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Development of heat storing poly(acrylonitrile) nanofibers by coaxial electrospinning

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ABSTRACT

New thermal energy storage materials were developed as poly(acrylonitrile) (PAN) nanofibers with encapsulated phase change materials (PCMs). Sixteen samples composed of PAN shells and PEG or PEGME cores, and one control sample composed of only a PAN shell, were manufactured by coaxial electrospinning. SEM images revealed the formation of randomly distributed, distinct nanofibers with smooth surfaces and cylindrical shapes along their lengths. FTIR results confirmed bicomponent nanofiber structures and TGA results demonstrated their thermal stabilities. Phase change performances of nanofibers were repeatedly examined by DSC analyzes; heating enthalpies ranged from 38 to 133 J g^{-1} and from 29 to 60 J g^{-1} for PAN-PEGs and PAN-PEGME samples, respectively, corresponding to good encapsulation efficiencies. These remarkable thermal energy storages were achieved at different melting temperatures (−1 to 60 °C). Textile based sandwich structures containing three different types of PAN-PCM nanowebs demonstrated enhanced thermal properties and buffering function against temperature changes in surrounding.

1. Introduction

Growing awareness of energy efficiency, attempts for avoiding environmental pollution as well as new lifestyle trends towards more comfortable and well-being products have become the main drivers to create alternative materials providing enhanced thermal management solutions [1]. The latent heat storage materials, commonly known as phase change materials (PCMs), that are capable of absorbing and releasing large quantities of latent heat during solid-solid or solid-liquid phase transitions, possess significant potential to fulfill the thermal management requirements for cooling and heating applications in various research fields and industries such as space heating and cooling [2], solar energy storage [3], temperature sensitive textiles and clothing [4], transportation packaging [5], healthcare [6] and electronics etc. [7].

Various storage processes such as microencapsulation [8,9], shape stabilization [10,11], foam production [12–14], filling hollow fibers [15] have been applied to PCMs prior to their integration into different composites in order to prevent their interaction with the surrounding medium and their leaching throughout the phase change process, to increase their mechanical and thermal stabilities and to enhance their ease of handling [4]. On the other hand, each method has some drawbacks such as reduced thermal conductivity, softness, flexibility, breathability or moisture transport capability in the final products [16]. Currently, developing new temperature regulating composites produced by single or coaxial electrospinning with improved thermal, mechanical and physical performances has received great attention for endorsing the applicability of PCMs [17–19]. Electrospun form stable PCMs exhibit remarkable advantages, such as forming a large surface area with the numerous nanofibers, being lightweight, and allowing direct use in various composites, etc. [20]. The method of single nozzle electrospinning, concerning with mixing or grafting of PCMs in the host polymer matrix, is the most common approach for fabricating ultrafine PCM fibers due to the easiness of electrospinning process. The greatest disadvantage of single electrospinning is the insufficient encapsulation and partial leakage of PCM through the fibers causing the PCM's interaction with the surrounding medium [19]. Over the past decade, the method of coaxial electrospinning, namely simultaneous electrospinning of two or more different materials into core-shell structured nanofibers, has attracted more and more attention [16–18] for encapsulating both hydrophilic and oleophilic PCMs in a variety of polymers, achieving high encapsulation efficiencies, preventing the leakage of PCMs and enhancing the mechanical properties of the composite PCM electrospun fibers [19,21]. Bringing in these advantages, various PCMs and polymers have recently been explored as core and shell materials in coaxial electrospinning processes to

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manufacture a number of form-stable PCM nanofibers [22–29].

Among the various organic PCMs, poly(ethylene glycols) (PEGs), composed of linear dimethyl ether chains with hydroxyl end groups [H−(O−CH_2−CH_2)$_n$−OH], have attracted attention for diverse thermal storage applications due to their desirable characteristics, such as their capability for repeatable solid-liquid phase changes at low and moderate temperature intervals, high heat of fusion (ΔH_{fus}), non-volatility, chemical and thermal stability, solubility both in water and organic solvents, biocompatibility, non-toxicity and low price [1,30–32]. Poly (ethylene glycol) methyl ethers (PEGMEs) [CH_3−(O−CH_2−CH_2)$_n$−OH], which are the methyl-terminated (CH_3) derivatives of PEGs, also have suitable characteristics for thermal storage utilization [33]. Along with the utilization of PEGs in the preparation of nanowebs through single axial electrospinning [34–37], PEGs have recently been tested as core material in the production of coaxial electrospun PCMs by Park's research group [29,38,39], Rezai et al. [28], Sun et al. [24], Chen et al. [26], Golestaneh et al. [25], Babapoor et al. [40]. They all observed that the heat capacity values and phase change temperature intervals of the nanofibers produced through coaxial electrospinning had varied in a wide range as a function of the molecular weight of PEG selected as core as well as the concentration, solvent type and pumping rate of PEG solution.

In the fabrication of coaxial nanofibers of PCMs, various types of polymers have been tested as shell material such as cellulose acetate (CA) [26,28], poly(vinyl pyrrolidone) (PVP) [22], poly(vinylidene fluoride) (PVDF) [27], polyurethane (PU) nanofibers [23,41], polyethylene terephthalate (PET) [25] and polyamide 6 (PA6) [40]. The results of these studies demonstrated that the average fiber diameter and fiber length as well as the mechanical properties of nanofibers dependent on the type of polymer picked as shell, concentration and pumping rate of polymer solution under given electrospinning conditions.

