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ORIGINAL ARTICLE

Foamy phase change materials based on linear low-density polyethylene and paraffin wax blends

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Abstract
Foamy phase-change materials (FPCMs) based on linear low-density polyethylene (LLDPE) blended with 30 wt.% of paraffin wax (W) were successfully prepared for the first time. The advantage of these materials is their double functionality. First, they serve as standard thermal insulators, and second, the paraffin wax acts as a phase change component that absorbs thermal energy (the latent heat) during melting if the temperature increases above its melting point, which ensures better heat protection of buildings, for instance, against overheating. The density of the porous fabricated FPCM was 0.2898 g/cm^3 with pore content 69 vol.% and gel portion achieved 27.5 wt.%. The thermal conductivity of the LLDPE/W foam was 0.09 W/m.K, whereas the thermal conductivity of the neat LLDPE foam prepared under the same conditions was 0.06 W/m.K, which caused a higher porosity of approximately 92 vol.%. The FPCM absorbed or released approximately 22–23 J/g during melting or cooling, respectively, and the material was stable under thermal and mechanical cycling.

Keywords Foams · Phase-change materials · Paraffin · Latent heat

1 Introduction

Approximately 30–40% of the world's energy obtained from fossil fuels is consumed by the building industry, which is responsible for one-third of the globe's greenhouse gas emissions [1]. One possibility of how to reduce energy consumption in buildings is based on effective thermal insulation. Plastic foams, such as polystyrene, polyethylene and polyurethane, are the most commonly used materials for this purpose due to their low thermal conductivity, appropriate specific mechanical properties and low density [2, 3].

Because of their excellent thermal insulation properties and low flammability, polyurethane (PU) foams in particular have been widely used in the field of thermal insulation in building envelopes to save energy.

In recent years, the combination of PU foams and phase-change materials (PCMs), such as paraffin waxes and fatty acids, has attracted increasing attention to realize the joint advantages of thermal insulation and thermal energy storage. It has been found that an appropriate amount of various PCMs or microencapsulated PCMs in a combined product enhances the thermal energy storage capacity [4–12].

Briefly, phase-change materials (PCMs) are substances with a high heat of fusion that are able to store or release thermal energy through melting and solidifying at certain temperatures [13]. The most common PCMs are inorganic salts as polyhydric alcohols, fatty acids, and paraffin waxes [14]. Paraffin waxes are the most promising PCMs due to their favorable characteristics, such as high latent heat of fusion, negligible super-cooling, stability, availability, and relative low price [15]. The melting temperature of these paraffin waxes ranges from 30 to 90 °C, depending on the number of carbons in the wax chains. The specific melting enthalpies of

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these waxes are between 180 and 230 kJ kg^{-1}, resulting in an excellent energy storage density for paraffin waxes [16, 17]. After melting, paraffin waxes have a tendency to leak from the system. For instance, paraffin waxes can be enclosed in containers of various shapes and size [14, 15]. The paraffin waxes can also be fixed in stable forms through encapsulation in a polymeric shell or by blending with suitable polymers [18–23]. Polymer matrices fix the material in a compact shape and suppress leaking after the wax melted. Polyethylene is widely used polymer for blending with paraffin waxes due to their structural and chemical similarity [24, 25]. It enables an incorporation of large amount of wax within polyethylene matrices without significant wax leaking.

PCMs have received growing interest for use in many applications, particularly in the building [26], textile and automotive industries, and as a solar energy storage medium [27]. Paraffin waxes are the most promising PCMs because of their desirable characteristics, such as high latent heat of fusion and a broad range of melting temperatures. Their properties, including melting points ranging from 30 °C to 90 °C and melting enthalpies that lie between 180 and 230 kJ kg^{-1}, indicate that paraffin waxes are excellent energy storage materials [16].

In addition to polyurethane and polystyrene foams, polyolefin, and particularly polyethylene foams, are another type of insulating materials that are traditionally used in a wide range of applications such as construction, packaging, buoyancy, automotive, and medical [28–31].

Despite the fact that the foaming of neat polyethylene is well known, the preparation of foams from polyethylene/wax blends has not been described in the literature until now, and it represents a unique solution patented by our team very recently [32]. On the other hand, polyethylene itself is the most frequently used polymer for blending with paraffin waxes. The blending of polyethylene with paraffin waxes is conducted because their chemical and structural similarity afford a final product that keeps a compact solid state, even after the melting of the wax. This type of material belongs to the category of materials often called shape-stabilized PCMs [17, 23, 33–35].

