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Shape Stabilised Phase Change Materials (SSPCMs): High Density Polyethylene and Hydrocarbon Waxes

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Abstract - Shape stabilised phase change materials (SSPCMs) based on high density polyethylene (HDPE) with high (H-PW, $T_m=56-58$ °C) and low (L-PW, $T_m=18-23$ °C) melting point waxes were prepared by melt-mixing in a twin-screw extruder and their potential in latent heat thermal energy storage (LHTES) applications for housing assessed. The structure and morphology of these blends were investigated by scanning electron microscopy (SEM). Both H-PW and L-PW were uniformly distributed throughout the HDPE matrix. The melting point and latent heat of the SSPCMs were determined by differential scanning calorimetry (DSC). The results demonstrated that both H-PW and L-PW have a plasticisation effect on the HDPE matrix. The tensile and flexural properties of the samples were measured at room temperature (RT, 20 ± 2 °C) and 70 °C, respectively. All mechanical properties of HDPE/H-PW and HDPE/L-PW blends decreased from RT to 70 °C. In all instances at RT, modulus and stress, irrespective of the mode of deformation was greater for the HDPE/H-PW blends. However, at 70 °C, there was no significant difference in mechanical properties between the HDPE/H-PW and HDPE/L-PW blends.

Keywords: Shape stabilised phase change materials; High density polyethylene; Wax; Energy storage

INTRODUCTION

Phase change materials (PCMs) are substances with a high heat of fusion which, through melting and solidifying at certain temperatures, are capable of storing or releasing large amounts of energy [1]. Shape stable phase change materials (SSPCMs) based on high density polyethylene (HDPE) and wax as latent heat storage systems have gained great interest in many applications such as in solar energy systems and in energy-conserving buildings [2,3]. Wax is mainly consisted of mixtures of linear chain alkanes C_nH_{2n+2} ($n=1-100$). Increased length of the carbon atom chains results in a higher melting temperature of the material [4]. Waxes with different melting points have been used for SSPCMs. Inaba and Hu described the testing methods for the thermo-physical properties of HDPE/wax blends. The wax used consisted mainly of pentacosane ($C_{25}H_{52}$, $T_m=54.2$ °C) [5]. Lee and Choi studied the durability of these materials by investigation of the seepage behaviour of the SSPCM with the wax ($C_{24}H_{50}$) for LHTES [6]. Kaygusuz and Sari investigated the thermal properties of the SSPCMs for heating systems based on HDPE and four different types of waxes with melting points in the ranges, 42-44 °C, 48-50 °C, 56-58 °C, and 63-65 °C, respectively [7]. Molefi *et al.* studied the difference in thermo-physical properties of SSPCMs based on low density polyethylene, linear low density polyethylene and HDPE blended with a soft wax ($T_m=40-60$ °C) for LHTES [8]. Mngomezulu *et al.* prepared an SSPCM blend by mixing HDPE, soft Fisher-Tropsch wax ($T_m=40-60$ °C) and alkali-treated wood flour for LHTES. The natural filler enhanced mechanical

properties and thermal stability [9]. Quanying prepared SSPCMs based on HDPE with four types of waxes with the melting points, 26.6 °C, 25.5 °C, 24 °C and 20.8 °C, respectively. The SSPCMs prepared had large latent heats and could be used for wallboard [10].

Therefore, it is worthwhile to note that SSPCMs can be used in certain applications by selecting a suitable wax in terms of melting temperature and latent heat. However, there is little fundamental research on the impact of different melting point of waxes on the thermo-physical properties of SSPCMs blends and no study about the mechanical properties of the SSPCMs when the wax is in melt state while the HDPE is in solid state. In this sense, the objective of this study is to prepare two different types of SSPCMs based on HDPE/H-PW and HDPE/L-PW and investigate their micro-structure and thermo-physical properties. The mechanical properties of the SSPCMs at RT and 70 °C are investigated, so the effect of the wax when in the liquid and solid state while part of the blend can be assessed.

