Manufacturing of nano-enhanced shape stabilized phase change materials with montmorillonite by Banbury oval rotor mixer for buildings applications

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Abstract

The use of adequate thermal energy storage (TES) systems has shown the potential to increase energy efficiency in many fields, such as the building sector. Shape-stabilized phase change materials (SS-PCMs) have attracted attention to address one of the key barriers of phase change materials (PCMs), the leakage during the liquid state, that nowadays limits its applicability. However, SS-PCMs still have drawbacks to overcome, such as poor fire reaction and thermal stability. In the present study, polymeric SS-PCMs are nano-enhanced with layered silicates to overcome these drawbacks. The new shape-stabilized nano-enhanced phase change material (SS-NEPCM) is based on ethylene propylene diene monomer (EPDM) as a polymeric matrix, palmitic acid (PA) as PCM and montmorillonite (MMT) as the layered silicate. An innovative method based on a Banbury mixer was used to prepare it, which is an industrially scalable fabrication method. To evaluate the effect of each component, eight different formulations were prepared: pure EPDM, EPDM with MMT additions (1 wt.%, 3 wt.% and 5 wt.%), EPDM with PA additions (5 wt.% and 10 wt.%) and EPDM with MMT (3 wt.%) and PA additions (5 wt.% and 10 wt.%). The composite materials obtained were not degraded by processing as FT-IR results show. The results obtained by X-ray diffraction showed that an ordered intercalated morphology is formed between EPDM chains and MMT. Thermogravimetric experimental results revealed an increase in the thermal stability of SS-NEPCM as a result of the barrier effect provided by MMT. Moreover, SS-NEPCM fire resistance was improved with a great reduction or avoidance of the dripping phenomenon.

Keywords*: Thermal Energy Storage (TES); Shape-stabilized phase change materials (SS-PCM); shape-stabilized nano-enhanced phase change material (SS-NEPCM); Phase change material (PCM); Montmorillonite (MMT); Polymer layered silicate (PLS); Nanocomposite*

1   Introduction

According to the International Energy Agency [1], the world energy consumption, which is the total energy produced and used by the entire human civilization, grew by 2.3% in 2019. In the current energy scenario, all possible projections foretell that this trend will be maintained in the following decades. On top of that, the energy demand is mainly satisfied by non-renewable energies; renewable energy sources only covered one-quarter of 2018's global energy demand growth [2]. The building sector has one of the greatest decarbonisation potentials, particularly in Europe heating, ventilating and air conditioning (HVAC) services represent a remarkable 50% of the total buildings energy consumption [3]. In this respect, thermal energy storage (TES) is considered a cross-cutting technology [4] that can increase energy system flexibility and facilitate renewable energy implementation. Thermal energy storage, and phase change materials (PCMs) in particular, can decrease HVAC energy consumption in buildings. PCMs enable the storage of a large amount of heat in a short temperature range by means of latent heat. Fatty acids show great properties to be used as PCM, such as congruent melting, high heat capacity, low vapour pressure, non-toxicity, low cost and small volume change [5]. Despite these great advantages, fatty acids have a low flash point and do not show good fire reactivity [6].

One of the main drawbacks of PCM technology that usually restricts its application is the management of the PCM in the liquid state. In this regard, researchers have followed different approaches, such as microencapsulation or PCM stabilization. Shape-stabilization of phase change materials (SS-PCMs) can avoid this issue containing the liquid PCM in a matrix. Materials with very different chemical natures can be used as matrices, such as inorganic cementitious materials [7] and carbon-based materials including nanoscale materials [8]. The use of polymer as matrix still has problems to be addressed, such as low thermal stability, poor mechanical properties, slight leakage over cycling, and flammability [8].

Nanocomposite materials, based on polymer layered silicate (PLS), could have the potential to overcome several latent heat storage challenges, such as the polymeric SS-PCM leakage, thermal stability and fire reactivity. The fundamental idea of dispersing a layered silicate, also known as phyllosilicate or clay, within a polymer is to obtain a polymeric matrix with homogeneously dispersed inorganic plates with a nanoscale thickness. The aspect ratio, the chemical composition and the dispersion degree of the clay considerably affect the final properties of the nanocomposite. The preferred structure is exfoliated since the efficiency of the reinforcing agent is proportional to its degree of dispersion [9]. Thus, the modification of the

clay is required to obtain the desired exfoliation of the clay layers in the polymer matrix. Even with the low content of reinforcing material, layered silicates can provide key properties to polymeric SS-PCM, such as higher thermal stability, and enhanced mechanical and barrier properties [9]. In addition, in thermoplastics even modified with flame retardant additives, dripping of the flaming melt is an issue [10]. The nanostructures formed by the clays acting as a barrier have the potential to address this dripping phenomenon. Nonetheless, up to now, only two studies have been carried out regarding SS-PCM nano-enhanced by layered silicates.

