

Discontinuous carbon fiber/polyamide composites with microencapsulated paraffin for thermal energy storage

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ABSTRACT: This work focuses on the development of multifunctional thermoplastic composites with thermal energy storage capability. A polyamide 12 (PA12) matrix was filled with a phase change material (PCM), constituted by paraffin microcapsules ($T_{melt} = 43 \text{ °C}$), and reinforced with carbon fibers (CFs) of two different lengths (chopped/CF "long"[CFL] and milled/CF "short" [CFS]). DSC tests showed that the melting/crystallization enthalpy values increase with the PCM weight fraction up to 60 J/g. The enthalpy was 41–94% of the expected value and decreased with an increase in the fiber content, because the capsules were damaged by the increasing viscosity and shear stresses during compounding. Long CFs increased the elastic modulus (+316%), tensile strength (+26%), and thermal conductivity (+54%) with respect to neat PA12. Thermal imaging tests evidenced a slower cooling for the samples containing PCM, and once again the CFS-containing samples outperformed those with CFL, due to the higher effective PCM content. © 2018 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2019**, *136*, 47408.

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INTRODUCTION

Multifunctional materials combine different kinds of properties (structural, electrical, magnetic, thermal, etc.), which makes them suitable for performing multiple tasks simultaneously, and for being applied when stimuli of different nature are involved. The interest in multifunctional materials is increasing in both the scientific and industrial community, as demonstrated by the considerable growth of the number of publications.¹⁻³ Among the different classes of materials, composites are particularly suitable to be designed as multifunctional materials.^{2,4} One of the main reasons to combine structural and non-structural properties in the same material is the need to save weight and volume, which is crucial, for example, in automotive/aerospace applications and in the portable electronics field. In this perspective, polymermatrix composites are attractive because they combine the remarkable features of a polymeric matrix, such as the low density, ease of processability and relatively low cost, and the considerable stiffness and strength of fibrous reinforcing phases, thereby allowing the production of composites with high specific mechanical properties.⁵

In a polymer composite, the matrix can be thermoplastic or thermosetting. Thermoplastic composites are generally less expensive, exhibit infinite shelf life at room conditions, and have a shorter fabrication time. They can be more easily recycled, reprocessed, post-thermoformed, repaired, and welded. Moreover, they feature interesting mechanical and physical properties, such as the high toughness, impact resistance, and fracture resistance, which make them highly damage-tolerant.⁵⁻⁷ Short-fiber thermoplastic composites have been increasingly employed as structural and semistructural materials in various fields, such as the automotive industry.⁸⁻¹⁰ Among all the thermoplastic fiber composites, those having a polyamide (PA) matrix and a discontinuous fiber reinforcement are the most widely used today, due to their high mechanical properties and relatively low cost.9 The most diffused reinforcement in a PA matrix is represented by discontinuous glass fibers, but carbon fibers (CFs) are also employed, especially when higher stiffness and lower density are required. CFs are a multifunctional filler themselves because, besides enhancing the mechanical properties, they can be used to impart specific physical properties, such as a higher thermal or electrical conductivity.⁸

Multifunctional polymer composites find application in many different fields. An interesting field where the multifunctionality could be exploited, although not yet thoroughly investigated, is that of the structural composites with thermal energy storage (TES) capability. TES can be defined as the storage of heat that can be released where and when needed, which considerably

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reduces the mismatch between thermal energy availability and request.¹¹⁻¹⁴ TES technologies can be applied (1) to accumulate excess or waste heat for a later use, for example, in the solar thermal power plants, or to recover waste industrial heat,^{15,16} (2) to store heat for temperature control, for example, in the buildings industry^{17,18} or to produce smart textiles for body temperature regulation,^{19,20} or (3) to temporarily store heat that could damage a component, as in the cooling systems for electronic devices.²¹ Therefore, multifunctional composites combining good mechanical properties and TES capability could be usefully employed in those fields where weight and volume savings are crucial parameters, but also the TES capability or the temperature control must be considered. Examples of such applications are the automotive industry, where the increasing use of polymer composite structures could complicate the thermal management inside the cockpit or of other heat sensitive components; the portable electronics field, where the weight and volume reduction is limiting the space available for the cooling systems; the smart technical garments industries, where there is the need for tailored mechanical properties and body temperature regulation.

TES can be divided in sensible, thermochemical, or latent TES. Among these, the most widely employed TES technique, especially in the low-mid temperature range (0-100 °C), is to accumulate and release latent heat through phase change materials (PCMs), which generally undergo a endo/exothermic solid-solid or solid-liquid transition and are categorized as organic, inorganic, or eutectic.¹¹ PCMs can store a high amount of heat per unit mass, at a nearly constant temperature, with a limited volume variation.^{11,22} Organic PCMs, represented by oligomers or polymers such as paraffins, poly(ethylene glycol)s, and fatty acids, are widely used as PCMs thanks to their high specific phase change enthalpy, small temperature range, negligible supercooling, low density, and cheapness. Their diffusion in a wide range of applications originates from their tunable melting/crystallization temperature, which can be varied by changing the molecular weight.^{11,23-26} The main disadvantages of organic PCMs are their poor thermal conductivity and the need to be confined to avoid leakage in the molten state.^{27,28} To avoid leakage, PCMs can be either encapsulated in micro- or nano-shells,²⁹⁻³¹ or confined ("shape-stabilized") in a polymer matrix,^{32–35} a layered/porous structure,^{21,36} or an inorganic nanofiller.^{19,37,38} In the latter case, the use of a thermally conductive filler also increases the total thermal conductivity, thereby improving the overall thermal exchange.

