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Preparation and Characterization of Poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane Nanocapsules as a Fiber Additive for Thermal Energy Storage

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Abstract: The interest to innovative products with high added values and processes in textile field has been rapidly increasing among the other industrial fields. One of innovations in this field is to produce of innovative textiles containing phase change material (PCMs) that have thermal storage and thermo-regulation properties. This study deals with preparation and characterization of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules containing n-hexadecane as phase change material for thermal energy storage. The chemical characterization of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules was made by fourier transform infrared (FT-IR) spectroscopy method as particle size and its distribution (PSD) were studied by scanning electron microscopy (SEM). Thermal properties of nanoencapsulated n-hexadecane were determined using differential scanning calorimetry (DSC). The melting and freezing temperatures of the nanoencapsulated n-hexadecane were 17.23 and 14.85 °C respectively as the latent heats of melting and crystallization were 148.05 and −147.63 J/g respectively. Produced nanocapsules were applied to polyacrylonitrile (PAN) by means of electrospinning and surface morphology of the fibers was investigated by SEM analysis. Based on the results, it can be considered that the nanoencapsulated n-hexadecane in poly(methylmethacrylate-co-glycidyl methacrylate) have good energy storage potential to be used in fibers.

Keywords: PCM, Smart textiles, Thermal comfort, Thermal energy storage

Introduction

Phase change materials (PCMs) have been one of the main topics in the energy research studies for several decades. They are used for ice storage, building applications, solar energy storage, heat pumps, heat distribution systems, air conditioning, green houses, solar collectors, solar cookers, thermal comfort and the conservation etc. Recently, PCMs have entered the textile market for use in increasing the thermal comfort of garments [1,2]. Although all of the traditional insulation materials supply extended insulation, they are not sufficient to serve the needs arising from engagement in extreme sports and some activities at extreme working conditions. In such extreme applications of textiles as diving suits, ski wear, and underwear, PCMs impart outstanding properties to garments. For instance, their insulating properties may prevent the wearer from fatal consequences. The clothing having thermal storage property absorbs or release heat during rapid temperature changes therefore they maintain the skin temperature constant or delay the temperature changing rapidly. The new textile insulation materials have become important because they provide temperature regulation according to the environment and body temperature. These interactive insulation textiles are called as heat storage and thermo-regulated textiles, and contain phase change materials (PCMs) and plastic crystals [3,4]. For textile applications, the melting temperature of PCMs (heat-absorbing) is 20 to 40 °C close to body temperature [5].

Many substances have been studied as potential PCMs, but only a few have commercial importance. PCMs are divided into two main groups, namely inorganic PCMs and organic PCMs. Hydrated salts as inorganic PCMs have a wide range of melting temperatures between 8.1 and 130 °C. However their heat absorbing and releasing temperature interval is usually between 20 and 40 °C. They require a great deal of heat for fusion and have limited life cycles. Organic PCMs; parafins, fatty acids and low melting polymers have more uses due to their outstanding properties. Especially parrafinic hydrocarbons are widely used in textiles and have been discussed in many papers and used in many inventions. Because the melting point of paraffin which is dependent on the number of C molecules is very close to the temperature of the body. Textiles and garments containing PCMs are still being widely investigated for many possible applications as reported by Zhang in 2001 [2].

There are four methods of integration of PCM into textile substrates. The first method is to add the PCM into fibres by filling hollow fibres [3]. The spinning of fibre with PCM is the second one [6]. The third method involves coating with the fibre with foam such as polyurethane or by padding crosslinking agents [7-10]. And, the last one is the lamination process in which PCMs are first incorporated into

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a polymer film [5-11]. The polymer film is then laminated onto the surface of the textile. In this study, n-hexadecane with challenging properties as a PCM [12] was nano encapsulated by emulsion copolymerization of methyl metacrylate and glycidyl methacrylate and produced nanocapsules were electrospinned in polyacrylonitrile (PAN) for textile application.

Experimental

Materials

n-Hexadecane was analytical grade and used as received. Methyl methacrylate and glycidly methacrylate (Merck grade) were double distilled before use. Triton X100, tertbutylhydroperoxide, ferrous sulphate heptehydrate, and ammonium persulphate were purchased from Merck company and used as received.

Preparation and Characterization of Poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane Nanocapsules

The procedure applied was the same with Alkan *et al.* works [13,14]. Methylmethacrylate monomer and n-hexadecane were assembled as oil phase. Tertbutylhydroperoxide (degradates at 90 °C) was used as an initiator. Suitable mixing speed was determined as 2000 rpm. Reaction balloon was mixed for a half hour before polymerization. 94 m*l* deionized water, 25 g n-hexadecane, and 2.00 g of Triton X-100 (surfactant) were used. Then, the mixture was heated above melting point of n-hexadecane under nitrogen atmosphere. 25 m*l* methylmethacrylate, 2.50 g glycidly methacrylate and 1 m*l* freshly prepared $FeSO_4.7H_2O$ solution prepared by mixing 0.30 g of $FeSO_4.7H_2O$ with 200 m*l* water and 0.25 gr of ammonium persulphate were added. Addition of a crosslinking agent during polymerization can prevent formation of secondary particles, thereby producing uniformly sized and shaped nanocapsules. In addition, addition of a secondary initiator during polymerization can produce uniformly sized and shaped nanocapsules in high yield without a separate subsequent process.

