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**POLYMER LAYERED SILICATE NANOCOMPOSITES FOR LATENT
HEAT THERMAL ENERGY STORAGE**

Master's degree thesis

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Polymer layered silicate nanocomposites for latent heat thermal energy storage

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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-PCM) have attracted attention to address one of the key barriers of phase change materials (PCM), the liquid management, that nowadays limits its applicability. However, SS-PCM still have drawbacks to overcome, such as poor mechanical properties, fire reaction and thermal stability. In the present study, polymeric SS-PCM 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 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, that 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.%). As it was investigated by Fourier-transform infrared (FT-IR) spectroscopy, the composite materials obtained were not degraded by processing. 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. Additionally, dynamic mechanical thermal analyses demonstrated that 3 wt.% MMT is an optimum content to enhance thermomechanical properties in the EPDM rubbery region.

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 2018. 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 sector is still high-carbon dependent and penetration of renewables is under expectations. The energy demand is mainly satisfied by non-renewable energies; renewable energy sources only covered one-quarter of the 2018's global energy demand growth [2]. This has drawn an uncertain and unsustainable scenario for future generations given the urgent need of tackling climate change by reducing greenhouse gas emissions and decarbonising the energy sector. Building sector has one of the greatest decarbonization 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 (PCM) in particular, can

decrease HVAC energy consumption in buildings. PCM enable the storage of large amount of heat in a short temperature range by means of the latent heat. There are several materials that involve solid-solid transitions, however, the most studied are solid-liquid since it usually involves latent heat values (J/g). 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]. In spite of these great advantages, fatty acids has 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 liquid state. In this regard, researchers have followed different approaches, such as microencapsulation or PCM stabilization. Shape-stabilization of phase change materials (SS-PCM) can avoid this issue containing the liquid PCM in a matrix. Materials with very different chemical nature can be used as matrix, such as inorganic cementitious materials [7] and carbon-based materials including nanoscale materials [8]. Although the wide variety of materials used, polymers excel in this purpose because of its ability to easily integrate organic PCM in its three-dimensional structure. In this way, polymeric SS-PCM take advantage of polymeric materials

shaping and retention capabilities. However, the use of polymers as matrix still have 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 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 the exfoliated since the efficiency of the reinforcing agent is proportional to its degree of dispersion. However, polymers and clays with distinct hydrophobicity are poorly compatible preventing the formation of exfoliated and intercalated structures [9]. Additionally, great differences in hydrophobicity might generate microcomposite instead of nanocomposite materials. Thus, the modification of the clay is required to obtain the desired exfoliation of the clay layers in the polymer matrix. Even with low content of reinforcing material, layered silicates can provide key properties to polymeric SS-PCM, such as: higher thermal stability, 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]. Polymeric SS-PCM dripping can be specially challenging to solve since it usually contains organic compounds in liquid state in its structure. The nanostructures formed by the clays, and so the barrier effect, 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. 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. Authors also demonstrated that the adequate dispersion of the PCM within the three-dimensional polymer network prevented leakage. One of the phenomena found in this study was the absorption effect of the flame retardant, which would decrease the latent heat of the PCM. A similar work published by these authors [12], 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 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 by ethylene propylene diene monomer (EPDM) as polymeric matrix, a fatty acid PCM and montmorillonite as the layered silicate. EPDM present 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.
- To carry out an exhaustive set of characterization techniques to properly understand the interactions and synergies between the polymeric matrix, the PCM and the layered silicates. It includes thermal stability, chemical stability, fire reactivity, and thermomechanical properties.
- To elucidate the degree of dispersion of the layered silicate within the polymer.

Experimental

Materials

The SS-NEPCM are composed by 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, is an amorphous terpolymer with low ethylene content (57.5 wt.%) and ethylidene norbornene (4.7 wt.%) provides the double bounds in the backbone chain. It has a broad molecular weight distribution and excellent workability. It is intended for moulded mechanical goods such as precision seals, brake parts and gaskets. Palmitic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$, or Hexadecanoic acid, was purchased from Merck with $\geq 99\%$ of purity. Palmitic acid has a melting point of 60.45 ± 0.14 °C and a latent heat of $221.42 \text{ J/g} \pm 1.65 \text{ J/g}$ [13]. The layered silicate used was a montmorillonite (MMT), trade name Nanomer® I.44P, provided by Sigma-Aldrich. It contains 35-45 wt.% dimethyl dialkyl (C14-C18) amine as surface modifying agent. The basal distance of silicate layers (d_{001}), indicated in the technical data sheet and calculated using Bragg's law, is 24-26 Å.

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 the Banbury. Afterwards, the resulting low viscosity material was rolled by using a hot rolling mill (80 °C), and 1 cm thick sheets 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. As it is shown in Table 1, the first six formulations were prepared to study the effect of each component in the EPDM matrix. Moreover, the last two formulations, which are a combination of the MMT and the PA loadings, were prepared with the aim of studying the interaction between MMT and PA. The last column shows 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.

Characterization techniques

X-ray diffraction (XRD) measurements were carried out using a PANalytical X'Pert PRO MPD θ/θ powder diffractometer of 240 millimeters of a radius, in a configuration of convergent beam with a focalizing mirror and with flat samples sandwiched between low absorbing films. Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), voltage of 45 kV and a tube current of 40 mA were used. The diffractogram was obtained in continuous scan mode in the 2θ range from 1° to 40° with a step size of $0.026^\circ 2\theta$ and a measuring time of 300 seconds per step. The powder samples were sandwiched between films of polyimide (kapton) of 7.5 μm thick.

