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Preparation of alternating multilayered polyethylene oxide/poly(ε-caprolactone) and the confined crystallization of the composites

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Abstract: In this paper, polyethylene oxide (PEO) and poly(ε-caprolactone) (PCL) were co-extruded to form the alternating multilayered structure with different layer numbers. For a given film thickness, the layers were thinner as the layer numbers became higher, and more interfaces were observed. The crystallization behaviors of these two polymers varied distinguishably as the layer number became higher. For the crystallization of PEO, the molten PCL layers promoted the crystallization rate of PEO, while the spatial confinement of the layer thickness significantly suppressed the crystallization rate of PEO at higher layer numbers. In the case of PCL layers, the effect of spatial confinement on the crystallization of PCL was negligible due to the small crystal size of PCL, while the interfacial interaction between PEO and PCL layers suppressed the crystallization rate of PCL in the layer interfaces. Meanwhile, the degree of crystallinity ($X_c$) of PEO decreased from 70.2% to 40.0% when the layer number increased from 2 to 128, while the $X_c$ of PCL did not vary much.

KEYWORDS: Confined crystallization, multilayered structure, interfacial interaction, poly(ε-caprolactone), polyethylene oxide

1. Introduction

In recent years, an increased demand for biodegradable materials in many industrial applications has been induced by environmental concerns, due to their excellent biocompatibility, degradability, and nontoxicity.\textsuperscript{1, 2} As one of the most important synthetic biodegradable polymers, poly(ε-caprolactone) (PCL) has been used extensively in drug delivery,\textsuperscript{3-7} tissue engineering,\textsuperscript{8,10} and food industries.\textsuperscript{11} However, the strong hydrophobicity of PCL usually made the degradation rate slow,\textsuperscript{12} which would limit its applications. Thus, some hydrophilic biodegradable polymers, such as polyethylene oxide (PEO), have been added to adjust the degradation behavior and hydrophilicity of PCL.

As two semicrystalline polymers, the properties of the PEO/PCL blends strongly depended on the morphology and crystallization of the two polymers. Therefore, it is important to investigate the crystallization behaviors of PEO/PCL blends under various processing conditions. In the case of binary blends of two crystalline polymers, it is complicated to investigate the crystallization behavior since both
components are able to crystallize, and the crystallinity of one component affects the crystallization process of the other.\textsuperscript{13,14} Qiu et al.\textsuperscript{15} prepared PEO/PCL blends through solution casting process, it was reported that the miscibility and crystallization kinetics of PEO and PCL was adjusted by the variation of the PEO/PCL weight ratio. The crystallization rate of PEO decreased with the increase of PCL in the blends, while the change in the crystallization rate of PCL was not very big at higher PEO contents.\textsuperscript{15} Huo et al.\textsuperscript{16} investigated the effect of the interface between PEO and PCL domains on the crystallization of the PEO/PCL blends, it was concluded that the condition of PEO (melted or not) significantly affected the nucleation behavior of the PCL chains at the interface. To the best of our knowledge, most previous studies focused on the crystallization behaviors of the blends, such as the size-dependence of the nucleation and the crystallization rates.\textsuperscript{15-17} However, due to the limitation of the conventional processing methods, (solution casting and hot-melt extrusion, etc), the domain size and the distribution of the two polymers in the blends were not that controllable or uniform.\textsuperscript{17-19} Thus the influence of geometrical confinement on the crystallization of the PEO/PCL blends was not fully understood. In order to easily adjust the confined space and further study its effect on the crystallization of PEO and PCL in the blends, a novel and efficient preparation was needed.

Our previous work showed that different polymer components could be forcedly distributed in the confined layer space through microlayered coextrusion technology, and various composites with excellent properties were obtained.\textsuperscript{20,21} Based on this technology, alternating PEO and PCL layers with adjustable layer thicknesses were obtained. Thus, the effects of the spatial confinement on the crystallization behavior of PEO and PCL in the multilayered composites can be easily investigated. Meanwhile, the continuous and parallel interfaces between PEO and PCL layers provide a suitable model
to investigate the interfacial interaction between PEO and PCL during the crystallization. Thus the fundamental of the crystallization of PEO and PCL in the composites was discussed.

2. Experimental

2.1 Materials

Poly(ε-caprolactone) (PCL, CAPA6800, Mw=80,000), with a melt index of 0.74 g/10 min (100˚C /2.16 kg), was purchased from Perstorp Corp. (UK). Polyethylene oxide (PEO, Mw=50,000) was supplied by Sumitomo Chemical Corp. (Japan), with a melt index of 1.56 g/10 min (100˚C/2.16 kg). The materials were vacuum dried at 40˚C for 12 h before use.

