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Electrospinning of poly(butylene-carbonate):Effect of Solvents on the Properties of the Nanofibers Film

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The aim of this work was to learn the solvent effect on preparation of poly(butylenes-carbonate) (PBC) electrospinning nanofiber filmes. For this purpose, the dissolvability and electro-spinnability of PBC in seventeen pure solvents and two blend solvents, together with morphology of the result PBC nanofiber films were investigated in detail. Results revealed that the solvent dielectric constant had a strong influence on the split process, and that affected the morphology of as-spun PBC nanofibers. Compared with poly(ε-caprolactone) (PCL) nanofibers, PBC nanofiber films appeared better hydrophilic performance, and enhanced mechanical property which can be attributed to its low crystallization speed.

Keywords: Poly(butylene-carbonate); Electrospinning; Nanofibers；Morphology；organic solvents

1. INTRODUCTION

Today, biomaterials play much more important role in human health. Due to excellent biocompatibility, biodegradability and biopolymers, especially polyesters such as poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(ε-caprolactone) (PCL) and their copolymers have been widely used in medical field[1] .

In past decades, nanostructures have aroused people’s interest since their unique prosperities and potential fascinating applications in many fields. For biopolymers, electrospinning is the most frequently-used method to generate nanoscale materials. Through this simple technique, biopolymer fibers can be obtained with a far diameter ranging, from 2nm to several micrometers using natural or synthetic polymer solutions. These nonwoven fabrics have versatility and potential for applications in diverse fields, like tissue engineering, biosensors, clean energy, filtration, drug delivery, and so on [3,4]. Therefore, people have put a tremendous attention and research on electrospinning [5,6], and a few companies such as Donaldson and Finetex even have been using electrospun nanofibers in their products [7].

Because of its excellent performances on mechanical property and drug permeability, PCL electrospinning nanofibers got a very comprehensive research [8,9,10]. However, PCL have a hydrophobic nature resulted by its high crystallinity and relatively hydrophobic chemical structure (five continuous methyl groups connect with one carbonyl group, showed in Fig.1), which limits its application. Further development is also impeded for its poor wettability, bad cell attachment, and rather slow degradable rate (a degradation cycle of 2~3 years in human body) [2]. Poly(butylene carbonate) (PBC), a new biodegradable polyester[11], has a similar backbone structure with PCL, just the methyl group connected with carbonyl is substituted by an oxygen atom. This chemical structure indicates that PBC may have better hydrophilic and improved biodegradability. Furthermore, PBC had the good ability to form miscible blends with a wide range of polymers [12,13,14]. Thus, PBC can be regarded as a twin material of PCL with different degradation characteristic, and may be a potential biomedical polymer with a splendid prospect.

In this work, effects of PBC in some solvents and the as-prepared solutions of electro-spinnability were investigated. The properties of the PBC nanofibers films were investigated through scanning electron microscopy (SEM), contact angle and X-ray diffraction (XRD).

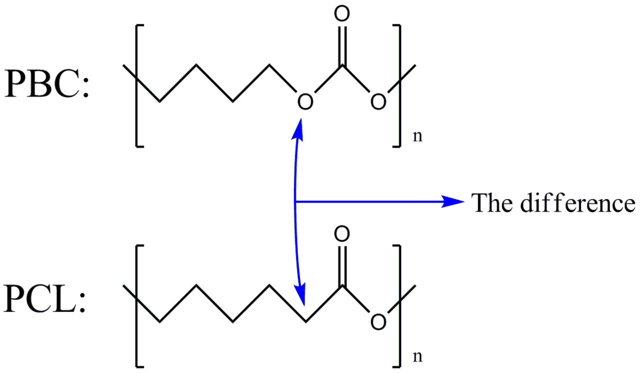


Figure 1. Structure of PBC and PCL

2. EXPERIMENTAL DETAILS

2.1. Materials

Poly(butylene-carbonate)(PBC) (Mn=7.0×105 Da, PDI=1.77) was provided from Sanfangxiang Group CO., LTD (Jiangsu, China), stoving the material in a vacuum drying chamber at 35ºC for one day before use. The poly(ε-caprolactone) (PCL) (Mn =8.0×105Da) was obtained from Tianqing Biological Material Co., LTD (Shanghai, China).

