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Shape-stabilized poly(ethylene glycol) (PEG)-cellulose acetate blend preparation with superior PEG loading via microwave-assisted blending

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ABSTRACT

Poly(ethylene glycol) (PEG) is known to be very effective phase change material (PCM), which has been processed by various techniques. Efforts for development of better processing technique are always on, to make the process product and performance superior. Microwave technology based process development for the preparation of form stable phase change composites was attempted, with the motivation of establishing a green technique, which will be energy and time efficient and require minimum amount of solvent. The process could easily be scaled for large scale production of PCM blends. The microwave-assisted blending of PEG and cellulose acetate (CA) was carried out in various ratios resulting in the formation of biodegradable form-stable PCM. PEG acted as the latent heat storage material and cellulose acetate as the supporting material. As a result of microwave treatment, a high loading capacity of 96.5 wt% PEG was achieved without any leakage during the transition process. The blending was confirmed by Fourier-transform infrared spectroscopy (FTIR) analysis which showed no chemical bonds between PEG and CA. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) indicated that maximum enthalpy of 155 J/g was attained and the material was found to have good thermal stability. The surface properties of these materials were studied by using contact angle for various weight percentages of PEG. The X-ray diffraction (XRD) investigation revealed that the crystallinity of the PEG-CA blend increased with increasing concentration of PEG. The morphology was studied with field-emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) suggesting a homogeneous network formation of the blend.

1. Introduction

The depletion of non-renewable sources of energy coupled with escalating world demand for energy has gathered focus on the research for alternative sources of energy. Thermal energy storage systems can be used to address this global issue partially. Latent heat storage systems, also known as Phase Change Materials (PCMs) are gaining popularity due to their high energy storage density and ease of temperature control (Kenisarin, 2014; Samui et al., 2015). Solid-solid PCMs can be prepared by using both physical methods (adsorption, blending, soaking) and chemical methods (grafting, crosslinking, copolymerization) (Kumar et al., 2014). Various form-stable blends have been developed using inorganic hard segments but it leads to supercooling and phase separation over repeated cycling (Qian et al., 2013). Therefore, organic form-stable blends offer better performance with good thermal efficiency. PEG is a versatile PCM with attractive properties such as high storage capacity per unit volume, ease of chemical modification, adjustable temperature range, non-toxicity, good chemical and thermal reliability (Alkan et al., 2012a; Qi et al., 2014; Samui et al., 2015; Sundararajan et al., 2016).

Many shape-stabilized PCMs have been prepared using natural, biodegradable polymers such as cellulose (Liang et al., 1995; Şentürk et al., 2011), cellulose acetate (Chen et al., 2007; Ding et al., 2001; Guo et al., 2003; Jiang et al., 2002), chitosan (Şentürk et al., 2011), agarose (Şentürk et al., 2011), sugars (Alkan et al., 2012b) and starch (Pielichowska and Pielichowski, 2010) as hard segments and PEG as the working material. Cellulose obtained from wood pulp was used to prepare PEG-cellulose blend using coagulation method with a maximum encapsulation of 40 wt% PEG (Liang et al., 1995). The crystalline to amorphous solid-solid phase transition was studied and melting enthalpy of 143 J/g was obtained. Guo et al. prepared PEG and CA physical blends by solution casting up to maximum loading of 85% PEG and the phase

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change behavior was investigated (Guo et al., 2003). Phase change enthalpy of 142 J/g was recorded for PEG-CA blend with PEG 6000. Another study was performed by preparing PEG and CA containing PCMs by using physical blending and chemical bonding methods (Ding et al., 2001). A loading of 80 wt% of PEG was achieved by using the same solution casting technique and latent enthalpy of 105 J/g was observed for the physically bonded PEG-CA PCM exhibiting solid-liquid phase transition. PEG-cellulose acetate thermoregulating ultrafine fibres were prepared by Chen et al. via electrospinning with 50 wt% PEG and fusion enthalpy values reaching 86 J/g (Chen et al., 2007). In a study performed by Senturk et al., biodegradable blends of PEG with cellulose, chitosan and agarose were prepared by solution casting method having maximum loading of 60 wt% PEG, 70 wt% PEG and 80 wt% PEG respectively (Şentürk et al., 2011). The latent heat of melting was found to be 85 J/g for PEG/cellulose blend, 111 J/g for PEG/agarose blend and 152 J/g for PEG/chitosan blend. Alkan et al. prepared PEG blends with sugars (fructose, lactose and glucose) using solution casting method with maximum 90 wt% PEG (Alkan et al., 2012). PEG of different molecular weights 1000, 6000 and 10,000 was used for preparation of blends and enthalpy as high as 156 J/g was achieved. Solution casting technique was used to prepare PEG-potato starch blends with a high loading of 75 wt% PEG and enthalpy reaching a maximum of 97 J/g (Pielichowska and Pielichowski, 2010).

