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Material Properties

Natural aging of shape stabilized phase change materials based on paraffin wax

Igor Krupa [a, *], Patrik Sobolčiak [a], Haneen Abdelrazeq [a, b], Mabrouk Ouederni [c], Mariam A. Al-Maadeed [a, b]

[a] Center for Advanced Materials, Qatar University, Doha 2713, Qatar
[b] Materials Science and Technology Program, College of Arts and Sciences, Qatar University, Doha 2713, Qatar
[c] Qatar Petrochemical Company (QAPCO), Doha 756, Qatar

ARTICLE INFO

ABSTRACT

Natural aging of shape-stabilized phase change materials containing linear low density polyethylene (LLDPE), paraffin wax and expanded graphite (EG) in Qatari climate has been studied. It was found that expanded graphite significantly improved the performance of prepared SSPCMs in multiple ways. Firstly, EG suppressed leakage of paraffin wax from the compact shape of SSPCMs. The addition of 15 wt% of EG to shape stabilized phase change materials (SSPCMs) containing 50 wt% of wax caused a decreasing in the leakage of wax by 50% over 210 days of natural aging.

Secondly, \expanded graphite enhanced the photochemical stability of the blends; this was confirmed by FTIR analysis, where carbonyl index decreased with EG content.

1. Introduction

In hot countries, such as Qatar, climatic conditions lead to the increase in temperatures up to 45 °C during summer and as low as 5 °C during the winter which results in large energy consumption, particularly for air conditioning. In general, it has been estimated that buildings consume up to 40% of global energy use [1]. Building designs that consider the local climate and utilize energy from the environment are called bioclimatic buildings. The sun is the most common source of energy that can be used to fulfill the energetic requirements of buildings. For this reason it is challenging to design elements which effectively absorb and release thermal energy from the sun to ensure thermal comfort with minimal use of electrical energy.

Materials which can be used for this purpose are called Phase Change Materials (PCMs). Their primary characteristics are the ability to undergo phase transition (usually from a solid to a liquid) at relatively low temperatures while absorbing or releasing a large amount of energy proportional to their specific enthalpy of melting

[2]. PCMs have received growing interest for use in many applications, particularly in the building industry. Various inorganic and organic compounds can be used as PCMs. The most common are inorganic salts (e.g., polyhydric alcohols), fatty acids, and paraffin waxes [2]. 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 relatively low price [3]. 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 these waxes are between 180 and 230 kJ kg^{-1}, resulting in an excellent energy storage density for paraffin waxes [4]. After melting, paraffin waxes have a tendency to leak from the system. To suppress this effect, paraffin waxes are enclosed in tanks or containers during heating to suppress leakage [2], they can be fixed in stable forms via encapsulation in a polymeric shell or by blending with certain polymers [3–9]. This type of materials is called Shape Stabilized Phase Change Materials (SSPCMs). The blending of suitable polymers with paraffin waxes leads to the fixation of the paraffin wax within a matrix resulting in a suppression of leakage during melting of wax. On the other hand, some amount of paraffin always leaks out the polymeric matrix, even in the case when paraffin is incorporated into a thermosetting (epoxy matrix) [10]. In this case, epoxy/paraffin mixture can be

considered as a composite with epoxy matrix and paraffin particles filler. Another design is based on the immiscible polymer/paraffin wax blends. It seems that polyethylene is the most convenient polymer for blending with paraffin waxes due to their chemical and structural similarities [11–13], which leads to the incorporation of a large amount of wax in polyethylene matrix without significant wax leakage due to incompatibility between the components.

Expanded graphite is commonly used in PCM design because it significantly improves their thermal conductivity [14–21], and suppresses PCM flammability [22].

