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Experimental investigations on heat transfer in phase change materials (PCMs)

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Abstract : This work focuses on the study of heat transfer mechanisms in composites materials which may be used for Latent Heat Thermal Energy Storage applications. Indeed they contain phase change material (PCM) which may absorb and release energy during thermal cycling. The PCM is paraffin microencapsulated in PMMA, the microencapsulation allows avoiding the flow of paraffin at liquid state. Samples with different weight fractions were prepared. Particles shape and distribution, and composites morphology were studied by Scanning Electron Microscopy (SEM). Differential Scanning Calorimetry (DSC) was used to perform measurements of phase changes temperatures and enthalpies. A periodic method (DICO) allowed measuring thermal conductivity (λ) and diffusivity (a) at different temperatures. Measurements were done at two temperatures away from phase change peaks. The interest of these samples is that thermophysical properties have been measured with the same method at two temperatures on solid composites containing solid or liquid paraffin.

Keywords :

Phase Change Materials, Thermal analysis, Thermophysical properties, Energy storage, DSC.

1. Introduction

Renewable energy is energy that comes from resources which are continually replenished such as sunlight, wind, geothermal heat…But one way to save energy is to store it. The use of phase change materials (PCM) is a solution to absorb, store and restore large amounts of heat avoiding energy consumption.

Different inorganic as well as organic substances have already been used for the processing of phase change materials [20]. Among the investigated PCMs, paraffins have been widely used for different Latent Heat Thermal Energy Storage (LHTES) applications due to their large latent heat and proper thermal characteristics such as little or no super cooling, low vapor pressure, good thermal and chemical stability, and self-nucleating behavior. The heat capacity of latent heat paraffin waxes is about $2.1\ Jg^{-1}K^{-1}$. Their melting enthalpy lies between 180 and $230\ Jg^{-1}$, which is quite high for organic materials. The combination of these two results in an excellent energy storage density. Waxes are also readily available and inexpensive [1].

Paraffin waxes have low thermal conductivity, around $0.2\ Wm^{-1}K^{-1}$ [17]. This results in a decrease of the rate of heat storage/retrieval during melting/solidification processes [2]. A wide range of investigations were carried out to enhance the thermal conductivity of the organic PCMs. The often used method is to disperse solid particles with high thermal conductivity, such as carbon nanofibers, metal particles and so on, or to insert the organic PCMs into metal matrix [3,4].

Microencapsulation allows to avoid the leakage of paraffin during the melting. The advantages of microencapsulated PCMs are (a) a protection of PCM against the influences of the outside environment, (b) an increasing specific heat transfer area, and (c) to permit the core material, due to coating, to withstand changes in volume of the PCM, as the phase change occurs [11,12]. The choice of the shell materials for the microencapsulation of paraffin plays an important role in regulating the properties of the microcapsules. Several polymers have been employed as shell materials, such as polyurethane [13], polystyrene [14,15] and poly(methylmethacrylate) (PMMA) [16]. At this time, the main manufacturer of PCM microcapsules is BASF. BASF manufactures its microcapsules from a polymerization process of a PCM emulsion.

The objective of the present study is to investigate the thermophysical properties of composite materials containing the phase change material (PCM) dispersed in a polymeric matrix. The phase change material used is a paraffin which has a phase change temperature of 26°C, microencapsulated in PMMA, and marketed by BASF. Polycaprolactone was chosen as polymeric matrix of composites because its melting temperature is below the PMMA softening temperature. The thermal conductivity and diffusivity were studied for different concentrations of filler (up to 50 wt%) at solid state (-10°C) and liquid state (35°C).

2. Experimental

2.1. Materials

In this study Polycaprolactone (PCL) CAPA® 6800 produced by Solvay has been used. It has a molecular weight of 80 000 g/mol. Its density is 1.14 g/cm^3, its glass transition is located at -60°C and its melting temperature between 58°C and 61°C. Its cristallinity is 67% and its Young's modulus is 190 MPa [5].

