



Fabrication of polyethylene glycol/polyvinylidene fluoride core/shell nanofibers via melt electrospinning and their characteristics

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ABSTRACT

Polyethylene glycol (PEG)/polyvinylidene fluoride (PVDF) core/shell nanofibers were fabricated using coaxial electrospinning. In the core/shell composite nanofibers, melted PEG and PVDF solutions were coaxially electrospun (e-spun) through a double spinneret as a core layer and as a shell layer, respectively. The PEG of the core layer in the e-spun composite nanofibers is a phase-change material (PCM) that is able to store and release large amounts of thermal energy at a constant phase transition temperature. PEG was encapsulated with a PVDF shell to prevent its leakage and reduce the effect of the external environment during usage. The core/shell structure of the e-spun composite nanofiber was confirmed using water contact angle (WCA) measurements, X-ray photoelectron spectroscopy (XPS) analysis, and transmission electron microscopy (TEM). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) showed that the e-spun composite nanofibers had good thermal stability and energy storage capacity. PEG of three different molecular weights (MWs: 1000 Da, 2000 Da and 4000 Da) was used as the core material to prepare e-spun composite nanofibers with different melting/crystallization temperature ranges and thermal storage capacities. Among these PEGs, the WCA value of 106° of e-spun PEG4000/PVDF core/shell nanofibers is similar to that of e-spun PVDF nanofibers confirming that the core/shell nanofibers could completely encapsulate 4000 Da PEG at the highest core feed rate of 0.210 mL/h. Regarding in terms of energy storage capacity, core/shell nanofibers, fabricated at the core feed rate of 0.210 mL/h, had the largest content of PEG in the core up to 42.5 wt% with a latent heat of 68 J/g and a melting temperature of 62.8 °C. These shape-stabilized core/shell nanofibers showed good thermal reliability and sufficiently high tensile strength, leading to various potential applications related to energy storage.

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1. Introduction

In recent decades, the ever-increasing demand for energy and the weather changes due to global warming have been a big challenge. Therefore, the development of new energy resources as well as the energy storage systems that are environmentally friendly has been received much attention. Since phase-change materials (PCMs) can absorb a large amount of energy as latent heat and release a large amount of the passively stored heat into the surrounding environment at a constant phase transition temperature, they have become high-performance materials for thermal energy storage [1,2]. Various inorganic compounds, organic compounds, and their mixtures have been used as PCMs (hydrated salts, paraffin waxes, fatty acids, and eutectic systems of organic and non-organic compounds) [1–3]. PCMs undergo solid–liquid state changes repeatedly during repeated cycles of

melting and cooling processes, and leakage into the surrounding environment is unavoidable. This leakage could shorten their usable lifetimes [4]. Recently, encapsulation of PCMs in a solid matrix has been found to be a good method of stabilizing PCMs during usage. Many attempts have been carried out to encapsulate PCMs with supporting polymers via coating [5], blending [6–10], interfacial polymerization [11,12], coacervation [13,14]. The two former methods could produce PCM-containing materials with high latent heats due to the higher content of PCMs in the blends or composites. However, the leakage of PCM from these materials might occur partially because of the phase separation of the PCM and the solid matrix. The latter methods allow PCMs to be completely encapsulated by a polymer shell and increase the total heat transfer between the PCMs and the external environment. Uddin et al. [11] prepared phase-change microcapsules by using a mixture of poly(methyl methacrylate) (PMMA) and silica as the shell material and n-octadecane as the core in the sol–gel process. Hawlader et al. [12] prepared microcapsules comprising PMMA as the shell material and n-octacosane as the core via emulsion polymerization. Chang et al. [13] reported that the

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paraffin microcapsules prepared by a simple coacervation technique showed large energy storage and release capacity (56–58 J/g) during its phase change. Using complex coacervation or spray drying methods, paraffin microcapsules having higher energy storage and release capacity (145–240 J/g) could be fabricated by Sari et al. [14]. However, the direct use of these microencapsulated PCMs is relatively difficult, particularly in textiles. To overcome this problem, the fabrication of macro- and/or micro-encapsulated PCM/polymer composite fibers via the electrospinning technique was introduced [15]. These PCMs contained in electrospun (e-spun) nanofibers showed some attractive advantages, such as flexibility, high latent heat, mechanical strength, a specific surface area per unit weight, and, in particular, a wide variety of applications. So far, several PCM/polymer composite e-spun nanofibers, such as lauric acid/poly(ethylene terephthalate) (PET) [16], stearyl stearate/PET [17], polyethylene glycol (PEG)/cellulose acetate (CA) [18], and polyethylene glycol (PEG)/polyvinylidene fluoride (PVDF) [19], have been fabricated via electrospinning of mixtures of polymer solutions.

Coaxial electrospinning is a very useful electrospinning technique used to fabricate core/shell e-spun nanofibers in which PCMs are in the core and are wrapped inside the polymeric materials making up the shell. The polymeric shell can help maintain the shape of the e-spun nanofiber and prevent PCM leakage from it during the phase-change process. McCane et al. [20] fabricated core/shell structured PCM/polymer composite nanofibers containing 45 wt% of octadecane as the core material encapsulated by a shell of polyvinylpyrrolidone (PVP) via melt electrospinning. Melt electrospinning has some advantages over solution electrospinning, such as environmental friendliness and low costs, because it is a solvent-free process.

