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Shape stabilised phase change materials based on a high melt viscosity HDPE and paraffin waxes

Mulan Mu [a], P.A.M. Basheer [b], Wei Sha [a], Yun Bai [c], Tony McNally [d,*]

[a] School of Planning, Architecture & Civil Engineering, Queen's University Belfast, BT9 5AG, UK
[b] School of Civil Engineering, University of Leeds, LS2 9JT, UK
[c] Department of Civil, Environmental & Geomatic Engineering, University College London, WC1E 6BT, UK
[d] International Institute for Nanocomposites Manufacturing (IINM), WMG, University of Warwick, CV4 7AL, UK

HIGHLIGHTS

- SSPCM's based on HDPE/paraffin waxes can be prepared using twin-screw extrusion.
- The waxes were uniformly dispersed and distributed in the polymer matrix.
- SSPCM's with a high melting point wax (T_m = 56–58 °C) had latent heats up to 89 J/g.
- The waxes had a strong plasticising effect on the HDPE.
- SSPCM's with the higher melting point wax were mechanically superior.

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ABSTRACT

Shape stabilised phase change materials (SSPCMs) based on a high density poly(ethylene)(hv-HDPE) with high (H-PW, T_m = 56–58 °C) and low (L-PW, T_m = 18–23 °C) melting point paraffin waxes were readily prepared using twin-screw extrusion. The thermo-physical properties of these materials were assessed using a combination of techniques and their suitability for latent heat thermal energy storage (LHTES) assessed. The melt processing temperature (160 °C) of the HDPE used was well below the onset of thermal decomposition of H-PW (220 °C), but above that for L-PW (130 °C), although the decomposition process extended over a range of 120 °C and the residence time of L-PW in the extruder was <30 s. The SSPCMs prepared had latent heats up to 89 J/g and the enthalpy values for H-PW in the respective blends decreased with increasing H-PW loading, as a consequence of co-crystallisation of H-PW and hv-HDPE. Static and dynamic mechanical analysis confirmed both waxes have a plasticisation effect on this HDPE. Irrespective of the mode of deformation (tension, flexural, compression) modulus and stress decreased with increased wax loading in the blend, but the H-PW blends were mechanically superior to those with L-PW.

1. Introduction

Thermal energy storage through the use of phase change materials (PCMs) in building applications has attracted much attention recently, their use having the potential to improve energy efficiency in buildings [1–3]. PCMs are substances with a high heat of fusion, which on changing phase over a certain temperature window are capable of storing and releasing large amounts of energy. The most effective method of storing thermal energy is via latent heat, which can be given by:

$$Q = \int_{T_i}^{T_m} mC_p \cdot dT + ma_m \cdot \Delta H_m + \int_{T_m}^{T_f} mC_p \cdot dT \quad (1)$$

where, Q = the quantity of heat stored, T_m = melting temperature, T_i = initial temperature, T_f = final temperature, m = mass of storage medium, a_m = fraction of material melted, ΔH_m = heat of melting per unit mass (J/kg) and C_p = specific heat capacity (J/kg/K). This process creates the opportunity for utilising renewable natural energy, such as solar energy and night ventilation by incorporating PCMs into buildings [4–7]. Many different types of PCMs have been studied, such as those based on hydrated salts, paraffins, fatty acids and polyols [8–11]. Paraffin is the most attractive PCM used in buildings as it is one of the cheapest and most readily available, being derived from petroleum and having relatively good

* Corresponding author.
E-mail address: t.mcnally@warwick.ac.uk (T. McNally).

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thermo-physical properties, such as high latent heat, negligible super-cooling and a suitable transition point [12]. A paraffin wax consists typically of a mixture of hydrocarbon molecules, C_nH_{2n+2} (n = 1–100), with each specific wax having a range of about 8 to 15 carbon numbers. Latent heat is stored as a consequence of the crystallisation of these hydrocarbon molecules. With a melting point adjustable to climate specific requirements, the length of the hydrocarbon chain dictates both the melting point of the PCM and the heat of fusion. Hydrocarbon waxes have a wide range of melting temperatures, from −5 °C to 61 °C [13]. This when combined with their high heats of fusion, up to 266 J/g, makes them suitable for space heating applications.

However, it cannot be used in buildings directly as the phase changes of paraffin waxes are between the solid and liquid states. To overcome this, researchers have developed shape stable phase change materials (SSPCMs), which use certain polymers as a supporting matrix and paraffin wax as the functional core material. By melting and mixing polymer and wax together, the polymer can form a three dimensional network structure to envelop the wax. The melting point of the polymer is always higher than that of the paraffin wax. Thus, when paraffin wax changes from solid to liquid, the supporting matrix remains solid and the paraffin wax will not leak, although there may be seepage with time, from the polymer network structure [9,14]. The composite material, therefore, can be used as laminated SSPCM wallboards with no need to incorporate them into building materials. A range of polymers can be used as the structural supporting component/matrix, including high- (HDPE), low- (LDPE) and linear low-density (LLDPE) poly (ethylene), styrene–butadiene–styrene (SBS) tri-block copolymer and poly(propylene) (PP), although the poly(ethylene) family have been most widely studied for SSPCM application with paraffin waxes, due to their similar chemical structures [15–19].