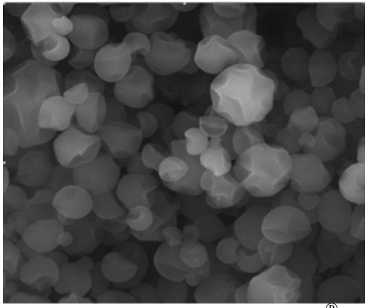

Figure 1: SEM micrographs of BASF Micronal® DS 5001 X.

Micronal® DS 5001 X from BASF® with a melting temperature of 26ºC has been used as the active CM component. Its common application is for summertime excessive heating protection in an operational range from 10 to 30°C. The overall storage capacity is approximately of 145 kJ/kg and its latent heat capacity of 110 kJ/kg. Its apparent density is approximately of 250 – 350 kg/m^3 [6]. Micronal® is formed by paraffin wax core and PMMA thin shell, it forms microcapsules. The shape of microcapsules is shown in figure 1. SEM observations have allowed to see that 7 µm micronals form aggregates of approximately 35 µm.

2.2. Sample preparation

The microcapsules of paraffin encapsulated in crosslinked PMMA were mixed with PCL to form composites. Several sets of mixtures were made for mass concentrations over the range of 10 to 50%. The mixtures were blended in the 30 ml mixing chamber of the blending machine (Brabender Plasticorder PLE 331, Germany) at 80 °C for 6 minutes at a mixing speed of 35 rpm. Samples of required shape we prepared by hot pressing in the laboratory press (Fontijne SRA 100, The Netherlands) at 80°C for 5 minutes and cooled slowly. Different proportions of the two basic components, micronals and PCL, were studied in order to obtain a material having a high heat of melting.

2.3. SEM

The morphology of composites was investigated by a Scanning Electron Microscope (SEM, JSM 6301F), all samples were examined at various magnifications.

2.4. Differential Scanning Calorimetry (DSC)

A Perkin-Elmer Diamond DSC differential scanning calorimeter was used with an intracooler. It was calibrated in temperature with indium, tin and benzyl. To measure phase change temperatures and enthalpies, samples were sealed in non-hermetic aluminum pans with lids. The weight of each sample was in the range from 10 to 20mg. Tests were performed between -20°C and 75°C at a heating rate of 10°C/min.

2.5. Thermophysical properties (device DICO)

A periodical method was used to estimate simultaneously thermal conductivity, diffusivity and specific heat of polymer composite materials. This method is based on the use of a small temperature modulation in a parallelepiped-shape sample (44 mm of side and 3 mm of thickness) and allows obtaining thermophysical parameters in only one measurement with their corresponding statistical confidence bounds [7]. The composite sample is fixed between two metallic plates. A good thermal exchange between the different plates and the sample is ensured by using a conducting grease. A parameter estimation technique is then applied to estimate simultaneously both thermal conductivity (λ) and diffusivity (a).

3. Results and discussion

3.1. Morphology of composites

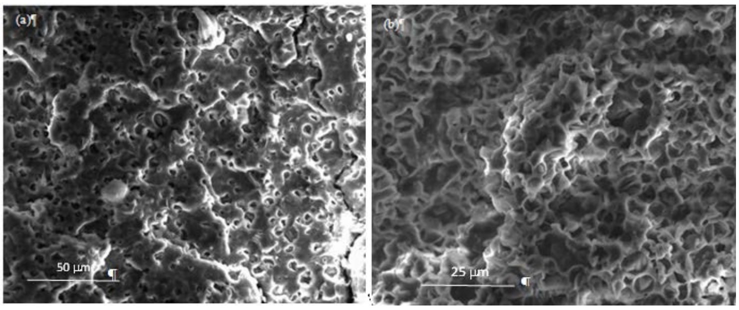

Figure 2: SEM micrographs of composites: (a) PCL / paraffin microcapsules (90/10 wt)
(b) PCL / paraffin microcapsules (50/50 wt).