Although PCMs are a hot topic and a large amount of information concerning their various types and different properties is available in literature, there is very limited information about their long term thermal performance when exposed to artificial or natural aging. As recently mentioned by Behzadi and Farid: "***This is an area that has been previously overlooked and requires further research***" [23]. These authors investigated thermal characteristics of two commercial organic PCMs (paraffin wax mixture, propyl stearic and palmitate mixture) when exposed to a constant temperature above their melting point. The thermal characteristic (i.e. melting range and latent heat of fusion) were tested after an exposure to storage temperatures of 30 and 55 °C. The results obtained indicated that the paraffin significantly and irreversibly changed with time. It was found that the peak of melting point shifted from 21 to 28 °C and latent heat of fusion increased from 134 to 170 J/g over a period of 120 days when kept at a temperature of 55 °C. Fauzi et al. [24] investigated the thermo-physical stability of fatty acids eutectic mixtures exposed to accelerated number of melting/solidification processes. The stability of phase transition temperature, latent heat of fusion, chemical structure and volume changes of selected mixtures after 200, 500, 1000 and 1500 thermal cycles were evaluated. J. Giro-Paloma et al. [25] studied cycling of PCM within slurries because of the breakage of microcapsules during charging/discharging and the subsequent loss of effectiveness. Sobolciak et al. investigated artificial aging of PCMs based on linear low density polyethylene and paraffin wax modified with various amounts of expanded graphite. It was found that expanded graphite significantly suppresses leakage of paraffin wax from the material over time and also improves their photo oxidation stability [26]. Accelerated thermal cycle test of polyethylene glycol of molecular weight 6000, as PCM for solar thermal energy storage was realized by Sharma et al. [27]. 1500 melt/freeze cycles were performed. The melting temperature was found to be stable in the quoted range of 55–60 °C with a maximum deviation of 6.5% when compared to that of at 0th cycle, but a gradual drop in the latent heat of fusion with the increasing number of thermal cycles was observed. The FT-IR spectra did not show any noticeable changes in the peaks which confirmed its compositional stability even after the higher number of thermal cycles.

In this paper, we report the results for prepared specimens utilizing local produced polyethylene as the raw materials. A significant natural aging approach was carried out to further study the photochemical and thermal degradation of the prepared PCM materials. Various analytical tools such as FTIR-spectroscopy, DSC were used to characterize prepared PCMs during natural aging.

FTIR-spectroscopy is simple and quick analytical method often used to identify certain functional groups in molecule [28]. In brief, infrared spectroscopy is based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule. Therefore, FTIR spectroscopy is helpful tool to study aging of PCMs by characterizing creation of various functional groups

(such as carbonyl, hydroxyl, carboxyl, etc.) created due to exposing of material to heat, sun and humid environment [26].

DSC measurement is a commonly used method for the thermal analysis of PCMs, providing accurate information of phase change temperature range and heat of fusion/solidification [29]. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions.

2. Experimental

2.1. Materials

Linear low-density of polyethylene (LLDPE) (MFI = 1 g/10 min, QAPCO, Qatar), paraffin wax (W) (Grade RT42, Rubitherm Technologies, Germany), and expanded graphite (EG) consisting of average size of 200 μm (GFG200, SGL Carbon, Germany) were used for the preparation of phase change materials blends.

2.2. Preparation of SSPCM blends based on LLDPE//W/EG

For preparation of SSPCMs, LLDPE powder was blended with W by Barbender (Plasticorder PLE 331, Germany) at 150 °C. The blends were then hot pressed (Fontijne TP 50, The Netherland) at 150 °C for 2 min. The LLDPE/W ratio was 50/50. Expanded graphite was added in concentration of 5 wt% and 15 wt% for improving thermal conductivity of SSPCMs. The parallelepiped shapes of SSPCMs were cooled down at room temperature between two thick metallic plates to obtain 1 mm thin sheets of SSPCMs.

2.3. Arrangement of specimens

The prepared SSPCM specimens were exposed to the outdoor environment at Qatar University in Doha, Qatar (25°22′44.2″N 51°29′19.7″ from 1st May to 25th November with the front and back sides facing the south east and North West, respectively. Whole set of holders were placed and fixed into separate metal plates and placed on a table in the outside atmosphere.

