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Effect of phase change microcapsules on the thermo-mechanical, fracture and heat storage properties of unidirectional carbon/epoxy laminates

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ABSTRACT

This work aims at producing and characterizing unidirectional carbon/epoxy composites containing different fractions of paraffin microcapsules (MC) for thermal management applications. The viscosity of the epoxy/MC mixtures increases with the MC content, thereby increasing the final matrix weight and volume fraction and reducing that of the fibers. This is at the basis of the decrease in mechanical properties of the laminates with high MC concentration (the elastic modulus decreases up to 53% and the flexural strength up to 67%), but the application of theoretical models shows that this decrease is only due to the lower fiber volume fraction, and not to a change in the properties of the constituents or the fiber/matrix interaction. The MC phase is preferentially distributed in the interlaminar zone, which leads to a thickening of this region and a decrease in matrix-related properties, such as the interlaminar shear strength, which decreases of up to 70%. However, a modest MC fraction causes an increase in the mode I interlaminar fracture toughness of 48%, due to the introduction of new toughening mechanisms. On the other hand, an excessive MC content lets the crack propagating through the matrix and not at the fiber/matrix interface, thereby reducing the toughening mechanism provided by fiber bridging. For the thermal properties, the phase change enthalpy increases with the MC fraction up to 48.7 J/g, and this is reflected in better thermal management performance, as proven by thermal imaging tests. These results are promising for the development of multifunctional polymer composites with thermal energy storage and thermal management properties, and future works will be focused on a deeper study of the micromechanical properties of PCM microcapsules and on the improvement of the capsule/matrix adhesion.

1. Introduction

The interest in fiber reinforced polymers (FRPs) has considerably grown in the last decades: their high specific mechanical properties, easy processability, high fatigue life and corrosion resistance have broadened the market of lightweight composite structures with complex geometries, especially in weight-critical applications such as the transportation, sports and energy industries [1–3].

Polymer composites have recently attracted increasing attention also because they are suitable to produce multifunctional structures, as they achieve multifunctionality by gathering in one material the properties of multiple phases [4]. The combination of different fillers results in a unique set of properties, which can be tailored to respond to stimuli of different nature and perform different tasks at the same time. Most of the recent effort in multifunctional materials consists in the development of polymer-matrix structural composites featuring one or more additional non-structural functions. This strategy allows large weight savings at the system level, through the elimination or reduction in the number of multiple monofunctional constituents, and it gives better results than the conventional approach of optimizing the weight and geometry of the single subsystems individually [5,6].

An interesting non-structural feature that could be added to a structural composite is the thermal energy storage (TES) capability, i.e. the ability to store heat that can be released where and when needed [7]. TES technologies have the feature of reducing the gap between thermal energy demand and availability and are nowadays employed to accumulate excess heat in the solar-thermal power plants [8,9], to recover waste industrial heat [10], to store hot or cold water [11], but also for

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thermal management applications such as the indoor thermal regulation in buildings [12–15].

Thermal energy can be stored and released as sensible heat, latent heat, or through a reversible thermochemical reaction. Nowadays, latent heat TES is the most widely used TES method, especially in the low-medium temperature range (0-100 °C) [7,16]. Latent heat TES is mostly performed through organic phase change materials (PCMs) such as paraffins, poly(ethylene glycol)s or fatty acids [17], which store a considerable amount of latent heat at a nearly constant temperature and are chemically inert, inexpensive and easy to handle [7,18-21]. They also show small volume variation upon phase transition, congruent melting, negligible supercooling, low density, large availability, and non-corrosiveness [22-25]. On the other hand, as they are subjected to a solid-liquid phase change, they need to be confined to avoid leakage of material above the melting temperature [26–29]. Among all available confinement techniques, encapsulation in micrometric shells is the most common and effective method, because the shell additionally protects the PCM from the surrounding environment, enhances thermal stability, and contributes to accommodate the core's volume variation during melting and crystallization [30-33]. Other solutions involve the production of shape-stabilized PCMs, in which polymer matrices, nanofillers, layered or porous materials can be used as the shape stabilizing agent and prevent leakage of the PCM also in the molten state. More specifically, such nanofillers or porous materials, thanks to their high specific surface area, grasp the PCM molecules and avoid leakage even when the temperature is above the melting point of the PCM [34–36].

Due to their ability of maintaining the temperature nearly constant throughout the whole phase transition while absorbing or releasing a considerable amount of heat, organic PCMs are strategic for thermal management applications, aimed at maintaining the temperature in the human comfort range [12,37–39], producing thermoregulating textiles [40–42], protecting perishable goods such as food or drugs [43], preventing overheating of electronic components [44–48], or avoiding the formation of ice on critical structures such as aircrafts and wind turbine blades [49]. Moreover, PCMs have been added to concrete materials for enhancing their thermal storage ability [50] or for reducing concrete cracking caused by temperature variations [51].

Apart from the case of concrete structures, the PCM is generally placed in a supplementary module specifically designed for TES and added to the main structure of a component. This can increase the weight and volume of the component, which can be unacceptable for all those applications in which weight saving is a critical performance parameter. On the contrary, it would be advantageous to embed the thermal management function in the structural elements. Therefore, lightweight polymer composites performing structural and TES functions could be employed where it is critical to deal with weight saving and heat management simultaneously, such as in the fields of transportation and portable electronics [52,53].

Although the literature reports many examples of polymer matrices containing PCMs [37,54-60], little has been done so far to deeply investigate their mechanical properties and to enhance them by adding reinforcing fibers [61]. Our group has recently focused on investigating how the introduction of a PCM impacts the thermo-mechanical properties of several classes of fiber-reinforced polymers. For example, many research efforts were devoted to the development of bidirectional epoxy/carbon laminates containing paraffin stabilized with carbon nanotubes (CNTs) [62-64], polyamide composites enhanced with a microencapsulated paraffinic PCM and reinforced with continuous or discontinuous fibers [65-69], and a fully biodegradable laminate based on thermoplastic starch, ultra-thin wood laminae and poly(ethylene glycol) [70]. The characterization of bidirectional laminates highlighted that the PCM content influences the thickness of the interlaminar region and the properties dependent on the matrix. However, a better understanding of how the PCM addition influences the fiber-related and matrix-related properties distinctly can be reached by characterizing a PCM-containing unidirectional laminate, which has never been

described in the open scientific literature, to the best of the authors' knowledge.

This work aims at producing unidirectional carbon/epoxy laminates containing a microencapsulated PCM in different weight fractions, and at characterizing in a comprehensive way the physical, thermal and mechanical properties to assess how they vary with the PCM content. More specifically, the thermal characterization aimed at measuring the total phase change enthalpy measured with differential scanning calorimetry (DSC) and at correlating it with the thermal management capability measured with thermal camera imaging. The dynamicmechanical analysis (DMA) aimed at measuring how the PCM phase change influences the viscoelastic parameters of the composites with single-frequency, multifrequency and cyclic heating-cooling tests. The mechanical characterization not only assessed the tensile and flexural properties in the longitudinal and transversal directions below and above the melting temperature of the PCM, but evaluated also the impact of PCM microcapsules on the interlaminar fracture toughness, which has been investigated only once in the open scientific literature (i. e. on bidirectional glass/epoxy laminates [71]).