Thermogravimetric analyser (TGA) from TA Instrument (SDTQ600, New Castle, Delaware, USA), was used to study the thermal stability of the materials. The TGA were performed under 50 mL/min air flow to simulate the worst case scenario. The heating rate used was $10^\circ\text{C}/\text{min}$ from 50°C to 600°C . Opened 100 μL alumina crucibles were filled with around 12 mg of sample. The mass sensitivity was 0.1 μg and the temperature sensitivity was 0.001°C .

Fourier-transform infrared (FT-IR) spectroscopy functionality is based on the characteristic wavenumbers at which the molecules vibrate in infrared frequencies. The FT-IR analyses were carried out in a Spectrum TwoTM from Perkin Elmer (Waltham, Massachusetts, USA), coupled with attenuated total reflectance (ATR), which allows obtaining IR spectra directly without any specific sample preparation.

The FT-IR equipment has a spectral resolution of 0.5 cm^{-1} and 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 10TM software).

Dynamic mechanical thermal analyses (DMTA) were performed by using a TA Instruments Q800 analyser (New Castle, Delaware, USA). Prismatic rectangular samples, 35 mm length, 5 mm thick and 15 mm wide, were analysed using the dual cantilever clamp. The frequency sweep mode was set, and the deformation was strain controlled (0.1%). A temperature ramp was applied from -80°C to 60°C at a heating rate of $3^\circ\text{C}/\text{min}$. The stress was applied at two different frequencies, 1 Hz and 10 Hz. In this study, storage modulus is taken as a stiffness indicator and loss modulus (E'') as the glass transition region start. Furthermore, $\tan \delta$ maximum value ($\tan \delta_{\text{max}}$) is taken as the glass transition temperature (T_g) and as an indicator of the damping properties of the material.

In the present study 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. The square shaped samples (90 mm x 90 mm x 10 mm) were exposed to a heat lamp radiating with heat flux of $3 \text{ W}/\text{cm}^2$. When ignition starts radiation is removed and ignition time measured, this procedure is repeated during 5 minutes or until the complete combustion of the material. Moreover, dripping was evaluated taking into consideration UNE 23725-90 standard guidelines. However, it was not possible to follow these two standards strictly. In the second place, limit oxygen index (LOI) is the minimum fraction of O_2 in a mixture of O_2 and N_2 that will maintain a flaming combustion, it was measured following the UNE-EN ISO 4589-2. It is one of the most used methods for assessing flammability of plastics. In this test, samples were maintained vertically inside a glass chamber, where O_2 and N_2 flow under a controlled ratio at $23^\circ\text{C} \pm 2^\circ\text{C}$. 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 $40 \text{ mm}/\text{s} \pm 2 \text{ mm}/\text{s}$, was used. For statistical purposes, a total of five specimens with type I shape (90 mm x 9.5 mm x 4 mm), were tested under described conditions.

Table 1. EPDM based formulations under study.

Sample name	EPDM (wt.%)	Montmorillonite (wt.%)	Palmitic acid (wt.%)	Latent heat (J/g)
EPDM	100	0	0	0
EPDM+1% MMT	99	1	0	0
EPDM+3% MMT	97	3	0	0
EPDM+5% MMT	95	5	0	0
EPDM+5% PA	95	0	5	11.1
EPDM+10% PA	90	0	10	22.1
EPDM+10% PA+3% MMT	87	3	10	22.1
EPDM+5% PA+3% MMT	92	3	5	11.1

Results and discussion

Dispersion state

X-ray diffraction (XRD) technique was used to determine the dispersion state of silicates within the polymer. The dispersion state 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 of this interlayer spacing. Notice that the position of the diffraction peak d_{001} is found at low angle values and it is related to the extent of the basal spacing. X-ray diffraction (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 do not present clear crystallization peaks, hence, its amorphous structure can be confirmed. The basal reflection of MMT located at $2\theta = 3.04^\circ$ (d_{001}) correspond 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 of 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 was increased due to polymer intercalation, these strong peaks indicate that the silicate layers are stacked in crystallographic order inside the EPDM [14]. 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.

In this respect and in view of the results, it is clear that the total exfoliation of the nanoclay was not achieved. Although the basal distance was slightly increased, the amount of intercalated polymer was not high enough to completely split the layers away from each other. In the case of MMT d_{001} , it is estimated to collapse at around 4.10 nm [15]. Considering the increase in basal spacing, i.e. 1 nm maximum, it is suggested that an intercalated nanocomposite structure was obtained. In this nanocomposite materials the polymer chains are inserted into the gallery space between the silicate layers. Nevertheless, in order to reinforce this hypothesis and fully characterize the dispersion state of the silicate layers transmission electron microscopy (TEM) images would be necessary.

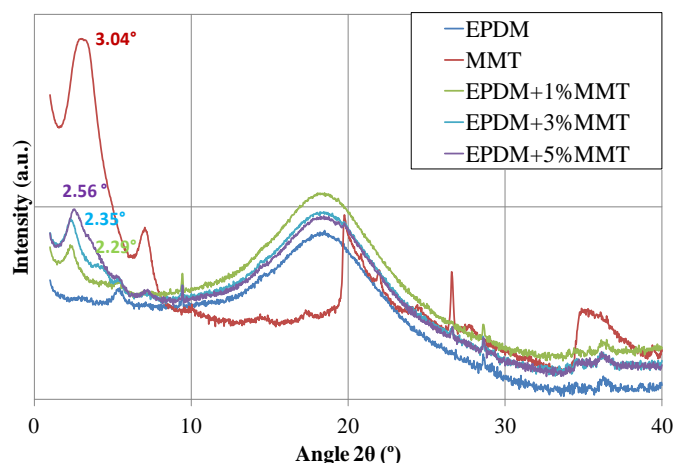


Figure 1. X-ray diffraction patterns of EPDM, MMT, EPDM+1% MMT, EPDM+3% MMT and EPDM+5% MMT.