Cai et al. [11] prepared a nano-enhanced SS-PCM based on high-density polyethylene/ethylene-vinyl acetate (HDPE/EVA) as a matrix, paraffin as a PCM, organophilic montmorillonite and an intumescent flame retardant. The authors prepared organophilic montmorillonite by cationic exchange of natural counter ions with hexadecyl trimethyl ammonium bromide (C16). The X-ray analysis and transmission electron microscopy confirmed that an exfoliated nanostructure was achieved. The authors also demonstrated that the adequate dispersion of the PCM within the three-dimensional polymer network prevented leakage [12]. A similar work published by these authors [13], studied magnesium hydroxide and microencapsulated red phosphorus instead of intumescent flame retardant, which lead to improvements in terms of thermal and flammability performances. Such improvements are the result of the synergistic effect between these flame-retardant additives and MMT.

In the present work, a shape-stabilized nano-enhanced phase change material (SS-NEPCM) based on layered silicates is developed with an emphasis on industrially scalable methods. A Banbury mixer was used for the preparation, it is one of the most used technologies for rubber mastication and mixing. The nanocomposite material is composed of ethylene propylene diene rubber (EPDM) as a polymeric matrix, a palmitic fatty acid PCM and montmorillonite as the layered silicate. EPDM presents good crack resistance and weather resistance, which make it an ideal material for several building applications, such as membrane or coating for roofs and components for the HVAC system. The novelty of the work relies on two aspects the preparation method used, and the materials involved. The main objectives of this study are to develop a completely new type of SS-NEPCM based on PLS with an industrially scalable method and carry out an exhaustive characterization to understand properly the interactions and synergies between the polymeric matrix, the PCM and the layered silicates.

2   Experimental Procedure

2.1   Materials

The SS-NEPCMs are composed of three main components: a polymer, an organic phase change material and layered silicates. The polymer, ethylene propylene diene monomer (EPDM) rubber, acts as a matrix embedding the phase change material and the nanostructures. The EPDM rubber (VistalonTM 2504) was provided by ExxonMobil, which is an amorphous terpolymer with low ethylene content (57.5 wt.%) and ethylidene norbornene (4.7 wt.%). Palmitic acid, $CH_3(CH_2)14COOH$ was purchased from Merck with ≥99% of purity. Palmitic acid has a melting point of 60.45 ± 0.14 ºC and latent heat of 221.42 J/g ± 1.65 J/g [14]. The layered silicate used was montmorillonite (MMT), trade name Nanomer® I.44P, provided by Sigma-Aldrich, which the mean particle size is 14-18 μm provided by the product specifications. It contains 35-45 wt.% dimethyl dialkyl (C14-C18) amine as a surface modifying agent. The basal distance of silicate layers (d001) is 24-26 Å.

2.2   Sample preparation

In this study, 600 g of each formulation were prepared. EPDM was added to a laboratory-scale Banbury oval rotor mixer from Werner & Pfleiderer Bakery Technologies and then additives were weighted and added according to the established formulations (see Table 1).

Thus, the mixtures of EPDM and either MMT or PA are heated and mixed inside Banbury. Afterwards, the resulting low viscosity material was rolled using a hot rolling mill (80 ºC), and 0,5 cm thick sheets were obtained. MMT was added first in the formulations that contained both components (i.e., MMT and PA) since better mixing results were obtained using this procedure. Table 1 shows the prepared formulations and the expected latent heat storage capacity. It was estimated using the rule of mixtures and taking 221.42 J/g as the PA latent heat.

Table 1. EPDM-based formulations under study.

Sample name	EPDM (wt.%)	Montmorillonite (wt.%)	Palmitic acid (wt.%)
EPDM	100	---	---
EPDM+1%MMT	99	1	---
EPDM+3%MMT	97	3	---
EPDM+5%MMT	95	5	---
EPDM+5%PA	95	---	5
EPDM+10%PA	90	---	10
EPDM+10%PA+3%MMT	87	3	10
EPDM+5%PA+3%MMT	92	3	5

2.3.Experimental Characterization

X-ray powder diffraction (XRD) was used to determine the dispersion state of silicates within the polymer. Measurements were carried out using a PANalytical X'Pert PRO MPD θ/θ powder diffractometer of 240 mm of a radius. Cu Kα radiation (λ= 1.5418 Å), a voltage of 45 kV and a tube current of 40 mA were used. The measurements were obtained in continuous scan mode and the 2θ range from 1° to 40° with a step size of 0.026º 2θ and a measuring time of 300 seconds per step.

