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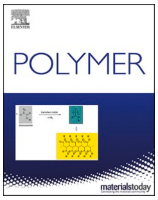

Supercooling suppression and mechanical property improvement of phase change nanofibers by optimizing core distribution

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ABSTRACT

Phase change fibers (PCFs) as a kind of composite material, the composition and spatial distribution of each phase have a great influence on its thermal and mechanical properties. In this article, PCFs with polyvinylpyrrolidone (PVP), polyvinyl butyral (PVB), and polyacrylonitrile (PAN) as sheath and 30% octadecane kerosene as core were prepared by coaxial electrospinning. It was found that octadecane had the highest supercooling degree when it was encapsulated in PVB. Thus, we used pure octadecane, 30% octadecane of isopropanol, chloroform, and kerosene solutions as core solutions, adjusted the fine structure of octadecane in PVB sheath, and four kinds of PCFs with different octadecane particle size and spacing were prepared. Successfully reduced the supercooling degree of octadecane. To compare the mechanical properties of the four fibers. It was found that the composite fiber obtained by using isopropanol as octadecane solvent had the most comprehensive mechanical performance. To find a universal method to control the distribution structure of phase change materials (PCMs) in fibers by coaxial electrospinning, we used PAN and PVDF as the sheath solution, pure octadecane, 30% octadecane in isopropanol, chloroform, petroleum ether, and kerosene solutions as a core solution to prepare the PCFs. Characterization results and analysis of the properties of solutions showed that only when the viscosity of the core and sheath solution was relatively low, it could obtain the bamboo-like structured fibers. And continuous core-sheath structured fibers could be obtained in two situations. First, the low viscosity of sheath solution and high viscosity of core solution; second, the high viscosity of sheath solution.

1. Introduction

Phase change fibers (PCFs) is a kind of functional fiber developed by combining phase change materials (PCMs) and fiber manufacturing technology [1–4]. When the temperature of the external environment changes, the PCMs inside the fibers can absorb- and store energy during the melting process, and release energy during the solidification process [5–9]. Through heat exchange with the external environment, the fibers realize energy storage or temperature adjustment function. It can be applied to many fields such as food packaging, clothing, energy storage, and industrial waste heat recovery [10–15].

Supercooling refers to the phenomenon that liquid does not solidify after reaching the freezing point under certain pressure, and understanding the means and factors to suppress supercooling is basic to advance thermal energy research and technology [16–19]. Adding nucleating agents is the most common method used by researchers to reduce supercooling degree [19–22], but the consequent reduction of latent heat is a serious drawback. A study has pointed out that the supercooling degree of PCMs in microcapsules will be affected by the composition and structure of the microcapsules. Cao et al. [23] created a new method to suppress supercooling by changing the synthesis parameters and optimizing the sheath composition and structure, but the specific structural changes had not been illustrated. Will the supercooling degree of PCMs in nanofibers be affected by the composition and structure of the nanofibers? As far as we know, there is no corresponding literature to demonstrate the relationship between fine structure and supercooling degree.

As a composite material, PCFs not only keep the advantages of each component but also can obtain the comprehensive properties that cannot be achieved by a single component material through the

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complementary and correlation of the properties of each component [24–26]. There is the great meaning of precisely controlling the content and distribution of each component. Electrospinning is a simple technology to prepare core-sheath PCFs. Researchers such as Sun et al. [27–32] have reported core-sheath structured PCFs, and periodic core filling structured PCFs have also been fabricated by other researchers [33–39] with a different method such as emulsion electrospinning, ordinary electrospun of a blend solution with core and sheath component and melt coaxial electrospinning. However, as far as we know, there is almost no literature that has reported that how to control the distribution structure of PCMs in fibers. And there is a lack of purposeful synthesis of specifically structured PCFs, almost no people have studied the controlled synthesis of the two structures, especially the precise regulation of the core distribution in the sheath. In fact, it is usual to load some functional substances of small molecules in the polymer fibers to synthesize composite functional nanofibers by coaxial electrospinning, but this will lead to the mechanical properties of the whole material decreased [2,40–42]. Therefore, it is necessary to study the loading mode of small molecules to reduce the performance degradation. Zhou et al. [43,44]synthesized a series of bamboo-like fibers by microfluidic-electrospinning technology, which precisely controlled the fine structure of hollow fibers. Analyzed the mechanical properties of an individual fiber and found that the bamboo-shaped fibers have great toughness, which has great application value. Though the fiber is hollow, the studied performance is relatively simple [43,45,46]. So there is great potential to accurately synthesize bamboo-structured nanofibers and loaded with PCMs to be applied to the relative fields and study their comprehensive performances.

In this study, a series of phase change nanofibers with different periodic core filling structures and core-sheath structures were respectively prepared via the coaxial electrospinning technique. By changing the octadecane solvent, we successfully regulated the distribution of octadecane in the fibers. The thermal and mechanical properties of PCFs and the viscosity of each sheath solution and core solution were tested and analyzed. It was found that the supercooling degree of PCMs in the fibers was affected by the composition and structure of the fibers. By controlling the viscosity of the sheath solution and the core solution, two kinds of fibers with core-sheath structure and different periodic core filling structures could be synthesized purposefully, which had certain application values.

2. Experimental procedure

Materials. Kerosene, polyvinyl butyral (PVB, B-98, Mw = 40000–70000), petroleum ether, N, *N*-dimethylacetamide (DMAc), poly (vinylidene fluoride) (PVDF, Mw = 400000) were purchased from Aladdin Chemistry Co. Ltd. Isopropyl alcohol, chloroform, sodium chloride, ethanol, and N, *N*-dimethyl formamide (DMF) was purchased from Hangzhou Gaojing Fine Chemical Industry Co. Ltd. Octadecane (99%, melting point is about 28.2 °C) and Polyvinylpyrrolidone (PVP, K88-96, Mw = 1300000) were purchased from Macklin Biochemical Technology Co., Ltd. Polyacrylonitrile (PAN, Mw = 140000) was purchased from Sinopec Shanghai Petrochemical Co. Ltd. China.

