Effect of different solvents on poly(caprolactone) (PCL) electrospun nonwoven membranes

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Abstract Poly(caprolactone) (PCL) is one of biodegradable and biocompatible polymers, which have received significant attention because they are environmentally friendly and are extensively used in biomedical applications. Electrospinning was a straightforward method to produce nanofibers from polymer solutions in a wide submicron range around 100 nm. However, no clear standard had been established for judging whether a solvent of high solubility for a polymer would produce a solution good for electrospinning. Considering the above-mentioned cause, we explored the effect of solvent on fibrous morphology, FT–IR spectra and ^{1}H NMR spectra, viscosity and shearing strength, differential scanning calorimetry (DSC) of PCL electrospun nonwoven membranes in this article. When NMP and AC were used as the solvent for PCL electrospinning, all of them were composed of smooth and nanosized fibers with similar fiber surface morphologies. Meanwhile, when DCM and CF were used as solvent, there were lots of holes in fibers due to high evaporation. The electrospinnability was good when CA was chosen as solvent due to its lowest viscosity.

Keywords Poly(caprolactone) (PCL) · Differential scanning calorimetry (DSC) · Electrospinning · Solvents

Introduction

The idea of using an electric field to spin fibers from a charged polymer melt or solution was conceived in the 1930s. Electrospinning, as the process was called, was a straightforward method to produce nanofibers from polymer solutions in a wide submicron range around 100 nm [1–5].

The basic principle of the process involves an application of a high electric potential (10–30 kV) to a polymer melt or solution across a finite distance between a conductive needle and a grounded collector. Electrically charged polymer solution forms a conical shape, called a Taylor cone, at the tip of the needle. When the electric charge at the needle tip overcomes the force due to surface tension and viscosity, a whipping polymer jet is ejected from the apex of the cone. The jet is directed toward the grounded collector, during this period the solvent evaporates and fibers deposit on the collector in form of a randomly oriented non-woven fabric.

Due to the physical uniqueness of high surface area, ultra-fine electrospun fibers of many biodegradable polymers have been proposed for biomedical applications such as drug delivery, wound dressing, and scaffolds for tissue engineering. Electrospun fibers have attracted a great deal of attention as tissue scaffolds that mimic the nano-features of natural extracellular matrix [6].

The structure of electrospun nonwoven membrane is under the influence of a large number of interrelated variables, including operating parameters (such as applied voltage, flow rate, collection distance), polymer molecular chain length, attributes of the solution (such as concentration, solvent, and solution properties), size of the nozzle orifice. Much effort has been made to fabricate demanded electrospun nonwovern. However, due to the lack of a complete understanding of the importance of electrospun solvent, the effects of solvent on electrospun nonwoven membrane structure and thermodynamics properties are very limited.

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To produce nanofibers, one of the most influential variables to be considered is polymer solution concentration. A critical minimum concentration Ce is needed to allow for molecular chain entanglements and electrospinning proceeding. This critical minimum concentration is defined as the minimum concentration required for forming beaded nanofibers [7, 8]. Concentrations below Ce will produce droplets during electrifying (electrospraying). At concentrations above Ce, electrospun fiber diameter increases and frequency of bead-on-string formation decreases with increasing concentration. However, the value of Ce is dependent on the molecular chain length, the chemical nature of the polymer and the solvents selected for the polymer solution. When a particular polymer of specific average molecular weight and molecular chain length is used in electrospinning, the selection of solvents for the polymer solutions plays a pivotal role in determining the value of Ce. Consequently, the selection of a suitable solvent is fundamental to the success of an electrospinning process for nanofiber production.

Solubility parameters are used to aid the search for suitable solvents and solvent systems for polymers used in electrospinning. It has been reported that the characteristics of electrospun fibers depend on the solution properties such as viscosity, surface tension, conductivity, and also the operation conditions [3, 9, 10]. The effect of increasing the concentration of the solution on fibers morphology and diameter has been investigated for many systems [11].

Several literatures reported the effect of solvent on the morphology of electrospun nanofibers membrane [12]. Especially solvents diversely positioned on the Teas graph were studied for their solubility and electrospinnability for making polymethylsilsesquioxane solutions [13]. But it can hardly find literatures on the effects of solvent on electrospun nonwoven membranes structure and thermodynamics properties. Moreover, this research content is very essential to broaden applications of electrospun nonwoven membranes.

