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Calorimetric and dynamic mechanical behavior of phase change materials based on paraffin wax supported by expanded graphite

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ABSTRACT

This study addressed the characterization and description of calorimetric and dynamic mechanical properties of phase change materials (PCMs) based on linear low-density polyethylene (LLDPE), paraffin wax (W) and expanded graphite (EG). The mentioned properties were evaluated over the temperature range from 0 °C to 60 °C, which is the expected range for practical applications of these materials. The appropriate dispersion of EG particles within the LLDPE/W blends was confirmed using XRD measurements. Moreover, the partial intercalation of the W between the graphite layers was confirmed. The broad investigation of the dynamic mechanical properties at various temperatures and frequencies provides complex information concerning the mechanical behavior of LLDPE/W blends as well as LLDPE/W/EG composites. The results showed that incorporation of EG into LLDPE/W blends led to a significant increase in their dynamic mechanical properties, which was proportional to the EG content.

Moreover, it was shown that the melting and crystallization characteristics of the investigated materials did not change upon cycling (30 heating/cooling cycles), and their dynamic mechanical properties stayed constant over five thermal cycles.

1. Introduction

PCMs are substances with a high heat of fusion that can store or release thermal energy by melting and solidifying at certain temperatures [1]. The primary characteristics of these materials are the ability to undergo phase transitions (typically from solid to liquid phase) at relatively low temperatures while absorbing or releasing a high amount of energy, proportional to their specific enthalpy of melting. PCMs have received increasing interest for their use in many applications, such thermal protection systems, active and passive electronic device cooling and, particularly, in the building industry [2] and as a solar energy storage medium [3]. Various inorganic and organic substances have been employed in PCMs, and the most common additives include various types of inorganic salts (e.g., polyhydric alcohols) and their eutectics, fatty acids, and paraffins [4]. Paraffins are the most promising PCMs because of their desirable characteristics, such as a high latent heat of fusion, a broad range of melting temperatures ranging from 20 to 90 °C, negligible super-cooling, low vapor pressure and relatively low price. The specific melting enthalpy of paraffin is between 180 and 230 $\mathrm{kJ\,kg^{-1}}$, leading to an excellent energy storage density [4].

After melting, paraffins used as PCMs have a tendency to leach from the system to which they are applied. In many civil engineering applications, paraffins are stored in closed tanks or containers during heating to suppress leaching [4]. Other methods to maintain waxes in stable forms during their application involve blending with convenient polymers [5–8] or encapsulating within a polymeric or inorganic shell to form microcapsules [9–13]. Similarly, the ability to stabilize paraffin wax using graphite particles has been reported [14–16]. Blends of paraffins with appropriate polymers (termed shape-stabilized PCMs) are good candidates for the preparation of smart polymeric PCMs for different applications, such as thermal storage of solar energy, thermal protection of electronic devices, food and medical goods, passive storage in bioclimatic buildings, and thermal comfort in vehicles [3,4]. The blending of paraffins with polymers provides an opportunity to utilize PCMs with unique, controlled structures. Polymeric matrices fix the paraffins in a compact form to suppress leaching, even after melting. These materials are also easily shaped, and the polymeric phase provides its own specific properties. A variety of polymer matrices are available with a large range of chemical and mechanical properties [17,18]. For example, thermosetting resins, such as epoxy, are

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Nomenclatures

DSC	differential scanning calorimetry
E_m	additional energy required for the system to reach the phase transition
EG	expanded graphite
F	tested frequency
F_0	constant frequency characteristic
HDPE	high density polyethylene
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
LVR	linear viscosity region
MFI	melt flow index
PCM	phase change material
PE	polyethylene
PP	polypropylene
R	universal gas constant
T	temperature
T_g	phase transition
T_{s-s}	melting point of solid–solid transition
T_{s-l}	melting point of solid–liquid transition
X	Röntgen
XRD	Röntgen ray diffraction
ΔH_{s-l}	melting enthalpy of solid–liquid transitions
ΔH_{s-s}	melting enthalpy of solid–solid transition