Methods. To obtain the sheath solution, PVB with the concentration of 14 wt% was added into ethanol with magnetic stirring for 24 h, and PVP and PAN with the concentration of 14 wt% were added into DMF with magnetic stirring for 24 h. PVDF with the concentration of 24 wt% was added into DMAc, and 0.1 wt% NaCl was also added into the blended solution with violent magnetic stirring in a 50 °C water bath for 10 h. Core solutions were pure octadecane, 30% octadecane of isopropanol, chloroform, petroleum ether, and kerosene solutions. The samples were fabricated by the coaxial electrospinning technique. The in-line stainless-steel needles consisted of an outer needle (outer/inner diameters were 1.49/1.01 mm) and an inner needle (outer/inner diameters were 0.72/0.41 mm). The ambient temperature was controlled at 40–50 °C to completely melt and dissolve octadecane and prevent them from cooling too fast to clog the needle, and the relative humidity was 45%.

To obtain the fibers with PVB as sheath and octadecane as core, four kinds of different core solutions were all used respectively. The sheath feed rate was 0.5 mL/h, the core feed rate was 0.08 mL/h. For the sample with pure octadecane as core solution, the core feed rate was adjusted to 0.042 mL/h to ensure a similar latent heat with other samples. To obtain the fibers with PVP as sheath and 30% octadecane of kerosene solution as the core solution. The solutions were electrospun at different combinations of 0.5 ml/h sheath feed rate and 0.08 and 0.1 ml/h core feed rates. To obtain the fiber with PAN and PVDF as sheath and octadecane as core, pure octadecane, 30% octadecane of isopropanol, chloroform, petroleum ether, and kerosene solutions as the core solution. The solutions were electrospun at different combinations of 0.5 ml/h sheath feed rates and 0.08, 0.09, and 0.1 ml/h core feed rates. For the sample with pure octadecane as core solution, the core feed rate was adjusted to 0.040 mL/h to ensure a similar latent heat with other samples. The applied high voltage was 16.1 kV and the distance from tip to the collector was about 13.5 cm for samples with PVB, PAN, PVP as the sheath. 30 kV and 25 cm for samples with PVDF as the sheath.

Characterizations. The morphology of the prepared nanofibers was observed by field emission scanning electron microscope (FE-SEM, ULTRA55, Zeiss), and the acceleration voltage was 3 kV. Before observation, the sample was pre-soaked in petroleum ether for 24 h and then coated with a thin layer of gold. The diameters of 100 random fibers were measured by ImageJ software, and their mean values were calculated. A transmission electron microscope (TEM, JEM-2100, JOEL) was used to investigate the interior structure of the nanofibers and the acceleration voltage was 200 kV. All TEM samples were prepared by directly depositing the electrospun nanofibers onto 400-mesh carbon-coated Cu grids, and then immerse the grids in petroleum ether for 24 h to remove octadecane. The tensile property was measured by a multifunctional mechanical tester (KES-G1) with an extension rate of 0.1 cm/s at 25 °C. The samples were cut into 0.5 × 2 cm pieces, and seven samples of each type were all measured and the thickness accurate to 1 μm. Differential scanning calorimetry (DSC, Q2000) was implemented in nitrogen flow with a heating and cooling rate of 10 K/min, the samples were heated from 0 to 50 °C and cooled from 50 to 0 °C. Solution viscosity was measured by Anton Paar MCR 301 with a shear rate from 0.1 to 100 1/s, the test temperature of pure octadecane was 50 °C, and for isopropanol, chloroform, petroleum ether, kerosene solution of octadecane, the test temperature was 40 °C.

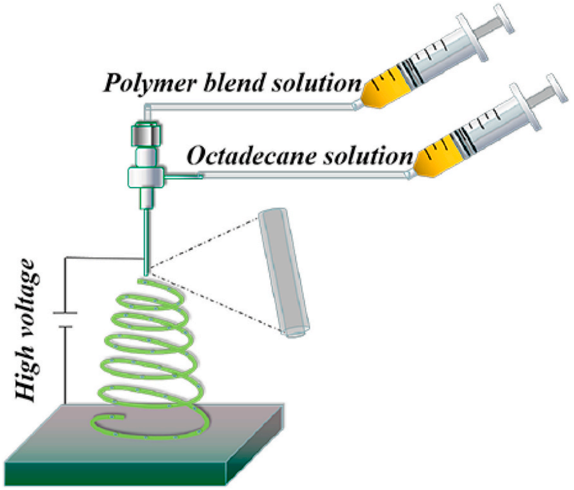

Fig. 1. Schematic diagram of coaxial electrospinning.

3. Results and discussion

Briefly, all samples were fabricated via the coaxial electrospinning technique as shown in Fig. 1. The sheath and core solutions were poured into two 10 mL plastic syringes and connected to two in-line stainless-steel needles. When a high voltage was applied on the needles, a jet would be formed, then the solvent vaporizes during the jet process, and the fibers could be obtained on the collector. Table S1 was the list of reagent and material nomenclature abbreviations. Table S2 was a summary of the experimental design.

