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ARTICLE

Detailed experimental and theoretical investigation of the thermomechanical properties of epoxy composites containing paraffin microcapsules for thermal management

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Abstract

Microencapsulated phase change materials (PCMs) are being increasingly employed as functional fillers in polymer matrices for thermal management. Therefore, the effect of PCM microcapsules on the rheological, microstructural, thermal and mechanical properties of the host polymer matrices must be understood. This work concerned the preparation of epoxy polymers filled with PCM microcapsules (MC) in various concentrations and their subsequent characterization. The MC phase increases the viscosity of epoxy before curing, thereby reducing castability and hindering elimination of air bubbles. The latter was reflected in an increase in porosity for highly filled compositions, as elucidated by density measurements and microscopic investigation. SEM micrographs showed that the adhesion between the capsule shell and the epoxy matrix was not optimal. The interfacial weakness and the intrinsic low stiffness and strength of MC caused a reduction in mechanical properties, as evidenced by the Nicolais-Narkis and Pukanszky models. On the other hand, at zero or low deformation levels, the interface presents no gaps and is able to transfer load and heat, as demonstrated by the data of elastic modulus, modeled with the Halpin-Tsai and Lewis-Nielsen models, and those of thermal conductivity, in excellent agreement with the Pal model.

K E Y W O R D S

interfaces, mechanical properties, microencapsulation, thermal properties, thermosets

1 | INTRODUCTION

Organic phase change materials (PCMs) are the most commonly employed materials for thermal energy storage (TES), particularly at 0 to 100° C.^[1] PCMs represent an innovative, renewable and clean energy technology that can rise the heat storage/release efficiency and improve thermal management in many applications.^[2–5] Since organic PCMs can store a considerable amount of latent heat at a nearly constant temperature, their use is advantageous for temporarily accumulating excess heat for a later use. In this way, they lead to a reduction of the mismatch between energy need and availability, thereby increasing the efficiency in energy utilization, saving primary energy resources and reducing emissions.^[6–8] Some current applications of organic PCMs in TES include temporary energy storage in solar-thermal power plants and recovery of waste industrial heat.^[9,10] However, organic PCMs can be also used for thermal management applications, aimed at maintaining the indoor temperature in the comfort range,^[11-13] at avoiding the formation of ice,^[14] or at preventing overheating of electronic components.^[15-19]

comprised Organic PCMs are of paraffins, poly(ethylene glycol)s, and fatty acids. These materials are the most widely used as they feature many other advantages over other TES materials (ie, inorganic and eutectic PCMs), such as small volume variation upon phase transition, congruent melting, negligible supercooling, low density, large availability, inexpensiveness, chemical stability, and noncorrosiveness.^[3,20,21] As organic PCMs undergo a solid-liquid phase transition, their main disadvantage is the need for confinement to avoid leakage in the molten state.^[22,23] Leakage can be addressed either by macro- or micro- or nanoencapsulation,^[24-26] by shape-stabilization within a polymer matrix,^[27-32] by using layered/porous materials^[33,34] or by a nanofiller network.^[35–38] which also generally increase the thermal conductivity.^[39] Among these techniques, encapsulation in micrometric shells is the most common and effective method, as the shell also protects the PCM from the environment, facilitates handing, increases thermal stability, and partially accommodates the volume variation during the core's phase change.^[24,40,41]

In most applications where a PCM is employed, this material is placed in a supplementary module specifically designed for TES or thermal management and added to the main structure of a component. Such design concept unavoidably increases the weight and volume of the component, which can be unacceptable for some applications. In these cases, embedding the heat storage function directly in the structural parts would be advantageous and, in this perspective, polymer-matrix composites offer wide possibilities for multifunctionality.^[42] Lightweight composites performing structural and thermal management functions simultaneously could be employed where weight reduction and temperature management are equally important, such as in the automotive, portable electronics and smart technical garments sectors.^[43,44]

The scientific literature reports many examples of thermoplastic or thermosetting matrices containing microencapsulated or shape-stabilized PCMs.^[12,20,31,45-49] Our group has recently developed and characterized a variety of polymer matrices and reinforced polymer composites that combine good mechanical properties and TES capability, for example epoxy/carbon laminates containing paraffin shape-stabilized with carbon nanotubes (CNTs),^[50-52] polyamide/glass laminates enhanced with a microencapsulated or a shape-stabilized paraffinic PCM,^[53,54] polyamide-based composites reinforced with discontinuous carbon fibers and containing paraffin microcapsules,^[55] and a fully biodegradable laminate



based on thermoplastic starch, ultra-thin wood laminae and a poly(ethylene glycol) as the PCM.^[56]

The impact of the PCM on the thermomechanical properties an processability of the host polymer must be understood. A highly fluid polymer or precursor can be more easily processable to fabricate parts in polymer composite, and the addition of a solid filler, especially in high volume fractions as in the case of a PCM, unavoidably affects the rheological behavior and thus the processability and castability.

This work aims at producing epoxy composites containing microencapsulated paraffin in various concentrations and characterizing these composites thoroughly in terms of rheological, microstructural, thermal and mechanical properties. More specifically, the processability was assessed through measurements of the viscosity of the mixture before curing. To the best of the authors' knowledge, no studies have been performed that investigate how the addition of PCM microcapsules affects the viscosity of an epoxy formulation. Thermal properties were evaluated with a broad spectrum of characterization techniques, comprising not only the state-of-the-art experimental methods normally applied on PCM-containing systems, for example, the assessment of the phase change enthalpy though differential scanning calorimetry (DSC), but also more sophisticated techniques such as the evaluation of the thermal conductivity, which is an important property influencing the heat transfer inside the composite and thus the overall thermal management performance. The importance of measuring and tuning the thermal conductivity on PCM-filled polymer composites has already been stressed by Su et al.^[57,58] This group also identified key parameters influencing the conductivity by considering theoretical models. However, this group did not apply the models to their experimental data. The present work does so, by selecting the most appropriate theoretical models that take into account the core-shell particle morphology and the high volume fraction of the most highly loaded compositions. Finally, this work investigates how the introduction of microencapsulated PCM affects the mechanical performance of the host epoxy resin, not only with quasi-static tests but also with fracture mechanics and impact characterization techniques. The experimental data were then fitted with theoretical models, to understand the role of the filler's stiffness and strength and the interfacial properties on the overall mechanical performance.

MATERIALS AND METHODS 2

2.1 Materials

The epoxy base Elan-tech EC157 (density = 1.15 g/ cm^3 , viscosity at $25^{\circ}C = 550 \text{ mPa} \cdot \text{s}$) and the hardener Elan-tech W342 (density = 0.95 g/cm^3 , viscosity at $25^\circ\text{C} = 50 \text{ mPa}\cdot\text{s}$) were kindly provided by Elantas Europe Srl (Collecchio, Italy), while the microencapsulated PCM Microtek MPCM43D was purchased from Microtek Laboratories (Dayton, OH). In this product, the PCM phase consists of a paraffin wax (declared melting temperature 43°C) encapsulated inside a melamine-formaldehyde-based shell, which represents approximately the 10-15% of the total mass. These microcapsules are characterized by a diameter of 15-30 µm, and the declared melting enthalpy is 200-210 J/g. All materials were used as received.

