC-Ag microcapsules may be more suitable for applications where a high melting enthalpy is required, while the MC-Ni microcapsules could be more indicated when a high thermal diffusivity is needed.

When incorporated into flexible epoxy composites, the metallized microcapsules provide significant mechanical reinforcement while maintaining thermal management functionality. The elastic modulus reaches 140–150 MPa at 40 wt% loading, representing a substantial increase over previous neat and PDA-coated MCs (95–110 MPa). All composite systems retain good ductility with ϵ_b values of 20%–60%, demonstrating the successful combination of stiffness enhancement and deformation capability.

This research extends the capabilities of PDA surface modification beyond simple adhesion enhancement. The metallized microcapsules open new possibilities for applications in thermal interface materials (TIMs), smart textiles, building envelope systems, and electronics packaging, where the combination of mechanical reinforcement, heat management, and enhanced thermal transport is advantageous. Future work should focus on optimizing the metallization parameters to completely remove volatile compounds after metallization, particularly for nickel treatments, and developing strategies to restore interfacial adhesion. Additionally, investigating the electromagnetic properties of these metallized composites could unlock further functionalities, such as electromagnetic interference (EMI) shielding or wireless heating capabilities, further expanding their application potential in advanced thermal management systems.

Author Contributions

Giulia Fredi: conceptualization (equal), data curation (equal), funding acquisition (equal), investigation (lead), methodology (equal), resources (supporting), validation (equal), visualization (lead), writing – original draft (lead), writing – review and editing (lead). **Sascha Putzke:** investigation (equal), methodology (equal), writing – review and editing (supporting). **Christina Scheffler:** funding acquisition (equal), methodology (equal), project administration (lead), resources (equal), supervision (lead), writing – review and editing (equal). **Cordelia Zimmerer:** conceptualization (equal), funding acquisition (equal), investigation (equal), methodology (equal), project administration (equal), resources (equal), supervision (equal), writing – review and editing (equal).

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data will be made available on request.

References

1. K. Pielichowska and K. Pielichowski, “Phase Change Materials for Thermal Energy Storage,” *Progress in Materials Science* 65 (2014): 67–123, <https://doi.org/10.1016/j.pmatsci.2014.03.005>.
2. H. M. Ali, T.-u. Rehman, M. Arıcı, et al., “Advances in Thermal Energy Storage: Fundamentals and Applications,” *Progress in Energy and Combustion Science* 100 (2024): 101109, <https://doi.org/10.1016/j.pecs.2023.101109>.
3. G. Fredi, *Thermal Energy Storage Composites. Multifunctional Structural Polymer Composites for Thermal Energy Storage and Management* (Walter de Gruyter GmbH, 2025).
4. S. K. Pathak, V. V. Tyagi, K. Chopra, and A. K. Pandey, “Solar Thermal Potential of Phase Change Material Based U-Pipe ETSCs for Different Climatic Zones: Evaluating Energy Matrices and Economic Viability,”

Sustainable Materials and Technologies 40 (2024): e00857, <https://doi.org/10.1016/j.susmat.2024.e00857>.

