THERMAL PROTECTION OF ELECTRONIC DEVICES WITH THE NYLON6/66-PEG NANOFIBER MEMBRANES

by

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Phase change materials for thermal energy storage have been widely applied to clothing insulation, electronic products of heat energy storage. The thermal storage potential of the nanofiber membranes was analyzed using the differential scanning calorimetry. Effect of microstructure of the membrane on energy storage was analyzed, and its applications to electronic devices were elucidated.

Key words: *phase change materials, nylon6/66 nanofiber membranes, electronic devices, thermal protection, electrospinning introduction*

Introduction

Management of the generated heat arising in an electronic device is becoming an ever-more important issue with the decrease of its size and the increase of its operation speed. Ineffective dissipation of the thermal energy threatens not only its performance but also its life cycle and its reliability as well. As a result, electronic packaging has transitioned from playing the significant roles of providing interconnection and protection to the enclosed semiconducting device to serving as a conduit for transferring the heat from such a device to the environment [1].

To reduce the thermal effect from a semiconductor package, a variety of materials commonly referred to be thermal interface materials have been developed [2]. These materials are used to reduce or completely eliminate the air gaps from the contact interfaces by conforming to the rough and uneven mating surfaces. However, phase change materials (PCM) are subjected to a phase change process kept at an almost constant temperature, they can absorb or release a quantity of heat as much as their latent heat.

Latent heat thermal energy storage in PCM is considered as a developing energy technology, and there has been increasing interest in using this essential technique for thermal applications such as hot water, air conditioning and so on [3]. The method of using PCM to store and retrieve thermal energy has been studied extensively due to advantageous properties including high storage density as well as small temperature variation between storage and retrieval [4-7].

Nanofibers mats possess remarkable advantages and excellent properties such as light weight, small diameter, controllable and multiscaled porous structure, and high surface-

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to-volume ratio and so on. The advantages of strong interface interaction can reveal their possibility for a thermal conductivity enhancer for the PCM.

Electrospinning is a simple, convenient, and versatile technique for generating polymer nanofibers from solutions [8, 9] and melts [10, 11]. A pendant droplet of the polymer solution at the syringe tip is deformed into a conical shape under an electrostatic field. When the electrostatic force overcomes the surface tension, a charged jet is ejected. In the process of electrospinning, the phenomenon of bending instability results in the electrospinning jet being elongated over 10,000 times in a short distance and in less than one second [12-14]. This extremely large effective draw ratio will likely align anisotropic nanofibers, such as dispersed layered silicates or carbon nanotubes, as well as extend polymer chain conformations and influence the formation and structure of polymer crystallites.

Nylon6/66 nanofibers with diameters of 200 nm were prepared by the electrospinning, and the obtained nanofibers exhibited a large exothermic peak before eventual melting of nylon6 crystals at 220 °C. Nylon6 fibers exhibit both crystalline and amorphous phases, with the amorphous phase consisting of isotropic and anisotropic components. It is believed that the detailed structures and morphologies of the crystalline phases are important to the nylon6 properties [15].

Since polyethylene glycol (PEG) is a flexible, water-soluble polymer, it can be used to create very high osmotic pressures (on the order of tens of atmospheres). Polyethylene glycol is also commonly used as a polar stationary phase for gas chromatography, as well as a heat transfer fluid in electronic testers.

Cai *et al.* [16] reported the preparation of phase change ultrafine fibers with sheaths being LA-TiO_2-PET-done, and the fibers were prepared through electrospinning. Chen *et al.* [17] reported that the ultrafine fibers of polyethylene glycol/cellulose acetate (PEG/CA) composites could be prepared through electrospinning the mixture solutions of PEG and CA; in their composite fibers, PEG acted as the phase change material while CA acted as the supporting material. Their results indicated that the composite fibers had high thermal stability due to the supporting and/or shielding effect of the CA matrix [17].

Experimental

Materials

Nylon6/66 with the molecular weight of 10485, which was obtained from Sigma Alorich, was dissolved into anhydrous formic acid with the concentration of 88 wt.% which was purchased from Sinopharm Chemical Reagent Co, Ltd. PEG 20000 from Sinopharm Chemical Reagent Co, Ltd., was scattered in anhydrous formic acid with the concentration of 88 wt.%.

Preparation of the PEG/nylon6/66 membranes

PEG with the concentration of 20 wt.% blending with nylon6/66 with the concentration of 60 wt.% at varying ratios (9/1, 8/2, 7/3, 6/4) consists the four kinds of mixture. The final volume of each polymer blend solution was 3 ml. Each polymer solution was added into a 5 ml syringe with a needle and then mounted in a programmable syringe pump (model 210, KD Scientific Inc., USA) operated at 0.2 ml/h. The positive lead from high voltage power generator (CPS-40K03VIT, Chungpa EMT Co., Korea) was connected to the needle tip and a DC voltage of 15 kV was applied. Stretched and solidified polymeric fibers were deposited on a rotating mandrel-type collector placed 12 cm away from the needle. All electrospinning processes were carried out under ambient conditions.

