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Department of Industrial Engineering

MULTIFUNCTIONAL CARBON/EPOXY LAMINATES WITH THERMAL ENERGY STORAGE/RELEASE CAPABILITY

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23rd International Conference on Composite Materials (ICCM23)

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Thermal Energy Storage and Thermal Management systems

The demand of energy is growing → ***Environmental pollution***

- ❑ Introduction **of renewable sources of energy** to reduce the use of fossil fuels
- ❑ Improve the efficiency of the traditional sources of energy
- ❑ **Better management of energy**

↓

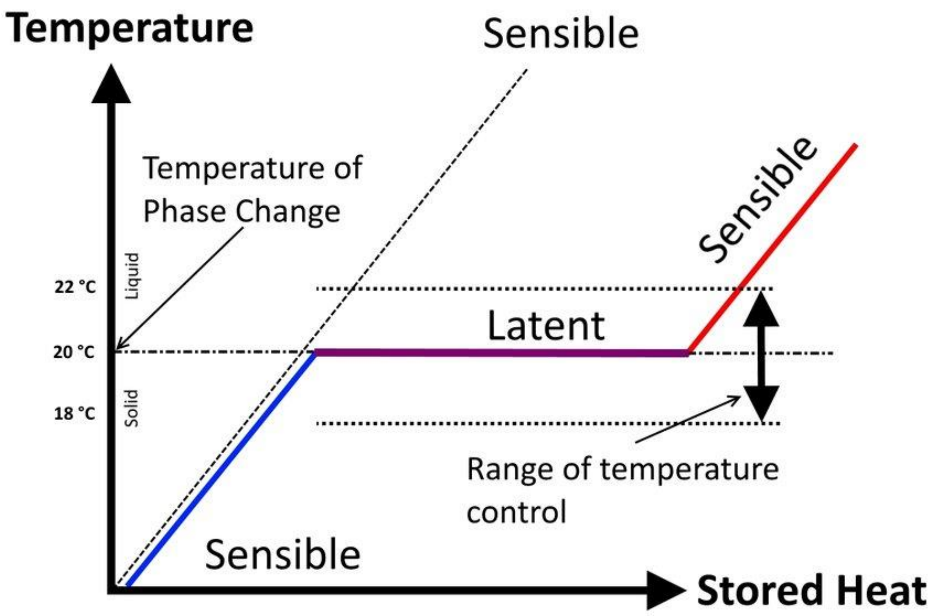
Thermal energy storage (TES)

Examples of applications

- ✓ Heating solar plants to store the excess of heat
- ✓ Indoor building comfort
- ✓ Thermal management in electronic devices
- ✓ Smart textiles

Dorigato et al., Express Polymer Letters, 11, 9, 738 (2017)
Dorigato et al., Rubber Chemistry and Technology, 90, 3, 575 (2017)

Phase Change Materials (PCM)

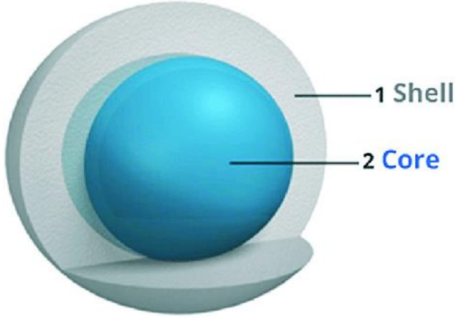


Organic Phase Change Materials (OPCMs)

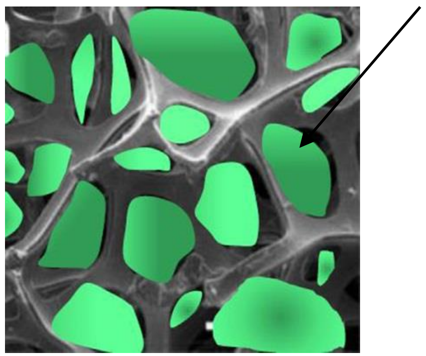
- High latent heat of fusion (200-300 kJ/kg)
- Melting temperature in the range 10-70 °C
- High thermal and physical stability
- Little volume variation
- Low thermal conductivity
- High flammability

Incorporation techniques for PCMs

- ✓ Encapsulation methods
- ✓ Shape-stabilization methods



Porous structure



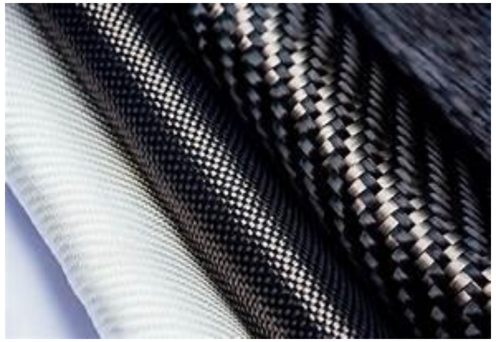
Fredi et al., Polymers, 9, 405 (2017)
Fredi et al., Composites Science and Technology, 158, 101 (2018)

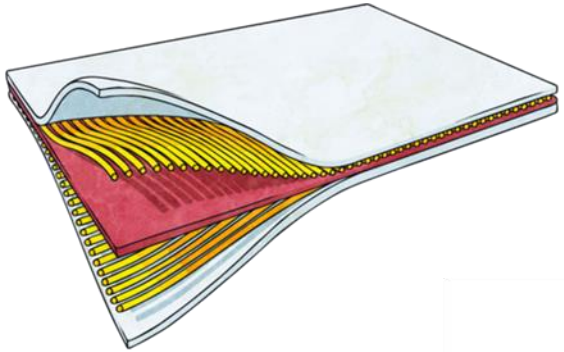
Multifunctional composite materials

Composite materials

"A composite material is a material composed by two or more distinct phases, which work synergy to improve the performance of the material"

- Mechanical properties
- Thermal properties
- Physical properties
- Conductivity properties





Carbon fiber laminates with TES materials

- ✓ Generally PCM are used alone or added as a supplementary material in a structural device
- ✓ Innovative material with both TES and structural features

MULTIFUNCTIONAL MATERIALS

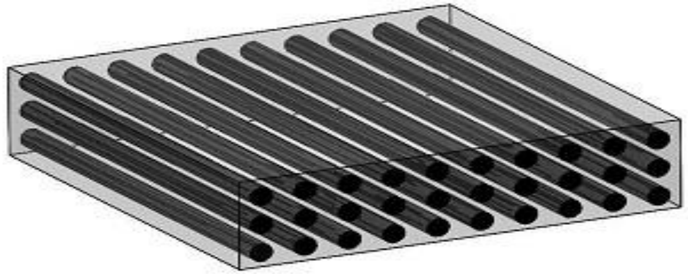
Coupling thermal management with structural properties (weight and volume saving)

Fredi et al., Multifunctional Materials, 3, 042001 (2020)

Aim of the work

Evaluate the influence of PCM (i.e. paraffin microcapsules) on the microstructural, thermal and mechanical properties of unidirectional epoxy/carbon fiber laminates with TES capability

- Melting enthalpy of the laminates
- Viscoelastic properties of the laminates
- Through-thickness thermal conductivity
- Temperature profiles during the heating and cooling phases of the laminates
- Flexural properties of the laminates
- Fracture toughness of the laminates



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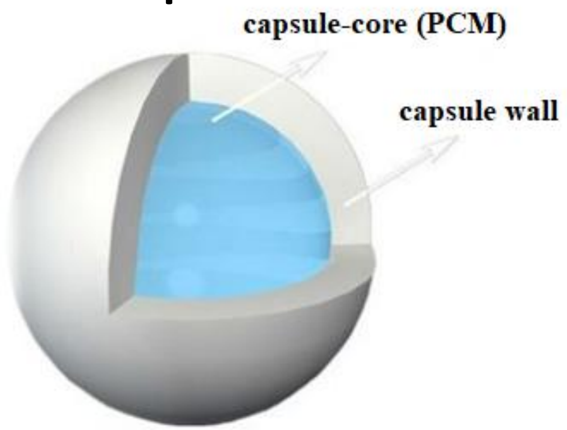


Fredi et al., Polymer Testing, 91, 106747 (2020)

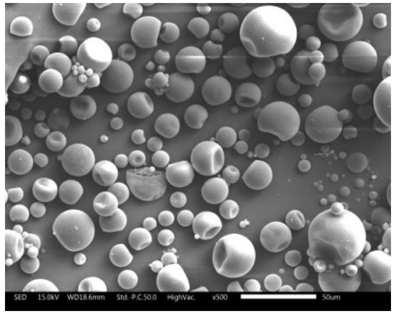
Materials

- **PCM: Microtek MPCM43 D ➡ MC (Paraffin microcapsules)**

  Purchased by Microtek Laboratories Inc. (Dayton, OH)

  Paraffin wax core with melamine-formaldehyde shell

  - ✓ Melting enthalpy 190-200 J/g
  - ✓ Melting temperature 43 °C
  - ✓ Capsule diameter ≈ 20 µm