Even though the literature reports many examples of polymer matrices containing PCMs,^{16,18,25,31,39-42} little has been done so far to investigate the possibility to produce a multifunctional polymer-matrix composite that presents TES features and simultaneously carry high mechanical loads, although it would be undoubtedly advantageous to have a multifunctional structure that is also involved in heat storage/management. Some examples from the literature deal with composite sandwich structures with temperature control function,^{21,43,44} or epoxy/glass fiber laminates with a microencapsulated paraffin.^{45,46} Recently, our group prepared multifunctional epoxy/CF composites containing CNT-stabilized paraffinic wax,^{47,48} and a thermoplastic PA12/glass fiber laminate containing a microencapsulated and a shape-stabilized PCM and

reinforced with continuous glass fiber fabrics.⁴⁹ However, to the best of the authors' knowledge, no works on the production of thermoplastic short-fiber composites with good mechanical properties and TES capability can be found in the open literature.

The aim of the present work is to develop and characterize multifunctional composites combining good mechanical properties and the ability of thermal energy storage/management. These composites were obtained by combining a polyamide 12 (PA12) matrix, a commercial microencapsulated paraffin wax (PCM) and two kinds of discontinuous CFs (chopped and milled), in various concentrations. PA12 was chosen over the more common PA6 and PA66 due to the lower melting temperature, compatible with the processing of the microcapsules, and the lower moisture sensitivity, related to its high methylene/amide ratio (11/1).^{50–52} The PCM phase consists of a paraffin wax, with a melting temperature of 43 °C, encapsulated in a stable melamine-formaldehyde shell. After the production of composites with different weight fraction of the constituents, an extensive characterization of their microstructural, rheological, thermal, and mechanical properties was performed.

EXPERIMENTAL

Materials

MPCM 43D microencapsulated PCM was provided by Microtek Laboratories Inc. (Dayton, OH). In these microcapsules, prepared via *in situ* polymerization, the PCM is a paraffin wax with a melting temperature of 43 °C, encapsulated within a stable melamine-formaldehyde shell, which constitutes 10–15% of the mass. The microcapsules have a mean diameter of 17–20 μ m, and the melting enthalpy reported on the product data sheet is 190–200 J/g.

The thermoplastic matrix was Rilsan PA12, provided by Arkema Group (Lyon, France) in form of polymer granules (density 1.01 g/cm³, melting temperature 174 °C). Two types of CFs were employed, both supplied from Zoltek Corporation (Bridgeton, MO) and belonging to the category Panex PX35. This category has a nominal elastic modulus of 242 GPa and a density of 1.81 g/cm³. The two selected fiber types are the chopped CFs Panex PX35 type 65 (sizing content 2.75 wt %, average fiber length 6 mm) and the milled CFs Panex PX35 MF150 (unsized, average fiber length 100 μ m). Since these two CF types differ mainly in length, they will be denoted as CF "long" (CFL) and CF "short" (CFS), respectively.

Sample Preparation

The composites were prepared by melt compounding and hotplate pressing. Microencapsulated PCM, CFL, and CFS were mixed in different weight concentrations with the PA12 granules. The mixtures were melt compounded through a Thermo Haake Rheomix 600 internal mixer equipped with counter-rotating rotors, operating at 40 rpm for 6 min at a temperature of 190 °C. The resulting composites were subsequently compression molded in a Carver hot-plate press at 190 °C for 10 min, under an applied pressure of 1.2 MPa, to obtain square sheets of $200 \times 200 \times 1.5 \text{ mm}^3$. The samples were denoted as PA12-capx-CFLy or PA12-capx-CFSy, where "PA12" represents the matrix, "cap" the PCM microcapsules, and "CFL" and "CFS" the long and short CFs, respectively; "x" is the weight fraction of microcapsules in the matrix (with respect to the amount of PA12 and capsules), and "y" is the weight fraction of CFs with respect to



the total mass of the composite. Samples of neat PA12 and samples containing only one type of filler (PA12-capx, PA12-CFLy, and PA12-CFSy) were also prepared to understand the effect of each single filler on the properties of the matrix. All the prepared compositions with the weight fractions of the constituents are reported in Table I.

Testing Techniques

Scanning electron microscopy (SEM) images of the cryofractured surfaces of all samples were acquired through a Zeiss Supra 40 field emission scanning electron microscope at an accelerating voltage of 4 kV, after Pt-Pd sputtering.

Differential scanning calorimetry (DSC) tests were performed with a Mettler DSC30 machine under a N₂ flow of 150 mL/min, between -20 and 240 °C, at a heating/cooling rate of 10 °C/min. All the specimens, with a weight of ~15 mg each, were subjected to a first heating scan, a cooling scan, and a second heating scan. In this way, melting/crystallization temperatures (T_m , T_c) and enthalpies (ΔH_m , ΔH_c) of the PCM were determined. Moreover, relative melting/crystallization enthalpies ($\Delta H^R_{m\nu} \Delta H^R_c$) were calculated by dividing the ΔH_m and ΔH_c values by the melting/crystallization enthalpy of the neat microcapsules, and normalizing by the nominal PCM content in the composites. The thermal transitions of the PA12 were also measured, namely the glass transition temperature (T_g) and the melting and crystallization temperatures, and enthalpies ($T^m_{\mu\nu} T^c_c, \Delta H^m_{\mu\nu}$ and ΔH^c_c).

