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Preparation of thiol-ene based photo-crosslinked polymer as a potential phase change material

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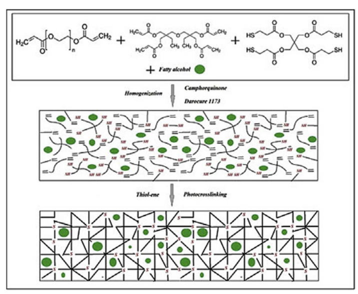
HIGHLIGHTS

- Photo-crosslinked thiol-ene based shape-stabilized phase change materials (PCMs) have been developed.
- The fatty alcohol containing PCMs exhibit endothermic and exothermic behaviors.
- The melting and freezing temperature of thiol-ene based UV-cured PCMs is remarkably decreased compared to that of pristine fatty alcohols.
- The latent heat enthalpies of heating and freezing cycle varied from 27 to 43 J/g, and 20–39 J/g, respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of novel photo-crosslinked thiol-ene based shape-stabilized phase change materials (PCMs) have been prepared for the use of thermal energy storage applications. Four types of formulations were prepared with different fatty alcohols by adding di(trimethylolpropane) tetraacrylate (TMPTA), polyethylene (glycol) diacrylate (PEGDA) and pentaerythritoltetrakis(3-mercaptopropionate) (4-SH) in which we investigated their properties as shape-stabilized PCMs. Fatty alcohols, 1-Octadecanol, 1-Eicosanol and 1-Docosanol, were added to the formulations, respectively. The characterization tests were performed by ATR-FTIR spectroscopy. Phase change behaviors and thermal performances were investigated by using differential scanning calorimetry (DSC) and thermogravimetric analysis system (TGA).The heating cycle phase change enthalpy is measured between 27 and 43 J/g, and the freezing cycle phase change enthalpy is found between 20 and 39 J/g. The decomposition of UV-cured PCMs started at 413 °C.The results indicate that the photo-crosslinked thiol-ene based PCMs possess good phase change properties and have an applicable temperature range. With the obtained results these materials promise a great potential in thermal energy storage applications.

1. Introduction

Energy storage technology offers new ways to meet the demand to obtain efficient and reliable energy storage materials. Thermal energy storage systems provide the potential to acquire energy savings, which in return decrease the environmental impact related to energy usage. For this purpose phase change materials (PCMs) that work as “latent heat storage units” which can store or release large amounts of energy are preferred. PCMs have found different

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application areas such as solar energy storage and transfer [1–3], HVAC (Heating, Ventilating and Air Conditioning) systems, thermal comfort in vehicles [4], passive cooling, temperature controlled distributions, industrial waste heat recovery [5], under floor heating systems [6,7] and modified fabrics in textiles [8].

Thermal energy can be stored by using sensible energy of solids or liquids, latent heat of phase change materials or chemical reaction of some chemicals. Thermal energy storage methods can be classified as sensible heat thermal energy storage or latent heat thermal energy storage technology segments [9,10].Latent heat storage, which is the most efficient method, relies on the storage material, absorbing or releasing heat as it undergoes a solid to solid, solid to liquid or liquid to gas phase change or vice versa [11–13].

Nowadays PCMs have attracted many interests to the researchers due to their capabilities to store high latent heat per unit volume via phase change at an almost constant temperature. Sarı et al. [14] synthesized a series of poly(styrene-co-allyalcohol)-graft-stearic acid copolymers for solid-solid PCMs for thermal energy storage applications. Stearic acid was used as precursors and poly(styrene-co-stearoyloxyethylen), poly(styrene-co-stearoyloxyethylen) and poly(styrene-co-stearoyloxyethylen) was synthesized. FT-IR, TGA analysis were conducted. Thermal characteristics of the copolymers were investigated with DSC. They reported that, copolymers could be used in thermal energy storage applications for solar space heating and cooling of buildings or greenhouses.

We see in recent studies that polymers are designed to prevent leaking of oils. Loxley et al. [15] introduced a phase separation method to encapsulate *n*-hexadecane with poly(-methylmethacrylate) (PMMA) and obtained the capsules with shells of different thickness by changing the concentration of polymer in the oil phase. Cemil Alkan et al. reported another similar research, in which they microencapsulated docosane, *n*-eicosane, *n*-octacosane and *n*-heptadecane with PMMA [16–19].

PCMs can be also obtained from composites. Cao et al. encapsulated fatty acid eutectics and cellulose to obtain shape-stabilized composite PCMs. The fatty acid eutectics were prepared from lauric acid and stearic acid. Results indicate that the composite is suitable to be used as the supporting materials for the preparation of shape-stabilized PCMs for the thermal properties of which DSC and TGA analysis were conducted. Also it has been observed that its thermal properties are well maintained after 100 thermal cycles [20].