2. Materials and methods

2.1. Materials

The epoxy base Elan-tech EC157 (density = 1.15 + 0.1 g/cm³, viscosity at 25 $^\circ\text{C}$ = 550 + 50 mPa s) and the hardener Elan-tech W342 (density = 0.95 + 0.1 g/cm³, viscosity at $25 \degree C = 50 + 20$ mPa s) were kindly provided by Elantas Europe Srl (Collecchio, Italy). Microencapsulated PCM Microtek MPCM43D was supplied by Microtek Laboratories (Dayton, OH, US). The PCM phase consists of a paraffin wax (declared melting temperature 43 °C) encapsulated inside a melamineformaldehyde-based shell, which constitutes approx. 10-15% of the total mass. The average diameter is 15–30 µm, and the melting enthalpy is 200-210 J/g, as declared on the product's datasheet. Previous works of our group highlighted that these microcapsules retain their thermal and TES properties for up to 50 heating/cooling thermal cycles [72]. Unidirectional carbon fiber fabric UCD-15060 was kindly provided by Mike Compositi (Milano, Italy). The nominal areal weight was 150 g/m^2 . The supplier declared that the carbon fibers composing the fabric are the Zoltek PX35 (Zoltek Corporation, Bridgeton, MO, US), having a nominal diameter of 7.2 µm, a nominal elastic modulus of 242 GPa and a nominal density of 1.81 g/cm³. All materials were used as received.

2.2. Sample preparation

The epoxy base and the hardener were mixed at room temperature (23 °C) at a weight ratio of 100:30, as suggested by the producer, and magnetically stirred at 500 rpm for 5 min. The PCM microcapsules were then added at different weight concentrations, i.e. 20 wt%, 30 wt% or 40 wt%. These weight fractions were selected from a previous work on epoxy matrices containing the same microcapsules [72]. The resulting mixtures were vigorously stirred manually for 2 min to obtain a homogeneous dispersion of the microcapsules in the resin. These mixtures were used as matrices to prepare laminates via a wet lay-up technique. Eight plies were stacked together, and the resulting unidirectional laminates had an in-plane area of $130 \times 200 \text{ mm}^2$. The laminates were vacuum-bagged, left to cure at room temperature for 24 h and post-cured in an oven at 100 °C for 10 h. A carbon fiber/epoxy laminate without MC was prepared with the same procedure for comparison. The same route was followed to produce additional laminates with 16 laminae. In such laminates, a poly(ethylene terephthalate) (PET) film with a thickness of 26 μm was placed in the mid plane to generate a pre-crack for mode I interlaminar fracture toughness tests. Table 1 displays the list of prepared laminates. The composites were denoted as EP-MCx-CFu, where EP, MC and CFu are the labels for the epoxy resin, PCM microcapsules and unidirectional carbon fibers, respectively, and x

Table 1

List of	the prei	pared EP	-MCx-C	'Fu la	minates.
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Sample	MC content in the initial matrix formulation (wt%)	Number of laminae	PET film (y/n)	Thickness (mm)
EP-CFu-A	0	8	n	1.33 ± 0.03
EP-MC20-CFu-A	20	8	n	2.00 ± 0.05
EP-MC30-CFu-A	30	8	n	2.13 ± 0.03
EP-MC40-CFu-A	40	8	n	$\textbf{2.42} \pm \textbf{0.07}$
EP-CFu-B	0	16	у	3.00 ± 0.17
EP-MC20-CFu-B	20	16	У	4.71 ± 0.19
EP-MC30-CFu-B	30	16	у	$\textbf{4.84} \pm \textbf{0.04}$
EP-MC40-CFu-B	40	16	у	5.58 ± 0.13

represents the initial weight percentage of MC on the total mass of the matrix (i.e. 20, 30 and 40 wt%). The laminates labelled "-A" have 8 plies, while those labelled "-B" have 16 plies and the PET film in the mid plane. From the thicker laminates, labelled "-B", specimens were used only for mode I fracture toughness and short-beam shear strength tests. All the other mechanical and dynamic-mechanical tests were performed on the thinner laminates, labelled "-A".

2.3. Characterization

The experimental density of the prepared laminates was measured through helium pycnometry, performed with a Micromeritics AccuPyc 1330 helium pycnometer (Micromeritics Instrument Corp., Norcross, GA, US) at 23 °C. For each specimen, 99 consecutive measurements were acquired, to reach stationary conditions. The same technique was applied to measure the density of the constituents, namely the carbon fibers, paraffin microcapsules and cured epoxy resin.

The microstructure of the prepared laminates was evaluated by obtaining optical microscope (OM) images of polished cross sections at different magnification levels, through an upright incident-light optical microscope Zeiss (Oberkochen, Germany) Axiophot featuring Epiplan Neofluar objectives. For the polishing procedure, specimens were embedded in epoxy resin beads and polished with grinding papers with a grit polishing size of 240, 500, 800, 1200, and then with polishing clothes wetted with a 3-µm and 1-µm diamond particle solution.

Differential scanning calorimetry (DSC) was performed to investigate the melting and crystallization temperature and enthalpy of the PCM (T_m , T_c , ΔH_m , ΔH_c) and the glass transition temperature of the epoxy resin (T_g). All DSC tests were performed on a Mettler DSC30 instrument (Mettler Toledo, Columbus, OH, US), 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. 10–20 mg each (cut through the whole laminate thickness), underwent a first heating scan, a cooling scan, and a second heating scan.

Thermogravimetric analysis (TGA) was performed through a Mettler TG50 instrument (Mettler Toledo, Columbus, OH, US) on specimens of approximately 20–25 mg cut through the whole laminate specimens, at a heating rate of 10 °C/min, up to 700 °C, under a nitrogen flow of 15 ml/min. The tests allowed the determination of the temperatures corresponding to a mass loss of 1 wt%, 3 wt%, 5 wt% ($T_{1\%}$, $T_{3\%}$, $T_{5\%}$), and the degradation temperature (T_d), intended as the temperature at the maximum degradation rate (i.e. the position of the mass loss derivative peak).

To check the overall thermal management capacity of the laminates, a simple test was performed with a thermal camera, both on heating and on cooling stages. For the tests on heating ramp, the laminates were inserted in an oven at a temperature of 70 $^{\circ}$ C, and their surface temperature was recorded through an infrared thermal imaging camera FLIR E60 (FLIR® Systems, Inc., Wilsonville, OR, US), placed at a fixed distance of 30 cm from the laminate surface. For the tests during the cooling stage, the laminates were first heated in an oven at 70 $^{\circ}$ C, then taken out and left cooling to room temperature, while their surface

temperature was measured with the same thermal camera.

The thermal conductivity of the prepared laminates was measured via Laser Flash Analysis (LFA), implemented on a Netzsch LFA 447 instrument (Netzsch GmbH, Selb, Germany). Square samples with a side length of 12.7 mm were cut from the prepared specimens. Each specimen was tested at various temperatures (25 °C, 35 °C, 45 °C, 55 °C), and three pulses were performed for each temperature. Data were analyzed with the software Proteus (Netzsch). Thermal diffusivity (α) was determined using the Cowan method with pulse correction. For the calculation of the specific heat capacity (c_P), the reference material Pyrex 7740, was employed, according to the standard ASTM-E 1461. The thermal conductivity (λ) was calculated according to Equation (1) as

$$\lambda = \alpha \rho c_P \tag{1}$$

where ρ is the sample density (g/cm³) determined by helium pycnometry.