In this work, seventeen solvents were hexafluoroisopropanol (HFIP) [Aladdin, China], chloroform [Enox, China], formic acid (FA) [Sinopharm, China], acetic acid (HAc) [Sinopharm, China], dimethylformamide (DMF) [Sinopharm, China], dichloromethane [Sinopharm, China], dichloroethane [Sinopharm, China], dimethylacetylamide [Sinopharm, China], carbinol [Sinopharm, China], ethanol [Sinopharm, China], acetone [Sinopharm, China], diethylether [Sinopharm, China], tetrahydrofuran [Sinopharm, China], ethyl acetate [Sinopharm, China], toluene [Sinopharm, China], dimethylsulfoxide [Sinopharm, China] and acetonitrile [Sinopharm, China]. All of these solvents were analytical research and used without further purification. PBC can dissolve in first seven solvents, which basic properties (i.e. chemical structure, density, viscosity, boiling point, conductivity, dielectric constant, and surface tension) are summarized in Table.1.

2.2. Electrospinning

All the solutions were electrospun at room temperature. Electrospinning setup consisted of a high voltage DC power supply (JG 50-1,Shanghai Shenfa Detection Device CO.,LTD) with a charged electrode wires held by a teflon stick. The blunt needle tip is clamped in the alligator clip. The collector is a grounded aluminium foil set on a circular framework. The process parameters are set as follow: electrostatic field strength (EFS) is 18kV/18cm, feed rate is 0.5 $mL\cdot h^{-1}$. The ambient condition keep constant: a humidity of 50% and room temperature.

2.3. Morphological observation

The morphology of the PBC nanofibers was studied by scanning electron microscopy (SEM) with a JSM 5600LV instrument (JEOL, Tokyo, Japan). The specimens for SEM observation were prepared by cutting an Al sheet covered with the as-spun products and the cut section was carefully affixed on a copper stub. Each specimen was gold-coated by a Balzers Union SCD 040 sputtering device.

2.4. Contact angle

Contact angle observation of the PBC and PCL nanofibers was observed by a Micro Optical Angle Measurement (OCA40, Dataphysics, Germany). The specimens for contact angle observation were prepared by cutting the as-spun nonwoven mats into strips (20×5 mm). Drip a distilled water drop (diameter: 0.5 mm) on the sample and take a photo after they contacted for 20 seconds. The contact angle data were calculated by the accompanying software.

2.5. Mechanical properties

Mechanical properties of electrospun PBC nanofibers films were investigated with a universal testing machine (Kexin WDW3020, Changchun, China). The specimens for mechanical testing were cut into 70×13 mm rectangular samples, following a steel pattern of the same dimensions. Sample thickness was measured with a microcalliper. All samples were mounted between holders at a distance of 50 mm. Tensile testing was conducted at a rate of 10 mm/min. The tenacity and extension at break of the PBC fibers were calculated as the average of at least 5 measurements and chosen the most typical one. All measurements were performed at room temperature and 65% relative humidity. The samples were tested under same conditions.

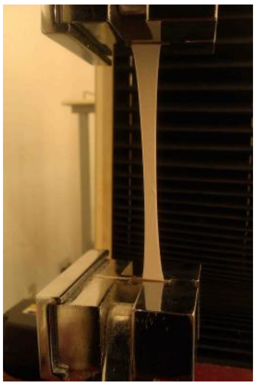


Figure 2. showed a photo taken from the tensile test.

2.6. Wide angle X-ray diffraction (WAXD) analysis

The crystallinity of the samples was examined using a wide angle X-ray diffractometer (D/max-2550 PC, Japan). The samples were scanned from $2\theta = 5° \sim 60°$, and the operating voltage and current were 40 kV and 200 mA, respectively. The radiation was Ni-filtered Cu-Kα radiation of wavelength 1.54056 Å.