Electrospinning has many applications and it is a technique to fabricate nanofibrous PCMs. Cai et al. used polyacrylonitrile and carbonized polyacrylonitrile for the fabrication of the PCMs. FT-IR and DSC was used to identify both morphological and thermal behaviors. Nanofiber diameter was between 300 and 400 nm and this high porosity caused by the absorption of a large amount of PCMs. Heat threated polyacrylonitrile found to have more desired thermal properties [21].

Furthermore, bio-based PCMs are a type of organic fatty acid ester PCMs made from underused and renewable feedstock, like vegetable oils, which make them cheaper and efficient to apply to fields that need large application scope. According to a survey found in literature, bio-based PCM composites had good thermal durability in the working temperature ranges. Therefore, bio-based PCMs can be considered as suitable candidates for latent heat thermal energy storage, with high thermal performance. In the research that Yu et al. conducted bio-based carbon composites were prepared and their thermal behavior was investigated. DSC and TGA studies were performed. According to TGA curves, all composites show thermal stability at room temperature [22].

Ultraviolet (UV)-curing technology has many advantages, which made it applicable in many different fields. Low energy consumption, high speed, room-temperature operation, low processing costs, high chemical stability, and being environmental friendly are some of its main benefits. UV-curing technique has many applications. Electrospinning, which is now very popular, is one of them. Yuksel-Deniz et al. prepared nanofibers using UV-reactive electrospinning technique and investigated the morphology of the nanofibers as well as their applications in cell culture [23].

Since thiol-ene functionality offers many advantages like oxygen inhibition, fast curing, uniform networks, delayed gel points and reduced polymer shrinkage [24,25], it has gained a lot of interests from industry and researchers in the recent years. Thiol-ene based UV-cured systems exhibit rapid rates of polymerization. They, in fact, quickly form a uniform crosslinked network, they have good adhesion and also UV-curable thiol-ene systems have the flexibility for the phase transitions to occur [26,27].However, as can be seen from the above-cited works, the research of UV cured thiol-ene based fatty alcohols containing PCMs has not yet been presented.

One of the many advantages of UV-cured PCMs is that they prevent the interior PCMs from leaking. Shape-stabilized PCM is prepared by blending the PCM with a supporting material, usually polymers. In our study this problem is minimized by coating the fatty alcohols with a photo-crosslinked thiol-ene based polymeric system. Leakage is minimized because photo-crosslinked polymer acts a matrix.

The aim of this paper is to introduce a novel thiol-ene based shape-stabilized PCM, which is not present in the literature survey. Photo-crosslinked thiol-ene based polymers containing fatty alcohols were prepared and characterized for the purpose of phase change materials (PCMs). Different types of fatty alcohols were used in order to investigate their properties as shape-stable PCMs [28–32]. The structure of the PCMs was confirmed by ATR–FTIR techniques. The phase transition behaviors, thermal stability of the prepared photo-crosslinked PCMs were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

Polyethylene (glycol) diacrylate(M_n = 575), pentaerythritoltetrakis(3-mercaptopropionate)(M_w = 466 g/mol), di(trimethylolpropane) tetraacrylate(M_w = 488.66 g/mol) and Camphorquinone (CQ) are purchased from Sigma Aldrich.1-Octadecanol (97%), 1-Eicosanol (96%) and 1-Docosanol were purchased from Alfa Aesar. Darocure 1173 was obtained from Ciba.

2.2. Preparation of photocrosslinked phase change materials (PCMs)

Di(trimethylolpropane) tetraacrylate (TMPTA) (1.50 mmol) and polyethylene (glycol) diacrylate (PEGDA) (0.52 mmol) were added in a three necked flask with constant stirring, photoinitator darocure 1173 and Camphorquinone was added.

Thiol-ene based PCMs formulations were prepared by heating the mixture to 80 °C by stirring until the fatty alcohols were melted and dissolved homogeneously. Pentaerythritoltetrakis(3-mercaptopropionate) (4-SH) was added with an amount that is indicated in Table 1. Four types of formulations [TMPTA/PEGDA/4-SH], [TMPTA/PEGDA/4-SH/1- Octadecanol], [TMPTA/PEGDA/4-SH/1- Eicosanol], and [TMPTA/PEGDA/4-SH/1-Docasanol] were prepared with having different fatty alcohols. TMPTA/PEGDA/4-SH was chosen as the base formulation. The formulations are presented in Table 1.

Afterwards, the mixture was put inside the oven. The PCMs were prepared by pouring the samples into Teflon™ wells (10 mm × 5 mm × 1 mm). They were exposed to UV light, which is