

Preparation and Characterization of High Latent Heat Thermal Regulating Fiber Made of PVA and Paraffin

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ABSTRACT

A convenient method for preparing the thermal regulating fibers with high latent heat has been developed. PVA thermal regulating fibers were prepared via a wet spinning process, with paraffin being the phase change material. The structures and properties of these fibers were investigated by SEM, TGA, DSC and tensile strength tester. With the paraffin content in the fibers increasing from 30wt% to 70wt%, the latent heat of the fibers increases from 42.8J/g to 87.8J/g and the paraffin phase structures change from separation into partial interconnection. PVA matrix can not wrap paraffin effectively when the paraffin content increases up to 50wt%, so the paraffin loss in the spinning process increases. The thermal stability of fibers with low paraffin content is better than that of fibers with high paraffin content. After 100 heat-and-cool cycles, the latent heat of fibers lose a little. The tensile strength of these thermal regulating fibers is good enough for application in wrapping, filling, and nonwovens.

INTRODUCTION

With the development of the textile and clothing industry, more and more functional and intelligent fibers are needed to create new types of textiles. Thermal regulating fiber is one of these intelligent fibers which has attracted much attention due to its special function of regulating environment temperature [1, 2]. Thermal regulating fibers contain phase change materials (PCMs) which absorb energy from environment in the heating process as phase change takes place and releases the latent energy to the environment in a reverse cooling process. Clothing made from thermal regulating fibers can moderate the temperature of the human body from being too hot or too cold and functions as an air-conditioner [2].

Thermal regulating fibers are prepared by combining PCMs with a fiber matrix. The percentage of PCM in fibers remarkably affects the energy storage properties of the fibers. Ordinarily speaking, a high percentage of PCM in fibers is expected to obtain

fibers with high latent heat. However, high PCM content would worsen the spinnability of the spinning fluid and cause the mechanical properties of the fibers to decline [3, 4]. Most PCMs applied in thermal-regulating fibers are solid-liquid PCMs. These PCMs are usually encapsulated into microcapsules before being combined with fibers. Microcapsules can prevent the leaking of PCMs, while decrease the energy storage density of PCMs [3, 5, 6]. Therefore, the traditional microcapsule method will lead to the low latent heats of thermal regulating fibers, which are commonly below 20J/g [4]. Such low latent heats make the thermal regulating fibers difficult to apply in the textile and clothing industries.

In this study, the thermal regulating fibers with high latent heat were made of polyvinyl alcohol (PVA) and paraffin by wet composite spinning. As the fiber matrix, PVA has good spinnability, mechanical properties and excellent barrier ability against non-polar substance. As the PCM, paraffin is a non-polar material with high energy storage density. The characteristics of PVA and paraffin make it possible to prepare thermal regulating fibers with high latent heat, acceptable mechanical strength and good durability. Previous studies show that paraffin could be well wrapped in a PVA fiber matrix when the paraffin content in the fiber was 30wt% [7, 8]. In this study, high paraffin contents were applied to obtain fibers with high latent heat. The structure and properties of the composite fibers were investigated by DSC, SEM, TGA and tensile strength tests.

EXPERIMENT

Materials

PVA (DP=1700, alcoholysis degree>99%), industrially pure, was obtained from Sichuan Vinylon Workers, China, which was washed in advanced by water; Paraffin (Melt point= 31.7°C, Melting enthalpy =156J/g), chemically pure, was purchased from Rubitherm, German; Tween-80, chemically pure, was obtained from Kelong Chemical Reagent Factory, Sichuan, China; Sodium sulfate, industrially pure,

was obtained from Sichuan Chuan Mei Co., Ltd., China.

Preparation

PVA was dissolved in water with a concentration of 16wt% at 95°C for about 4 hours. Then the paraffin and Tween-80(3wt% of paraffin) were added to the PVA solution and mixed together to form the spinning solution. The spinning solution was extruded into a sodium sulfate coagulating bath from a spinneret ($\phi=0.08\text{mm}$) to form the as-spun composite fiber. The as-spun composite fiber was drawn and collected on a bobbin. A series of composite fibers were obtained by changing the content of the paraffin. The compositions of the thermal regulating fibers are listed in *Table I*.