In the past decade, biodegradable and biocompatible polymers have received significant attention because they are environmentally friendly and are extensively used in biomedical applications. In this direction, poly(caprolactone) (PCL) is one of the most promising polymers, and it can be used in many medical applications, such as drug delivery, scaffolds, and guided bone regeneration [14]. PCL has been investigated and reported by many groups [15, 16]. Its long degradation time, documented bioactivity for endothelial cells and smooth muscle cells [16, 17], and innate compliance make it a suitable candidate for a vascular graft material. In this manuscript, PCL in different solvent will be chosen as electrospun solution to investigate the structure and properties of electrospun nonwoven membranes.

Experimental

Materials

Poly(caprolactone) (PCL) (Mn 80,000 g/mol) was obtained from J & K chemica®. N,N-dimethylformamide (DMF), 1-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), dichloromethane (DCM), acetone (AC), chloroform (CF), and dimethyl sulfoxide (DMSO) were used as the solvent. 15 wt% PCL solutions were prepared in different solvents to use in the following experiments.

Electrospinning set-up

The experiments were conducted with other experimental parameters unchanged. The applied voltage is 20 kV, the distance between the needle and the collector was 15 cm and the diameter of needle was 1 mm. The flow rate was 3 mL/h. Figure 1 showed a schematic diagram of the homemade electrospinning set-up. All experiments were performed under ambient conditions at room temperature and relative humidity of about 50%.

Measurements

DDSJ-308A intelligent conductivity meter was used to measure the conductance of PCL polymer solution. JSM-5600LV digital vacuum scanning electron microscope, which was produced by Japan Electron Optical Laboratory, was used to observe the morphology of nanofiber mats.

Mettler Toledo DSC 822e was used to the thermal behavior of PCL electrospun fibers of different solvents.

Haake RS150 Rheometer is used to measure the rheological property. Before measuring, the samples are put
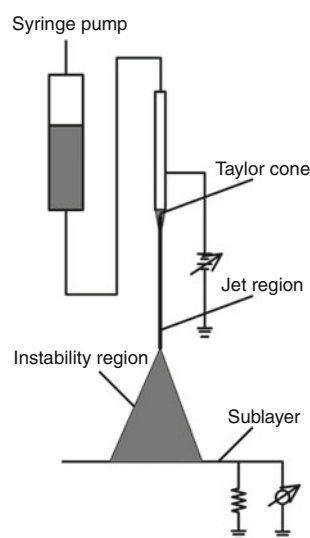
Fig. 1 Experimental set-up device

into rheometer for 20 min at constant temperature. Measuring method of balance flow curve was used (equilibrium time of each measured value is set as 5 s). At the same shear rate range, the method of shearing rate is used. The process that shearing rate increases from low to high gradually and then decreases gradually is set. Variation curve that shearing strength and apparent viscosity of specimens change along with the change of shearing rate is measured.

Results and discussion

The effect of solvents on electrospun fibrous morphology

PCL was dissolved in different solvents such as DMF, NMP, THF, DCM, AC, CF, and DMSO. To prepare for excellent electrospun PCL solution, dissolvable temperature and dissolvable time were recorded in Table 1. It is found that DCM, CF, as well as THF are the most dissolvent for PCL. Especially, PCL was dissolved immediately in DCM and CF. Meanwhile, PCL can not be dissolved in DMSO.

Comparison of solvent properties is showed in Table 2. The decreasing order of conductivity is NMP > DMF > DMSO > AC > THF > DCM > CF. As known, if the solution is absolutely insulating, or the applied voltage is not high enough, electrostatic force can not overcome the surface tension. However, if the conductivity is higher, the spinnability of a polymer solution is better. Therefore, we found that it was very fluent to electrospin fibers when NMP was used as solvent. (see Fig. 3b).

Figure 2 shows the appearance of PCL dissolved in different solvents such as NMP, AC, and DMF, which form uniform electrospun solution but need higher dissolvable temperature of about 80 °C and longer dissolvable time (NMP 30 min, AC and DMF 10 min, respectively). However, we found that PCL was easily separated out when DMF was used, see Fig. 2.