DMA tests were performed with a TA Q800 DMA instrument in single cantilever bending mode, with a distance between the grips of 17.5 mm and an applied strain of 0.05%. Three testing modes were applied, i.e. single-frequency scans, heating-cooling cycles, and multifrequency scans. In single frequency scans (1 Hz), the storage modulus (E'), loss modulus (E''), and loss factor (tan δ) were measured between -20 °C and 160 °C at 3 °C/min. Heating-cooling cycles were carried out between -40 °C and 60 °C, at the scanning speed of 3 °C/min, at a frequency of 1 Hz. All laminates were subjected to a heating-cooling-heating cycle (sequence h-c-h), and the laminate with the highest PCM fraction (EP-MC40-CFu-A) was subjected to an additional complete cycle (sequence h-c-h-c-h). Multifrequency scans were carried out at the frequency values of 0.3, 1, 3, 10, and 30 Hz and heating rate of 0.3 °C/min. The activation energy (E_a) at the glass transition peak was determined through the Arrhenius approach, from the slope of the linear regression of the natural logarithm of the applied frequency plotted versus the reverse of the $tan\delta$ peak temperatures, as reported in Equation (2):

$$E_a = R\left(\frac{d(ln\nu)}{d(1/T_p)}\right) \tag{2}$$

where *R* is the universal gas constant, equal to 8.314 J/molK, ν is the applied frequency, and T_P is the *E*^{*} or $tan\delta$ peak temperature at the glass transition. A similar approach was also used to tentatively evaluate the activation energy involved at the PCM melting in the interval 10–50 °C.

Quasi-static tensile tests were performed with a universal testing machine Instron 5969 (Instron, Norwood, MA, US), equipped with a 50 kN load cell. Rectangular specimens of $10 \times 120 \text{ mm}^2$ were cut out of the prepared laminates with a diamond saw. The tests were carried out with an initial distance between the grips of 80 mm. The specimens were tabbed at both ends with glass fiber composite tabs, to avoid damages in the gripping zone. 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. Tests were performed in the longitudinal (fiber) and transversal directions, and five specimens were tested for each sample and each direction.

Flexural tests were performed at room temperature and at 65 °C with a three-point bending configuration, according to the standard ASTM D790, with a universal testing machine Instron 5969 equipped with a 50 kN load cell, on specimens with nominal in-plane dimensions of 10 × 120 mm². The span length was 85 mm, the crosshead speed was fixed at 9 mm/min, and at least five specimens were tested for each sample, in the longitudinal direction. 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 (3)–(5):

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

$$\sigma_{fM} = \frac{3PL}{2bd^2} \left[1 + 6\left(\frac{D}{L}\right)^2 - 4\left(\frac{D}{L}\right)\left(\frac{d}{L}\right) \right] \tag{4}$$

$$\varepsilon_{fb} = \frac{6Dd}{L^2} \tag{5}$$

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.

Short-beam shear (SBS) tests were performed on the laminates type B to assess the interlaminar shear strength (ILSS), following the standard ASTM D 2344, with an Instron 5969 universal testing machine equipped with a 50 kN load cell, in a three-point bending configuration, at a crosshead speed of 1 mm/min. Specimens were cut out of the prepared laminates with a diamond saw, and their dimensions were chosen to meet the conditions prescribed by the ASTM standard: named *d* the laminate thickness, the specimen width was 2*d*, the length 6*d* and the support span 4*d*.

Mode I interlaminar fracture toughness was evaluated on the type B laminates according to the standard ASTM D5528-13, with an Instron 5969 universal testing machine equipped with a 50 kN load cell. The

tests were performed on specimens with in-plane dimensions of 20 \times 130 mm², cut out of the prepared laminates with a diamond saw. At least three specimens were tested for each composition. The initial crack formed in the middle plane was made by inserting a PET film with a thickness of 26 µm in the stacking process of the laminates. In this way, a pre-crack of 55 mm was produced. Specimens were loaded at 0.25 mm/min until an increment of delamination crack growth of 3–5 mm and then unloaded at 25 mm/min, and the tip of the pre-crack was noted. The specimens were then reloaded at 2.5 mm/min until the crack had propagated for at least 50 mm from the tip of the pre-crack. The test was recorded with a LogiTech C920 USB video camera, to correlate each advancement of the crack tip with the corresponding load value. The specimens were finally unloaded at 25 mm/min. The value of critical strain energy release rate (G_{IC}) was calculated with Equation (6):

$$G_{IC} = \frac{3P\delta}{2b(a+|\Delta|)} \tag{6}$$

where *P* is the applied load, δ is the load point displacement, *b* is the specimen width, *a* is the delamination length, and the term $|\Delta|$ is introduced to take into account the rotations that may occur at the delamination front. Δ was determined experimentally by generating a least squares plot of the cube root of compliance ($C^{1/3}$) as a function of delamination length *a*, where $C = \delta/P$, as specified in the standard.

3. Results and discussion

The optical microscope (OM) images of the polished cross sections of the laminates are shown in Fig. 1(a-d). The neat EP-CFu laminate Fig. 1 (a) shows fibers homogeneously distributed in the laminate thickness, without evident matrix-rich zones. The porosity present in this laminate derives from the hand lay-up technique, and it is evident also in the other compositions. For the laminates containing MC (Fig. 1(b-d)), the micrographs show zones rich in CF and other zones rich in MC, and the PCM phase is preferentially distributed in the interlaminar region and



Fig. 1. Optical microscope micrographs of the polished cross section of the laminates EP-MCx-CFu-A. (a) EP-CFu-A; (b) EP-MC20-CFu-A; (c) EP-MC30-CFu-A; (d) EP-MC40-CFu-A.

not among the fibers of the same tow. This phenomenon, also due to the relative sizes of microcapsules (average diameter 20 μ m) and fibers (average diameter 7 μ m), could decrease the interlaminar properties of the laminate and create a preferential path for damage propagation, as described more in detail with the results of the mode I interlaminar fracture toughness test. Moreover, the thickness of the interlaminar region increases with the initial MC fraction in the epoxy/MC mixtures, with a consequent decrease in the relative fiber volume fraction in the laminates, as described hereafter. The concentration of the PCM phase in the interlaminar region and the thickness of this zone were also observed in previous works on laminates containing bidirectional carbon fibers [63,73].

Fig. 2 shows representative DSC thermograms of the laminates EP-MCx-CFu-A, while the main DSC results for type A and type B composites are summarized in Table 2. The thermograms of the type B laminates were not reported for the sake of brevity, as they are qualitatively similar to those of the corresponding type A samples.

All samples exhibit glass transition at approx. 100 °C, and the samples containing MC also show endo-/exothermic peaks at the PCM phase change. The endothermic melting peak is observable in the heating scan at 40–60 °C, while the exothermic crystallization peak is appreciable in the cooling scan at 40-15 °C, as observed in previous works on the same PCM microcapsules [74,75]. The glass transition is shifted to slightly higher temperatures with an increase in the MC loading, while the rise in melting temperature and the decrease in crystallization temperature are probably linked to a reduction in thermal diffusivity and conductivity of the samples, as confirmed by the results of the LFA analysis presented hereafter. Moreover, the melting temperature of the PCM in the type B laminates is generally higher and the crystallization temperature generally lower than those measured on the type A laminates; this can be due to the fact that the specimens cut out of the type B laminates are generally thicker than those obtained from type A laminates, which could have slightly modified the heat transmission in the specimen during the test. However, the melting and crystallization temperature intervals are not considerably affected by the composition of the laminate, which indicates that the working temperature interval of the PCM remains almost constant in the range 20-40 °C, independently from the MC content.