2.2 | Sample preparation

The epoxy base and the hardener were combined in a weight ratio of 100:30, as indicated by the producer, and vigorously stirred for 5 minutes to ensure an intimate mixing. PCM microcapsules (MC) without any solvents were subsequently added in different weight fractions (10, 20, 30, 40, and 50 wt%) and the mixtures were stirred again to ensure a homogeneous dispersion of the MC phase. The resulting mixtures were degassed under vacuum and casted into rectangular silicon molds of different sizes to prepare specimens for the subsequent characterization. The specimens were cured at room temperature for 24 hours and post-cured at 100°C for 10 hours. Neat epoxy specimens (EP) were also prepared for comparison. Table 1 lists the prepared compositions with the nominal weight fractions of the components.

2.3 | Characterization techniques

The viscosity of the as-prepared base-hardener-MC mixtures was evaluated at room temperature (23°C) with a Brookfield viscometer. The epoxy base and the MC were first mixed to ensure a homogeneous dispersion. The hardener was added to the mixture just before the test, to

TABLE 1List of the prepared samples with the nominalweight composition

Sample	EP (wt%)	MC (wt%)
EP	100	0
EP-MC10	90	10
EP-MC20	80	20
EP-MC30	70	30
EP-MC40	60	40
EP-MC50	50	50
MC	0	100

avoid a further increase in viscosity due to crosslinking. The tests were performed at room temperature with a Brookfield Viscometer Model RVT (Brookfield Engineering Laboratories, Inc., MA), with spindles chosen among the set RV and the small sample adapter, according to the viscosity of the mixture. The viscosity was determined in the speed range between 5 and 100 rounds per minute (rpm), and all the measurements were acquired within 15 minutes since the addition of the hardener.

Density measurements were acquired to evaluate how the MC addition modifies the porosity of the final cured samples. The experimental density of the samples EP and EP-MCx (x = $10 \div 50$) was determined with the liquid displacement method, performed according to the standard ASTM D792 with a Gibertini E42 analytical balance (Gibertini Elettronica Srl, Milano, Italy). The selected liquid was ethanol (purity 99%), purchased by Sigma-Aldrich. At least three specimens were measured for each sample. The density of ethanol was measured with a metallic sphere of known and calibrated volume at the beginning and at the end of each measuring session. The bulk density of MC was measured with a Micromeritics AccuPyc 1330 helium pycnometer (Micromeritics Instrument Corp., Norcross, GA) at 23.0°C, and the density was calculated as the average of 99 consecutive measurements. The theoretical density of the prepared samples was calculated through the mixture rule, starting from the density of EP and MC. From a comparison between the experimental and theoretical density, the volume fraction of pores could then be calculated.

Scanning electron microscopy (SEM) micrographs of the cryofracture surfaces of the prepared samples were acquired using a Zeiss Supra 60 field emission scanning electron microscope (FESEM; Oberkochen, Germany), after Pt-Pd sputtering.

Differential scanning calorimetry (DSC) was performed to investigate the melting and crystallization enthalpy and temperature values (T_m , T_c , ΔH_m , ΔH_c), which are the main parameters determining the TES capability of a sample containing a PCM in a specific temperature range. Moreover, a volumetric melting enthalpy was calculated by multiplying the values of ΔH_m by the experimental density. DSC analysis also allowed the measurement of the glass transition temperature of the EP matrix (T_g) , which provides information about the degree of curing. All DSC tests were performed on a Mettler DSC30 instrument (Mettler Toledo, Columbus, OH), in the temperature interval 0-120°C, at a heating/cooling rate of 10°C/min, under a nitrogen flow of 100 mL/min. All specimens, with a mass of approx. 10 mg each, underwent a first heating scan, a cooling scan, and a second heating scan. Additionally, cyclic DSC tests were performed to evaluate the stability of the

thermal properties after several thermal cycles. The test was run in the temperature interval 0-100°C, and fifty subsequent cycles were performed.

Thermogravimetric analysis (TGA) was performed to assess how the resistance to the thermal degradation varies upon PCM addition. The tests were performed through a Mettler TG50 instrument (Mettler Toledo, Columbus, OH) on specimens of approximately 20-25 mg at a heating rate of 10°C/min, up to 700°C, under a nitrogen flow of 150 mL/min. The tests allowed the determination of the temperatures corresponding to a mass loss of 1 wt%, 3 wt%, 5 wt% ($T_{1\%}$, $T_{3\%}$, $T_{5\%}$), of the degradation temperature (T_d) , intended as the temperature at the maximum degradation rate and measured as the position of the mass loss derivative peak, as well as the residual mass after the test (m_r) .

Thermal conductivity was measured with a Hot Disk Thermal Constants Analyzer Model TPS 2500S (Hot Disk AB, Göteborg, Sweden), capable of precise measurement of thermal conductivity, thermal diffusivity and specific heat capacity. This machine uses the transient plane source method and theory in accordance with ISO Standard 22 007-2:2015. To perform the measurement, the sensor, made of a double spiral nickel wire insulated in a thin layer of Kapton, was placed between two sheets of material with planar and parallel surfaces. In this work, specimens were analyzed with sensor no. 5465 (radius 3.189 mm). The measurement is performed by sending a current through the nickel sensor and measuring the temperature rise of the sensor itself, evaluated through a change in electrical resistance. The temperature rise is influenced by the thermal properties of the sample material that surrounds the sensor, which are evaluated by the instrument software. Important measurement parameters are the power input and the measurement time, which must be chosen so that they produce a temperature increment of 2-5 K, as recommended by the instrument manual. At least three measurements were performed for each sample, in different zones of the specimen and/or with a different power input. The bulk isotropic module was chosen for all the investigated samples. For these measurement, specimens were prepared with an in-plane dimension of $100 \times 50 \text{ mm}^2$ and a thickness of 5 mm.

Although the DSC test is the most accurate technique to produce quantitative information on the TES capability of a sample, the small dimensions of the investigated specimen can lead to results that are not fully representative of the macroscopic properties of the prepared samples. Therefore, to check the overall thermal management capacity of the MC-enhanced epoxy composites, a simple test was performed with a thermal camera. Specimens of $100 \times 100 \times 5 \text{ mm}^3$ were heated in an oven at 80° C for



30 minutes, then removed and left cooling to room temperature. During the cooling step, the surface temperature was recorded with an infrared thermal imaging camera FLIR E60 (FLIR Systems, Inc., Wilsonville, OR), placed at a fixed distance of 30 cm from the sample surface. The tests allowed the evaluation of the effects of the latent heat of crystallization released during cooling, which slowed down the temperature decrease.

Quasi-static tensile tests were performed with a universal testing machine Instron 5969 (Instron, Norwood, MA), equipped with a 50 kN load cell. The test was performed on 1BA specimens (standard ISO 527) prepared by casting. The measurement of the elastic modulus (E)was performed at a crosshead speed of 0.25 mm/min. The strain was measured with a resistance extensometer Instron 2620 with a gauge length of 12.5 mm, and five specimens were tested for each sample. According to the standard ISO 527, the elastic modulus was measured as the secant of the stress-strain curve between the strain values of 0.05% and 0.25%. For each composition, five additional specimens were tested until failure, at a crosshead speed of 1 mm/min. This test allowed the determination of the maximum stress and the corresponding strain (σ_{MAX} , ε_{MAX} ,), as well as the stress and strain at break (σ_h, ε_h).