**Table 1** Conditions for PCL dissolve in different solvents

Solvent	Dissolvable temperature/°C	Dissolvable time/min
DMF	80	10
NMP	80	30
THF	40	10
DCM	Room temperature	2
AC	50	10
CF	Room temperature	2
DMSO	80	–

Table 2 Comparison of solvent properties

| Solvent	T_b/°C	ε (20 °C)	Dipole	Conductivity/S cm^{-1}
DMF	152.8	36.7	3.82	1.59E−7
NMP	202.2	32.2	4.09	6E−7
THF	64	7.58	1.7	1.5E−8
DCM	40	9.1	1.8	4.31E−11
AC	56	20.7	2.9	2E−8
CF	61.7	5.2	4.78	0
DMSO	189	47	3.96	3E−8
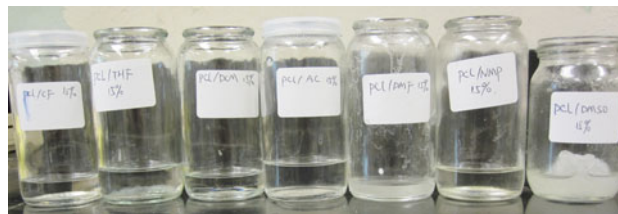
Fig. 2 The solution appearance when PCL dissolved in different solvents (containing DMF, NMP, THF, DCM, AC, CF, and DMSO)
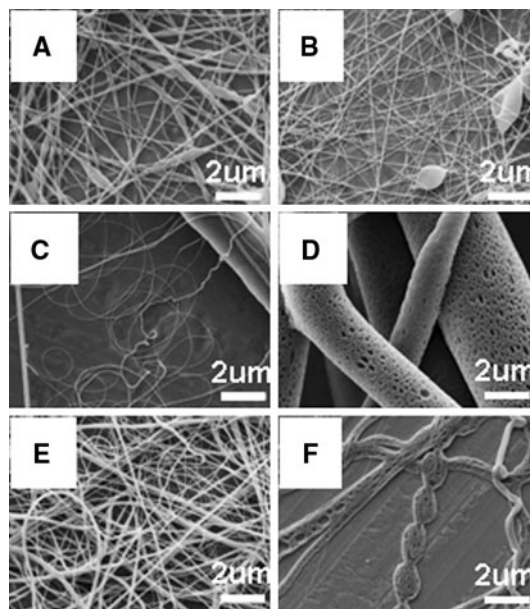
Fig. 3 Morphologies of electrospun PCL nonwoven mats produced with different solvents: **a** DMF, **b** NMP, **c** THF, **d** DCM, **e** AC, **f** CF, concentration = 15%

The morphologies of electrospun PCL mats produced with different solvents were observed with SEM, and the results were shown in Fig. 3. Fiber size distribution and average fiber diameters were showed in Fig. 4. When NMP, AC as well as DMF were used as the solvents for PCL electrospinning, the resulting of PCL fibers not only showed much smaller fiber diameters than those from DCM, CF, and THF, but also could be collected
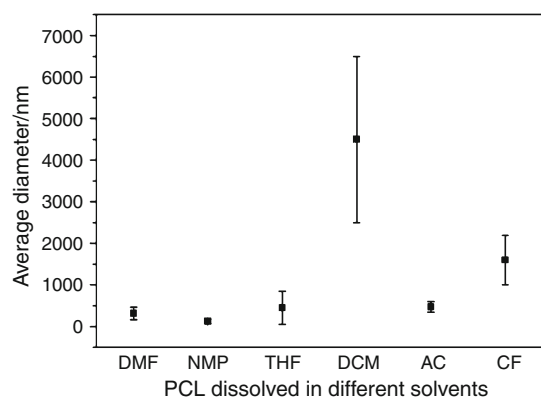
Fig. 4 Fiber size distribution and average fiber diameters

continuously for several hours without disruption because the blockage problem of a syringe needle was eliminate. Though DCM, CF, and THF have higher solubility for PCL they can not produce electrospun nonwoven mats with higher quality, the reason is due to their higher volatility. Furthermore, fibers diameter and fiber size distribution are very larger when DCM, CF, and THF was used (see Fig. 4), and it is interesting to find that there are lots of holes appeared in each single fiber (see Fig. 3d, f).

Obviously, when NMP and AC were used as the solvents for PCL electrospinning, both of them were composed of smooth and nanosized fibers with similar fiber surface morphologies. The average fiber diameters varied from 100 to 500 nm depending on the solvent being used. When NMP was used, fibers were very tiny and the distribution is very small. But there were some beads appeared there. When DMF was used, there were lots of beads and fibers were not smoothly, which demonstrate a transition state from electrospraying to electrospinning (Fig. 3a, b). Moreover, NMP, AC, and DMF showed partial solubility but high electrospinning productivity.