To study the thermal stability of the materials thermogravimetric analyses (TGA) were carried out with a TA Instrument (SDTQ600, New Castle, Delaware, USA). The TGA was performed under 50 mL/min air flow. The heating rate used was 10 °C/min from 50 ℃ to 600 °C. Opened 100 µL alumina crucibles were filled with around 12 mg of sample.

Differential scanning calorimetry (DSC) analysis with DSC 822e from Mettler Toledo, was used to study the thermophysical behaviour. The DSC was performed under a N_2 flux of 50 mL/min, with a heating rate of 10 ℃/min from 20 ℃ to 90 ℃. 40 µL aluminium closed crucibles with around 8 mg of sample were used. The cooling process of these materials is not studied based on previous experiences [15-16].

Changes in the chemical functional groups may be produced by undesired chemical degradation and are evaluated with Fourier-transform infrared (FT-IR). The FTIR analyses were carried out in a Spectrum Two™ from Perkin Elmer (Waltham, Massachusetts, USA),

coupled with attenuated total reflectance (ATR). It was optimized for a wavenumber range between 4000 cm^{-1} and 500 cm^{-1}. The data recorded for each analysis is the mean of four infrared scans (Spectrum 10™ software).

Fire reactivity is evaluated by two means. In the first place, a radiation test taking into consideration UNE 23721-90 recommendations was performed considering that the material has a thickness higher than 5 mm. Square-shaped samples (90 mm x 90 mm x 10 mm) were exposed to a heat lamp radiating with a heat flux of 3 W/cm^2. When ignition starts radiation is removed and ignition time measured, this procedure is repeated for 5 minutes or until the complete combustion of the material. Moreover, dripping was evaluated taking into consideration UNE 23725-90 standard guidelines. In the second place, limit oxygen index (LOI) was measured following the UNE-EN ISO 4589-2. LOI is the minimum concentration of oxygen that a specimen will support combustion under the criteria defined in the standard. In this test, samples were maintained vertically inside a glass chamber, where O_2 and N_2 flow under a controlled ratio at 23 ºC ± 2 ºC. The top of the sample was ignited under different O_2/N_2 ratios to determine the LOI. A paramagnetic analyser with an accuracy of 0.5%, when the flow velocity is 40 mm/s ± 2 mm/s, was used. For statistical purposes, five specimens with type I shape (90 mm x 9.5 mm x 4 mm), were tested under described conditions.

3   Results

3.1   Dispersion state

The dispersion state studied with XRD is determined by the comparison between the diffraction peak position of the MMT and the MMT inside the polymer. Bragg's law ($n\lambda = 2d \sin \theta$) relates the measured angles of incidence (θ) and interlayer spacing (d), so the shift of a diffraction peak towards a lower value indicates an increase in this interlayer spacing.

Notice that the position of the diffraction peak d001 was found at low angle values and it is related to the extent of the basal spacing. XRD measurements were taken on powdered MMT, EPDM, EPDM+1%MMT, EPDM+3%MMT and EPDM+5%MMT. Hence, the clay basal spacing can be measured, and so the degree of clay dispersion within the polymer determined.

As **Figure 1** shows, EPDM presented a low crystallinity phase, being the main phase amorphous. The basal reflection of MMT located at $2\theta = 3.04°$ (d001) corresponds to an interlayer distance of 2.90 nm. The EPDM+MMT formulations basal diffraction peaks are shifted to lower angle values. It corroborates an increase in the basal spacing (d_{001}) due to the

intercalation of the polymer chains within the silicate layers. The basal spacing of EPDM+1%MMT is 3.85 nm, which represents an inter-gallery distance increase of 0.95 nm, an increase of 32% compared to pure MMT. The basal spacing increase of EPDM+3%MMT and EPDM+5%MMT was 0.85 nm (22%) and 0.54 nm (14%), respectively. Despite basal spacing being increased due to polymer intercalation, these strong peaks indicate that the silicate layers are stacked in crystallographic order inside the EPDM [17]. Additionally, as MMT content increases from 1 wt.% to 5 wt.% the relative intensity of the peak increases and the basal space increase is slightly reduced.