3. RESULTS AND DISCUSSION

3.1. Effect of solutions on the electrospinning of PBC

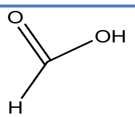
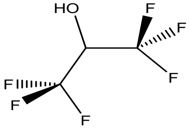
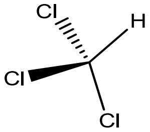
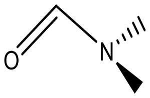
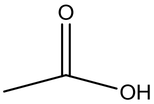
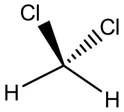
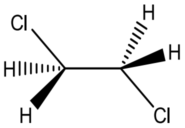
3.1.1. Solubility properties and electro-spinnability

In present study, seventeen pure solvents, including hexafluoroisopropanol (HFIP), formic acid (FA), dimethylformamide (DMF), chloroform, acetic acid, dichloromethane, dichloroethane, dimethylacetylamide, carbinol, ethanol, acetone, diethylether, tetrahydrofuran, ethyl acetate, toluene, dimethylsulfoxide and acetonitrile,were chosen to tese the PBC solubility in different mediums. The results showed that PBC have good solubility in dichloromethane, dichloroethane, chloroform, HFIP and FA without any additional conditions. While, PBC could also be well dissolved in DMF, acetic acid, tetrahydrofuran, dimethylacetylamide, dimethylsulfoxide and acetone *via* heighten temperature. When remove heating apparatus, the uniform solutions become solidification at room temperature. But PBC cannot dissolve in other six solvents at all.

After solubility test, PBC electro-spinnability experiments were performed in these good solvents. It is found that the PBC solutions in HFIP, FA and $CHCl_3$ can be electrospun, while the productivity of PBC/$CHCl_3$ was very low and a long bunch of solution was hung over at the needle tip after several minutes. Solutions with PBC dissolved in dichloromethane and dichloroethane cannot be electrospun even raising the voltage to 30 kV.

For PBC dissolved in acetic acid and DMF, the solubility was very low, far from the requirement to form electrospinning solutions. And PBC cannot dissolve in tetrahydrofuran, dimethylacetylamide, dimethylsulfoxide and acetone unless heating up the temperature to 50~60ºC, so we amplified additive amount of PBC to these solvents and heated them up to get proper concentration and viscosity, then put the solution into syringe and boosted the voltage at a high temperature of 45~50ºC, but only PBC/DMF can cover the aluminium foil with nonwoven fabrics.

Table 1. Properties of partial solvents used in this work

Solvent	Structure	Density (g·cm^{-3})	Viscosity (mPa·s)	Boiling Point (℃)	Conductivity (S·m^{-1})	Dielectric constant (F/m)	Surface tension (mN·m^{-1})
Formic acid (FA)		1.21	1.96	100.6	6.4×10^{-7}	58	37
Hexafluoroisopropanol (HFIP)		1.60	1.65	58.2	-	16.7	16.1
Chloroform		1.49	0.56	61.2	$<10^{-10}$	4.9	27.14
Dimethylformamide (DMF)		0.94	0.80	153	6×10^{-8}	36.7	35.2
Acetic acid		1.04	1.12	118.1	6×10^{-9}	6.15	26.9
Dichloromethane		1.33	0.42	39.8	4.3×10^{-11}	9.1	28.1
Dichloroethane		1.26	0.84	83.5	3×10^{-8}	10.45	32.23

In summary, for the seventeen solvents we attempted in the initial stage of the work, there were four solvents can produce electrospinnable solutions which were HFIP, FA, $CHCl_3$ and DMF. Among these solvents, HFIP and FA could dissolve and make PBC electrospinning to nanofibers successfully and the others appeared some problems in this process more or less.

From Table.1, we can find the reason why some solvents can dissolve PBC favourably but cannot form electrospinning solutions. Conductivity and dielectric constant of the solutions are two key factors of electrospinning solutions and highly depend on the solvents [15]. The comprehensive effect of low conductivity and dielectric constant are the main cruxes for this performance. Dichloromethane and dichloroethane can dissolve PBC successfully, but their conductivity and dielectric constant are too low to help PBC electrospinning into nanofibers.

3.1.2. Single solvents used for electrospinning

The nanofibers prepared from different PBC solutions were shown in Fig.3. Two kinds of magnification for each solvent were chosen. The low magnification gave us a broad vision in the nonwoven mats, and we had a legible view on regional fibers .