During the period of natural aging, values of both temperature and humidity were regularly recorded (Fig. 1).

2.4. Scanning electron microscopy (SEM)

The surfaces of the samples were investigated using a Nova Nano SEM 450 Scanning Electron Microscope. The specimen surfaces were sputtered with an Au layer (4 mm) using a Baltec-SDC 050 sputter-coater.

2.5. Differential scanning calorimetry (DSC)

DSC measurements were performed using Perkin Elmer model DSC 8500 (Perkin Elmer, USA) at temperature range from 0 °C to 60 °C at a heating rate of 1 °C/min under nitrogen atmosphere. Enthalpy was calculated from the second heating curve in order to erase the thermal history of the samples. Nitrogen gas was passed through the instrument at a flow rate of 20 ml·min^{-1}.

Results of DSC measurement were calculated from at least 3 measurements and average values with standard deviation are presented. The weight of the samples varied from 3.5 to 6.5 mg.

2.6. FTIR spectroscopy

Fourier transform infrared (FTIR) spectrometry was used to identify the chemical changes and degradation (photo-oxidation) in the SSPCMs structure during aging exposure. FTIR data were
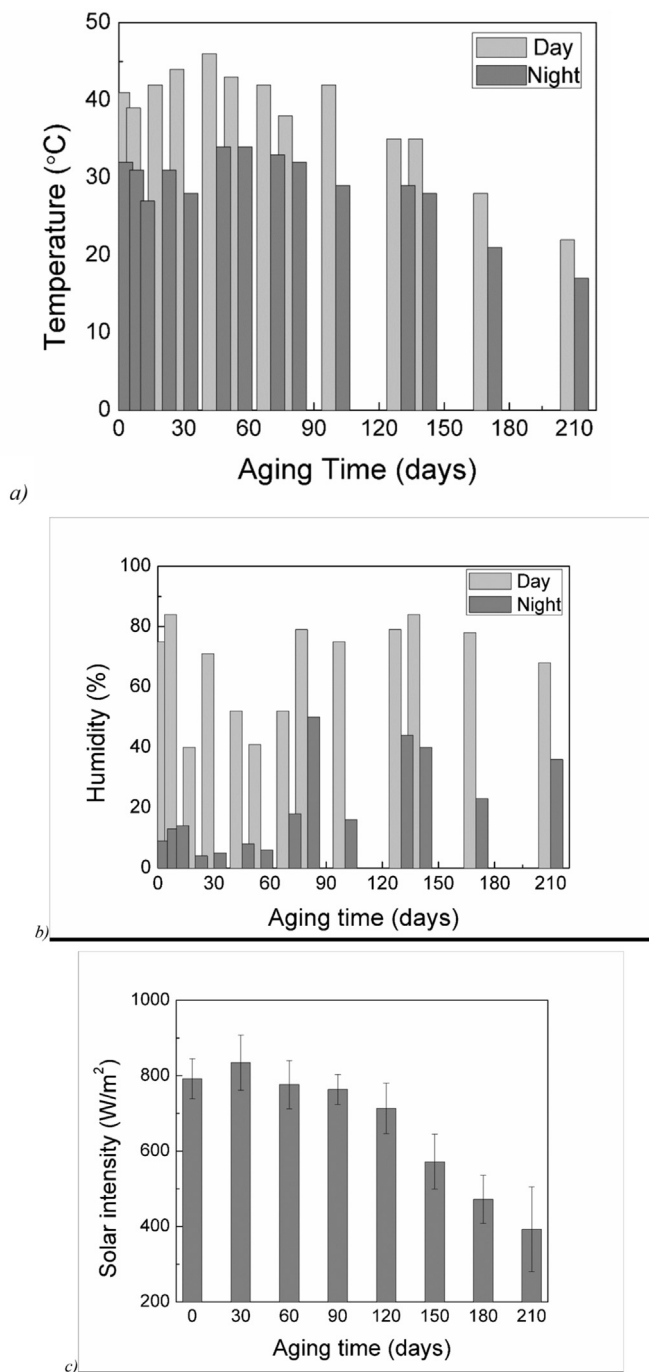
a)

b)

c)

Fig. 1. Records of outdoor conditions of a) temperature b) humidity and c) solar intensity during natural aging.

recorded on FTIR spectrometer Spectrum 400 (Perkin Elmer).