5. Y. A. Bhutto, A. K. Pandey, R. Saidur, Y. N. Mishra, and V. V. Tyagi, “Synergistic Impact Investigation of 1D/2D Hybrid Nanoparticles on Lauric Acid Phase Change Material for Thermoelectric Generator and Heat Sink Cooling Application,” *Sustainable Materials and Technologies* 40 (2024): e00926, <https://doi.org/10.1016/j.susmat.2024.e00926>.
6. A. Nemš, S. Daniarta, M. Nemš, P. Kolasiński, and S. Ushak, “A Review of Artificial Intelligence to Thermal Energy Storage and Heat Transfer Improvement in Phase Change Materials,” *Sustainable Materials and Technologies* 44 (2025): e01348, <https://doi.org/10.1016/j.susmat.2025.e01348>.
7. Y. Hu, Y. Huang, X. Liu, et al., “Synergistically Enhanced NF/CNTs@PDA/PEG Composite Phase Change Materials for High-Efficiency Solar-Thermal Energy Storage and Conversion,” *Solar Energy Materials and Solar Cells* 290 (2025): 2902025, <https://doi.org/10.1016/j.solmat.2025.113714>.
8. D. Lincu, S. Ioniță, M. Deaconu, et al., “Optimizing Nanocasting Techniques for Stable Bismuth-Mesoporous Silica Composites in Thermal Energy Storage Application,” *Sustainable Materials and Technologies* 42 (2024): e01157, <https://doi.org/10.1016/j.susmat.2024.e01157>.
9. S. Wang, X. Gu, T. Kar, et al., “Improved Form Stability, Thermal Storage Capacity and Thermal Conductivity of Polyurethane based Waste Sponge Carbon/Expanded Graphite/Organic Phase Change Materials Coated by Ag Nanoparticles,” *Sustainable Materials and Technologies* 43 (2025): e01245, <https://doi.org/10.1016/j.susmat.2025.e01245>.
10. M. Yadav, N. Pasarkar, A. Naikwadi, and P. Mahanwar, “A Review on Microencapsulation, Thermal Energy Storage Applications, Thermal Conductivity and Modification of Polymeric Phase Change Material for Thermal Energy Storage Applications,” *Polymer Bulletin* 80 (2022): 5897–5927, <https://doi.org/10.1007/s00289-022-04369-x>.
11. S. Shoeibi, F. Jamil, S. M. Parsa, et al., *Journal of Energy Storage* 94 (2024): 112401, <https://doi.org/10.1016/j.est.2024.112401>.
12. G. B. Hamad, Z. Younsi, H. Naji, and F. Salaün, “A Comprehensive Review of Microencapsulated Phase Change Materials Synthesis for Low-Temperature Energy Storage Applications,” *Applied Sciences* 11 (2021): 112021, <https://doi.org/10.3390/app11241900>.
13. G. Fredi, A. Dorigato, L. Fambri, and A. Pegoretti, “Multifunctional Structural Composites for Thermal Energy Storage,” *Multifunctional Materials* 3 (2020): 042001, <https://doi.org/10.1088/2399-7532/abc60c>.
14. W. Chalco-Sandoval, M. J. Fabra, A. López-Rubio, and J. M. Lagaron, “Use of Phase Change Materials to Develop Electrospun Coatings of Interest in Food Packaging Applications,” *Journal of Food Engineering* 192 (2017): 122–128, <https://doi.org/10.1016/j.jfoodeng.2015.01.019>.
15. Q. Huang, X. Li, G. Zhang, et al., “Flexible Composite Phase Change Material With Anti-Leakage and Anti-Vibration Properties for Battery Thermal Management,” *Applied Energy* 309 (2022): 118434, <https://doi.org/10.1016/j.apenergy.2021.118434>.
16. H. Baniasadi, R. Abidnejad, C. D. Cruz, et al., “Sustainable Multifunctional Foams for Cold-Chain Packaging: Stabilizing Polyethylene Glycol With Cellulose and Pomegranate Peel for Antibacterial Protection and Temperature Control,” *Sustainable Materials and Technologies* 43 (2025): e01312, <https://doi.org/10.1016/j.susmat.2025.e01312>.
17. Y. Huang, W. Luo, W. Chen, et al., “Self-Healing, Adaptive and Shape Memory Polymer-Based Thermal Interface Phase Change Materials via Boron Ester Cross-Linking,” *Chemical Engineering Journal* 496 (2024): 153789, <https://doi.org/10.1016/j.cej.2024.153789>.
18. S. A. Abdul Jaleel, M. Alayli, S. Cheon, and S. Baik, “Independent Control of Electrical and Thermal Properties of Polymer Composites for Low Thermal Resistance Interface Materials,” *Advanced Engineering Materials* 27 (2025): 2402732, <https://doi.org/10.1002/adem.202402732>.