Thermal stability

Thermal stability is considered of crucial importance when designing a thermal energy storage (TES) system [16]. In this regard, TGA has been performed to essentially study two aspects; the thermal decomposition of the nanocomposite materials and to ensure that initial degradation temperature is higher than the PCM working temperature. In order to ensure the operability of the PCM, the working temperature range is considered 20 °C above and below phase change temperature (i.e. between 43 °C and 83 °C). The degradation of the materials under study consists of three steps. The first step, which accounts for a 10 wt.% of mass loss, starts at around 250 °C and has a minor slope than the second and third steps. The second degradation step that accounts for 80 wt.% of mass loss starts at around 350 °C and is the fastest compared to the other degradation steps. Finally, the third step is similar for all the formulations starting at around 430 °C and concluding with the char residue. It is also important to note that the hydrophobic character of EPDM [17] was confirmed since less than 1 wt.% of mass was lost between 50 °C and 100 °C.

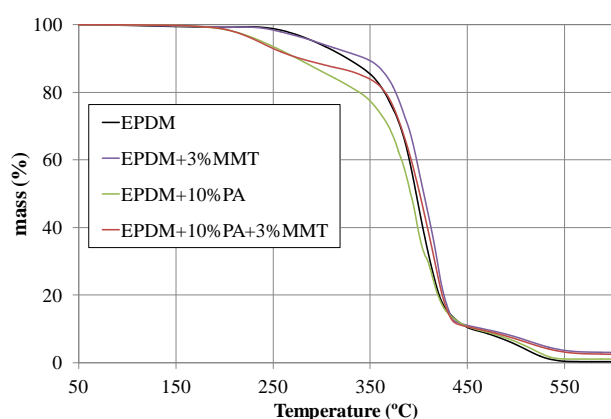
The thermal decomposition of nanocomposites is improved compared to the pure counterpart primarily in the second degradation step, after the 10 wt.% mass loss. This phenomenon can be explained by two synergetic mechanisms provided by the intercalated clays [18,19]. First, intercalated silicate layers increase the mean free path inside the bulk polymer (**Figure 2**) slowing down oxygen input and generated volatiles output. This barrier effect provided by MMT is able to decrease the thermo-oxidative degradation kinetics. In second place, the thermal resistance effect, which may slow down the sample heating. Nevertheless, analysing the MMT containing formulations results (**Supplementary information figure 1**) it is important to note that the further addition of clay (>5 wt.%) probably will not provide a superior thermal performance.



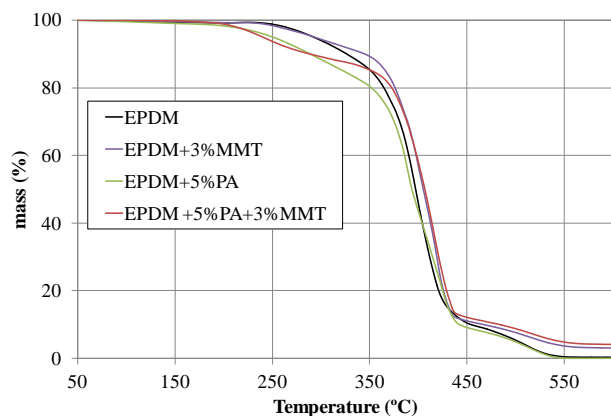
Figure 2. Schematic representation of physical barrier effect provided by the MMT in a polymeric matrix. Extracted from [19].

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

Figure 3 a and **b** shows the comparison of SS-NEPCM with 10 wt.% and 5 wt.% PA content, respectively, with pure EPDM, EPDM+3%MMT and EPDM+PA formulations. As it can be seen in the comparison between the PA formulations and SS-NEPCM formulations, MMT is able improve the thermal stability of the nanocomposite in the second degradation step (>270 °C).



a)



b)

Figure 3. Thermograms, wt.% mass 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.

Therefore, the 3 wt.% MMT content is able to thermally stabilize the polymer but not the PA inside the polymer. It is in accordance to other works, Fitaroni et al. [19] also demonstrated that MMT acts as stabilizer agent in polypropylene (PP) after this temperature. All the materials under study are considered stable 20 °C above palmitic acid phase change (83 °C), so no thermal degradation is expected in operation conditions. Furthermore, it should be made clear that the TGA were performed assuming the worst-case scenario, which is air continuously flowing around the material. In real thermal applications it is difficult to achieve such disadvantageous conditions.