Although the basal distance was slightly increased, the amount of intercalated polymer was not high enough to split completely the layers away from each other. Therefore, the total exfoliation of the nanoclay was not achieved in the case of MMT d_{001}, it is estimated to collapse at around 4.10 nm [18]. Considering the increase in basal spacing, *i.e.,* 1 nm maximum, it is suggested that an intercalated nanocomposite structure was obtained. The polymer chains are inserted into the gallery spaces between the silicate layers, in these nanocomposite materials.
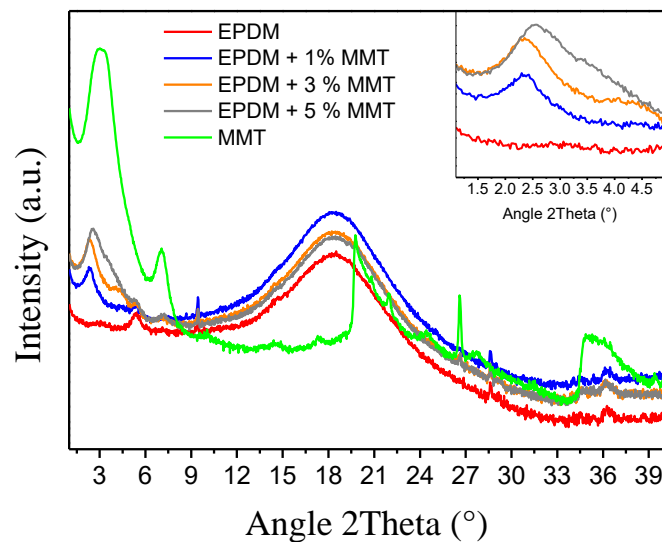

Figure 1. X-ray diffraction patterns of EPDM, MMT, EPDM+1%MMT, EPDM+3%MMT and EPDM+5%MMT.

3.2   *Thermal characterization*

3.2.1   Thermal Stability

Thermal stability is considered of crucial importance when designing a thermal energy storage (TES) system [19]. TGA has been performed to essentially study two aspects; the thermal decomposition of the SS-NEPCM and to ensure that the initial degradation temperature is higher than the PCM working temperature.

The degradation of the materials under study consists of three steps as shown the **Figure** *2*. The first stage starts at 250 ℃ being this temperature the maximum working temperature of those materials under study. This temperature is higher than the maximum working temperature required for building applications. The first stem of thermal degradation is shown from 250 to 325 ℃, is the minor weight loss stage, 10 wt.%, due to the degradation of the low molecular weight substances that the EPDM contains [20]. The second stage, from 325 to 450 ℃, which accounts for 80 wt.% of mass loss is the fastest stage that happens due to the decomposition of the EPDM [20]. Moreover, this stage has overlapped the decomposition of the PA [21]. Finally, the third stage, from 450 to 550 ℃, is similar to all the formulations and ends with a char residue. It is also important to note that the hydrophobic character of EPDM [22] was confirmed since less than 1 wt.% of mass was lost between 50 ℃ and 100 ℃.

The thermal decomposition of the MMT containing samples is improved compared to the pure EPDM, in the second degradation stage. This behaviour can be explained by two synergetic mechanisms provided by the intercalated clays, MMT. First, intercalated silicate layers increase the mean free path inside the bulk polymer slowing down oxygen input and generating volatiles output. This barrier effect decreases the thermo-oxidative degradation kinetics. Second, the thermal resistance effect, which may slow down the sample heating [23,24]. Nevertheless, analysing the MMT containing formulations results in **Figure** *2* (a) it is important to note that the further addition of clay (>5 wt.%) probably will not provide superior thermal performance.

For the PA containing formulations, the thermal decomposition is accelerated compared to pure EPDM, **Figure** *2* (b), the higher the PA content the faster the thermal degradation. In addition, the initial degradation temperature is reduced, so the first degradation step starts 50 ℃ earlier (200 ℃) compared to other formulations. Notice that the EPDM formulation had a weight loss of 1.06 wt.% at 250 ℃ while EPDM+5%PA lost 4.86 wt.%, hence, the 76% of the PA addition was lost at this temperature.

Moreover, in **Figure 2** (a) can be seen the comparison between the PA formulations and SS-NEPCM formulations, where the MMT addition improves the thermal stability in the second degradation step. Therefore, the 3 wt.% MMT content is able to thermally stabilize the polymer but not the PA inside the polymer. The stabilization of the polymer degradation is in accordance with other works, Fitaroni et al. [24] also demonstrated that MMT acts as a stabilizer agent in polypropylene (PP) after this temperature.