In this study, PEG/PVDF core/shell nanofibers were fabricated by using a melt-solution coaxial electrospinning system. PEG is a polyether compound that is widely utilized as a PCM because of its high heat of fusion, good chemical stability, and ability to be frozen without supercooling. PEG of three different MWs (1000 Da, 2000 Da, and 4000 Da) with different melting/solidifying temperature ranges and thermal storage capacities was used. PVDF is a semicrystalline polymer with high mechanical strength and good thermal properties; it was employed as the polymeric shell. The melt-solution coaxial electrospinning system involves the use of a spinneret composed of two coaxial capillaries, and melted PEG and PVDF solution were pumped through the inner and outer capillary, respectively. Thus, the core and shell of the e-spun nanofibers were formed simultaneously. In our previous study [21], the PEG/PVDF core/shell nanofibers obtained by coaxial electrospinning of PEG (1000 Da) solution as the core layer and PVDF solution as the shell layer showed a low content of PEG in the e-spun nanofibers (20 wt%), resulting low thermal storage capacity. This was caused by the dilution of PEG by the solvent in the PEG solution. The combination of melt electrospinning and solution electrospinning is expected to enhance the PEG loading in the core of the composite nanofibers in comparison with the solution coaxial electrospinning. The core/shell structure of the e-spun composite nanofibers was analyzed using water contact angle (WCA) measurements, transmission electron microscopy (TEM) observations, and X-ray photoelectron spectroscopy (XPS). The morphology and size of the e-spun nanofibers was investigated using field-emission scanning electron microscopy (FE-SEM) images. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were employed to investigate the thermal properties and the thermal reliability of the PEG/PVDF composite nanofibers. In addition, the tensile properties of nonwoven mats of PEG/PVDF core/sheath nanofibers were evaluated.

2. Experimental

2.1. Materials

PEG with an average MW of 1000 Da (PEG1000) was purchased from Samchun Co. (Korea), while PEG with average MWs of 2000 (PEG2000) and 4000 Da (PEG4000) was supplied by Dae Jung Co. (Korea). Kynar[®] 761 PVDF was used. *N,N*-dimethylformamide (DMF) was purchased from Samchun Co. (Korea). All of the chemicals were used without further purification.

2.2. Coaxial electrospinning

PVDF was dissolved in DMF, and a 20 wt% solution of PVDF was placed in a plastic syringe. Fig. 1 shows the scheme for the melt coaxial electrospinning. PEG was put into a stainless steel syringe that was preheated to 70 °C. PEG melt and PVDF solution (20 wt%) were injected into the coaxial composite spinneret, which consisted of two concentrically arranged capillaries. The inner capillary has an inner diameter (ID) of 0.35 mm and an outer diameter (OD) of 0.65 mm, while the outer capillary has an ID of 1.05 mm and an OD of 1.20 mm. The flow rates in the capillaries were controlled by two separate pumps (Nano NC, Korea). Both capillaries were connected to the same high-voltage power supply. The e-spun nanofibers were collected on aluminum foil placed above the flat, grounded metal plate. The applied voltage and the distance between the tip of the spinneret and the collector were maintained at 12 kV and 17 cm, respectively. The shell flow rate was set to be constant at 1.5 mL/h, while the core flow rate was varied from 0.09 to 0.24 mL/h.

2.3. Characterization

WCA measurements were used to evaluate the hydrophilicity of a nonwoven mat of PVDF and nonwoven mats of PEG/PVDF core/shell composite nanofibers prepared at different core feed rates. The WCA was measured using a video contact angle instrument (Samsung FA-CED camera, Korea) and was recorded immediately after deionized water was dropped freely onto the surfaces of the flat nonwoven mats. For each case, the WCA reported was the average of the values recorded in five measurements.

The melt viscosity of PEG was measured using a viscometer (LVDVII, Brookfield, USA). The PEG was first placed into the viscometer chamber kept at a constant temperature of 70 °C by the circulation of silicon oil through the steel jacket. Viscosity measurements were conducted using a #18 cylindrical spindle at 70 °C.

The structure of the coaxially e-spun core/shell nanofibers was determined using XPS (Thermo, MultiLab 2000) and TEM observations (TecnaïG², USA), for which carbon-coated copper grids were used to collect the coaxial e-spun fibers.

The morphology of the nonwoven mats was observed in images captured by an FE-SEM (HITACHI S-4700, Japan) machine using a coating system (BAL-TEC MED020). The average diameter of the e-spun fibers was determined from the FE-SEM images using the visualization software TOMORO Scope Eye 3.6.

The transition temperatures and latent heats of the e-spun PEG/PVDF composite nanofibers were analyzed using DSC (SH IN2920, TA Instruments, USA) with a heating/cooling rate of 10 °C/min under a constant nitrogen flow. In order to determine the thermal reliability of the PEG-PVDF core/sheath nonwoven mats, a thermal cycling test involving 100 consecutive melting and cooling cycles was conducted. Thermogravimetric analysis (TGA, TA Instruments, USA) was performed to determine the content of PCM in the coaxial e-spun fibers using a thermal analyzer (EXSTAR 6000, Seiko instruments Inc., USA) at

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