19. K. Iqbal, A. Khan, D. Sun, et al., "Phase Change Materials, Their Synthesis and Application in Textiles—A Review," *Journal of the Textile Institute* 110 (2019): 625–638, <https://doi.org/10.1080/00405000.2018.1548088>.
20. K. Yang, M. Venkataraman, X. Zhang, et al., "Review: Incorporation of Organic PCMs Into Textiles," *Journal of Materials Science* 57 (2022): 798–847, <https://doi.org/10.1007/s10853-021-06641-3>.
21. I. Alfonso, T. Calvo-Correias, A. Eceiza, et al., "Recycling Bovine Ear Tags for Phase Change Material Encapsulation via Electrospinning," *Sustainable Materials and Technologies* 45 (2025): e01449, <https://doi.org/10.1016/j.susmat.2025.e01449>.
22. B. M. Tripathi and S. K. Shukla, "A Comprehensive Review of the Thermal Performance in Energy Efficient Building Envelope Incorporated With Phase Change Materials," *Journal of Energy Storage* 79 (2024): 110128, <https://doi.org/10.1016/j.est.2023.110128>.
23. X. Wang, W. Li, Z. Luo, K. Wang, and S. P. Shah, "A Critical Review on Phase Change Materials (PCM) for Sustainable and Energy Efficient Building: Design, Characteristic, Performance and Application," *Energy and Buildings* 260 (2022): 111923, <https://doi.org/10.1016/j.enbuild.2022.111923>.
24. H. B. Ghadim, A. Godin, A. Veillere, M. Duquesne, and D. Hailot, "Review of Thermal Management of Electronics and Phase Change Materials," *Renewable and Sustainable Energy Reviews* 208 (2025): 115039, <https://doi.org/10.1016/j.rser.2024.115039>.
25. X. Wang, H. Liu, and S. Ouyang, "Damping Properties of Flexible Epoxy Resin," *Journal of Wuhan University of Technology-Mater. Sci. Ed* 23 (2008): 411, <https://doi.org/10.1007/s11595-007-3411-4>.
26. H. J. Kim, H. G. Kim, B. Seo, and C. S. Lim, "Synthesis of Acid Anhydride-Modified Flexible Epoxy Resins and Enhancement of Impact Resistance in the Epoxy Composites," *Journal of Applied Polymer Science* 140 (2022): e53249, <https://doi.org/10.1002/app.53249>.
27. N. Burger, A. Laachachi, M. Ferriol, M. Lutz, V. Toniazzi, and D. Ruch, "Review of Thermal Conductivity in Composites: Mechanisms, Parameters and Theory," *Progress in Polymer Science* 61 (2016): 1–28, <https://doi.org/10.1016/j.progpolymsci.2016.05.001>.
28. J.-F. Su, Y.-H. Zhao, X.-Y. Wang, H. Dong, and S.-B. Wang, "Effect of Interface Debonding on the Thermal Conductivity of Microencapsulated-Paraffin Filled Epoxy Matrix Composites," *Composites Part A: Applied Science and Manufacturing* 43 (2012): 325–332, <https://doi.org/10.1016/j.compositesa.2011.12.003>.
29. J.-F. Su, X.-Y. Wang, S.-B. Wang, Y.-H. Zhao, K.-Y. Zhu, and X.-Y. Yuan, "Interface Stability Behaviors of Methanol-Melamine-Formaldehyde Shell microPCMs/Epoxy Matrix Composites," *Polymer Composites* 32 (2011): 810–820, <https://doi.org/10.1002/pc.21102>.
30. G. Fredi, F. Simon, D. Sychev, et al., "Bioinspired Polydopamine Coating as an Adhesion Enhancer Between Paraffin Microcapsules and an Epoxy Matrix," *ACS Omega* 5 (2020): 19639–19653, <https://doi.org/10.1021/acsomega.0c02271>.
31. G. Fredi, A. Dorigato, L. Fambri, and A. Pegoretti, "Detailed Experimental and Theoretical Investigation of the Thermomechanical Properties of Epoxy Composites Containing Paraffin Microcapsules for Thermal Management," *Polymer Engineering and Science* 60 (2020): 1202, <https://doi.org/10.1002/PEN.25374>.