The use of PAN in the manufacture of electrospun form-stable PCM nanofibers has recently been studied due to its very good filament forming properties, high tensile strength and elastic modulus, thermal stability and low density [42–46]. Ke et al. fabricated a form-stable composite PCM with the methyl stearate (MES) mixed in the supporting matrix of PAN (50,000–60,000 g mol^{-1}) using simple electrospinning method and investigated the composite nanofibrous mats for their changing thermal and mechanical properties when loaded with various contents of graphene oxide [47]. Esmaeilzadeh et al. prepared PEG-PAN nanofibers with different amounts of multi walled carbon nanotubes (MWCNTs) through single electrospinning [48]. The number of published articles concerning with PAN-PCM shell/core structures is limited as well. Wan et al. studied PAN-co-IA/isopropyl palmitate and paraffin oil (PCM) sheath/core nano-fibers by coaxial electrospinning, reporting phase change enthalpies for only PAN-co-IA/isopropyl palmitate nano-fibers but no thermal transition for PAN/paraffin oil nanofibers [49]. Very recently, Haghighat et al. studied the encapsulation of *n*-alkanes in PVP, PVDF and PAN [50], concluding that PAN solution was not suitable for embedding *n*-octadecane into the core.

Although the coaxial electrospinning has become a promising method to develop form-stable PCMs, the use of PAN in shell/core nano structures is quite new and the information on their chemical, structural and thermal phenomena is quite limited. There still exists a knowledge gap with respect to coaxial electrospinning of PAN and PCMs to develop diversified dynamic heat storage materials suitable for different industrial energy applications. More specifically, the coaxial electrospinning of PAN-PEG and PAN-PEGME shell/core nanofibers has never been reported in the previous studies. PEGMEs are good PCM candidates; however, to the best of our knowledge, their thermal properties have not yet been addressed in this respect despite they provide phase transitions with considerable heat enthalpies in different temperature intervals. The objective of the present study is to design and develop bicomponent nanofibers composed of PAN shells and various PEG and PEGME cores for use as novel thermal energy storage materials that ensure the continuity of the microclimate of the system despite fluctuations in the temperature of the surrounding medium and are suitable for further manufacturing practices. The shell material of PAN (150,000 g mol^{-1}) is preferred considering its good thermal, chemical and fiber forming properties as well as its potential use in both energy and nanofiber applications. A number of low molecular weight PEGs (400–2000 g mol^{-1}) are selected due to their perfect thermal properties, especially the high latent heat of fusions at relatively low and normal temperatures, chemical stabilities and biodegradability. Similarly, three PEGMEs (550–5000 g mol^{-1}) for the first time are chosen regarding the lack of their applications in the shape stabilized PCM manufacture. The coaxial electrospinning is applied at optimized processing conditions to produce uniformly shaped bicomponent nanofibers. Structural and thermal characterizations of the as-spun nanofibers are investigated in depth by using Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetry (TGA). Scanning electron microscopy (SEM) is used to identify the morphologies of the electrospun PAN-PEG and PAN-PEGME nanofibers. In addition, to seek the potential use of PAN-PCM nanofibers in textile-based composites, four sandwich-like structures were developed and characterized for their thermal properties.

2. Experimental study

2.1. Materials

A PAN copolymer, which consists of 99.5% acrylonitrile (AN) and 0.5% maleic anhydride (MAH), (H_2CHCN)$_n$, was supplied by Good Fellow Cambridge Limited (Ermine Business Park, Huntingdon, England; CAS No: 25014-41-9) in powder form and used as the shell material in the coaxial electrospinning process. Its average molecular weight was 150,000 g mol^{-1}, its density was 1.18 g cm^{-3}, and its mean particle size was 50 μm [51].

Eight different types of organic PCMs were used as core materials in the same process to enhance the thermal properties of the PAN-based nanofibers. Poly(ethylene glycols) (PEGs) with molecular weights of 400 g mol^{-1} (PEG400), 600 g mol^{-1} (PEG600), 1000 g mol^{-1} (PEG1000), 1500 g mol^{-1} (PEG1500) and 2000 g mol^{-1} (PEG2000) and PEG methyl ethers (PEGMEs) with molecular weights of 550 g mol^{-1} (PEGME550), 750 g mol^{-1} (PEGME750) and 5000 g mol^{-1} (PEGME5000) along with the chemical reagent dimethyl acetamide (DMAc, C_4H_9NO) were purchased from Sigma-Aldrich Inc. These materials were all technical grade and used without further purification.

2.2. Coaxial electrospinning of PAN-PCM nanofibers

The PAN-PCM nanofibers were produced using a coaxial electrospinning device (Yflow Co., Spain) [52], which was suitable for the fabrication of shell/core structures in one step. The spinneret of the device consists of two stainless steel coaxial needles with outer diameters (ODs) of 0.9 and 1.7 mm and inner diameters (IDs) of 0.6 and 1.4 mm, respectively, connected to a reservoir. The grounded flat stainless steel plate was placed 15 cm from the coaxial nozzles, and a double polarized system (−30 kV, +30 kV) was used to effectively collect the nanowebs. The system was equipped with a Taylor cone visualization system.

To produce electrospun heat storing bicomponent nanofibers, the shell and core solutions were prepared by separately dissolving PAN and each of the PCMs in DMAc. To prepare the shell solution, 150 mL of DMAc and 6% PAN (by weight) were added to a glass sample bottle and stirred at 500 rpm using a magnetic stirrer at 35–40 °C for 4 h to obtain transparent solutions. The core solutions were prepared at two different concentrations: either 40 wt% or 30 wt% PEG in DMAc and either 30 wt % or 20 wt% PEGME in DMAc. Therefore, the weight ratios of the core materials in the core/shell compositions (RW_{core}) were calculated as