The resultant mixture was vigorously mixed at 2000 rpm for 30 min. An extra of 0.25 gr $(NH_4)_2S_2O_7$ and 1.00 gr 70 % tertbutyl hydroperoxide solution were added at this point and the reaction medium was heated to 90 °C for an extra hour. The colloidal emulsion concentrated by casting water. The precipitate was dried under vacuum at 40 °C for 24 h.

The spectroscopic analysis was performed on a KBr disk using a Jasco 430 model FT-IR spectrophotometer. The morphology of the form-stable composite was investigated using a Scanning Electron Microscopy SEM LEO 440 and particle size was determined upon measuring more than 500 particles in SEM micrographs by a Lucia 32G 4.11 software program. Electrospinning process was exploited using single syring spinning system represented by Granier *et al.* [15].

Electrospining of Polyacrylonitrile with Poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane Nanocapsules as Phase Change Material for Thermal Comfort

In electrospinning of PAN with nanoencapsulated PCMs, PAN was dissolved in DMF to prepare 12 % PAN solution. Electrospinning apparatus founded by a project [16] supported by Turkish Scientific Council was used. Electrodes were placed with a distance of 17 cm and 20 kV potential was applied to PAN to produce electrospun fibers in the electrospinning system. Nanoencapsulated PCMs were added to PAN to adjust their concentration to 15 % by weight. Nanoencapsulated PCM containing PAN solution was electrospun under the same conditions with PAN at room temperature.

Determination of Thermal Properties of Poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane Nanocapsules

Thermal properties of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules such as melting and crystallizing points and latent heats were measured by DSC technique (Perkin Elmer Jade DSC, 2009). The analyses were carried out at 5 °C/min heating rate under a constant stream of argon at flow rate of 60 m*l*/min. Reproducibility was tested by conducting three measurements.

Results and Discussion

Chemical characterization of produced poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules performed using FT-IR spectroscopy method revealed the co-presence of methylmethacrylate, n-hexadecane and glycidylmethacrylate in the nanocapsules. Figure 1 shows the transmittance spectra of the characteristic peaks for

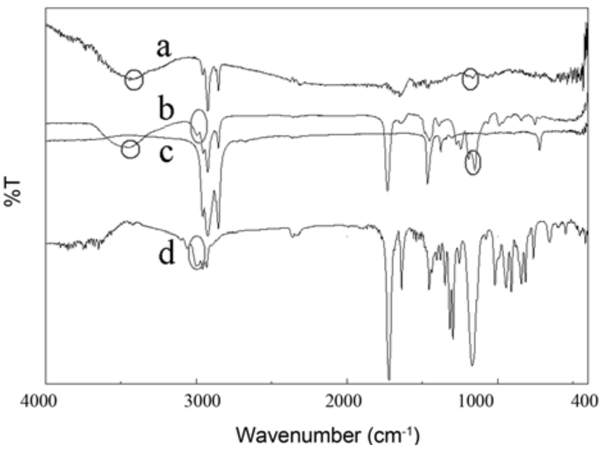

Figure 1. (a) FT-IR spectra of PMMA, (b) poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules, (c) pure n-hexadecane, and (d) glycidyl methacrylate.

PMMA (a), poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules (b), pure n-hexadecane (c) and glycidyl methacrylate (d). In the pure n-hexadecane spectrum (Figure 1(c)), the peaks at 2956, 2916, and 2848 cm^{-1} are C-H stretching peaks and the peaks at 1471, 1461, 1377, and 729 cm^{-1} are characteristic for paraffin compounds. The peaks are all present and observable in the spectrum of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules due to high concentration of n-hexadecane in the nanocapsules. In the spectrum of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules, the broad band marked at around 3500 cm^{-1} is characteristic to PMMA (as can be seen in Figure 1(a)). Proving the constitution of glycidylmethacrylate in poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules is the most difficult part due to its low concentration in the nanocapsules. Figure 1(d) shows the FT-IR spectrum of glycidylmethacrylate and the peak at 3099 cm^{-1} marked in both spectra of nanocapsules and glycidylmethacrylate proves the presence of glycidyl methacrylate crosslinker in the nanocapsules.