Thermogravimetric analysis (TGA) was carried out by using a TGAQ500 instrument under a N₂ flow of 200 mL/min, in a temperature interval between room temperature and 700 °C, at a heating rate of 10°C/min. The test allowed the determination of

Table I. List of the Prepared Samples

Sample	PA12 wt %	Capsules wt %	CF wt %
PA12	100	-	-
PA12-cap20	80	20	-
PA12-cap40	60	40	-
PA12-cap50	50	50	-
PA12-cap60	40	60	-
PA12-CFL10	90	-	10
PA12-CFL20	80	-	20
PA12-CFL30	70	-	30
PA12-cap20-CFL20	64	16	20
PA12-cap40-CFL20	48	32	20
PA12-cap50-CFL20	40	40	20
PA12-cap60-CFL20	32	48	20
PA12-CFS10	90	-	10
PA12-CFS20	80	-	20
PA12-CFS30	70	-	30
PA12-cap20-CFS20	64	16	20
PA12-cap40-CFS20	48	32	20
PA12-cap50-CFS20	40	40	20
PA12-cap60-CFS20	32	48	20

the temperatures associated to a mass loss of 1 wt % $(T_{1\%})$, 3 wt % $(T_{3\%})$, and 5 wt % $(T_{5\%})$, as well as the temperature corresponding to the maximum degradation rate (T_d) , taken as the maximum of the mass loss derivative signal.

The Vicat softening temperature (VST) was determined according to the ASTM D1525 standard to evaluate the dimensional stability of the resulting matrices and the maximum temperature of continuous use. The tests were carried out at a heating rate of 120 $^{\circ}$ C/h under an applied load of 10 N, with the samples immersed in a bath of silicone oil. Three specimens were tested for each sample.

Thermal conductivity and diffusivity were measured through laser flash analysis (LFA) with a Netzsch LFA 447 instrument. Square samples with a side length of 12.7 mm were cut from the composite sheets. Each specimen was tested at three temperatures (20, 40, and 60 °C) and three pulses were performed for each temperature. Data were analyzed with the software Proteus (Netzsch). Thermal diffusivity (α) was calculated using the Cowan method with pulse correction. For the determination of the heat capacity (c_P), the reference material Pyrex 7740 (ASTM E1461), was employed, according to the standard ASTM-E 1461. The thermal conductivity (λ) was calculated according to eq. (1):

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

where ρ is the sample density (g/cm³), using the data of α and c_P obtained from the LFA test.

A test with a thermal imaging camera was performed to verify the macroscopic thermal performance of the laminates. Specimens with a surface area of $70 \times 60 \text{ mm}^2$ were cut from the sheets. They were heated in an oven at 60 °C for 30 min, then taken out and left cooling down to room temperature. During cooling, their surface temperature was measured with a thermal imaging camera (FLIR E60), placed at a distance of 30 cm.

Dynamic rheological tests were conducted with a Haake Mars III dynamic shear rheometer in parallel plate configuration, in isothermal conditions at a temperature of 190 °C, on square samples of $20 \times 20 \times 1.5 \text{ mm}^3$. A maximum shear strain (γ_0) of 1% was applied, while the frequency range was varied between 0.02 and 20 Hz. This test allowed the measurement of the shear viscosity (η), and the shear dynamic storage modulus (*G*'), loss modulus (*G*''), and loss factor (tan δ) in the selected frequency range.

Quasi-static tensile tests were performed with a universal testing machine Instron 4502, equipped with a 1 kN load cell. 1BA specimens (according to ISO 527 standard) were cut through a specimen die-cutter Ceast 6051. The measurement of the elastic modulus 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 ISO 527 standard, an elastic modulus (*E*) was measured as the secant of the stress–strain curve between the strain values of 0.05 and 0.25%. For each sample, five additional specimens were tested until failure, at a crosshead speed of 10 mm/min. The test allowed the determination of the maximum stress and the corresponding strain (σ_{MAX} , ε_{MAX}) and the stress and strain at break ($\sigma_{\rm b}$, $\varepsilon_{\rm b}$).