To study the relationship between PCFs composition and supercooling, we prepared PCFs with PVP, PAN, PVB as sheath, and octadecane as core. As shown in Fig. 2 a-b, a slight increase in loading capacity has almost no effect on the supercooling degree. Fig. 2 d compares the crystallization peaks of the three. Three kinds of PCFs appear supercooling. PAN/octa has only one crystallization peak, and the supercooling degree was the smallest. The supercooling degree of PVP/octa was greater than PAN/octa, with two crystalline peaks. The PVB/octa supercooling degree was the largest, there were three crystallization peaks, and the crystallization temperature range was very wide. This may lead to partial latent heat values that cannot be used effectively in actual use. The following was a further study of PVB/octa, hoping to find a way to alleviate the severe supercooling of the fibers.

Inspired by a study that the supercooling degree of PCMs in the microcapsule was affected by the composition and structure of the microcapsule, we guess the supercooling degree of PCMs in fiber have similar performance. It was verified in the previous experiment that the supercooling degree was affected by fiber composition, and the supercooling degree of octadecane in the PVB sheath was the largest. Next, it was necessary to control the distribution structure of octadecane in the PVB sheath to verify the influence of different structures on the supercooling degree of PCMs. To achieve this, the method adopted in this article was to change the solvent of octadecane. Because for a successful coaxial electrospinning process, the two-layer solution of the sheath and the core were immiscible, and the amount of charge distribution in the sheath and core solution was not equal, and the charge was basically on the surface of the sheath solution, which causes the driving forces of the two layers of solutions were inconsistent, resulting in large shear stress between the sheath and the core solution. It was guessed that the magnitude of the shear stress and the viscosity of the core solution were the keys to obtaining PCFs with different internal structures. Therefore, we tried many-core solvents with differences in properties to prepare PCFs and found that not all solvents can successfully load octadecane into the fibers. Choosing isopropanol, kerosene, and chloroform to dissolve octadecane can be successful, and the pure molten octadecane is also selected as the core solution because its viscosity is the largest.

Fig. 3 is the FE-SEM image of PVB/octa fibers prepared with different core solvents. The four kinds of fibers have been soaked in petroleum ether for 24 h to remove the internal PCMs. From Fig. 3a, b, and 3c, it can be found that there are many depressions on the fibers, and these depressions show a bamboo-like form. This depression was left after octadecane was washed off, proving that octadecane was loaded into fibers successfully. However, when pure octadecane was the core solution, the obtained fibers can hardly see the depressions (Fig. 3d). The reason may be that the octadecane was distributed in PCFs in the form of the continuous core-sheath structure so that the diameter of the core layer will be smaller. When the octadecane was washed away, the remaining polymer layer was thicker than 3a, 3*b*, and 3c. Therefore, it was not easy to collapse.

The TEM image in Fig. 4 clearly shows the different internal structures of the PVB/octa fibers prepared with different core solvents. Fig. 4a was PVB/octa fibers prepared by using isopropanol as the core solvent, which was later named STR-1. The octadecane was distributed in the PVB sheath with small particles and short spacing. Fig. 4b uses chloroform as the core solvent(STR-2), the particle size was similar to the former, but the spacing was larger than the former. Fig. 4c uses kerosene as the core solvent(STR-3). Compared with the former two, the morphology of the octadecane particles has a great change. The particle size was becoming increasingly narrow and long. The spacing between the particles has also increased a lot. In Fig. 4d, the core solution was

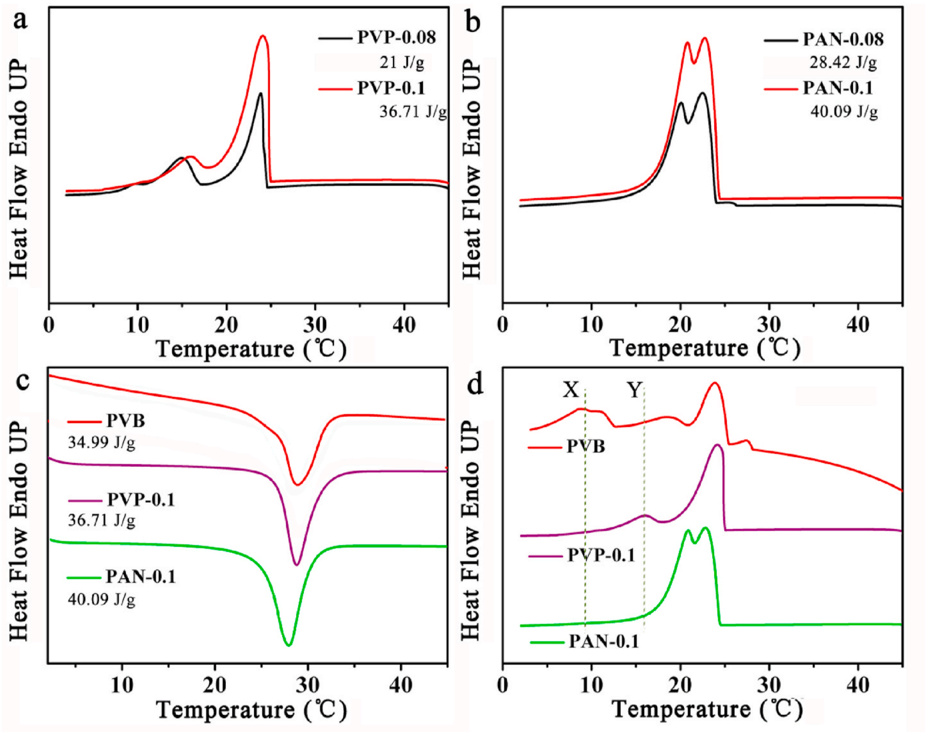

Fig. 2. DSC curves of samples with (a) PVP and (b) PAN as sheath (0.08 and 0.1 means the core feed rate). DSC curves of samples with different polymers as sheath, (c) heating stage, (d) cooling stage.