TABLE I. Sample composition.

Sample Number	1 [#]	2 [#]	3 [#]	4 [#]	5 [#]
PVA (w): paraffin (w)	7:3	6:4	5:5	4:6	3:7

Measurement and Instrument

The phase structure of the spinning solution was observed with an optical microscope (XSP-8C, Changfang, China).

The morphology of the composite fibers was observed with an SEM (JSM-5900, JEOL, Japan).

Fiber samples for SEM were extracted by petroleum ether to remove the paraffin phase, and fractured in liquid nitrogen before testing.

The thermal stability of fibers was studied with a TGA (WRT-2R, China).

The thermal properties of thermal regulating fibers were measured with a DSC (DSC200, NETZSCH, Germany) at the ramping rate of 5°C/min in the range of 0–150°C under N₂ atmosphere.

The mechanical properties of fibers were measured with a tensile strength tester (YG001A, China). Initial length is 20 mm; Tensile testing speed was 20mm/min.

The thermal cycle tests were preceded as following: the test tubes loaded with 0.5g fibers were put into an 0°C ice water bath for 10mins, then into a 50°C water bath for 10mins. This process was repeated 100 times.

RESULTS AND DISCUSSION

The Phase Structure of Spinning Solution

Uniform and stable spinning solution is the prerequisite for spinning. The paraffin and PVA aqueous solution is a thermodynamic incompatible system. Emulsifier must be used to make the system stable. In this study, Tween-80 was selected as the emulsifier to make the paraffin dispersible in the PVA aqueous solution. It can be seen from *Figure 1* that paraffin phases were dispersed in the PVA aqueous solution uniformly. The average diameter of paraffin droplets is about 3.8 μm . 99% of paraffin droplets are smaller than 10 μm . Therefore, in the spinning process, these paraffin droplets could easily pass through the nozzle hole of 80 microns, and not lead to fiber to breakage. In the coagulation bath, these paraffin droplets were frozen in the PVA fiber matrix.

Morphology Analysis of Composite Fibers

Figure 2 presents that the composite fibers have typical fibrous appearances. These fibers are form-stable even after thermal cycles. *Figure 3* shows the SEM photos of fiber cross-sections and surface structures. The holes in the fibers are caused by paraffin phases which have been etched out. In fiber 1[#], the holes are separated from each other; while in fiber 5[#], the holes are intensive, even some are interconnected. There are fewer holes on the surface of fiber 1[#] in comparison with fiber 5[#]. This indicates that the paraffin changes from dispersed phase to partial continuous phase with the increase of content in the fibers. When paraffin presents in partial continuous phase structure, the fiber matrix could not wrap paraffin very well. Some paraffin would move through continuous channels to the fiber surface easily. Therefore, the high paraffin contents are detrimental to the durability of the composite fibers.

Thermogravimetry Analysis

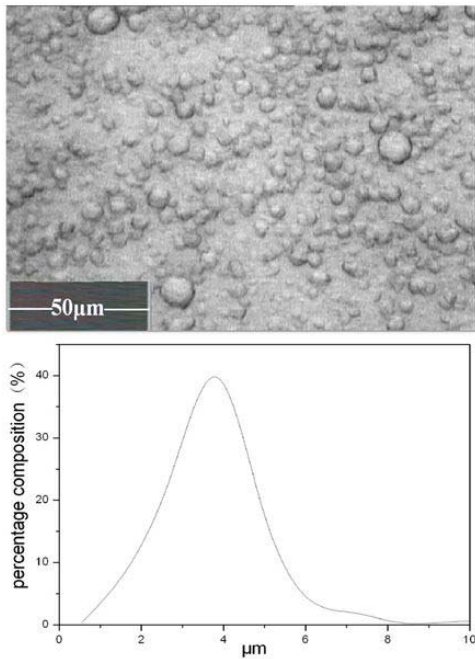


FIGURE 1. The optical microscope photo of spinning solution and its particle-size analysis (PVA (w): paraffin (w)=6:4)



FIGURE 2. The digital photo of PVA paraffin thermal regulating fibers.

