Energy Conversion and Management 87 (2014) 400–409

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Phase change materials based on high-density polyethylene filled with microencapsulated paraffin wax

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ARTICLE INFO

Article history:
Received 20 February 2014
Accepted 18 June 2014
Available online 1 August 2014

Keywords:
Paraffin wax
Microencapsulation
High density polyethylene
Blends
Phase change materials

ABSTRACT

A modified *in situ* polymerization microencapsulation procedure for the preparation of microcapsules with paraffin wax cores (43 wt.%) and melamine–formaldehyde resin shells having a uniform size distribution and a spherical shape with average diameters of approximately 15 μm was developed. The high-density polyethylene/microcapsule blends were prepared via two routes. In the first case, the dry high-density polyethylene powder covered by microcapsules was simply hot pressed, whereas, in the second case, the dry high density polyethylene/capsule powder was first blended in the molten state to obtain better homogeneity before hot pressing. It was observed that both systems behave qualitatively the same with comparable mechanical properties and thermal behavior.

The thermal stability of high-density polyethylene/microcapsule blends characterized by thermogravimetry is significantly lower than that of neat high-density polyethylene. The selected characteristic temperatures of degradation decreased by more than 200 °C compared with the related temperatures for neat high-density polyethylene.

An analysis based on Differential Scanning Calorimetry revealed separated melting and crystallization behavior of wax within the capsules and high density polyethylene in the blends. The enthalpies of melting and crystallization are proportional to the amount of individual components in the material. The capsules have a strong plasticizing effect on the high density polyethylene, resulting in a significant decrease in the melting and crystallization temperatures. The plasticizing effect was also confirmed by measurements of the tensile mechanical properties and rheological behavior.

1. Introduction

Thermal and electrical energy storage is recognized as one of the key technologies for energy supply in the future. The reasons are that energy storage (i) contributes to efficient energy use and the related conservation of fossil fuels; (ii) enables the use of renewable energy sources; (iii) reduces required power generating capacity through peak (energy) shaving; and (iv) simplifies the control of energy supply systems and improves their reliability. Attractive approaches to solving the aforementioned issues are based on phase change materials (PCM), which are substances with a high heat of fusion that are capable of storing or releasing large amounts of energy by melting and solidifying at certain temperatures [1]. Paraffin waxes are the most promising PCM because of their many desirable characteristics, such as high latent heat of fusion, negligible super-cooling, low vapor pressure and stability. These materials are chemically inert, non-corrosive, and non-toxic. Their properties, including a melting point ranging between 30 °C and 90 °C and a melting enthalpy that lies between 180 and 230 kJ kg^{-1}, indicate that paraffin waxes are excellent energy storage materials [2]. These materials are also produced in large quantities by various petrochemical companies, and therefore, they are readily available and inexpensive. However, there are also a few problems related to their real applications. One issue involves how to keep the paraffin wax in the compact shape and fixed volume even after melting as well as how to suppress the undesirable leaching effect, which is associated with the low viscosity of waxes after melting [3]. In many civil engineering applications, paraffin

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http://dx.doi.org/10.1016/j.enconman.2014.06.061
0196-8904/

waxes are kept in closed tanks or containers during heating to suppress leaching [4,5]. This solution is a quite acceptable and simple method but has many limitations. Other methods focus on how to keep waxes in stable form during applications that involve blending the waxes with plaster or with convenient polymers [6–10] or on their encapsulation within a polymeric shell to form microcapsules of a desired size [11,12].

According to scientific publications, microencapsulated PCM have been produced by different microencapsulation methods. For instance, Chen et al. [13] microencapsulated butyl stearate PCM in polyurea walls using interfacial polycondensation method of toluene-2,4-diisocyanate and ethylenediamine as monomers. Zhang et al. [14] fabricated microencapsulated PCM based on stearic acid core and polycarbonate wall by a solution casting method. Fang et al. [15] prepared polystyrene/*n*-tetradecane composite nanoencapsulated phase change material by ultrasonic-assistant miniemulsion *in situ* polymerization method, and used them as latent functionally thermal fluid for cold thermal energy storage. Alkan et al. [16] microencapsulated *n*-eicosane as a PCM for thermal energy storage, using emulsion polymerization technique and polymethylmethacrylate as the wall material. Aidin [17] described an *in situ* microencapsulation method to encapsulate a commercial PCM Cetiol MM (a high-chain fatty acid ester) in poly(urethane-urea) walls, by using a poly-functional amino alcohol N-(2-hydroxyethyl) ethylenediamine, and toluene diisocyanate as the monomers.