Flexural tests were performed with a three-point bending configuration, according to the standard ASTM D790, with a universal testing machine Instron 5969 (Instron, Norwood, MA) equipped with a 50 kN load cell. Tests were performed on rectangular specimens with nominal dimensions of $70 \times 10 \times 3 \text{ mm}^3$. Span length was fixed at 50 mm and the crosshead speed at 1.5 mm/ min. At least five specimens were tested for each composition. The flexural modulus of elasticity (E_f) , the flexural strength (σ_{fM}) and the flexural strain at break (ε_{fb}) were determined for each specimen as described in Equations (1), (2) and (3), respectively:

$$E_f = \frac{mL^3}{4bd^3} \tag{1}$$

$$\sigma_{fM} = \frac{3PL}{2bd^2} \tag{2}$$

$$\varepsilon_{fb} = \frac{6Dd}{L^2} \tag{3}$$

where L is the support span, m is the slope of the tangent to the initial portion of the load-deflection curve, b and d are the specimen width and thickness, P is the maximum load and D is the deflection at the break point.

Mode I fracture toughness tests were performed with a universal testing machine Instron 5969 (Instron, Norwood, MA) equipped with a 50 kN load cell. Tests were performed on single edge notched beam (SENB) specimens with nominal dimensions $80 \times 10 \times 4 \text{ mm}^3$. A sharp notch was machined with a depth of 4.5 mm, and a sharp crack was subsequently initiated by sliding a fresh razor blade in the notch. Three specimens were tested for each composition. The measurements were carried out according to the standard ASTM D5045, in a three-point bending configuration, with a span length of 40 mm and crosshead speed of 10 mm/min. A conditional value (K_Q) of the critical stress intensity factor was determined for each specimen through Equation (4) as:

$$K_Q = \left(\frac{P_Q}{B\sqrt{W}}\right) f(x),\tag{4}$$

where P_Q is the load value determined as described in the standard ASTM D5045, *B* and *W* are the specimen thickness and depth, respectively, and f(x) is a geometrical function defined in the Equation (5) as:

$$f(x) = 6\sqrt{x} \frac{1.99 - x(1 - x)(2.15 - 3.93x + 2.7x^2)}{(1 + 2x)(1 - x)^{\frac{3}{2}}}$$
(5)

where *x* is the ratio between the initial notch length (*a*) and the specimen depth (*W*). To produce a valid value of K_Q , the ratio P_{max}/P_Q should not be greater than 1.1, where P_{max} is the maximum load reached during the test. The calculated K_Q can be considered as the critical stress intensity factor K_{IC} only when the condition of plane-strain defined in Equation (6) are satisfied:

$$B, a, (W-a) > 2.5 \left(\frac{K_Q}{\sigma_y}\right)^2, \tag{6}$$

where σ_y is the yield stress, evaluated in this case as the maximum load in the uniaxial tensile tests.

For the measurement of the critical strain energy release rate, G_{IC} , the displacement correction was performed to account for system compliance, loading-pin penetration, and sample compression. The displacement correction for each specimen was performed by loading an uncracked specimen with the support span reduced to zero, as described in the standard ASTM 5045.

Charpy impact tests were performed according to ISO 179 with a Ceast 6549 impactor. The hammer had a mass of 1.18 kg and was placed at an angle of 39°, so that the impact speed resulted of 1 m/s and the impact energy of 0.6 J. The test was performed on rectangular samples of $80 \times 10 \times 4 \text{ mm}^3$ with a notch depth of 2 mm and a notch tip radius of 0.25 mm. A span length of 62 mm was

used, and at least five specimens were tested for each sample. The test allowed the measurement of the maximum load reached during the tests (F_{max}), the and the total absorbed specific energy (E_{tot}).

3 | RESULTS AND DISCUSSION

3.1 | Viscosity

Results of the Brookfield viscosity tests are reported in Figure 1. The mixture containing 50 wt% of MC (EP-MC50) could not be tested because its viscosity was out of the range investigable with the available equipment $(>4.10^4 \text{ cP})$. Due to the geometry of some of the spindles, a precise and uniform value of shear rate could not be calculated. Therefore, the values of viscosity were reported as a function of the rotation speed. However, since different spindles were used, a direct quantitative comparison could not be made. In any case, the obtained results were sufficient to draw important conclusions on the effect of MC on the sample viscosity and processability, at least from the qualitative point of view. The neat base/hardener mixture (EP) exhibits slight pseudo-plastic behavior, as the viscosity decreases with an increase in the rotation speed and is especially evident at the lower limit of the investigated rotation speed range. This behavior is observable also in the MC-filled mixtures, which do not exhibit the dilatant (shear-thickening) behavior commonly observed in fluids containing particles.^[59] Since this behavior is generally associated to the particle order loss and aggregate formation at high shear stresses, it can be concluded that the aggregation tendency of MC is low,



FIGURE 1 Results of the Brookfield viscosity tests on the EP/MC uncured mixtures [Color figure can be viewed at wileyonlinelibrary.com]

which is also reasonable considering the particles are of micrometric size. For a fixed rotation speed the viscosity increases remarkably with MC loading, as commonly reported in the literature for uncured epoxy systems containing micro- or nano-particles.^[60] For example, at 20 rpm, the viscosity of the neat EP was measured as 390 cP, while that of the EP-MC30 mixture is 3200 cP and that of the EP-MC40 mixture is as high as 15 400 cP. It should be stressed that the comparison between the different compositions cannot be made from a quantitative point of view because the test was performed by using different spindles. However, these results give at least an idea of the increase in viscosity due to the MC addition. Such a large increase was observed also on polypropylene samples containing the same type of paraffin microcapsules.^[61] This result suggests that an increase in the MC fraction decreases the processability of the mixtures in terms of degassing and casting, thereby



hindering the possibility to obtain defect-free and perfectly dense specimens, as confirmed by the increase in porosity with the PCM content, described in Section 3.3.