EXPERIMENTAL

Materials

The HDPE (Marlex® HHM TR-144 Polyethylene) used in this study was supplied by Qatar Chemical Company LTD in pellet form, with a MFI=0.18 g/10 min (190 °C/2.16kg). The H-PW was supplied in pellet form by TCS Biosciences Ltd. It has a melting point range around 56-58 °C. The L-PW wax was supplied by Rubitherm Technologies GmbH and has a melting range around 18-23 °C.

Sample preparation

The ratios of the blends of HDPE/H-PW and HDPE/L-PW prepared are shown in Table 1. All the blends were melt mixed using a Dr Collin ZK25 twin-screw extruder. For HDPE/H-PW blends, the temperature profile of the extruder was 120, 150, 170, 170, 170, 170 °C from the feeder (zone 1) to the extruder end (zone 6). The extruder screw speed was set at 175 rpm. For HDPE/L-PW blends, the temperature profile of the extruder was 150, 165, 150, 160, 160, 160 °C from the feeder (zone 1) to the extruder end (zone 6). The extruder screw speed was set at 300 rpm. The extruded blends obtained were compression moulded into 2 mm (for tensile test) and 4 mm (for flexural test) thick sheets in Dr. Collin P200P platen press machine. The sheets were preheated at 170 °C for 2 minutes between the platens then formed using a pressure of 70 bar for 5 minutes. The sheets were then quenched from 170 °C to 120 °C in 2 minutes and from 120 °C to 50 °C in 3 minutes, then cooled to room temperature.

Characterization & Testing Methods

SEM: The blend morphology and surfaces were examined using a JEOL 6500 JSM840A scanning electron microscope with operating voltages of 3.0 kV. The samples used were taken from compression moulding samples. Specimens were mounted on 25 mm×1 mm aluminium discs using Araldite rapid epoxy adhesive, allowed to cure for 24 h and subsequently sputtered with 10-20 nm thick coating of gold on the sample surface to impede charging effects and induce conductivity prior to SEM examination.

DSC: Measurements were performed using a Perkin-Elmer DSC 6 instrument under flowing nitrogen (flow rate 20 mL min⁻¹) for all samples. Samples (5–10 mg) were sealed in aluminium pans and heated from 30 to 160 °C at a heating rate of 10 K min⁻¹, and cooled at the same rate.

Mechanical testing: Tensile testing was carried out using an Instron 5564 twin column tensile tester with a 5 kN load cell. A minimum of five dumbbell samples for each blend composition were loaded to the maximum strain of 1 mm at crosshead speeds of 5 mm min⁻¹ at RT and 70°C in an atmosphere oven, respectively. The dumbbell samples had a total length of 75mm, a gauge length of 24 mm, a neck width of 5mm, and a thickness of 2 mm. All tensile properties (including Young's modulus, and yield stress) were extracted from stress-strain curves using Merlin software (Version 5.51). The flexural modulus and stress of the samples were measured in three-point bending tests using the same machine as for tensile testing. The crosshead speed was set to 5 mm min⁻¹ and the test specimens with dimensions of 80 mm × 10 mm × 4mm were used.

TABLE 1 - Compositions of blends prepared

Sample code	HDPE (wt %)	H-PW (wt %)	L-PW (wt %)
HDPE ₅₀ H-PW ₅₀	50	50	0
HDPE ₃₅ H-PW ₆₅	35	65	0
HDPE ₂₅ H-PW ₇₅	25	75	0
HDPE ₆₀ L-PW ₄₀	60	0	40
HDPE ₅₀ L-PW ₅₀	50	0	50
HDPE ₃₅ L-PW ₆₅	35	0	65

RESULTS AND DISCUSSION

SEM

By way of example, the surfaces of the HDPE₃₅H-PW₆₅ and HDPE₃₅L-PW₆₅ blends are shown in Figure 1 a) and b), respectively. The white striations are HDPE while the black component is the wax phase [5]. Both of the images indicate that the HDPE forms a three dimensional netted structure and the waxes are well dispersed within it. The HDPE provides mechanical strength to the whole compound, and so the composite keeps its shape in the solid state [2]. There are some holes as indicated by arrows in Fig.1 (b) in the L-PW blend surface, which may be caused by air trapped during the manufacturing process.