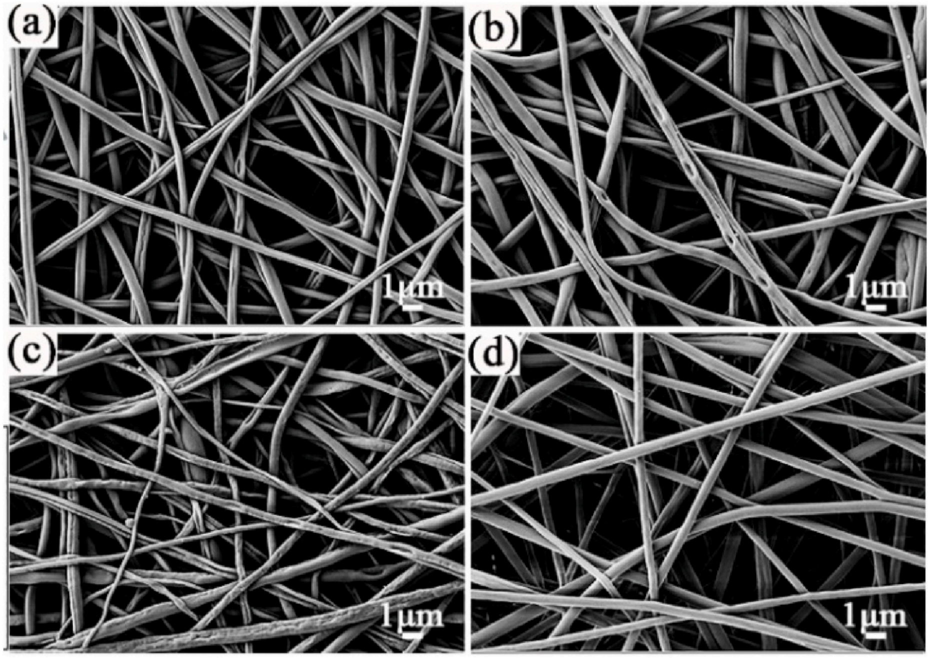

Fig. 3. SEM images of PVB/octa fibers prepared with 30% octadecane of (a) isopropyl alcohol, (b) chloroform, (c) kerosene solutions, and (d) pure octadecane as the core solution.

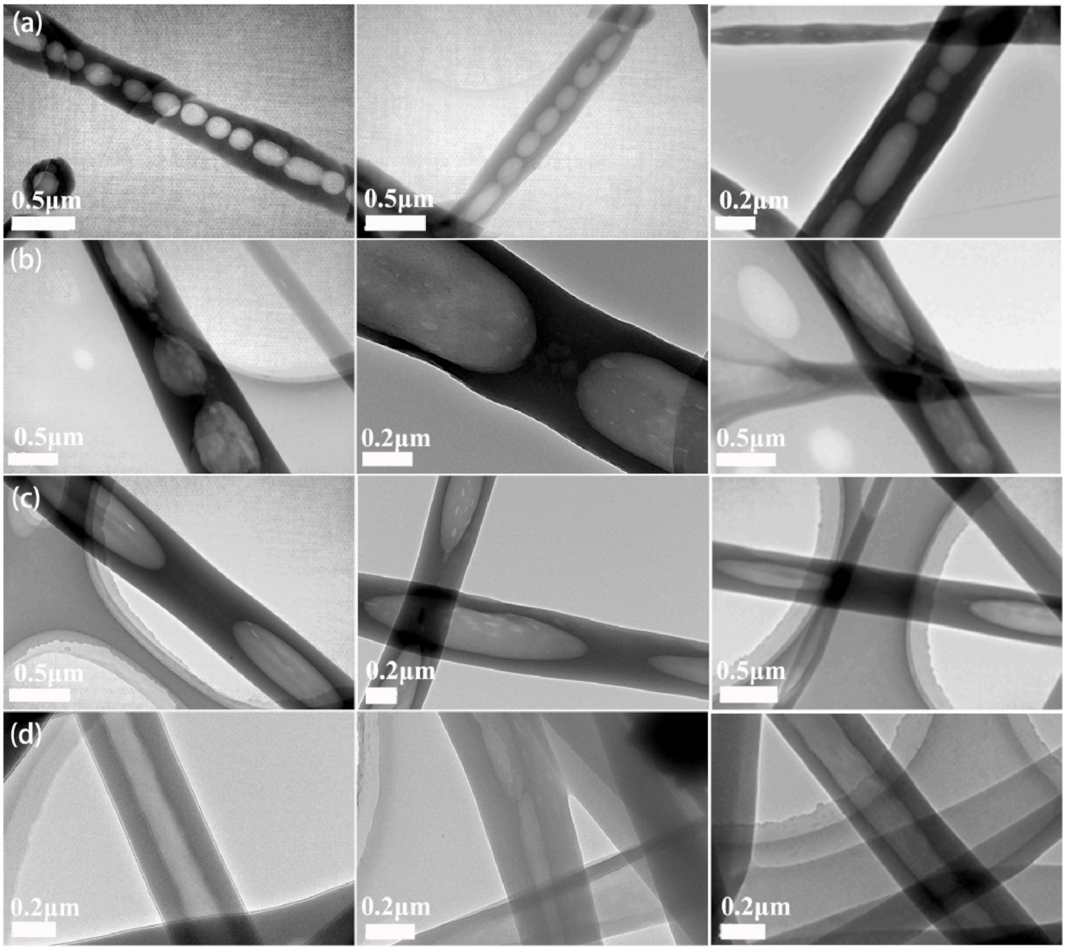

Fig. 4. TEM images of (a) STR-1, (b) STR-2, (c) STR-3, (d) STR-4.

pure melted octadecane (STR-4), the distributes of octadecane in the PCFs with a form of continuous core-sheath structure.

