Thermo-physical characteristics, mechanical performance and long-term stability of high temperature latent heat storages based on paraffin-polymer compounds

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A B S T R A C T

Different polyolefin matrix materials were melt-blended with high-molecular weight paraffin waxes as phase change materials (PCM) on a lab-scale extruder. Afterwards, the compounds were converted into latent heat storage plates via compression molding. Detailed morphological investigations of the functional materials with Differential Scanning Calorimetry and Small Angle X-ray Scattering revealed various types of interaction between the applied components. Distinct correlations between the material formulation, the resulting overall compound morphology and the mechanical characteristics of the compounds were established. Moreover, a high long-term stability in terms of latent heat storage capacity, morphology and mechanical properties was ascertained, which emphasizes a high application potential of the functional materials. However, since the mechanical characteristics of the compounds deteriorated significantly upon the melting of the PCM (i.e. beginning storage of latent heat), latent heat storages in the form of polymeric compounds are not applicable as load-bearing component.

1. Introduction and scope

Due to its high heat of fusion, little or no sub-cooling, outstanding cycle stability, non-toxicity, environmental safety and low price, paraffin wax is a powerful phase change material (PCM). Moreover, paraffin wax is available on the market at a wide variety of melting temperatures [e.g. 1–3]. All these aspects make paraffin wax highly interesting for the production of efficient latent heat storages, which shall be applied for the heat management of buildings, where − depending on the application (e.g. enhancing the energy efficiency of buildings; assuring the thermal room comfort in buildings with solar thermal facades; thermal energy storage) – phase change temperatures between ~25 and 85 °C are required [e.g. 4–11]. In order to suppress the leaking of molten paraffin wax, the PCM has to be encapsulated properly [3]. Thus, the blending/compounding of the paraffin wax and convenient polymers (stabilization which fixes the PCM in compact form and suppresses leaking) represents a very promising and flexible approach [e.g. 12–15]. These so called shape-stabilized latent heat storages based on PCM-polymer compounds are cheap and easy to produce in any size and geometry by applying conventional polymeric processing techniques. The phase change temperature and temperature

range and the latent heat storage capacity can be adjusted by varying the paraffin type and concentration. PCM-polymer compounds have already been investigated and discussed extensively in the scientific literature [12–31]. However, most studies deal with PCM, which exhibit phase change temperatures below 60 °C. Typically, merely small amounts of functional materials are prepared by melt blending of the components in a mixer (kneading blocks). Moreover, the effect of blending a polyolefin matrix with paraffin wax on the overall mechanical characteristics as well as the application relevant long-term stability (static and dynamic thermal load) in terms of thermo-physical and mechanical characteristics are not yet addressed systematically and comprehensively in the scientific literature so far. Thus, the present study aims at formulating PCM-polymer compounds also with elevated phase change temperature ranges (> 60 °C) by applying industrial processing techniques. Different matrix materials (polyethylene (PE), ethylene/propylene copolymer (E/P) and polypropylene (PP)) as well as paraffin waxes (different molecular weight and thus melting temperature) are blended/compounded on a lab-scale extruder. The process ability, the interactions between wax and matrix polymer as well as the effect of the wax type on the morphology, thermo-physical and mechanical characteristics of the compounds are examined in detail.

Specific focus is on assessing the application relevant thermo-physical and mechanical long-term stability of the functional materials.

2. Experimental

2.1. Materials

The matrix materials were selected according to maximum operating temperature, compatibility with the applied phase change materials ((PCM) paraffin waxes; see below) and price. Phase change temperatures below 90 °C allow for the application of cost-efficient commodity plastics (< 2 €/kg) such as polyethylene, polypropylene and copolymers thereof, which exhibit a long term service temperature range between 80 and 130 °C. Thus, as matrix materials high density polyethylene (HDPE) HE1123 (MFR 8.0 g/10 min (2.16 kg and 190 °C)) – in the following referred to as PE –, ethylene/propylene copolymer (E/P) BB412E (MFR 1.3 g/10 min (2.16 kg and 230 °C)) k in the following referred to as E/P –, and polypropylene (PP) HD905CF (MFR 6.5 g/10 min (2.16 kg and 230 °C)) – in the following referred to as PP – were selected. All matrix materials were supplied by Borealis Polyolefine GmbH (Linz, AT). The paraffin waxes Sasolwax 3456 (supplied by Sasol Germany GmbH (Hamburg, DE); melting peak temperature ~60 °C) – in the following referred to as PCM/S – and Rubitherm RT 82 (supplied by Rubitherm Technologies GmbH (Berlin, DE); melting peak temperature 82 °C) – in the following referred to as PCM/R – were selected as PCM. All materials were used as received without any further modification.