Inaba and Hu proposed, more than 15 years ago, the concept of HDPE/wax blends as a new type of SSPCM by melting and mixing paraffin and HDPE for thermal energy storage applications without encapsulation and determining the thermo-physical properties of the blend. The blend was composed of 26% HDPE and 74% paraffin by weight. The wax used consisted mainly of pentacosane ($C_{25}H_{52}$, T_m = 54.2 °C) [9]. Lee and Choi studied the durability of SSPCMs by investigating the seepage behaviour of a paraffin ($C_{24}H_{50}$) [20]. The SSPCMs based on this paraffin wax with two different types of HDPE were prepared by simple physical mixing at a paraffin content of 70 wt%. The authors reported the effect of HDPE crystalline morphology on the seepage behaviour of the paraffin and concluded that a higher molecular weight HDPE was required for better sealant properties. More recently, Chen and Wolcott identified co-continuous structures for blends of HDPE, LLDPE and LDPE with a C_{18} based paraffin wax [21]. They concluded that the co-continuous structure formed was the main cause of paraffin leakage from the respective blends, and the rate of leakage from HDPE was significantly lower than that from LLDPE and LDPE, for the same test conditions. Blends of six types of HDPE with varying melt indices and paraffins were evaluated as candidate materials for SSPCMs by Hong and Ge [14]. The HDPEs were mixed (detail not given) with refined or semi-refined paraffin waxes of different melting points (the T_m of the waxes was not reported) at wax contents as high as 75 wt%. The authors showed a SSPCM based on a HDPE with a MFI = 11 g/10 min and semi-refined paraffin which could be used in LHTES applications. Zhang et al. developed SSPCMs for building applications using paraffin waxes having T_m = 20 °C and 60 °C as the PCM, but studied SBS as well as HDPE as the supporting matrix [22]. The authors explored strategies to enhance the thermal conductivity of these systems by adding graphite or carbon fibre and reduce leakage of the wax from the matrix by employing surface treatments, e.g. grafting or crosslinking. However, the authors provided no information about the influence of different waxes, polymer matrices or additives on the mechanical properties of the SSPCM blends. Kaygusuz and Sari investigated the thermal properties of an SSPCM based on HDPE and four different types of waxes with T_m = 42–44 °C, 48–50 °C, 56–58 °C, and 63–65 °C [23,24]. They found that the mass fraction of paraffin wax in the SSPCM could be as high as 77% without any seepage of the paraffin, for the conditions tested. The thermal conductivity of the SSPCMs, although from a low level, was improved by as much as 52% on addition of exfoliated graphite at a loading of 3 wt%. Al Maadeed et al. also reported that addition of up to 15 wt% of expanded graphite (EG) to HDPE/paraffin wax blends increased both thermal stability and thermal conductivity of the blends [25]. Even the addition of small quantities of EG reduced crystallisation time and thus increased the latent heat storage. Hato and Luyt studied the influence of wax type and content on miscibility when blended with HDPE, LDPE and LLDPE [26]. The thermal behaviour of the wax is greatly influenced by the degree of miscibility with the polymer matrix. All three polymers were initially melt-mixed with a hard wax (H1), (T_m = 59.4 °C) and an oxidised wax (A1) (T_m = 55.4 °C) in a Brabender Plastograph (screw speed = 30 rpm for 15 min). Interestingly, all HDPE/wax blends were completely miscible at both 10 wt% and 20 wt% wax content, but only partially miscible when 30 wt% wax was added. LDPE/hard paraffin wax blends were partially miscible at all wax loadings investigated, while only completely miscible for a low loading of 10 wt% oxidised wax. Complete miscibility was observed for all the LLDPE/oxidised wax blends. Further work by the same group on SSPCMs consisting of HDPE, alkali-treated wood flour (WF) and either M3 or H1 waxes (where M3 wax has T_m = 40–60 °C, average M_w = 440 g mol^{-1}; for H1, T_m = 107 °C, average M_w = 785 g mol^{-1}) explored the effectiveness of WF in improving the mechanical properties and thermal stability of the SSPCM [27,28]. Poor filler dispersion and interfacial adhesion were observed between the WF particles and HDPE matrix. Partial miscibility of the HDPE with both M3/H1 waxes was observed, with the WF particles covered by wax. The presence of either wax (M3 or H1) reduced the thermal stability and mechanical properties of all blends. With regard to the use of these SSPCMs in building applications increased M3 wax content resulted in a decrease in water uptake. Chen and Wolcott also studied the miscibility of HDPE, LLDPE and LDPE with a C_{18} paraffin wax and showed all three polymers were partially miscible with this wax [29]. The miscibility between the HDPE and wax was the weakest and thus from a phase change material perspective this blend is preferred for LHTES. Yan et al. prepared SSPCMs based on HDPE with four different types of waxes with T_m between 21 °C and 27 °C and up to 70% mass content [30]. The SSPCMs prepared had large latent heats, up to 177 J/g and were good candidates for LHTES. Co-crystallisation of paraffin waxes with poly(ethylene)s must also be considered when preparing SSPCMs based on these materials. Luyt and Brüll studied the extent of co-crystallisation of SSPCMs based on an oxidised wax (average M_w = 785 g mol^{-1}, *C/O* ratio 18.8/1) with HDPE, LDPE and LLDPE [31]. The authors demonstrated extensive co-crystallisation of the wax with LLDPE, but little or no co-crystallisation with HDPE and LDPE. From an applications point of view the flame retardant properties of SSPCM's are very important. Recently, Wang et al. examined the effect of organo- modified montmorillonite(OMMT), EG and crosslinking the polymer matrix on the burning time (related to flame retardant performance) of a blend of SBS/HDPE/paraffin wax (30/10/60) [32]. The best flame retardance was achieved when both OMMT and EG was added to the blend and the polymer matrix crosslinked by tert-butyl hydroperoxide.

However, there has been little research on the impact of different melting point waxes on the thermo-physical properties of the SSPCMs which are also prepared using a continuous, scalable and