2.2 Preparation of the multilayered PEO/PCL composites

PEO and PCL were coextruded through the layer-multiplying coextrusion technology, the mechanism of which has been described in our previous work. A schematic of the multilayered coextrusion equipment is shown in Fig. 1, the equipment is consisted of two single-screw extruders, a feedblock and some multiplying elements. PEO and PCL were extruded from extruders A and B, respectively, the feeding and rotation ratios of the extruders were 1:1. These two melt streams were combined and controlled in the feedblock as two parallel layers. From the feedblock the two layers flowed through a series of multiplying elements and each element doubled the number of layers. An assembly of n multiplying elements produced a tape with $2^{(n+1)}$ layers, where n was the number of multiplying elements. In this work, the multilayered composites were fabricated with 2, 16, 64, and 128 layers, respectively. The temperatures from the hopper to the die were 40˚C, 80˚C and 140˚C, and the screw rotation was maintained at 15 rpm. The layer structure is shown in Figure 1b, where the PEO and PCL layers arranged alternately along the extrusion direction (Y direction). The thickness of the samples ranged from 2000 to 2200 μm, and the width was about 40 mm.
Fig. 1 (a) Schematic of multilayered coextrusion system: A and B - single screw extruder; C - connector; D - coextrusion block; E - layer multiplying elements; F - die. (b) Schematic of multilayered PEO/PCL composites, the Y-axis represents the extrusion direction.

For comparison, pure PEO, PCL and conventional PEO/PCL blends were extruded through a single-screw extruder, the heat condition (the temperatures from the hopper to the die were 40°C, 80°C and 140°C) and the sample size (sample thickness ranged from 2000 to 2200 μm, and the width was about 40 mm) were the same as the multilayered composites.

2.3 Characterization and testing

2.3.1 Nonisothermal crystallization

The crystalline analysis of the samples was performed using a Q20 DSC instrument (TA Instrument Co., USA) under a nitrogen atmosphere. The samples (6-8 mg) were heated from 0 to 140°C at a rate of 10°C/min, and maintained for 3 min to erase any thermal history. Then the samples were cooled down to 0°C at a cooling rate of 10°C/min and maintained for 3 min. After that, the samples were reheated to 140°C at a rate of 10°C/min.

The densities of the samples were measured through a high-precision density tester (GH-120M, MatsuHaku, China). Then the weight ratios of PEO and PCL were obtained. Thus the degree of crystallinity ($X_c$, %) for PEO and PCL in each sample was calculated as follows:

$$X_c (\%) = \frac{\Delta H_m}{\Delta H_m^0 \times W_x} \times 100\%$$ (1)
where $\Delta H^m$ is the enthalpy of PEO or PCL obtained from the second heating process, $\Delta H^0_m$ is the theoretical enthalpy of the completely crystalline PEO or PCL, which are 197.37 and 135.5 J/g for PEO and PCL, respectively, and $W_i$ is the weight fraction of PEO or PCL in the multilayered sample.

### 2.3.2 Isothermal crystallization

The isothermal crystallization behaviors of the composites were also investigated using the Q20 DSC instrument under a nitrogen atmosphere. A two-step isothermal crystallization testing was performed. The samples (6-8 mg) were first heated from 0 to 140°C at a rate of 10°C/min and maintained for 3 min. Then the samples were cooled down to 53°C at a cooling rate of 80°C/min and isothermally treated for 30 min. After that, the samples were cooled down to 40°C at a cooling rate of 80°C/min and isothermally treated for another 30 min. These two isothermal crystallization processes were recorded.

### 2.3.3 Polarized optical microscope (POM)

A thin slice with a thickness of 15 μm was obtained by a rotary microtome (YD-2508B, Jinhua Yidi Medical Equipment Factory, China) along the thickness direction of the samples. And the thickness of a single layer for PEO and PCL was measured based on the POM micrographs using a scaling bar. More than five slices were used for each sample, and the average thickness of the layer was calculated.

The crystalline morphologies of the multilayered composites were observed using an Olympus BX51 polarizing microscope (Japan) equipped with a camera. In order to study the crystallization kinetics of the multilayered PEO/PCL composites, a hot-stage POM was performed. The specimen was placed between a microscope glass slide and a cover slip, and heated on an Instec HCS302 hot stage (China). The samples were first heated to 100°C and kept for 5 min, then quenched to 55°C and isothermally treated for 30 min. After the completion of the crystallization of PEO, the samples were quenched to 40°C and isothermally treated for another 30 min for the crystallization of PCL.