To analyze the thermal properties of the above four samples. It can be seen from Fig. 5 that there were great differences in the DSC curves of STR-1, 2, 3, and 4. When used pure octadecane as the core solution, we reduced its feed rate to ensure that all samples have a similar phase change enthalpy, so that the latent heat value of the fiber was about 30 J/g. During the heating stage, the melt peaks of STR-1 to STR-4 gradually broadening, because the inside octadecane particles became larger, and it took a long time to melt larger particles. This may be applied in the actual use of PCFs. The wider the melting peak was, the less heat it absorbs and releases instantly, but the duration time was longer. The narrower the melting peak was, the more heat it absorbs and releases instantly, but the duration time became shorter. During the cooling stage, all samples have the phenomenon of supercooling, and from STR-1 to STR-4, the supercooling degree gradually increases, which the α peak of STR-4 was the largest, and the β peak also appears the latest, and the supercooling phenomenon was the most serious. The explanation for this was that octadecane was heterogeneous crystallize on the PVB layer, and the supercooling degree was bound up with the curvature of the crystalline substrate. It can be seen from the previous TEM image that the curvature of octadecane particles was very different, which may be the reason for the difference in the supercooling degree. Therefore, it was confirmed that the supercooling degree of PVB/octa fiber was greatly affected by its structure, and the composite fiber obtained by using isopropanol as solvent has the lowest supercooling degree.

PCFs as a composite material, the distribution form of each phase has a great influence on its mechanical properties. Therefore, study the mechanical properties of the above four samples. The selection of the sample strip area was shown in Figure S1. Each sample tested seven copies and removed the best and worst mechanical dates of each sample. Average the remaining five sets of data to obtain the mechanical data in the following Table 1.

Table 1
Mechanical data of STR-1, 2, 3, 4.

Sample	Average tensile stregth (MPa)	Average elongation rate (%)
STR-1	2.0	16.8
STR-2	2.18	12.7
STR-3	1.71	17.8
STR-4	2.52	9.0

Fig. 6 shown the stress-strain curves of the above four types of fiber mats. Fig. 7 clearly shown the fracture illustration of nanofibers with core-sheath structure and periodic core filling structure. First of all, it can be seen that STR-4 has the highest tensile strength, but its elongation rate was much lower than the other three. Although STR-3 has a higher elongation rate, its tensile strength was the lowest. STR-2 and STR-1 have similar tensile strength, but the former has a lower elongation rate. In summary, the STR-1 obtained with isopropanol as the core solvent has better mechanical properties. The explanation was as follows: when the tension force was applied to the core-sheath structured fibers, the internal octadecane in the fibers was always under a tensile force from the beginning until it breaks. When STR-1, 2, 3 of the periodic core filling structure were stretched, the initial force between the octadecane and the PVB layer was static friction force, and then it has been the sliding friction force. Compare to the magnitude of these forces, we found the tensile force of octadecane in STR-4 was far greater than the friction force produced by other fibers. Therefore, the initial slope of the stress-strain curve of STR-4 should be greater than that of STR-1, STR-2, and STR-3. When the tensile force continues to act on fiber, the octadecane inside the STR-4 will inevitably break first, and then the fiber will become a tubular structure. The octadecane inside the fiber will no longer affect its subsequent mechanical properties. Therefore, STR-4 has the lowest elongation. For STR-3, the large particles of octadecane and its large spacing distribution make the friction force generated by the PVB layer less than STR-1 and STR-2, so its initial slope should be lower than that of STR-1 and STR-2. Therefore, the STR-1 has better mechanical properties. The octadecane in STR-1, 2, 3 gradually separates from PVB as the stretching progresses, and the friction between the two becomes smaller as the contact area decreases. The modulus of the tubular structure fibers was undoubtedly greater than that of the bamboo-like structure, and many researchers have been confirmed this conclusion [43]. This explains that the stress-strain curve of STR-4 was so steep, while the stress-strain curve of STR-1, 2, and 3 was much gentler. In addition, the mechanical properties of phase change fibers can also be improved by thermal crosslinking [47] or improving fiber morphology [48,49].

In the previous section, we used PVB as the sheath solution, and finely controlled the distribution of octadecane in the fibers by changing the core solvent. Next, we need to find a general method of fine structure adjustment. We used different sheath solutions and different core solvents to prepare PCFs. Fig. 8 was the FE-SEM image of PCFs prepared with PVDF as the sheath solution, pure octadecane, 30% octadecane in chloroform, kerosene solutions as the core solution. The three kinds of fibers have been soaked in petroleum ether for 24 h to remove the internal PCMs. All PCFs have good morphology, the surface was smooth, there were no depressions and beads, and the average diameters of the three fibers were similar.

Fig. 9 was the FE-SEM image of PCFs prepared with PAN as the sheath solution and 30% octadecane of chloroform, kerosene, and petroleum ether solutions as the core solution. All fibers have a smooth surface, uniform thickness, without depressions or beads. The average diameters of the three types of fibers vary greatly. N-2 has the largest average diameter and N-1 has the smallest average diameter.

The TEM image shown in Fig. 10 clearly shows the internal structures of the PVDF/octa and the PAN/octa fibers prepared with different core solvents. In Fig. 10a (F-1), octadecane was distributed in PVDF with large particles and short spacing. In Fig. 10b (F-2) and Fig. 10c (F-3), octadecane was distributed in PVDF continuously. In Fig. 10d (N-1), e

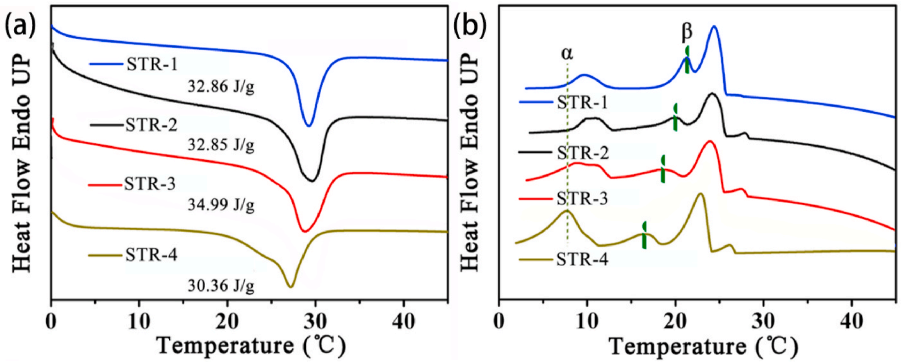

Fig. 5. DSC curves of STR-1, 2, 3, 4, (a) heating stage, (b) cooling stage.

