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Energy storage polymer/MicroPCMs blended chips and thermo-regulated fibers

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The thermo-regulated sheath/core composite fibers containing 4–24 wt% of microencapsulated *n*-octadecane (MicroPCMs) were melt-spun with a 24-holes spinneret at a speed of 720 m/min. The polyethylene chips containing 10–60 wt% of MicroPCMs were used as the core and polypropylene chips were used as the sheath. The morphologies and properties of the chips and fibers were investigated by using SEM, DSC, WAXD and Melting Index tester etc. The microcapsules in the chips containing 10–40 wt% of MicroPCMs are evenly inserted inside the polymer matrix and their respective phase change temperatures are almost the same. The enthalpies rise steadily as the content of MicroPCMs increased from 10 wt% to 40 wt%. The efficiency of enthalpy of the chip containing more than 30 wt% MicroPCMs depends on the extruding procedure. For the same MicroPCMs content, the efficiency of enthalpy of the chip fabricated directly with MicroPCMs and polyethylene are significantly lower than that of the chips fabricated with polyethylene, MicroPCMs and chips containing MicroPCMs by progressively increase the MicroPCMs contents. Nonetheless, the spinnability of the chips decrease as the contents of MicroPCMs exceed 50 wt%. The micrographs of the spun fibers containing 4–24 wt% of MicroPCMs also indicate that the core of the fibers was evenly surrounded by the sheath component. The heat absorbing and evolving temperatures of the fibers remain unchanged with the increase of MicroPCMs content and keep at approximately 32 and 15°C, respectively. The enthalpy, tensile strength and strain of the fiber containing 20 wt% of MicroPCMs are 11J/g, 1.8cN/dtex and 30.2%, respectively. The spun fibers can be used for the production of fabric materials.

1. Introduction

Microcapsules are tiny particles that the core materials are surrounded with wax, salts, clays, macromolecules or metals etc. The core materials can be drugs, paper coatings, enzymes, dyes, fragrant oils, solvents or salts, etc. [1]. Microencapsulation is a process in which tiny core materials are wrapped with a protective coating yielding microcapsules for countless applications. Microencapsulated phase change materials (MicroPCMs) have attracted more and more attention since 1980's, as they are regarded as renewable and clean energy storage materials [2, 3]. MicroPCMs have been widely studied in roles such as active or pumped coolants [4–7], solar and nuclear heat storage system [8] and heat exchanger [9]. MicroPCMs have also been used in the manufacture of thermo-regulated fibers, fabrics, foams and coating [10–15]. The thermo-regulated textiles containing phase change materials (PCM) can regulate the inner temperature as the ambient temperature altered by absorbing heat from the environment or evolving heat to the environment corresponding to the PCM changing their phases from solid to liquid or from liquid to solid [16].

Amongst, the techniques to embed MicroPCMs into the fibers by spinning were studied by Bryant and Colvin who invented a fiber with integral microcapsules filled with phase change materials (PCM) or plastic crystals in 1988 [10]. This fiber hadenhanced thermal

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properties at predetermined temperature and the function of smart temperature regulation [17]. The wet spun polyacrylonitrile (PAN) fibers that contain 7 wt% of MicroPCMs have been put onto market since 1997 [11]. They have been used as jacket liners, long underwear, boot liners, glove liners, sleeping bags and socks etc. With melt-spun technologies using nylons, polypropylenes and polyesters as raw materials, the global markets could potentially increase ten-fold [18]. However, the contents of MicroPCMs in the polypropylene or poly(butylene terephthalate) fibers that had been made were only 3 wt% [12], and the structures and properties were not disclosed. It is crucial to fabricate and investigate the structures and properties of the fibers with higher contents of MicroPCMs, as their temperature regulating ability is governed by the PCM contents in the fibers [19]. In this study, the structures and properties of increased content of MicroPCMs melt spun fibers will be investigated.

2. Experiments

2.1. Fabrication of MicroPCMs

The microcapsules containing *n*-octadecane with urea-melamine-formaldehyde copolymers shell were synthesized by in-situ polymerization. According to the results, the thermal stable temperature of the MicroPCMs, approximately 200°C, is improved by copolymerization [20]. The *n*-octadecane content in the microcapsule is approximately 72 wt%. The diameters of the microcapsules are in the range of 0.4–4.5 micron, whilst most of them are in the range of 1–2 micron. The diameters of the microcapsules are lower than that of reported in the literature [12].