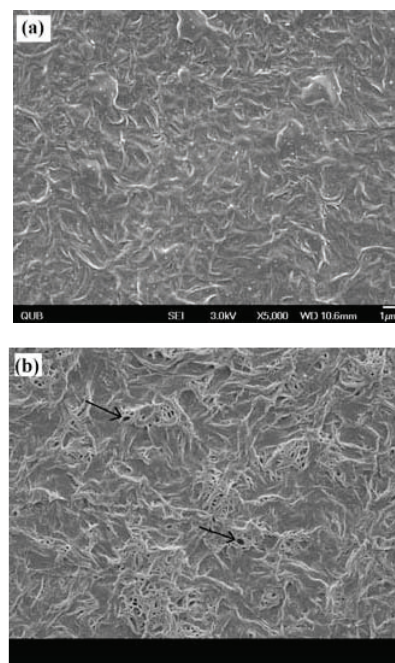


FIGURE 1 - SEM micrographs: (a) HDPE₃₅H-PW₆₅; (b) HDPE₃₅H-LW₆₅.

DSC

As shown in Figure 2 a) and b), both the H-PW and L-PW was observed to melt separately from the HDPE. The melting temperatures of H-PW remained fairly constant, within experimental error, with increasing wax content in all blends. However, an increase in wax content resulted in a decrease in the melting temperatures of HDPE. The same trends were found for the HDPE/L-PW blends. This is probably the result

of the plasticisation effect of both the H-PW and L-PW on the HDPE matrix and the wax component altering HDPE crystallization behaviour [9].

As it can be seen from Table 2, the experimentally observed melting enthalpies of the H-PW are lower than the calculated enthalpies for all wax contents studied. The calculated enthalpies were determined from the melting enthalpy of the unblended wax and the fractions of wax in the HDPE/H-PW blends. The difference between the two enthalpies decreased with an increase in wax content. These observations indicate that some portion of the H-PW wax partially co-crystallised with HDPE [9]. The trend was less pronounced in HDPE/L-PW blends as can be seen from the data in Table 3, and requires further investigation.

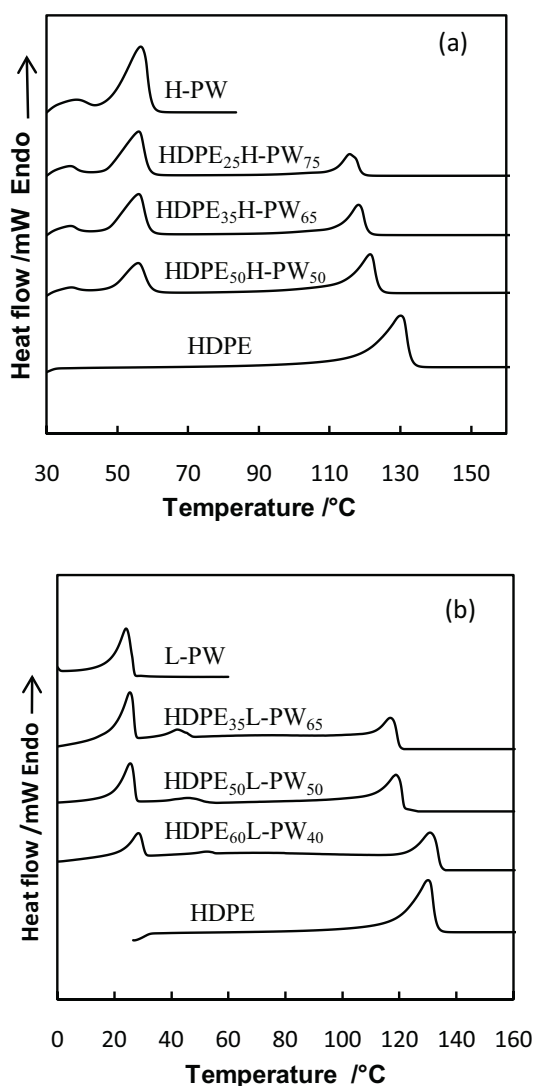


FIGURE 2 - DSC heating curves for (a) HDPE/H-PW blends and (b) HDPE/L-PW blends

TABLE 2 -Thermal characteristics of H-PW, HDPE and HDPE/H-PW blends from DSC (melting).