All the materials under study are considered stable 20 ℃ above palmitic acid phase change (83 ℃), so no thermal degradation is expected in operation conditions.
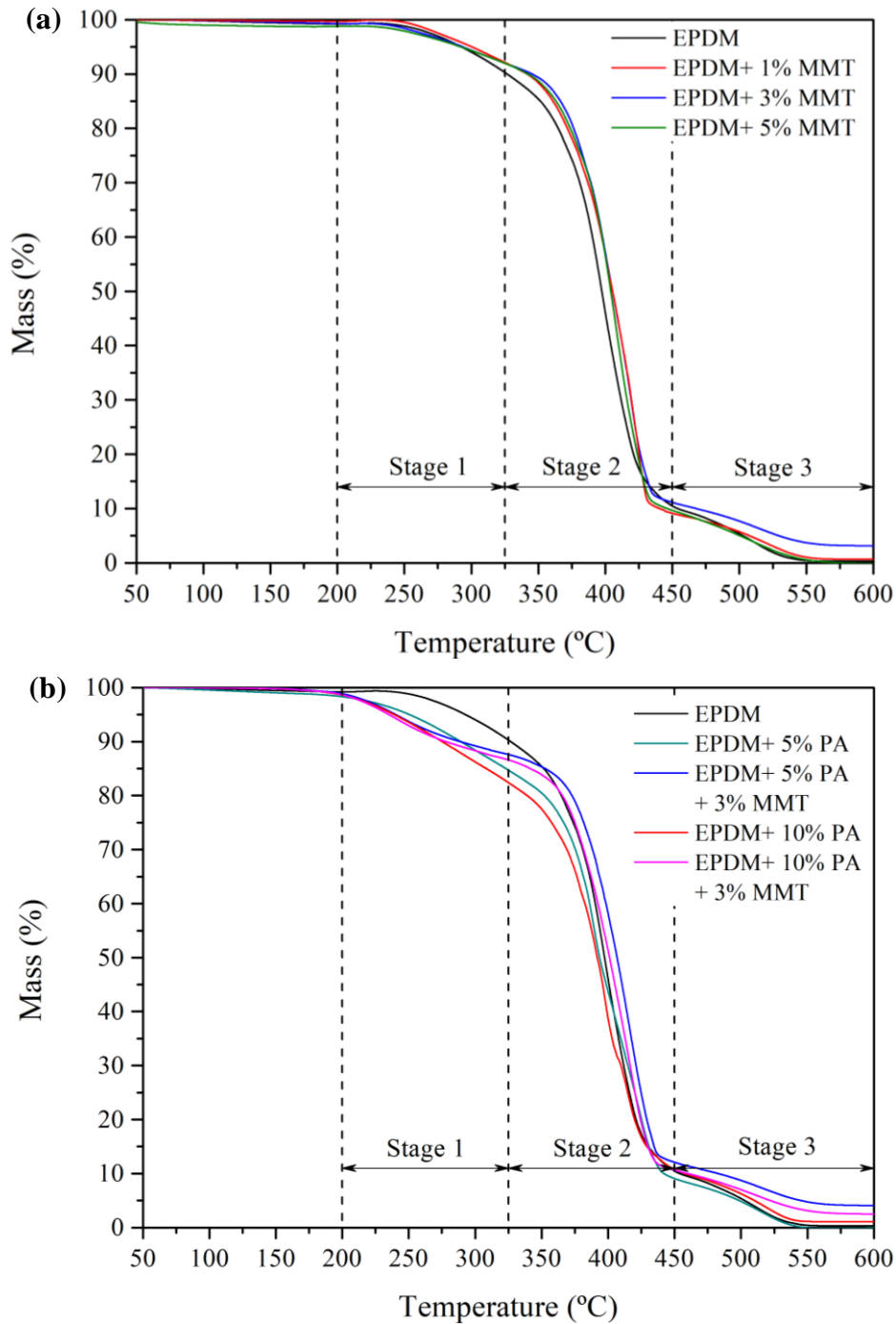

Figure 2. Thermograms, wt.% mass loss as function of temperature, of EPDM and a) EPDM+3MMT, EPDM+10%PA and EPDM+10%PA+3%MMT b) EPDM+3MMT, EPDM+5%PA and EPDM+5%PA+3%MMT.

Notice that, the samples that have MMT content also have a small residue when the TGA experiment ends that correspond to the MMT content. In addition, the differences in this residue content in Figure 2. (b) are due to a sample issue and it is absolutely normal when several samples of composite material are under study.