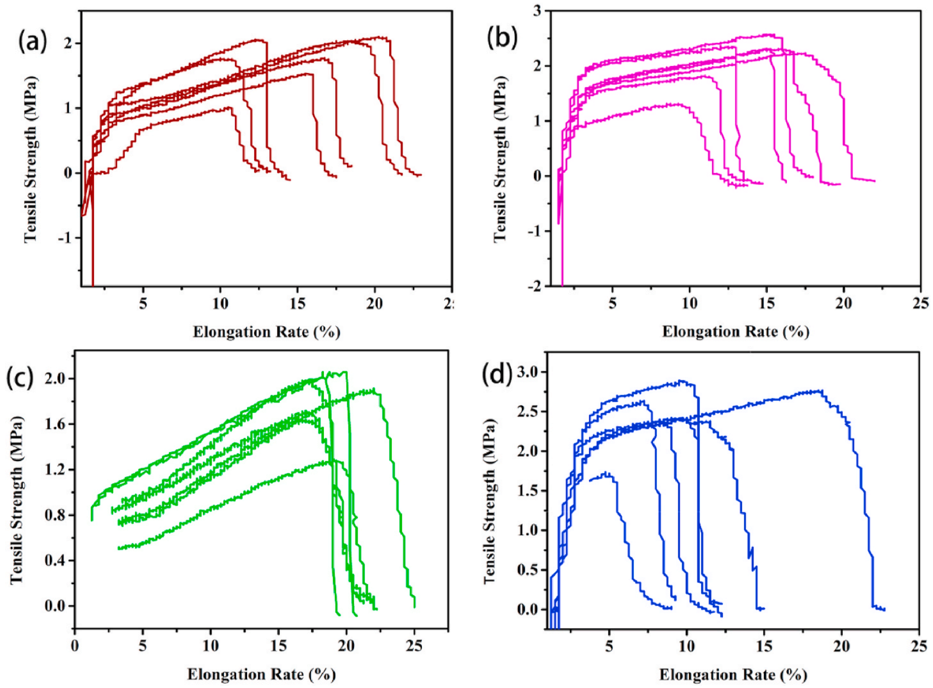

Fig. 6. Stress-strain curves of STR-1, 2, 3, 4 and solid PVB fiber.

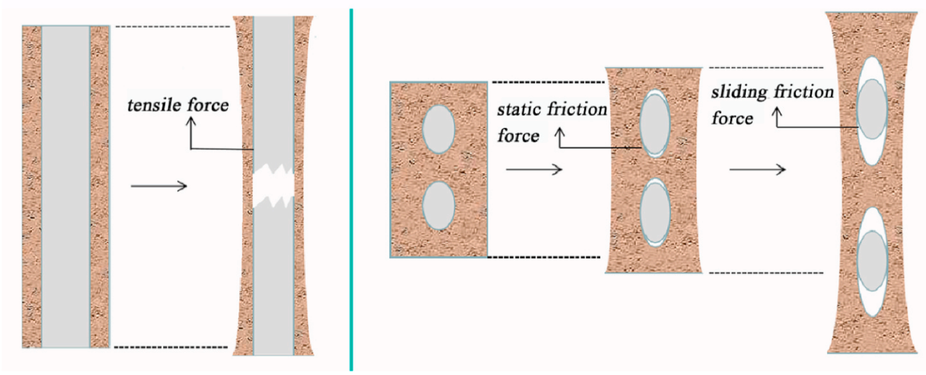

Fig. 7. Fracture illustration of nanofibers with core-sheath structure (left) and periodic core filling structure (right).

(N-2), and f (N-3), octadecane was distributed in PAN continuously.

To explore the reasons for the difference in the internal structure of PVB, PVDF, and PAN fibers, we tested the viscosity of all the solutions used in this experiment. Fig. 11a shown the viscosity of PVB, PAN, and PVDF solutions. It can be seen that the viscosity of PVB solution was the smallest, and it was much smaller than that of PVDF and PAN solution, and the viscosity of PAN solution was the largest. Fig. 11b was the viscosity of pure octadecane, 30% octadecane of isopropanol, chloroform, petroleum ether, and kerosene solutions. It can be seen that the viscosity of petroleum ether of octadecane has the smallest solution viscosity, pure octadecane was the largest, and the viscosity of pure octadecane was much larger than that of the other core solutions.

