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POLYMERIC PHASE CHANGE MATERIALS FOR THERMAL ENERGY STORAGE

Among polymeric phase change materials a low-molecular weight polyethylene has been characterised based on differential scanning calorimetry (DSC) and DSC with modulated temperature. Such a polymer can be used for environmentally-friendly energy storage. The enthalpy of melting and crystallisation of the polyethylene were 77–136 and 69–129 J/g, respectively, and the phase transition temperature was in two ranges, i.e., from 92.5 to 113.9 °C and from 74.0 to 98.9 °C. The quantity of the non-reversible component of heat flow is small which testifies to the recrystallisation and reversibility of the process.

1. INTRODUCTION

A proper management of thermal energy requires both a gradual replacement of traditional energy sources by alternative ones as well as development of effective, environmentally-friendly and sustainable ways of energy storage. The latter may be accomplished by design and fabrication of thermal energy storing materials (TESMs) which belong to the phase change materials (PCMs) that are able to store energy in the form of sensible heat, latent heat and heat associated with a chemical reaction [1], [2]. A major problem in using traditional PVMs, such as inorganic salt hydrates and their mixtures, stems from the fact that most of them melt incongruently, i.e., they melt down into a saturated aqueous phase and a solid phase that is generally a lower hydrate of the same salt. The other problem is that salt hydrates have poor nucleating properties, resulting in the supercooling of the liquid salt hydrate prior to freezing. A third problem is corrosion, which means that they have short service lives or high packing and maintenance costs [3], [4]. For these reasons in recent years there has been a considerable interest in developing novel polymeric materials that would show better properties of thermal energy storage than traditional ones. One of the most

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promising compounds is poly(ethylene oxide) (PEO) due to its relatively large heat of fusion, congruent melting behaviour, non-corrosiveness and wide range of melting point [5], [6]. Another polymeric material that can be applied is polyethylene (PE) [7]. Exact data on thermal phenomena can be obtained by using differential scanning calorimetry (DSC) that makes it possible to determine precisely the equilibrium regions, phase transitions and associated temperatures. Shape of the thermal signal may provide valuable information about the course of phase transition and evolution of compositional homogeneity.

In this paper, we deal with melting behaviour of low-molecular weight polyethylene investigated with DSC and MT-DSC techniques.

2. EXPERIMENTAL

2.1. MATERIALS

Polyethylene (PE) with molecular weight of 4000, 15000 or 35000 was produced by Aldrich (Steinheim, Germany).

2.2. TECHNIQUES

Differential scanning calorimetry (DSC). For the DSC measurements a Netzsch DSC 200, operating in a dynamic mode, was employed. Samples of ca. 4 mg weight were placed in sealed aluminium pans. The heating/cooling rate of 10 K/min was applied. Argon was used as an inert gas with the flow rate of 30 cm³/min. Prior to its use the calorimeter was calibrated with mercury and indium standards; an empty aluminium pan was used as reference. Liquid nitrogen was used as a cooling medium.

Step-scan alternating DSC (SSA-DSC). Step-scan alternating DSC investigations were performed by using a Perkin-Elmer Pyris Diamond DSC. Measurements were done in closed aluminium pans with sample mass of ca. 8 mg under argon flow of 20 cm³/min. Prior to its use the calorimeter was calibrated with indium standard. After a series of optimisation measurements, the following parameters have been chosen: length of the isothermal segment (t_{iso}) = 48 s; linear heating rate in dynamic segments (β) = 2 K/min and temperature jump between two subsequent isothermal segments (step) = 1 deg.

Modulated DSC offers extended capabilities of temperature profile by, e.g., superimposing a sinusoidal wave on the normal linear temperature range

$$T = T_0 + \beta t + B \cdot \sin(\omega t), \quad (1)$$

where:

T – the program temperature,

T_0 – the initial temperature,

β – the underlying average heating rate,

B – the amplitude of the temperature modulation,

$\omega = 2\pi/p$ [1/s] – the angular frequency of modulation.

The superimposition may be also in the form of oscillations, dynamic–isothermal heating and cooling segments, saw–tooth profile, etc.

The equation to describe heat flow is derived from a simple equation based on thermodynamic theory in which

$$dQ/dt = C_{pt} \cdot dT/dt + f(t, T), \quad (2)$$

where:

Q – the amount of heat absorbed by the sample,

C_{pt} – the thermodynamic heat capacity,

$f(t, T)$ – some function of time and temperature that governs the kinetic response of any physical or chemical transformation [8], [9].

3. RESULTS AND DISCUSSION

The degree of crystallinity (X_c) of PE samples was calculated on the basis of DSC measurements, assuming that the enthalpy of melting of 100% crystalline polymer is equal to 293.6 J/g, and the results are shown in the table. It can be seen that PE with the molecular weight of 15000 has the highest degree of crystallinity, i.e., the most regular crystalline structure.