3.2.2 Thermophysical characterization

The results obtained by the DSC in this study are summarised in Figure 3. The results show that all the materials containing PCM have the characteristic phase change peak response (endothermic, therefore, obtained during the heating process). The quantification values of each melting peak are listed in
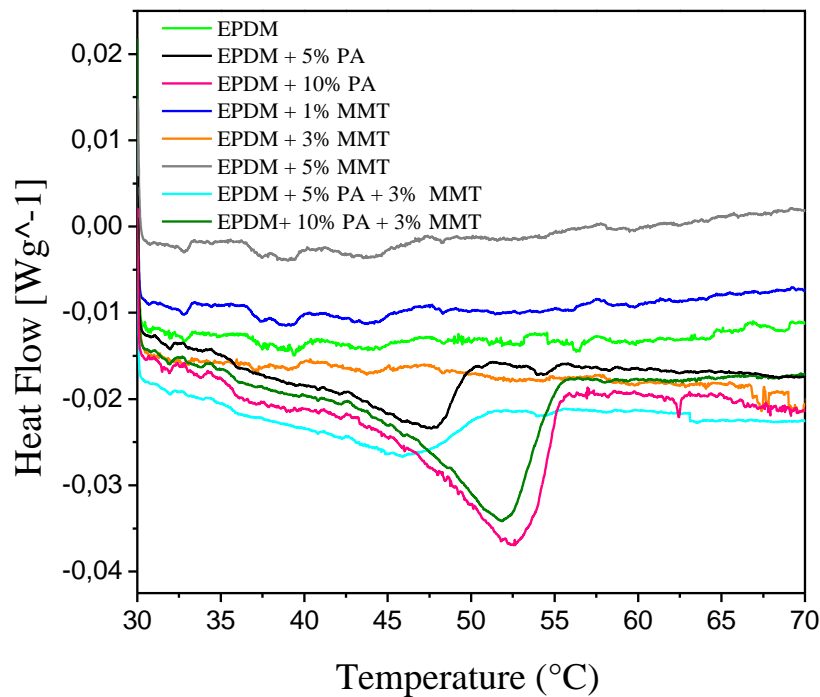

Table 2.

Figure 3. Heat flow vs. temperature of EPDM samples variating their composition with MMT and PA.

The peak temperature of phase change and the melting enthalpy (kJ/kg) are included in this table since it is the reference temperature for organic phase change materials characterization. The results showed that the materials with 10% wt. PCM has around 20 kJ/kg (proportional amount expected from the theoretical value calculated following the mixture law [25], corroborating that there is no loss of PCM during the material preparation. Based on previous

results [26], the peak temperature is slightly higher when the formulations have more PCM. This is due to the interaction between the PCM with the EPDM matrix.

Table 2 Enthalpy of fusion and temperature values.

Sample	Temperature$_{(peak)}$ (° C)	Enthalpy (kJ/kg)
EPDM + 5% PA	47.6	10.1
EPDM + 10% PA	57.6	21.7
EPDM + 5% PA + 3% MMT	45.9	8.2
EPDM + 10% PA + 3% MMT	51.9	21

3.3 Chemical Stability

FT-IR was performed to analyse the chemical stability and to control possible chemical degradation of the polymer during their processing, due to the relatively extreme conditions suffered by the components inside the Banbury (*i.e*., high shear forces and temperature). It can be monitored by the partial or total disappearance of characteristic IR peaks, or the appearance of new peaks associated with, for example, thermo-oxidative processes.

Characteristics IR peaks of EPDM were represented in **Figure 4** (Black Line). These peaks were the characteristic peaks of the three repetitive units that form the employed EPDM (terpolymer of ethylene, propylene and ethylidene norbornene). In the high wavenumber region (4000 to 1500 cm^{-1}), the 2922 cm^{-1} and 2853 cm^{-1} peaks can be associated with C-H stretching. Meanwhile, in the fingerprint region (1500 to 500 cm^{-1}), the band at 1470 cm^{-1} is associated to C-H scissoring [27], 1377 cm^{-1} to C-H methyl rocking [27], 911 cm^{-1} to the vinyl C=C [27,28], and 724 cm^{-1} to long-chain methyl rocking [28].

For comparison purposes, EPDM, EPDM+3%MMT, EPDM+10%PA and EPDM+10%PA+3%MMT samples were represented in **Figure 4.** As it can be seen in **Figure 4**, palmitic acid containing formulations show two characteristic peaks, one sharp peak at 1701

cm^{-1} attributed to the carbonyl C=O stretching mode and a broad band comprised between 3650 cm^{-1} and 3590 cm^{-1} related to OH vibrational modes. In addition, the peaks of -C-O- stretching (ester) can be identified between 1238 cm^{-1} and 1165 cm^{-1} [30].

MMT characteristics bands appeared superimposed with EPDM bands, only in EPDM+3%MMT it can be observed at 1032 cm^{-1} and 521 cm^{-1} [13]. The 1032 cm-1 peak does not appear in the EPDM+3%MMT FT-IR results due to the detection limit of the ATR accessory. As EPDM and EPDM+3%MMT spectra shows, EPDM does not suffer important chemical modifications due to the MMT addition.