In this paper, we present the method for the preparation of ***foamy PCMs based on linear low-density polyethylene and paraffin wax blends*** by chemical foaming using selected blowing agents. The materials were cross-linked by organic peroxides before the foaming step to prevent the collapse of the pores. These materials represent a new type of foamy PCMs, which were first described in our patent [32].

These materials primarily serve as standard thermal insulators, and second, paraffin wax acts as a component that absorbs thermal energy during melting if the temperature increases above its melting point, which ensures better heat protection of buildings, for instance, against overheating. Another application of these materials is the designing of special cabinets for the protection of valuable items against overheating (blood, CDs, wine, etc.) in case of an increase in the surrounding temperature, e.g., due to an accidental electricity shut down, etc.

Despite the fact that the heat storage capacity represented by the specific enthalpy of melting is relatively low – approximately 20 J/g – this value is comparable with values for the most common polyurethane-based foams modified by PCMs reported in the literature. The specific enthalpies of melting of PCM components, such as pure n-hexadecane, n-hexaoctane, and myristyl myristate, and/or their encapsulated forms incorporated within polyurethane foams are in the range from 4 to 77 J/g but are mostly from approximately 15 to 20 J/g. Our results are in line with the most common values of the reported enthalpies of melting [36].

2 Experimental

Foams were prepared from LLDPE (Lotrène®Q1018N, QAPCO, Qatar), paraffin wax (Rubitherm, Germany), a blowing agent (Genitron AC2, Schering Polymer Additives, England) and a cross-linking agent (dicumyl peroxide, SIGMA ALDRICH, USA) in a multistep process. At first, all substances (LLDPE/wax = 70/30 *w*/w, 10 wt.% of blowing agent, 1 wt.% of dicumyl peroxide – both relative to the LLDPE/wax mixture) were mixed for 5 min at 140 °C in a Plasticorder Brabender (Germany). Then, the material was hot pressed for 3 min at 140 °C in a cylinder-shaped mold to obtain the required shape, followed by further heating at 140 °C for 13 min to perform cross-linking of the blend. During this process, the blowing agent was decomposed to its volatile components, but high pressure in the press did not allow the release of the blowing agent from the blend before cross-linking, which plays an important role for obtaining a stable final foamy structure. After cooling down to room temperature, the sample was removed from the mold and placed into an oven at 140 °C for 25 min to allow decomposition of the blowing agent (masterbatch consisting of 40 wt.% 1,1′-azobiscarbamide within LDPE), which led to the formation of the foamy material. The route for FPCM preparation is shown in Fig. 1.

Scanning electron microscopy (SEM, Nova NanoSEM 450, FEI, USA) was used for the characterization of sample morphology.

DSC measurements were performed using a Perkin Elmer model DSC 8500 (Perkin Elmer, USA) in a temperature range from 0 °C to 140 °C at a heating rate 10 °C min^{-1} under a nitrogen atmosphere.

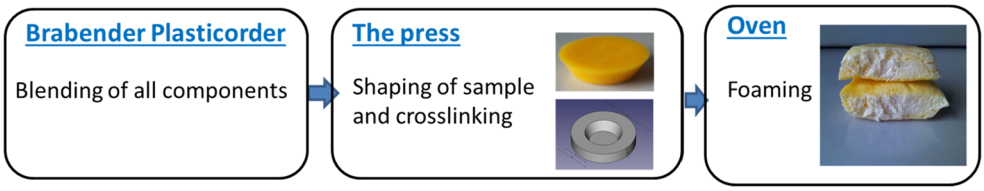

Fig. 1 FPCM preparation

DMA testing in compression mode was performed by an RSA-G2 (TA Instruments, USA). The samples were in the form of a cylinder with an 8 mm diameter and an 8 mm height. The initial preloads for the measurements were established at 0.02 N for 1 min. Then, all measurements were performed in the linear viscoelastic range (LVR) established from the strain dependence of the viscoelastic moduli. The frequency dependence was performed from 10^{-3} Hz to 10^{2} Hz. The temperature sweep was measured at 1 Hz from 0 °C to 60 °C at a heating rate of 3 °C min^{-1}, and 20 cycles of heating and cooling were performed to prove the repeatability of the phase-change phenomenon.