32. G. Fredi, A. Dorigato, L. Fambri, S. H. Unterberger, and A. Pegoretti, "Effect of Phase Change Microcapsules on the Thermo-Mechanical, Fracture and Heat Storage Properties of Unidirectional Carbon/Epoxy Laminates," *Polymer Testing* 91 (2020): 106747/1, <https://doi.org/10.1016/j.polymertesting.2020.106747>.
33. G. Fredi, C. Zimmerer, C. Scheffler, and A. Pegoretti, "Polydopamine-Coated Paraffin Microcapsules as a Multifunctional Filler Enhancing Thermal and Mechanical Performance of a Flexible Epoxy Resin," *Journal of Composites Science* 4 (2020): 174, <https://doi.org/10.3390/jcs4040174>.
34. C. Zimmerer, G. Fredi, S. Putzke, et al., "Dopamine as a Bioinspired Adhesion Promoter for the Metallization of Multi-Responsive Phase Change Microcapsules," *Journal of Materials Science* 57 (2022): 16755–16775, <https://doi.org/10.1007/s10853-022-07658-y>.
35. L. Shanmugam, X. Feng, and J. Yang, "Enhanced Interphase Between Thermoplastic Matrix and UHMWPE Fiber Sized With CNT-Modified Polydopamine Coating," *Composites Science and Technology* 174 (2019): 212–220, <https://doi.org/10.1016/j.compscitech.2019.03.001>.
36. M. Reinhardt, A. Drechsler, S. Putzke, F. Simon, and C. A. Zimmerer, "Bioinspired Adhesion Promoters for the Metalization of Polyethylene: A Comparison Between Polydopamine and Tannic Acid," *ACS Applied Polymer Materials* 6 (2024): 9694–9704, <https://doi.org/10.1021/acsapm.4c01571>.
37. N. Augustine, S. Putzke, A. Janke, F. Simon, A. Drechsler, and C. A. Zimmerer, "Dopamine-Supported Metallization of Polyolefins—A Contribution to Transfer to an Eco-Friendly and Efficient Technological Process," *ACS Applied Materials & Interfaces* 14 (2022): 5921–5931, <https://doi.org/10.1021/acsami.1c19575>.
38. C. Zimmerer, F. Simon, S. Putzke, A. Drechsler, A. Janke, and B. Krause, "N-Type Coating of Single-Walled Carbon Nanotubes by Polydopamine-Mediated Nickel Metallization," *Nanomaterials* 13 (2023): 2813, <https://doi.org/10.3390/nano13202813>.
39. S. Li, J. M. Scheiger, Z. Wang, et al., "Substrate-Independent and re-Writable Surface Patterning by Combining Polydopamine Coatings, Silanization, and Thiol-Ene Reaction," *Advanced Functional Materials* 31 (2021): 2107716, <https://doi.org/10.1002/adfm.202107716>.
40. X. Zhang, S. Yang, H. Zhang, H. Liu, and X. Wang, "Sustainable Solar-Powered Seawater Desalination Enabled by Phosphorene-Decorated Watermelon-Like Phase-Change Microcapsules," *Desalination* 594 (2025): 118283, <https://doi.org/10.1016/j.desal.2024.118283>.
41. F. Liu, G. Ge, W. Gu, P. Gong, D. Fan, and P. Guo, "Diatomite-Based Phase Change Composite Coatings Applied to Concrete Walls With Solar Thermal Storage and Preservation," *Solar Energy Materials and Solar Cells* 290 (2025): 113717, <https://doi.org/10.1016/j.solmat.2025.113717>.
42. S. Liu, S. Xin, X. Wei, and C. Shi, "Novel Composite Phase Change Material With Modified Melamine Foam as an Encapsulation Template for Use in Personal Cooling Suits," *Journal of Energy Storage* 101 (2024): 113796, <https://doi.org/10.1016/j.est.2024.113796>.
43. R. Suchentrunk, *Kunststoff-Metallisierung* (Eugen G. Leuze Verlag GmbH & Co. KG, 2007).

Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Figure S1:** EDX spectra of maps of C, O, Ni and Ag on (a) MC, (b) MC-Ag, (c) MC-NiS, and (d) MC-NiL. **Figure S2:** EDX maps of C, O, Ni and Ag on MC, MC-Ag, MC-NiS, and MC-NiL. **Figure S3:** Results of the cyclic DSC tests on the modified microcapsules. Phase change temperature and enthalpy as a function of the cycle number (only selected values are reported to improve clarity).

Polydopamine-mediated silver and nickel metallization of phase change microcapsules for multifunctional flexible epoxy composites

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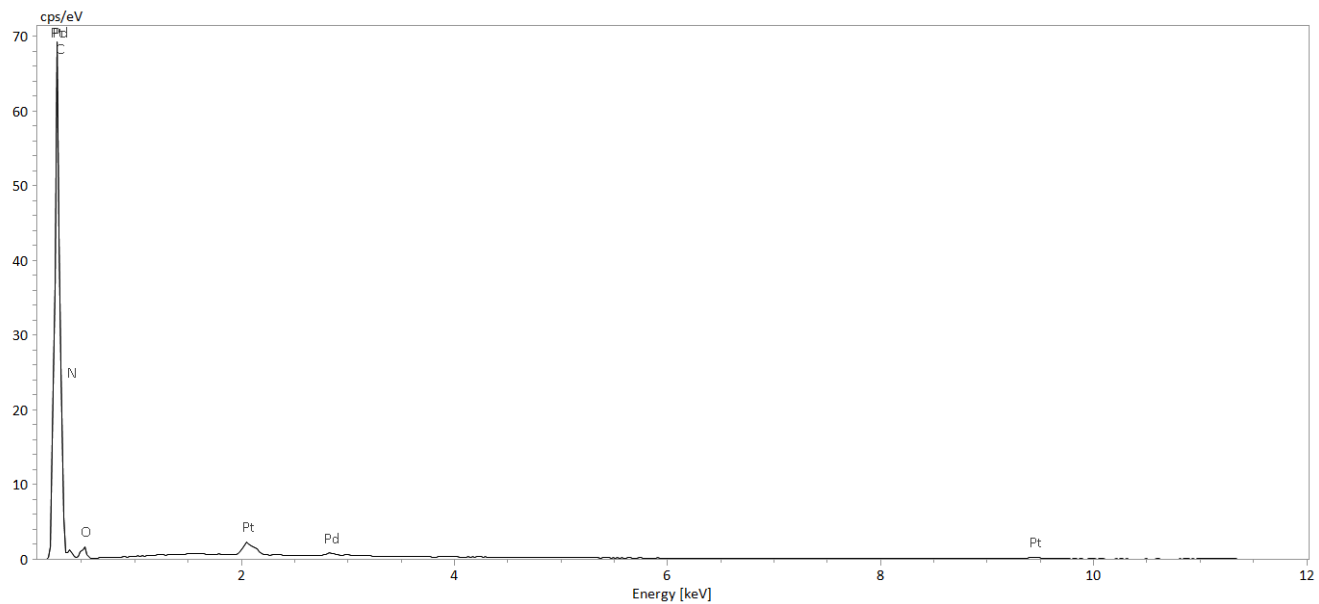
