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Composite nanofibrous sheets of fatty acids and polymers as thermo-regulating enclosures

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ABSTRACT

In this work we report fabrication and study of Polyvinyl Alcohol (PVA)-Fatty acids composite nanofibrous mats with an aim to develop thermo-regulating enclosures. Fatty acids, an important class of phase change materials (PCM), can serve as energy storage/recovery materials due to their high latent heats. PCM-PVA composite nanomats are fabricated by incorporating the PCMs into electrospun polymeric mats by two methods: (i) in 'drop-cast' composite mats, the molten liquid binary mixtures of the PCMs are gently dropped on to the electrospun PVA nanomats and fill the voids by capillary-suction, and (ii) in 'mixed-and-spun' composite mats, the fatty acid mixture solution is mixed with the PVA spinning solution and electrospun. The nanofibrous-mats of PVA and a series of mixtures of lauric acid (LA) and stearic acid (SA) prepared using the above two methods are characterized using differential scanning calorimetry (DSC), X-Ray diffractometry, and scanning electron microscopy. Phase diagrams constructed using the transition temperatures from DSC are interpreted as phase diagrams of the LASA binary mixture inside a nanofibrous polymeric medium, as opposed to its bulk phase diagram. The LASA mixture in PVA nanomats exhibits a eutectic phase diagram similar to their phase behavior in bulk. However, the eutectic temperature (T_e) is significantly altered in composite nanomats as compared to its bulk value of 39.5 °C: $T_e = 34$ °C in "drop cast" composite mats, and further drops to 30 °C in the "mixed-and-spun" composite mats. Tensile tests show considerable softening in the composite mats. Application of regular solution model suggests that an enhanced attraction between LA and SA components, attributed here to nanoconfinement, may be responsible for this change. SEM images show partial wetting of the PVA nanofibers by the fatty acids in "drop cast" composite mats and uniform fibers in "mixed-and-spun" composite mats samples. Thermoregulation ability of these mats is confirmed by monitoring the temperature vs. time profile inside a vial filled with hot water and wrapped around by the composite nanomats.

1. Introduction

Various approaches being pursued to meet the challenge of disparity between the demand and availability of energy include finding new sources of energy, utilizing the available resources in most efficient manner, increasing the efficiency of the energy conversion devices, proper planning of energy distribution, and energy conservation by storage. In this paper, we concern ourselves with the energy storage approach. Solar thermal energy leading to temperature rise in buildings is an important concern for energy conservationists as it increases load on air-conditioning. This presents an important challenge and any technique that may regulate the temperature of an enclosure is likely to offer a potential solution. To this end, we envisage a sheet like object containing the phase change materials (PCM) which can be wrapped around a volume and will be able to regulate the inside temperature by storing the latent heat of phase transformation of the PCM material dispersed inside the sheet-like medium. Use of PCMs as materials for thermal energy storage and retrieval has been studied extensively due to their advantageous properties including high storage density as well as small temperature variation between storage and retrieval [1–3]. The PCMs can be generally classified into inorganic materials, organic materials and their mixtures. Among the previously studied PCMs, fatty acids constitute an attractive class of materials from the point of view of solar thermal energy storage and have found use in areas such as building materials and air-conditioning. Owing to their attractive features such as an easily accessible transition temperature (in the range of 30 °C to 60 °C), high latent heat, chemical stability, non-toxicity, non-corrosiveness, and cost-effectiveness, these materials