- **Epoxy resin: EN 157/W 342 ➡ EP**

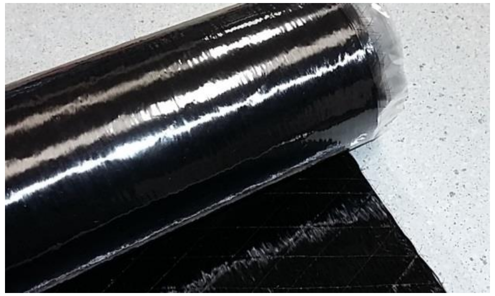
  Purchased by Elantas Europe (Parma, Italy)

  - ✓ Density 1.16 ± 0.01 g/cm^3
  - ✓ Time of gelation 6-8 hours
  - ✓ Glass transition temperature 60-100 °C

- **Unidirectional carbon fiber: UDC 15060 ➡ CF**

  Purchased by Mike Compositi (Milano, Italy)

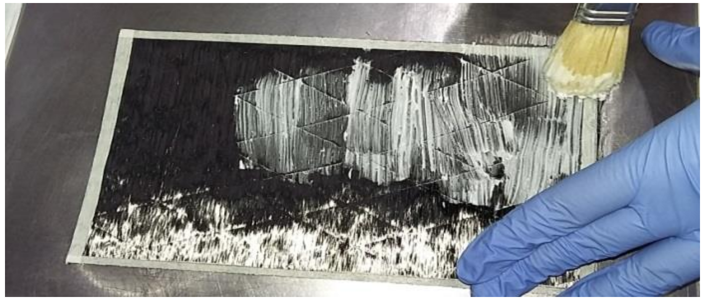
  - ✓ Elastic modulus 190 GPa
  - ✓ Density 1.63 g/cm^3
  - ✓ Areal density 150 g/m^2
  - ✓ Fiber diameter ≈ 7.7 µm

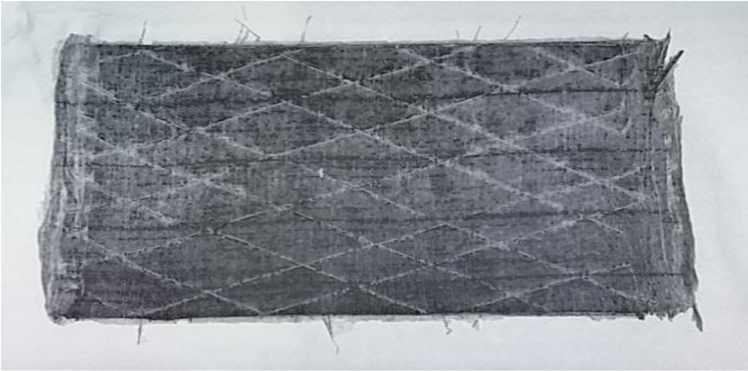


Samples preparation

Steps of the lamination process

- ✓ Preparation of the matrices
  Stirring at 500 rpm for 5 min and degassing
  - EP without MC
  - EP with 20 wt% of MC
  - EP with 30 wt% of MC
  - EP with 40 wt% of MC
- ✓ Hand lay-up process
  - 130x200 mm^2 CF plies
- ✓ Vacuum bag
  - 4 hours under vacuum
- ✓ Curing treatment
  - 24 hours at room temperature
  - 10 hours at 100 °C

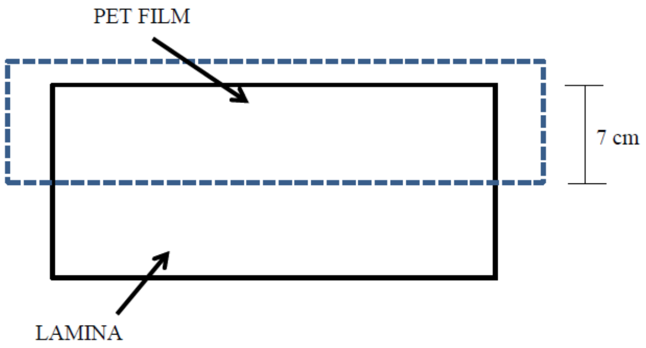




List of the prepared laminates

Sample	Matrix	Reinforcement	N. Laminae	Thickness (mm)
EP-CFu-A	Neat EP	Unidirectional CF	8	1.33 ± 0.03
EP-CFu20-A	EP + 20 wt% MC	Unidirectional CF	8	2.00 ± 0.05
EP-CFu30-A	EP + 30 wt% MC	Unidirectional CF	8	2.13 ± 0.03
EP-CFu40-A	EP + 40 wt% MC	Unidirectional CF	8	2.42 ± 0.07
EP-CFu-B	Neat EP	Unidirectional CF	16	3.00 ± 0.17
EP-CFu20-B	EP + 20 wt% MC	Unidirectional CF	16	4.71 ± 0.19
EP-CFu30-B	EP + 30 wt% MC	Unidirectional CF	16	4.84 ± 0.04
EP-CFu40-B	EP + 40 wt% MC	Unidirectional CF	16	5.58 ± 0.13

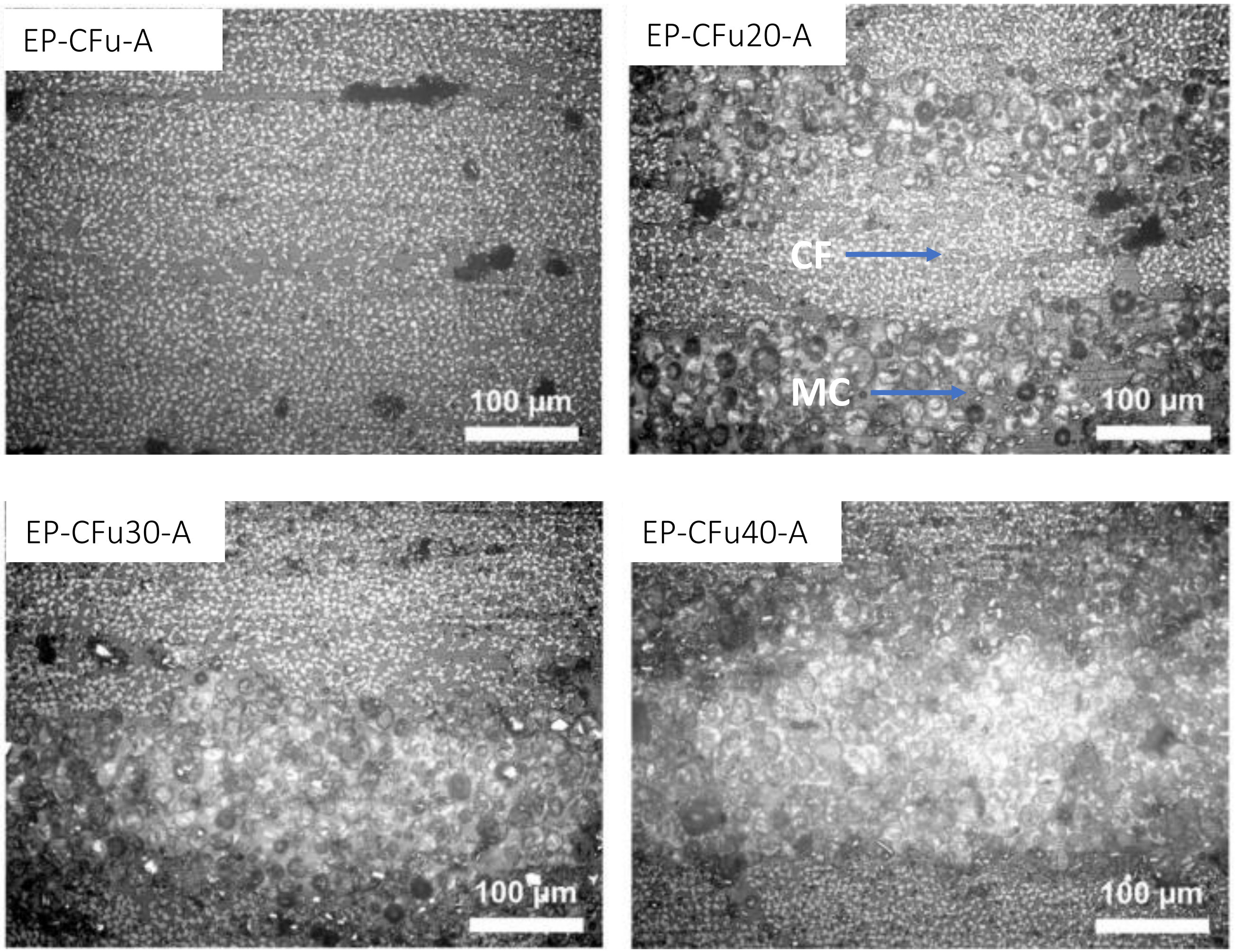
NB. In 16 layered laminates, a PET film 26 μm thick was placed in the mid-plane to generate a pre-crack for mode I interlaminar fracture toughness tests.