However, PCL solutions of DCM, CF, and THF produced uneven and high-discrete electrospun fibers of average diameters 450, 4500, and 1600 nm, respectively. Solutions in DCM, CF, and THF showed high solubility but low electrospinning productivity.

Previous literature has shown that solvent properties, such as density, boiling point, dielectric constant, conductivity, surface tension, and viscosity, influence the electrospun fiber morphology [18]. Solvent evaporation has been reported to decrease the elongation factor during electrospinning [19]. For instance, DCM and CF compared to other solvent, there were lots of holes in fibers (see Fig. 3d, f) because of high evaporation. This result demonstrates the rate of evaporation of solvents over other parameters on fiber diameter and morphologies.

The issue of solvent suitability for electrospinning is complex. Considerable efforts have been spent on the

development of suitable solvents and solvent systems for electrospinnable polymer solutions. The spinnability of a polymer solution has been explained based on solution concentration and solvent and solution properties. Solution properties including conductivity (see Table 2) and viscosity (see Fig. 8).

In this study, PCL is considered to exhibit good electrospinnability when continuous and stable fiber production with uniform fiber morphology and minimal "bead-on-string" formations. Therefore, we found that the decreasing electrospinnability order during experiments is NMP > AC > DMF > THF > DCM > CF.

The effect of solvents on FT–IR spectra and NMR spectra of poly(caprolactone) electrospun fiber

We re-analyze morphologies of electrospun PCL nonwoven mats produced with different solvents in Fig. 3. It is obvious that there are some beads in Fig. 3a, b. Meanwhile, there are lots of holes in Fig. 3d, f. It is not sure if there are remnant solvents in beads or in holes. Therefore, FT–IR spectra and NMR spectra are used to investigate PCL electrospun fibrous structure fabricated in different solvent. (see Figs. 5, 6).

The FTIR spectra of PCL electrospun fiber in different solvent are given in Fig. 5 and their infrared vibrations and assignments are also listed below: 2900–3000 cm^{-1}, C–H_2 asymmetric stretching; 2800–2900 cm^{-1}, C–H_2 symmetric stretching; 1700–1760 cm^{-1}, C=O stretching; 1350–1480 cm^{-1}, C–H scissoring and symmetric deformation; 1150–1200 cm^{-1}, O–C–O stretching; 1100–1150 cm^{-1}, C–O stretching; 1000–1100 cm^{-1}, C–C stretching; 900–1000 cm^{-1}, C–O–C symmetric stretching; and 500–900 cm^{-1}, CH_2 rocking. Whenever for any of the FT–IR spectra of PCL electrospun fiber in different solvent, there were no difference among them.
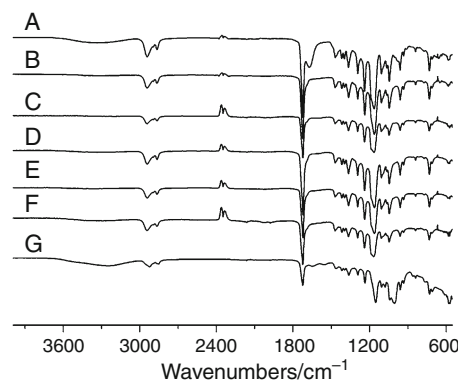
Fig. 5 FT–IR spectra of PCL electrospun fiber in different solvent. (A) PCL in NMP, (B) PCL in CF, (C) poly(caprolactone) in CA, (D) PCL in DCM, (E) PCL in THF, (F) PCL in DNF, (G) pure PCL
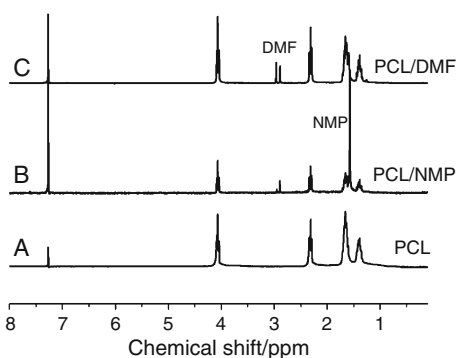
Fig. 6 ^{1}H NMR spectra of PCL electrospun fiber in CDCl$_3$. (*A*) PCL was dissolved in chloroform for electrospinning; (*B*) PCL was dissolved in NMP for electrospinning, and (*C*) PCL was dissolved in DMF for electrospinning