From the scanning electron microscopy photos, we can observe the morphology of the PBC nanofibers clearly. All of the PBC nanofibers were prepared from the same parameters (18kV/18cm, 0.5 $mL\cdot h^{-1}$) and different concentration depending on their disparate dissolubility and solution viscosity (the PBC mass fraction: 25% in FA solution, 20% in DMF, 12% in HFIP and 20% in chloroform).

Nanofibers coming from PBC/FA solution presented a smooth look and the diameter of the fibers distributed to a narrow scope while the morphology of the other nanofibers showed a wide distribution in fiber diameter. Especially, when we look at the pictures of nanofibers produced from PBC/HFIP, we can find some plait structure in 3(e). Promoting the magnification and comparing 3(e)-3(f) with 3(c)-3(d) and 3(g)-3(h), we conclude that it is a reflex of the incomplete split of the jet flow. The dielectric constant values of these solvents help us get this conclusion.

As we all known, the solution of dielectric constant is essentially a measure of the capability to hold electric charge when placed in an electric field, and highly depend on the solvents. For electrospinning, the accumulation of electric charge brings non-axial instability to the jet flow in the electric field, and then, this instability leads the jet flow split into thinner ones. That means a higher dielectric constant stands for a stronger capability for split which happen in the high electric field.

The value of Table.1 indicates that FA has a high dielectric constant and can get abundant electric charges from positive electrode. For DMF, HFIP and chloroform, the capacity of holding charge become weaker as this value descending successively. It is mutually supported with the Fig.3, and is also get support from the result of mixed solvents showed in Fig.4 which will be mentioned later.

Fig.3(a) and 3(b) reveal that after split, the jet flow also underwent sufficient stretching effect before arriving at the collector. So we could be convinced that PBC/FA jet flow accomplished its split process very fast, because its high dielectric constant can help it get a powerful Coulomb repulsion force to overcome its surface tension easily, then there was enough time left for the jet flow to stretch before deposition. And owed to its suitable concentration and sizable conductivity, nanofibers with homogeneous diameter and neat appearance were collected on the Al foil.

Though the surface tension of DMF is close with FA, the dielectric constant is much lower than FA, so the DMF system cannot yield uniform nanofibers like the former.

For PBC/HFIP, with solvent dielectric constant reducing to 16.7D, the split did not come out acutely. So the distance between needle tip and collector is not so ample for the jet flow to get a sufficient stretching. This braided pattern can be seen as an enlargement of the small fiber bundles in 3(c).

With a very low solvent dielectric constant of 4.9D, the electrospinning process of PBC/chloroform is really difficult and the productivity is very low. And from the Fig.3(h) we can find that when the split process is still proceeding, the fibers have already deposited on the Al foil. That’s also why the diameter of fiber in Fig.3(g) is so thick and the quantity of fibers in unit area is fewer than the others. In the final analysis, this system is short of split because of its low value of dielectric constant. That can also explain why Lien got microscale fibers when he used $CHCl_3$ as the solvent, but nanoscale fibers were produced while formic acid was used in his work[13].