RESULTS AND DISCUSSION

Microstructural Properties

Figure 1(a-f) reports the SEM micrographs of the cryofractured surface of some representative compositions, that is, PA12-CFL20, PA12-CFS20, PA12-cap50, and PA12-cap50-CFL20, taken at different magnifications. Both long [Figure 1(a,b)] and short [Figure 1 (c,d)] fibers are uniformly dispersed in the matrix, without agglomeration. This production process does not impart a

unidirectional fiber orientation, although the fibers may be preferentially oriented in the plane perpendicular to the pressing direction. The fiber/matrix adhesion is rather good for both long and short fibers, although it seems better for the longer fibers, as the short fibers are unsized. As observed in our previous work,⁴⁹ also the microcapsules [Figure 1(e)] are uniformly distributed in the matrix, and also this filler presents a good adhesion with the matrix. Even though some debonding can be detected, many



(c)





(e)

(**f**)



Figure 1. SEM micrographs of the cryofracture surface of the prepared samples (a) PA12-CFL20, 1000×; (b) PA12-CFL20, 5000×; (c) PA12-CFS20, 1000×; (d) PA12-CFS20, 5000×; (e) PA12-cap50, 5000×; and (f) PA12-cap50-CFL20, 5000×.



residues of the shells of broken capsules are observable, which implies that, in most cases, the fracture propagation did not occur at the capsule-matrix interface. The breakage of some capsules could have happened also during melt compounding and hot pressing. The same considerations can be made for the samples containing both capsules and fibers. The micrograph of the sample PA12-cap50-CFL20 is reported in Figure 1(f), while the composites containing capsules and short fibers are not reported for sake of brevity.

Thermal Properties

Figure 2(a,b) shows representative DSC thermograms of the first heating scan and the cooling scan of the PA12-capx-CFS20 samples ($x = 0 \div 60$), while the main parameters obtained by DSC analysis are summarized in Table II.

For the neat PA12, an endothermic melting peak can be observed in the heating scan at ~180 °C, followed by an exothermic crystallization peak observable in the cooling scan at ~155 °C. The glass transition of the PA12 is detectable at ~40°C, both in the neat PA12 and in the samples without capsules. The PA12 melting/crystallization peaks are clearly visible in all the other samples, while the T_g is detectable only in the samples without capsules, due to the fact that, when the PCM is present, the T_{σ} signal cannot be seen prominently in the DSC thermogram due to the high intensity of the melting and crystallization peaks of the microencapsulated paraffin at ~45 and 30°C, respectively. Considering the experimental errors associated to DSC measurements, it can be stated that the phase change temperatures of the PCM do not significantly vary with the CF content. The phase change enthalpy of the PCM (ΔH_m , ΔH_c) increases with the weight fraction of microcapsules, but the relative enthalpy ΔH^{R}_{m} (calculated as described in Testing techniques section) is generally <100% and decreases as the PCM content increases. This implies that the measured enthalpy is less than that expected considering the PCM weigh fraction, which suggests that a significant fraction of capsules was broken during the processing steps, and the paraffin leaked out of the composites. This hypothesized leakage of PCM is also confirmed by TGA results, in which the mass loss relative to the PCM is lower than what expected considering the nominal weight fraction of the microcapsules.

The decrease in ΔH^{R}_{m} is increasingly evident for higher PCM contents; this can be due to the higher melt viscosity and the consequently higher shear stresses to which the capsules are subjected during compounding [see Rheological Properties section, Figure 6(a), which leads to a damage of the thin capsule shell and leakage of the paraffin contained. Some paraffin was observed leaking out of the mixing chamber during the compounding process. Additionally, it is interesting to note that the relative phase change enthalpy is lower for samples containing long fibers respect to those containing short fibers with the same filler weight fraction. This can be due to the high shear stresses arisen during the melt compounding of composites with long fibers and the consequent damage of the PCM microcapsules. This is in good agreement with the results of the dynamic rheological tests (see Rheological Properties section). Nevertheless, most of the TES/release capability is retained, especially in the samples with a low fiber content.

Figure 3(a-b) reports representative TGA thermograms of the prepared samples, which represent the residual mass and the mass loss derivative as a function of temperature for the neat PA12, the microcapsules, and some representative compositions, namely PA12-capx-CFL20 ($x = 0 \div 60$).

The most important results of the TGA tests are reported in Table III. The thermal degradation of the neat PA12 happens in two steps, but the greatest part of the mass loss occurs in the first stage. The addition of CFs delays the beginning of thermal degradation, as the values of $T_{1\%}$, $T_{3\%}$, and $T_{5\%}$ increase with the CF content, which is especially true for the CFS-containing samples, but the value of T_d is almost never significantly different from that of the neat PA12 and does not follow a trend with the CF weight fraction. On the contrary, the thermal degradation resistance of the microcapsules is lower than that of the neat PA12, and the PCM addition shifts the curves toward lower temperatures. For the neat microcapsules the degradation begins with many small subsequent steps. Four steps can be identified, which correspond to four local maxima in the mass loss derivative



Figure 2. Representative DSC thermograms of the prepared samples: (a) first heating scan; (b) cooling scan. [Color figure can be viewed at wileyonlinelibrary.com]