When the PCL solutions were electrospun as fiber, the fibers were collected and dissolved in CDCl$_3$ immediately for ^{1}H NMR characterization. There was no solvent peak in ^{1}H NMR spectra for CA, THF, and DCM (data was not shown). Because of the PCL which was dissolved in chloroform, the solvent peak in ^{1}H NMR spectra was not observed due to the CDCl$_3$ as the ^{1}H NMR solvent. But seen from the ^{1}H NMR of PCL fiber electrospun from chloroform solution in DMSO-d$_6$, there was no chloroform solvent peak in the spectra (data was not shown). As shown in Fig. 6b, c, the solvent NMP and DMF peak was observed, which was due to the volatility of NMP and DMF. It is well known that CA, THF, and DCM can evaporate in the air easily while NMP and DMF are difficult to evaporate.

The effect of solvents on viscosity and shearing strength of PCL solution

Viscosity is one of the most important parameters in the manufacture of chemical fiber. In general, the viscosity of PCL polymer solution depends on the molecular weight of PCL polymer, the concentration and the solvent of solution. In this part, the effect of solvents on viscosity and shearing strength of PCL solution was investigated.

It is shown in Fig. 8 that flow curve describes viscosity of spinning fluid at biggish shearing rate range. That kind of flow curve is used to compare viscosity of different kinds of solutions and the change of shearing strength.

In Fig. 7, shearing strength increased along with the increasing of shearing rate; shearing viscosity decreased along with the increasing of shearing rate at preliminary stage of test. The main reason is that the concentration of entwisted points decreases. High molecular polymer can be regarded as instantaneous network structure. Homeostasis moves accordingly along with the change of shearing strength. When shearing rate increases, some of entwisted
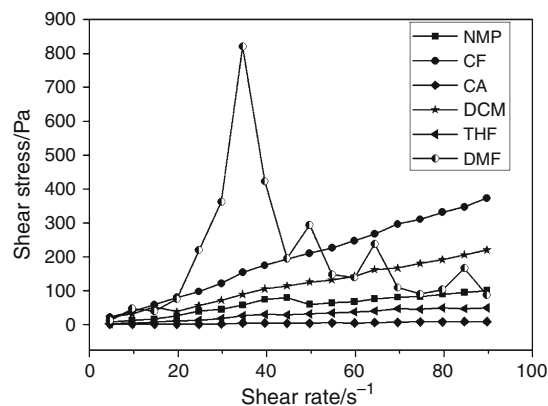
Fig. 7 Compare of shearing strength of PCL at different solvent
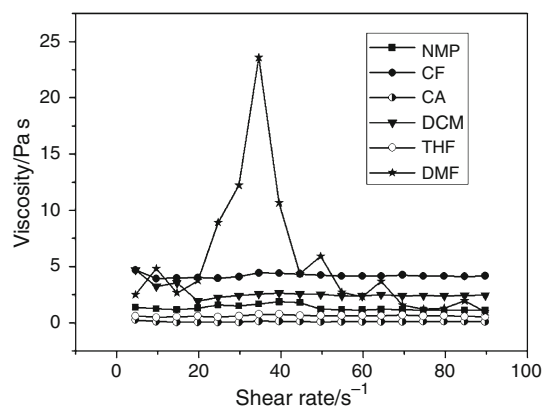
**Fig. 8** compare of viscosity of PCL at different solvent

points are removed. The decrease of entwisted points leads to the decrease of fluid viscosity. A majority of entwisted points in system are removed when the shearing rate comes to stated value, so between liquid flow layers, there are only friction force and applied shearing strength. The viscosity presents gently. That is the reason why the fluid viscosity that is researched in this paper is at stability condition. This article will omit original transilient situation in the flow curve figure at other conditions. We will mainly investigate the overall trend.

It is obvious from Figs. 7 and 8 that viscosity varies along with different solvents used. The sequence of viscosity is: CF > DCM > NMP > THF > CA. Lower the viscosity, higher is the electrospinnability. The sequence explained the reason why the electrospinnability was good when CA was chosen as solvent. Meanwhile, the shearing strength increases along with the increase of shearing rate. It is known from equation $\sigma = \eta \xi$ that shearing strength σ is proportional to shearing rate ζ and the slope of flow curve is the solution viscosity η. Meanwhile, we can know from Fig. 8 that solution viscosity will not change along with the change of shearing strength or shearing rate at stability condition.