2.2. Fabrication of polyethylene chips containing MicroPCMs

The mixture of 90–40 wt% of polyethylene (2911H, Fushun Ethylene Plastic Chemical Engineering Ltd., melting index 29 g/10 min) and 10–60 wt% of dried MicroPCMs were mixed and melt extruded in a twin screw extruder (Nanjing R ubber and Plastic Machinery Plant, SJSH30) at 100–180°C. In this study, the chips containing more than 30 wt% MicroPCMs were fabricated with two different procedures. In procedure I, chips were fabricated with a predetermined weight of microcapsules and PE, and extruded once. In procedure II, the microcapsules contents were increased progressively. Chips containing 40 wt% of MicroPCMs were fabricated with the chips containing 30 wt% of MicroPCMs, PE and MicroPCMs. And the chips containing 50–60 wt% of MicroPCMs were fabricated with the chips containing 40 wt% of MicroPCMs, PE and MicroPCMs. All of the chips were then dried at 80°C for 8 h.

The chips containing 35 wt% of MicroPCMs were fabricated with procedure II and then were extruded in the twin screw extruder for 5 times to examine the stability of the microcapsules during extruding procedure. The dried chips of every extruded cycle were used to investigate the stability of microcapsule in the heating and extruding process.

2.3. Fabrication of polypropylene sheath/core composite fibers

The dried chips containing less than 30 wt% (included) MicroPCMs fabricated in procedure I and the dried chips containing more than 30 wt% (excluded) MicroPCMs fabricated in procedure II were used as the core component, and the polypropylene chips (71735, PetroChina Liaoyang Petrochemical Company, melting index 35 g/10 min) were used as the sheath component. The weight ratio of the core and sheath is 2:3. The thermo-regulated fibers containing 4–24 wt% of MicroPCMs were melt spun in a spinning machine with a 24-holes sheath/core spinneret. The fibers were then wound at a speed of 720 m/min.

The as-spun fibers were stretched at 65°C water and 120°C vapor and relaxed heat setting at 120°C for 25 min.

2.4. Characterization of the chips and fibers

2.4.1. Scanning electronic microscope (SEM)

The chips were tested without further treatment. The fibers were broken in a liquid nitrogen bath. The micrographs of the gold-coated chips and fibers were obtained by using a scanning electronic microscope (SEM, Leica, Stereoscan 440).

2.4.2. Differential scanning calorimeter (DSC)

The phase change properties of the chips and fibers were obtained by using a differential scanning calorimeter (Perkin Elmer DSC-7) at a scanning rate of 10°C/min in a nitrogen atmosphere from −20 to 200°C, waiting for 3 min then cooled to −20°C at the same rate. The mass of the sample was 5.0–8.0 mg. Theoretical enthalpy equals to the average enthalpy of microcapsules multiply by the theoretical content of MicroPCMs in the chip. The efficiency of enthalpy is defined as the ratio of the theoretical enthalpy and the measured value.

2.4.3. Wide-angle X-ray diffraction (WAXD)

The X-ray diffraction patterns of the fiber powders were obtained by using X-ray diffraction (WAXD, Bruker Aux D8 Advance, 40 kV, 40 mA, Cu $K_{\alpha 1}$) at 22°C, with the scanning range of 5–40° (2theta). The WAXD pattern of the fibers containing 20 wt% of MicroPCMs was also obtained at 45°C.

2.4.4. Melting index tester

The Melting Index (MI) of the dried chips was measured in a Melting Index Tester (Jilin University, UPXRZ-400, measured at 190°C, cylinder diameter 2.095 mm, load 2160 g).

