Thermal properties of polyacrylonitrile and lauric acid and stearic acid composite fibers

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Abstract: Polyacrylonitrile and fatty acids(lauric acid and stearic acid) composite fibers were made through electrospinning. Scanning electron microscope images revealed that the composite fibers had smooth surface and good formation. Differential scanning calorimetry analysis indicated the temperature of the melting peak was around 37°C, and the composite fiber had considerable energy storage potential.

1. Introduction
As one of the representatives of smart materials, phase change materials (PCM) have been widely studied and applied in solar energy storage, air-conditioning building, temperature adjustable clothing and smart textiles and so on[1-3]. Among a large amount of PCMs, solid-liquid heat storage materials have been widely concerned. During phase change process, Solid-liquid PCMs have suitable phase change temperature range, relative high latent heat value, stable volume during phase change process[4-6]. Solid-liquid PCMs also have shortcomings. One disadvantage is liquid leakage during phase change process, which brings technical challenge and inconvenience to the practical application. There are many methods to solve this problem. For example, microcapsule encapsulation has been used as an effective way to solve this problem[7-10]. However, microcapsule encapsulation technology is rather complex. Another prosperous method is to develop a form-stable phase change material. Many researches showed a polymer-based shape stabilized PCM can effectively protect melted organic solid-liquid PCM from leaking[11-13]. Composite shape stabilized PCMs are generally composed of substrate matrix and phase change materials. Polymer material can be used as matrix to afford structural and mechanical supporting, solid-liquid PCMs are dispersed in the three-dimensional structure of the polymer to form a form-stable composite material. Polymer matrix can wrap and bound the core PCM to prevent PCMs from macroscopic flowing or leaking during the melting process. In order to make full use of the multi-scaled porous structure of electrospun fiber mats, polyacrylonitrile was electrospun to obtain a supporting matrix for PCMs in this study.

2. Experimental
2.1. Materials and chemicals
Polymer polyacrylonitrile (PAN), Lauric acid(LA), stearic acid(SA) and n,n-dimethyl-formicaci were obtained commercially.
2.2. Preparation of PAN/ LA-SA composite fiber
Fatty acids LA and SA were blended with molar ratio 8.67:1.33 and heated at 80°C for 2h. Then LA-SA mixture was cooled at environment temperature. 8~10%-wt polyacrylonitrile was dissolved in organic solvent n,n-dimethyl-formicaci. Different mass ration of LA-SA mixture was added into PAN solution and the solution was stirred magnetically for about 3h to obtain spinning solution. The spinning was conducted on a simple electrospinning device. Spinning dope was loaded in a 10ml plastic syringe with a stainless-steel needle(0.5mm in diameter).The flow rate of spinning dope was 1mL/h and static discharged voltage was 15kV. The electro-spun fibers were collected on aluminum foil with a 20cm received distance.

2.3. Characterization
The electrospun composite fibers were surveyed under scanning electron microscope(Japan Electron Optics Laboratory Co. Ltd. 6510LV) with 10kV acceleration voltage.

The phase change behaviors were examined with differential scanning calorimetry (DSC 204F1, NETZSCH). During DSC testing, temperature was increased form 25°C to 100°C with inflowing nitrogen atmosphere (50mL/min) at a rate of 8 degrees Celsius per minute. Approximately 5mg of each sample was prepared in an aluminum pan for the DSC test.

The electrospun fibrous mats(spinning for 6h) were cut into 50mm×20mm size for mechanical testing. Breaking strength and extension at break were measured using Instron5566 at 20°C, 65%R.H. Test speed was 10mm/min and clamp distance was 20mm. Breaking stress(MPa) was calculated using values of five samples.

3. Results and discussions

3.1. SEM Observation of PAN and LA-SA compound fibers
The SEM photos of pure PAN and the composite fiber with different mass ratio of LA-SA and PAN are shown in figure 1. Observed from figure 1, all pure PAN fibers and composite fibers have smooth and compact surface and cylindrical shape. With the increase of fatty acids LA and SA mixture contents in the composite fibers, fiber diameter increases and becomes uneven. On the whole, PAN and LA-SA electrospun composite fibers present good formation based on the protection and support of PAN matrix.

![Figure 1. SEM photos of pure PAN fibers and PAN/LA-SA composite fibers](image)

3.2 Thermal properties
The thermal properties of electrospun PAN(8wt%) and LA-SA composite fibers were analyzed with DSC as presented in figure 2. Phase change temperature and melting latent heat extracted from DSC curves are shown in Table 1. It is observed that phase change temperature of the composite fiber varies from 36.0~37.4°C. Mass ratio of LA-SA and PAN polymer produces little effects on phase change temperature. Onset melting temperature is around 37°C, which is a suitable temperature for energy storage application of composites fibers in textile and building fields.
Figure 2. DSC curves of electrospun PAN/LA-SA composite fibers (1,2,3,4 represents mass ratio of LA-SA and PAN is 0.5 : 1, 0.7 : 1, 1 : 1, 1.2 : 1 respectively)

Table 1. Thermal parameters the composite fibers

| LA-SA:PAN   | 0.5:1 | 0.7:1 | 1 : 1 | 1.2:1 |
|-------------|-------|-------|-------|-------|
| Melting temperature(°C) | 37.2  | 37.4  | 36.0  | 36.4  |
| Latent heat(kJ/kg) | 34.68 | 48.91 | 53.08 | 80.26 |

3.3 Tensile properties of PAN and LA-SA composite fibers

Breaking strength and extension at break of PAN and LA-SA composite fibers are given in Table 3. It is observed that the strength of PAN and LA-SA composite fiber is not high, when their mass ratio is 0.7:1, the composite fiber exhibits highest tensile strength (1.936MPa). In addition, the composite fiber with relative low LA-SA content shows high breaking elongation. This may be due to PAN is polymer matrix, supporting whole composite fibers, excessive addition of LA-SA eutectics may destroy the continuity of the PAN substrate structure. When the proportion of LA-SA and PAN is 0.7:1, LA-SA and PAN may have the most homogeneous mixture, the composite fibers obtain complete and stable shape thus better mechanical properties.

Table 2. Tensile properties of PAN and LA-SA composite fibers

| LA-SA:PAN   | 0.5:1 | 0.7:1 | 1 : 1 | 1.2:1 |
|-------------|-------|-------|-------|-------|
| Tensile stress(MPa) | 0.404 | 1.936 | 0.924 | 0.796 |
| Elongation(%) | 66.09 | 48.42 | 56.08 | 16.88 |

4. Conclusion

Polyacrylonitrile and lauric acid and stearic acid composite fibers were fabricated with electrospinning. The composite fiber presented good shape. The surface morphology, thermal properties and tensile properties were affected by lauric acid and stearic acid content. Phase transition temperature of the composite fibers was around 37°C, which means the composite fiber is suitable in application of phase change textile and building materials.

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