3.2 | Microstructural characterization

Figure 2A-H shows the SEM micrographs of the cryofracture surface of the prepared samples. The core-shellstructure of the microcapsules is well visible, together with their spherical morphology and diameter mainly in the range 10-30 μ m, as already evidenced in previous works^[62] and in good agreement with what reported in the producer's datasheet. From micrographs acquired at higher magnification (not reported) and image processing with the ImageJ software, it was possible to estimate the shell thickness as (0.150 ± 0.011) μ m. Micrographs at lower magnification (Figure 2A,C,E) show that the



FIGURE 2 Selected SEM micrographs of the cryofracture surface of the EP and EP-MCx (x = 10, 20, 30, 40, 50) samples at different magnification levels. (A,B) EP-MC10; (C,D) EP-MC30; (E,F) EP-MC50; (G) EP-MC10, with the indication of the interphase region; (H) EP-MC30, with the indication of the interphase region [Color figure can be viewed at wileyonlinelibrary.com]

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microcapsules are homogeneously distributed in the matrix, without evident aggregation or agglomeration. The micrograph of the sample EP-MC50 (Figure 2E,F) shows that, at such a high concentration, the microcapsules hinder one another and cause a deformation and partial loss of spherical shape. Micrographs at higher magnification (Figure 2B,D,F) indicate that nearly all microcapsules are broken, which implies that the fracture propagates across the capsules and not at the capsulematrix interface. Nevertheless, the capsule-matrix interfacial adhesion is poor, as evidenced by gaps and debonding zones. Poor interfacial adhesion was observed previously in polymer composites containing this kind of MC and having an $epoxy^{[62]}$ or an $acrylic^{[63,64]}$ matrix, and is mainly due to the lack of reactivity of the fully cured melamine-formaldehyde shell. The present work, focused on the effects of PCM introduction in an epoxy matrix, allowed a deeper investigation also on the properties of the interface and the interphase. As observable in Figure 2G,H, the region surrounding the capsules and evidenced with a red dashed line has a darker color than the matrix far from the capsules; it can be described as an interphase zone and shows the formation of microcracks along the stress propagation lines.

3.3 | Density and porosity

Figure 3 reports the results of the evaluation of density and porosity of the prepared samples. The neat cured EP has a measured density of $1.158 \pm 0.002 \text{ g/cm}^3$, while that of the MC phase was found to be 0.901



FIGURE 3 Theoretical density (ρ_{th}), experimental density (ρ_{exp}) and porosity of the EP and EP-MCx (x = 10, 20, 30, 40, 50) samples, as a function of the nominal MC weight fraction. The density of ethanol is ρ_{etOH} =0.793 ± 0.004 g/cm³ [Color figure can be viewed at wileyonlinelibrary.com]

 \pm 0.005 g/cm³, in excellent agreement with values from the datasheet. These two values allowed the calculation of the theoretical density of the EP-MCx samples via the mixture rule using volumetric compositions. These values, reported in Figure 3 as ρ_{th} , decrease with an increase in the MC fraction. Figure 3 also reports the experimental density (ρ_{exp}) for these samples, which is increasingly lower than ρ_{th} with an increase in the MC content. Therefore, the porosity increases from 1.64 vol% for Ep-MC10 to 7.78 vol% for EP-MC50 confirming the increasing difficulty to fabricate defect-free specimens for highly-filled compositions, consistent with the considerable increase in viscosity (see Section 3.1). The increase in porosity is modest up to an MC fraction of 30 wt% and increases considerably at higher MC fractions.

3.4 | Thermal characterization

Figure 4A,B show DSC thermograms of the first heating and cooling scans on the prepared samples, while the main results of the DSC tests for all the three scans are summarized in Table 2. All EP and EP-MCx samples show glass transition temperatures at 80-90°C, and small fluctuation in these values do not seem to show a trend with the MC weight fraction. Thermograms of all the samples containing MC show an endothermic peak at 45-49°C, which corresponds to the melting of the PCM contained in the microcapsules, and an exothermic peak at 25-30°C corresponding to the crystallization transition. For all compositions, both thermal transitions interest a temperature range of approx. 20-30°C; the melting transition is found in the temperature range between 35°C and 60°C, while the crystallization transition between 40°C and 15°C. Moreover, the breadth of the peak and the involved temperature range increases with the MC fraction, which indicates that the interval in which the material is active as a TES medium increases. Although the indicated temperature intervals are strictly a function of the applied heating/cooling rate (10° C/min), these results suggest that it is important to evaluate the interval of thermal transition for a specific sample, as this interval determines the temperature interval in which the sample is actively performing TES. As observable especially in the cooling scan (Figure 4B), these peaks are the superposition of at least two peaks attributable to a solid-solid and a solid-liquid transition as already observed in previous works on the same^[61] or similar^[65,66] paraffinic PCMs. The intensity of these peaks increases with the MC weight fraction. From peak areas, the experimental values of the melting and crystallization enthalpy were calculated and reported in Table 2 as ΔH_m and ΔH_c for the first heating and cooling scans, respectively. By a



FIGURE 4 DSC thermograms of the samples EP and EP-MCx (x = 10, 20, 30, 40, 50). (A) first heating scan; (B) cooling scan; (C) representative thermograms of the cyclic DSC test on the sample EP and EP-MC30, with the values of melting enthalpy (ΔH_m) measured at each cycle [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Results of DSC tests on EP and EP-MCx (x = 10, 20, 30, 40, 50) samples

Sample	<i>T</i> g (°C)	<i>Τ_m</i> (°C)	ΔH_m (J/g)	ΔH_m (J/cm ³)	ΔH_m^{rel} (%)	<i>T</i> _c (°C)	∆ <i>H</i> c (J/g)	ΔH_c^{rel} (%)	<i>T</i> _{g,} ₂ (°C)	<i>T_{m,}</i> ₂ (°C)	∆ <i>H_{m,}</i> ₂ (J/g)	$\Delta H^{rel}_{m,2}$ (%)
EP	96.2	—	—	_	—	—	_	—	97.6	—	—	—
EP-MC10	88.9	46.2	21.6	23.9	94.9	25.6	22.2	98.1	89.6	46.1	21.8	96.4
EP-MC20	94.9	46.5	43.9	46.7	96.4	25.4	44.0	97.3	96.6	46.5	43.4	95.9
EP-MC30	89.2	48.1	67.7	69.5	99.1	24.7	68.8	101.4	91.1	47.9	67.7	99.8
EP-MC40	95.3	51.1	86.3	84.3	94.8	21.9	88.9	98.3	96.3	50.9	88.2	97.5
EP-MC50	91.7	50.6	107.0	99.9	94.0	22.2	106.4	94.1	98.6	50.8	106.4	94.1
MC	_	44.7	227.7	204.9	100.0	29.0	226.2	100.0		44.4	226.2	100.0

Note: $T_g =$ glass transition temperature of the epoxy phase in the first heating scan (°C); $T_m =$ melting temperature of the PCM in the first heating scan (°C); $\Delta H_m = \text{PCM}$ melting enthalpy in the first heating scan (J/g); $\Delta H_m^{rel} = \text{relative PCM}$ melting enthalpy in the first heating scan (%); $T_c = \text{crystallization}$ temperature of the PCM (°C); $\Delta H_c =$ PCM crystallization enthalpy (J/g). $T_{g, 2} =$ glass transition temperature of the epoxy phase in the second heating scan (°C); $T_{m,2}$ = melting temperature of the PCM in the second heating scan (°C); $\Delta H_{m,2}$ = PCM melting enthalpy in the second heating scan (J/g); $\Delta H_{m,2}^{rel}$ = relative PCM melting enthalpy in the second heating scan (%).

comparison between the phase change enthalpy measured on the neat MC and that measured on the prepared EP-MCx samples, relative phase change enthalpy values $(\Delta H_m^{rel}, \Delta H_c^{rel})$ were calculated according to Equations (7) and (8), respectively:

$$\Delta H_m^{rel} = \frac{\Delta H_m}{w_{MC} \cdot \Delta H_m^{neat}} \tag{7}$$

$$\Delta H_c^{rel} = \frac{\Delta H_c}{w_{MC} \cdot \Delta H_c^{neat}} \tag{8}$$

where ΔH_m and ΔH_c are the melting and crystallization enthalpy values of the MC measured on the EP-MCx, w_{MC} is the nominal weight fraction of PCM in the sample and ΔH_m^{neat} and ΔH_c^{neat} are the melting and crystallization enthalpy values of the neat PCM. A relative phase change enthalpy close to 100% suggests that the PCM fraction contained in the composite after processing is close to the nominal (initial) fraction, and that the PCM preserves its capability of melting and crystallizing also when embedded in a polymer matrix.