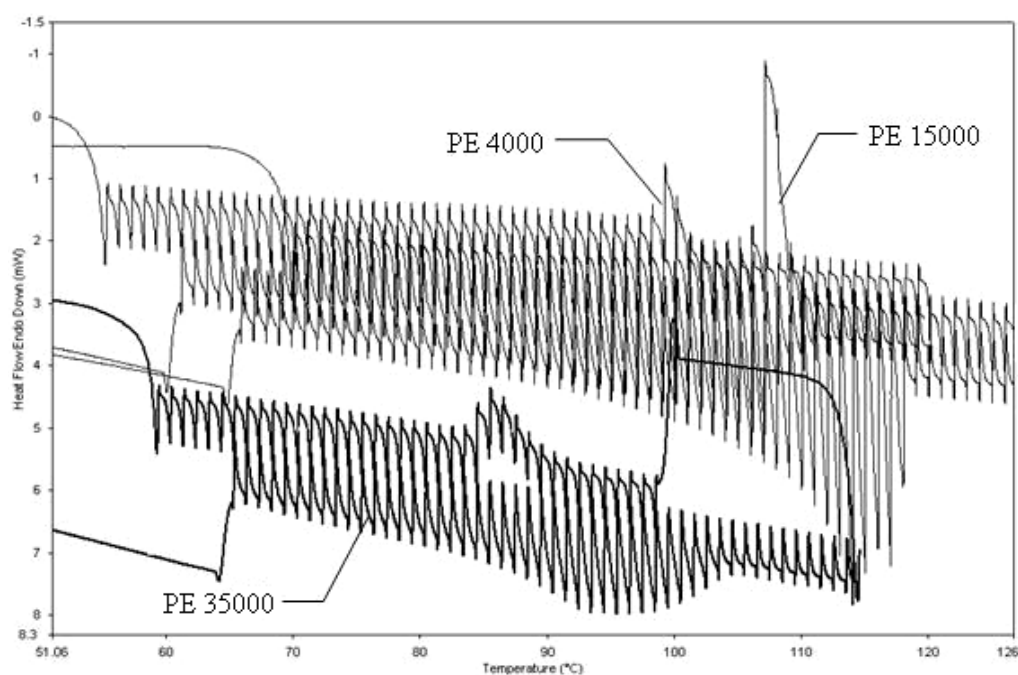
Table 1

Degree of crystallization (X_c) of PE	
PE	X_c [%]
PE 4000	38.8
PE 15000	46.3
PE 35000	26.2

In the next stage, SSA-DSC investigations were performed (the figure).

DSC profiles with modulated temperature show that non-reversing component obtained due to the melting of PE occurs in a small quantity. The profiles testify to the recrystallisation and reversibility of the process. Generally, the heat of phase transition in the range of 69–136 J/g is great enough to be used for space heating, for time shift-

ing of a maximum demand in energy supply systems, for internal heat gain which would otherwise be wasted (such as that derived from solar radiation, lights and appliances) and for improving the efficiencies of burners, chillers and heat pumps [10], [11]. Polymeric materials capable of storing thermal energy fulfil a number of criteria such as high heat of fusion and thermal conductivity, high specific heat capacity, small volume change, non-corrosiveness and non-toxicity. These advantages make them suitable for modern renewable energy installations applied, e.g., in order to preserve historical cities.



DSC results of the melting and crystallisation of PE with different molecular weights

4. CONCLUSIONS

By using DSC method it has been found that PE 15000 is characterised by the highest degree of crystallinity and by the highest melting temperature, as compared with other PE samples tested. The non-reversible component of the melting process (as evidenced by MT-DSC data) is obtained in a small quantity which testifies to the recrystallisation and reversibility of the whole process.

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FAZOWO ZMIENNE MATERIAŁY POLIMEROWE
DO AKUMULACJI ENERGII CIEPLNEJ

Polietylen o małym ciężarze cząsteczkowym jako jeden z fazowo zmiennych materiałów polimerowych został scharakteryzowany za pomocą metody różnicowej kalorymetrii skaningowej (DSC) oraz DSC z modulacją temperatury. Jest on stosowany do przyjaznej dla środowiska naturalnego akumulacji energii. Entalpia topnienia i krystalizacji wynosiła odpowiednio 77–136 i 69–129 J/g, a temperatury przemian fazowych – 92.5–113.9 i 74.0–98.9 °C. Wielkość wpływu składowej nieodwracalnej strumienia ciepła była niewielka, co potwierdza, że miała miejsce rekrytalizacja, i świadczy o odwracalności procesu.