HDPE/ H-PW	T_o (°C)	ΔH_m (Jg ⁻¹)	ΔH_c (Jg ⁻¹)	T'_o (°C)	$\Delta H'_m$ (Jg ⁻¹)
100/0	--	--	--	120	151
50/50	48	47	60	114	75
35/65	47	74	78	112	57
25/75	47	89	90	111	42
0/100	48	121	121	--	--

T_o , ΔH_m and ΔH_c are the melting onset temperature and observed melting enthalpy and calculated enthalpy of H-PW, respectively. T'_o and $\Delta H'_m$ are the melting onset temperature and observed melting enthalpy of the HDPE, respectively.

TABLE 3 -Thermal characteristics of L-PW, HDPE and HDPE/L-PW blends from DSC (melting).

HDPE/ L-PW	T_o (°C)	ΔH_m (Jg ⁻¹)	ΔH_c (Jg ⁻¹)	T'_o (°C)	$\Delta H'_m$ (Jg ⁻¹)
100/0	--	--	--	120	151
60/40	19.5	43	49	112	80
50/50	19.5	61	62	110	78
35/65	19.5	70	79	109	61
0/100	18	123	123	--	--

T_o , ΔH_m and ΔH_c are the melting onset temperature and observed melting enthalpy and calculated enthalpy of L-PW, respectively. T'_o and $\Delta H'_m$ are the melting onset temperature and observed melting enthalpy of the HDPE, respectively.

Mechanical testing

The results of the mechanical tests showed that the presence of wax generally causes a reduction in tensile and flexural modulus and stress, which is expected as a result of the more brittle nature of the low molecular weight waxes.

As is shown in Figure 3 a) and b), Young's modulus and yield stress of the HDPE/H-PW blends was greater than HDPE/L-PW blends at RT. This is associated with the higher degree of crystalline content of the H-PW based blends compared with that of L-PW, as L-PW is in molten state at RT. The same trends were observed in the case of flexural testing, see Figure 4 a) and b), and can be explained in a similar way. However, in all instances at 70 °C, modulus and stress, irrespective of the mode of deformation, there was no significant difference between the two sets of blends. At 70°C both waxes are in liquid state, since the movement of polymer chains mainly occurs in the amorphous part, shorter wax chains in the amorphous phase of polymer will promote chain mobility, which implies that the polymer chains are easier to draw from the lamellae [11]. On the other hand, the HDPE itself become more soften as some short chains start to become mobile at 70°C, which may induce a change in crystallinity compared with that at RT.

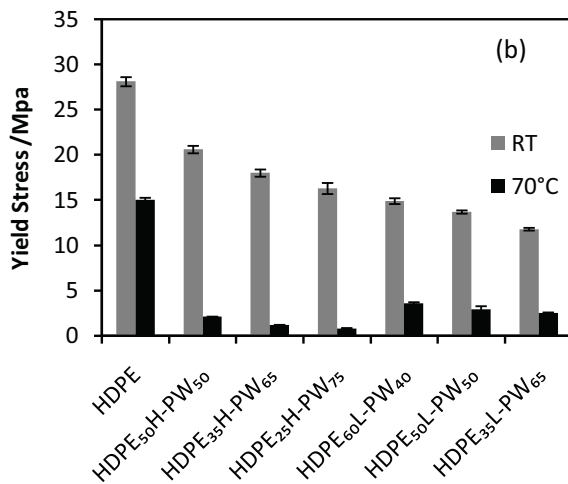
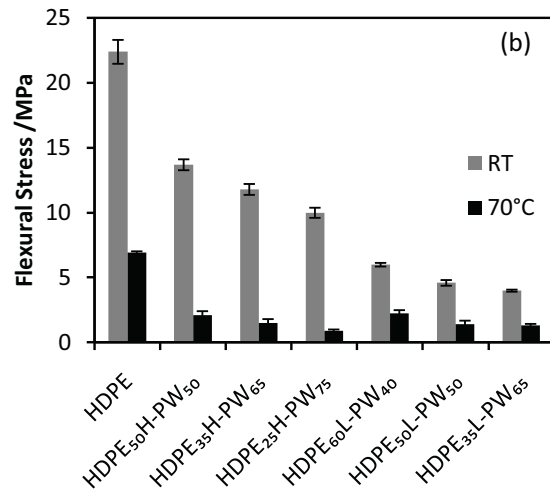
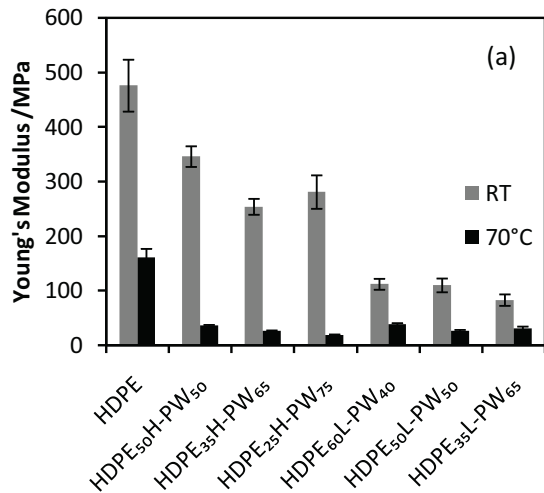