Microstructural analysis

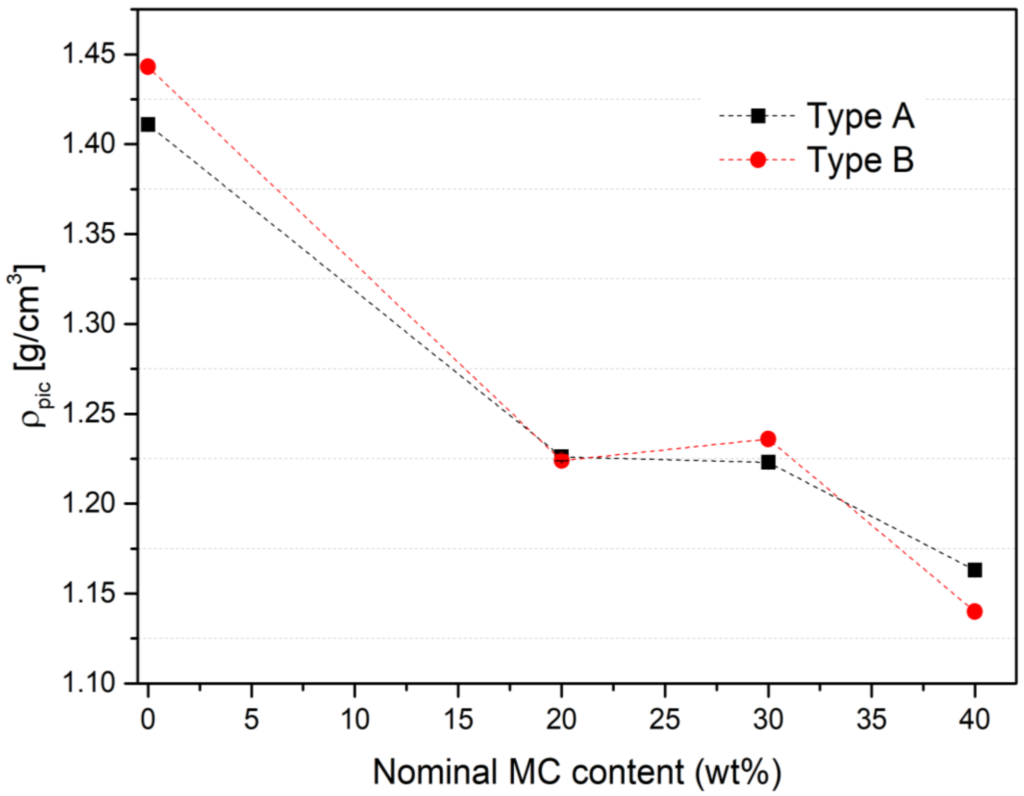
Optical microscope Zeiss Axiphot (Oberkochen, Germany)
Polished cross sections

- CF **homogeneously distributed** in the laminate thickness, without evident matrix-rich zones.
- **PCM phase preferentially distributed in the interlaminar region** and not among the fibers of the same tow.
- This phenomenon **could decrease the interlaminar properties** and create a preferential path for damage propagation.
- **The thickness of the interlaminar region increases with the MC concentration**, with a consequent decrease of CF volume fraction in the laminates.



Density evaluation

Helium Pycnometer AccuPyc 1330 (T = 23 °C)



$$Porosity = \frac{\rho_{the} - \rho_{exp}}{\rho_{the}}$$

Sample	Porosity [%]
EP-CFu-A	**2.3 ± 1.6**
EP-CFu20-A	7.1 ± 0.8
EP-CFu30-A	5.4 ± 0.5
EP-CFu40-A	**8.3 ± 1.9**
EP-CFu-B	0.1 ± 0.1
EP-CFu20-B	5.2 ± 0.5
EP-CFu30-B	1.7 ± 0.2
EP-CFu40-B	7.7 ± 0.7

The density of the laminates decreases with the MC loading

- Lower density of MC
- Lower weight fraction of CF
- **Increase of porosity**

The increase of MC loading causes an **increase in viscosity of the matrix** ➡ The air bubbles remain entrapped in the composite

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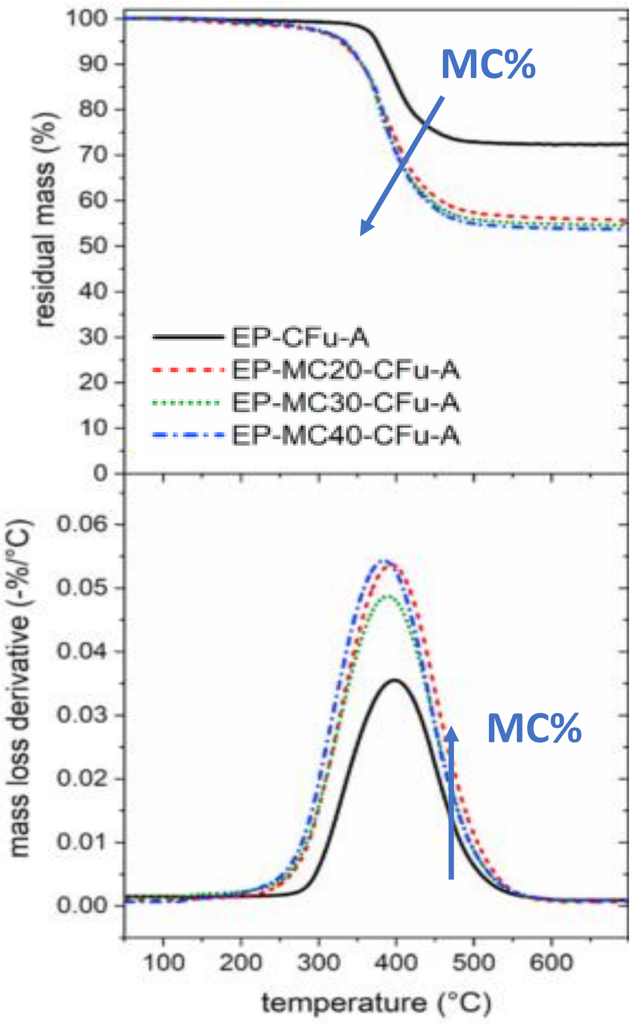
Thermogravimetric analysis (TGA)

Mettler TG50 M3 TGA instrument
v = 10 °C/min in nitrogen atmosphere (100 ml/min)

Sample	$T_{5\%}$ [°C]	T_d [°C]	$m_{r\%}$ [%]	CF content [wt%]
EP-CFu-A	**368 ± 9**	**401 ± 2**	**70 ± 3**	**68.0 ± 3.6**
EP-CFu20-A	330 ± 2	388 ± 1	56 ± 1	53.7 ± 0.7
EP-CFu30-A	328 ± 4	387 ± 2	54 ± 1	51.8 ± 0.9
EP-CFu40-A	**333 ± 1**	**387 ± 4**	**53 ± 1**	**50.2 ± 1.1**
EP-CFu-B	356 ± 5	397 ± 2	70 ±1	68.2 ± 0.1
EP-CFu20-B	330 ± 6	390 ± 3	50 ± 1	47.7 ± 0.1
EP-CFu30-B	329 ± 2	388 ± 1	47 ± 1	44.4 ± 1.5
EP-CFu40-B	323 ± 6	387 ± 2	44 ± 1	40.4 ± 0.3



- **MC addition reduces $T_{5\%}$, T_d and $m_{r\%}$** (lower CF amount in the laminates and lower thermal stability of MC).
- **A direct comparison of the mechanical properties** of the laminates is impossible.

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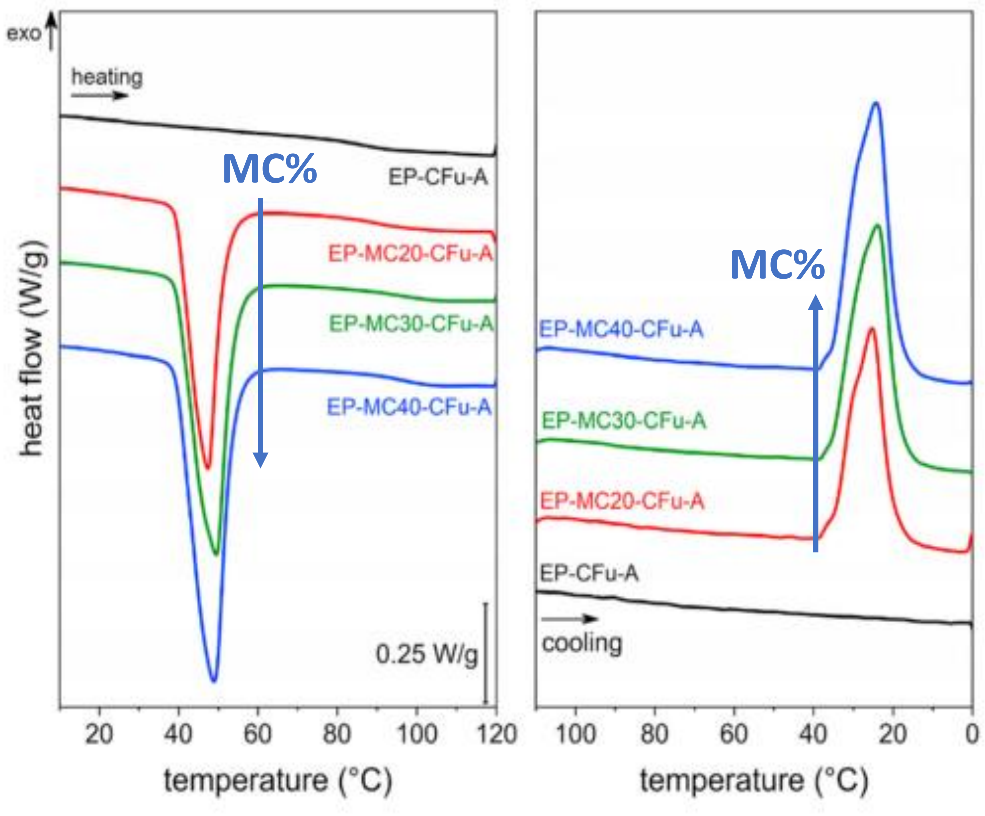
Differential scanning calorimetry (DSC)