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have gained popularity in thermal energy storage applications [4–8]. Two important aspects of these materials relevant to their utility in solar thermal energy storage, also the subjects of concern of this paper, are their transition temperature and ease in processing. Pure fatty acids undergo sharp crystalline transitions and one way to control the transition temperature of these materials is by using mixtures of varying compositions. However, phase separation on mixing may lead to severe inadequacies. Therefore a sound information regarding the phase behavior of the mixtures is extremely necessary in order to plan the processing aspects. The phase behavior of binary mixtures of fatty acids has been extensively studied [9–11]. Conceptually, the interaction between atoms and molecules are altered on mixing and the resulting thermodynamic changes occurring in the system that varies with the change in composition, temperature, and pressure, governs the phase behavior of the mixture. A phase diagram maps the equilibrium phases in the thermodynamic parameter space. Earlier studies on the phase behavior of the bulk binary mixtures of the fatty acids have found them to form simple eutectic systems [9,12–14]. Due to the fact that the PCM mixtures exhibit a eutectic behavior, they are useful materials for energy storage as energy can be stored and recovered over a wide range of temperatures, thus enabling a superior thermal control. However, these PCMs suffer from a severe inadequacy, that is, they melt on heating and tend to flow out of the supporting medium that holds them. Therefore, an appropriate medium which provides mechanical integrity to the PCM components such that it does not spill out on melting, and yet enough surface area to the PCM components for good heat transfer is desirable. Mixing fatty acids with polymers has been one of the approaches to overcome this limitation [17]. However compositing the PCMs with electrospun nanofibrous mats [15,16] appears to be a better approach owing to a high porosity and mechanical robustness possessed by the electrospun polyermeric mats. Their structure enables efficient use of heat in melting the PCMs and holds the molten PCM [2,18–20,34] by capillarity effect. Fabrication of such electrospun nanomats composited with the PCM materials has received interest recently. Chen et al. have reported fabrication of pure PCM materials on electrospun mats such as cellulose acetate with polyethylene glycol, [18] and fatty acids on polyethylene terephthalate [2]. Cai et al. [19] have reported fabrication of a composite mat of polyamide blended with pure lauric acid. There has also been studies on binary mixtures in the nanofibrous mats, but they have been limited to bulk eutectic mixtures only [20,21]. In a related study, Cai et al. have composited the fatty acid eutectics with electrospun polyacrylonitrile (PAN) mats and carbon mats obtained by carbonization of these PAN mats, by letting the mats absorb the fatty acid eutectic mixtures. Cai et al. have examined the microstructures and the thermal energy storage/release behavior of these composited mats. However, these authors have only considered eutectic composition of the fatty acid mixtures. Also, the composites were prepared by absorbing the fatty acid mixtures on to the mats. In this work we also fabricate nano-structured PCM fiber composites mats using the electrospinning method [20–23] but we consider range of compositions of fatty acid mixtures and construct a phase diagram. We have also fabricated composite mats by a different approach where the PCM-polymer solutions are mixed before spinning ("mixed-and-spun"). Our phase diagrams show that the eutectic temperature is significantly reduced by the compositing process and is even smaller in "mixed-and-spun" samples as compared to those formed by absorbing the PCM on to the polymer nanofibrous mats ("drop cast"). However, to authors' knowledge, there have been no studies on the detailed phase behavior studies of the mixtures when they are composited with the electrospun nanofibrous mats. As a proof of concept, we also demonstrate their ability to function as a heat storage material. We have chosen lauric acid (LA) and stearic acid (SA) as the fatty acid components of the binary mixtures, and poly-vinyl alcohol (PVA) is used for making the nanofibrous material in our proposed composite nanofibrous mats [24]. A high degree of crystallinity of the supporting polymer imparts a mechanical integrity and the high surface area of the mat enables higher loading capacity for fatty acids. The PVA mats also have high thermal stability of up to 250 °C. The developed fibrous composite materials (fiber mats) can regulate the temperature of a volume enveloped by these mats, with potential applications in textile industry such as in developing smart fabric, window glass coatings for thermal regulation of interiors of the buildings, and process intensification components such as micro-reactors and micro-heat-exchangers etc. In the present work, fatty acid binary mixtures are incorporated inside the PVA nanomats by employing two different approaches. In first approach, the molten fatty acid is gently dropped and spread over a pure PVA nanomat where the fatty acid spreads and fills in the pores of the nano-fibrous mats by capillary action. These samples are referred here as "drop-cast" composite mats. In the second approach, the fatty acid components are incorporated in the spinning solution itself. The latter is referred here as the "mixed-and-spun" composite mats samples. Composite mats prepared by both the methods are characterized using SEM, XRD, and DSC, and a qualitative phase diagram is mapped. The morphologies of these mats are imaged using SEM. The results on "drop-cast" composite mats are presented in Section 3.1, and those on "mixed-and-spun" composite mats in Section 3.2. Phase-diagrams of the binary mixtures of the fatty acids inside the nanofibrous mats show a considerable change in the eutectic temperature as compared to that of the bulk binary mixtures. The eutectic temperature of the bulk mixture is 39.5 °C, [13] whereas in "drop cast" composite mats, observed eutectic temperature is found to be around 34 °C, which further drops to a value of around 30 °C in the "mixed-and-spun" composite mats. In Section 3.3 we demonstrate temperature regulation which can possibly be achieved by using these mats as enclosures. The drop in eutectic temperature can be attributed to the altered interaction between the molecular species of the binary mixture. In Section 4 we show by using the regular solution model that enhancement in the attractive interaction between the molecular components in the liquid phase may be one reason for the reduction in the eutectic temperature. The enhanced attraction may originate from the nano-scale confinement of the molecular species of the fatty acids.

2. Material and methods

2.1. Materials

Polyvinyl alcohol (PVA) of M_w ranging from 85,000 to 124,000 as the supporting polymer, and powders of lauric acid (LA), stearic acid (SA) as the composite PCMs, were purchased from SD Fine Chem ltd. and were used without further purification.

2.2. Preparation of spinning solutions

9% PVA solution in DI water was prepared by mixing and stirring it for 3–4 h at 60 °C. Then the respective fatty acid solutions in ethanol (4% by weight) were prepared. Thereafter, the PCM solution was added drop-by-drop to the PVA solution, stirring simultaneously for a couple of hours more, so as to obtain the PVA-PCM solution for electrospinning. The solution of binary mixture of LA and SA was prepared in ethanol with increasing weight % of LA in the mixture ranging from 0.1 to 0.9. As mentioned earlier the PCM-fiber composite were prepared by two approaches.