Table II. Main Results of the DSC Tests on the Prepared Samples

Sample	<i>T_g</i> (°C)	<i>T_m</i> (°C)	<i>T'_m</i> (°C)	ΔH_m (J/g)	ΔH^{R}_{m} (%)	<i>T_c</i> (°C)	<i>T′_c</i> (°C)	ΔH_c (J/g)
Сар	-	44.1	-	220.1	100.0	30.2	-	208.2
PA12	40.7	-	179.9	-	-	-	155.0	-
PA12-cap20	-	46.2	178.7	44.5	101.1	26.7	154.2	38.1
PA12-cap40	-	47.3	178.6	91.8	104.3	26.4	153.3	84.1
PA12-cap50	-	49.9	180.0	100.8	91.6	25.3	152.5	93.8
PA12-cap60	-	47.8	177.6	116.6	88.3	24.1	151.8	108.9
PA12-CFL10	39.7	-	180.2	-	-	-	154.1	-
PA12-CFL20	39.4	-	181.2	-	-	-	152.4	-
PA12-CFL30	38.7	-	181.0	-	-	-	153.4	-
PA12-cap20-CFL20	-	44.8	178.9	30.5	86.0	31.0	153.6	22.0
PA12-cap40-CFL20	-	45.8	179.9	28.9	41.1	31.4	152.7	23.8
PA12-cap50-CFL20	-	46.6	178.2	46.9	53.3	26.1	151.6	40.9
PA12-cap60-CFL20	-	45.8	178.4	44.5	42.1	30.2	151.8	37.6
PA12-CFS10	41.0	-	180.4	-	-	-	156.7	-
PA12-CFS20	37.6	-	180.0	-	-	-	159.3	-
PA12-CFS30	37.1	-	180.6	-	-	-	157.5	-
PA12-cap20-CFS20	-	45	179.2	33.3	94.6	31.7	157	28.8
PA12-cap40-CFS20	-	48.1	179.6	58.8	83.5	25.2	155.6	54.3
PA12-cap50-CFS20	-	47.5	179.4	60.4	61.0	26.6	156.2	57.7
PA12-cap60-CFS20	-	44.8	177.8	54.6	51.7	24.5	156.2	51.4

 T_{g_r} glass transition temperature of PA12 (°C); T_{m_r} melting temperature of the PCM (°C); T'_{m_r} melting temperature of PA12 (°C); ΔH_{m_r} PCM melting enthalpy (J/g); $\Delta H^R_{m_r}$ relative PCM melting enthalpy (%); T_{c_r} crystallization temperature of the PCM (°C); T'_{c_r} crystallization temperature of PA12 (°C); and ΔH_{c_r} PCM crystallization enthalpy (J/g).



Figure 3. Representative TGA thermograms of the prepared samples. (a) Residual mass and (b) mass loss derivative as a function of temperature. [Color figure can be viewed at wileyonlinelibrary.com]

signal, as also reported by other studies from the literature dealing with paraffin encapsulated in melamine-formaldehyde-based microcapsules.⁵³ The mass loss during the first step (up to ~180 °C) can be attributed to absorbed water and residual lowmolecular-weight species not properly removed after the capsule synthesis. This step is not observed in the other samples containing capsules, as most of the low-molecular-weight compounds have probably been removed during the melt compounding and hot-pressing operations, performed at 190 °C. The subsequent steps are related to the thermal degradation of the paraffinic core and the melamine-formaldehyde shell. A previous work of our group⁴⁷ showed that a free (non-encapsulated) paraffin wax, with a similar molecular weight and melting point as the PCM contained in these microcapsules, is fully degraded already at 250 °C, which suggests that the melamine-formaldehyde shell also increases the thermal stability of the PCM core. The considerably high peak in the mass loss derivative signal indicates that most of the mass loss happens in a relatively narrow temperature interval. This mass loss can be associated to the damage of the microcapsule shell and the sudden release of the PCM core. This spike was



Table III. Main Results of the TGA Tests on the Prepared Samples

	T _{1%}	T _{3%}	T _{5%}	
Sample	(°C)	(°C)	(°C)	<i>T</i> _d (°C)
PA12	250.9	372.5	410.9	475.7
PA12-cap20	163.6	219.4	267.1	471.5
PA12-cap40	165.2	204.5	243.7	471.7
PA12-cap50	167.0	201.9	240.0	468.6
PA12-cap60	159.6	186.8	217.4	468.9
PA12-CFL10	263.8	388.0	414.3	481.8
PA12-CFL20	278.8	390.5	424.9	480.3
PA12-CFL30	291.2	396.9	422.8	476.6
PA12-cap20-CFL20	159.0	201.0	240.0	479.0
PA12-cap40-CFL20	161.0	204.6	243.2	476.2
PA12-cap50-CFL20	160.0	195.8	230.5	474.1
PA12-cap60-CFL20	159.9	196.2	231.5	474.0
PA12-CFS10	300.6	398.5	419.2	474.7
PA12-CFS20	311.0	403.0	421.1	471.5
PA12-CFS30	314.5	406.8	425.6	479.2
PA12-cap20-CFS20	171.1	230.2	285.0	474.1
PA12-cap40-CFS20	167.1	208.4	254.1	474.0
PA12-cap50-CFS20	165.5	197.4	235.8	475.0
PA12-cap60-CFS20	164.8	201.4	243.8	477.3
сар	118.4	164.0	241.0	421.2

observed also on the repeated measurement, but it was not observed in any of the PCM-containing composites. This can be due to the fact that the mass loss rate is modified by the presence of the surrounding polymer matrix, which is not yet degraded at the end of the degradation process of the PCM. The other steps observed for the neat microcapsules, between 200 and 420 °C are also observed for the samples containing microcapsules. The mass loss observed in this temperature range is less than what expected considering the nominal capsule weight fraction, but this result is in good agreement with the DSC results, where the phase change enthalpy is less than expected due to some leakage of the PCM during the melt compounding and hot-pressing operations.

