CRYSTALLOGRAPHIC MATCHING EFFECT IN SELF-INDUCED NANOHYBRID SHISH-KEBAB STRUCTURE OF POLY(E-CAPROLACTONE)

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Abstract

The shish-kebab structure has been investigated for many years and it has been widely applied in many fields, while the formation mechanism is attracting researchers. In this study, different electrospun poly(ε-caprolactone) (PCL) fibers were applied as shish materials in the self-induced crystallization and two different self-induced crystal structure were obtained. By comparing with the surface crystalline structure, it seems that the self-induced nanohybrid shish-kebab (SINSK) structure follows a crystallographic matching mechanism in the crystallization process. The PCL fibers with different internal crystalline structure led to different induced crystal lamella morphology. This study might help people to screen the materials for formation of SINSK structure.

Introduction

The shish-kebab structure is a classic polymer crystalline morphology which consists of a central fibril and perpendicularly oriented multiple disk-like crystal lamellae, and both the shish and kebab are formed in a shear flow field or other conditions. An as-existent shish materials make it easier to obtain the nanohybrid shish-kebab structure (NHSK) in a more common manner, such as solution incubation, solvent evaporation and etc. The NHSK has emerged widely application potential, such as, tissue engineering scaffold, bucky paper, mechanical enhancement, surface modification, mineralization enhancing collagen fiber-mimicking material.

The formation mechanism for the NHSK has been studied extensively and it is believed that soft epitaxy is the key mechanism in the crystallization process because of the small size of shish material which leads that it is difficult for the polymer chains forming a crystallographic matching. Even though interfacial crystallization follows the epitaxy mechanism that is crystalline lattice parameter and orientation matching when polymer nucleation and growth onto the shish surface, the small size and curvature of shish material distort the growing lattice and thus only allows nucleation to occur periodically. In the crystallization process, strict crystallographic matching does not occur but the molecular chains adsorb onto the surface of shish and form a homogenous coating and then the polymer chains orient, nucleate and grow. The concentration gradient between the growing lamellae causes a periodic structure of shish-kebabs. This theory is very well defined for describing the hybrid shish-kebab formation of the CNT as a shish material, carbon nanofiber and those being different for the kebab materials. However, for the self-induced nanohybrid shish kebab (SINSK) structure, the crystalline lattice parameters is identical for the crystal in the shish and kebab, and the physical and chemical characteristics are also the same, whether the epitaxy or soft epitaxy mechanism taking effect is still unclear.

To this end, electrospun PCL nanofibers with different fiber diameter and internal structure were applied as shish materials in a self-induced solution incubation crystallization process. The evolution of shish-kebab morphology in terms of fiber diameter, orientation and crystallization time was discussed. A phenomenological analysis was carried out based on the experimental results of both the shish-kebab structure and internal structure of PCL fibers.

Experimental

Materials

PCL (CAPA6500) was purchased from Perstop (London, UK). The average molecular weigh and melt flow index were 50,000 g/mol and 7 g/10 min (2.16 kg, 160 °C), respectively. Chloroform (CF), dimethyl-formamide (DMF), glacial acetic acid were bought from Tianjin Chemical Reagents. The deionized water was collected from Millipore Ultrapure Water System. All materials were used as received without any treatment.

Electrospinning of PCL fibers

The PCL pellets were vacuum dried at room temperature for 6 hours, and then were dissolved in a solvent mixture of CF and DMF (V/V 7/3) for 4 hours with magnetic stirring to obtain a homogenous solution. The concentration of 14 % and 25 wt. % were prepared respectively to obtain nanofibers and microfibers. 0.2 wt. % of NaCl macroparticles were dissolved in CF
and DMF solvent mixture by ultrasonication (ultrasonic cleaner, JP-020S, (Jiemeng, Shenzhen, China)) for 5 min to increase the conductivity of the solution. And then, the solution was filled into a 10 ml syringe with a needle diameter at 0.9 mm. For random PCL nanofibers, the applied voltage was 20 kV over a distance of 20 cm from the needle to the collector and for random PCL macrofibers, the voltage and the distance were 10 kV and 10 cm respectively. Moreover, to obtain aligned fibers a rotating ferrum frame with diameter of 40 cm and the rotating speed was 700 rpm.

Creation of PCL SINSK Structure

A controlled solution crystallization method was applied to obtain the SINSK structure. The electrospun PCL fibrous mats were immersed in the 1.5 wt. % PCL/(glacial acetic acid/deionized water mixture) solutions at room temperature (22℃) for 5 min, 10 min, 30 min, 60 min and 120 min. Then the PCL mat was rinsed with glacial acetic acid/deionized water mixed solvents for three times to remove the residual PCL on the mats. For PCL supersaturated solutions, 1.5 wt. % PCL were added in to the glacial acetic acid/deionized water (V/V = 75/25) mixed solvents at 70℃ with magnetic stirring for 3 hours then cooled to room temperature for later use.