Chemical stability

FT-IR was performed to control the possible chemical degradation of the polymer during processing due to the relatively extreme conditions suffered by the components inside the Banbury (i.e. high shear forces and temperature). It can be closely monitored by the partial or total disappearance of characteristic IR peaks or the appearance of new peaks associated to, for example, thermo-oxidative processes. In order to simplify the FT-IR results examination four characteristic formulations will be shown, however, the conclusions extracted can be extrapolated to the remaining formulations. The rest of IR spectra are provided as additional data in the Supplementary information section. Taking into account that the EPDM used is a terpolymer of ethylene, propylene and ethylidene norbornene, it is expected to found IR characteristic peaks of these three monomers. As an illustrative example several EPDM peaks can be distinguished in **Figure 4 a**. In the region known as the high wavenumber region (4000 to 1500 cm^{-1}), the 2922 cm^{-1} and 2853 cm^{-1} peaks can be associated to 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 [20], 1377 cm^{-1} to C-H methyl rocking [20], 911 cm^{-1} to the vinyl C=C [21], and 724 cm^{-1} to long chain methyl rocking [20]. The MMT spectra is shown in the **Supplementary information figure 3**, as it can be seen only EPDM+5%MMT displayed the characteristic MMT bands at 1032 cm^{-1} and 521 cm^{-1} [12]. EPDM+1%MMT and EPDM+3%MMT IR spectra appeared superimposed.

For comparison purposes, the four formulations plotted are EPDM, EPDM+3%MMT, EPDM+10%PA and EPDM+10%PA+3%MMT. As it can be seen in **Figure 4 b** and **Supplementary information 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} [22].

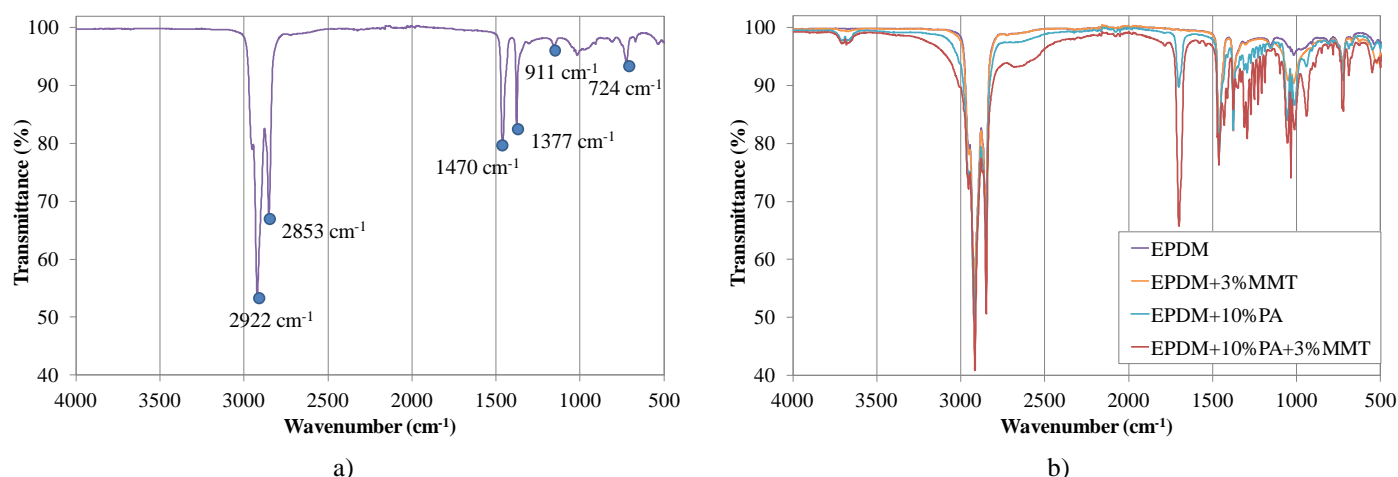


Figure 4. FT-IR spectroscopy results for a) EPDM b) EPDM, EPDM+3%MMT, EPDM+10%PA and EPDM+10%PA+3%MMT.

As EPDM and EPDM+3%MMT spectra shows, their peaks are almost superimposed, 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.

Thermomechanical properties

The results of the DMTA experiments are displayed in [Figure 5](#). The thermomechanical behaviour of all samples is similar since all are mainly constituted by EPDM.

[Figure 5 a](#) and [b](#) plots the storage modulus (E') that is related to the stiffness of the material, as a function of temperature. As it shows, all the curves present two clear plateaus: 1) at low temperatures, between -80 °C and -60 °C, the glassy plateau and 2) at medium temperatures, between -30 °C and 50 °C, the rubbery plateau. Between these two plateaus, there is the glass transition region that contains the glass transition temperature (T_g). On the one hand, comparing with pure EPDM, it can be clearly seen ([Figure 5 a](#)) that PA produces a decrease in the stiffness in the whole temperature range. This leads to the idea that PA seemed to act as a plasticizer increasing polymer free volume. A similar trend was observed during the preparation of EPDM+PA formulations, which showed a facilitated processing. On the other hand, 1 wt.% and 5 wt.% MMT containing formulations ([Figure 5 b](#)) showed a higher storage modulus in the glassy region whereas a slight decrease can be observed in the rubbery region. Meanwhile, The EPDM+3%MMT formulation presented a E' similar to EPDM in the glassy region and a slight increase within the rubbery region. Additionally, EPDM+10%PA+3%MMT formulation showed a higher E' than EPDM+10%PA formulation, but lower than EPDM+3%MMT. EPDM+5%PA+3%MMT showed a E' similar to EPDM at the glassy region, but surprisingly, a higher E' in the rubbery region.