### 2.3.4 Microscopic Fourier transform infrared spectroscopy (micro-FTIR)
The interfacial interaction between PEO and PCL layers was evaluated using a Thermo Nicolet infrared microscope (Thermo Fisher, USA). The multilayered composites were cut into thin slices by a YD-2508B rotary microtome along the thickness direction, with a thickness of 15 μm. The spectral range was 4000-400 cm\(^{-1}\), with the resolution being 2 cm\(^{-1}\) and the accumulation being 32 scans.

2.3.5 Wide angle X-ray diffraction (WAXD)

Two-dimensional WAXD (2D-WAXD) of the multilayered PEO/PCL composites were performed on a D8 discover X-ray diffractometer (Bruker, Germany), using Cu Kα radiation (\(\lambda=0.1542\) nm) operated at 40 kV and 40 mA. The scattered intensities were registered in the range of scattering ranges from 5° to 45°.

The testing surface is the cross section of specimens along the extrusion direction.

3. Results and discussion

3.1 Microstructure of the multilayered composites

Fig. 2 shows the POM micrographs of the multilayered PEO/PCL composites. The PEO and PCL layers were assembled alternately along the thickness direction of the specimens. With the layer number increased, numerous interfaces appeared between the PEO and PCL layers, while the thickness of each layer reduced proportionally since the total thickness of the samples remained the same (about 2 mm).

Controlling the coextruding speed, the volume ratio of PEO and PCL layers was close to 1:1. Based on the POM micrographs (Fig. 2), the average thickness of a single layer for PEO and PCL was obtained (Table 1).
3.2 Crystallization and melting behavior of the multilayered composites

3.2.1 Nonisothermal crystallization of multilayered PEO/PCL

The crystallization and melting behavior of multilayered PEO/PCL composites are shown in Fig. 3 and Fig. 4. And the crystallization temperature ($T_c$), melting temperature ($T_m$) and degree of crystallinity ($X_c$) of PEO and PCL are summarized in Table 2. As shown in Fig. 3 and Table 2, the $T_c$ of PEO from the multilayered composites was almost unchanged. The $X_c$ of PEO was sharply decreased from 70.2% to 40.0% when the layer number increased from 2 to 128, indicating that the crystallization of PEO was suppressed by the multilayered structure.

### Table 1 Volume ratio of PEO/PCL layers ($V_r$), the total film thickness ($T_{tot}$) and the average thickness of a single layer for PEO ($T_{PEO}$) and PCL ($T_{PCL}$).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$V_r$</th>
<th>$T_{tot}$ (μm)</th>
<th>$T_{PEO}$ (μm)</th>
<th>$T_{PCL}$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PEO</td>
<td></td>
<td>2090±82</td>
<td>2090±82</td>
<td>2010±63</td>
</tr>
<tr>
<td>Pure PCL</td>
<td></td>
<td>2010±63</td>
<td>1011±62</td>
<td>1049±57</td>
</tr>
<tr>
<td>PEO/PCL-2layer</td>
<td>1/1</td>
<td>2060±68</td>
<td>1011±62</td>
<td>1049±57</td>
</tr>
<tr>
<td>PEO/PCL-16layer</td>
<td>1/1</td>
<td>2000±45</td>
<td>124±32</td>
<td>126±37</td>
</tr>
<tr>
<td>PEO/PCL-64layer</td>
<td>1/1</td>
<td>2200±42</td>
<td>32±11</td>
<td>36±16</td>
</tr>
<tr>
<td>PEO/PCL-128layer</td>
<td>1/1</td>
<td>2260±52</td>
<td>17±8</td>
<td>18±9</td>
</tr>
</tbody>
</table>

Fig. 2 POM micrographs of the multilayered PEO/PCL composites with different layer numbers.
On the other hand, the $T_c$ of PCL, which was 30°C in the pure PCL, shifted to 26.3°C as the layer number being 128 (Fig. 3 and Table 2). It was indicated that the crystallization of PCL was also suppressed by the multilayered structure. However, compared with the reduced $X_c$ of PEO, the $X_c$ of PCL...
was almost unchanged as the layer number became higher. It was speculated that the multilayered structure induced different effects on the crystallization of PEO and PCL.