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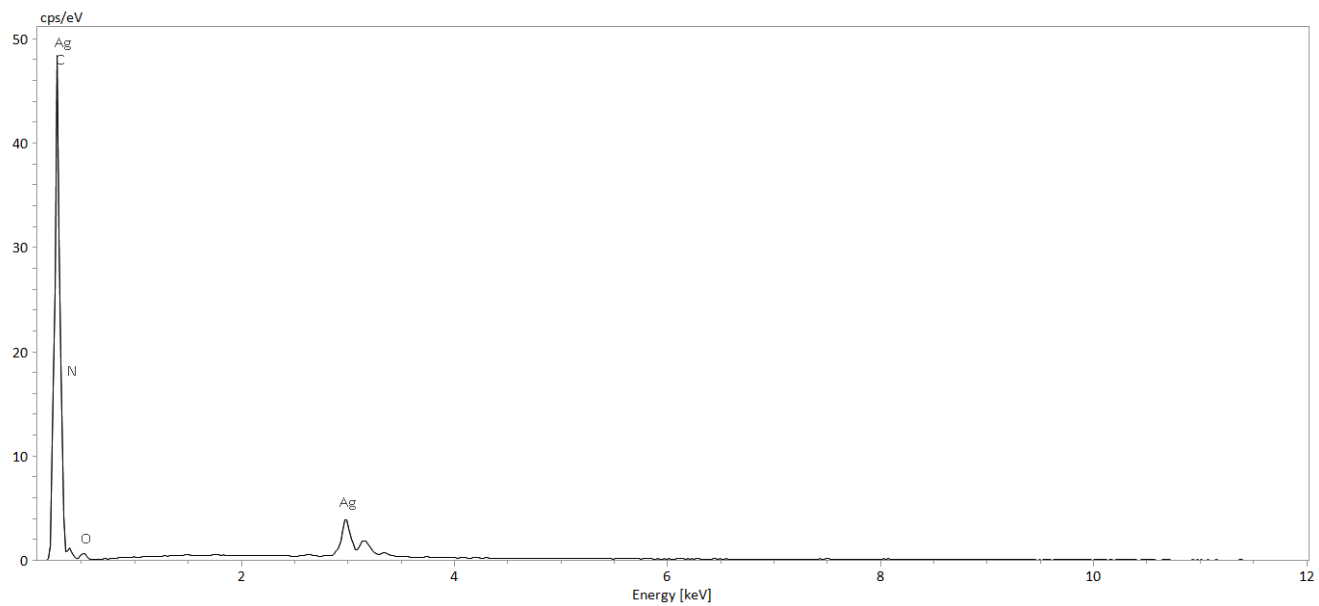
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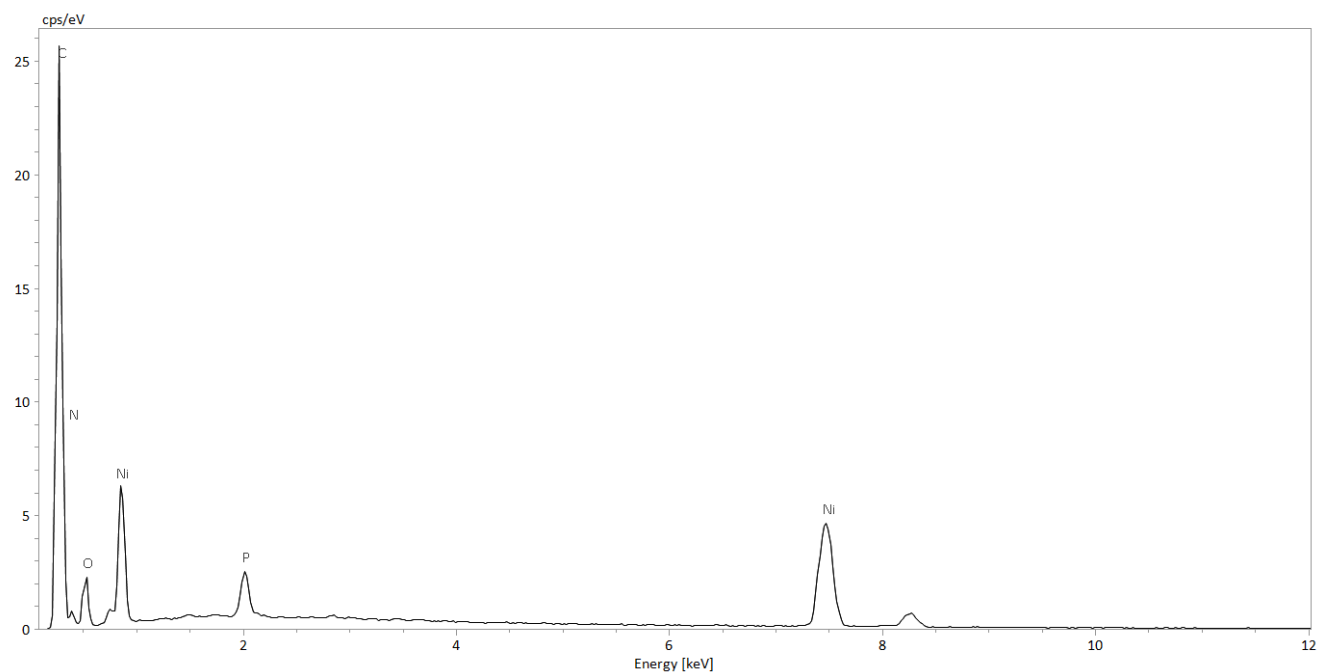
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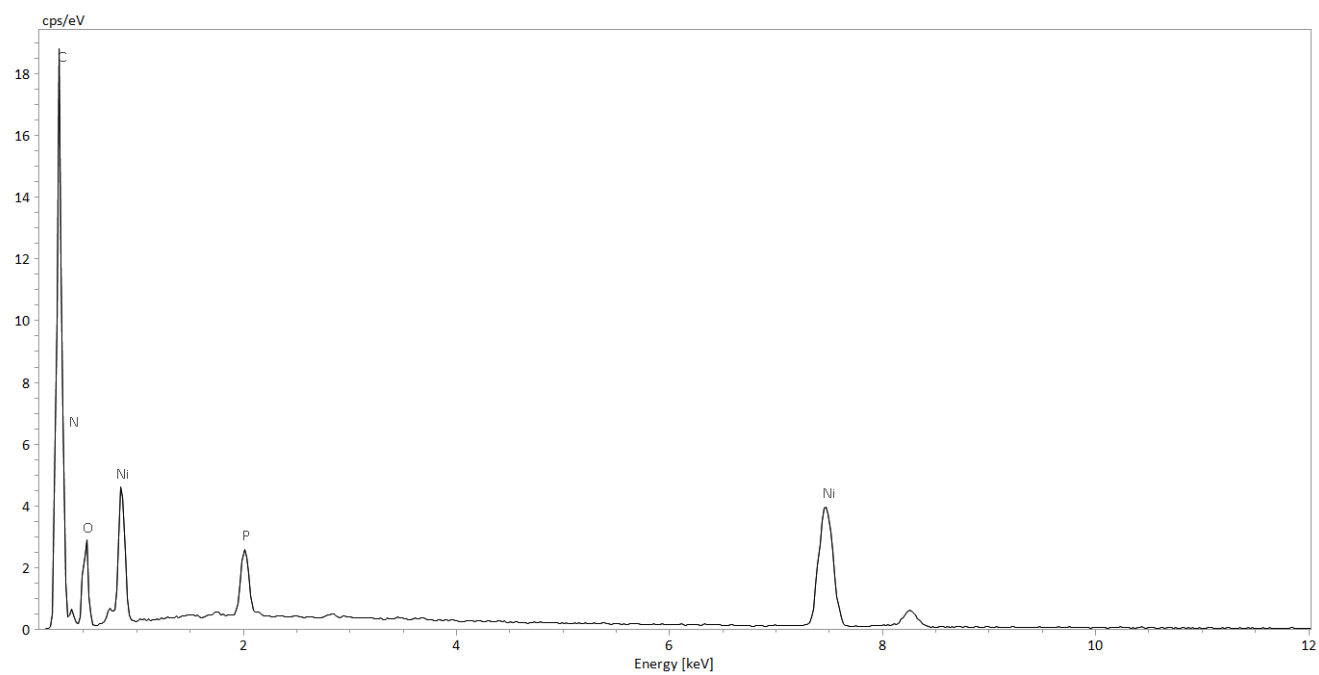
(a)