Furthermore, peaks associated to degradation processes were not identified and all the characteristic peaks of the compounds used remained after processing, as a result, it can be concluded that no chemical degradation was suffered during processing.
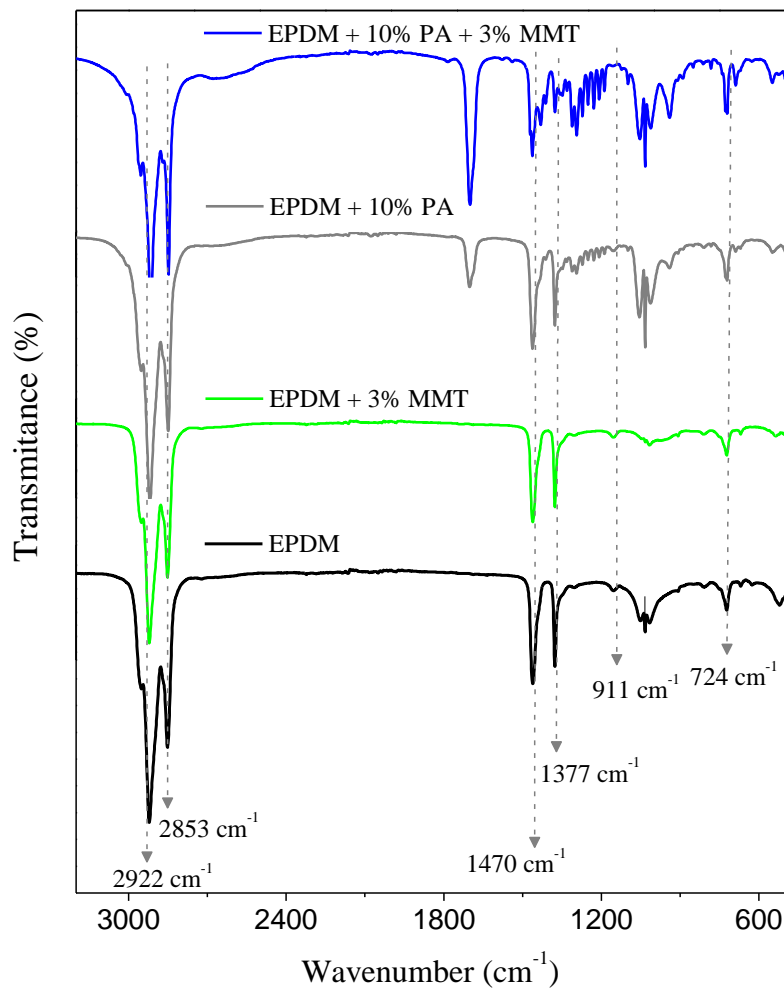

Figure 4. FT-IR spectroscopy results for EPDM, EPDM+3%MMT, EPDM+10%PA and EPDM+10%PA+3%MMT.

3.4 Fire reactivity

Fire is a complex exothermic process that involves combustible material and an oxidant, usually, atmospheric oxygen, accompanied by heat release, light and various reaction products. The chemical nature of polymers, usually long hydrocarbon chains, defines their flammability reaction. In many cases, for safety reasons, plastic flammability is an important issue in several applications such as textile, buildings, transportation and furniture. The fire reaction considers the performance of a material when it is exposed to radiation or a direct flame.

The flammability evaluation of the eight formulations was assessed by an LOI test and a radiation test. **Table 3** presents the LOI and radiation test results of the EPDM based materials.

Table 3 Results of Limit oxygen index (LOI) based on UNE-EN ISO 4589-2, and radiation test based on UNE 23721:90 and UNE 23725:90.

Formulation	LOI [vol.%]	Radiation test	
		Ignition to char time (min:s)	Dripping start time (min:s)
EPDM	19.5 ± 0.5	2:33	3:11
EPDM+1%MMT	20.5 ± 0.5	2:27	4:18
EPDM+3%MMT	20.5 ± 0.5	2:29	n.d.
EPDM+5%MMT	22.0 ± 0.5	2:32	n.d.
EPDM+5%PA	16.5 ± 0.5	1:43	2:01
EPDM+10%PA	16.0 ± 0.5	0:54	1:23
EPDM+10%PA+3%MMT	19.0 ± 0.5	1:07	2:10
EPDM+5%PA+3%MMT	19.0 ± 0.5	1:54	2:46

n.d.: non-dripping performance

The LOI value of pure EPDM was 19.5 vol.% O_2, which agrees with the data reported by other studies such as 19.5 vol.% [31] and 20.5 vol.% [32]. The incorporation of 1 wt.% and 3 wt.% of MMT resulted in an LOI enhancement to 20.5 vol.%, whereas the addition of 5 wt.% exhibited a greater increase up to 22.0 vol.%. The EPDM+5%MMT showed the highest LOI value and the only sample with an LOI value higher than the concentration of oxygen in the air (21 vol.%). Thereby, the LOI value was drastically reduced for the PA formulations from 16.0 vol.% for EPDM+10%PA to 16.5 vol.% for EPDM+5%PA samples, respectively. The PA and MMT combination led to LOI values (19.0 vol.%) close to pure EPDM (19.5 vol.%). Thus, the

3 wt.% MMT that contains these two formulations (i.e., EPDM+10%PA+3%MMT and EPDM+5%PA+3%MMT) is able to counter PA described phenomenon. This is explained taking into account the barrier properties provided by MMT.