3. Results and discussion

3.1. The phase change properties and morphologies of the chips

The phase change properties and the efficiency of enthalpy of the microencapsulated *n*-octadecane and the chips containing various contents of MicroPCMs are

TABLE I Phase change properties of microPCMs and chips[a]

Content of MicroPCMs (wt%)	Procedure no.	Tm (°C)	ΔH_m (J/g)	T_c /°C	ΔH_c (J/g)	Spinnability
10	I	29.7	4	16.2	4	Excellent
20	I	29.5	11	21.7	12	Excellent
30	I	30.0	24	25.6	25	Excellent
40	I	29.4	29	24.5	28	–
	II	29.6	42	23.8	44	Good
50	I	29.7	30	24.0	27	–
	II	29.3	60	26.4	65	Good
60	I	29.4	24	28.3	25	–
	II	29.7	72	28.7	74	Poor
100		30.0	175	27.4	176	–

[a]T_m- peak temperature on the DSC heating curve (at the lower temperature); ΔH_m-melting enthalpy on the DSC heating curve; T_c-peak temperature on the DSC cooling curve; ΔH_c-crystallization enthalpy on the DSC cooling curve.

listed in Table I. It is observed that the heat-absorbing temperatures (T_m) obtained from the chips with various contents of MicroPCMs are almost the same. Nevertheless, the heat-evolving temperatures (T_c) rise with the increased contents of MicroPCMs.

The relationship between the efficiency of enthalpy and the content of MicroPCMs is shown in Fig. 1. This is the integrated result of the poor thermal conductivity between polyethylene and the shell of microcapsule, and the damage of the microcapsules during heating and extrusion processes. The results reveal that when the content of MicroPCMs is more than 30 wt%, the chips fabricated with procedure I exhibit significant lower values of efficiency of enthalpy than those fabricated with procedure II. The chips fabricated with procedure I has reached the maximum efficiency of enthalpy (to approximately 47% efficiency) at 30 wt% of MicroPCMs. Further higher contents of MicroPCMs have resulted in significant reductions of efficiency of enthalpy. The efficiency of enthalpy is only 23% for the chip containing 60 wt% MicroPCMs. It is observed that *n*-octadecane is diffused from the chip when the MicroPCMs contents are higher than 50 wt%. As the MicroPCMs contents increased, more and more of the microcapsules were probably crushed by the friction and pressure in the melting and extruding procedures. For the chips fabricated with procedure II, the maximum efficiency of enthalpy (to approximately 71% efficiency) is obtained when the MicroPCMs content reaches 50 wt%. When the MicroPCMs contents further increase, the efficiency of enthalpy decreases slightly. In procedure II, the contents of microcapsules were increased progressively, some of the infusible MicroPCMs were wrapped and protected by the thermoplastic PE molecular chain, the friction and pressure from the screw and cylinder in the melting and extruding procedures decreased, the ratio of crushed microcapsules decreased.

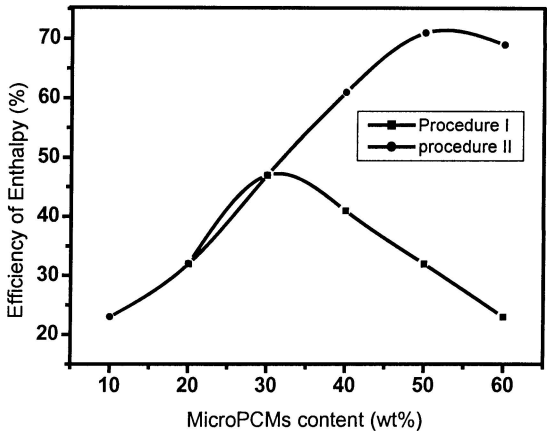

Figure 1 Relationship between the efficiency of enthalpy and the content of MicroPCMs in the chips fabricated with different procedures.

The micrographs of the chips containing various contents of MicroPCMs are shown in Fig. 2. The microcapsules in the chips containing 10–40 wt% of MicroPCMs are evenly inserted inside the polymer matrix and no broken microcapsule is observed. Nevertheless, when the content of MicroPCMs has been exceeded 50 wt%, some of the chips are damaged by the heating and extruding processes. No microcapsules with diameters higher than 3 micron are observed, they are probably crushed.

3.2. Spinnability of the chips

As can be seen from Table I, the content of MicroPCMs has significant effect on the spinnability. When it exceeds 40 wt%, especially 50 wt%, the spinnability of the chip decreases with the increased content of the microcapsules. As shown in Fig. 3, the chips containing 40–50 wt% of MicroPCMs result in significantly low melting index, and thus reduce the spinnability of the chips. Even though the melting index increase at 60 wt% of MicroPCMs, the spinnability decrease due to the increasing ratio of damaged microcapsules.