Consequently, poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules spectrum shows the characteristic peaks of PMMA, n-hexadecane, and glycidylmethacrylate in the nanocapsules together. The similar FT-IR results were reported for nanocapsules containing *n*-octadecane in which *n*-octadecane was fabricated as microcapsules and nanocapsules in melamine-formaldehyde shell respectively [18,19].

Morphology Investigation by SEM and PSD of Nanoencapsulated PCMs

Particle size and shape can dramatically alter the physical and therapeutic properties of a substance. The solubility, stability, chemical reactivity, opacity, flowability, and material strength of many materials are affected by the size and characteristics of the particles within them. Figure 2 represents the SEM images of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules. As it is seen in the figure, poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsule particles have a very uniform and unimodal distribution. The uniform distribution of the particles could only be supplied using a convenient crosslinker in the system. Therefore the uniform distribution of the nanocapsules can be meant the constitution of a crosslinker in the system.

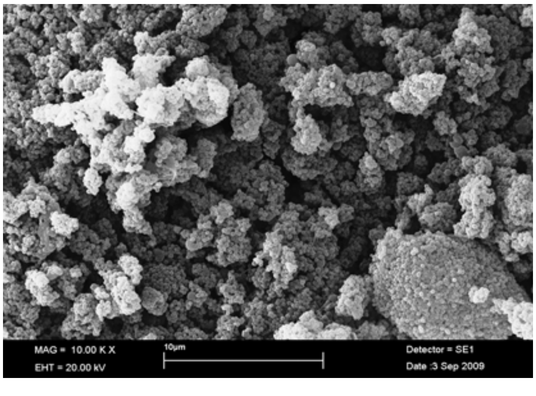

Figure 2. SEM of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules.

The appearance of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules is consistent with the nanocapsules prepared using different core materials and in the similar shape and particle size distribution [13,14]. PSD in Figure 3 represents almost monodispersity of the particles supplied using cross-linker comonomer in the system and the stirring speed. Cross-linker usage results in discrete and stable morphological structures as the thermal stability of microcapsule can be enhanced by the increase of the stirring speed [18]. The PSD in volume shows unimodal distributions of particle sizes ranging in the interval between 140 and 466 nm. The average diameter of nanocapsules was 260 nm.

Figure 4 shows the PAN nanofibers produced by electrospinning process as Figure 5 represents poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules incorporated PAN nanofibers produced under the same conditions. Compared to pure PAN fiber, poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules incorporated PAN nanofibers have lower diameters. Poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules incorporated PAN nanofibers are not smooth as PAN nanofibers and nanocapsules are distributed homogeneously or as oversaturated. The homogeneity of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules in PAN could be explained by

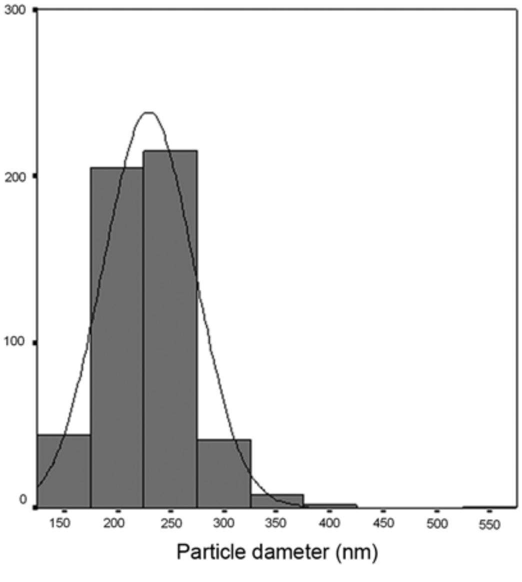

Figure 3. PSD of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules.

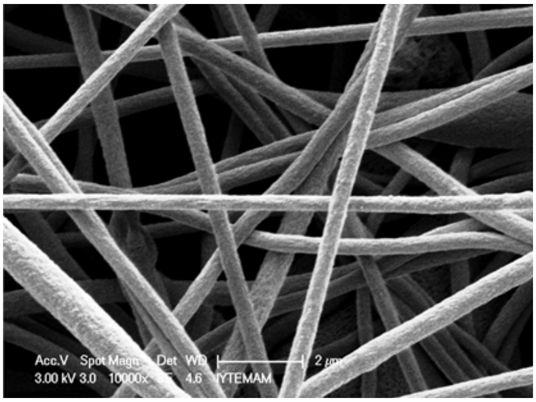

Figure 4. SEM image of PAN fiber.