Meanwhile, the change of viscosity with DMF solvent in PCL solution is quite different from other solvents. The reason is found that PCL dissolved in DMF solvent can not form homogeneous solution. Some white PCL polymer separated out the solution and deposited on the bottom.

The effect of solvents on thermal behaviors of poly(caprolactone) electrospun fibers

The thermal behavior of PCL electrospun fibers of different solvents were investigated by Differential scanning calorimetry (DSC) analysis and compared with PCL powder. The DSC curves were shown in Fig. 9. Both PCL powder and electrospun PCL (in different solvents) fibers showed quite different glass transition temperature T_g from -62.68 to -60.18 °C, i.e., -60.18 °C (PCL powder), -60.71 °C (PCL in NMP solvent), -61.19 °C (PCL in DMF solvent), -61.87 °C (PCL in THF solvent), -62.27 °C (PCL in DCM solvent), -62.68 °C (PCL in CA solvent), and -62.49 °C (PCL in CF solvent). That is, the glass transition temperature T_g of different PCL fibers from higher to lower is: pure PCL > NMP > DMF > THF > DCM > CA > CF, indicating solvent boiling point that might be responsible for the different T_g observed. Moreover, we can find the higher boiling point of solvent used, the higher T_g of fibers gotten. In addition, the volatilization of solvent will increase with decrease in boiling point. When the volatilization of solvent is very fast, fibers will be solidified suddenly, the jet has not got enough time for macromolecule crystallizing before solidifying. Therefore, T_g value will be low. The authors also observed that the melting temperature T_m showed different values when PCL was dissolved in different solvent, i.e., 8.51 °C (PCL in NMP solvent), 57.99 °C (PCL in DMF solvent), 57.85 °C (PCL in THF solvent), 57.40 °C (PCL in DCM solvent), 57.94 °C (PCL in CA solvent), and 57.33 °C (PCL in CF
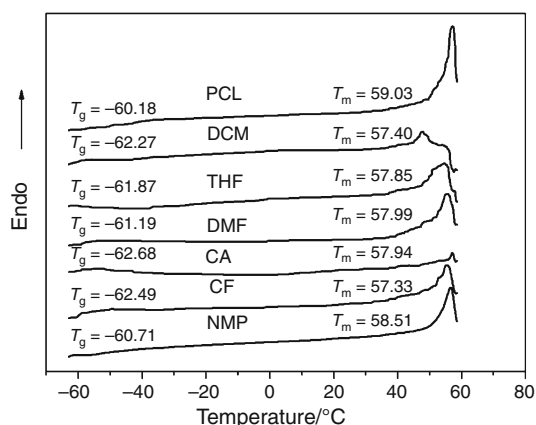
solvent). Furthermore, Lower T_m values have been observed for electrospinning fibers than PCL power, i.e., 59.03 °C (PCL powder). The melting temperature T_m of different PCL fibers from higher to lower is similar as T_g: pure PCL > NMP > DMF > THF > CA > DCM > CF. We can also found that when higher boiling point of solvent used, higher T_m of fibers was obtained.

The results obtained in these studies suggest that electrospinning may cause a lower glass transition, as well as a slightly lower melting temperature and crystallinity; all of these results are in close agreement with Chu's work [20].

We found the crystallinity of PCL nanofibers was a little lower than PCL powder. The crystallite destroyed when the PCL powder is prepared to solution. The stretching of electrostatic force is propitious to form crystal of PCL nanofibers either. But the solidifying speed of jet is almost millisecond level during electrospinning. The jet has not got enough time for macromolecule crystallizing before solidifying. So the crystallinity of PCL nanofibers is not very high. Figure 9 also showed that the crystallinity of nanofibers electrospun from solutions with low boiling point is lower than that with higher boiling point.

Conclusions

The effect of solvent on fibrous morphology, FT–IR spectra and ^{1}H NMR spectra, viscosity and shearing strength, thermal behaviors of PCL electrospun nonwoven membranes were investigated in this article. The results showed:

(1) When NMP, AC were used as the solvent for PCL electrospinning, all of them were composed of smooth and nanosized fibers with similar fiber surface morphologies. Meanwhile, when DCM and CF were as solvent, there were lots of holes in fibers due to high evaporation.
(2) There were remnant solvents in beads but not in holes by FT–IR spectra and ^{1}H NMR spectra analysis.
(3) The electrospinnability was good when CA was chosen as solvent due to its lowest viscosity.
(4) Differential scanning calorimetry indicated that solvent boiling point might be responsible for the different T_g and T_m observed. Moreover, when higher boiling point of solvent was used, higher T_g and T_m of fibers were obtained.