The measured values of ΔH_m and ΔH_c are in good agreement with those expected by considering the nominal MC weight fraction, and hence the values of ΔH_m^{rel} and ΔH_c^{rel} always close to 100%. This result indicates that the processing parameters are mild enough to preserve microcapsule integrity and the PCM meltingcrystallization capability, and the small positive or negative deviations from 100% could be attribute to slight inhomogeneities of the MC distribution inside the samples. Values relative to the second heating scan are nearly the same as those reported for the first, which indicates that the TES capability of the contained PCM are preserved after the first cycle. The ability of the samples to undergo many subsequent thermal cycles was studied more in detail via a cyclic DSC test. The results of this test for the sample EP-MC30 are reported in Figure 4C, which shows DSC thermograms relative to some representative cycles and the measured melting enthalpy for the cycles. Cycle shape, phase change temperature and enthalpy do not vary significantly indicating good thermal stability. The average melting enthalpy over the 50 thermal cycles is 99.8 ± 0.3 J/g, and the resulting average relative melting enthalpy (ΔH_m^{rel}) , normalized to that of the MC in the first heating scan is 99.8%. These cyclic DSC tests were run between 0°C and 100°C, a temperature interval abundantly broader than that to which the material will be subjected in service.

Figure 5A,B shows TGA thermograms while TGA results are shown in Table 3. As already observed.^[61,62] the initial thermal degradation of the MC consists of several small subsequent steps. The mass loss at lower temperature can be related to free (non-encapsulated) paraffin and some low molecular weight compounds, present as residuals of the capsule synthesis. Mass loss between 200°C and 300°C is observable also on the EP-MCx samples, and is responsible for the decrease in $T_{1\%}$, $T_{3\%}$, and $T_{5\%}$ with an increase in the MC loading. For MC alone the subsequent degradation step is related to the thermal degradation of the paraffin and the melamineformaldehyde shell. The narrow derivative peak indicates that most of the mass loss occurs in a small temperature interval. This mass loss is due to damage of the microcapsule shell and sudden release of the PCM core. This spike was observed also on repeated measurements on different specimens and in previous works on the same PCM,^[61,62]



FIGURE 5 TGA thermograms of the EP and EP-MCx (x = 10, 20, 30, 40, 50) samples. (A) residual mass as a function of temperature; (B) mass loss derivative as a function of temperature [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 Main results of TGA tests on the EP and EP-MCx (x = 10, 20, 30, 40, 50) samples

Sample	<i>T</i> _{1%} (°C)	T _{3%} (°C)	T _{5%} (°C)	<i>T_d</i> (°C)	m _r (%)
EP	213.6	325.0	351.8	378.8	5.99
EP-MC10	199.2	293.8	325.2	390.3	6.50
EP-MC20	201.4	294.7	324.4	370.0	5.40
EP-MC30	191.2	272.4	318.0	378.3	5.56
EP-MC40	189.1	239.5	294.9	379.8	5.55
EP-MC50	163.8	241.1	299.3	386.0	5.18
MC	184.8	233.6	299.7	465.8	0.46

Note: $T_{1\%}$ = temperature corresponding to a mass loss of 1 wt% (°C); $T_{3\%}$ = temperature corresponding to a mass loss of 3 wt% (°C); $T_{5\%}$ = temperature corresponding to a mass loss of 5 wt% (°C); T_d = degradation temperature (°C), corresponding to the peak of the mass loss derivative; m_r = residual mass at 700°C (%).

but is not observed in any of the EP-MCx sample, as the presence of the surrounding matrix may modify the heat transfer and the mass loss rate. In these samples, degradation of the EP and MC happens in a relatively narrow temperature interval making it difficult to separate the degradation steps and employ them to evaluate sample composition. Finally, the peak derivative temperature T_d is only marginally effected by the MC content, which implies that the MC addition does not impair the thermal degradation resistance of the EP phase.

The thermal imaging test, although simple, was able to give immediate information on the thermal management capability of the prepared EP-MCx samples. The results of this characterization for some compositions are reported in Figure 6A, B. Figure 6A reports some thermographic images acquired during the tests, while Figure 6B shows the trends of surface temperature (acquired in the center of the specimen) as a function of time after extraction from the oven. For the neat EP sample, the temperature decreases quickly, while in the samples containing MC the temperature exhibits a plateau-like trend, due to the heat released during crystallization of the PCM. This effect delays cooling to room temperature, and is increasingly evident with an increase in the MC weight fraction, as also appreciable from the reported thermographic images (Figure 6A). For instance, the sample EP takes 11.9 minutes to reach 35°C, while approx. 35.0 minutes are needed for the sample EP-MC20 and 48.5 minutes for the sample EP-MC40, with an increase of 194% and 307%, respectively.

The results of the Hot Disk test are reported in Table 4. The thermal conductivity is 0.222 W/mK for the neat epoxy resin, in good agreement with literature data,^[67] and increases slightly but significantly with the MC loading. This trend was found also for other epoxy-



based systems filled with microencapsulated PCM in the solid state and/or approaching the melting transition^[57] when the shell was not made of a highly conductive metal or ceramic material. On the other hand, values of thermal diffusivity and specific heat capacity do not follow a trend with MC content. However, these values are not as reliable as thermal conductivity measured with a Hot Disk Thermal Constant Analyzer. Although the scientific literature reports many experimental, theoretical and numerical studies on the thermal conductivity of two-phase polymer composites, little has been done to investigate the thermal conductivity of polymers filled with core-shell particles. Felske^[68] developed a model to predict the thermal conductivity (λ) of a non-dilute composite (volume fraction of filler does not tend to zero) filled with core-shell particles, as a function of the conductivity of the matrix (λ_m) , of the particle shell (λ_s) and the particle core (λ_c), the filler volume fraction (ϕ_f), and the ratio between the outer and the inner particle radius (δ) . The model describes the behavior of the relative thermal conductivity of the composite (λ_r) , defined as the ratio between the conductivity of the composite and that of the matrix. The model is reported in Equation (9)-(11) as

$$\lambda_r = \frac{\lambda}{\lambda_m} = \frac{2\left(1 - \phi_f\right) + \left(1 + 2\phi_f\right)(B/A)}{\left(2 + \phi_f\right) + \left(1 - \phi_f\right)(B/A)} \tag{9}$$

where

$$A = 1 + 2\delta^3 - (1 - \delta^3)(\lambda_c / \lambda_s) \tag{10}$$

$$B = \frac{(2+\delta^3)\lambda_c - 2(1-\delta^3)\lambda_s}{\lambda_m}$$
(11)