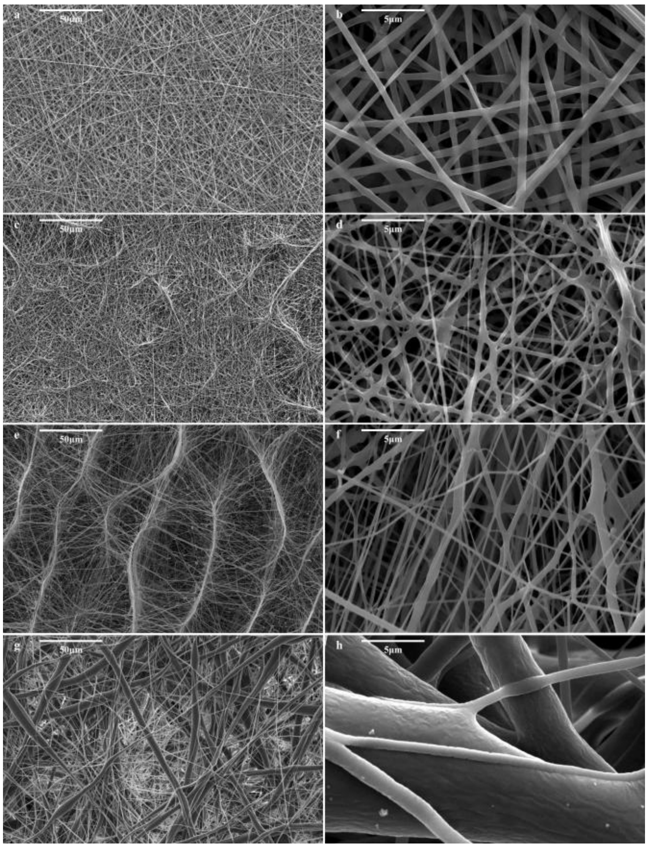


Figure 3. Scanning electron micrographs of PBC nanofibers prepared from single solvents (a-b: FA, c-d: DMF, e-f: HFIP, g-h: $CHCl_3$).

3.1.3. Mixed solvents used for electrospinning

For the solvents we tested, we found DMF cannot dissolve PBC in room temperature so there existed some question in electrospinning. And $CHCl_3$ has a good performance in dissolving PBC but the solution cannot be electrospun smoothly due to its low conductivity and dielectric constant. Coincidentally, DMF has considerable conductivity and dielectric constant which can cover the shortage of single $CHCl_3$. Then, these two solvents being blended to form a mixed solvent to dissolve PBC and produce an electrospinnable solution is a suitable method.

We mixed $CHCl_3$ with DMF in different weight ratio and dissolved PBC in them respectively (weight percent of PBC is 20%). For the ratio of $CHCl_3$-DMF is 9:1 and 1:9, the performance is similar to pure $CHCl_3$ or DMF being the solvent: the former had a too low productivity with a long bunch of solution hanging over at the needle tip, the latter cannot dissolve PBC in room temperature. This situation was changed when the weight ratio changed to 8:2 and 2:8. The solution can be electrospun successfully with a passable productivity by observing the collector.

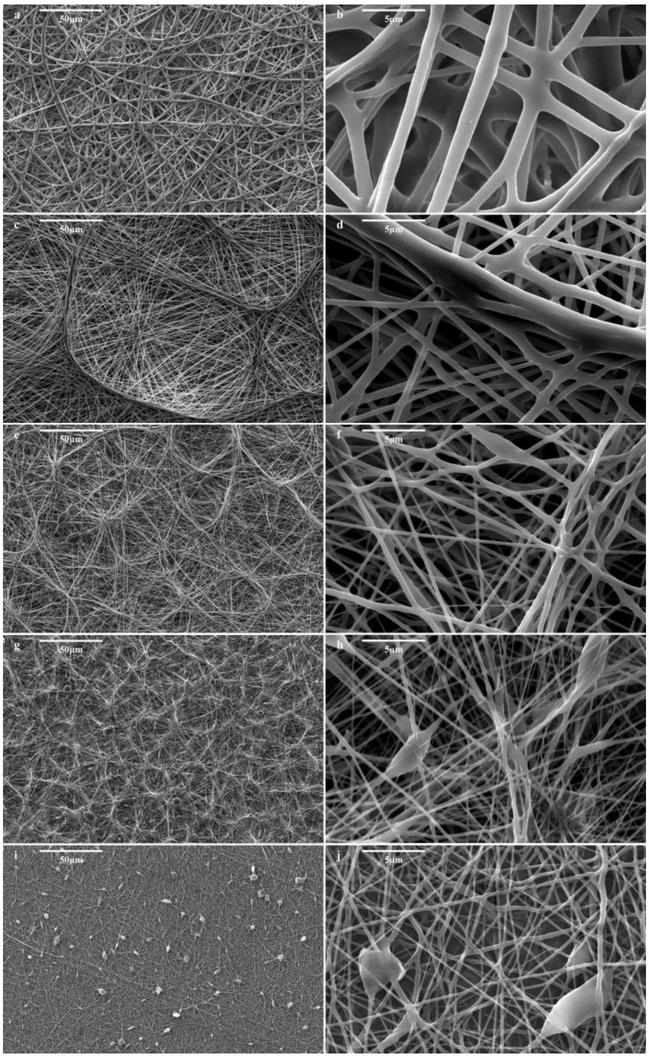


Figure 4. Scanning electron micrographs of PBC nanofibers prepared from $CHCl_3$-DMF mixed solvents(a,b-8:2, c,d-7:3, e,f-5:5, g,h-3:7, i,j-2:8).