T_g and $\tan \delta$ as function of temperature are shown in [Figure 5 c](#) and [d](#). The MMT and PA addition caused similar effects in T_g . Both components slightly shifted the $\tan \delta$ curve, and so displacing the T_g to lower temperatures. For instance, the EPDM+5%MMT formulation presented a T_g of -49.2 °C, which is 4 °C lower than pure EPDM. The intensity $\tan \delta_{\max}$ is related to the materials damping properties while the peak width is related to the mobility of the macromolecular chain segments [23]. In accordance to the intercalated structure demonstrated by XRD measurements, MMT narrowed the $\tan \delta$ peak reducing chain mobility ([Figure 5 b](#)). The MMT addition also produced an increased in $\tan \delta_{\max}$, which means that these composites will exhibit more damping than pure EPDM. Damping is related to acoustic insulation since high damping materials can dissipate vibrational energy before it can build up and propagate as sound. Likewise, storage modulus results, EPDM+5%PA+3%MMT presented improved results; a slightly higher T_g and a narrower $\tan \delta$ peak in comparison to pure EPDM.

Loss modulus maximum (E''_{\max}), and so the glass transition region start, was measured at -52.2 °C for pure EPDM. Similarly to what was demonstrated for T_g , MMT and PA addition slightly reduced the E''_{\max} temperatures ([Supplementary information figure 5](#) and [Supplementary information figure 6](#)). Restrictions in the main chain mobility are expected to decrease the area under the E'' against temperature curve, this phenomenon was not observed. Likewise, the measurements at 10 Hz showed similar results and the same trends can be identified in E' , E'' and $\tan \delta$.

In summary, the stiffness improvements observed are probably caused by the immobilization of the rubber chains due to the interaction within the MMT layers. However, it only occurs in the glassy region at low temperatures except for the EPDM+5%PA+3%MMT. That could be explained taking into account the limited degree of dispersion achieved by the layered silicates, which restricts the filler-matrix interactions.

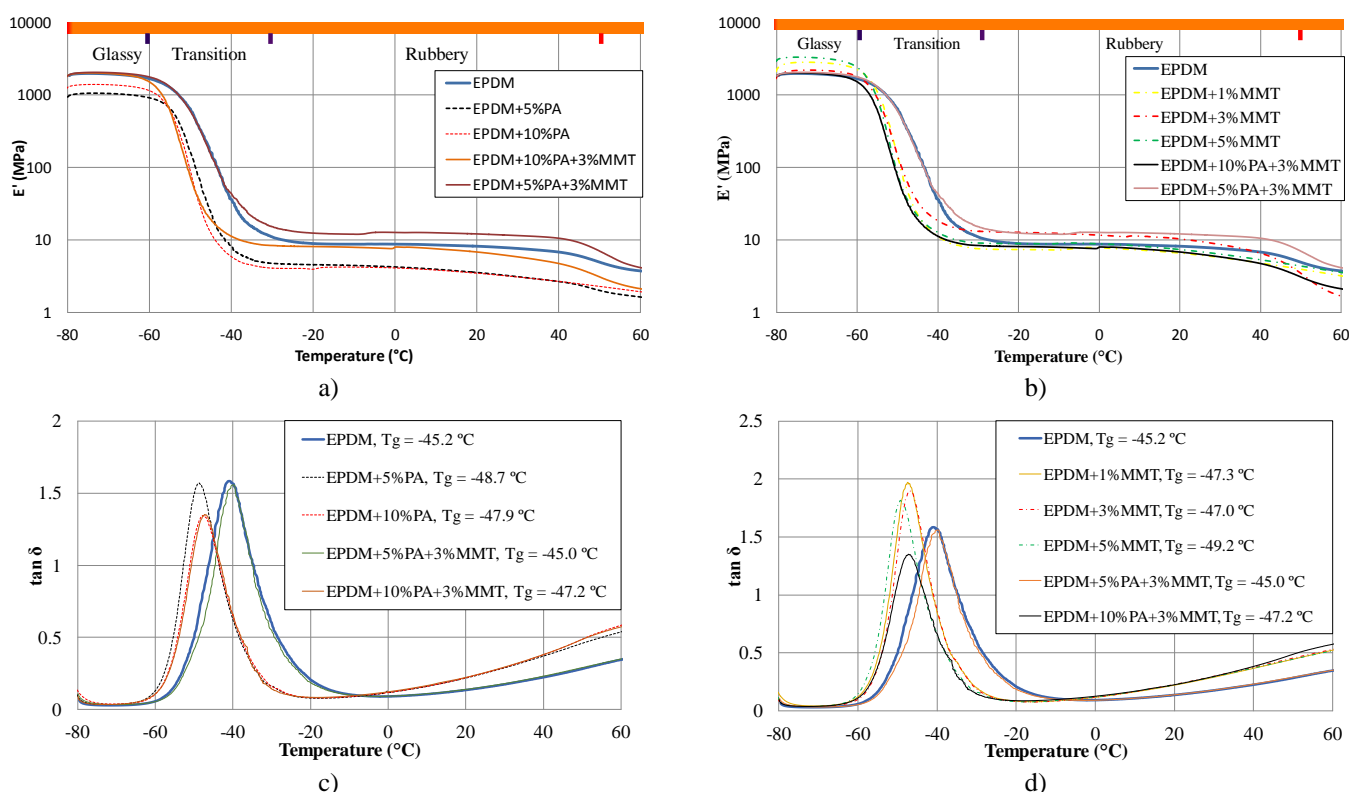


Figure 5. Dynamic mechanical properties measured at 1 Hz: a) Storage modulus vs. Temperature of PA containing formulations b) a) Storage modulus vs. Temperature of MMT containing formulations c) $\tan \delta$ vs. Temperature of PA containing formulations d) $\tan \delta$ vs. Temperature of MMT containing formulations.