The carbonyl index (CI) was used to characterize the degree of degradation of SSPCMs. The CI is defined as a ratio of the peak area of absorbance of carbonyl bands in range from 1680 to 1760 cm^{-1} and internal thickness band at 1463 cm^{-1}.

2.7. Leakage test

Leakage experiments were performed for characterization of weight loss of SSPCMs during natural aging. The samples were weighted using an analytical balance and subsequently weight loss

was calculated according to Eq. (1).

$$weight\ loss\ (\%) = 100 - \frac{(m_0 - m_x)}{m_0 * w} \times 100 \tag{1}$$

where m_0 is initial mass of specimen, m_x is actual mass of the specimen and w is mass fraction of paraffin wax.

3. Results and discussion

3.1. Scanning electronic microscope (SEM)

The Scanning Electron Microscopy (SEM) was used to observe the surface morphology of LLDPE/W/EG composites after natural aging period.

SEM micrographs (Fig. 2) show surface morphology of SSPCM contain 5 and 15 wt% of EG respectively. Both images contain different phases with belong different component of SSPCMs. EG showed as white parts are more pronounced in Fig. 2b due to higher content of EG within SSPCM.

It was previously reported [30], that paraffin can be absorbed into the pores of the expanded graphite and held by the capillary force and the surface tension force of the porous expanded graphite what significantly improve leakage stability of the blends. It can generally be pointed out that higher amount of the W can be absorbed and held within SSPCM contain 15 wt% of EG what was also confirmed by leakage experiment.

3.2. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy was used to identify photochemical degradation of SSPCM during natural aging. FTIR measurements were taken before and during the natural aging process. Fig. 3a illustrates the FTIR spectra for neat LLDPE before and after 30, 70, 100, 14, 210 days of natural aging. FTIR spectrum of LLDPE before natural aging shows characteristic peaks at 2917, 2843 cm^{-1} belonged to vibration mode of −CH$_2$ groups and scissoring vibration of −CH$_2$ at 1463 cm^{-1}. Another noticeable peaks around 1040 and at 729 cm^{-1} characterized C-C stretching vibration [31,32].

Exposing of LLDPE to natural aging led to photochemical degradation with main evidence in the range from 1700 to 1780 cm^{-1} belongs to creation of carbonyl structure such as aldehyde, ketones carboxylic acids *etc* [33,34].

Likewise changes in the amorphous phase (around 1300 cm^{-1}) and formation of peaks around 3400 cm^{-1} belongs to −OH vibration can be occurred.

Natural aging caused increasing of vibration band in mentioned areas and overlapping of the peaks especially in region around 1750 cm^{-1} due to multiple oxidation products contains carbonyl groups. In addition, natural aging caused degradation of amorphous phase as can be seen around 1250 cm^{-1}. Also slight broadening peak around 3400 cm^{-1} can be found which belongs to −OH bands.

Likewise, in Fig. 3b, creation of carbonyl groups was observed for SSPCM blends with composition LLDPE/W 50/50. W has similar structure as a LLDPE except the chain length which is much lower in case of paraffin therefore accelerated degradation compare to neat LLDPE and SSPCMs contain 50 wt% of LLDPE and W.