Characterization of electrospun fiber meshes

Before SEM observation, all of the samples were sputter-coated with gold. Morphologies of the electrospun nanofiber were carried out with a scanning electron microscope (SEM, Hitachi S4800, Japan) with an accelerating voltage of 3 kV and the obtained five pieces of images were analyzed by Image-Pro-Plus Tool software, and totals of 100 counts were used to calculate the average diameter of nanofibers.

Analysis of the composition

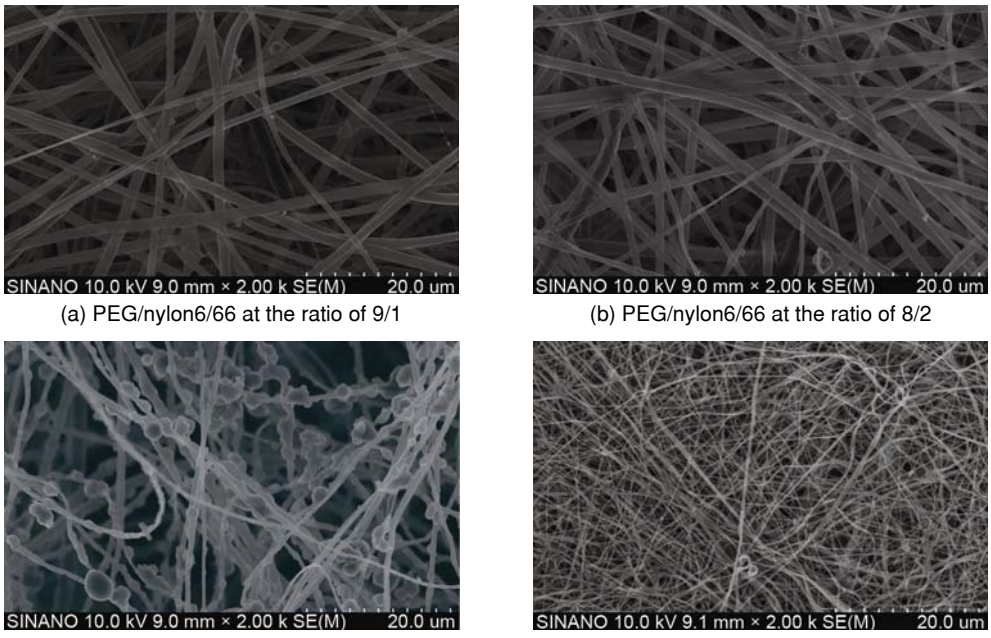
The composition of the 5 mg of electrospun nylon6/66-PEG membranes was achieved from the infrared spectra, which was measured by using Fourier transform infrared spectrometer (Nicolet 5700) and infrared microscope (Nicolet Centaurus).

The thermal behavior of nylon6/66-PEG electrospun membranes was determined with a differential scanning calorimeter (DSC, PE-S II) using 5.0 mg samples at a 10 °C/min heating rate in nitrogen. The degree of crystallinity was calculated by subtracting the measured heat of cold crystallization from the measured heat of fusion and dividing by the heat of fusion of the purely crystalline forms of nylon6/66-PEG.

Results and discussions

Material fabrication

Figure 1 shows typical FE-SEM micrographs of the nylon6/66-PEG nanofiber webs in the amplification of 2 Kx. The electrospun nylon6/66-PEG dissolved in the formic acid 88 wt.% nanofiber membrane is non-woven mesh of fiber with diameters ranging from 100 nm to 1500 nm (fig. 1) by the statistics and measurement of the software named Image-Pro-Plus.



(a) PEG/nylon6/66 at the ratio of 9/1 (b) PEG/nylon6/66 at the ratio of 8/2

(c) PEG/nylon6/66 at the ratio of 7/3 (d) PEG/nylon6/66 at the ratio of 6/4

Figure 1. FESEM micrograph of fibers electrospun from PEG and nylon6/66 dissolved in the formic acid 88 wt.% solutions at varying ratios: (a) 9/1, (b) 8/2, (c) 7/3, and (d) 6/4

Table 1. The average, the maximal and the minimal diameter at the ratios of 9/1, 8/2, 7/3, 6/4

Ratios	Average diameter [nm]	Maximal diameter [nm]	Minimal diameter [nm]
9/1	1309	1843	544
8/2	1323	1829	796
7/3	915.8	1739.6	477.6
6/4	212.1	439.3	141.6

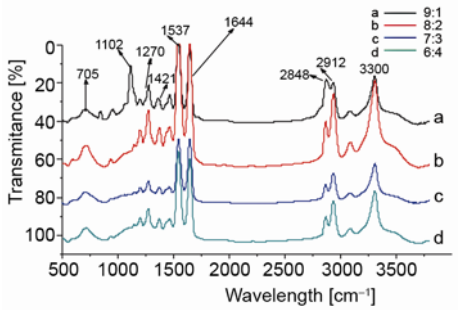


Figure 2. FTIR of electrospun PEG/nylon-6/66 (9/1, 8/2, 7/3, 6/4) blend fibrous mesh