Based on the internal structure of the fibers and the solution viscosity data, we can draw the following inference. When the viscosity of the sheath solution was high, it is easy to obtain fibers with a core-sheath structure. When the viscosity of the sheath solution is low, with high viscosity of core solution, it is easy to obtain fibers with core-sheath structure, and with low viscosity of core solution, it is easy to obtain fibers with bamboo-like structure. Thus, it can be inferred that the internal structure of PCFs can be adjusted by sheath and core solution viscosity. The explanation for the above inference is as follows: the driving force of the core and sheath solution is different, and there must be exit shear stress at their interface. When the viscosity of the sheath solution is low, which means that its fluidity is better, and the sheath is relatively ''soft''. So the core solution is easier to penetrate the sheath solution, resulting in a strong bond between the two phases. If the viscosity of the core solution is low, the shear stress between the two phases is much greater than the surface tension of the core solution. The core solution and sheath solution cannot form a continuous and stable composite jet, and the core solution liquid flow will be interrupted, thus forming the bamboo-like structure. If the viscosity of the core solution is high, the shear stress between the two phases can overcome the surface tension of the core solution. The core solution and sheath solution form a stable composite jet, thus forming a continuous core-sheath structure. Similarly, when the viscosity of the sheath solution is high, the combination of the sheath and the core is weak. The shear stress between the two phases can overcome the surface tension of the core solution and can stretch into a stable composite jet, so it is easy to form a continuous core-sheath structure. All in all, we believe that there are two keys to obtain the PCF bamboo structure: first, the binding force between the sheath and the core solution is strong enough; second, the shear stress between the two phases is much greater than the surface tension of the

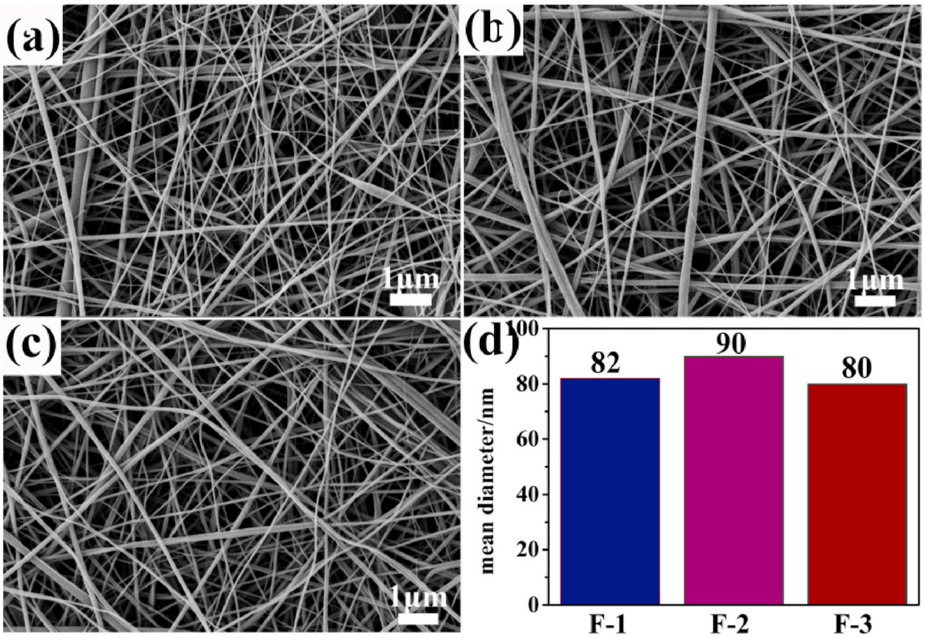

Fig. 8. SEM images of PVDF/octa fibers prepared with 30% octadecane of (a) chloroform, (b) kerosene solutions, and (c) pure octadecane as the core solution. (d) Histogram of fiber diameter with different core solutions.

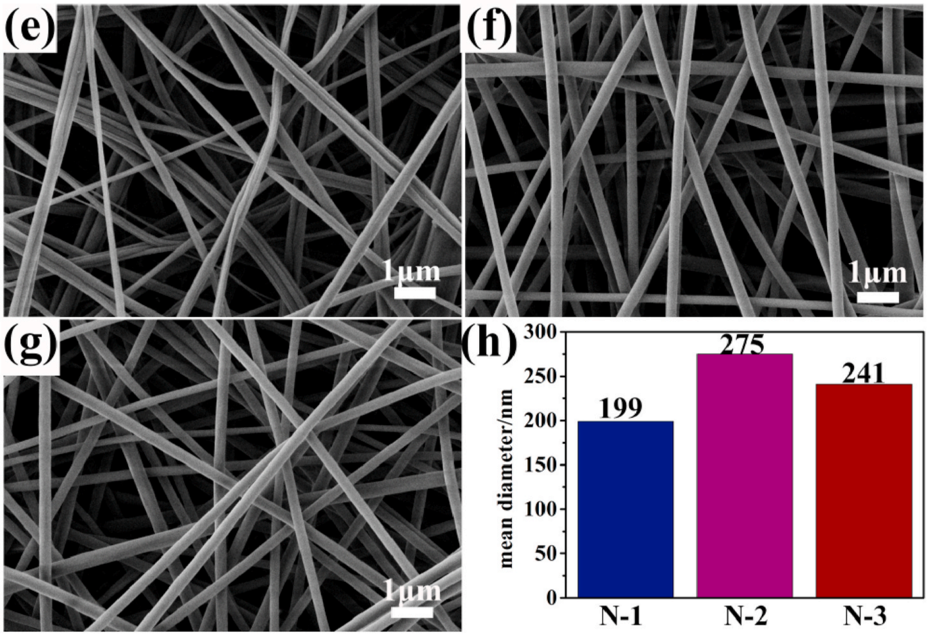

Fig. 9. SEM images of PAN/octa fibers prepared with 30% octadecane of (e) chloroform, (f) kerosene, and (g) petroleum ether solutions as the core solution. (h) Histogram of fiber diameter with different core solutions.

core solution.