The thermal conductivities of samples were measured by a hot disk thermal analyzer (Hot Disk 2500, Sweden) using the transient place source (TPS) method based on a transient technique. According to this method [37], a disk-shaped TPS sensor is placed between two circular sample pieces. The diameter of sensor is 3 mm. The measurement power ranged from 5 to 15 mW, and the time of the measurement varied between 10 and 40 s. At least three measurements for each sample were performed at 25 ºC with an accuracy within 3%.

The densities of the samples were determined gravimetrically.

The cross-linking efficiency has been evaluated by gravimetric measurements by analyzing of the insoluble part (gel) after a 12 h extraction of the FPCM samples using xylene heated at its boiling temperature.

3 Results and discussion

3.1 SEM analysis

Figure 2a shows relatively good distribution of the formed pores in a hexagonal shape in the neat LLDPE foam with pore sizes from approximately 100 to 200 μm. Figure 2b shows pores within the FPCM. The pore sizes also lie in the range from 100 to 200 μm; however, a less regular structure appeared due to possible melting of paraffin wax within the foam and subsequent coverage of the pores.

3.2 Pore content

The volume portion of the pores was calculated from Eq. (1):

$$\varphi_{pores}(\%) = 1 - \frac{\rho_{foamed}}{\rho_{unfoamed}} x100\% \quad (1)$$

where φ_{pores} is the volume portion of the pores and $\rho_{unfoamed/foamed}$ are the densities of the material before and after foaming, respectively. These values are summarized in Table 1 together with the gel portion that characterizes the degree of cross-linking of the materials. It is seen that the gel portion of cross-linked LLDPE is greater than gel portion of the LLDPE/W blend. This finding is because a proportional amount of peroxide is distributed in both the LLDPE and wax phase, and thus, an effective concentration of peroxide in LLDPE is lower than that in neat LLDPE. On the other hand, the low molecular weight wax is not cross-linked due to its short chains.

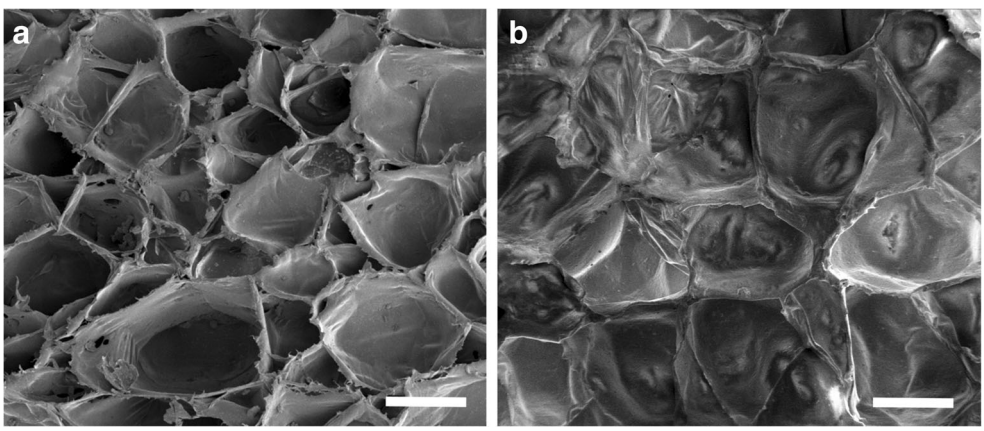

Fig. 2 SEM images of the LLDPE foam (**a**) and FPCM (**b**). The bar is equal to 100 μm

Table 1 Densities of the materials and volume portion of the pores

Sample	Density (g/cm^3)	φ_{pores} (vol.%)	Gel portion (wt.%)
LLDPE	0.9410	–	–
LLDPE/Wax	0.9177	–	–
LLDPE foam	0.0763	92	81.1
LLDPE/Wax foam	0.2898	69	27.5

The blends were cross-linked before blowing to suppress the collapse of the pores. This is a common procedure for the preparation of foamy polyethylene. The volume portion of the pores in the FPCM was 69%, whereas the volume portion of the pores in neat LLDPE was 92%.

3.3 DSC characterization

The DSC measurements were realized in the temperature range from 0 to 140 °C. The most important temperature region for the final PCMs applications is between 10 and 60 °C. The results are summarized in Table 2. Two transitions are observed in this range. The main peak at a temperature of approximately 42 °C is attributed to the solid-liquid transition of the paraffin wax (melting point of crystallites). A minor peak at 18 °C belongs to the solid-solid transition of the paraffin wax. This peak relates to the transition of one crystalline phase into another, as described by Genovese et al. in more details [37].