The thermal conductivity/diffusivity results of the LFA test are reported in Figure 4(a-c). The thermal diffusivity of the neat PA12 slightly decreases with increasing temperature and varies between 0.16 and 0.14 mm²/s. On the contrary, the specific heat and the thermal conductivity slightly increase with temperature. The thermal conductivity ranges between 0.26 and 0.28 W/mK, which is consistent with the values declared by the producer. The introduction of CFs increases the thermal diffusivity and consequently the thermal conductivity, as expected, which is positive for the overall thermal exchange. For TES applications, a higher thermal conductivity can be beneficial as it reduces the charging/ discharging periods of the PCM. For the samples containing only CFs (PA12-CFL20 and PA12-CFS20), the effect of CFL on the thermal diffusivity is slightly higher than that of CFS, but the thermal conductivity is not significantly different and is ~0.4 W/ mK for both samples. For the samples containing both CFs and microcapsules, the specific heat and the thermal conductivity show a maximum at 40 °C, because the PCM is approaching the melting temperature. This phenomenon has been already observed in our previous study with another PCM-containing system, and in some other works from the literature.^{49,54} This effect is more evident for the samples containing the shorter fibers than for those containing longer ones, as the real PCM content is higher in the case of the CFS-containing samples, which is consistent with the DSC and TGA results. The values of thermal conductivity of the composites are higher also than those of the samples containing only the microcapsules (not reported here for the sake of brevity), due to the positive contribution of the CFs in increasing the thermal diffusivity and conductivity.

Figure 5(a,b) shows the results of the thermal imaging test. Figure 5(a) reports the values of temperature as a function of time during the cooling to room temperature. In the samples containing the PCM, the temperature decreases more slowly than in the case of the neat PA12, and proceeds in a plateau-like fashion, as the heat stored by the microencapsulated paraffin during the heating step in the oven is released as the PCM crystallizes. The effect is much more evident for the sample PA12-cap50-CFS20 than for that containing CFL, as is also visible from the thermal camera pictures after 4 min, reported in Figure 5(b). This is due to the fact that the real PCM content is higher for the CFScontaining samples, and it agrees with the previous results. This test, although simple, gives a clear idea of the potential of these composites in thermal management applications.

Table IV reports the values of VST for the prepared samples. The VST of the PA12 is close to the melting enthalpy for this experimental setup, and it is slightly lowered by the introduction of microcapsules. On the contrary, the introduction of CFs increases the VST from 2 to 5 $^{\circ}$ C, thus improving the thermal stability of the composites.

Rheological Properties

The rheological behavior of the composites was investigated to link the degradation of TES properties of the microcapsules to the shear stresses developed during melt compounding. Since the purpose of the dynamical rheological test was limited to understand this specific point, only some representative compositions were analyzed. The test involved the study of the rheological properties only at low frequency (up to 20 Hz), because this is a good representation of the frequency range the materials are subjected to during processing, and also because the shear viscosity of microfilled composites generally present small differences at high shear rates, where the viscosity almost approaches that of the neat matrix, while larger differences can be detected at lower frequencies, as thoroughly reported in the literature.55-59 The results of the dynamical rheological test are reported in Figures 6 and 7. Figure 6 reports the frequency dependence of the shear viscosity for neat PA12 and some representative composites. The general trends of the viscosity for these composites reflect the well-known behavior of particulate-filled polymers.⁶⁰ The shear viscosity of neat PA12 is not heavily affected by the applied frequency in the investigated frequency range, presenting a Newtonian plateau nearly over the whole frequency interval considered. Upon filler addition, as shown in each panel of Figure 6, the





Figure 4. Results of the LFA test on the prepared samples. (a) Thermal diffusivity; (b) specific heat; (c) thermal conductivity. [Color figure can be viewed at wileyonlinelibrary.com]

viscosity increases more markedly at lower shear stresses and to a lesser degree while approaching the shear thinning region, and the onset of shear thinning is reached at lower frequencies (e.g., PA12-cap20 and PA12-cap40). The shear thinning behavior of molten highly filled polymers is extensively reported in the literature.^{55,60–62} With a further increase in the filler content, the

T (°C)

shear thinning region is further anticipated, and the presence of a yield stress becomes evident at the lowest limit of the considered frequency interval. The yield stress is caused by the interaction between the filler particles and the formation of a filler network. The portion of the curve dominated by the yield stress has a limited extension in frequency, also for the samples with the highest

T (°C)





Figure 5. Results of the thermal camera imaging test on the prepared samples. (a) Surface temperatures as a function of time during the cooling to room temperature. (b) Examples of thermographs at 4 min of (from left to right) PA12, PA12-cap50-CFL20, and PA12-cap50-CFS20. [Color figure can be viewed at wileyonlinelibrary.com]