4. Conclusions

In summary, a series of PCFs with different periodic core filling structures and core-sheath structures were respectively prepared via the coaxial electrospinning technique. Prepared the PCFs with PAN, PVP, PVB as the sheath, and octadecane as the core, and found that the supercooling degree of PVB/octa was the largest. Using PVB as the sheath, by replacing the solvent of octadecane, adjust the internal structure of the fibers successfully to reduce the supercooling degree. It was found that the fibers prepared with isopropanol as the core solvent have the lowest supercooling degree and the best mechanical properties. Finally, prepare the PCFs with PVDF and PAN as the sheath and octadecane solution in different solvents as the core. Characterization of fibers structure and solution viscosity data, we found that when the viscosity of the core and sheath solution was relatively low, it could obtain the bamboo-like structured fibers. And continuous core-sheath structured fibers could be obtained in two situations. First, the low viscosity of sheath solution and high viscosity of core solution; second, the high viscosity of sheath solution. This article provides a reference for the synthesis of different structured PCFs, which has certain significance

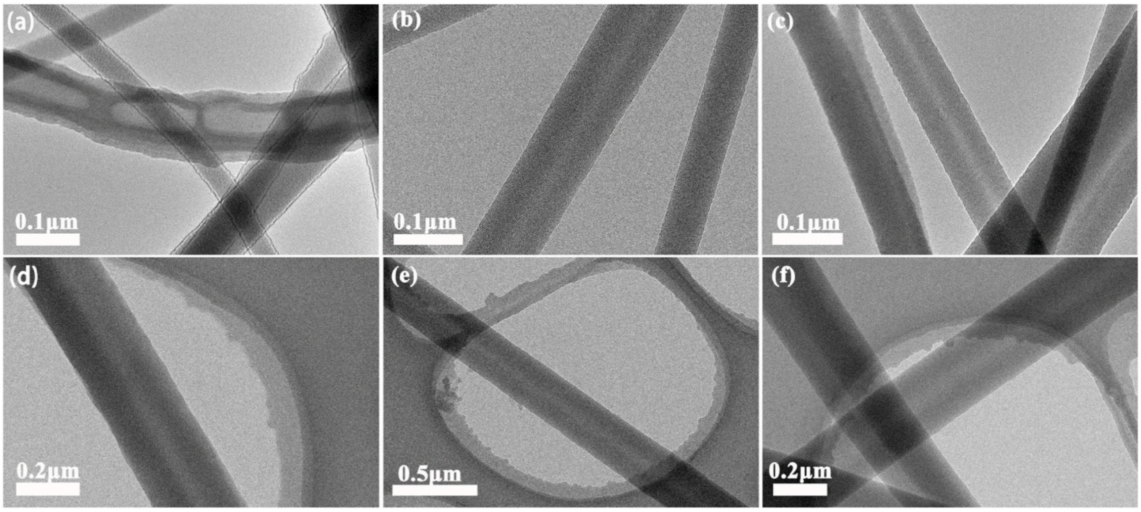

Fig. 10. TEM images of six samples with PVDF and PAN as the sheath solution. (a)F-1, (b)F-2, (c)F-3, (d) N-1, (e) N-2, (f) N-3.

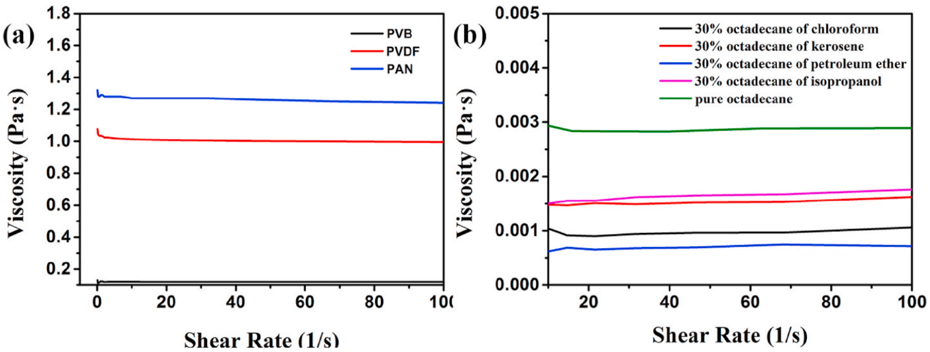

Fig. 11. The viscosity of (a) PVB, PAN, and PVDF (b) pure octadecane, 30% octadecane of isopropanol, chloroform, petroleum ether, and kerosene solutions at a shear rate from 0.1 to 100 1/s.

for its better practical application.

Notes

The authors declare no competing financial interests.

CRediT authorship contribution statement

Zhuofan Qin: Conceptualization, Methodology, Formal analysis, Validation, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Liqiang Yi:** Conceptualization, Methodology, Formal analysis, Validation, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Shuoshuo Wang:** Validation, Investigation. **Lina Wang:** Writing – original draft. **Juming Yao:** Writing – review & editing. **Guocheng Zhu:** Resources, Investigation. **Jiri Militky:** Resources, Investigation. **Mohanapriya Venkataramam:** Resources, Investigation. **Ming Zhang:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision.

Declaration of competing interest

This statement is to certify that all Authors have seen and approved the manuscript being submitted. We warrant that the article is the Authors' original work. We warrant that the article has not received prior publication and is not under consideration for publication elsewhere. On behalf of all Co-Authors, the corresponding Author shall bear full responsibility for the submission. This research has not been submitted for publication nor has it been published in whole or in part elsewhere. We attest to the fact that all Authors listed on the title page have contributed significantly to the work, have read the manuscript, attest to the validity and legitimacy of the data and its interpretation, and agree to its submission to the POLYMER. All authors agree that author list is correct in its content and order and that no modification to the author list can be made without the formal approval of the Editor-in-Chief, and all authors accept that the Editor-in-Chief's decisions over acceptance or rejection or in the event of any breach of the Principles of Ethical Publishing in the POLYMER being discovered of retraction are final. No additional authors will be added post submission, unless editors receive agreement from all authors and detailed information is supplied as to why the author list should be amended.

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Appendix A. Supplementary data

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