The phase change enthalpy increases with the MC loading up to 48.7 J/g for the sample EP-MC40-CFu-A. While preparing the laminates, the nominal and experimental weight fractions of MC in the initial EP/MC mixtures were known (0, 20, 30 and 40 wt%), but the MC weight fraction in the laminates is also influenced by the resultant weight fraction



Fig. 2. Representative DSC thermograms of laminates EP-MCx-CFu-A. First heating scan and cooling scan.

Table 2

Results of the DSC tests on the laminates EP-MCx-CFu-A and EP-MCx-CFu-B (first heating scan and cooling scan).

Sample	$T_g(^{\circ}C)$	$T_m(^{\circ}C)$	Δ <i>H</i> _m (J/ g)	$T_c(^{\circ}C)$	Δ <i>H</i> _c (J/ g)	<i>ω_{MC}</i> (wt %)
MC	-	46.5	221.7	27.6	223.5	100
EP-CFu-A	87.1	-	-	-	-	0
EP-MC20-	89.0	45.4	29.3	27.0	29.8	13.2
CFu-A						
EP-MC30-	95.9	47.8	40.3	25.5	40.2	18.2
CFu-A						
EP-MC40-	93.4	48.2	48.7	24.9	48.7	22.0
CFu-A						
EP-CFu-B	84.7	-	-	-	-	0
EP-MC20-	90.5	49.2	30.6	23.8	30.5	13.8
CFu-B						
EP-MC30-	93.1	51.0	42.0	21.9	41.9	19.0
CFu-B						
EP-MC40-	94.2	53.7	47.5	19.4	47.1	21.4
CFu-B						

 T_g = glass transition temperature of the epoxy phase (°C); T_m = melting temperature of the PCM (°C); ΔH_m = PCM melting enthalpy (J/g); T_c = crystallization temperature of the PCM (°C); ΔH_c = PCM crystallization enthalpy (J/g); ω_{MC} = experimental microcapsule weight fraction calculated from the measured melting enthalpy (wt%).

of fibers and matrix, which is affected by the matrix viscosity that in turn depends on the starting MC loading. Since the MC addition increases the viscosity of the EP/MC mixtures considerably, as demonstrated in a previous work on epoxy/MC samples [72], it is reasonable to expect that a high fraction of MC hinders the flowing of the matrix out of the carbon fabric during vacuum bagging, thereby increasing the final matrix weight fraction. This will be better described hereafter. The final MC weight fraction in the composites can be calculated from the phase change enthalpy measured with DSC, by dividing the melting enthalpy measured on the laminates by that measured on the neat MC. This can be done by assuming that the MC maintain their energy storage efficiency also after the lamination process, which is reasonable if considering the results of previous works on epoxy composites containing the same microcapsules used in this work [72,73]. The values of experimental MC weight fraction (ω_{MC}) are also reported in Table 2. The MC weight fraction increases with the initial MC loading in the epoxy mixture and ranges from 13.2 wt% to 22.0 wt%, without remarkable differences between the type A and type B laminates, which indicates that the final MC loading is not largely influenced by the number of layers in the laminate.

The effective fiber weight fraction of the laminates was then investigated through TGA, which was also useful to assess their thermal stability. The results of this characterization are reported in Fig. 3 and Table 3. All tested samples present a single degradation step, which corresponds to the degradation of the epoxy and MC phases and is observable as a single peak also in the signal of the mass loss derivative. This happens because the EP and MC phases degrade in the same temperature interval, and therefore it is impossible to measure the relative mass fraction of these two phases by studying the degradation profile [72]. On the other hand, the residual mass after the test (m_r) allowed the calculation of the fiber weight fraction, which was computed by considering the residual mass of the EP/MC systems determined in a previous work [72] and that of the employed carbon fibers that resulted as 96.0 wt%. The carbon fiber mass fraction (ω_f) can be determined with Equation (7) as:

$$\omega_f = \frac{m_r - R_m}{R_f - R_m} \tag{7}$$

where R_f and R_m are the residual masses of the fiber and the matrix phases after TGA test, respectively. The fiber weight fraction of the laminates calculated in this way is reported in Table 3. ω_f decreases with



Fig. 3. TGA thermograms of the laminates EP-MCx-CFu-A and EP-MCx-CFu-B. Residual mass and mass loss derivative as a function of temperature.

Table 3		
Results of the TGA tests on the	e laminates EP-MCx-CFu-A	and EP-MCx-CFu-B.

Sample	<i>T</i> _{1%} (°C)	<i>T</i> _{3%} (°C)	<i>T</i> _{5%} (°C)	<i>T</i> _d (°C)	<i>m</i> _r (%)	<i>ω_f</i> (wt %)
EP-CFu-A	310.5	358.1	368.9	401.2	70.6	71.5
EP-MC20-CFu- A	199.2	307.6	330.2	388.1	53.2	52.6
EP-MC30-CFu- A	207.3	301.1	328.4	387.2	51.9	51.0
EP-MC40-CFu- A	226.4	307.6	333.4	387.6	50.9	50.0
EP-CFu-B	301.3	357.5	365.5	397.2	67.0	67.5
EP-MC20-CFu- B	237.6	310.4	330.5	390.3	50.6	49.6
EP-MC30-CFu- B	215.3	306.6	329.5	388.2	48.4	47.2
EP-MC40-CFu- B	192.5	282.6	323.6	387.6	43.6	41.8

 $T_{1\%}$, $T_{3\%}$, $T_{5\%}$ = temperature corresponding to a mass loss of 1%, 3%, 5%; T_d = temperature of the maximum degradation kinetics (peak of the mass loss derivative); m_r = residual mass; ω_f = weight fraction of carbon fibers determined from the TGA residual mass.

an increase in the MC loading and it is lower for the type B laminates, which indicates that the flow of the matrix out of the CF fabric is hindered by the viscosity increase determined by the MC addition and by the increase in the laminate thickness. ω_f ranges from 71.5 wt% of the sample EP-CFu-A to 41.8 wt% for the sample EP-MC40-CFu-B, and the decrease does not follow a linear trend with the MC content. As the TGA

is performed on specimens of few milligrams, the test was repeated on at least three specimens and the standard deviation of the final calculated values of ω_f never overcomes 1.5 wt%. The lower fiber content, and the consequent higher epoxy and MC weight fraction, is probably at the basis of the reduced thermal stability of the laminates with the highest MC loading, as can be appreciated from the shift of $T_{1\%}$, $T_{3\%}$, and $T_{5\%}$ to lower temperatures. On the other hand, the degradation interval is not remarkably affected by the composition of the laminate, and the lowest degradation peak temperature is 387.6 °C, which is 14 °C lower than that of the laminate EP-CFu-A. In all cases, the thermal degradation is far above the operative temperature interval for which these materials are intended.