Mettler DSC 30 instrument
v = 10°C/min in nitrogen flux (100 ml/min)



Sample	T_g [°C]	T_m [°C]	T_c [°C]	ΔH_m [J/g]	ΔH_c [J/g]	MC cont. [wt%]
MC	-	47.0 ± 0.6	27.2 ± 0.8	221.7 ± 12.6	221.6 ± 15.7	100.0
EP-CFu-A	87.0 ± 1.7	-	-	-	-	0.0
EP-CFu20-A	89.0 ± 0.9	45.4 ± 0.5	27.0 ± 0.5	29.1 ± 2.6	29.8 ± 2.6	13.2
EP-CFu30-A	96.8 ± 1.3	47.8 ± 0.3	25.5 ± 0.2	39.7 ± 0.4	40.2 ± 0.7	18.2
EP-CFu40-A	**93.4 ± 2.9**	**48.2 ± 1.4**	**24.9 ± 1.4**	**48.2 ± 7.6**	**48.7 ± 7.9**	**22.0**

- **The T_g of EP is shifted to slightly higher temperatures** with the MC loading.
- **T_m and T_c of PCM are not considerably affected** by the composition of the laminates.
- **ΔH_m increases with the MC loading** up to 48 J/g.
- The effective MC content in the laminates was established.

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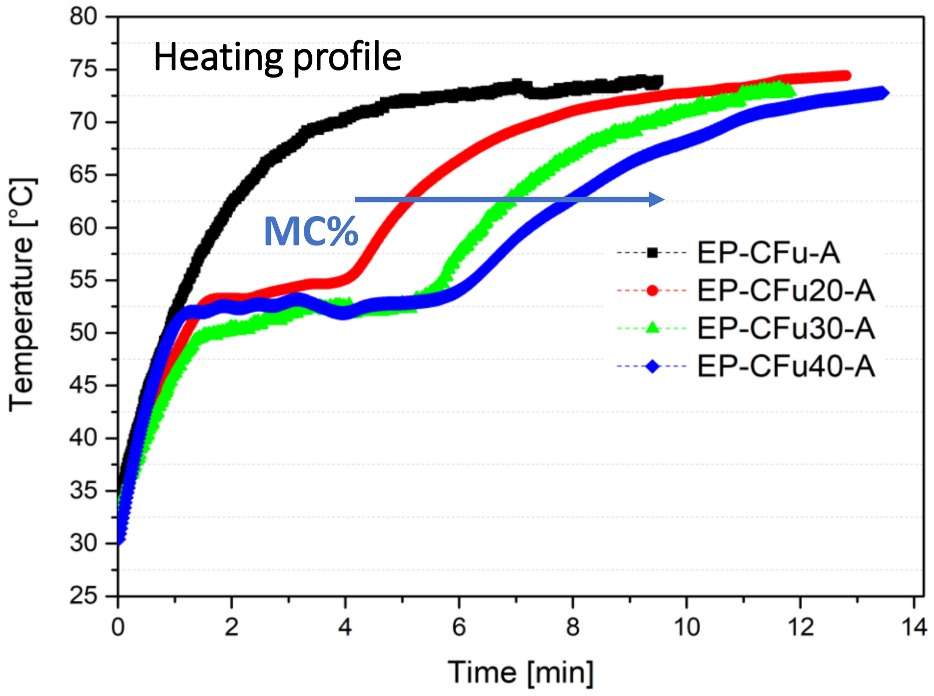
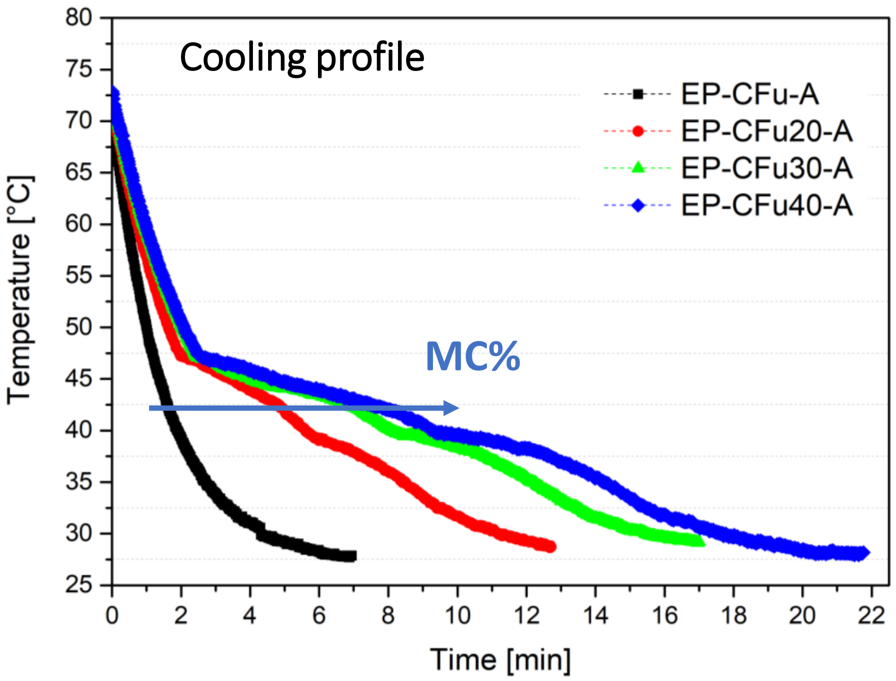
Infrared thermography

Thermal camera FLIR E6 3900 (Oregon)
Laminates dimensions 100 x 100 mm

Evaluation of the surface temperature





Sample	t_{70} [min]	t_{30} [min]
EP-CFu-A	**4.0**	**4.3**
EP-CFu20-A	7.7	10.7
EP-CFu30-A	9.6	14.8
EP-CFu40-A	**11.0**	**17.0**

- The MC introduction **promotes a temperature stabilization at T_m of microcapsules**
- **Both t_{70} and t_{40} increase** with the MC content

TES capability is confirmed !