The nanofiber in Fig.4 are all prepared from various $CHCl_3$-DMF weight ratio with the same experimental parameter. From Fig.4, it is clear that with increased DMF ratio, the fiber diameter decreased due to the higher conductivity and dielectric constant of DMF. At the same time, split phenomenon also happened more frequently which can be proved by the left five images with a magnification of 500. When the weight ratio of $CHCl_3$-DMF changed from 8:2 to 7:3, thick fibers split into thinner ones accompanied by the appearance of braided structure. The braided structure became unconspicuous and presented as the fiber bundle with a deeper degree of split when the ratio of DMF came higher to 50% and 70%. Ultimately, the fiber bundle also disappeared because of the reinforced stretching effect with the DMF ratio reaching to 80%.

The SEM images also showed that a few number of bead defects were generated. And the number of bead defects increased with the shape transformation from fusiform to olivary along with the increase of DMF proportion. This can be understood when we compared with the surface tension of $CHCl_3$ and DMF. This variation in morphology can be seen as the compromised product between stretching effect and different surface tensions.

According to the above reasons, the nanofibers got from the pure PBC/DMF solution would generate more beads. But we cannot find obvious beads from Fig.3(c)-3(d). The reason may due to that electrospun at a high temperature, so the viscosity and surface tension lessened to the low values while the solution conductivity increasing[18].

3.2. Properties of the PBC nanofiber film

3.2.1. Hydrophilic test

The hydrophily of a material is the key factor to affect the interactions between the biomaterial and cells in the first stage. Good hydrophily can promote cell attachment and proliferation[19,20,21,22]. And for degradable polyesters, good hydrophily may also induce a faster rate of biodegradation. So we tested the contact angle between water and the materials. PCL and PBC were firstly dissolved in FA with a concentration of 25% respectively, then the solutions were prepared into nanofiber fabrics under the same condition (18kV/18cm, 0.5 mL·h-1).

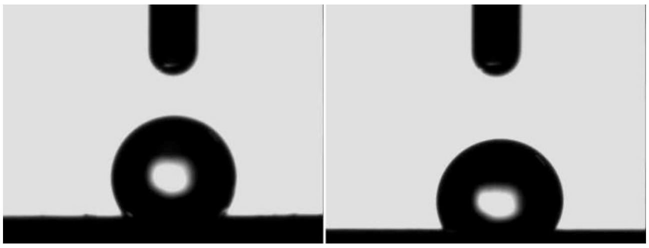


Figure 5. The water contact angle taken from two kinds of nanofiber films after contacted for 20 seconds: left-PCL; right-PBC

Fig.5 showed two photos taken during the hydrophilic test. From Fig.5 we can clearly find that, the PBC nanofiber fabric has a better hydrophily for whose contact angle is about 110° compared than that of 130°. This difference may caused by the chemical structure of these two polyesters. PBC has two oxygen atom connecting with its carbonyl, but for PCL there are five continuous methylenes in its construction unit. The different performance in hydrophily may lead PBC to be more favourable for cell adhesion and can have a faster degradation speed than PCL.

3.2.2. Crystallinity and mechanical test.

As a polyester with so little research, the biggest question of PBC may be its low speed in crystallization. The machining and application of PBC may be limited by this trait because of the puzzle in melt molding and solution curing process. Although electrospinning can help PBC shape into nanofibers smoothly, it still cannot change the peculiarity of low speed in crystallization of PBC. So, it’s a funny job to get a investigation on the relationship among crystallization time, crystallinity and mechanical properties.

In the earlier work, we found PBC can be dissolved and well electrospun by FA and HFIP, but FA is one of the least toxic and cheap solvent, so we select FA to dissolve PBC and for electrospinning.