More recently, Pal^[69] pointed out that the model described in Equation (9) succeeds in predicting the thermal conductivity of a composite only when ϕ_f is less than approx. 0.2, while it is less accurate when ϕ_f approaches ϕ_{max} , where ϕ_{max} is the maximum packing volume fraction. Therefore, Pal proposed a new model that is illustrated in Equation (12)-(13) as

$$\left(\lambda_r\right)^{1/3} \frac{\beta - 1}{\beta - \lambda_r} = \left(1 - \frac{\Phi_f}{\Phi_{max}}\right)^{-\Phi_{max}} \tag{12}$$

$$\beta = \frac{\left(2+\delta^3\right)\left(\lambda_c/\lambda_m\right) - 2\left(1-\delta^3\right)\left(\lambda_s/\lambda_m\right)}{\left(1+2\delta^3\right) - \left(1-\delta^3\right)\left(\lambda_c/\lambda_s\right)} \tag{13}$$

If, as in the present work, the particle shell is thin, and the shell material exhibits a thermal conductivity of



FIGURE 6 Results of the thermal imaging camera tests on the EP and EP-MCx (x = 20, 30, 40) samples. (A) Selected thermography images acquired during the test. (B) Values of surface temperature as a function of the cooling time [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 Results of the Hot Disk tests on the EP and EP-MCx (x = 20, 30, 40) samples

Sample	λ (W/mK)	<i>k</i> (mm ² /s)	$c_P (\mathrm{MJ/m^3K})$
EP	0.222 ± 0.003	0.156 ± 0.009	1.55 ± 0.07
EP-MC20	0.242 ± 0.002	0.170 ± 0.003	1.52 ± 0.02
EP-MC30	0.257 ± 0.002	0.173 ± 0.006	1.54 ± 0.04
EP-MC40	0.267 ± 0.002	0.156 ± 0.004	1.55 ± 0.03

Note: λ = thermal conductivity (W/mK); *k* = thermal diffusivity (mm²/s); *c*_P = specific heat capacity (MJ/m³K).

the same order of magnitude as the core and the surrounding matrix (λ_s does not tend to ∞), then the value of δ can be approximated to 1 and Equation (12) can be rewritten as the Equation (14) as

$$(\lambda_r)^{1/3} \frac{(\lambda_c/\lambda_m) - 1}{(\lambda_c/\lambda_m) - \lambda_r} = \left(1 - \frac{\Phi_f}{\Phi_{max}}\right)^{-\Phi_{max}}$$
(14)

The model described in Equation (14) was used to fit the experimental data of thermal conductivity. The value of ϕ_{max} was fixed at 0.637, which is the maximum packing volume fraction in the case of uniformly sized spherical particles.^[69] The value of λ_m was fixed as the measured thermal conductivity of the neat epoxy, while λ_c was treated as a free parameter. The results of this analysis are reported in Figure 7. The model estimates the thermal conductivity of the prepared composites well, as the fitting converges with a value of R² equal to 0.999. The value of the parameter λ_c , the thermal conductivity of the core material, results as (0.308 ± 0.003) W/mK, which is in good agreement with literature data on paraffinic PCMs.^[70,71] These results prove that the Pal model



FIGURE 7 Relative thermal conductivity of the prepared samples (λ_r) as a function of the MC volume fraction. Experimental data and fitting with the modified Pal model. The fitting converged with a value of R² of 0.999. (λ = thermal conductivity of the EP-MCx samples; λ_m = thermal conductivity of the neat EP) [Color figure can be viewed at wileyonlinelibrary.com]

with the approximation of thin shell is suitable to predict the thermal conductivity of these epoxy composites filled with core-shell paraffinic PCMs.

According to the model introduced by Pal^[69] and the results presented by Su et al.,^[58] when interfacial debonding occurs between the MC and the epoxy matrix, then the model can be rewritten with the ratio λ_c/λ_m tending to zero, as a considerable thermal resistance hinders the heat transfer between the matrix and the particles. Therefore, the model can be rewritten as shown in Equation (15):

$$\lambda_r = \left(1 - \frac{\Phi_f}{\Phi_{max}}\right)^{\frac{3\Phi_{max}}{2}} \tag{15}$$

Equation (15) indicates that the overall thermal conductivity of the composite should decrease with an increase in the MC fraction, but this is not the case with the experimental results. Tests were made on asproduced undeformed samples, and the results of the fitting implies that the condition of zero thermal resistance (and no gaps at the interface) is closer to reality than the condition in which gaps are present. This result implies that the gaps at the interface observed on the SEM micrographs are not generated during sample preparation (due to the different thermal expansion coefficient of MC and epoxy during cooling after the post curing step), but are generated at higher deformation levels, during the specimen fracture. These results agree SPEINSBURG PLASTICS POLYMER ENGINEERING_WILEY 1213 AND SCIENCE

with the modeling of the elastic modulus with the Lewis-Nielsen model, presented in Section 3.5.

3.5 | Mechanical characterization

Results of flexural tests are reported in Figure 8A,B, which show representative load-displacement curves and the trends of the flexural modulus, strength and strain at break as a function of the MC weight fraction. As already observed in previous works on MC-filled epoxy^[62] and acrylic^[63] resins, the elastic modulus decreases with an increase in the MC content. The lowest value is measured on the sample EP-MC50 and is equal to (0.87 ± 0.02) GPa, which implies a decrease of 68.7% compared to the neat EP resin, exhibiting a modulus of (2.78 ± 0.21) GPa. As expected, the flexural strength is also negatively affected by the MC addition, as it decreases from (112 \pm 15) MPa of the neat EP to (28 \pm 2) MPa of the sample EP-MC50. This decrease is probably associated to the lower stiffness and strength of the MC phase compared to EP, as well as to a non-optimal adhesion with the matrix. On the other hand, the strain at break is less affected by the MC fraction.

Similar comments can be made for the results of the quasi-static tensile tests, reported in Figure 9A,B. Also in this case, the mechanical properties are negatively affected by an increase in the MC fraction. The experimental data of elastic modulus were fitted with the Halpin-Tsai model, a useful tool to predict the stiffness of a composite containing a particulate filler.^[72,73] According to the Halpin-Tsai model, the modulus of the composites (E) can be computed through the Equation (16) as

$$\mathbf{E} = \frac{1 + \zeta \eta \phi_f}{1 - \eta \phi_f} E_m,\tag{16}$$

where E_m is the elastic modulus of the matrix, ϕ_f is the filler volume fraction, ζ is the shape factor of the filler, equal to 2 in the case of spherical particles, and η can be computed through Equation (17) as

$$\eta = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \zeta}.$$
(17)

where $E_f = E_{MC}$ is the elastic modulus of the filler (the MC phase). Considering an estimation of the value of E_f , it depends on the elastic moduli of the shell and the core. Since the shell is a thin membrane with a thickness of approx. 150 nm, if an average particle diameter of 20 µm