For inorganic form-stable PEG based PCMs, high loading capacity of 96% has been achieved so far (Qi et al., 2014) whereas for organic form-stable PEG based PCMs, maximum loading capacity of only 90% has been achieved (Alkan et al., 2012; Jiang et al., 2002). Shape-stabilized PCMs have also been prepared previously using ultrasound-assisted blending (Tang et al., 2013). However, the blending was preceded by the de-agglomeration step of the SiO_2 under ultrasonication. The methods of blending adopted earlier suffer from limitations such as complicated procedures, maximum PEG loading and lower phase change enthalpy. The absorption of microwaves by dipole active molecules induces intense heat and accelerates the reaction leading to time-effective product formation, in a matter of minutes which can be easily applied for commercial applications. The instant high temperature increases the mobility of components of blend and allows it to cool down at equilibrium position, which leads to maximum interpenetration and interpolymer interaction. Further, the use of microwave for blend production is fast, reliable, energy efficient green method with less solvent consumption and allows for higher incorporation of PCM without developing leakage problem during repeated use. The preparation of polymeric blends using microwave blending has previously been reported (Rivero et al., 2009). The microwave route of blending of organic form-stable PCMs was not reported earlier. It was assumed to reveal some interesting and facile features in blending.

In the present work, an efficient route for the preparation of shape-stabilized PEG-CA blend has been explored by using microwave synthesizer with the aim of enhancing the PEG proportion, minimizing the microwave contact time to make the process fast, while avoiding the degradation of polymers. Additionally, the presence of CA was expected to minimize the hydrophilic nature of PEG. The chemical characterization of these blends has been performed using Fourier-transform infrared spectroscopy (FTIR). The thermal characteristics have been found out with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Atomic force microscopy (AFM) and scanning electron microscopy (SEM) have been utilized to find out the morphology of the prepared PCMs. The contact angle studies have also been performed for finding the improvement in hydrophilicity of PEG.

2. Experimental section

2.1. Materials

Poly(ethylene glycol) with an average molecular weight of 8000 was purchased from Sigma-Aldrich and vacuum dried at 120 °C for 3–4 h before use. Cellulose acetate with $M_n = 37{,}000$ (40% substitution of acetyl groups) was supplied by Sigma-Aldrich and used after drying in vacuum oven for 4 h at 90 °C. Acetone was purified by drying over molecular sieves 3 Å. The CEM Discover microwave synthesizer (Model No.: 908010, USA) was used for the reaction.

2.2. Preparation of PEG-CA blend

The PEG-CA shape-stabilized PCM was prepared by using microwave-assisted blending and the reaction scheme is shown in Scheme 1. The dried PEG was dissolved in acetone and to the prepared solution; a known quantity of cellulose acetate was added. This reaction mixture was kept in microwave synthesizer under closed vessel conditions at 100 W and 70 °C for 20 min with stirring. The volume of acetone was maintained at 3 mL and the total blend weight which included both components (PEG + CA) remained the same, for all blend preparations. Only the ratio of both the components (PEG and CA) of the blend was varied accordingly. In a typical recipe for preparation of 90 wt% PEG-CA blend, 90 mg PEG was dissolved in 3 mL acetone to which 10 mg of cellulose acetate was added and this reaction mixture was microwave treated. The microwave treated mixture was dried on a glass plate at room temperature overnight to remove acetone and the shape-stabilization of the prepared blends could be investigated.

The PEG-CA blends were prepared in various ratios ranging from 10 wt% to 96.5 wt% PEG. When the composite with 97 wt% PEG was heated beyond 80 °C, the leakage of liquid could be observed. Therefore, a maximum loading of 96.5 wt% PEG could be achieved.

2.3. Characterization

Infrared spectroscopy information of the PEG-CA blend was obtained using ATR technique on Bruker–Alpha 200630, Germany. The samples were placed directly on the Zn-Se ATR crystal and the FTIR was recorded in the spectral range of 4000–500 cm^{-1} with 4 cm^{-1} resolution for every spectrum. Thermal transitions were evaluated using Perkin Elmer DSC 8500 (Serial No.:-534N1091601, USA). Approximately, 5 mg of the dry samples were heated from 35 °C to 150 °C at a heating rate of 10 °C/min under nitrogen atmosphere. XRD measurements were conducted using Bruker D8 Advance with Cu Kα radiation ($\lambda = 0.154$ nm) at step size/time of 0.02°/1 s. Thermogravimetric analysis was performed using Perkin Elmer simultaneous thermal analyser 6000. All the samples were heated from 30 °C to 800 °C at a rate of 20 °C/min in dry nitrogen. The surface morphology of the prepared blends was observed using Carl Zeiss's Scanning Electron Microscope (Σigma 03-18, Germany). AFM images of the samples were obtained in the tapping mode at room temperature with Asylum Research Atomic Force Microscope (Model No.: AC160TS). Silicon cantilevers coated with aluminum were used for the measurement with a resonance frequency close to 300 kHz. Water contact angles were measured by sessile drop method using Holmarc contact angle measuring instrument (Model No.: HO-IAD-CAM-01A), India. The specimens were prepared by depositing on clean glass slides and 5 μL of deionised water was added for every measurement.