Fig. 9 DSC curves of electrospun PCL fibers with different solvents: from *up* to *down* PCL, DMF, THF, DCM, CA, CF, and NMP

References

1. Reneker DH, Yarin AL, Fong H, Koombhongse S. Bending instability of electrically charged liquid jets of polymer solutions in electrospinning. J Appl Phys. 2000;87:4531–48.

2. Ma QA, Cebe P. Phase structure of electrospun poly(trimethylene terephthalate) composite nanofibers containing carbon nanotubes. J Therm Anal Calorim. 2010;102:425–34.

3. Reneker DH, Chun I. Nanometre diameter fibres of polymer, produced by electrospinning. Nanotechnology. 1996;7:216–23.

4. Qin XH. Structure and property of electrospinning PAN nanofibers by different preoxidation temperature. J Therm Anal Calorim. 2010;99:571–5.

5. Stephens JS, Frisk S, Megelski S, Rabolt JF, Chase DB. "Real time" Raman studies of electrospun fibers. Appl Spectrosc. 2001; 55:1287–90.

6. Kim HS, Lee BH, Lee S, Kim HJ, Dorgan J. Enhanced interfacial adhesion, mechanical, and thermal properties of natural flour-filled biodegradable polymer bio-composites. J Therm Anal Calorim. 2011;104:331–8.

7. Mckee MG, Hunley MT, Layman JM. Long TE solution rheological behavior and electrospinning of cationic polyelectrolytes. Macromolecules. 2006;39:575–83.

8. Colby RH, Fetters LJ, Funk WG, Graessley WW. Effects of concentration and thermodynamic interaction on the viscoelastic properties of polymer-solutions. Macromolecules. 1991;24:3873–82.

9. Megelski S, Stephens JS, Chase DB, Rabolt JF. Micro- and nanostructured surface morphology on electrospun polymer fibers. Macromolecules. 2002;35:8456–66.

10. Lee KH, Kim HY, La YM, Lee DR, Sung NH. Influence of a mixing solvent with tetrahydrofuran, N,N-dimethylformamide on electrospun poly(vinyl chloride) nonwoven mats. J Polym Sci B Polym Phys. 2002;40:2259–68.

11. Fong H, Chun I, Reneker DH. Beaded nanofibers formed during electrospinning. Polymer. 1999;40:4585–92.

12. Olaru N, Olaru L. Electrospinning of cellulose acetate phthalate from different solvent systems. Ind Eng Chem Res. 2010;49: 1953–7.

13. Luo CJ, Nangrejo M, Edirisinghe M. A novel method of selecting solvents for polymer electrospinning. Polymer. 2010;51:1654–62.

14. Romeo V, Gorrasi G, Vittoria V. Encapsulation and exfoliation of inorganic lamellar fillers into polycaprolactone by electrospinning. Biomacromolecules. 2007;8:3147–52.

15. Hirose S, Hatakeyama T, Izuta Y, Hatakeyama H. TG-FTIR studies on lignin-based polycaprolactones. J Therm Anal Calorim. 2002;70:853–60.

16. Szamel G, Klebert S, Sajo I, Pukanszky B. Thermal analysis of cellulose acetate modified with caprolactone. J Therm Anal Calorim. 2008;91:715–22.

17. Del Gaudio C, Bianco A, Folin M, Baiguera S, Grigioni M. Structural characterization and cell response evaluation of electrospun PCL membranes: micrometric versus submicrometric fibers. J Biomed Mater Res A. 2009;89:1028–39.

18. Deitzel JM, Kleinmeyer JD, Harris D, Tan NC. The effect of processing variables on the morphology of electrospun nanofibers and textiles. Polymer. 2001;42:261–72.

19. Reneker DH, Yarin A, Zussman E, Koombhongse S, Kataphinan W. Nanofiber manufacturing: toward better process control. In: Reneker DH, Fong H, editors. Washington, DC: ACS Symposium Series; 2006. p. 7–20.

20. Zong X, Kim K, Fang D, Ran S, Hsiao BJ, Chu B. Structure and process relationship of electrospun bioabsorbable nanofiber membranes. Polymer. 2002;43:4403–12.