FIGURE 8 Results of the three-point bending tests on the EP and EP-MCx (x = 10, 20, 30, 40, 50) samples. (A) Representative loaddeflection curves; (B) values of flexural modulus (E_f), strength (σ_{fM}) and strain at break (ε_{fb}) as a function of the nominal MC weight content [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 9 Results of the quasi-static tensile tests on the samples EP and EP-MCx (x = 10, 20, 30, 40, 50). (A) Representative stress-strain curves; (B) values of tensile modulus (*E*), strength (σ_{max}) and strain at break (ε_b) as a function of the nominal MC weight content [Color figure can be viewed at wileyonlinelibrary.com]

is considered, the shell accounts for only 4.5% of the total MC volume. Since also the shell is polymeric (melamineformaldehyde resin), it is reasonable to suppose that its elastic modulus is of the same order of magnitude of the epoxy resin and the paraffinic core, and not orders of magnitude greater as if it was made of a ceramic or a metallic material. Therefore, the shell contribution to the total elastic modulus can be in a first approximation neglected. The elastic modulus of a solid paraffin wax with a melting temperature of around 50°C is approx. 150-250 MPa,^[74] therefore a tentative value of 200 MPa was put in the model as E_f , and the results of this evaluation are reported in Figure 10A. The model succeeds in predicting the elastic modulus for low MC volume fraction but tends to overestimate the experimental results above a MC content of 20 vol%. A more accurate fit is found if the value of E_{MC} is put equal to 28 MPa. This value was found in a previous work of our group on PCM-enhanced thermoplastic polyurethane (TPU) blends.^[75] In that work, the employed microcapsules had a liquid core, as the melting temperature of the paraffin applied in that work was below room temperature. The results of the model would not be considerably different if E_{MC} is put equal to 0 MPa instead of 28 MPa, which would result if the filler behaved mechanically like spherical porosity. The effect of the adhesion between the epoxy matrix and the MC shell can be taken into account by applying the Lewis-Nielsen model,^[76,77] reported in Equation (18) as

$$\mathbf{E} = \frac{1 + (k_E - 1)\beta \phi_f}{1 - \beta \mu \phi_f} E_m, \tag{18}$$

where k_E is the generalized Einstein coefficient, ϕ_f is the filler volume fraction, E_m is the modulus of the matrix, and β and μ are coefficients defined through Equations (19) and (20), respectively, as

$$\beta = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + (k_E - 1)},$$
(19)

$$\mu = 1 + \frac{1 - \phi_f}{\phi_{max}} \left[\phi_{max} \phi_f + (1 - \phi_{max}) \left(1 - \phi_f \right) \right], \qquad (20)$$

where $E_f = E_{MC}$ is the elastic modulus of the filler (the MC phase) and ϕ_{max} is the maximum filler volume fraction, as in the case of Equation (14). The value of k_E depends on the filler-matrix adhesion. According to Nielsen and Landel,^[78] for a matrix with a Poisson's ratio of 0.5 containing dispersed spheres, k_E assumes the value 2.5 if there is no slippage at the interface and 1.0 if there is slippage, but k_E is decreased if the Poisson's ratio of the matrix is lower than 0.5. The literature value for the Poisson's ratio of epoxy resins is 0.30-0.35, so a value of 0.35 was selected here, following also what reported elsewhere in the literature for particulate-filled epoxy composites^[77,79] so values of k_E are reduced by a factor of 0.867. Hence, $k_E = 2.167$ if there is no slippage and k_E



= 0.867 if there is slippage.^[78] Both values were used to fit the data and the results are reported in Figure 10B. For the case with $k_E = 2.167$, the value of E_{MC} was alternatively set to 0.200 GPa or 0.028 GPa. It can be observed that the model with $k_E = 2.167$ results in a good fitting of the experimental data when E_{MC} = 0.200 GPa and slightly underestimates the data when E_{MC} = 0.028 GPa, although the two trends do not differ remarkably. On the other hand, the model with the hypothesis of slippage ($k_E = 0.867$) largely underestimates the data and fails in fitting the experimental results. This result suggests that the hypothesis of no slippage is closer to the experimental data, thus the adhesion is good, there are no evident gaps at the interface and the interphase is able to transfer load from the matrix to the fillers, at least at zero or low deformation levels where the elastic modulus is calculated. These results agree with those made for the thermal conductivity results.

On the other hand, tensile strengths were fitted with two theoretical models that both account for adhesion and interfacial properties related to the capability of the interface to transfer load from the matrix to the fillers. The selected model was that proposed by Nicolais-Narkis and that developed by Pukanszky. The model of Nicolais-Narkis is reported in Equation (21) as:

$$\frac{\sigma_{MAX,c}}{\sigma_{MAX,m}} = 1 - K \left(\phi_f\right)^{2/3} \tag{21}$$

where $\sigma_{MAX, c}$ and $\sigma_{MAX, m}$ are the tensile strength of the composite and the matrix, respectively, ϕ_f is the filler volume fraction and *K* is a parameter that takes into account the interfacial adhesion between the filler and the matrix and assumes a maximum value of 1.21 for a scarce



FIGURE 10 Application of theoretical models to the values of tensile modulus of the EP and EP-MCx (x = 10, 20, 30, 40, 50) samples. (A) Halpin-Tsai model; (B) Lewis-Nielsen model [Color figure can be viewed at wileyonlinelibrary.com]

adhesion. The model of Pukanszky is reported in Equation (22) as:

$$\frac{\sigma_{MAX,c}}{\sigma_{MAX,m}} = \frac{1 - \phi_f}{1 + 2.5\phi_f} e^{B\phi_f}$$
(22)

where $\sigma_{MAX, c}$, $\sigma_{MAX, m}$, and ϕ_f assume the same meanings as for Equation (21), and *B* is an empirical parameter that considers the load-transfer capability of the interphase. Tensile strengths were fitted with both models with either *K* or *B* as free parameters and results are reported in Figure 11. The model of Nicolais-Narkis converged with a value of R² of 0.992 with a value of *K* equal



FIGURE 11 Application of Nicolais-Narkis and Pukanszky models to the values of tensile strength of the EP and EP-MCx (x = 10, 20, 30, 40, 50) samples [Color figure can be viewed at wileyonlinelibrary.com]

to 1.21, which represents very low capsule-matrix interfacial adhesion. Analogous results emerged from the fitting with the Pukanszky model, which converged with a value of R^2 of 0.993 and a coefficient *B* equal to 0.272. This value of *B* indicates an interphase with low mechanical properties that, although able to transfer load between the matrix and the fillers, is a weak point in the composite.

Composites were also investigated trough a Charpy *impact* tests, and the results of this characterization are reported in Figure 12A,B. Also in this case, MC addition impairs the mechanical properties of the composites, as both the absorbed total specific energy and the maximum load decrease noticeably with an increase in the MC fraction. For example, the total specific energy decreases from 6.37 kJ/m² of the neat EP sample to 1.21 kJ/m² of the sample EP-MC30 and 0.87 kJ/m² of the sample EP-MC50, with a decrease of 81% and 86%, respectively. This effect, observed also in a previous study,^[62] is another consequence of the embrittlement and the defectiveness brought by MC insertion.