At the beginning, the MicroPCMs act as plasticizer, the MI increases with the increasing of the content of MicroPCMs. When the content of MicroPCMs exceeds 10 wt%, the infusible microcapsules prohibit the polyethylene molecular chain from flow freely, the MI decreases. The MI of the chips containing approximately 50 wt% of MicroPCMs reaches the lowest. Continuously increasing the content of MicroPCMs, the friction between the microcapsules and cylinder breaks them down, the *n*-octadecane is released. The released *n*-octadecane in the chips acts as plasticizer too, the MI increases again. Such speculation is proved by the micrographs, efficiency of enthalpy of the chips and the experimental results in Table II.

The phase change properties and softness of the chips that were extruded in the twin screw extruder for 1–5 cycles are listed in Table II. As the extruding cycles increasing, the heat absorbing and heat evolving

TABLE II Enthalpies of the chips containing 35 wt% of MicroPCMs during extruding processes

Extruding times	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	Softness of the chips
1	30.9	29	25.8	32	Rigid
2	31.1	26	25.8	29	Rigid
3	31.3	26	25.4	30	Soft
4	30.8	22	25.8	25	Very soft
5	30.7	21	25.7	26	Very soft

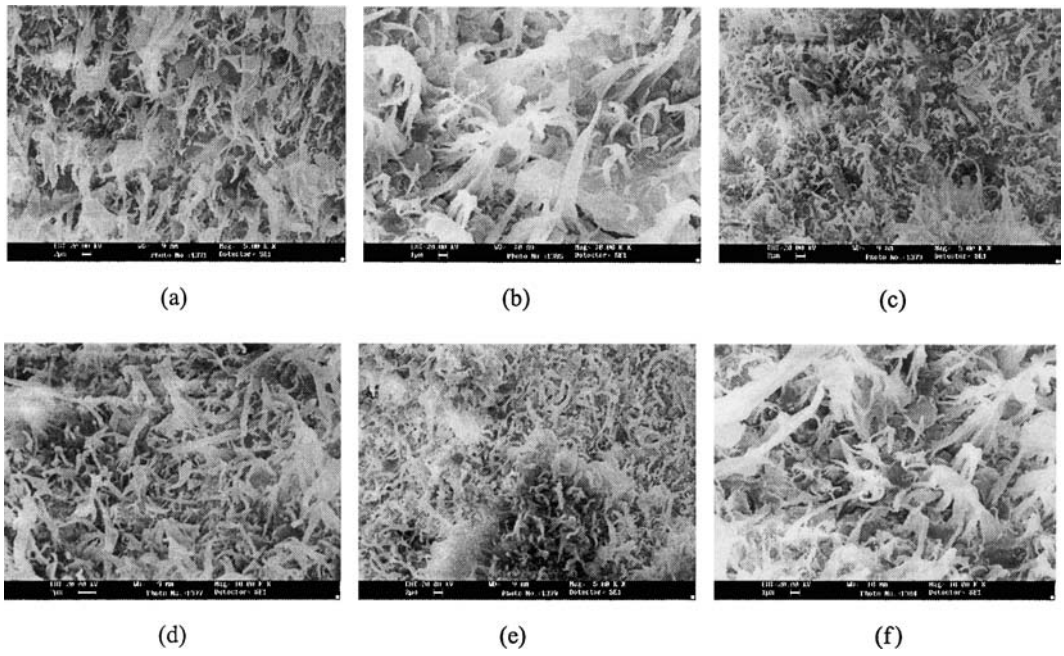

Figure 2 Cross-section SEM micrographs of the chips (a)-30 wt%(5000×); (b)-30 wt%(10000×); (c)-40 wt%(5000×); (d)-40 wt%(10000×); (e)-50 wt%(5000×) and (f)-50 wt%(10000×).