The FPCM absorbed or released approximately 22–23 J/g during melting or cooling of paraffin wax component, respectively. Twenty heating and cooling cycles were performed during the cyclic variation in temperature from 0 °C to 60 °C, and excellent reproducibility demonstrating the material's stability was shown (Fig. 3). The results indicate that only the differences between the first cycle and all the remaining cycles are identical. This difference is attributed to the thermal history of the sample. Furthermore, no degradation or other

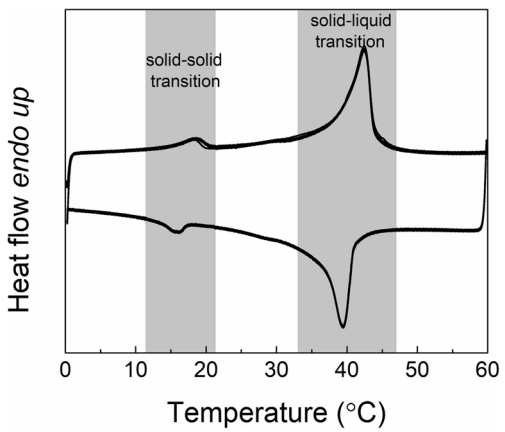

Fig. 3 Heat flux evolution of FPCM during a cyclic variation in temperature from 0 to 60 °C

Table 2 Temperatures for the solid-solid(T_{s-s}) and solid-liquid transitions (T_{s-l}) and the specific enthalpies of the solid-solid($\Delta H_{s-s,}$) and solid-liquid transitions (ΔH_{s-l}), of paraffin wax within FPCM during the cyclic variation in the temperature range from 0 to 60 °C

No. of cycles	Heating				Cooling			
	T_{s-s} °C	ΔH_{s-s} J/g	T_{s-l} °C	ΔH_{s-l} J/g	T_{s-s} °C	ΔH_{s-s} J/g	T_{s-l} °C	ΔH_{s-l} J/g
1	18.2	1.4	42.4	23.0	16.2	−1.2	39.6	−21.7
2	18.7	1.4	42.4	20.9	16.2	−1.3	39.6	−21.4
10	18.7	1.4	42.4	21.2	16.2	−1.3	36.6	−21.8

changes in the DSC curves were observed over the entire twenty cycles of the heating and cooling period.

The DSC measurements performed at higher temperatures up to 140 °C characterize the melting behavior of the LLDPE phase in the FPCM compared to neat LLDPE and foamed LLDPE. These results are summarized in Table 2. The FPCM absorbed or released approximately 22–23 J/g during melting or cooling of paraffin wax component, respectively. Twenty heating and cooling cycles were performed during the cyclic variation in temperature from 0 °C to 60 °C, and excellent reproducibility demonstrating the material's stability was shown.

As it has been previously found, the adding of paraffin wax into polyethylene, as well as crosslinking of polyethylene and polyethylene/paraffin wax blends with organic peroxides, results in theo changes in the melting temperature and specific enthalpy of melting of the polyethylene [38]. The melting and crystallization temperatures, and the specific enthalpies of melting and crystallization of neat LLDPE, foamed LLDPE, and FPCM are summarized in Table 3.

The melting temperature of pure LLDPE was found to be 120.8 °C. In the foamed LLDPE it decreased to 110.7 °C due to the cross-linking by dicumyl peroxide, which causes the creation of defects in the crystalline structure. It results in the formation of smaller crystallites and the lower melting temperature [39]. In the FPCM the melting temperature decreased to 116.1 °C, which is lower than the melting temperature of neat LLDPE, but higher than the melting point of the foamed

Table 3 The parameters obtained from DSC measurements of neat LLDPE, foamed LLDPE, and FPCM. T is temperature, ΔH is specific enthalpy, m – melting, c – crystallization

	Cooling		Heating	
	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
Neat LLDPE	104.9 (0.4)	99.3 (4.5)	120.8 (0.4)	100.3 (2.1)
Foamed LLDPE	96.1 (0.4)	63.4 (0.8)	110.7 (0.1)	65.4 (0.7)
FPCM	100 (0.3)	43.5 (1.5)	116.1 (0.9)	42.8/ 61.1[+] (1.2)