particularly useful in applications in which blending with paraffins at room temperature is required for the low transition temperature PCM to stay in the solid phase during composite processing [19]. Polyethylene (PE) polymers are used most frequently to blend with paraffins to obtain shape-stabilized PCMs because they are chemically and structurally similar to paraffin [20,21]. Thus, it is possible to incorporate large amounts of wax into polyethylene, which is the most important requirement for these materials. For example, Inaba and Tu [20] investigated a shape-stabilized paraffin system based on paraffin blended with high-density polyethylene (HDPE). The resulting composite consisted of 74 wt% paraffin and 26 wt% HDPE. Conversely, our results based on an investigation of low-density polyethylene (LDPE)/W blends were not as promising [22]. The dynamic mechanical analysis (DMA) of the blends highlighted the importance of the basic question regarding the component that forms the continuous phase and the component that forms the discontinuous phase. Although LDPE forms the continuous phase at up to 50 wt% wax [22], the amount of LDPE is unable to maintain the material structure in a consistent shape. Controlled-force ramp testing during the DMA confirmed poor material strength, especially at temperatures higher than the melting point of the wax (i.e., temperatures that are interesting for energy storage applications). The highest paraffin concentration able to sustain external forces and thermal cycling was 40 wt%. This value was even lower when polypropylene (PP) was used as the matrix [23]. The shape-stabilized PCMs based on isotactic PP blended with soft and hard Fischer–Tropsch paraffin showed strong phase separations. Paraffin melted separately in the PP matrix (up to 40 wt% wax), whereas the PP remained in the solid state [23]. Thus, attention should be focused on the miscibility or improved compatibility between the components. The degree of miscibility between the polymer pairs may also influence the energy efficiency in many applications. Chen and Wolcott [24] investigated binary polyethylene–paraffin blends that were melt compounded at different ratios of high-density polyethylene, low-density polyethylene, and linear low-density polyethylene using a parallel co-rotating twin screw extruder. The miscibility of the paraffin in the three types of polyethylene was evaluated using differential scanning calorimetry (DSC) and atomic force microscopy. The DSC data demonstrated two melting temperatures with a depression of the equilibrium melting temperature for the polyethylene in the mixture. Two distinct phases and an intermediate phase were evident in the atomic force microscopy images. This structure verified the partial miscibility of paraffin in polyethylene. The crystallinity of each component depends on the blend concentration. Two paraffin crystallization peaks for the PE/paraffin blends were observed, with the enthalpy of one peak increasing as that of the other decreased. The lowest paraffin miscibility in polyethylene was found in the paraffin/high density polyethylene blend [24].

This study is focused on a mechanical and calorimetric investigation of PCMs with paraffin wax as an active phase change substance over the temperature range from 0 to 60 °C. XRD analysis confirmed a good dispersion of expanded graphite (EG) within the blends as well as exfoliation of graphite due to the penetration of paraffin between the graphite layers.

EG is commonly used in PCMs designing because it significantly improves their thermal conductivity [25–27], decreases flammability [28] and suppresses a leaching of paraffin from mixtures [29,30].

Incorporation of the EG particles into blends significantly improved the mechanical properties and provided the systems with promising phase-change behavior as well as mechanical support over many phase-change cycles.

The melting point of paraffin wax used in this study is around 42 °C. Investigated PCMs are potentially applicable in outdoor building applications in the regions where heat accumulates at a higher temperature [31]. Furthermore, it can be useful for a heat protection of solar collectors [32].

2. Materials

Linear low-density polyethylene (MFI = 1 g/10 min, QAPCO, Qatar), paraffin wax (Grade RT42, Rubitherm Technologies, Germany) and expanded graphite (GFG200, SGL Carbon, Germany) with an average size of 200 μm were used for the preparation of the PCMs.

2.1. Preparation of the composites

LLDPE was mixed with W and EG in various ratios in a Brabender (Plasticorder PLE 331, Germany) for 7 min at 140 °C. Paraffin contents greater than 50 wt% led to significant phase separation of the blends and loss of their mechanical integrity. To improve the thermal conductivity of the materials, EG was added.

Subsequently, the blends were hot pressed (Fontijne TP 50, The Netherlands) at 140 °C for 5 min.

2.2. Characterization

2.2.1. X-ray diffraction

The suitable incorporation of EG and W in the LLDPE/W/EG blends as well as intercalation of W between the graphite layers was confirmed and characterized using an X-ray diffractometer X'Pert PRO X-ray (PANalytical, The Netherlands) with a Cu-K$_\alpha$ X-ray source (λ = 1.5418 Å) over the diffraction angle range of $2\theta = 5–85°$.

2.2.2. Differential scanning calorimetry

DSC measurements were performed using a Perkin Elmer model DSC 8500 (Perkin Elmer, USA) over a temperature range from 0 °C to 60 °C at a heating rate of 2 °C/min under a nitrogen atmosphere. The second scan was evaluated to investigate the melting enthalpy as well as the melting and crystallization temperatures. As crystallization and melting temperature was taken the peak temperature of corresponding peak. Indium was used for calibrating the