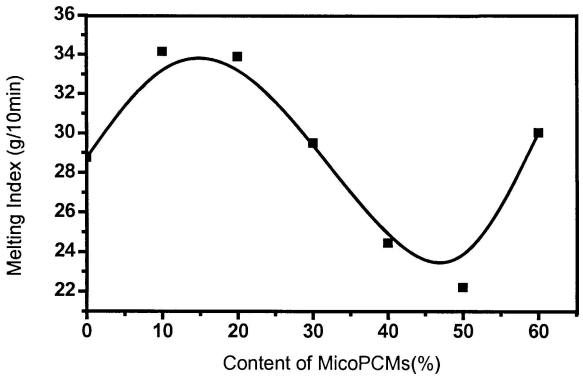

Figure 3 Relationship between Melting Index and the content of MicroPCMs in the chips.

temperatures fluctuate slightly, however, the enthalpies decrease significantly. And the meanwhile, the softness of the chips increases quickly. More and more microcapsules are broken in the repeated extruding processes even though they are wrapped and protected by the thermoplastic PE. Therefore, fewer extruding cycle is also preferable for improving the efficiency of enthalpy of the chip.

It may also be noteworthy that, as reported by Bryant [12], spinnability of the chips may also be affected by the diameter of the microcapsule, the larger the diameter of the microcapsule, the poor the spinnability for the same MicroPCMs content. Since the diameters of the microcapsules used in this paper are lower than that of in the literature [12], the spinnability of the chip is better than that of in the literature. The content of MicroPCMs in the fiber is increased from 3 to 20 wt%.

3.3. The morphologies and phase change properties of the fibers

The micrographs of the fibers containing 16, 20 and 24 wt% of MicroPCMs are shown in Fig. 4. The cores were evenly surrounded by the sheath, the dense sheath strengthens the fiber, the loose core containing MicroPCMs endows the fiber with heat-storage ability.

The phase change properties of the composite fibers containing various contents of MicroPCMs are listed in Table III. The heat absorbing and heat evolving temperatures of the fibers are approximately 32 and 15°C, respectively. No significant relationship has been observed between the contents of MicroPCMs and the heat absorbing and heat evolving temperatures of the fibers. In contrast, the enthalpies of the fibers rise steadily with the increase of the contents of MicroPCMs. The enthalpy of the fibers containing 20 wt% of MicroPCMs is approximately 11 J/g that is significantly higher than the expected value-4 J/g by Lennox-Kerr [21].

As shown in Fig. 5, with the increased contents of MicroPCMs, there is a maximum value of the efficiency of enthalpy. The fibers containing approximately 12 wt% of MicroPCMs exhibit the highest efficiency of enthalpy, that is approximately 43%. This result is dramatically lower than the literature efficiency value of-75–80%[12], however. The undesirable lower efficiency of enthalpy is probably due to the relatively lower thermal stable temperature caused by the smaller size and thinner shell thickness of the microcapsules compared with that of in the literature [12]. When the

TABLE III Phase change properties of the sheath/core composite fibers containing various contents of MicroPCMs

MicroPCMs content (wt%)	T_m(°C)			Tc(°C)		
	Onset	Peak	ΔH_m (J/g)	Onset	Peak	ΔH_c(J/g)
4	30.4	31.3	1	16.2	14.7	1
8	30.2	31.5	4	18.7	14.8	4
12	30.0	31.9	9	18.3	13.8	9
16	31.0	32.6	10	16.8	14.6	10
20	31.4	32.7	11	17.8	16.2	11
24	31.1	32.7	13	17.4	15.4	13