[+] The specific enthalpy of melting related to the LLDPE phase

LLDPE. In this case, the system is more complex. Firstly, the crosslinking by dicumyl peroxide (by any peroxide in general) contributed to the lowering of melting point of LLDPE phase. The degree of crosslinking of LLDPE phase within FPCM wassignificantly lower than the degree of crosslinking of neat LLDPE as shown in Table 1 (the crosslinking density is represented by the gel content), because dicumyl peroxide has been evenly distributed in both the LLDPE and paraffin wax phase, and thus the concentration of dicumyl peroxide in the LLDPE phase has been proportionally lower. This led to the less pronounced decrease in the melting temperature compared to the crosslinked neat LLDPE foam. Secondly, the paraffin wax acted as a plasticizer and therefore also reduced the melting temperature of the LLDPE phase [33]. However, the effect was lower than the effect of crosslinking. The combination of these two effects resulted in the decrease in the melting temperature, but to a lower extent than what was observed for neat LLDPE. The same consideration is also valid for the temperature of crystallization. The effect of crosslinking is also clearly visible from the enthalpies of melting (crystallization). The specific enthalpies of melting of both the foamed LLDPE and the FPCM significantly decreased compared to the enthalpy of melting of neat LLDPE because a formation of imperfections in the crystalline structure due to complicated folding of the crosslinked polymeric chains.

3.4 Thermogravimetric analysis

The integral and derivative dependences of weight loss on the temperature are shown in Fig. 4. The results indicate that the thermal stability of the FPCM is lower than that of the foamed LLDPE because of the lower thermal stability of the wax. It is seen that the FPCM degraded in two clearly distinguishable steps due to the mutual immiscibility and the different thermal stabilities of the two components (LLDPE, wax).

3.5 DMA analysis

The dynamic mechanical properties of the prepared samples were investigated in the linear viscoelastic range, where the viscoelastic moduli were independent of the strain deformation (Fig. 5a). The LLDPE foam is stable to higher deformations in comparison to FPCM due to better structural properties. However, the absolute value of the elastic modulus was higher for the FPCM sample, indicating that this sample exhibits better mechanical behavior and is stiffer than pure LLDPE foam. From Fig. 5b, in both samples, the viscoelastic moduli slightly increase with increasing frequency, resulting from the good mechanical behavior of the samples. Since LLDPE can provide suitable properties for higher strain deformation, as previously mentioned, the FPCM has higher elastic modulus values and therefore have higher mechanical energy, which can be stored in the material. Furthermore, as shown in Fig. 5c, the FPCM is more dependent on the temperature, resulting from the phase change of the wax within the measured temperature range, while neat LLDPE does not exhibit this behavior due to the absence of wax. Finally, Fig. 5d presents a peak in tan δ at 42 °C. This temperature is the typical melting point of wax and was also obtained from the DSC measurement. This peak clearly indicates the phase change of the FPCM. To evaluate the quantitative amount of energy from this phase transition, the mechanical properties in a wide temperature range and various frequencies (1, 2.5, 5 and 10 Hz) were measured. Using a modified Arrhenius equation [10], the activation energy of the phase change was quantified. This energy was calculated to be 428 kJ/mol.

3.6 Thermal conductivity and diffusivity

The comparison of thermal conductivities of foamed and unfoamed samples is shown in Fig. 6. The thermal conductivity of the LLDPE foam was 0.06 W/m.K, whereas thermal conductivity of the FPCM was 0.09 W/m.K, mainly due to its lower porosity. Unfoamed LLDPE exhibited a thermal conductivity of 0.38 W/m.K, and the addition of wax caused the thermal conductivity to decrease to 0.33 W/m.K due to the lower thermal conductivity of wax (approximately 0.2 W/m.K) compared with that of pure polyethylene (0.42 W/m.K). The thermal diffusivities range from 0.27 mm^2/s for LLDPE foam to 0.22 mm^2/s for the FPCM.