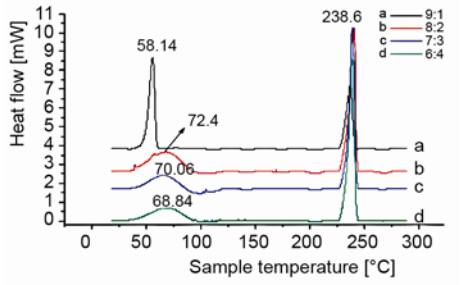


Figure 3. Differential scanning calorimetric thermograms of electrospun PEG/nylon-6/66 (9/1, 8/2, 7/3, 6/4) blend a fibrous mesh as function of sample temperature

From tab. 1 and fig. 1, some porous meshes resulted from the crossed nanofibers were observed. Multi-scaled porous structure and high surface-to-volume ratio promoted the channel to the heat dissipation from the electronic devices. The best fiber-formed nanofiber and the smoothest nanofiber appeared at the ratio of 9/1. The nylon6/66 nanofiber meshes acted as the gross roots to protect the melted PEG from flowing to the waste of PCM.

Analysis of the FTIR

In order to examine whether nylon6/66 reacted with polyethylene glycol through the specific chemical bond, IR spectra of the four electrospun nylon6/66-PEG membranes were measured as shown in fig. 2. The characteristic absorption bands at 1644 per cm induced from C=O [18] and 1537 per cm from N-H [18] consistent with a trans-conformation absorptions of nylon6/66 in four curves. $(C\text{-}H)_n$ ($n > 4$) in the nylon6/66 exhibited stretching vibration band at the 705 per cm and 1421 per cm. The characteristic absorption bands at 3300 per cm were due to the superposition of stretching vibration of O-H [19] in the PEG. The characteristic absorption bands at 1270 per cm were due to the vibration of O-H [19] in the PEG. Figure 2(a) shows the characteristic absorption bands at 1270 per cm produced due to the vibration of O-C=O because of O-H in the PEG reaction with the HO-C=O. The reaction increased the connection of the double polymer. When added in PEG, the double absorption bands appeared at 2848 per cm due to the symmetrical absorption produced from the C-H of the nylon6/66 and C-H of the PEG.

In order to examine thermal morphological changes occurring in the PEG/nylon6/66 blend mesh during incubation, differential scanning calorimetric study was performed. As shown in fig. 3, melting temperatures for PEG and nylon6/66 as-spun fibers were observed around 50 °C, and around 238.6 °C, respectively. When blended at the ratio of 9/1, melting temperature of PEG appeared at 58.14 °C was lower than the other ratios. The four temperatures fundamentally lived up to that of the protection of electronic devices. However, the heat flow tended to reach the peak at the ratio was higher than the others. While the mentioned PEG was embedded in the broad melting nylon6/66, suggesting that PEG and nylon6/66 were slightly phase-mixed.

Figure 4 shows that the heat flow varied with the change of the time. When the fiber mesh melt, the heat of the release summed up to 485.28 mJ by using the integral area under the curve. Furthermore, the remaining weight at the 58.18 °C was 3.49 mg, just as shown in fig. 5. The enthalpy of the mixing membranes reached 139.05 J/g corresponding to the enthalpy of PCM acted as the protection of electronic devices.

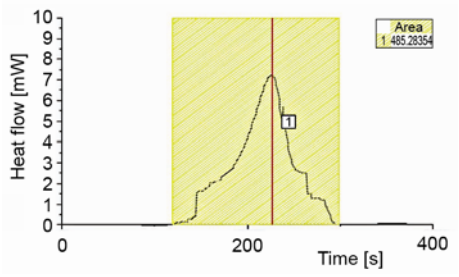


Figure 4. Heat flow changing curve with the changing of time

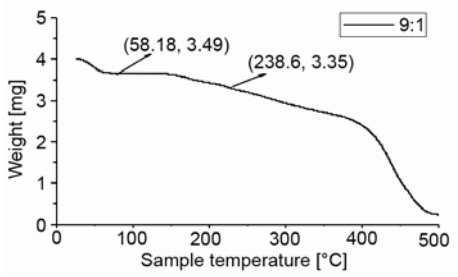


Figure 5. Remaining weight of electrospun membranes of the PEG/nylon6/66 blend fibers 9/1

Conclusions

- Multi-scaled porous structure and high surface to volume ratio promoted the channel to the heat dissipation from the electronic devices. When the ratio was 9/1, the mesh exhibited the best performance.
- The four temperatures fundamentally lived up to that of the protection of electronic devices.
- The enthalpy of the mixing membranes produced from the solution at the ratio of 9/1 reached to 139.05 J/g corresponding to the enthalpy of PCM acted as the protection of electronic devices.

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