Table IV. Vicat Softening Temperature (VST) of the Prepared Samples

Sample	VST (°C)
PA12	176.8 ± 0.4
PA12-cap20	174.7 ± 0.3
PA12-cap40	173.9 ± 0.4
PA12-cap50	174.1 ± 1.6
PA12-cap60	175.7 ± 1.3
PA12-CFL10	181.2 ± 0.4
PA12-CFL20	182.2 ± 0.6
PA12-CFL30	183.2 ± 0.4
PA12-cap20-CFL20	179.9 ± 0.7
PA12-cap40-CFL20	179.5 ± 0.4
PA12-cap50-CFL20	180.2 ± 0.7
PA12-cap60-CFL20	180.8 ± 0.6
PA12-CFS10	179.0 ± 0.3
PA12-CFS20	176.9 ± 0.3
PA12-CFS30	179.9 ± 0.3
PA12-cap20-CFS20	177.6 ± 0.3
PA12-cap40-CFS20	176.1 ± 0.6
PA12-cap50-CFS20	176.4 ± 0.3
PA12-cap60-CFS20	177.9 ± 0.6

filler content (PA12-cap50-CFS20), and thus it does not suppress completely the Newtonian region. By a comparison among the three panels of Figure 6, it can be observed that the presence of microcapsules alone brings a significative increase in viscosity only at elevated concentrations (i.e., sample PA12-cap40). Conversely, when fibers and capsules are present together, the increase in viscosity, the rise of the yield stress, and the anticipation of the shear thinning region at lower frequencies are more evident. It is interesting to observe that the viscosity is higher for the samples containing long fibers than for those containing short fibers with the same nominal weight fraction of microcapsules. This is an indication that the CFL produce a higher increase in viscosity also in the melt compounding process, which raises the shear stresses and could damage the capsules, thereby causing paraffin leakage and decreasing the total melting enthalpy. This is in good agreement with the DSC results (see Thermal Properties section), in which the total and relative phase change enthalpy of the composites containing short fibers is higher than that of the CFL-containing samples. This increase in viscosity brought by the CFL with respect to CFS might not seem enough to justify such discrepancies in the DSC results. It should be considered, though, that the samples subjected to the rheological test have been prepared through melt compounding and hot pressing, and thus the fiber length could be inferior than the initial one (see also Mechanical Properties section). As the viscosity generally increases with the fiber aspect ratio,⁵⁵ it is reasonable to





Figure 6. Values of viscosity as a function of the frequency for some representative compositions. [Color figure can be viewed at wileyonlinelibrary.com]

hypothesize that the shear stresses in the melt compounder are higher at the beginning of the compounding stage, thus causing an even higher microcapsule damage.

It can be also interesting to observe the trends of the shear storage modulus (G'), loss modulus (G''), and loss factor ($tan\delta$) as a function of frequency for the prepared materials (Figure 7). Only the results of the most promising compositions from the TES point of view, that is, the composites with CFS, are presented. As expected, the filler addition considerably modifies the viscoelastic properties of PA12. The presence of fillers causes an increase in G' and G'', and this increase is more marked at low frequencies. On the contrary, the values of $tan\delta$ decrease with an increase in the filler content, and the peak of $tan\delta$ shifts to higher frequencies. The peak of $tan\delta$ can be associated to the breakdown of the filler network, and thus the shift of the peak to higher frequencies can be linked to a stronger interparticle interaction.⁶³

Mechanical Properties

The results of the mechanical test are shown in Figure 8(a–c), which report the elastic modulus (*E*), the maximum stress (σ_{MAX}), and the strain at break (ε_b) as a function of the capsule volume fraction.

It can be observed that the elastic modulus [Figure 8(a)] of the neat PA12 is 1.20 ± 0.07 GPa, and it decreases with an increase of the PCM content, down to 0.59 ± 0.07 GPa for the sample PA12-cap60. The introduction of a reinforcing agent such as the CFs, as expected, increases the elastic modulus. This effect is more evident for the CFL than for the CFS, which is due to the higher load transfer length and therefore a higher stiffening and reinforcing capability, as widely reported in the literature.^{10,64} Also in the samples containing CFs, the Young's modulus decreases with an increase in the content of microcapsules. Similar considerations are also valid for the values of σ_{MAX} , [Figure 8(b)], which decrease with an increase in the PCM content and increase with the addition of CFs. Once again, the CFL is more effective in enhancing the mechanical strength of these composites. Lastly, the addition of microcapsules causes a strong decrease in the strain at break [-Figure 8(c)] and brings to an embrittlement of the material, and this happens already with a capsule weight fraction as low as 20%, while the further decrease for higher capsule loadings is almost negligible. This effect, already observed in our previous work,49 could be due to the poor mechanical properties of the microcapsules or to the not optimal adhesion between the matrix and the capsules. Also the presence of CFs, as expected, decreases the ductility of the composites, and also in this case the measured $\varepsilon_{\rm b}$ is not heavily affected by the capsule content.

The Halpin–Tsai model is a useful tool to predict the stiffness of a composite reinforced with discontinuous fibers.^{65,66} The analytical model allows the calculation of the longitudinal and transversal moduli (E_L , E_C), assuming that the fibers are aligned in the L direction, and with a modified mixture rule it is possible to determine the modulus for a random fiber 2D or 3D orientation. In the present work, for each composition, E_L and E_C were determined through eqs. (2) and (3), respectively, as:

$$E_L = E_m \frac{1 + \frac{l}{r} \eta_L v_f}{1 - \eta_L v_f} \tag{2}$$

$$E_T = E_m \frac{1 + 2\eta_T \nu_f}{1 - \eta_T \nu_f} \tag{3}$$

where E_m is the modulus of the matrix, measured on the neat PA12 and the samples PA12-capx, ν_f is the fiber volume fraction, and η_L and η_T were determined through eqs. (4) and (5), respectively, as:

$$\eta_L = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_f} + \frac{1}{r}} \tag{4}$$

$$\eta_T = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + 2} \tag{5}$$

where E_f is the nominal fiber modulus (242 GPa), and *l* and *r* are the fiber average length and radius, respectively. Finally, E_C could be calculated through eq. (6), as:

$$E_C = aE_L + (1-a)E_T \tag{6}$$

where a = 0.375 for a 2D (in-plane) random orientation and 0.185 for a 3D random orientation. In this work, a 3D random orientation was assumed.