2.2. Processing and sample preparation

The PCM-polymer compound (5 kg) was produced by mixing PE, E/P, or PP with PCM/S and PCM/R, respectively, on a semi-industrial compounder (synchronous twin screw-extruder ZSK25 (Coperion GmbH, Stuttgart, DE)). The screw speed was 250 rpm and the material throughput was 6 kg/h. The processing, the tailoring of the PCM concentration and the production of homogeneous compounds was rather difficult by applying conventional gravimetric metering: the significant differences in the melt viscosity of matrix and PCM at the standard matrix processing temperatures provoked a distinct phase separation (the effect was detected for all applied material combinations). Consequently, the PCM spilled through the extruder vents, especially if the PCM concentration exceeded 30 wt.%. As a first measure the processing temperatures were changed to reduce the viscosity difference between the materials while maintaining a homogeneous mixture and a good post-processing (pulling) quality. The selected temperature profiles of the extruder are presented in Table 1. Secondly, the compounding was done in two steps: initially a compound, which exhibited a PCM concentration of ~20–25 wt.% was produced. In order to increase the PCM concentration, this compound was further compounded with PCM. By this way mixtures which exhibit a PCM concentration of up to 40 wt.% (based on compound weight) were produced.

Afterwards, the compounds were melt-pressed into plates with dimensions of $160 \times 160 \times 0.8$ mm^3 by vacuum press molding (P 200 PV (Dr. Colin GmbH, Ebersberg, DE)). The molding temperature was 195 °C. The processing parameters are summarized in Table 2. The

Table 1
Temperature profile of the synchronous twin screw-extruder ZSK25 (Coperion GmbH, Stuttgart, DE) for the compounding process.

Zone		1	2	3	4	5	6
Temperature °C	PCM/S-polymer compounds	135	155	160	170	175	175
	PCM/R-polymer compounds	135	155	160	165	170	165

Table 2
Parameters of the compression molding process.

Phase	1	2	3	4	5
Function	Heating (melting)	Compression (shaping)			Cooling (solidification)
Time [min]	15	5	3	2	20
Temperature [°C]	195	195	195	195	20
Pump pressure (PE,E/P/PP) [bar]	2/1	45/65	65/100	100/150	100/150
Surface pressure (PE,E/P/PP) [N/cm^2]	1/0.5	23/33	33/50	50/75	50/75

produced samples along with their nomenclature are outlined in Table 3.

Investigations regarding the long-term stability covered the exposure of samples (plates) to static thermal load and thermal cycling, respectively, followed by analyzing their weight, thermo-physical and mechanical characteristics. Thus, tensile test specimens of the S2 type (DIN 53504) with an overall length of 75 mm were machined from the polymer plates with a puncher and fixed on grill grids using paper clips. The exposure to static thermal load (hot air) was done in a standard heating furnace (Thermo Fischer Scientific Inc., Waltham, MA, US). The exposure temperature was 80 °C for compounds produced from PCM/S and 100 °C for compounds produced from PCM/R. The sampling was done after 10, 20, 50, 100, 200, and 500 h. The thermal cycling was done using a climatic exposure test cabinet VC7020 (Vötsch Industrietechnik GmbH, Balingen, DE). The samples were heated/cooled between 10 and 80 °C (compounds produced from PCM/S) and between 10 and 100 °C (compounds produced from PCM/R), respectively. The heating/cooling rate was 1 K/min, whereas the relative humidity was not regulated. The sampling was done after 10, 20, 50, 100, 200, and 500 cycles.

2.3. Material characterization

2.3.1. Thermo-physical properties

The thermophysical characteristics (solid state transition temperature, melting temperature, heat of fusion) of PCM, polymer matrix, and PCM-polymer compounds (granulates) as well as of the samples (plates) which were exposed to static and dynamic thermal load (Section 2.2) were determined by Differential Scanning Calorimetry (DSC). Thermograms were recorded under static air on a DSC1 (Mettler Toledo GmbH, Schwerzenbach, CH) in the temperature range between 10 and 120 °C (PCM) and 200 °C (matrix and compound), respectively. A heating/cooling rate of 10 K/min was applied. 40 μl aluminum crucibles were used. The sample mass was 10 ± 1 mg. The instrument was calibrated using the onset temperatures of melting as well as the melting enthalpy of indium and zinc standards. All evaluations were done on thermograms from second heating according to ISO 11357-3. The presented data represent the average of three measurements. The PCM concentration (w_{PCM}) was determined via the heat of fusion according to Eq. (1):

$$W_{PCM} = (\Delta H_{m,PCM-C})/(\Delta H_{m,PCM-P}) \times 100 \, [\%] \tag{1}$$

where $\Delta H_{m,PCM-P}$ and $\Delta H_{m,PCM-C}$ denote the heat of fusion of PCM pure and in the compound, respectively. The theoretic overall heat of fusion of the compound ($\Delta H_{m,calc}$) for the actual PCM concentration was determined via the additive rule given in Eq. (2):

$$\Delta H_{m,calc} = W_{E/P} \times \Delta H_{m,E/P} + W_{PCM} \times \Delta H_{m,PCM-P} \tag{2}$$

where $\Delta H_{m,E/P}$ and $\Delta H_{m,PCM-P}$ are the heat of fusion of matrix and pure PCM, respectively, and $w_{E/P}$ and w_{PCM} are the weight fractions of