FTIR spectra of SSPCMs containing 5 and 15 wt% of EG are shown in Fig. 3c and d. Creation of carbonyl structures in both types of SSPCM was suppressed (in comparison to blends without EG) due to enhancement of photostability of SSPCM blends caused by addition of EG because EG, similarly as other carbon fillers (carbon black, carbon nanotubes) acts as free radicals scavenger.
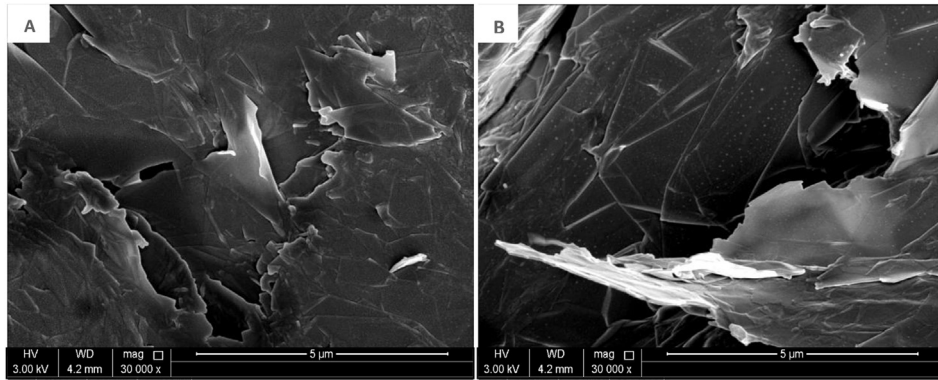
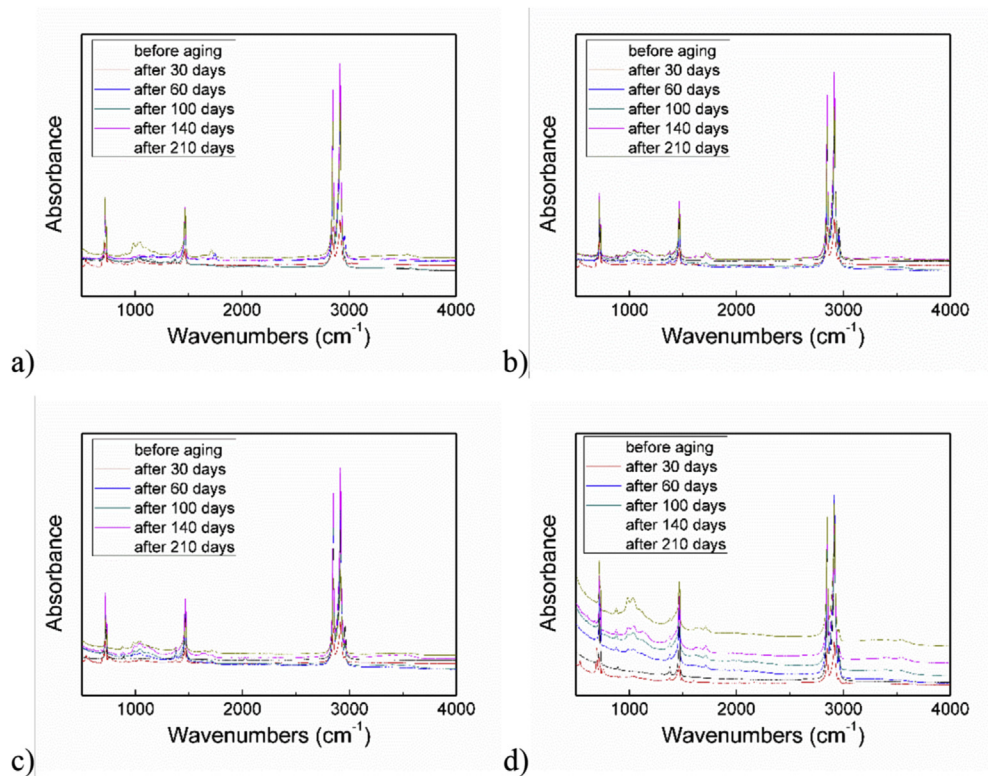Fig. 2. SEM micrographs for SSPCMs contain LLDPE/W/EG (w/w/w) A) 45/50/5; B) 35/50/15.