When the samples were reheated to 140°C, the melting temperatures ($T_m$) of PEO and PCL were recorded (Fig. 4 and Table 2). The $T_m$ of PEO slightly decreased as the layer number varied from 2 to 128, while the $T_m$ of PCL did not vary much. The lack of significant movement of the $T_m$ implies that these two polymers crystallized separately, which is in good accord with the results of the conventional PEO/PCL blends reported elsewhere.\textsuperscript{26}

### 3.2.2 Isothermal crystallization of multilayered PEO/PCL

In order to further study the crystallization behavior of the multilayered PEO/PCL composites, a two-step isothermal crystallization process was carried out. The crystallization temperature was first selected as 53°C for the crystallization of PEO,\textsuperscript{24} and then cooled to 40°C for the crystallization of PCL.\textsuperscript{25} As a result, the crystallization of PCL occurred in the presence of crystallized PEO layers. The isothermal DSC curves of the multilayered composites exhibited a single peak at each crystallization temperature as is typical for isothermal polymer crystallization (data not shown). The relative crystallinity $X_t$, defined as the ratio of crystallinity at time $t$ to the crystallinity when time approached infinity, was given as follows\textsuperscript{15,25}:

$$X_t = \frac{\Delta H_t}{\Delta H_\infty} = \int_0^t \left( \frac{dH}{dt} \right) dt / \int_0^\infty \left( \frac{dH}{dt} \right) dt$$

where $dH/dt$ is the rate of heat evolution, $\Delta H_t$ is the total heat evolved at time $t$, and $\Delta H_\infty$ is the total heat evolved as time approaches infinity.

Plots of the $X_t$ as a function of time of PEO and PCL layers are shown in Fig. 5. The crystallization kinetics of PEO and PCL layers is plotted in Fig. 6, according to the classic Avrami equation\textsuperscript{27}:

$$\ln \left[ -\ln \left( 1 - X_t \right) \right] = n \ln t + \ln k$$
where $n$ is the Avrami exponent describing the crystal growth geometry and the nucleation mechanism, and $k$ is the crystallization rate constant.

Fig. 5 Relative crystallinity ($X_t$) versus time ($t$) for the isothermal crystallization of multilayered PEO/PCL composites (a): PEO layers at 53°C and (b): PCL layers at 40°C.

Fig. 6 Avrami plots of the isothermal crystallization of multilayered PEO/PCL composites (a): PEO layers at 53°C and (b): PCL layers at 40°C. The solid lines are fits using equation (3).

The early stage of the crystallization was linear in the Avrami plot, while a gradual deviation from linearity was observed at higher $X_t$. For consistency, the slope $n$ and the intercept ln$k$ were taken from the linear portion with $X_t$ value ranging from 0.1 to 0.75. The Avrami exponent $n$ and the crystallization rate constant $k$ for the PEO and PCL layers are listed in Table 3.
Table 3 The Avrami exponent $n$ and the crystallization rate constant $k$ of PCL and PEO layers in the multilayered composites with different layer numbers.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>PEO layers</th>
<th>PCL layers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n$</td>
<td>$k$ (min$^{-1}$)</td>
</tr>
<tr>
<td>Pure polymer</td>
<td>2.2</td>
<td>0.087</td>
</tr>
<tr>
<td>PEO/PCL-2layer</td>
<td>2.1</td>
<td>0.244</td>
</tr>
<tr>
<td>PEO/PCL-16layer</td>
<td>2.1</td>
<td>0.258</td>
</tr>
<tr>
<td>PEO/PCL-64layer</td>
<td>2.2</td>
<td>0.242</td>
</tr>
<tr>
<td>PEO/PCL-128layer</td>
<td>2.1</td>
<td>0.208</td>
</tr>
</tbody>
</table>