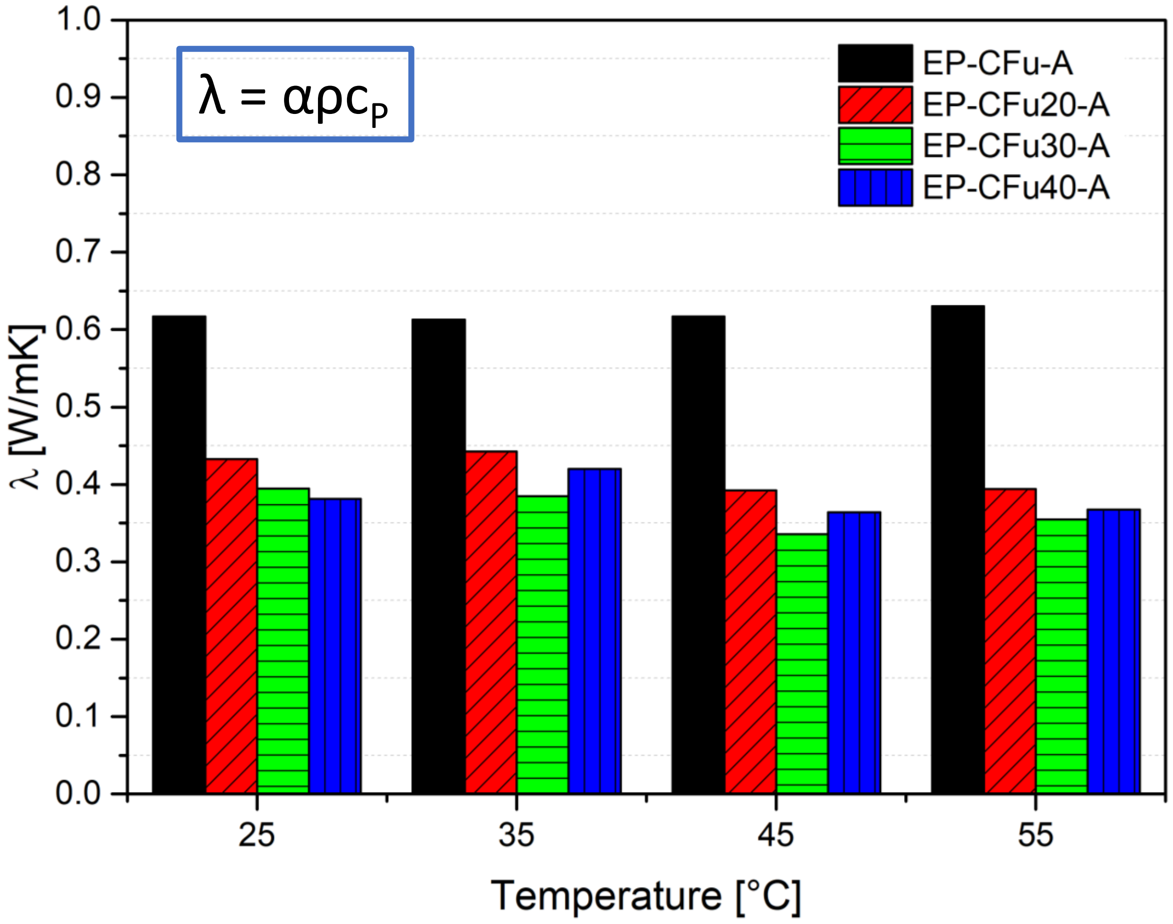
Through-thickness thermal conductivity

Netzsch LFA 447 Laser Flash Apparatus
Testing temperatures: 25 °C; 35 °C, 45 °C; 55 °C
Samples dimensions: 10 x 10 mm

- For the laminates containing MC, **the thermal conductivity is lower than that of the neat laminate**, mainly because of the lower CF fraction and not for the different λ of the MC.

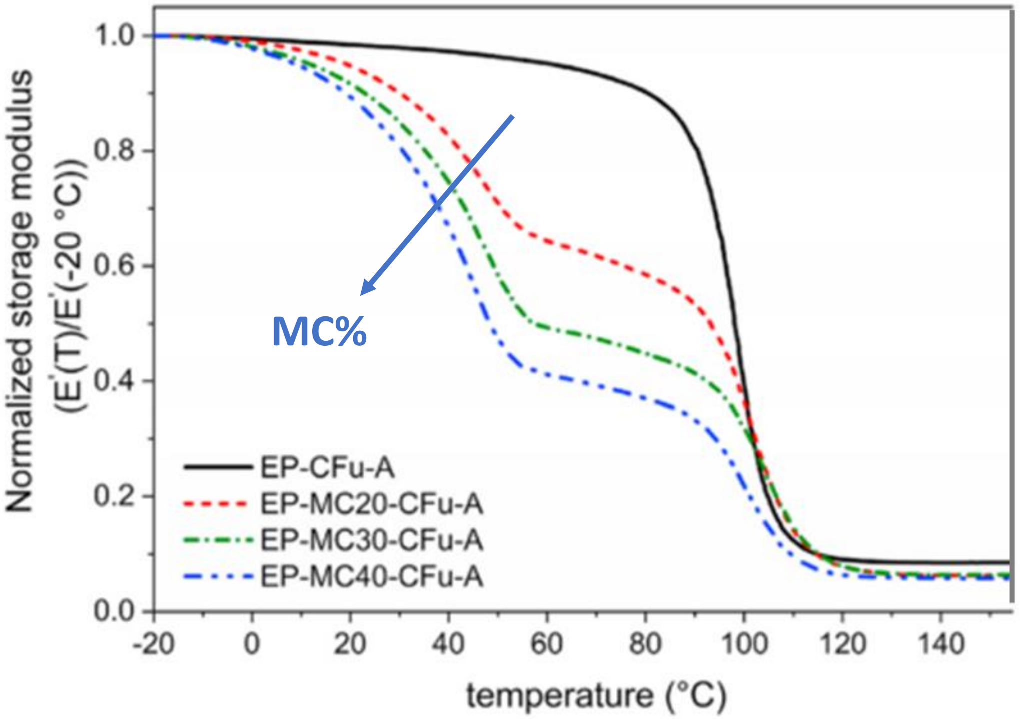
- **For the laminates containing MC, thermal conductivity shows a maximum at 35 °C**, as the PCM is approaching the solid-liquid phase change.

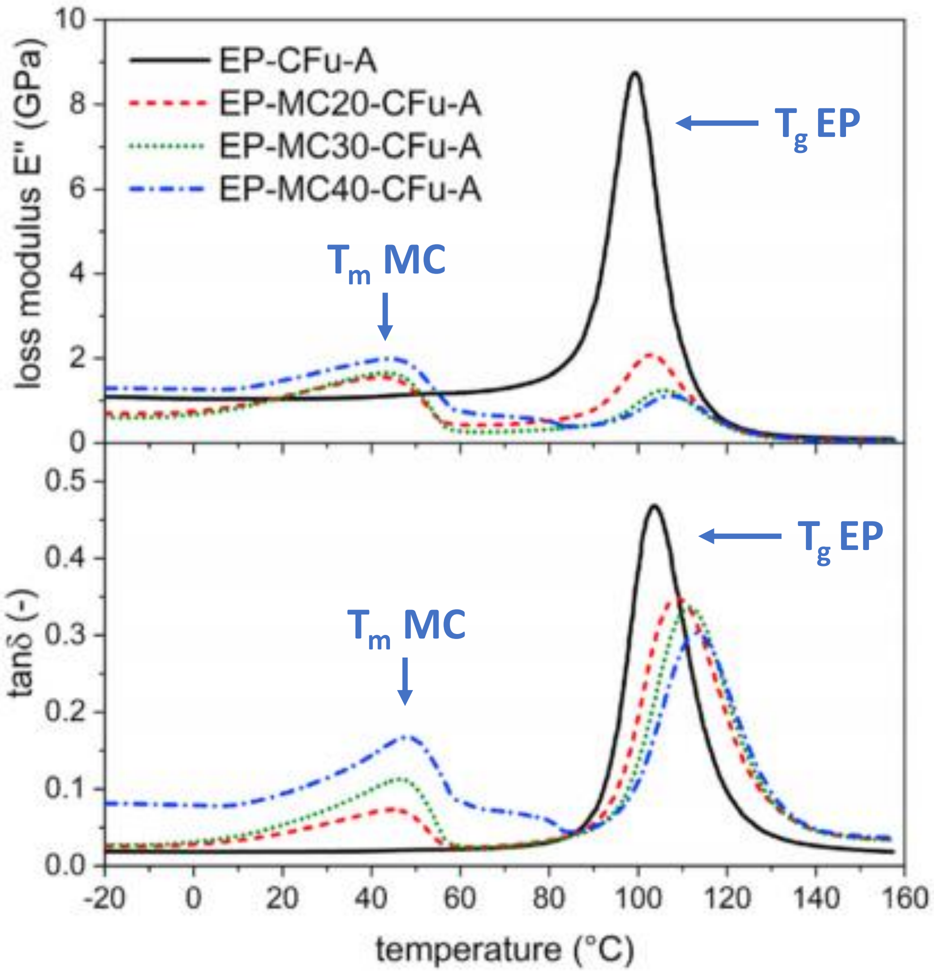
- **Thermal conductivity is slightly lower when the PCM is completely molten** (i.e. at 55 °C) than when the PCM is completely solid (i.e. at 25 °C).



Dynamical mechanical analysis (DMA)

TA Q800 DMA, single cantilever mode
v = 3 °C/min, maximum strain amplitude = 0.05 %, frequency = 1 Hz