Fig. 3. FTIR spectroscopy of a) neat LLDPE and SSPCMs contain b) 50/50/0, c) 45/50/5 and d) 35/50/15 w/w/w over time of natural aging.

One of the possibilities of determination of thermal stability of materials is based on comparing amount of carbonyl structures created over time. Carbonyl index can be calculated from FTIR spectra by dividing area of the peaks belonging to carbonyl structures (1650–1780 cm^{-1}) and peak which is considered unchanged during aging such as CH$_2$ vibration at 1463 cm^{-1}. Fig. 4 illustrated CI for neat LLDPE and various SSPCMs during natural aging.

The higher photostability of SSPCM contain 50 wt% of LLDPE and W have been observed compared to pure LLDPE in terms of creation carbonyl structures which can by caused by differences in the structure of LLDPE and W, where narrow structure of W chains compare to branched polymer chains of LLDPE containing tertiary carbons can play role.

Blends containing EG assigned lowering of CI values due to increasing stability of blend caused by presence of EG. Similar trend, increasing of photostability of SSPCMs based on W was due

to presence of EG [26].

3.3. Leakage measurements

Leakage of W from SSPCMs is a serious issue which affects usability of those types of materials for thermal energy utilization and therefore there is a need to properly address this matter. Fig. 5 shows the weight loss of LLDPE and various SSPCMs during natural aging. Expectedly, weight of LLDPE did not show any significant change over time.

On the other hand, leakage of W for all SSPCMs has been observed. It can be seen from Fig. 5 that the major leakage for the samples was pronounced after 5 days of natural aging due to release of W from surface layers (or close to surface) of SSPCMs. However, after a longer time has passed, the reduction in leakage became much lower, and started to become almost constant
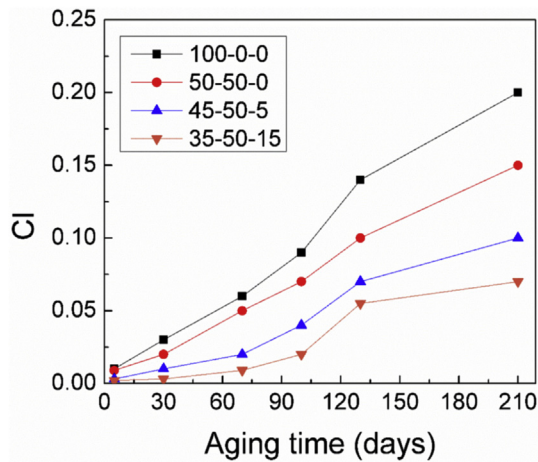
Fig. 4. Carbonyl index of LLDPE/PW/EG phase change materials blends from 1780 to 1660 cm^{-1} spectra during natural aging experiment.

Fig. 6. Comparison of DSC thermographs during natural aging for SSPCM contains 15 wt% of W.

influence of natural aging on the polyethylene phase was not investigated in this work.

Fig. 7 shows melting enthalpy of SSPCMs during natural aging experiment for various SSPCMs. It is clearly seen that SSPCM without EG exhibited the largest decrease of melting enthalpy during natural aging due to noticeable leakage of W from blend, where melting enthalpy dropped from 54 J/g to 27 J/g.

For the sample consisting of 5 wt% of EG, melting enthalpy changed from 55 J/g (before natural aging) to 32 J/g (after natural aging). Adding to this, specific enthalpy of melting for the SSCPM containing 15 wt% of EG decreased from 58 J/g to 46 J/g. This supports the observation noted from the leakage experiment in which the increasing addition of EG within the SSCPMs improve the stability of prepared blends. Similarly, the increase in stability of SSPCMs was observed during artificial aging as reported elsewhere [26].