Lastly, the results of fracture toughness tests are reported in Figure 13 and in Table 5. The evaluation of the fracture propagation in an epoxy composite is important and the literature reports many studies on the methods and techniques to improve the fracture toughness of epoxy resins.^[80,81] For all specimens considered in the calculation, both the condition expressed in Equation (6) and the condition $P_{max}/P_Q < 1.1$ were always verified, as recommended by the ASTM standard. The values of fracture toughness K_{IC} are negatively affected by an increase in the MC weight fraction. A Student's *t*test was performed between each pair of samples (EP and



FIGURE 12 Results of the Charpy impact tests on the EP and EP-MCx (x = 10, 20, 30, 40, 50) samples. (A) Representative load-time curves; (B) values of total specific energy ($E_{sp, tot}$, kJ/m²) and maximum load (F_{max} , N) as a function of the nominal MC weight fraction [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 13 Representative load-displacement curves obtained during the fracture toughness tests on the samples EP and EP-MCx (x = 10, 20, 30, 40, 50) [Color figure can be viewed at wileyonlinelibrary.com]

EP-MC10, EP-MC10 and EP-MC20, etc.) to evaluate the significance of the variation. A value of P < .05 was considered statistically significant in all testing. It was found that p is always higher than 0.05 for each pair of samples except for the comparison between EP-MC20 and EP-MC30. Therefore, the decreases are not statistically significant for a capsule weight fraction of up to 20%, while the decrease becomes significant for MC contents of 30 wt% and above. For example, the value of K_{IC} is 1.28 $\pm \ 0.34 \ \text{MPa}{\cdot}\text{m}^{1/2}$ for EP but decreases to 1.11 \pm 0.10 MPa·m^{1/2} for EP-MC20 and 0.57 \pm 0.04 MPa·m^{1/2} for EP-MC50. In a similar way, the value of G_{IC} slightly increases up to 20 wt% of MC, and then decreases with a further increase in the MC content. The value of G_{IC} increases from $400 \pm 158 \text{ J/m}^2$ of the neat EP to 634 \pm 42 J/m² of the sample EP-MC20, with an increase for the mean value of 58.5%. A Student's t-test performed on the G_{IC} values gave the same results as that performed on the data of K_{IC} . MC addition modifies also the behavior of the material during the test. The compositions with up to 20 wt% of MC fail suddenly and break in two pieces after reaching the maximum load, while the formulations with an MC content above 30 wt% absorb a significant amount of energy also after the maximum load. This effect can be quantified through the parameter E_p/E_i , which is the ratio between the energy absorbed after the maximum load $(E_p, propagation energy)$ and that absorbed before the maximum load $(E_i, initiation)$ energy), reported in Table 5. This parameter increases considerably with MC addition, especially for an MC content above 30 wt%, and is probably due to the crushing



TABLE 5 Results of the fracture toughness tests on the EP and EP-MCx (x = 10, 20, 30, 40, 50) samples

Sample	K_{IC} (MPa·m ^{1/2})	E_p/E_i (%)	G_{IC} (J/m ²)
EP	1.28 ± 0.34	4.3 ± 1.0	400 ± 158
EP-MC10	0.95 ± 0.12	4.4 ± 1.7	404 ± 72
EP-MC20	1.11 ± 0.10	3.6 ± 0.1	634 ± 42
EP-MC30	0.77 ± 0.10	50.7 ± 11.6	417 ± 102
EP-MC40	0.64 ± 0.07	61.9 ± 6.2	333 ± 23
EP-MC50	0.57 ± 0.04	77.5 ± 3.2	269 ± 25

Note: K_{IC} = mode I fracture toughness (MPa·m^{1/2}); E_p/E_i = ratio between the energy absorbed after the maximum load (E_p , propagation energy) and the energy absorbed before the maximum load (E_i , initiation energy); G_{IC} = critical strain energy release rate (J/m²).

and deformation of the capsules that collapse onto each other. Although the maximum load and thus the value of K_{IC} decrease with an increase in the MC content, the ability of the material to absorb a non-negligible amount of energy during crack propagation helps slow crack advancement, thus making the material somewhat more reliable. The microcapsules introduce new toughening mechanisms, such as the crack deflection, crack pinning, microcracking, and debonding, as commonly observed for brittle matrices containing micro- or nanofillers.^[82-84] These mechanisms are also observable from the SEM micrographs of the fracture surfaces after the test (Figure 14A-D), especially up to a MC content of 20 wt%. The cracks are similar to those propagating from the equatorial region of the particles in brittle polymers toughened with rubber domains (eg, high-impact polystyrene, HIPS^[85]). On the other hand, for the samples with a high MC concentration, the crack propagation also causes deformation and crashing of the microcapsules one over the other, which is likely the main reason for the energy absorption during crack propagation.

4 | CONCLUSIONS

This work reported detailed thermal and mechanical characterization of epoxy samples filled with microencapsulated paraffin. Brookfield viscosity tests evidenced that the MC addition strongly increases the viscosity of the resin/hardener mixture, thereby decreasing the processability of the mixtures and making the casting and degassing steps more difficult. These effects are the basis of an increase in porosity with an increase in the MC content, as evidenced by density measurements and SEM micrography. Microstructural characterization also highlighted that the MC phase is uniformly distributed in the matrix and that the



FIGURE 14 SEM micrographs of the fracture surface of representative compositions after fracture toughness tests. (A) EP; (B) EP-MC10; (C) EP-MC30; (D) EP-MC50 [Color figure can be viewed at wileyonlinelibrary.com]

adhesion between the matrix and the MC shell is not optimal causing a considerable decrease in the mechanical strength of the prepared samples, as also demonstrated by the fitting of the experimental data with the models of Nicolais-Narkis and Pukanszky, both of which are consistent with considerable interphase weakness. The Halpin-Tsai model was used to predict the tensile elastic modulus of the composites. When employing a filler modulus of 0.2 GPa, which is that of a solid paraffin wax, the Halpin-Tsai model resulted in a slight overestimation of the experimental data for a high MC concentration (above 30 wt%), while a much more accurate prediction resulted when employing a filler modulus of 0 GPa (porosity) or 0.028 GPa (found in a previous work for microcapsules containing a liquid PCM). The modeling of the elastic modulus with the Lewis-Nielsen approach evidenced that, at low deformations, the interfacial interaction between fillers and matrix is good. This good interactions agrees with thermal conductivity data, which showed excellent agreement with the Pal model calculated considering no gaps at the interface. Fitting of the thermal conductivity data allowed the estimation of the thermal also

conductivity of the MC phase as (0.308 ± 0.003) W/mK, in good accordance with data from the literature. Fracture mechanics experiments also showed that an increase in MC content causes a decrease in fracture toughness, but above an MC fraction of 30 wt % the material absorbs a considerable amount of energy after maximum load. In this perspective, the sample EP-MC30 can be considered the most promising composition, as it shows a good TES capability, but also a reasonably low porosity, acceptable mechanical properties and an interesting behavior in fracture propagation tests. The phase change enthalpy of the prepared composites was proportional to the MC weight fraction, which indicated that the processing parameters were mild enough to preserve the MC integrity and avoid PCM degradation. Further assessment of the thermal management capability of the prepared samples was made through a test with a thermal camera, which evidenced that the heat released during PCM crystallization slows down the cooling of the material considerably. This work sheds light on the impact of adding a core-shell PCM to an epoxy matrix and helps pave the way for using such

systems in applications of thermal energy storage and temperature management.

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