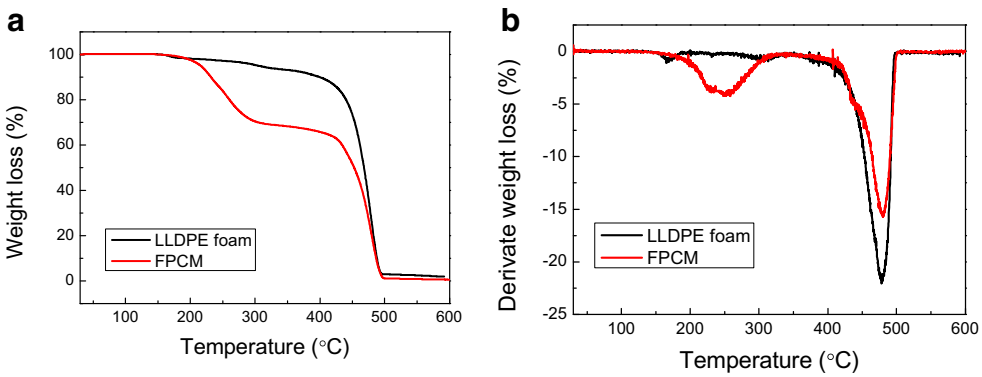

Fig. 4 Thermogravimetric curves of foamed LLDPE and FPCM

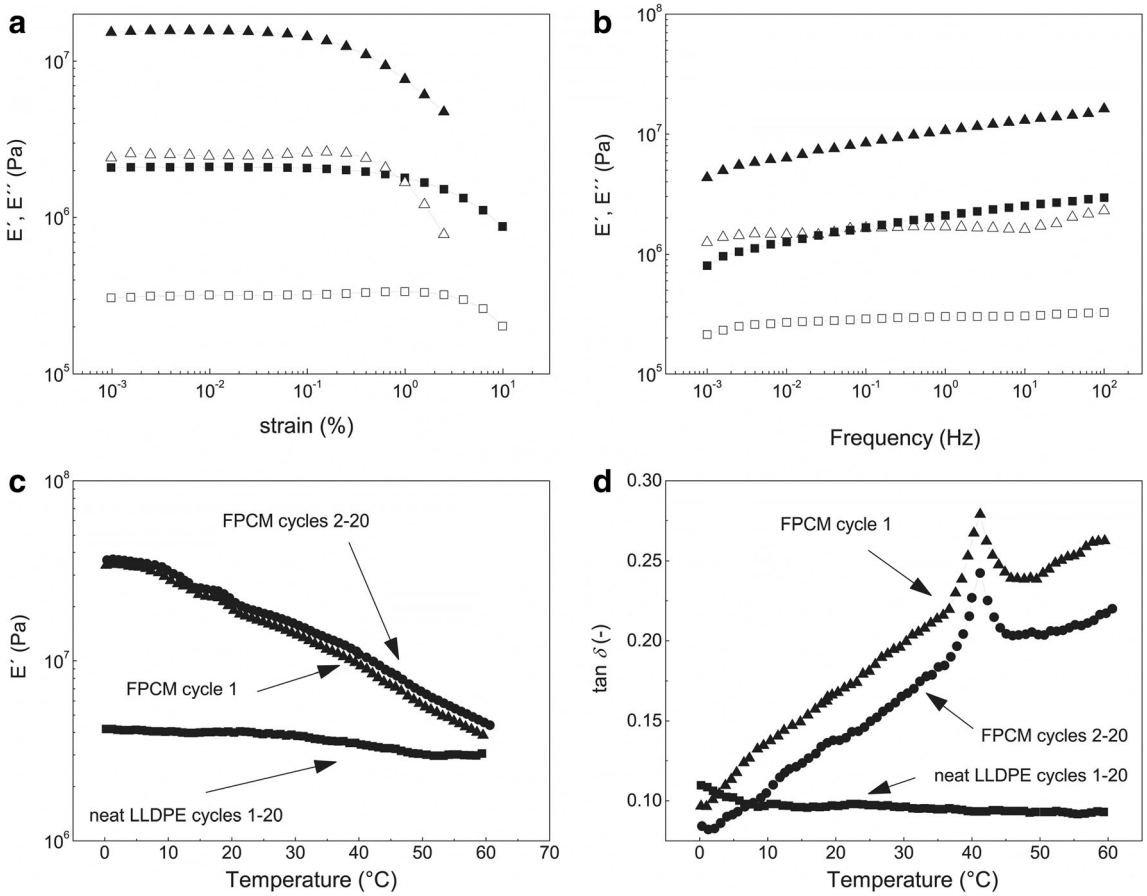

Fig. 5 Dependence of the elastic modulus E′ (solid symbols) and loss modulus E′′ (empty symbols) versus strain (**a**) and frequency (**b**). Dependence of the elastic modulus E′ versus temperature (**c**) and the dependence of tan δ versus temperature (**d**), where (■, □) corresponds to the neat LLDPE foam, (▲, Δ) corresponds to FPCM cycle 1, and (●) corresponds to FPCM cycles 2–20