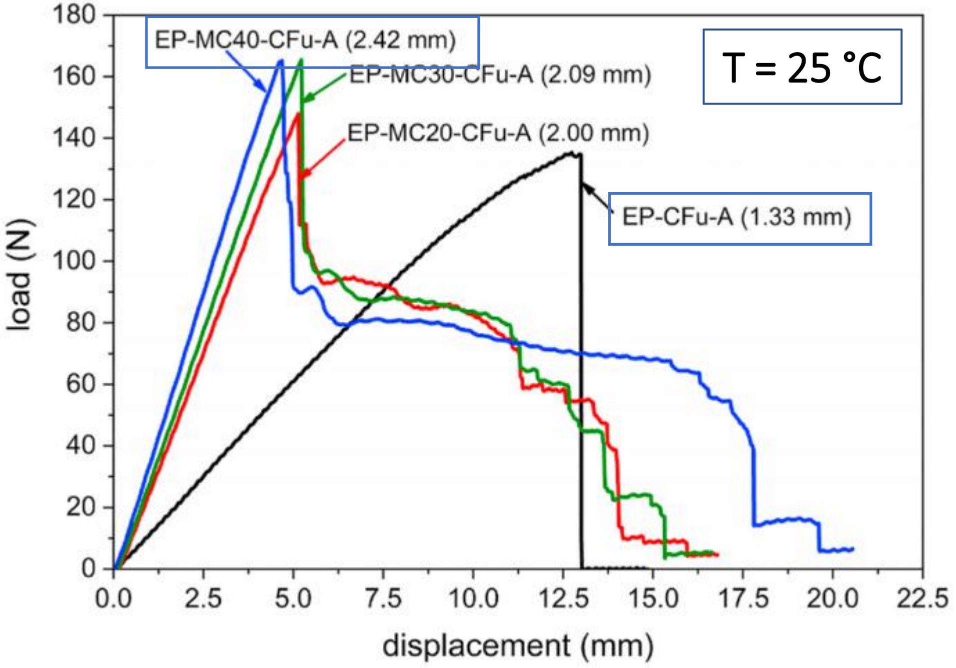




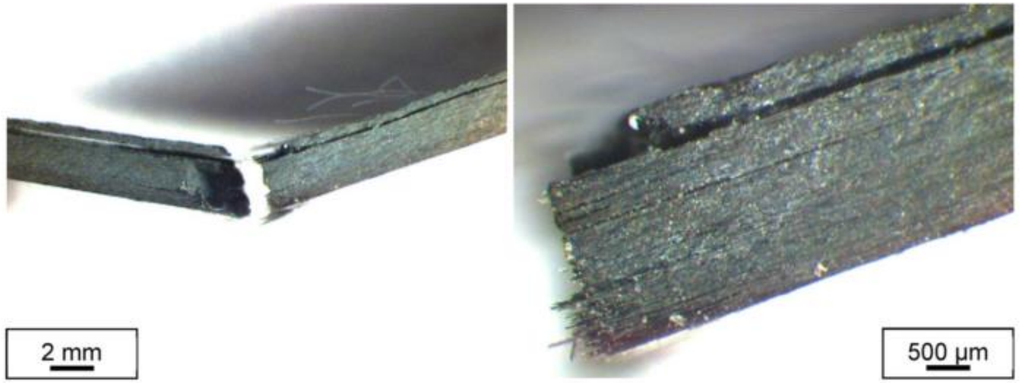
- **Two main decreasing steps of E'**, i.e. at the paraffin T_m and at the T_g of EP.
- **E″ and tanδ peaks at the MC T_m**, proportionally to the MC content.

Flexural properties

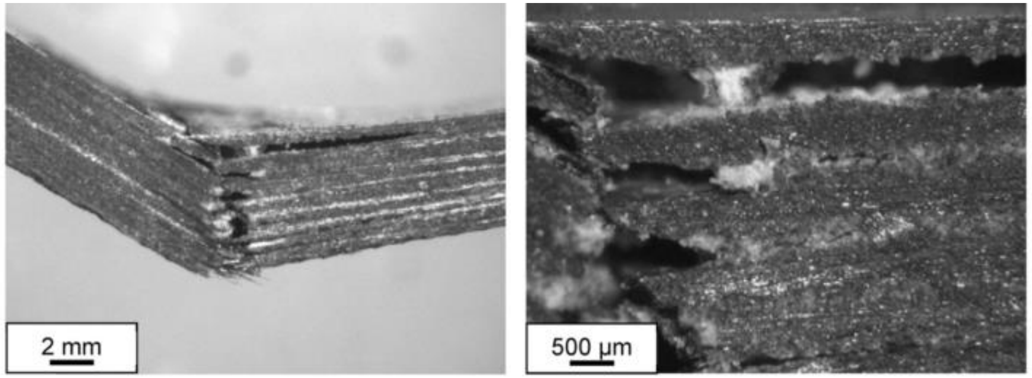
Instron 5969
v = 1.5 mm/min, span length = 50 mm



EP-CFu-A



EP-CFu40-A



- **The neat laminate is subjected to a catastrophic failure** (good interlaminar adhesion).
- **The PCM-containing laminates are subjected to a progressive failure**, with energy dissipation during damage propagation (the in-plane strength is considerably higher than the ILSS).

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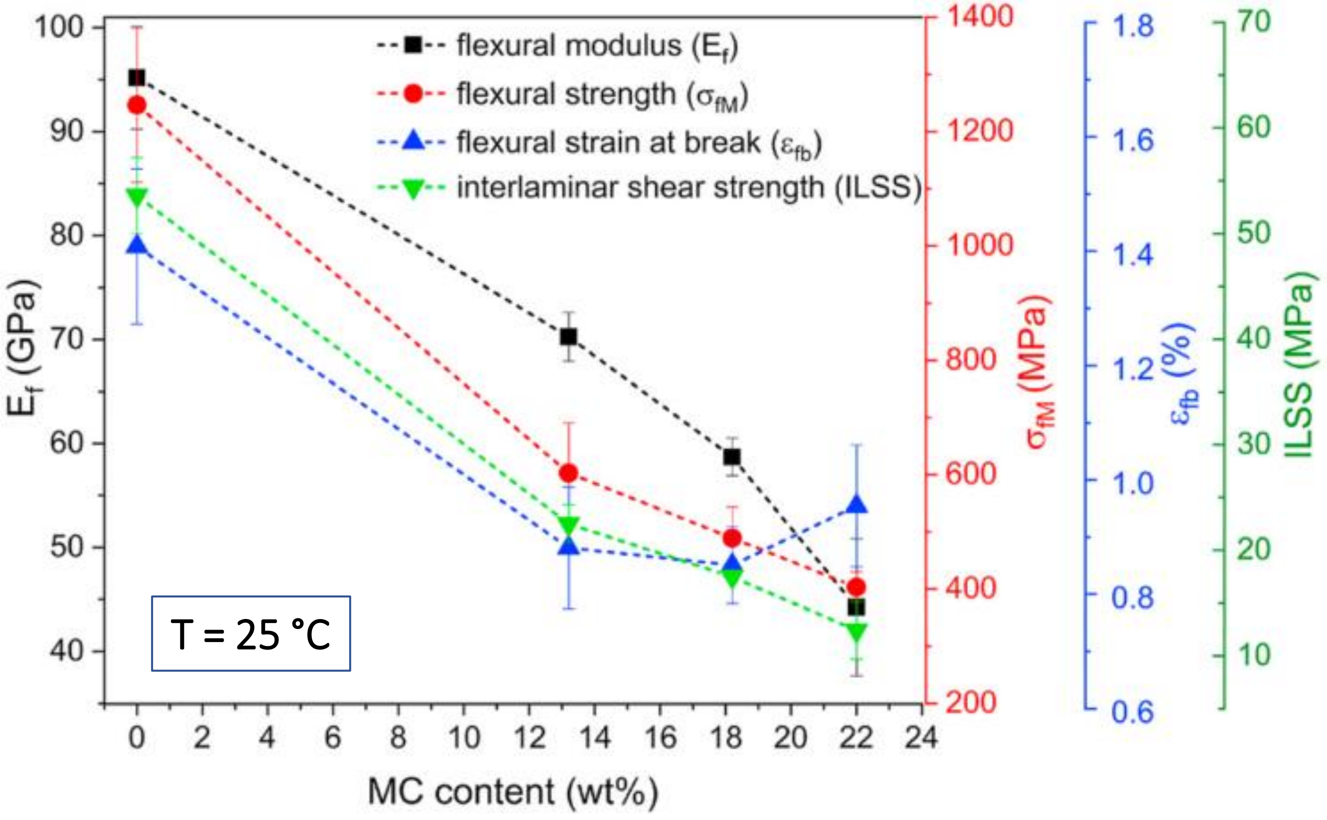
Flexural properties

Instron 5969
v = 1.5 mm/min



- **The elastic modulus is seen decreasing** with an increase in the MC content, **which is due ONLY to the reduction in the CF volume fraction**.
- **Also the flexural strength and the strain at break decrease,** because of the introduction of new damaging mechanisms (delamination and interlaminar fracturing).
- The same phenomena are also at the basis of the **observed reduction of the ILSS**.