Some authors reported on microencapsulation of PCM by *in situ* polymerization method, similar to the method described in this paper. For instance, Su et al. [18] microencapsulated dodecanol PCM by *in situ* polymerization using methanol-modified melamine–formaldehyde prepolymer as the wall material. In their next publication, Su et al. [19] applied a similar *in situ* polymerization method, using methanol-modified melamine–formaldehyde prepolymer as a wall material, to encapsulate a paraffinic PCM for gypsum-matrix thermal energy storage building materials. However, as the melting point of both PCM was around the room temperature, no temperature adjustments were necessary in the emulsification and polymerization processes of the *in situ* microencapsulation procedure. In addition, residual formaldehyde was not removed from the final suspension of microcapsules. In our work, a molten PCM with the higher melting point of about 49 °C was microencapsulated in the oil-in-water emulsion system. The temperature regime of emulsification and polycondensation steps in the *in situ* process were modified and optimized to avoid the premature polycondensation reaction of the melamine–formaldehyde pre-polymer. In addition, ammonia was used as a scavenger at the final stage of microcapsule preparation, to reduce the concentration of formaldehyde residues in the final suspension of microcapsules to a concentration lower than 0.5%.

Finally, the latter two methods can be combined, as reported in this paper. This approach leads to one significant advantage and one drawback. The advantage is that the material behaves as a common composite based on the polymeric matrix filled with solid particles. Here, even if the constituents are not compatible each other, the leaching effect is negligible due to the viscosity limitation. The disadvantage is related to the fact that part of the volume of the composite is occupied by the encapsulating shell, which is not effectively usable for the designed functionality, namely, for heat absorption. In brief, the portion of the effective PCM component (wax) incorporated within a composite structure is lower than that if the wax had been directly mixed with the polymeric matrix. However, for some reasons, especially thermodynamic ones, the approach based on the direct mixing of the polymer with paraffin is more problematic than the previous one. First, only a few polymers are at least partly compatible with paraffin waxes, enabling a reasonable amount of wax to be incorporated into them [20,21]. In fact, only polyethylene (PE), and partly polypropylene (PP), can be applied with reasonable success to obtain a mixture that is stable if composed of 40–50 wt.% wax [22,23]. The second problem is associated with the leaching of waxes as well with the unstable morphology of materials upon cycled heating and cooling, as we demonstrated in previous papers [22,23]. For this reason, we investigated HDPE blended with encapsulated paraffin wax.

2. Experimental

2.1. Preparation of PCM microcapsules

Samples of microcapsules were prepared via the *in situ* polymerization of aminoaldehyde pre-polymers in a semi-industrial (10 l) reactor. A commercial grade paraffin wax (grade RT50: melting point between 45 and 51 °C, typically 49 °C) from Rubitherm (Germany) was microencapsulated using a thin polymeric shell of melamine–formaldehyde resin via *in situ* polymerization in an oil-in-water emulsion system. Partly methylated trimethylolmelamine (MF pre-polymer) (Melamin, Slovenia) was used as a pre-polymer for the microcapsule wall, and a styrene-maleic acid anhydride copolymer (SMA) with an average molecular weight of 350,000 (Hercules) was added as an emulsifier and modifying agent/polycondensation initiator. Analytical grade sodium hydroxide (Kemika) was used for termination of the polycondensation reaction and pH neutralization. To remove the formaldehyde released during the polycondensation, ammonia (Kemika) was added to the suspension of microcapsules as a scavenger. The microencapsulation process scheme is depicted in Fig. 1.

The *in situ* polymerization microencapsulation process consisted of the following steps (Fig. 1): (1) preparation of an aqueous solution of SMA modifying agent, (2) emulsification of future cores of microcapsules at a temperature above the melting point of the paraffinic PCM, i.e. at $T = 55$ °C, (3) addition of MF pre-polymer for wall formation at $T = 55$ °C, (4) induction of the polycondensation reaction by increasing the temperature to $T = 80–85$ °C, (5) polycondensation process occurring for approximately 90 min at $T = 80–85$ °C, (6) termination of polycondensation by increasing the pH value from 5.5 to 7.0, (7) removal of residual formaldehyde by adding the ammonia scavenger at $T = 50$ °C, and (8) cooling down to room temperature.

2.2. Preparation of composites

High-density polyethylene (HDPE BP 5740 3VA, British Petrol, UK, melting temperature = 129.4 °C, melting enthalpy = 160 J/g) was mixed with the water suspension of microcapsules to obtain the required composition with the fixed HDPE/microcapsules ratio. The HDPE/microcapsules ratio was = 60/40, 50/50 and 40/60 w/w. After that, water was evaporated in the oven at 50 °C. Then, two routes were employed for the preparation of the composites. In the first case, the dry powder was simply hot pressed in the laboratory press (Fontijne SRA 100, The Netherlands) at 160 °C for 5 min to obtain samples of the required shapes for the following testing. In the second case, the powder was first mixed in the 30 ml mixing chamber of the blending machine (BrabenderPlasticorder PLE 331, Germany) at 160 °C for 8 min at a mixing speed of 35 rpm to obtain better homogeneity, and then, the samples of required shape were pressed in the same manner as in the previous case. The two methods were tested because it is clear that hot blending of the components prior to the testing sample preparation leads to a much better homogeneity of composites than if only mechanical mixing is used. However, from a practical and economical viewpoint, it is desirable if composites with adequate