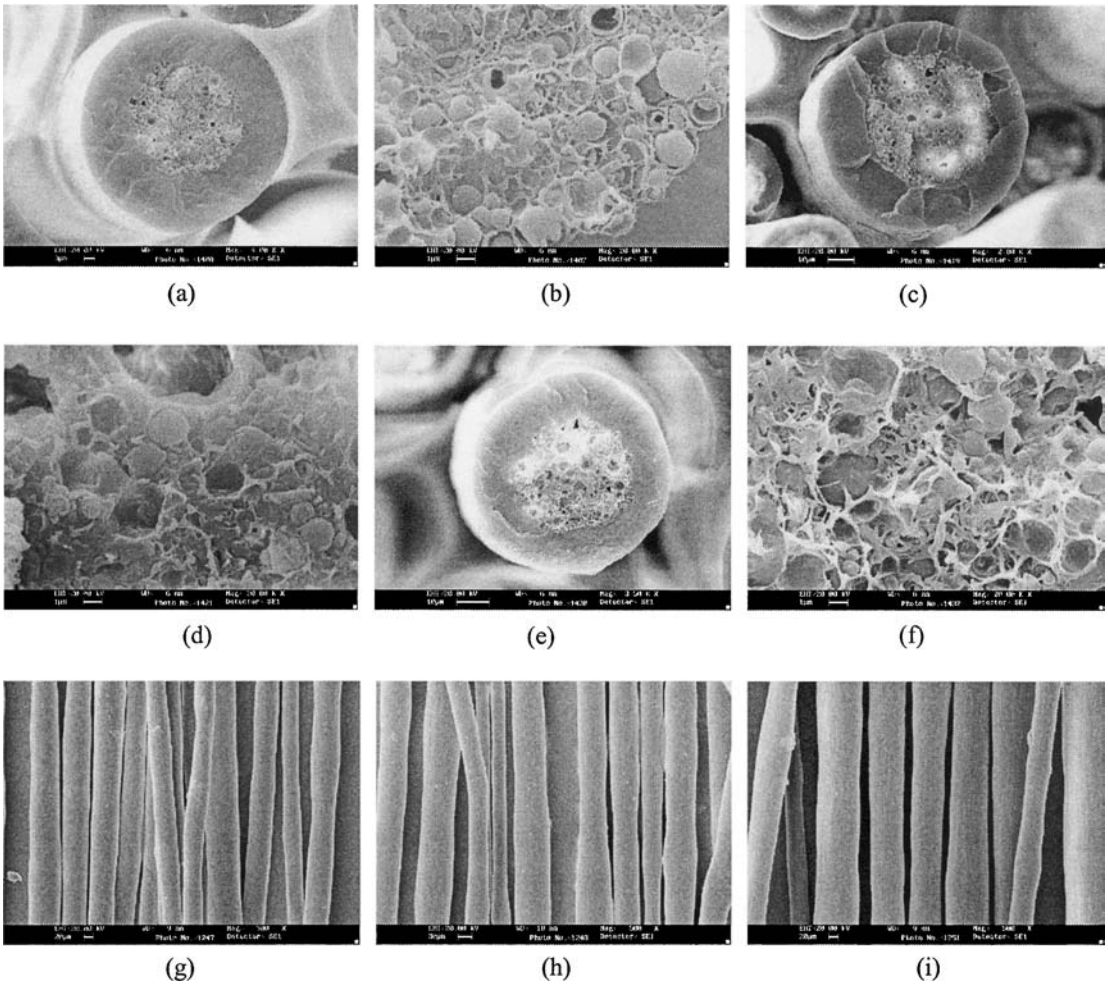

Figure 4 SEM micrographs of the stretched thermo-regulated fibers profiles and side surface (a-16 wt% MicroPCMs fibre (4000×); b-16 wt% MicroPCMs fibre (20000×); c-20 wt% MicroPCMs fibre (3800×); d-20 wt% MicroPCMs fibre (20000×); e-24 wt% MicroPCMs fibre (3500×); f-24 wt% MicroPCMs fibre (20000×); g-16 wt% MicroPCMs fibre (500×); h-20 wt% MicroPCMs fibre (500×) and i-24 wt% MicroPCMs fibre (500×)).

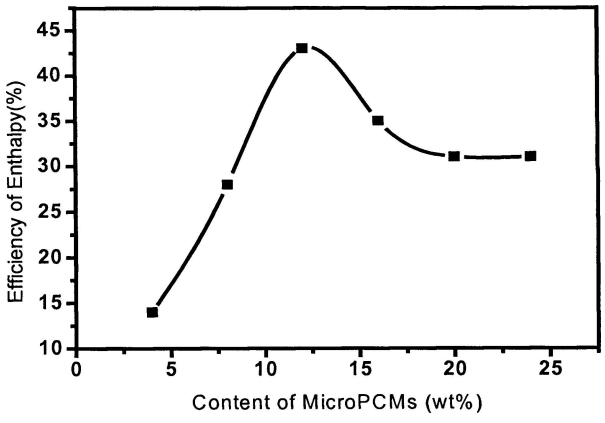

Figure 5 The efficiency of enthalpy and the content of MicroPCMs in the fibres.