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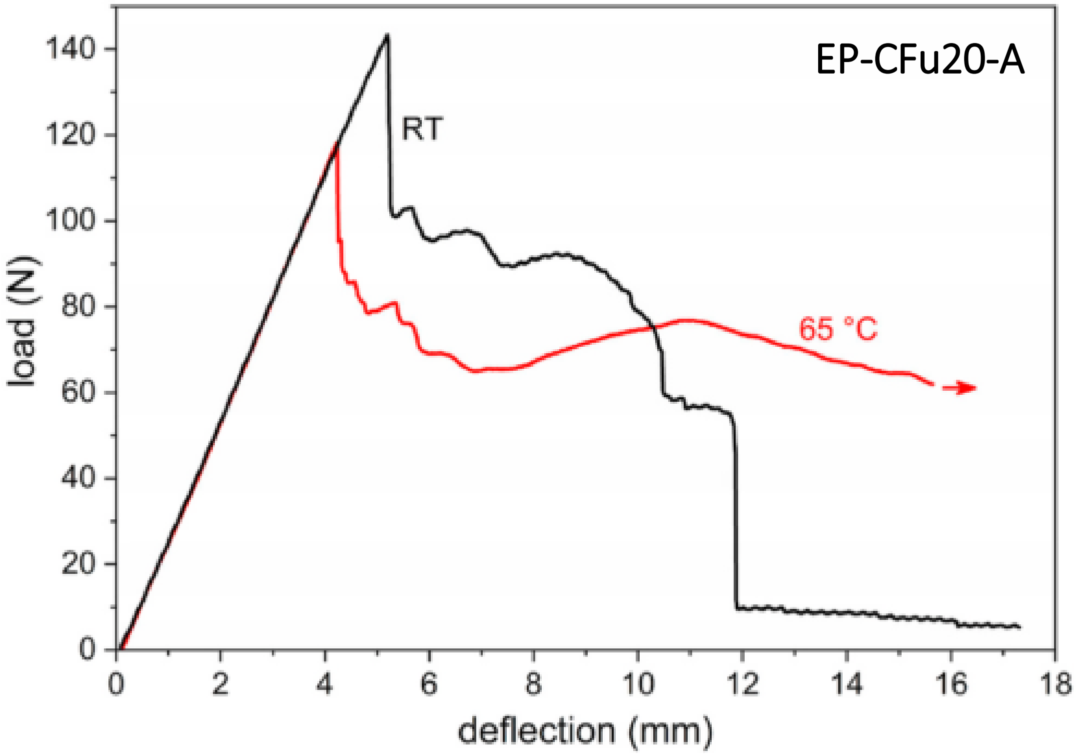
Flexural properties

Instron 5969
v = 1.5 mm/min

T = 65 °C



Difference with respect to the room temperature values

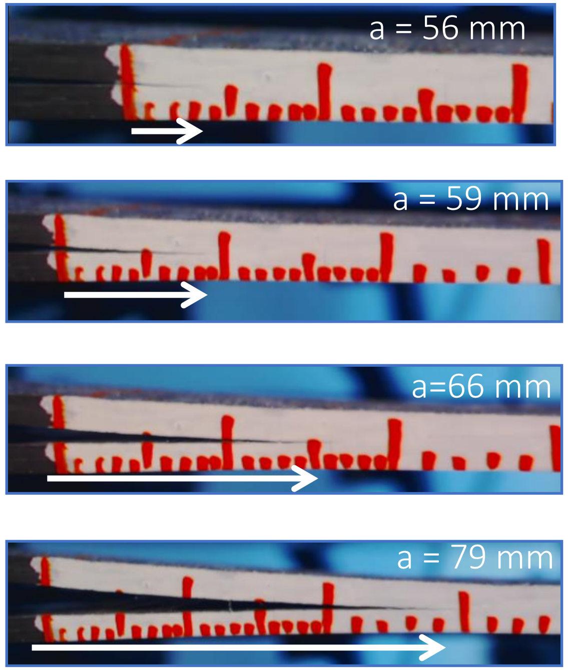
Sample	ΔE_F [%]	$\Delta \sigma_F$ [%]	$\Delta \varepsilon_b$ [%]
EP-CFu20-A	99	74	78
EP-CFu30-A	85	59	70
EP-CFu40-A	93	59	70

- **The load-deflection curve in the crack propagation zone is different from that observed at RT**, as specimens containing MC presented a long plateau.
- **The elastic modulus is only marginally affected by temperature, while the decrease in the flexural strength and strain at break is more evident**, especially at higher MC contents.
- The decrease in the mechanical properties of the MC at the molten state **causes a further decrease in the mechanical properties of the interlaminar region.**

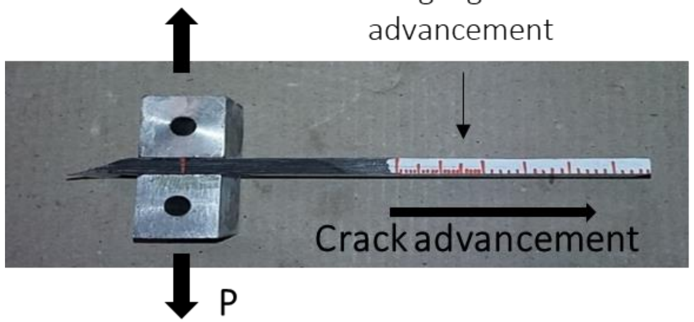
Mode I interlaminar fracture toughness

Instron 5969
v = 2.5 mm/min
pre-crack dimension = 50 mm

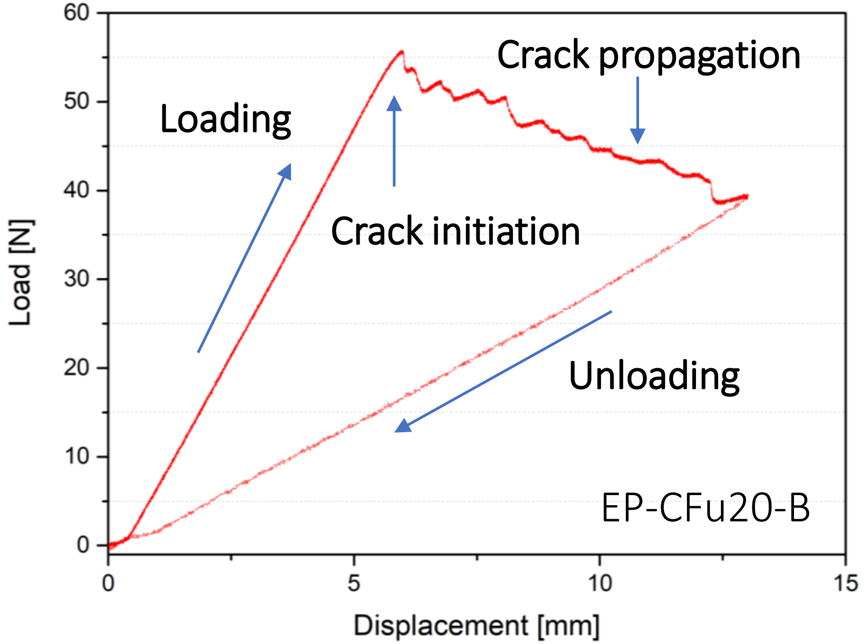
Crack propagation monitoring



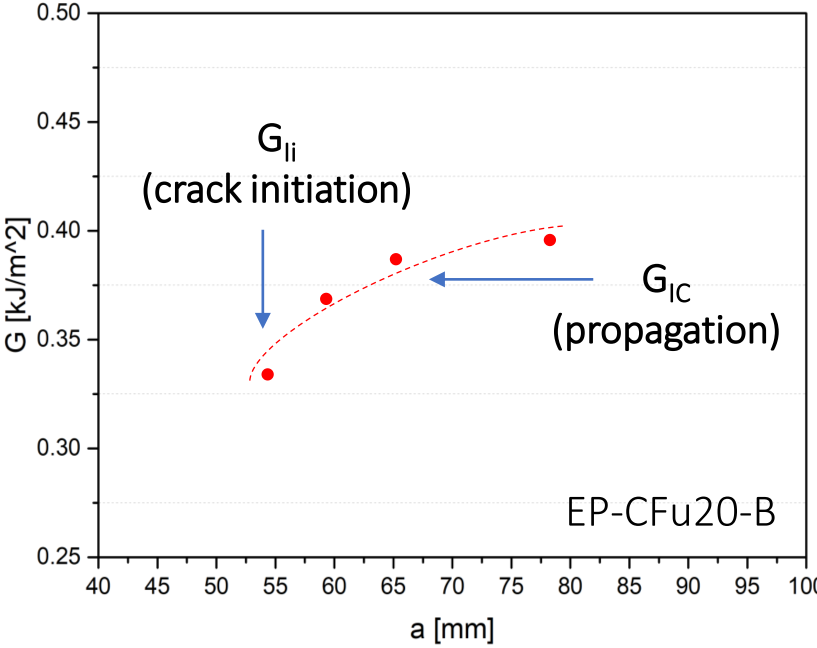
Scale to highlight the crack advancement



