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Material Properties

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

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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

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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 $ml \cdot min^{-1}$.

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