FIGURE 3- Variation in; (a) Young's modulus and (b) Yield stress for HDPE/wax blends at RT and 70°C.

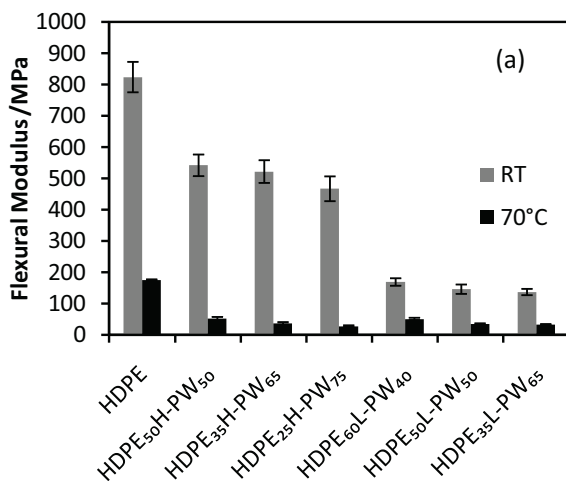


FIGURE 4 - Variation in; (a) Flexural modulus and (b) Flexural stress for HDPE/wax blends at RT and 70°C.

CONCLUSIONS

Both the H-PW and L-PW waxes could be mixed uniformly with HDPE to form SSPCMs. The SSPCMs had large latent heat, as determined from DSC analysis and thus these materials are suitable for LHTES applications. The mechanical properties of the blends decreased from RT to 70 °C for both HDPE/H-PW and HDPE/L-PW blends. The tensile and flexural strength of HDPE/H-PW blends were much greater than HDPE/L-PW blends at RT, but similar at 70 °C. The change in the mechanical properties at elevated temperatures should be taken into consideration when designing SSPCMs as wallboard in buildings for warmer climates.

REFERENCES

1. A.M. Khudhair; M.M. Farid. *Energ Convers Manage.* 2004, 45, 263.
2. A. Sari. *Energ Convers Manage.* 2004, 45, 2033.
3. G. Susman; Z. Dehouche; T. Cheechern; S.Craig. *Applied Thermal Engineering.* 2011, 31,717.
4. S. Himran; A. Suwono; A.G. Mansoori. *Energy Sources.* 1994, 16, 117.
5. H. Inaba; P. Tu. *Heat Mass Transfer.* 1997, 32, 307.
6. C.H. Lee; H.K. Choi. *Polymer composites.* 1998, 19, 704.
7. K. Kaygusuz; A. Sari. *Energ Source.* 2007, 29, 261.
8. J.A. Molefi; A.S. Luyt; I. Krupa. *Thermochim Acta.* 2010, 500, 88.
9. M. Mngomezulu; A. Luyt; I. Krupa. *J Appl Polym Sci.* 2010, 118, 1541.
10. Q. Yan; L. Li; D. Shen. *International Journal of Sustainable Energy.* 2010, 29, 87.
11. M.J. Hato; A.S. Luyt. *J Appl Polym Sci.* 2007, 104, 2225.