Morphology characterization

SEM (Agilent 8500) was employed to observe the PCL fibers and the shish-kebab morphology. The fibers were gold coated for better imaging. The ImageJ software was used to measure the distribution of PCL fibers with the number of 100 different fibers diameters. To investigate the surface topography of nanofibers, the Atomic Force Microscopy (AFM, KEYSIGHT 7500) was applied to image. The PCL fibers were transferred onto the silicon wafer for sample preparing.

Results and Discussion

Morphology of PCL fibers

Different electrospun PCL nanofibers were obtained by varying the solution concentration and collecting method (cf. Figure 1). For the solution concentration at 14 wt. %, the fibers on flat collector showed a random oriented fiber morphology and the fiber diameter was about 230 ± 80 nm (R-14), while the fibers on rotation drum showed an aligned morphology and the fiber diameter was about 205 ± 94 nm (A-14). For the solution concentration at 25 wt. %, the random oriented fiber on flat collector was about 2104 ± 175 nm (R-25), while the aligned fibers on rotation drum was about 902 ± 256 nm (A-25). All the four kind of fibers showed smooth fiber surface.

It can be clearly seen that the fiber diameter were varied from hundreds of nanometer to several microns by varying the solution concentration and collecting method. For the solution concentration at 14%, there was not a significant difference between the flat collector and rotation drum. However, for the solution concentration at 25%, the fiber diameter decreased dramatically when the collecting method was altered from a flat collector to a rotation drum, and it is believed that the additional tension force by the rotation collector played an important role in decreasing the fiber diameter. This effect become more significant for a higher solution concentration.

Table 1. Statistical result of the PCL fiber diameter.

<table>
<thead>
<tr>
<th>Solution Concentration</th>
<th>Flat plate / nm</th>
<th>Rotation drum / nm</th>
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<tbody>
<tr>
<td>14%</td>
<td>230 ± 80</td>
<td>205 ± 94</td>
</tr>
<tr>
<td>25%</td>
<td>2104 ± 175</td>
<td>902 ± 256</td>
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Morphology of SISK with different diameters of PCL fibers

PCL crystal lamellae successfully decorated on the PCL fibers and the morphology of PCL crystal lamellae differs with the different types of PCL fibers. For PCL nanofibers, (both R-14 & A-14) the nanofiber shish-kebab were uniformly formed. PCL crystal lamellae were decorated on the nanofibers periodically, completely wrapped around PCL nanofibers, and perpendicular to the long axis of PCL nanofibers. The periodicity of the crystal lamellae was about 400 nm. For PCL microfibers (R-25),
the PCL kebabs wrapped randomly around the fibers compared with PCL nanofibers and PCL lamellae were randomly orientated on the microfiber surface, but no clear classical shish-kebab structure was observed. Figure 2(d) shows that when the PCL fibers diameter decreases to about 750 nm (A-25), the crystal structure were similar to that of R-14 & A-14. Interestingly, there were several PCL microfibers (A-25) which formed the similar structure with PCL random microfibers in Figure 2(c).

![Figure 2](image)

Figure 2. SEM images of PCL fibers incubated in 1.5 % PCL / glacial acetic acid/ deionized water supersaturated solutions for 120 min: (a) R-14, (b) A-14, (c) R-25 and (d) A-25. Scale bar is 5 μm.

The result suggested that the crystal morphology in self-induced crystallization is affected by the characteristics of the shish-fiber which might be fiber diameter and / or internal crystalline morphology of the PCL fibers.

**SINSK morphology evolution over crystallization time**

To further investigate the formation mechanism of SINSK structure on different fibers, the surface morphology evolution over crystallization time was obtained. Figure 3. Shows the morphology of PCL crystal lamellae attached on PCL parallel macrofibers (A-25) at different incubation time. At 5 min, PCL crystal lamellae formed on the surface of PCL fibers (Figure 3(a)), the kebabs were very small and the periodicity was around 300 nm. With the incubation increases, the crystal lamellae grew and completely wrapped around the macrofibers. Moreover, the kebab periodicity increased to about 500 nm. When the incubation time reached 120 min, the crystal lamella collapsed down and the adjacent kebabs merged with each other. Consequently, the periodicity increased to 1169 nm as shown in Figure 4.

![Figure 3](image)

Figure 3. SEM images of PCL parallel macrofibers (A-25) incubating at different time: (a) 15 min, (b) 30 min, (c) 60 min, (d) 120 min. Scale bar is 2 μm.

![Figure 4](image)

Figure 4. Kebab periodicity on PCL fibers at different incubation time.

The crystallization morphology evolution of PCL random macrofiber (R-25) was very different from their aligned counterparts. After 10 min incubation, a number of small tiny crystallites decorate on the PCL macrofibers as shown in Figure 5(a). At the time point of 15 min, the crystallites become a little bit larger and more crystallites were observed on the fiber surface. With the increase of incubation time, the little visible PCL crystal became larger (cf. Figure 5(b) and (c)). After 120 min of the incubation, the PCL macrofiber was completely wrapped by larger PCL lamellae in Figure 5(d). While the PCL crystal lamellae did not grow periodically on the surface of R-25 macrofibers which was very different from that of
A-25 in Figure 3(d). The crystals show multiple orientation directions, perpendicular, slant, or even parallel to the axis of PCL macrofiber. A great number of crystal lamellae wrapped up the fibers, and an irregular coral-surface-like structure was formed.