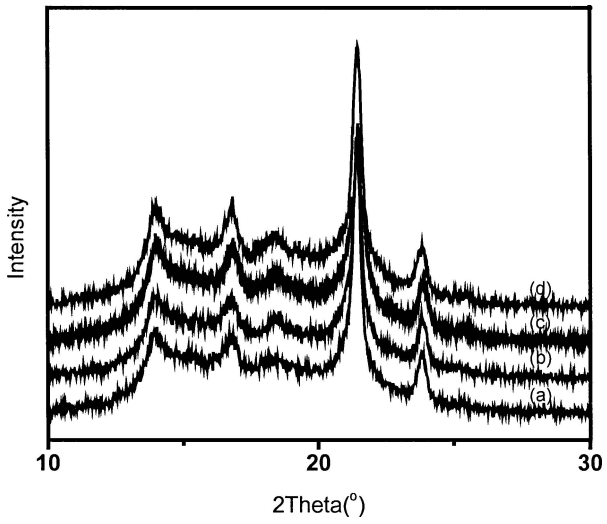

Figure 6 WAXD patterns of the fibers containing various contents of MicroPCMs (a-8 wt%; b-12 wt%; c-20 wt% and d-20 wt% at 45°C).

content of MicroPCMs exceeds 12 wt%, the efficiency of enthalpy decreases readily. This can be explained by the poor conductivity between microcapsule and PE and the damage of the microcapsules during the extrusion process.

3.4. Crystallization of the fibers

The WAXD patterns of the fibers containing various contents of MicroPCMs are shown in Fig. 6. Results indicated that they are all highly crystallized, however, fibers containing various contents of MicroPCMs exhibit similar WAXD patterns. Similar WAXD patterns are also obtained when the fibers containing 20 wt% of MicroPCMs were measured at 22 and 45°C respectively. In this respect, the contribution of *n*-octadecane

TABLE IV The physical mechanical properties of the sheath/core composite thermo-regulated fibers

Content of MicroPCMs in fiber (wt%)	0	4	8	12	16	20
Titer/dtex	5.0	5.0	5.6	6.2	6.4	5.5
Strain /cN/dtex	3.1	2.8	2.7	2.4	1.9	1.8
Stress (%)	38.1	24.4	38.8	29.7	33.5	30.2

crystallization to the diffraction intensity is hard to distinguish.

3.5. Physical mechanical properties of the fibers

The physical mechanical properties of the fibers containing less than 20 wt% of MicroPCMs are listed in Table IV. Results indicate that fibers containing higher MicroPCMs contents tend to have lower values of the tensile strain. However, no significant relationship exists between the fiber tensile stress and various contents of MicroPCMs in the fiber. It is also evident that fibers containing less than 20 wt% are able to withstand the strength required at fabric production processes.

4. Conclusions

In this study, the experiment results have revealed that the extruding procedure during the chips fabrication has a major effect on the efficiency of enthalpy, particularly for the chips containing more than 30 wt% MicroPCMs. The efficiencies of enthalpy of the chips fabricated directly with MicroPCMs and polyethylene are significantly lower than that of the chips fabricated with polyethylene, MicroPCMs and chips containing MicroPCMs for the same MicroPCMs content. Melting and extruding procedures have tremendous effects on the integrality of the microcapsules. The tests have shown that microcapsules in the chips containing 10–40 wt% of MicroPCMs are evenly inserted inside the polymer matrix and their respective phase change temperatures are somewhat similar. Also, the spinnability of the chips decrease dramatically. Results also indicate that as the thermo-regulated sheath/core composite fibers containing 4–24 wt% of MicroPCMs were melt-spun with a 24-holes spinneret at a speed of 720 m/min, the core was evenly surrounded by the sheath component. The heat absorbing and heat evolving temperatures of the fibers remain unchanged (at approximately 32 and15°C, respectively) with the increasing content of MicroPCMs. The enthalpy of the fibers is approximately 11 J/g. The fibers also exhibit acceptable mechanical properties, as the content of MicroPCMs is not exceed 20 wt%, which can be used for fabric production.

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