A comment shall be made on the degradation behavior in TGA of the carbon fibers used in this work, for which the residual mass is 96.0 wt%, with a mass loss of 4.0 wt%. For other continuous carbon fibers used in combination with the same epoxy resin in previous works [63,76], the mass loss in TGA performed with the same instrument and at the same testing conditions resulted as approx. 99 wt%, with a mass loss of less than 1 wt% attributed to the sizing agent. This implies that the fraction of organic degradable phase over these CFu is not negligible and claimed a deeper investigation of their surface. Such investigation, performed with SEM (not reported for the sake of brevity), revealed a certain amount of organic residues on the fiber surface, which could explain their degradation behavior. In fact, this residues were not anymore present on the surface of the fibers after TGA. This surface state could not only influence the degradation behavior of the fibers, but also their mechanical properties and the fiber/matrix adhesion, of the final composites. However, the aim of this work is to study the effect of the introduction of microcapsules in a unidirectional epoxy composite and

make a comparison between the neat epoxy/carbon laminate and those containing MC. Therefore, the fibers were used as received and the properties of the MC-containing laminates were compared to those measured on the neat laminate without MC.

The DSC and TGA data allowed the calculation of the weight fractions of MC and CFu in the laminates, respectively. These data, reported in Table 4, allowed the calculation of the theoretical density (ρ_{th}) of the laminates, by knowing the density of the microcapsules (0.923 \pm 0.002 g/cm³), of the CFu (1.633 \pm 0.027 g/cm³) and of the EP phase (1.158 \pm 0.002 g/cm³), all measured via helium pycnometry. It is worth noting that the density measured for the fibers is lower than that indicated on the producer's datasheet (1.75–1.80 g/cm³), which matches the values of density for carbon fibers generally reported in the literature. This could be partially attributed to the organic residues on the fiber surface and agrees with the results of TGA.

The same helium pycnometry technique was employed to measure the experimental density (ρ_{exp}) of the prepared laminates, reported in Table 4. The comparison between ρ_{th} and ρ_{exp} allowed the calculation of the porosity, and then of the volume fraction of the fibers, the microcapsules and the EP phase. As already reported in previous works [73], the fiber volume fraction and the MC volume fraction follow opposite trends. This is mainly due to the viscosity increase of the EP/MC mixtures, which reduces the matrix flowing out of the carbon fabric during the vacuum bag process. Moreover, for the same initial MC fraction, the fiber volume fraction is lower for the laminates type B than for the type A. Additionally, it can be observed that the experimental MC weight fraction in the matrix, reported in Table 4 as MC/(MC + EP), is almost everywhere higher than the initial nominal one, equal to 0 wt%, 20 wt%, 30 wt% or 40 wt%. This implies that during vacuum bagging the EP phase flows out of the carbon fabric more easily than the microcapsules. thereby increasing the resulting MC concentration in the matrix. Finally, the porosity (ϑ_v) increases with the MC concentration, which is once again linked to the increased matrix viscosity, but is not remarkably different for the laminates type A and type B.

Although the DSC test is the main characterization technique that gives quantitative information on the heat absorption and release in a certain temperature range, it has the limitation of being performed on samples of few milligrams. Therefore, to study the thermal management properties of the prepared laminates on a slightly bigger scale, a simple yet effective test was performed with thermal imaging techniques. Fig. 4 reports the values of the surface temperature of the laminates as a function of time during both the heating and the cooling stages. As observed for other PCM-containing laminates [67,73,76], the temperature trend shows plateau-like regions, caused by the latent heat absorbed during melting and released during crystallization of the PCM, and this phenomenon causes a remarkable increase in the time needed to reach the temperature of the surrounding environment. For example, on the heating phase, the neat EP-CFu-A laminate reaches the temperature of 60 °C in 2.3 min, while the same temperature is reached by the laminate EP-MC40-CFu-A in 8.2 min. In the same way, in the experiment on cooling, the two laminates reach the temperature of 30 °C in 3.4 min

and 15.8 min, respectively. It should be pointed out that the rate of heating/cooling is also dependent on the laminate mass, which varies as a consequence of the variation in the matrix weight fraction. However, the observed plateau-like trends are a clear sign of the variation in the thermal behavior of the laminates (and therefore of the thermal management capability) as a function of the MC content.

The results of the LFA tests on the laminates EP-MCx-CFu-A are shown in Fig. 5. The thermal diffusivity of the neat EP-CFu-A decreases slightly at higher temperatures and ranges from 0.40 mm²/s to 0.42 mm²/s, while the specific heat capacity and thermal conductivity follow the opposite trend. The thermal conductivity varies in the range 0.61-0.63 W/(m·K). For the laminates containing MC, the thermal diffusivity and thermal conductivity are lower than those of the neat laminate EP-CFu-A, which is in large part due to the lower fraction of carbon fibers and not to the thermal conductivity of the MC phase, since it was observed that the thermal conductivity of the epoxy/MC samples slightly increases with the MC content [72]. On the other hand, for these laminates, the specific heat increases with the MC content. The thermal conductivity shows a maximum at 35 °C, as the PCM is approaching the solid-liquid phase change, as already observed in previous works of our group [63,67] and in other works from the literature [77]. However, the variations are small and the bands of standard deviation partially overlap, which suggests that this effect might be not significant with these compositions. Moreover, it can be generally observed that the thermal conductivity is lower when the PCM is completely molten (i.e. at 55 °C) than when the PCM is completely solid (i.e. at 25 °C).

As reported in the experimental section, DMA characterization comprises single-frequency, multifrequency and heating/cooling cyclic tests, all performed in single cantilever mode. This analysis was carried out to understand how the PCM addition affects the viscoelastic properties and the glass transition of the host laminate, and how these parameters change before, during and after the PCM phase change temperature. Moreover, this study aims at assessing the suitability of the DMA techniques to study the PCM phase transition, which is an unusual application for this test.

The results of the single-frequency scans are illustrated in Fig. 6(a-c). To facilitate the comparison among the samples, the values of E' have been normalized to the value at -20 °C. The storage modulus of the laminate EP-CFu-A (Fig. 6(a)) decreases with increasing temperature throughout all the investigated temperature interval, but the decrease is particularly evident at the glass transition of the epoxy phase. At this temperature, E'' and $tan\delta$ peaks can be detected (Fig. 6(b)). In the MCcontaining composites, two main steps are observable in the trend of E'; the first at the paraffin melting, the second at the glass transition of the EP phase. The drop of *E*' at the first step increases with the MC fraction. Interestingly, the correlation between the \vec{E} drop amplitude and the MC weight fraction or the melting enthalpy is linear, with R² values of 0.998 (Fig. 6(c)). This was observed also in other works on thermoplastic polymer laminates containing a PCM [73]. These trends were obtained by dividing each value of E' by the value at 0 °C. However, if a normalization is made to the initial value of E' at -20 °C, the slope of the

Table 4

Theoretical and experimental	density and rela	tive concentration	of the constituents	s of the prepared laminates.
1	2			1 1

Sample	<i>ω</i> _f (wt%)	ω _{MC} (wt%)	$\frac{MC}{MC+EP}$ (wt%)	$\rho_{th}(g/cm^3)$	$\rho_{exp}(g/cm^3)$	ϑ_{v} (vol%)	ϑ_f (vol%)	ϑ_{MC} (vol%)
EP-CFu-A	71.5	0	0	1.462 ± 0.003	1.428	2.31	62.5	0.0
EP-MC20-CFu-A	52.6	13.2	27.8	1.315 ± 0.002	1.226	6.78	39.4	17.5
EP-MC30-CFu-A	51.0	18.2	37.1	1.290 ± 0.002	1.223	5.14	38.2	24.1
EP-MC40-CFu-A	50.0	22.0	44.0	1.272 ± 0.002	1.163	8.53	35.6	27.7
EP-CFu-B	67.5	0	0	1.441 ± 0.003	1.423	1.25	58.8	0.0
EP-MC20-CFu-B	49.6	13.8	27.4	1.300 ± 0.004	1.236	4.90	37.6	18.5
EP-MC30-CFu-B	47.2	19.0	36.0	1.271 ± 0.003	1.225	3.68	35.4	25.1
EP-MC40-CFu-B	41.8	21.4	36.8	1.241 ± 0.002	1.140	8.14	29.2	26.5

 ω_f = fiber weight fraction determined through TGA; ω_{MC} = MC weight fraction determined via DSC; ρ_{th} = theoretical density; ρ_{exp} = experimental density measured via pycnometry; θ_{ν} = porosity; = fiber volume fraction; = MC volume fraction.