3.7 Fourier-transform infrared spectroscopy (FTIR)

The chemical composition of the samples was investigated by FTIR. The FTIR spectra of the neat LLDPE, foamed LLDPE and FPCM are shown in Fig. 7. The absorption bands relative to the products formed during the crosslinking process cannot be directly detected by FITR, conclusions may be drawn from changes in some of the bands appeared as an decomposition of dicumyl peroxide representing crosslinking agent. The existence of byproducts originating from the crosslinking reaction

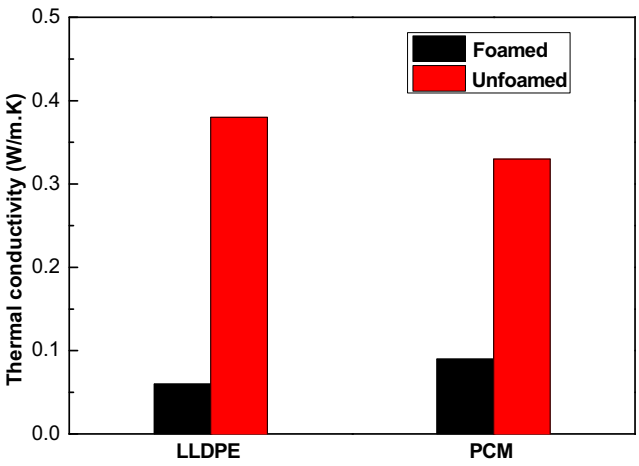

Fig. 6 Comparison of the thermal conductivities of the foamed and unfoamed samples

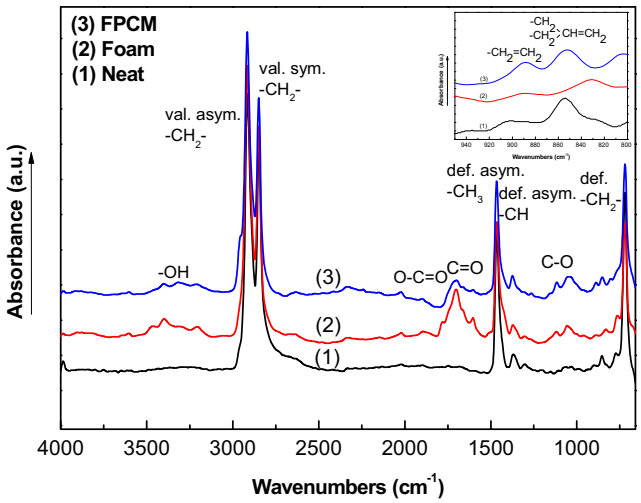

Fig. 7 FTIR spectra of samples

was determined as acetophenone and cumyl alcohol, and also as the ketones created as results of the thermo-processes. Moreover, some unsaturations observed in neat LLDPE at 860 cm^{-1} (vinylidene absorption) were more intense than at 909 cm^{-1} (vinyl band). The crosslinking process was responsible for a decrease in the intensity of the vinylidene absorption band and a slight increase in the intensity of the vinyl absorption band in FPCM [40].

4 Conclusions

Foamy phase-change materials consisted of polyethylene and paraffin wax were successfully prepared for the first time. The wax content was kept constant at 30 wt.%. The content of pores was 69 vol.%, and that of the foam prepared under the same conditions as neat LLDPE for comparison was 92 vol.%. The crosslinking effect of the prepared FPCM was proven by gel portion analyses using extraction by boiling xylene and by FTIR analysis. The thermal conductivity of the LLDPE foam was 0.06 W/m.K, whereas the thermal conductivity of the FPCM was 0.09 W/m.K, mainly due to lower porosity. The FPCM absorbed or released approximately 22–23 J/g during melting or cooling, respectively, which is in line with the results reported for the most common foamy PCMs, namely, polyurethane foams modified with encapsulated paraffin. The DSC and DMA measurements proved the excellent stability of the materials under cyclic heating/cooling and under dynamic mechanical stresses, while the FPCM properties were sustained at the same level. Forthcoming research will be focused on the incorporation of higher paraffin content within polyethylene-based foams to increase the heat storage capacity.

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