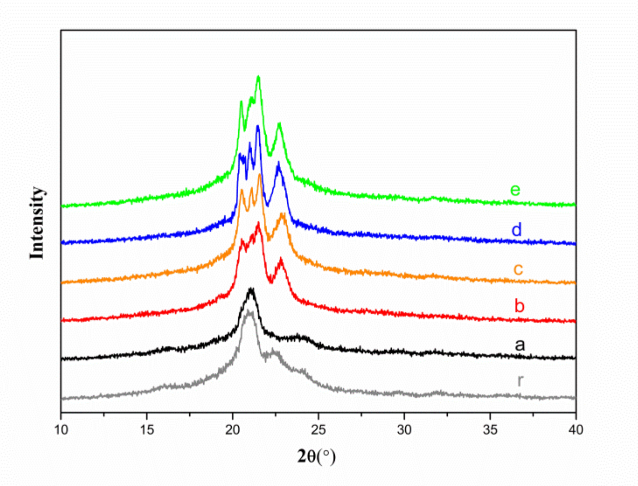


Figure 6. XRD patterns of the PBC nanofiber films (r: raw material, a: just prepared, b: 1 day after prepared, c: 2 days, d: 4 days, e: 10 days)

Fig.6 shows the WAXD patterns for series nonwoven mats which electrospun from a 25 wt% solution dissolved in FA and had different crystallization time. These patterns imply that the PBC nanofibers have a very slow crystallization rate. Startlingly, the degree of crystallinity is increasing successively even several days later.

At the same time, we tested the mechanical properties of the nonwoven mats with different crystallization time. Logically, the material strength heightened with the crystallization time, in other words, the incremental crystallinity. The most representative stain-stress curves for these five different crystallization time are showed in Fig.7.

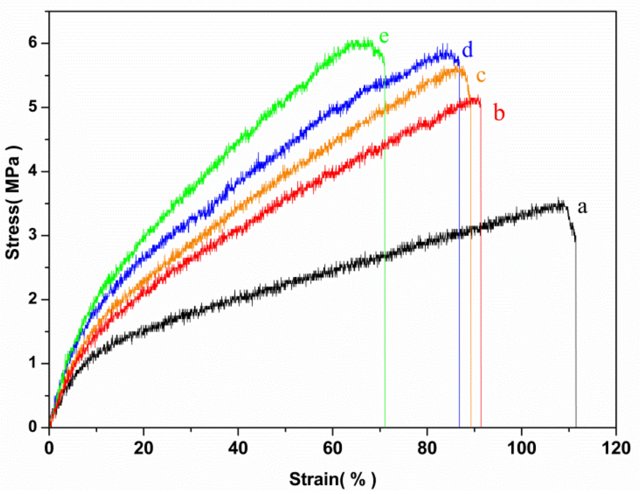


Figure 7. Strain-Stress curve of the PBC nanofiber films (a: tested that right day, b: 1 day after prepared, c: 2 days, d: 4 days, e: 10 days)

With the crystallinity increasing, the modulus, broken strength and yield strength all have an obvious promotion after crystallization of one day, but the tendency became weaker in the following days. The result also showed that with the crystallization process nearly get accomplished and the broken strength is almost as twice as that of the new prepared ones. The strength of this material is also suitable for biomedical application.

4. CONCLUSIONS

In this study, PBC solubility test in seventeen pure solvents and two blend solvents were carried out firstly. The PBC electro-spinnability in good solvents was following studied, and got PBC nanofibers successfully. Results displayed that the morphology of PBC nanofibers was strongly depended on solvents's dielectric constant, higher dielectric constant would lead split to happen in a faster speed and got a neat look. In the condition of low dielectric constant, Jet flow split reluctantly has a trendency to form plait structure in the SEM pattern. This phenomenon was also supported in $CHCl_3$-DMF mixed solvent systems. With increasing DMF content, split happened more acutely and left the mats with more thin fiber bundles.

The contact angle test showed that PBC nanofiber films present relatively hydrophilic characteristic. Its contact angle is 110°, less than PCL nanofiber films that of 130°. The different performance in hydrophily may lead PBC to be more suitable in biomedical application.

An interesting phenomenon arouses our attention in polymer crystallization test. PBC has slow crystallization speed, and appears enhancement mechanical property in beginning ten days. Its excellent mechanical performance meets the biomedical materials requirement.

Other experimental methods and physical and chemical properties of PBC nanofiber films, such as degradation and biocompatibility are still under research, will be reported in the following papers.

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