Fig. 4. Results of the thermal camera imaging tests on the laminates EP-MCx-CFu-A. Surface temperature of the laminates as a function of the testing time.

linear fitting and the value of R² would have resulted 89 ± 3 J/g and 0.998, respectively. These values are not significantly different from those reported in Fig. 6(c), which indicates that the variation in *E*' between -20 °C and 0 °C is negligible. The trends of *E*" and *tan* δ show peaks in correspondence of the melting step. These peaks shift to higher temperatures and their intensity increases with the PCM content.

As the structural TES composites must withstand repeated thermal cycles around the phase change temperature of the PCM, the variation of the dynamic-mechanical behavior was investigated not only on heating, but also on cooling, between -40 °C and 60 °C. The results of this analysis are reported in Fig. 7(a), which shows the trend of \vec{E} in a heating-cooling-heating (h-c-h) scan performed at 3 °C/min on the prepared laminates. To verify the behavior after the first cycle and detect any first-cycle effects, two complete cycles (sequence h-c-h-c-h) were performed on the laminate with the highest PCM content, i.e. EP-MC40-CFu-A. E' decreases with increasing MC concentration and manifests a decreasing step at the PCM melting, which is almost completely recovered on cooling as it reaches approx. 95% of the initial value. More specifically, this value is 99.6% of the initial value for the neat EP-CFu-A laminate, 94.4% for the laminate EP-MC20-CFu-A, 94.6% for the laminate EP-MC30-CFu-A, and 95.8% for the laminate EP-MC40-CFu-A (95.0% of the initial value after the second full cycle). This recovery happens with a certain hysteresis, which can be also observed in the trends of E'' (Fig. 7(b)) and tan δ (not reported), for which the crystallization peaks occur at a lower temperature than the melting peaks. A similar result was evidenced also in our previous works on carbon fiber laminates containing a PCM [73,78].

Multifrequency DMA scans were performed to assess the effect of frequency on the PCM melting and the glass transition of the matrix in the prepared composites. The results of the laminates EP-CFu-A and EP-MC40-CFu-A are shown in Fig. 8(a–c).

For the composite EP-CFu-A (Fig. 8(a)), the frequency increase determines a shift of all parameters to higher temperatures; this effect, although present in the whole investigated temperature range, is more evident at the glass transition of the EP phase. For the composite EP-MC40-CFu-A (Fig. 8(b)), and for the other MC-containing laminates, the frequency dependence is observable not only at the glass transition, but also at the PCM melting between 5 °C and 45 °C. It is worth noting that the melting peak is located at lower temperatures that those measured in DSC, which is a direct consequence of the lower heating rate (0.3 °C/min instead of 10 °C/min). Moreover, in this temperature range, the frequency sensitivity of all the viscoelastic parameters is

higher below the melting peak temperature than above it. Therefore, when the PCM is almost completely molten, the frequency dependence weakens considerably. This was observed also for other polymer laminates containing the same microencapsulated PCM [73].

These tests allowed the calculation of the activation energy of the glass transition $(E_a(T_g))$ from the $tan\delta$ peak temperatures through the Arrhenius approach. The results of this analysis, presented in Fig. 8(c) and Table 5, show that $E_a(T_g)$ generally increases with the MC concentration, which implies that the glass transition is hindered by the presence of an increasing amount of filler [79,80].

Since the peaks of E'' and $tan\delta$ at the PCM melting also appear to depend on frequency, an attempt was made to apply the Arrhenius approach to calculate the activation energy of the melting transition. The results of this attempt are also reported in Fig. 8(c). It can be clearly seen that the linear fitting of these data is considerably less precise than that of the data at the glass transition. In any case, the calculated results for the activation energy of the melting transition, $E_a(T_m)$, are also reported in Table 5. The higher activation energy for the laminates EP-MC30-CFu-A and E-MC40-CFu-A could be attributed to the combined effect of the real melting temperature of PCM, the apparent shifting at higher temperature proportional to PCM content, and the frequency dependence of the polymer mobility and its viscosity in the mushy and molten state. However, the large standard deviations, which follow the poor linear fitting and are reflected in a small R^2 , hinder an accurate data analysis. Moreover, the authors are aware that this provisional interpretation should be further investigated with other compositions and systems.

This investigation contributed to provide an interesting insight on the use of DMA to study a melting/crystallization phase change and the effects of such transition on the dynamic-mechanical properties of the host laminate, which is extremely important for composites designed to combine the structural and TES functions and to work across the PCM phase change temperature. This approach also experimented the uncommon use of DMA to study a melting/crystallization phase change and found noteworthy correlations between DMA and DSC parameters.

To assess the mechanical properties of the prepared laminates, four techniques were applied, i.e. quasi-static tensile tests, three-point bending tests, short-beam shear tests and mode I interlaminar fracture toughness tests.

The results of the tensile tests are reported in Fig. 9, in which the values of tensile moduli in the fiber direction (longitudinal, E_L) and in the transversal direction (E_T) are plotted as a function of the MC content.



Fig. 5. Results of the LFA measurements on the laminates EP-MCx-CFu-A in the temperature interval 25–55 $^\circ\text{C}.$

 E_L decreases with an increase in the MC fraction, which is mostly due to the decrease in the fiber volume fraction. To separate the contribution of the decrease in the fiber content to that of the change in the properties of the matrix due to MC addition, a theoretical elastic modulus was calculated via the mixture rule reported in Equation (8) [1]:

$$E_c = E_f \cdot \vartheta_f + E_m \cdot \left(1 - \vartheta_f\right) \tag{8}$$

where E_c is the longitudinal modulus of the composite, E_f and E_m are the moduli of the fibers and the matrix, respectively, and ∂_f is the fiber volume fraction.

The calculation of the theoretical elastic modulus was performed as follows. First, the experimental value of elastic modulus of the neat laminate EP-CFu-A was used to calculate an experimental value of E_f via the mixture rule reported in Equation (8), by knowing ϑ_f (calculated with data from TGA) and E_m (measured on neat epoxy samples) for this laminate. This value of E_f was applied to calculate theoretical values of



Fig. 6. Results of the single-frequency DMA tests on the laminates EP-MCx-CFu-A. (a) Storage modulus as a function of temperature, normalized to the value at the beginning of the test (-20 °C); (b) Loss modulus and *tan* δ as a function of temperature; (c) Value of *E*' after PCM melting (60 °C) normalized to the value at 0 °C, as a function of the melting enthalpy, with the results of the linear fitting.