TGA was used to assess the thermal stability property of the composite fibers. TGA curves of fibers 1[#] to 5[#] are shown in *Figure 4*. Results show that all the TGA curves have two stages of weight loss. The first stage begins at about 150°C, and the second stage begins at about 220°C. This phenomenon is due to the different weight loss temperatures of paraffin and PVA. 150°C is the temperature at which paraffin begins to evaporate, while 220°C is the temperature at which PVA begins to thermally degrade. With the increase of paraffin content, the first stage of weight loss becomes more and more obvious. It can be concluded from *Figure 4* that the paraffin in fiber 1[#] and 2[#] has

only a small weight loss and the majority can keep stable until PVA begins to thermal degrade at 220°C, while the paraffin in fiber 3[#] to 5[#] is almost completely lost before the thermal degradation of PVA. This means that the high paraffin contents would make the fiber structure fail to wrap paraffin effectively. This also can be proved by the microstructure of the fibers shown in the morphology analysis of composite fibers. The paraffin in fiber 3[#] to 5[#] can be a continuous phase structure. During TG analysis, the paraffin contained in the fiber would be evaporated through the continuous phase channels.

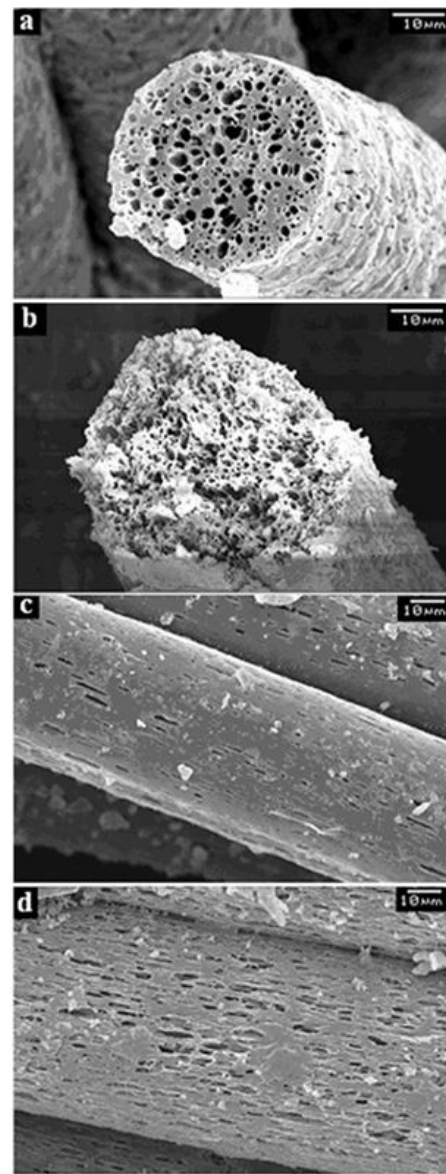


FIGURE 3. The SEM photographs of composite fibers. (a, b) the cross section of 1# fiber and 5# fiber ; (c, d) the surface of 1# fiber and 5# fiber.

Differential Scanning Calorimetry

The DSC curves of composite fibers are shown in Figure 5. The results from the detailed data of DSC analysis are also summarized in Table II. With the increase of the paraffin contents, the latent heats of composite the fibers increase from 42.8J/g to 87.8J/g. Due to the high paraffin contents, the latent heats of these composite fibers are much higher than many other thermal regulating fibers which are made of microencapsulated PCMs. The properties of high latent heat provide these fibers with more potential application fields. Table III gives the theoretical latent heats and experimental latent heats of composite fibers, in which the theoretical latent heats of composite fibers are calculated based on the

paraffin content in the fibers and the latent heat of pure paraffin. During the spinning process, the fibers were affected by outside forces. Part of the paraffin in the fibers would be lost in the spinning processes especially in the coagulation bath. As a result, the actual paraffin contents are lower than the calculated values. The loss ratio of ΔH_m can be considered equal to that of paraffin. Results show that the loss ratio of paraffin increases gradually with the increase in paraffin contents. The microstructures of composite fibers can also explain the relationships between paraffin contents and paraffin loss ratio during spinning process. When the paraffin contents exceed 50wt%, the paraffin loss ratio becomes stable, which is about 19%.