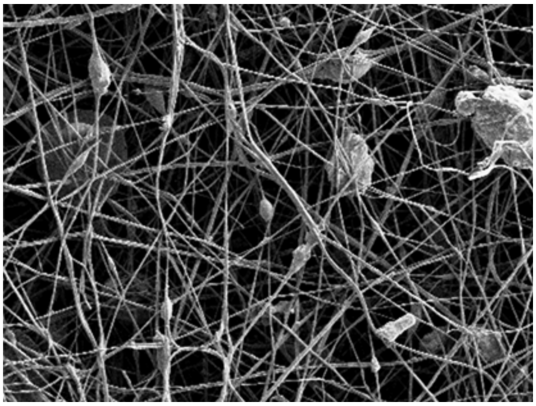

Figure 5. SEM image of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules incorporated PAN fiber.

the positive interactions between cyanoacrylates of PAN and oxygenes of acrylic polymer. The interactions between the PAN and the nanocapsules effected PAN to be electrospinned therefore some parts in the matrix left as plastic PAN coated nanocapsules. The other reason for the coagulation of the capsules is probably oversaturation of the capsules in PAN.

As a result poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanoparticles could be spinned in a fiber material homogenously at a considerably low fiber diameters which makes it possible to validate nanocapsules easily. Also nanofiber form of shape stabilized phase change materials have extended surface area and therefore high heat transfer ability.

Thermal Properties and Thermal Stability of Nanocapsules

A workable microencapsulated PCM should posses several properties like high specific heat storage density and a suitable phase temperatures [14]. Thermal properties evaluated from the DSC curve of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules in Figure 6 indicated that poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules melts at 17.23 °C and crystallizes at 14.85 °C as pure n-hexadecane has a melting point of 18.30 °C and crystallization point of 13.82 °C. Besides the latent heats of melting and freezing of poly (methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules were found to be 148.05 J/g and –147.63 J/g respectively as the latent heats of melting and crystallization of pure hexadecane were measured as 237.05 and –228.95 J/g respectively. The encapsulation ratio of n-hexadecane was calculated as 62.46 % with the following equation based on enthalpy values [13,14].

$$hexadecane\ (wt\%) = \frac{\Delta H_{MicroPCM}}{\Delta H_{PCM}} \times 100$$

where $\Delta H_{NanoPCM}$, ΔH_{PCM} are measured enthalpies of nanocapsules containing n-hexadecane and n-hexadecane itself, respectively.

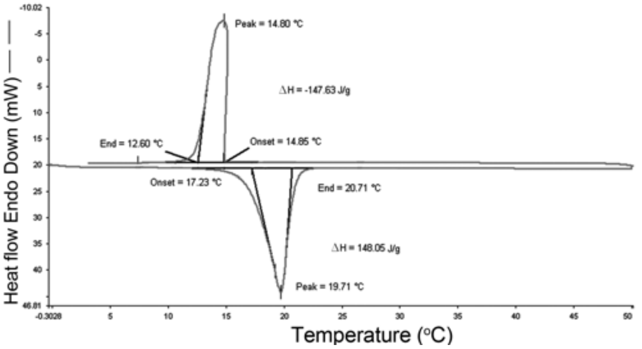

Figure 6. DSC thermogram of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules.

Thermal performance of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules is better than thermal performance of other PMMA nanocapsules with other alkanes (n-docosane, n-octacosane, and n-heptadecane) and allymethacrylate as crosslinker [13,14,20]. The thermal performance of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules are also better than the other acrylic polymer (polyethylacrylate) containing the same alkane (n-hexadecane) but different cross-linkers (allymethacrylate, ethylene glycol dimethacrylate, and glycidylmethacylate) [21,22].

The poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules incorporated PAN revealed 36.80 J/g enthalpy sorption between 1 and 18 °C upon DSC measurement under the same conditions with poly (methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules and further studies are going on.

Conclusion

PMMA nanocapsules containing n-hexadecane are successfully prepared with a narrow particle size distribution properly controlled by the emulsion stirring rate of 2000 rpm.

Glycidyl methacrylate is used as a comonomer at low mole fractions to supply cross-links between the chains which is important for stability of the capsules. FT-IR results have confirmed that the PMMA shell nanocapsules are successfully fabricated by emulsion polymerization. SEM analysis and particle size distribution determined via direct analysis of SEM images indicated that the prepared nanoencapsulated PCMs have smooth and compact surface with an average diameter of 260 nm. The temperatures and latent heats of melting and crystallization of n-hexadecane in PMMA nanocapsules were found considerably high as compared to the other acrylic shell microcapsules or PMMA shell microcapsules produced with other alkanes and crosslinkers. PMMA nanocapsules were found consisting 62.46 wt% n-hexadecane. The thermal endurance is an important property and it is proved by 1000 thermal cycling.

Pure PAN and poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanocapsules incorporated PAN were electrospun individually and it was observed that poly (methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanoparticles could be organised in a nano fiber. It extends the possible application fields of poly(methylmethacrylate-co-glycidyl methacrylate)/n-hexadecane nanoparticles. The enthalpy of sorption measured from the nanofiber promises a good future for phase change materials in nanofiber form.

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