A series of composites was prepared at different weight fractions of Micronal® ranged from 10 to 50wt.%. Samples were broken in nitrogen, the morphology of the composites was examined at the rupture face. Micrographs obtained by Scanning Electron Microscopy (SEM) are presented in figure 2. Composites morphology indicates a good dispersion of microcapsules in the polymer.

3.1. Differential Scanning Calorimetry

Microcapsules, PCL and composites were studied by DSC between -20°C and 75°C at 10°C/mn. For paraffin microencapsulated in PMMA two endothermic peaks are observed. The first peak located at 2°C may correspond to a solid-solid phase transition as can be seen on the n-heptadecane [18,19]. The second peak corresponds to the melting of the paraffin with an onset temperature near 26°C. The PCL is a semi-crystalline polymer, its melting is observed around 60°C.

Table 1 : Phase transitions temperatures and latent heat of Micronal® DS 5001 X from BASF®, PCL and composites obtained by DSC

Samples	Micronal® weight fraction (%)	Sample mass (mg)	Paraffin solid - solid transition		Paraffin melting		PCL melting	
			T_o (*°C*)	ΔH (*J/g*)	T_o (*°C*)	ΔH (*J/g*)	T_o (*°C*)	ΔH (*J/g*)
PCL	0	18.46					57.43	72.68
M10	10	17.14	0.43	0.94	25.81	9.60	57.44	64.31
M20	20	17.06	0.87	2.08	26.13	19.70	58.51	58.20
M30	30	14.92	0.89	3.32	25.85	29.79	57.55	51.15
M40	40	17.99	1.26	4.50	25.73	41.23	57.72	44.19
M50	50	16.77	1.14	5.16	25.99	47.33	57.26	38.53
micronals	100	6.12	1.99	12.43	26.31	109.40		

The extrapolated peak onset temperature (T_o) and latent heat obtained by DSC measurements are listed in table 1. For PCL/micronals composites, we found all endothermic phenomena associated with the phase changes of various constituents, the peak area varies in proportion to their mass fractions (table 1).

As visible by SEM, Micronal® are well dispersed in PCL. The onset temperature of the three peaks remain the same for all composites. The area of the melting peak of PCL decreases when PCL quantity decrease. The latent heat of melting of paraffin in each composite has been calculated and is presented in table 2.

3.2. Thermophysical properties

Thermal conductivity (λ) and diffusivity (a) measurements were performed at -10°C and 35°C on all composites. These temperatures were chosen where none endothermic phenomenon has been observed in DSC. The initial objective was to obtain the thermophysical properties of composites when the paraffin is solid and liquid. The values of the thermal conductivity, diffusivity, heat capacity, density and phase change temperatures of the constituents of composites are presented in table 2.

Table 2: Thermal conductivity, diffusivity, heat capacity, density and phase change temperatures of the constituents of PCL / microencapsulated paraffin composites

		Thermal conductivity *($W.m^{-1}.K^{-1}$)*	Thermal diffusivity *($\times 10^{-7}\ m^2s^{-1}$)*	Heat capacity *($J\ .g^{-1}.K^{-1}$)*	Density *($g.cm^{-3}$)*	Phase change temperatures
Micronal®		LT : 0.24 HT : 0.15 [8]		LT : 1.6105 HT : 1.995	0.92	$T_m = 26°C$
PMMA		0.21 [9,10]			1.18	$T_g = 90°C$
PCL	-10°C	0.246 ± 0.007	1.439 ± 0.21	1.545 ± 0.005	1.11	$T_g = -60$ °C $T_m = 58$ °C
	35°C	0.219 ± 0.006	1.231 ± 0.15	1.60 ± 0.20		

The evolution of thermal conductivity and diffusivity with filler volume fraction is shown in figure 3 (a) and (b), respectively. At -10°C, an increase of thermal conductivity (λ) and thermal diffusivity (a) with increasing filler volume fraction was observed, while at 35°C the opposite happens. Which is normal, when we compare the results with the values of the thermal conductivity of paraffin and PCL found in literature (table 2).