TABLE II. The thermal properties of composite fibers.

Sample No.	ΔH_m (J/g)	T_m (°C)	ΔH_c (J/g)	T_c (°C)
1 [#]	42.8	30.3	45.6	18.8
2 [#]	55.4	31.2	52.6	20.1
3 [#]	63.6	31.2	65.6	22.7
4 [#]	75.4	31.7	77.9	22.3
5 [#]	87.8	31.7	96.2	18.9

Note: T_m - peak temperature on the DSC heating curve; T_c -peak temperature on the DSC cooling curve; ΔH_m -melting enthalpy on the DSC heating curve; ΔH_c -crystallization enthalpy on the DSC cooling curve.

TABLE III. The theoretical latent heat and experimental latent heat of composite fibers.

Sample No.	Theoretical ΔH_m (J/g)	Experimental ΔH_m (J/g)	Loss rate (%)
1 [#]	46.8	42.8	8.6
2 [#]	62.4	55.4	11.3
3 [#]	78.0	63.6	18.5
4 [#]	93.6	75.4	19.5
5 [#]	109.2	87.8	19.6

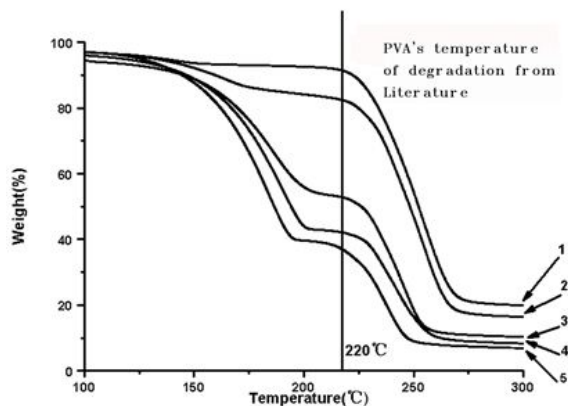


FIGURE 4. The TGA curves of composite fibers.

Thermal Cycle Tests of Composite Fibers

The thermal properties of composite fibers after 100 heating-cooling thermal cycles are shown in Table IV. All the latent heats of the composite fibers decrease after thermal cycling. Latent heats of fibers with higher paraffin contents reduce more after thermal cycling. The decrease in latent heats may be caused by the loss of paraffin. In fiber 4[#] and 5[#], paraffin can easily diffuse to the fiber surface and volatilize through the continuous channels during the thermal cycles. Therefore, the latent heat loss ratio of fiber 4[#] and 5[#] are relatively large. Table IV also shows that T_c and T_m of composite fibers do not change much after thermal cycling, which demonstrates that these composite fibers have stable thermal properties and no apparent super cooling.

TABLE IV. The thermal properties of composite fibers after 100 thermal cycles.

Sample No.	ΔH_m (J/g)	T_m (°C)	ΔH_c (J/g)	T_c (°C)	$\Delta H_{m, Loss}$ ratio (%)
1	39.7	31.3	43.1	19.2	7.11
2	47.9	32.0	49.3	20.8	13.5
3	52.4	31.8	53.3	21.7	17.6
4	57.1	33.0	60.2	22.1	24.3
5	68.2	31.8	70.5	22.8	22.3

Mechanical Properties of Composite Fibers

Figure 6 shows the stress-strain curve of the composite fibers. Table V shows that the mechanical strengths of these composite fibers are much weaker than normal PVA fibers. Thus, these fibers cannot be applied directly as materials for weaving. But these fibers still have an acceptable strength to be applied in filling, wrapping, and other nonwoven applications.