Nevertheless, it seems that the 5 wt.% of PA acts as a coupling agent between MMT and EPDM, favouring the filler-matrix interactions since better results were demonstrated for this formulation. In the nanocomposite with 10 wt.% PA (EPDM+10%PA+3%MMT), the phenomenon was not observed, which means that this PA content excessively penalizes thermomechanical properties. Additionally, the 3 wt.% MMT content seems to be an optimum content since it showed a greater thermomechanical performance than 1 wt.% and 5 wt.% in the rubbery region.

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 carbon and hydrogen chains, ultimately defines its flammability. In many cases, for safety reasons, plastics flammability is an important issue in several applications such as textile, building, transportation and furniture. Hereof, there are two main terms that comprehend the study of fire safety. On the one hand, resistance to fire is the ability of a structure, such as a wall, a door, or a beam, to maintain its integrity, stability and isolation capability for a certain amount of time. On the other hand, the fire reactivity considers the behaviour or reaction of a material, when it is exposed to radiation or a direct flame. In this study fire reactivity is studied by LOI and radiation tests.

The flammability evaluation of the eight formulations was assessed by LOI test and a radiation test. **Table 2** presents the LOI and radiation test results of the EPDM based materials.

The LOI value of pure EPDM was 19.5 vol.%, which is in agreement with the data reported by other studies such as 19.5 vol.% [24] and 20.5 vol.% [25]. The incorporation of 1 wt.% and 3 wt.% of MMT resulted in a 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 one with a LOI greater than the concentration of oxygen in the air (21 vol.%). Conversely, for the PA formulations the LOI value was drastically reduced to 16.0 vol.% and 16.5 vol.% for EPDM+10%PA and EPDM+5%PA, 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 contain these two formulations (i.e. EPDM+10%PA+3%MMT and EPDM+5%PA+3%MMT) is able to counter PA described phenomenon. That could be explained taking into account the barrier properties provided by MMT as has been explained in the Thermal stability section. PA has a relatively low flashpoint (206 $^{\circ}\text{C}$), 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.

Table 2. 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 ± 00:01	3:11 ± 00:01
EPDM+1% MMT	20.5 ± 0.5	2:27 ± 00:01	4:18 ± 00:01
EPDM+3% MMT	20.5 ± 0.5	2:29 ± 00:01	no dripping
EPDM+5% MMT	22.0 ± 0.5	2:32 ± 00:01	no dripping
EPDM+5% PA	16.5 ± 0.5	1:43 ± 00:01	2:01 ± 00:01
EPDM+10% PA	16.0 ± 0.5	0:54 ± 00:01	1:23 ± 00:01
EPDM+10% PA+3% MMT	19.0 ± 0.5	1:07 ± 00:01	2:10 ± 00:01
EPDM+5% PA+3% MMT	19.0 ± 0.5	1:54 ± 00:01	2:46 ± 00:01

Nevertheless, to meet the requirements of self-extinguishable a material has to achieve a LOI value greater than 26 vol.%, and it was not achieved in any formulation.

In the radiation tests, all samples completely burned to char residue in less than three minutes of experiment. Nonetheless, value information can be retrieved from the fire reactivity behaviour observed. As it can be seen in [Table 2](#), MMT content slightly reduced time to final ignition. It is correlated with a previous work [26], which studied poly (methyl methacrylate) (PMMA)/montmorillonite (MMT) nanocomposite fire retardancy. In contrast to MMT, PA greatly reduced this time by almost 50 second in the EPDM+5%PA formulation and around 100 second 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 contains PA(i.e. 5 wt.% and 10 wt.) around 10 second. In contrast to ignition to char time, even a small amount of MMT (e.g. 1 wt.%) greatly improved dripping time, delaying this fire propagation phenomenon almost two minutes. The formulations containing 3 wt.% and 5 wt.% MMT do not showed 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 taking into account the barrier effect provided by the intercalated silicates that acted as a protective wall reducing heat and mass transfer [26]. Additionally, a lower smoke production was observed in formulations that contained MMT compared to non-MMT formulations.

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, it is not always achieved with the addition of layered silicates. This is due to the fact that 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.% O₂).

Conclusions

In this work it has been demonstrated that an industrially scalable method based on Banbury mixer can be used to develop a new kind of SS-NEPCM with a rubber matrix. As FT-IR results showed, the demanding processing conditions employed did not degrade the composite materials obtained. Once the production process was validated, the synergies between EPDM, PA and MMT were also studied, which is outstanding data for researchers in the field since this combinations have not been reported before in the literature.

The XRD results showed that an intercalated structure is obtained. Unlike full exfoliated structures, in intercalated structures the silicate layers remain ordered with the polymer chains inserted into the space between. Furthermore, it was observed that as MMT content increases the basal spacing enhancement was reduced.

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

The DMTA results clearly showed two distinct behaviours. On the one hand, upon increasing MMT content an increase in E' is observed in the glassy region. On the other hand, PA containing formulations decreased E' in the whole temperature range, so PA seemed to act as a plasticizer increasing polymer free volume, and so facilitating its processing. It is important to highlight that the thermomechanical improvements provided by 1 wt.% and 5 wt.% MMT are observed only at low temperatures, and therefore outside of the material's temperature range of application. Nevertheless, EPDM+3%MMT showed a greater thermomechanical performance than EPDM+1%MMT and EPDM+5%MMT in the rubbery region.