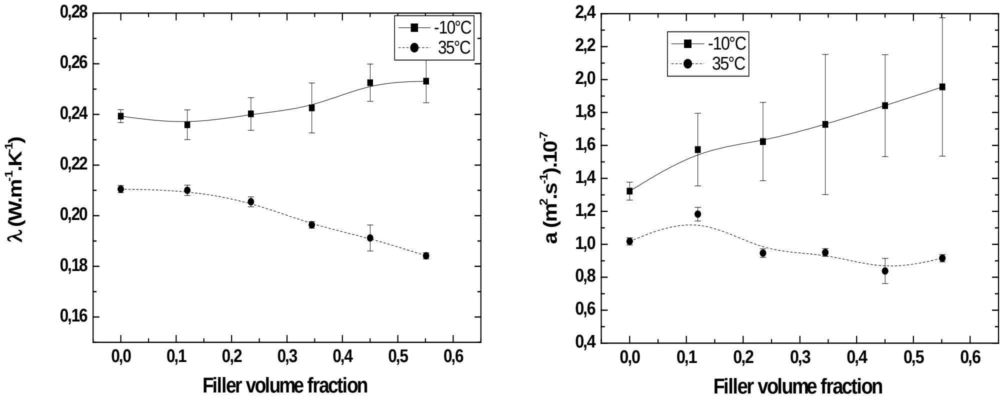

Figure 3: Effect of filler content and temperature on thermal conductivity (a) and diffusivity (b) of PCL / microencapsulated paraffin composites.

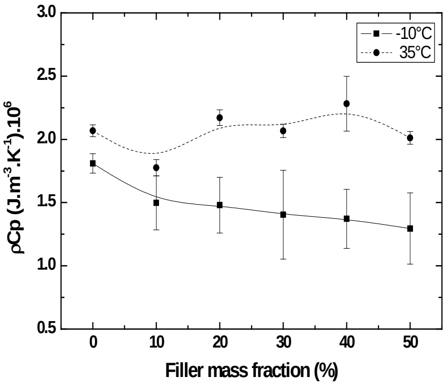

Figure 4: ρCp of PCL / microencapsulated paraffin composites at -10°C and 35°C

As shown in figures 3 (a) and (b) respectively, the influence of the temperature on the thermophysical properties of composites is not negligible. It is observed that the thermal conductivity decreases with increasing temperature which is normal because on the one hand, for a semicrystalline polymer, the thermal conductivity decreases steadily with increasing temperature below the melting point [9] and, moreover, as can be seen in table 2, paraffin see also a reduction of its thermal conductivity especially when it changes its state from solid to liquid (ie above 26°C). However, the relative thermal diffusivity uncertainties are more significant (up to 10%) at higher than those noted for the thermal conductivity (up to 3%). From the values of thermal conductivity and diffusivity obtained with the DICO device, ρC_p can be calculated (C_p = □/□a). Figure 4 of volumic heat capacity (ρCp) as function of temperature. It can be seen that when the temperature increases, a significant increase of the factor (ρCp) is noted.

4. Conclusion

This study is focused on the thermophysical characterization of a new composite material containing microencapsulated paraffin acting as a phase change materials (PCM) for Latent Heat Thermal Energy Storage applications. Thermophysical properties have been studied for different concentrations at different temperatures. Two measurement methods were used, the first is DSC and the second was developed in the laboratory (DICO). DSC and DICO are complementary characterization methods. DSC was used to measure melting temperatures, latent heats of PCL/Micronal® composites. DICO was used to measure thermal conductivity and diffusivity outside from melting phenomena. The material characterization was performed on a temperature range that extends from -20°C to 75°C. This complete characterization of composite samples may allow modeling the thermal response of these samples in the case of Latent Heat Thermal Energy Storage applications

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