Fig. 7. Cyclic DMA tests. (a) Storage modulus as a function of temperature during the thermal cycles; (b) Loss modulus as a function of temperature during the thermal cycles (1 = first heating scan; 2 = first cooling scan; 3 = second heating scan; 4 = second cooling scan; 5 = third heating scan.

 E_c for the MC-containing laminates, with the previously measured values of ϑ_f for these laminates, via the mixture rule reported in Equation (8). As the mixture rule requires the value of E_m , two approaches were adopted: the first was to put E_m equal to that of the neat epoxy resin in all cases (i.e. 2.5 ± 0.3 GPa, see Ref. [72]), and the second was to vary E_m according to the MC content, by considering the elastic moduli of the epoxy/MC samples measured in a previous work on epoxy/MC samples [72]. The results of the calculations with these two approaches are reported in Fig. 9, as "E_L theoretical (matrix is EP)" and "E_L theoretical (matrix varies)", respectively.

The two theoretical approaches give approximately the same results, which was expected as the elastic modulus of the matrix has little relevance when calculating the modulus of a unidirectional carbonreinforced composite in the fiber direction. Additionally, the theoretical values of E_L are equal to (or in some cases even lower than) the experimental values, which means that the decrease in elastic modulus with an increase in MC concentration is entirely due to a decrease in the fiber volume fraction, and the MC introduction does not actively contribute to decrease it, which could have been the case if the MC decreased the fiber alignment. In some cases, as for the laminate EP-MC20-CFu-A, the MC phase seems even to contribute positively to the elastic modulus, as the experimental value deviates positively from the



Fig. 8. Results on the DMA multifrequency scans on the samples EP-MCx-CFu-A. Investigated frequencies: 0.3-1-3-10-30 Hz. (a) Sample EP-CFu-A; (b) Sample EP-MC40-CFu-A; (c) Natural logarithm of frequency as a function of 1000/T (peaks of *tanð* at glass transition (left) and at paraffin melting (right). The solid lines represent the result of the linear fitting.

Table 5	
Results of the multifrequency DMA scans on the samples EP-MCx-CFu-A.	
	i

Sample	EP-CFu- A	EP-MC20-CFu- A	EP-MC30-CFu- A	EP-MC40-CFu- A
$E_a(T_g)$ (kJ/mol)	$\begin{array}{c} 365 \pm \\ 14 \end{array}$	395 ± 9	434 ± 17	419 ± 13
$R^2(T_g)$	0.996	0.998	0.995	0.997
$E_a(T_m)$ (kJ/mol)	-	615 ± 63	955 ± 100	865 ± 102
$R^2(T_m)$	-	0.97	0.97	0.96

 $E_a(T_g)$ = activation energy of the glass transition calculated from the $tan\delta$ peaks; $E_a(T_m)$ = activation energy of the melting transition calculated from the $tan\delta$ peaks; R^2 = values of R^2 of the linear regression.

n(frequency)



Fig. 9. Experimental and theoretical tensile moduli of the laminates EP-MCx-CFu-A. The theoretical moduli E_L and E_T were calculated via the direct and inverse mixture rule, respectively, starting from the properties measured on the neat laminate EP-CFu-A.

theoretical trend, but further analysis is needed to verify this hypothesis. This approach is conservative, as it does not take into account the pore volume fraction in the calculation of the theoretical moduli, which would have resulted in even lower values.

A similar analysis was performed on the values of the transversal modulus, but in this case the inverse mixture rule was applied, as reported in Equation (9) [1]:

$$\frac{1}{E_c} = \frac{\vartheta_f}{E_f} + \frac{1 - \vartheta_f}{E_m} \ . \tag{9}$$

The results of this calculation are reported in Fig. 9.

In this case, the two approaches for the calculation of the theoretical moduli gave remarkably different results, because a variation in E_m determines important variations in the transversal modulus, and since the elastic modulus of the epoxy/MC samples decreases with an increase in the MC content, also the theoretical transversal modulus of the composites is lower when in is calculated with the approach "matrix varies". The experimental values of E_T are higher than the theoretical values calculated with this approach, so a much lower decrease in E_T was expected if considering the elastic moduli of the epoxy/MC samples. On the other hand, the experimental values of E_T are closer to those calculated only by considering a decrease in the fiber volume fraction (approach "matrix is EP"). Therefore, it can be concluded that the longitudinal and transversal moduli of these composites are affected by the MC phase only because it determines an increase in the matrix viscosity and thus a decrease in the final fiber volume fraction. This conclusion is similar to that obtained in a previous study on epoxy/carbon laminates containing a shape-stabilized PCM [63]. In those laminates, the fiber volume fraction was almost independent from the PCM content, and in fact the flexural elastic modulus was not significantly affected by the laminate composition.

The results of the three-point bending tests are shown in Fig. 10(a-b). Fig. 10(a) shows representative load-displacement curves, which show a behavior similar to that observed on other PCM-containing laminates [63,73].

The curves of all samples present an initial linear zone, but the



Fig. 10. (a) Representative load-displacement curves obtained in three-point bending tests on the laminates EP-MCx-CFu-A at room temperature. The value in brackets represents the laminate thickness; (b) Flexural modulus (E_f), strength (σ_{fM}), and strain at break (ε_{fb}), and interlaminar shear strength (*ILSS*) as a function of the MC weight fraction.

behavior after the maximum load of the neat EP-CFu laminate is different from that of the MC-containing laminates. The neat laminate is subjected to a catastrophic failure, which always started from the tensile-stressed mid-lower region of the specimen. Such failure mode is often associated to a good interlaminar adhesion [81,82]. On the other hand, the PCM-containing laminates are subjected to a progressive failure and present a drop-plateau sequence, which indicates a dissipation of mechanical energy also during damage propagation. The damage was observed starting either in the mid-upper zone, subjected to compression, or in the interlaminar zone. This is observable also from the optical microscope micrographs of the specimens after the tests, shown in Fig. 11(a-h). This failure mode has been described as typical of materials having a tensile in-plane strength considerably higher than the interlaminar shear strength, which is the case for the MC-containing laminates reported in this work.

Fig. 10(b) summarizes the main results of the three-point bending tests, as it shows the trends of the flexural elastic modulus, stress and strain at break as a function of the MC weight fraction. Fig. 10(b) also shows the values of interlaminar shear strength (*ILSS*) obtained during short-beam shear tests on the type B laminates. The elastic modulus is seen decreasing with an increase in the MC content, which is due to the reduction in the fiber volume fraction. However, also the flexural strength decreases, and this is probably related to the introduction of new damaging mechanisms such as the delamination and interlaminar fracturing. The same phenomena are also at the basis of the observed



Fig. 11. Optical microscope micrographs of the specimens after three-point bending tests at room temperature. (a–b) EP-CFu-A; (c–d) EP-MC20-CFu-A; (e–f) EP-MC30-CFu-A; (g–h) EP-MC40-CFu-A.

reduction of the ILSS.

The same three-point bending tests were performed at 65 °C, above the PCM melting temperature. Fig. 12 shows a representative load-displacement curve with a comparison between the laminate EP-MC20-CFu-A tested at room temperature and at 65 °C, while the results of this characterization are reported in Table 6.