The MMT content greatly increased LOI value, while only 5.0 wt.% PA decreased this value down to 16.5 vol.%. Nonetheless, 3 wt.% MMT is able to counter the

LOI decrease caused by PA and almost re-establish it. In spite of the great enhancements observed, any formulation reached the self-extinguishing grade. From the radiation test, it was demonstrated that MMT does not significantly alter ignition time. In contrast, dripping that 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.

Moreover, the formulation with 3 wt.% MMT and 5 wt.% PA showed significantly better results in terms of thermomechanical properties compared to the rest. Additionally, it presented an acceptable balance between PCM content, fire reactivity and thermal stability.

In conclusion, this work was focused on the study of a new kind of SS-NEPCM based on a rubber matrix and prepared by an industrial fabrication method. However, given the different nature of the components and the multiple interactions that can arise between them, further studies are required to validate this kind of materials viability. Future work should include the characterization of leakage over thermal cycling, evaluating in this way the possible barrier effect provided by layered silicates. Other important aspects regarding these materials might be studied, such as the effect of the components on the crosslinking chemistry, weathering resistance, sustainability, and other industrially feasible methods such as extrusion.

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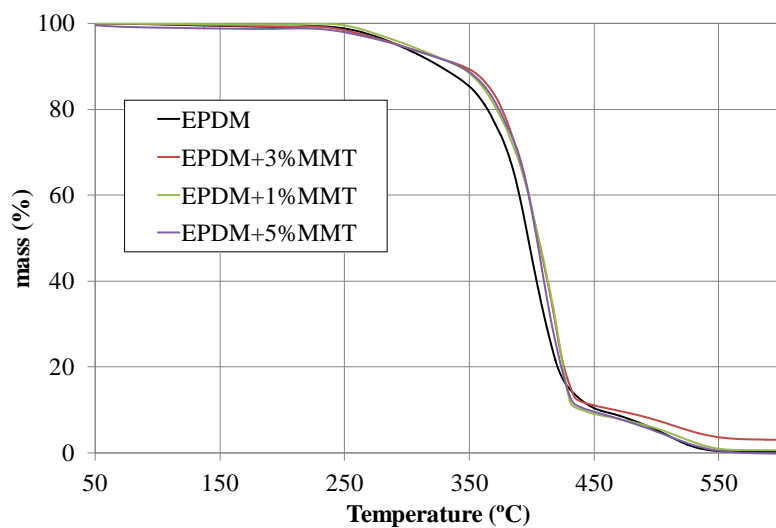
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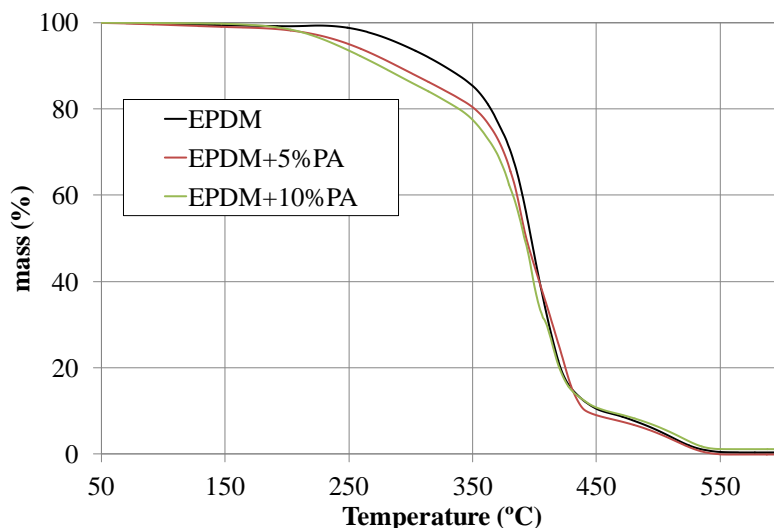
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Supplementary Information

Thermogravimetric analyses (TGA)

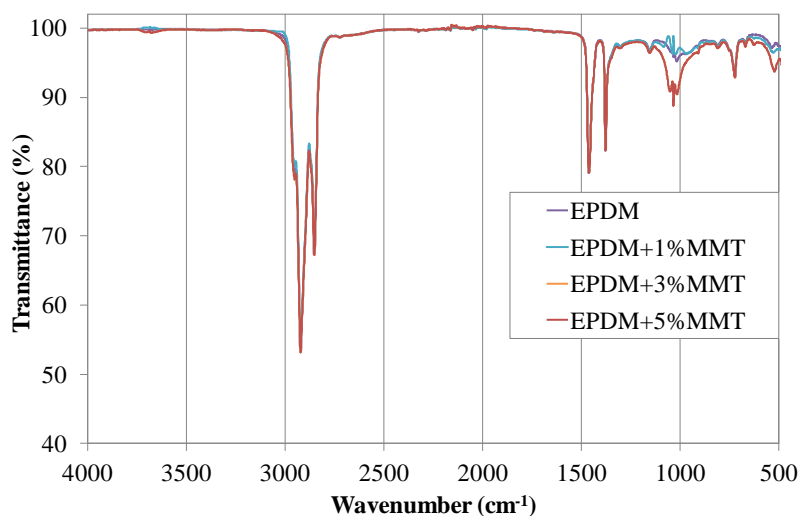


Supplementary information figure 1. Thermograms of EPDM with MMT addition.