One can clearly see that the fiber served as the shish and PCL crystal lamellae grew to be a very different structure comparing with the classical shish-kebab structure. The kebab aligned irregularly on the fiber surface when they were nucleating at the very beginning, and with the crystallization time increasing, the kebab keep growing around the kebab crystal nucleus. When two adjacent kebab met each other, they might merged together and kept growing. As a result, the irregular coral-surface-like structure was formed. It should be noted that in the self induced crystallization process, the solvent might also affect the morphology of the shish fiber itself, therefore it seems like the diameter of shish decreased by some extent.

Figure 5. SEM images of PCL random macrofibers (R-25) incubating at different time (a) 15 min, (b) 30 min, (c) 60 min, (d) 120 min. Scale bar is 2 μm.

Figure 6 and Figure 7 are the SINSK morphology over incubation time of A-14 & R-14. The result reveals that for both two shish fibers, the SINSK kebabs became larger as an increase in incubation time which is very similar to that of A-25. While the periodicity variation of the three different types of kebabs was shown in Figure 4. All the three kinds shish-kebab periodicities show a nearly linear relationship with an increase in crystallization time (incubation time). The reason is that when the PCL kebab lamellae was growing to be larger, the capillary force between the adjacent lamellae pulled them to merge with each other leading to a more stable lamellae, therefore the periodicity of the kebabs shows an proportional increase with the increasing of incubation time.

Figure 6. SEM images of PCL parallel nanofibers (A-14) incubated at different time (a) 5 min; (b) 30 min; (c) 60 min; (d) 120 min.

Figure 7. SEM images of PCL random nanofibers (R-14) incubated at different time: (a) 30 min, (b) 60 min, (c) 120 min.

For the four types of PCL fibers, PCL crystal lamellae attached on the fiber surface, while the attaching manner are very different from each other. In general, it is
much easier to form SK structure on nanofibers (A-14 & R-14) comparing with the macrofibers which can be seen from the time sequence image. For macro fibers, aligned fibers are able to induced SK crystallization, while it shows complicated crystallites morphology instead of SK structure and the crystallization process is also in a slower developing rate.

Figure 8. AFM phase contrast images of PCL electrospun nanofibers and macrofibers: (a) R-14, (b) A-14, (c) R-25, (d) A-25.

Crystallographic matching effect

We then investigated the crystalline morphology of PCL fibers. The band pattern of dark and light was observed in the red boxes in Figure 8 which suggested the orientation of PCL crystal lamellae. It showed a very random orientation of the crystal lamellae in the fiber of R-25, while a parallel orientation was observed in A-25, which is perpendicular to the fiber axis. While it seems that the collecting method did not affect much on the orientation of PCL crystal lamellae in the fiber of R-14 & A-14, both of which showed a parallel orientation. A similar result was also reported.

Recall that the shish-kebab structure formation was failed when the fibers of R-25 were applied as the shish material. While for the fibers of R-14, A-14 & A-25, the shish-kebab structure was successfully grown on the fiber surface. The as-existed theory that is soft epitaxy on the formation the nanohybrid shish-kebab structure for the shish material like carbon nanotube and others deteriorates to the crystallographic matching effect in the formation of SINSK structure. Because of the confinement crystallization in the electrospinning process, the PCL crystal lamellae show a parallel orientation structure which is favor for the generation of SINSK structure. When the PCL molecular chains in the solution attached on the PCL fiber, they behaved as a most stable manner which was that the PCL chains oriented themselves perfectly matching the crystalline structure on the fiber surface. The same orientation of the crystallites allowed them to keep growing to be a disk-like lamellae fashion, which for those fibers with random oriented crystal lamellae morphology, the shish-kebab structure was failed to form instead of a coral-surface-like structure.

Moreover, the coral-surface-like stature on some A-25 fibers showed in Figure 2(d) might also suggest that the size effect of soft epitaxy theory is not dominant in SINSK structure formation. The reason is that for the fibers with similar diameter, two completely different crystal structures are formed. More investigation needs to be done about the SINSK structure of other polymers for a better understanding of the formation mechanism of SINSK structure.

Conclusions

This study investigated the self-induced nanohybrid shish-kebab structure by employing four different kinds of PCL fibers. The result suggested that different from the classic soft-epitaxy theory, the crystallographic matching played the dominant role in the formation of SINSK structure. The new crystal lamellae grew as extension part of the lamellae in the shish fibers which showed parallel morphology and random orientation morphology, corresponding to shish-kebab structure and coral-surface-like structure. This study shows potential application in selecting the material for obtaining SINSK structure.

References