The results of the quasistatic tensile test have been modeled with the Halpin–Tsai approach, and the results of the model are compared in Figure 9(a,b) with the experimental data. For the





Figure 7. Shear storage modulus (G'), loss modulus (G''), and loss factor (tan δ) as a function of the frequency for the samples containing CFS. [Color figure can be viewed at wileyonlinelibrary.com]

samples containing the CFL [Figure 9(a)], the use of the nominal fiber length in the model leads to an overestimation of the elastic modulus. This can be explained by considering that, during the melt compounding process, the fibers are subjected to shear stresses that cause fiber breakage and reduction of the average length. To verify this hypothesis, small pieces of CFL composites were dissolved in concentrated formic acid, the fibers were recovered, and their length was measured with an optical microscope. The measured average length was 0.4 mm for the sample



Figure 8. Results of the quasi-static tensile test as a function of the volume fraction of the capsules. (a) Elastic modulus (*E*); (b) maximum stress (σ_{MAX}); and (c) strain at break (ε_b). [Color figure can be viewed at wileyonli nelibrary.com]

PA12-CFL20 and 0.3 mm for the samples containing also the microcapsules, which highlights that the shear stresses to which the fibers are subjected increase with microcapsule addition and is also compatible with the increases in viscosity presented before (see Rheological Properties section). The experimental values of fiber length were used in the Halpin–Tsai model and the results are reported in Figure 9(a). It is evident that the model fits the experimental data more precisely, even though the data are slightly underestimated. This could be due to the fact that the





Figure 9. Results of the Halpin–Tsai modeling of the tensile test data. (a) CFL-containing samples; (b) CFS-containing samples. [Color figure can be viewed at wileyonlinelibrary.com]

fibers may have some preferential orientation in the plane rather than in the thickness direction, and thus the hypothesis of the 3D random orientation may not be fully verified. The same fitting was performed on the samples containing CFS and, as observable from Figure 9(b), the model fits the experimental data also with the nominal fiber length. This can be explained by considering that the milled fibers have an initial short fiber length, and further reduction during processing is negligible,⁵⁵ as was also experimentally verified by measuring the residual CFS length in the same way. Therefore, during the production process of thermoplastic, short fiber composites, is extremely important to evaluate the effect of viscosity on the residual fiber length.

CONCLUSIONS

This work concerned the preparation and characterization of novel multifunctional thermoplastic composites with TES capability. A PA12 matrix was combined with a commercial microencapsulated paraffin and CFs of different lengths (chopped/CFL and milled/CFS), in various weight fractions, and the obtained composites were thoroughly characterized. SEM micrographs highlighted a good dispersion of capsules, CFL and CFS, and a rather good adhesion was detected between the fillers and the matrix. DSC tests allowed the measurement of the phase change temperatures and enthalpies of the PCM; the temperatures were not affected by the composition, while the enthalpy values increase with the PCM weight fraction. A relative phase change enthalpy was calculated by normalizing the measured enthalpy to the expected enthalpy calculated by considering the nominal PCM weight fraction. In the composites, it was observed that the relative enthalpy was always below 100%, decreased with an increase of the PCM content and it was lower for the CFLcontaining composites than for those containing CFS. This was attributed to the increasing viscosity and shear stresses during the melt compounding step, which caused capsule damage and paraffin leakage. To verify this hypothesis, dynamic shear measurements were performed, which evidenced a considerable increase in viscosity with an increase in the filler content and, as expected, a higher impact of CFL in changing the rheological properties. TGA tests showed that the CFs increased the thermal stability of the composites, while the degradation temperature decreases with an increase of the microcapsules, as they are less thermally stable than PA12. The presence of CFs also gave a positive contribution in increasing the thermal diffusivity and conductivity of the composites, as shown by the LFA measurements, thus improving the overall thermal exchange. LFA also evidenced an increase of specific heat and thermal conductivity in correspondence of the initial steps of the phase change, as well documented in the literature. Thermal imaging tests evidenced a slower cooling for the samples containing PCM, and once again the CFS-containing samples outperformed those with CFL, due to the higher real PCM content. Finally, quasi-static tensile tests highlighted a decrease in mechanical properties upon PCM addition, while the presence of CF positively contributed to increase the elastic modulus. As expected, the experimental data and the Halpin-Tsai modeling evidenced a higher effect of CFL, due to the higher aspect ratio, even though the residual fiber length was much lower than the initial one. This work contributed to investigate the concept of multifunctional structural TES composites. Future work will be devoted to optimizing the processing parameters to reduce the capsule damage, as well as to considering other types of microcapsules with a stronger shell, that can sustain the shear stresses developed during processing.

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