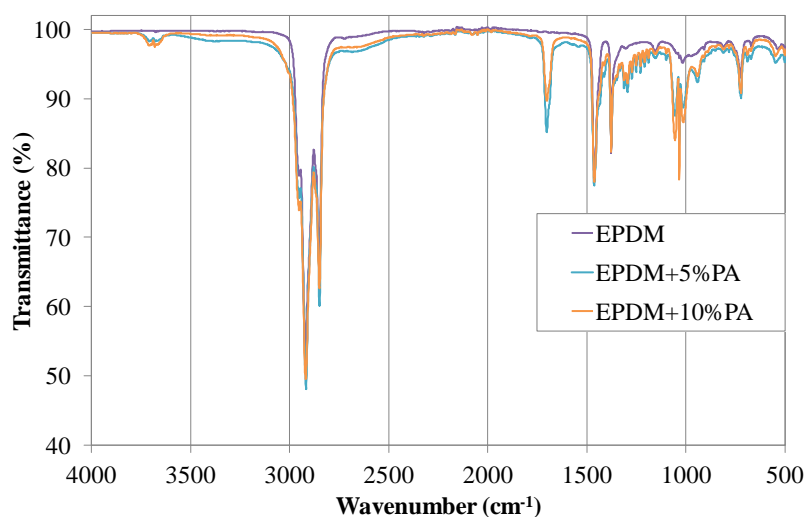


Supplementary information figure 2. Thermograms of EPDM with PA addition.

Fourier-transform infrared (FT-IR) spectroscopy

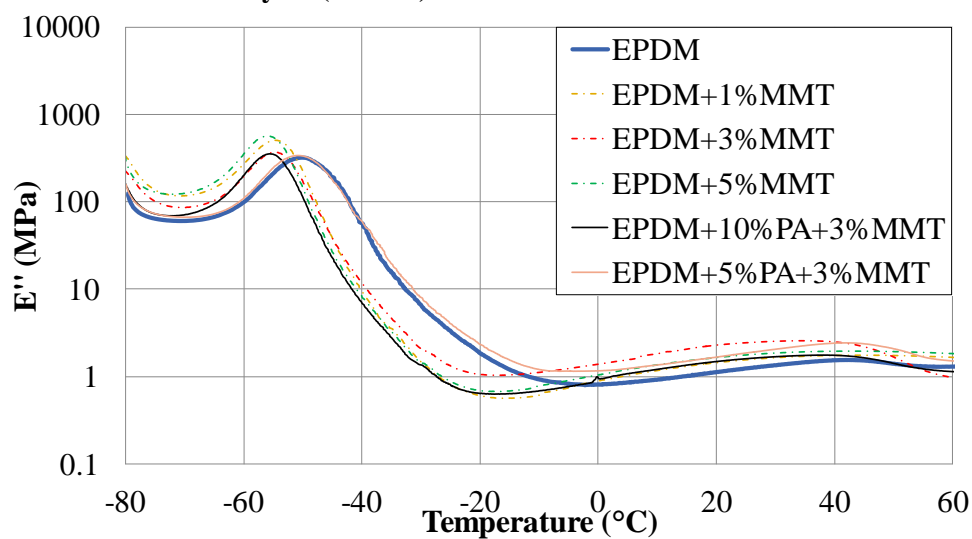


Supplementary information figure 3. IR spectra of EPDM with MMT addition.

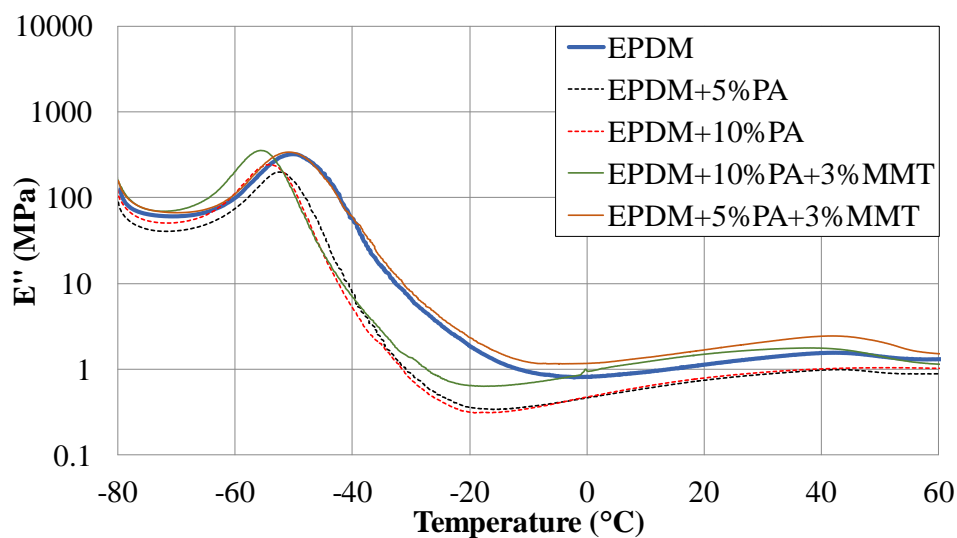


Supplementary information figure 4. IR spectra of EPDM with PA addition.

Dynamic mechanical thermal analyses (DMTA)



Supplementary information figure 5. Loss modulus (E'') vs. Temperature of MMT containing formulations measured at 1 Hz.



Supplementary information figure 6. Loss modulus (E'') vs. Temperature of PA containing formulations measured at 1 Hz.