The elastic modulus is only marginally affected by temperature, as

the values are approximately the same as those measured at room temperature for the laminate EP-MC20-CFu-A and slightly lower for greater MC concentrations. On the other hand, the decrease in the properties at failure (flexural strength and strain at break) is more dramatic, and the decrease is higher for higher MC content. This is probably due to a decrease in the mechanical properties of the microcapsules when the core is melted, which causes further decrease in the



Fig. 12. Representative load-deflection curves obtained during three-point bending tests on the laminate EP-MC20-CFu-A at room temperature (RT) and at 65 $^\circ\text{C}.$

Table 6

Results of the three-point bending tests on the laminates EP-MCx-CFu-A performed at 65 °C. Values of flexural modulus (E_f), strength (σ_{fM}), and strain at break (e_{fb}) and relative values compared to the results at room temperature.

Sample	<i>E</i> _{<i>f</i>} ^{65 °<i>C</i>} (GPa)	$\frac{E_{f}^{65 \ \circ C}}{E_{f}^{RT}}(\%)$	$\sigma_{fM}^{65 \ \circ C}$ (MPa)	$\frac{\sigma_{fM}^{65 \ \circ C}}{\sigma_{fM}^{RT}}(\%)$	$arepsilon_{fb}^{65 \ \circ C}$ (%)	$rac{arepsilon_{fb}^{65\ \circ C}}{arepsilon_{fb}^{RT}}(\%)$
EP- MC20- CFu-A	$\begin{array}{c} 69.8 \pm \\ 0.9 \end{array}$	99.2	447 ± 26	74.1	$\begin{array}{c} \textbf{0.69} \pm \\ \textbf{0.05} \end{array}$	78.6
EP- MC30- CFu-A	$\begin{array}{c} 50.1 \pm \\ 2.2 \end{array}$	85.3	290 ± 1	59.2	$\begin{array}{c} \textbf{0.60} \pm \\ \textbf{0.06} \end{array}$	70.2
EP- MC40- CFu-A	$\begin{array}{c} 40.9 \pm \\ 2.1 \end{array}$	92.6	238 ± 1	58.9	$\begin{array}{c} \textbf{0.67} \pm \\ \textbf{0.10} \end{array}$	70.0

mechanical properties of the interlaminar region. Moreover, the behavior of the load-deflection curve in the region of the defect propagation was different from that observed at room temperature, as reported in Fig. 12; all tested specimens containing MC presented a long plateau, and for some of them the load did not drop to zero.

Fig. 13(a) shows representative load-displacement curves obtained in mode I interlaminar fracture toughness tests, while Fig. 13(b) shows the obtained R-curves, i.e. the delamination resistance as a function of the crack length, for the four prepared compositions. All loaddisplacement curves are a subsequence of load drops and plateaus, especially that of the neat laminate EP-CFu-B, which may impair the reliability of the results.

Table 7 collects the mode I critical strain energy release rates for crack initiation (G_{li}) and steady-state propagation (G_{lc}). The G_{li} is determined at the initial delamination of the specimen, when the precrack start to grow. The first point of G_{li} can be evaluated in different ways; the way adopted in this work is the deviation from the linearity of the load-displacement curve. The G_{lc} is obtained as the average value in the steady state region, after approx. 5–10 mm of crack propagation (a >60 mm).

Generally, G_{li} is independent from the fiber volume fraction, while G_{lc} can vary as a function of this parameter [83,84]. For the laminate EP-MC20-CFu-B, both G_{li} and G_{lc} are higher than those of the neat EP-CFu-B, which implies that the introduction of a modest amount of MC activates different toughening mechanisms; such mechanisms could be the particle debonding, crack pinning, crack deflection and micro-cracking. On the other hand, above a certain MC concentration, both G_{li} and G_{lc} decrease with increasing MC content, which can be due



Fig. 13. (a) Load-displacement curves obtained in mode I interlaminar fracture toughness tests on the laminates EP-MCx-CFu-B; (b) R-curves of the laminates EP-MCx-CFu-B. The results of two to four specimens are shown for each sample.

Table 7

Mode I critical strain energy release rates for crack initiation (G_{Ii}) and steadystate propagation (G_{Ic}) for the laminates EP-MCx-CFu-B.

Sample	$G_{li}(\text{kJ/m}^2)$	$G_{Ic}(kJ/m^2)$
EP-CFu-B EP-MC20-CFu-B EP-MC30-CFu-B EP-MC40-CFu-B	$\begin{array}{l} 0.15 \pm 0.03 \\ 0.34 \pm 0.02 \\ 0.27 \pm 0.02 \\ 0.24 \pm 0.02 \end{array}$	$\begin{array}{c} 0.27 \pm 0.01 \\ 0.40 \pm 0.01 \\ 0.32 \pm 0.01 \\ 0.30 \pm 0.02 \end{array}$

to an excessive thickening and decrease in the mechanical properties of the interlaminar region, in turn caused by a poor capsule/matrix adhesion and by the intrinsic low mechanical properties of the MC.

From a visual observation of the specimens during the test, the samples EP-CFu-B and EP-MC20-CFu-B showed fiber bridging, while this phenomenon was not observed for the laminates with a higher MC concentration, for which the crack propagated mostly through the matrix (Fig. 14(a-b)).

4. Conclusions

This work presented the thermo-mechanical characterization of unidirectional carbon/epoxy composites containing paraffin microcapsules. The MC phase increased the viscosity of the epoxy matrix, which limited the flow of the epoxy/MC mixtures out of the fiber fabric, thereby increasing the matrix weight (and volume) fraction and



Fig. 14. Specimens during the mode I interlaminar fracture toughness tests. (a) EP-MC20-CFu-B, with evidence of fiber bridging; (b) EP-MC40-CFu-B, without evidence of fiber bridging.

reducing that of the fibers. This was at the basis of a decrease in the mechanical properties of the prepared laminates with high MC concentration, but the application of theoretical models showed that this decrease was only due to the decrease in the volume fraction of the reinforcement and not to a change in the matrix composition.

The MC phase was preferentially distributed in the interlaminar region, which led to a thickening of this region and a decrease in matrixrelated properties such as the interlaminar shear strength. On the other hand, a modest MC fraction led to an increase in the mode I interlaminar fracture toughness, probably due to the introduction of new toughening mechanisms, such as the debonding, crack deflection, and microcracking. However, an excessive MC content reduced the values of G_{lc} , because the crack propagated through the matrix and not at the fiber/ matrix interface, thereby reducing the fundamental toughening mechanism of fiber bridging.

For the thermal properties, the melting enthalpy increased with the initial MC fraction and reached a value of 48.7 J/g. Therefore, the TES and thermal management capability of the prepared laminates increased with the MC fraction, as also demonstrated by thermal imaging tests. The DMA characterization highlighted the variation of the viscoelastic parameters as a function of temperature, composition and testing mode (single-frequency, multifrequency, cyclic heating-cooling tests). This technique was proven a useful complement to DSC to study the melting and crystallization process of a PCM when embedded in a polymer composites.

These results are promising for the development of multifunctional polymer composites with thermal energy storage and thermal management properties in the temperature range 10–50 °C. Future works will focus on a deeper study of the micromechanical properties of PCM microcapsules and on the improvement of the capsule/matrix adhesion.

Data availability

The raw/process data required to reproduce these findings will be made available on request.

CRediT authorship contribution statement

Giulia Fredi: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Visualization. Andrea Dorigato: Conceptualization, Writing - review & editing, Supervision. Luca Fambri: Writing - review & editing. Seraphin Hubert Unterberger: Investigation, Validation. Alessandro Pegoretti: Writing - review & editing, Supervision.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2020.106747.

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