Detailed melting and crystallization temperatures as well as melting and crystallization enthalpies for various SSPCMs are listed in Table 1.

The highest decrease (over 50%) in melting enthalpy was noted for the 50/50 blend during natural aging in compared to the lowest decrease (around 20%) for SSPCM contains 15 wt% of EG. The decrease of the melting enthalpy with time is reasonable, because W leaked from the samples should be proportional to changing of melting enthalpy of SSPCMs.
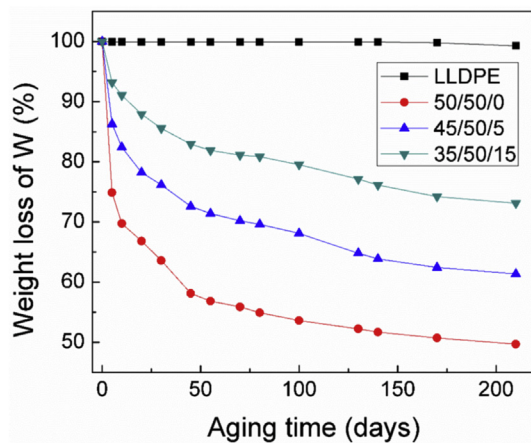

Fig. 5. The leakage of SSPCM blends based on LLDPE, 50 wt% of W and EG over the time.

towards the end.

The SSPCM containing 15 wt% of EG exhibited the lowest paraffin loss of 25% in compared to the high paraffin loss of 50% in the 50/50 SSPCM blend.

Hence, this confirms that the addition of expanded graphite stabilized SSPCMs partially due to trapping of W between graphene layers of EG and subsequent difficulties to diffuse small W chains out of the graphene sheets of EG. Also, presence of EG particles increased the viscosity of the SSPCMs [26].

3.4. Differential scanning calorimetry (DSC)

Specific enthalpy of melting of SSPCMs during natural aging was determined by DSC. Since W is an active component in SSPCM and leakage experiment showed decreasing of W within SSPCM over the time, the specific enthalpy of melting decreased proportionally to the leakage amount of W.

Fig. 6 shows DSC thermographs for SSPCM contains 15 wt% of EG before and after 30, 70, 100, 140 and 210 days of natural aging. Generally, DSC thermographs contain two peaks. Minor peaks around 18 °C which belongs to solid-solid transition of W crystalline region occurred due to their reorganization and solid-liquid transition belongs to melting of crystalline phase of W. The
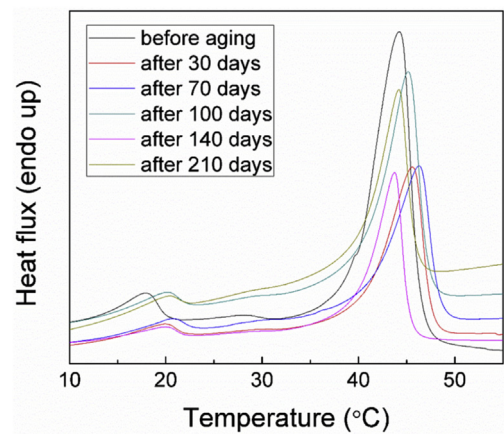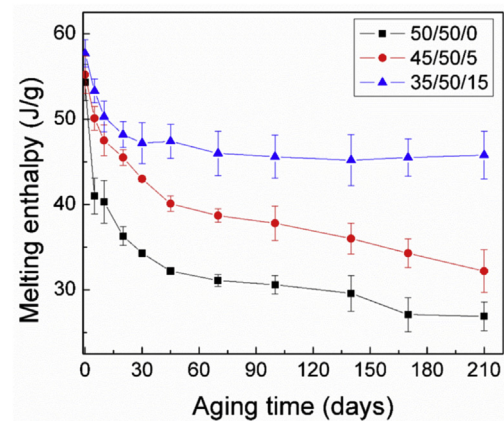

Fig. 7. Melting enthalpy for various SSPCMs over time of natural aging.