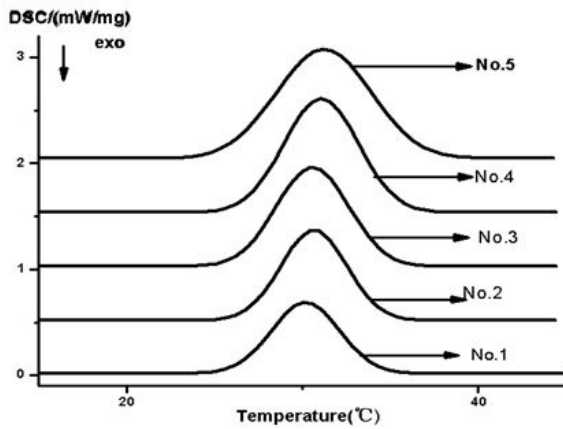


FIGURE 5. The DSC curves of composite fibers.

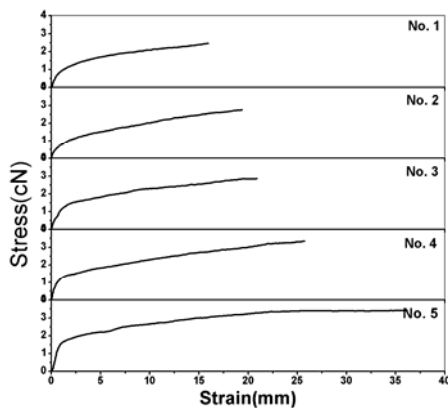


FIGURE 6. The stress-strain curve of composite fibers.

TABLE V. The mechanical properties of composite fibers.

Sample No.	Breaking strength (cN/dtex)	Elongation (%)
1 [#]	0.68±0.03	180.8±18.0
2 [#]	0.66±0.03	130.9±15.0
3 [#]	0.57±0.04	104.3±10.0
4 [#]	0.55±0.03	95.8±11.3
5 [#]	0.49±0.02	79.7±12.4

CONCLUSION

In this study, thermal regulating fibers made of PVA and paraffin were prepared by a wet spinning process, which had high latent heats and almost no super cooling. With the different contents of paraffin, the fibers presented different microstructures. When paraffin content exceed 50wt%, the paraffin phases in the fibers became inter-connected, which caused a decrease in the thermal stability of these composite fibers. These thermal regulating fibers also have nice durability. The latent heats decreased slightly after 100 heat-and-cool cycles. These fibers are form-stable and have acceptable mechanical strength, which means they could be applied in nonwoven fields such as wrapping, filling, and packing.

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REFERENCES

- [1] Mohammed M. Farid; Amar M. Khudhair; Siddique Ali K. Razack; etc. A review on phase change energy storage: materials and applications. *Energy Conversion and Management* 2004, (45):1597-1615.
- [2] S.X. Wang; Y. Li; J.Y. Hu; et al. Effect of phase-change material on energy consumption of intelligent thermal- protective clothing. *Polymer Testing*, 2006, (25):580-587.

- [3] Cosimo Carfagna; Paola Persico. Functional Textiles Based on Polymer Composites. *Macromol. Symp.* 2006, (245-246): 355-362.
- [4] Qinghao Meng; Jinlian Hu. A temperature-regulating fiber made of PEG-based smart copolymer. *Solar Energy Materials & Solar Cells.* 2008, (92):1245-1252.
- [5] X. X. ZHANG; X. C. WANG; X. M. TAO; et al. Energy storage polymer/MicroPCMs blended chips and thermo- regulated fibers. *Journal of materials science.* 2005, (40): 3729-3734.
- [6] Changzhong Chen; Linge Wang; Yong Huang. Morphology and thermal properties of electrospun fatty acids/polyethylene terephthalate composite fibers as novel form-stable phase change materials. *Solar Energy Materials & Solar Cells.* 2008, (92):1382-1387.
- [7] Jiang Mengjin; Song Xiaoqing; Xu Jianjun; et al. Preparation of a new thermal regulating fiber based on PVA and paraffin. *Solar Energy Materials & Solar Cells.* 2008, (92):1657-1660.
- [8] Mengjin Jiang; Xiaoqing Song; Guangdou Ye; et al. Preparation of PVA/paraffin thermal regulating fiber by in situ microencapsulation. *Composites Science and Technology.* 2008, (68):2231-2237.

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