(b)



(c)



(d)

Figure S1. EDX spectra of maps of C, O, Ni and Ag on (a) MC, (b) MC-Ag, (c) MC-NiS, and (d) MC-NiL.

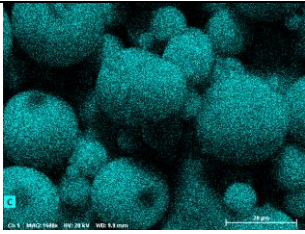
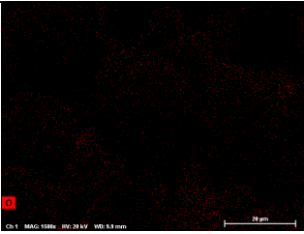
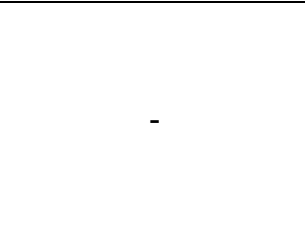
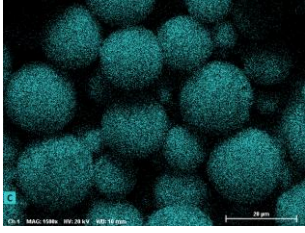
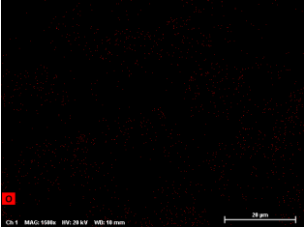
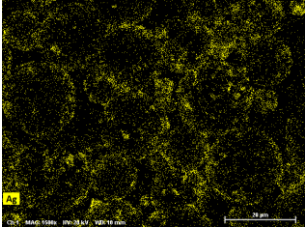
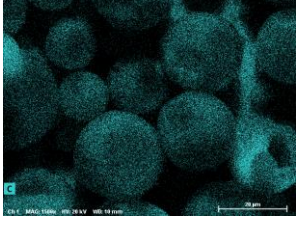
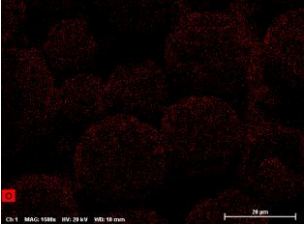
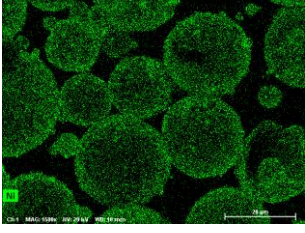
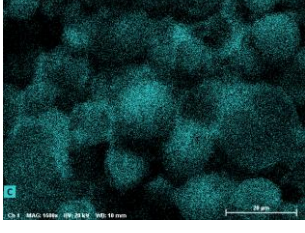
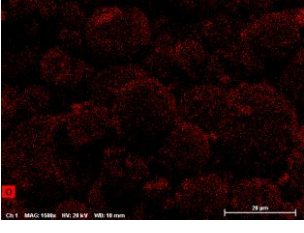
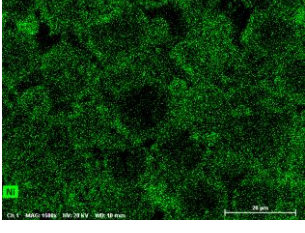
	C	O	Ag/Ni
MC			
MC-Ag			
MC-NiS			
MC-NiL			

Figure S2. EDX maps of C, O, Ni and Ag on MC, MC-Ag, MC-NiS, and MC-NiL.

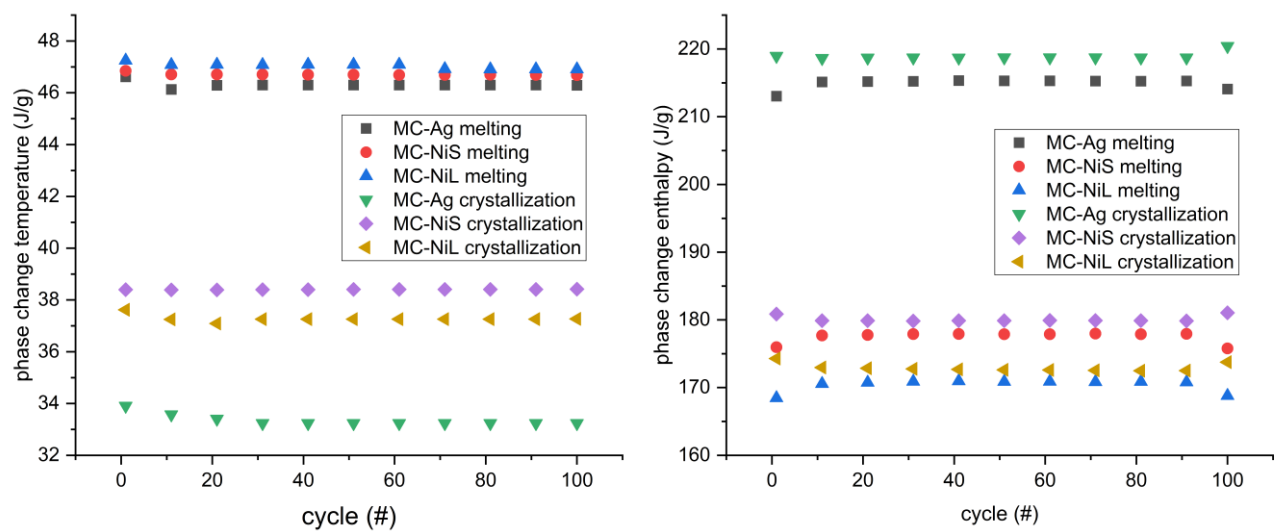


Figure S3. Results of the cyclic DSC tests on the modified microcapsules. Phase change temperature and enthalpy as a function of the cycle number (only selected values are reported to improve clarity).