PA has a relatively low flashpoint (206 ºC), that is, given an ignition source, the lowest temperature at which vapours of the material will ignite. Therefore, the intercalated MMT inside the polymer matrix is able to effectively reduce oxygen availability and hold the generated vapours by increasing its mean free path. Nevertheless, to meet the requirements of self-extinguishable a material must achieve an LOI value higher than 26 vol.%, and it was not achieved in any formulation under study.

In the radiation tests, all samples were completely burned to char residue in less than three minutes of the experiment. Nonetheless, value information can be retrieved from the fire reaction performance. As it can be seen in Table 3, MMT content slightly reduced the time to final ignition. It is in concordance with a previous work [32], which studied poly (methyl methacrylate) (PMMA)/montmorillonite (MMT) nanocomposite fire retardancy where they stated that ignition times for PMMA/MMT nanocomposite were early than virgin polymer due to the decomposition of MMT clay at a lower temperature.

In contrast to MMT, PA greatly reduced this time by almost 50 s in the EPDM+5%PA formulation and around 100 s in the EPDM+10%PA formulation. The addition of 3 wt.% MMT increased the time required for the ignition to char of the formulations that contain PA (i.e., 5 wt.% and 10 wt.) around 10 s. In contrast to ignition to char time, even a small amount of MMT (e.g., 1 wt.%) improves dripping time, delaying this fire propagation phenomenon by almost 2 min.

The formulations containing 3 wt.% and 5 wt.% MMT do not show dripping during the whole experiment. While EPDM+5%PA and EPDM+10%PA dripped after around 20 seconds of the ignition time, EPDM+5%PA+3%MMT and EPDM+10%PA+3%MMT required around two minutes more to start it. It can also be explained by taking into account the barrier effect provided by the intercalated silicates that acted as a protective wall reducing heat and mass transfer [32]. Additionally, a lower smoke production was observed in formulations that contained MMT compared to the ones formulated without MMT.

As a summary, the results of radiation tests demonstrated that the addition of MMT does not cause a significant improvement of ignition to char time. An increase in the ignition time is desirable. However, the addition of layered silicates is not always achieved. This is because the

mechanism of action of these nanostructures is by a mean free path increase, and so it reduced dripping and delayed flame propagation instead of the ignitability in atmospheric conditions (21 vol.% O_2).

4   Conclusions

In this work, it has been demonstrated that a scalable method based on the Banbury mixer can be used to develop a new SS-NEPCM with a rubber matrix, by the manufacture of eight formulations based on EPDM with different content of MMT, that acts as a nanocomponent enhancer and PA as PCM component. The naib outputs of the present research are listed below:

- The demanding processing conditions did not degrade the composite materials obtained, as shown in the FT-IR results. Moreover, the synergies between EPDM, PA and MMT were also studied, which is outstanding data for researchers in the field since these combinations have not been reported before in the literature.

- An intercalated structure is obtained by the XRD results, unlike full exfoliated structures, in intercalated structures, the silicate layers remain ordered with the polymer chains inserted into the space between.

- MMT could effectively improve thermal stability, although this phenomenon is emphasized at high temperatures. Nevertheless, the initial degradation temperature is higher than the PCM phase change temperature, so the thermal stability is not compromised within the working temperature range.

- The samples containing PA increase their thermal storage capacity in proportion to the amount of PA added. The one containing 10 wt. % can store around 20 kJ/kg of latent heat. Therefore, MMT does not affect the thermal energy storage capacity.

- The LOI value greatly increases by the content of MMT, however in the 5.0 wt.% PA sample the value decreased down to 16.5 vol.%, but with an addition of 3 wt.% MMT the LOI values are almost re-establish. Despite the great enhancements observed, any formulation reached the self-extinguishing grade. In the radiation test, it was demonstrated that MMT does not significantly alter ignition time. In contrast, dripping which is a key propagation mechanism in many building fires was reduced or avoided

In the light of the results of fire reactivity tests, MMT should be considered as a reinforcement when preparing rubber-based SS-NEPCM. Additionally, it presented an acceptable balance between PCM content, fire reactivity and thermal stability.

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