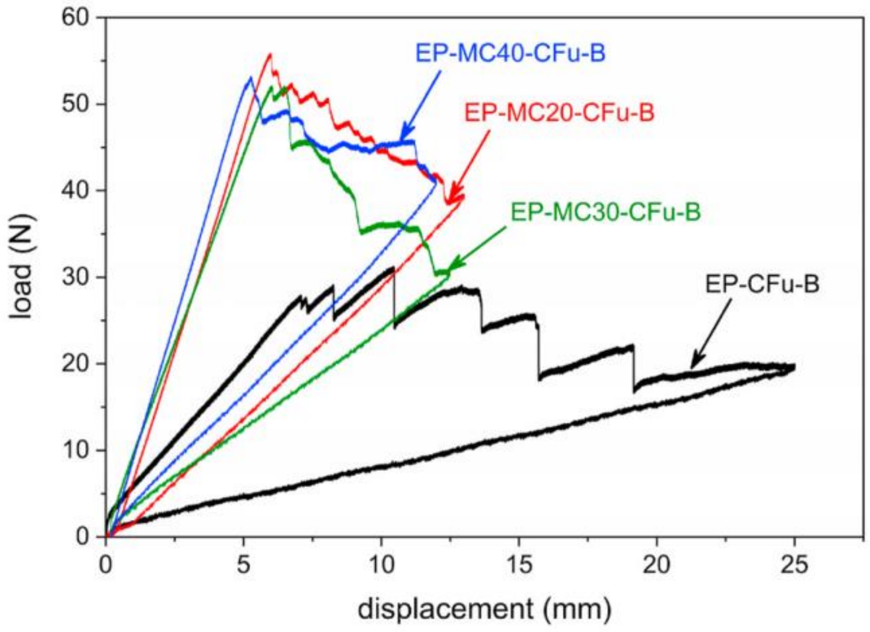
$$G_I = \frac{3P\delta}{2b(a+\Delta)}$$



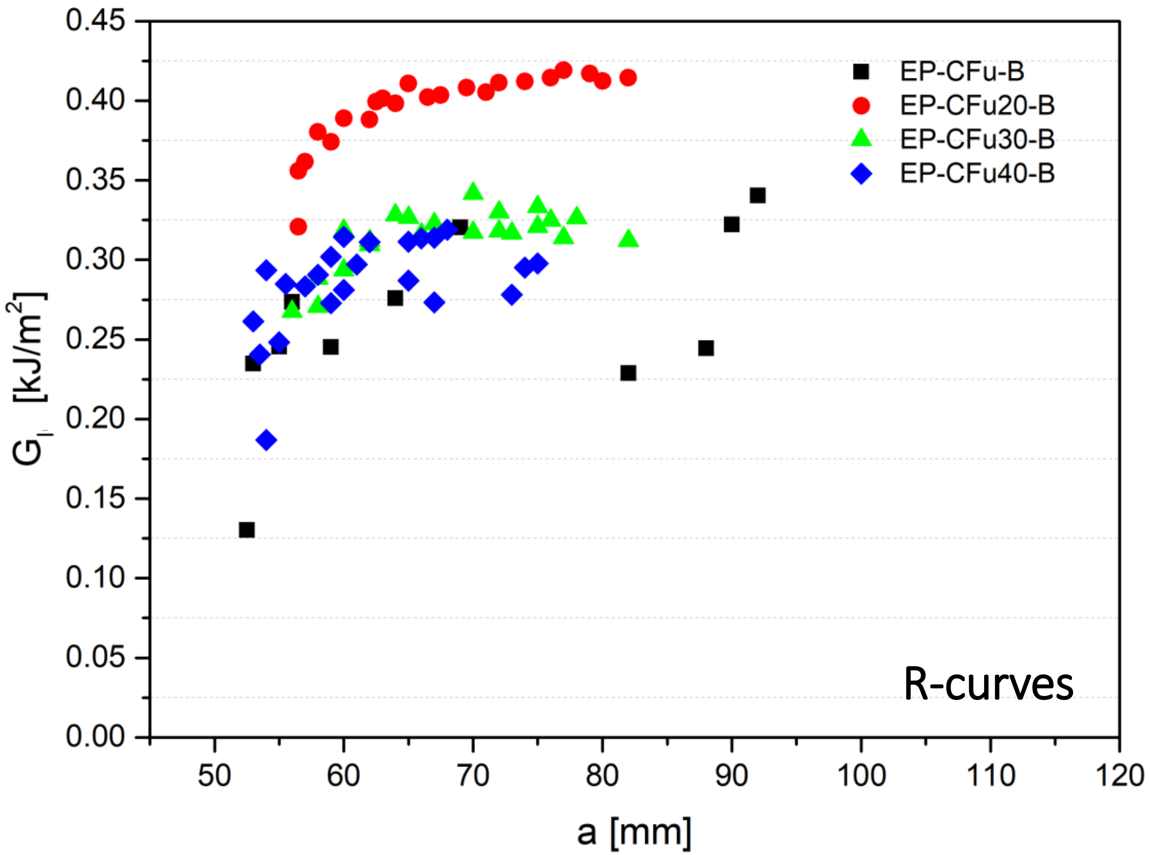
Construction of the R-curve



Mode I interlaminar fracture toughness



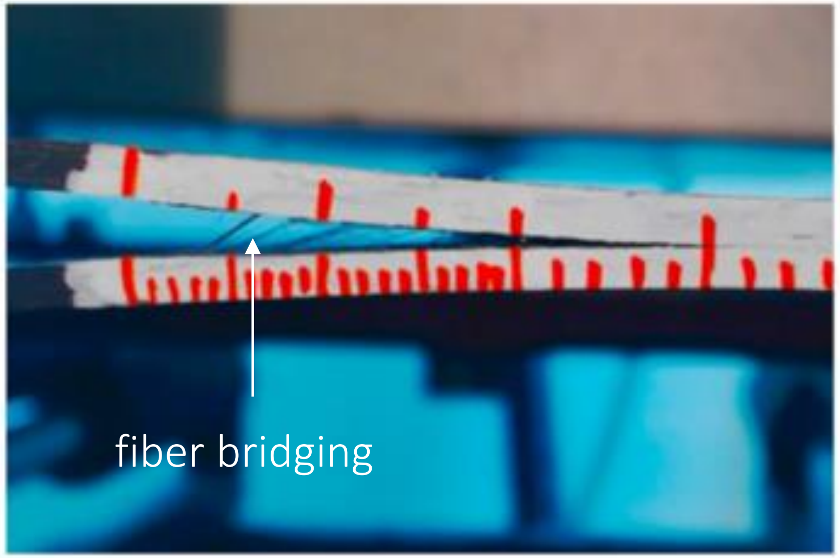
Sample	G_{Ii} [kJ/m^2]	G_{IC} [kJ/m^2]
EP-CFu-B	0.15 ± 0.03	0.27 ± 0.01
EP-CFu20-B	0.34 ± 0.02	0.40 ± 0.01
EP-CFu30-B	0.27 ± 0.02	0.32 ± 0.01
EP-CFu40-B	0.24 ± 0.02	0.30 ± 0.02



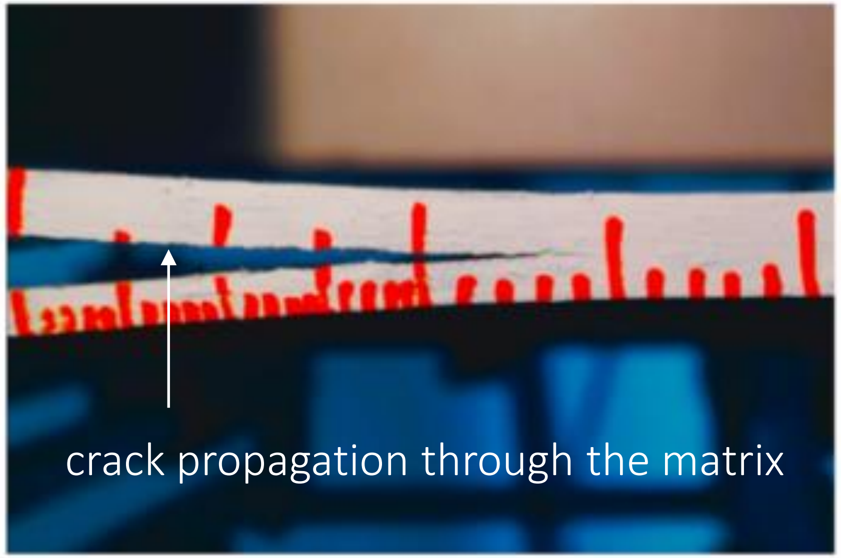
Toughening effect of at low MC amounts (20 wt%)

Mode I interlaminar fracture toughness

EP-CFu20-A



EP-CFu40-A



- **The introduction of a modest amount of MC (20 wt%) activates different toughening mechanisms,** i.e. particle debonding, crack deflection and fiber bridging.
- **Above a certain MC concentration, both G_{Ii} and G_{IC} decrease**, because of the 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.

Conclusions

In this work a thermo-mechanical characterization of unidirectional carbon/epoxy composites containing paraffin microcapsules for TES applications **was successfully performed.**

- **MC introduction increased the viscosity of the epoxy matrix**, limiting the flow of the epoxy/MC mixtures out of the CF fabric, **thereby increasing the matrix concentration and reducing the CF amounts**. This was at the basis of a decrease in the mechanical properties of the prepared laminates at high MC concentration.
- **MC were preferentially distributed in the interlaminar region, with a thickening of this region and a decrease in matrix-related properties**, such as the interlaminar shear strength. On the other hand, **a modest MC fraction led to an increase in the G_{IC}**, probably due to the introduction of new toughening mechanisms.
- **The TES and thermal management capability of the prepared laminates increased with the MC fraction**, as also demonstrated by thermal imaging tests.

Future works will focus on a deeper study of the **micromechanical properties of PCM microcapsules and on the improvement of the capsules/matrix adhesion**.

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