Table 1
Average temperature (Tm-melting and Tc-cooling) and enthalpy (ΔHm-melting and ΔHc-cooling) values obtained from DSC measurements for various SSPCMs.

DAY	50/50				45/50/5				35/50/15			
	Tm	ΔHm	Tc	ΔHc	Tm	ΔHm	Tc	ΔHc	Tm	ΔHm	Tc	ΔHc
	°C	J/g	°C	J/g	°C	J/g	°C	J/g	°C	J/g	°C	J/g
0	43.5 (0.3)	54 (2)	35.4 (0.1)	57 (2)	44.2 (0.3)	55 (2)	35.6 (0.4)	53 (1)	43.4 (0.2)	58 (2)	36.8 (0.3)	56 (2)
5	44.2 (0.6)	41 (2)	34.3 (0.3)	45 (2)	44.8 (0.5)	50 (1)	34.9 (0.2)	51 (2)	44.5 (0.2)	53 (1)	36.9 (0.3)	53 (1)
10	44.4 (0.5)	40 (3)	34.6 (0.4)	44 (1)	44.4 (0.1)	48 (2)	35.4 (0.4)	49 (2)	43.8 (0.4)	50 (2)	36.9 (0.2)	52 (3)
20	44.2 (0.5)	36 (1)	35.2 (0.2)	35 (2)	44.7 (0.3)	46 (1)	35.8 (0.1)	47 (3)	45.6 (0.5)	48 (2)	35.3 (0.4)	51 (2)
30	44.7 (0.2)	34 (1)	34.9 (0.6)	35 (1)	45.6 (1.0)	43 (1)	36.0 (0.2)	43 (2)	46.6 (0.2)	47 (2)	35.9 (0.5)	49 (1)
45	44.4 (0.2)	32 (1)	35.6 (0.1)	33 (2)	47.4 (1.5)	40 (1)	36.2 (0.4)	41 (1)	45.6 (0.4)	47 (2)	35.5 (0.1)	48 (2)
70	44.0 (0.3)	31 (1)	35.8 (0.4)	30 (2)	46.3 (0.8)	39 (1)	35.4 (0.3)	37 (2)	46.1 (0.6)	46 (3)	34.9 (0.1)	48 (2)
100	45.5 (0.1)	31 (1)	35.6 (0.3)	30 (1)	46.5 (0.6)	38 (2)	36.2 (0.6)	36 (2)	45.6 (0.3)	46 (3)	36.5 (0.4)	45 (3)
140	44.1 (0.1)	30 (2)	36.9 (0.2)	29 (2)	45.0 (0.2)	36 (2)	37.7 (0.2)	34 (3)	44.4 (0.3)	45 (3)	38.4 (0.3)	45 (2)
170	44.3 (0.6)	27 (2)	37.2 (0.1)	28 (3)	44.9 (0.5)	34 (2)	38.5 (0.2)	35 (2)	45.3 (0.2)	46 (2)	38.6 (0.5)	45 (2)
210	45.2 (0.3)	27 (2)	37.2 (0.8)	26 (3)	46.4 (0.3)	32 (3)	38.2 (0.4)	32 (3)	45.6 (0.1)	46 (3)	38.6 (0.2)	45 (2)

4. Conclusions

SSPCMs containing linear low density polyethylene, paraffin wax and expanded graphite have been exposed to natural aging in Qatar climate.

Natural aging caused leakage of paraffin wax from compact shape of SSPCMs. The SSPCMs without EG showed around 50% weight loss of paraffin wax, whereas SSPCMs containing 15 wt% EG showed 25% weight loss over 210 days of natural aging.

Also, photochemical degradation over time has been observed. The creation of carbonyl groups has been studied by FTIR spectroscopy. It can be concluded, that the addition of EG caused decreasing of carbonyl groups over time which was confirmed by the carbonyl index analysis.

Acknowledgement

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