For the PEO layers in the multilayered composites, the plot of the $X_t$ as a function of time (Fig. 5a) exhibited a higher crystallization rate than that of pure PEO. It was indicated that the presence of the adjacent PCL layers promoted the nucleation of PEO spherulites. The effect of a molten polymer on the crystallization behavior of the other polymer layer has been researched by Zhang et al. $^{28}$ PEG or PEO thin film was covered on a molten PLA film to form a double-layer film, the molten PEG or PEO layer could greatly accelerate the crystallization of the beneath PLA layer, which was in accordance with our results. It should be noted that the crystallization rate constant $k$ (Table 3) decreased from 0.258 to 0.208 min$^{-1}$ with layer number varied from 16 to 128. Similar results were reported by Qiu and co-workers. $^{15}$ In the conventional PEO/PCL blends, the crystallization rate of PEO decreased with the increase of PCL, which was due to the smaller domain size of PEO. $^{15}$ For our multilayered composites, the layers were thinner as the layer numbers became higher, thus the slow-down of the crystallization of PEO may be considered to occur from a physical restriction to the growth by the PCL layers. And it was also reported in the literature that when the confined space (11μm) was comparable with the crystal size of PCL (10 μm$^{29}$), the crystallization rate was decreased. $^{25}$ Thus it was reasonable that the crystallization rate constant $k$ decreased to 0.208 min$^{-1}$ when the layer thickness (17±8μm for 128-layer sample) was significantly smaller than the crystal size of PEO (about 160 μm$^{29}$). For the samples with 16 and 64 layers, the spatial confinement effect was not significant. Quite similar PEO crystallization rates are observed for these two samples, which was due to the combination effect of the interfacial interaction and the spatial
In the case of PCL layers (Fig. 5b and Table 3), the crystallization of PCL occurred with PEO being in the crystalline solid state, which restricted the mobility of PCL chains at the interface due to the interfacial interaction or interdiffusion between PEO and PCL layers, leading to a slower crystallization rate than that of pure PCL. Considering the small crystal size of PCL (about 10 μm), the spatial confinement of the layer thickness (the minimum value was 17±8 μm, for 128-layer sample) had little effect on the crystallization rate of PCL.

Considering the crystallization behaviour of the two polymers in the multilayered composites, the different variation of $X_c$ for PEO and PCL were reasonable as the layer number became higher (Table 2). It was reported that for conventional PEO/PCL blends, the crystallization of PEO (or PCL) was not observed when the weight content of PEO (or PCL) was relatively small (less than 20% of the blend). That is, the domain size of PEO (or PCL), in other words, the spatial confinement affected the crystallization degree of the polymer. In our experiments, the crystal size of PEO was much larger than that of PCL, so the same spatial confinement significantly influenced the crystallization of PEO, while litter effect was observed for that of PCL. As a result, The $X_c$ of PEO was sharply decreased from 70.2% to 40.0% when the layer number increased from 2 to 128, while the $X_c$ of PCL did not vary much.

The Avrami exponent values $n$ of the PEO and PCL layers were almost unchanged, indicating that the crystallization mechanism of PEO and PCL did not change when the layer number became higher (Table 3).

### 3.2.3 The growth behavior of the PEO and PCL crystals

In order to further investigate the growth behavior of the PEO and PCL crystals in the multilayered composites, the hot-stage POM was performed. As shown in Fig. 7, when the molten multilayered PEO/PCL composites quenched to 55°C, the PEO crystals started to grow. For the 2-layer and 16-layer
samples, the initial crystallization rate of PEO was higher than that of pure PEO (samples in 40s and 2 min), which was attributed to the interfacial interaction of PEO and PCL layers. When the layer thickness of PEO became small enough (comparable with the spherulite size of PEO), that is, for samples with 16 layers and above, the PEO spherulites deformed greatly. Discoidal crystals of the PEO were observed, which was concluded that the crystallization behavior of PEO was also affected by the growth space of the PEO crystals. As a result, the crystallization rate of PEO in the multilayered composites increased first and then decreased when the layer number became higher.

![PEO/PCL multilayered composites](image)

**Fig. 7** Hot-stage POM photographs of PEO with different layer numbers: (a) Pure PEO, (b) PED/2-layer, (c) PEO/16-layer, (d) PEO/PCL-128-layer, isothermal crystallized at 55°C.

After maintained at 55°C for 30 minutes, the multilayered composites were quenched to 40°C and maintained for another 30 min. The growth behavior of PCL crystals is shown in Fig. 8. It was noticeable that the isothermal crystallization of PCL in the middle of the layers was faster than that from the interface. Because the 2-layer sample had the largest thickness for a single layer, the crystallization
difference between the middle and the interface was more clearly compared with other samples. Since the crystallized PEO lamella has invaded into the PCL layers during the isothermal crystallization of PEO (Fig. 7 and 8), it was speculated that the existed PEO crystals retarded the mobility of PCL chains and then suppressed the crystallization of PCL in the interface. As a result, the crystallization rate of PCL was suppressed significantly with higher layers, which was in accordance with our DSC isothermal crystallization results. Moreover, since the spherulite size of PCL (about 10 μm) was smaller than the thickness of one single PCL layers (17±8 μm for 128-layer sample), the effect of spatial confinement on the crystallization of PCL was negligible. This speculation was also in accordance with the DSC isothermal crystallization results.

![Figure 8](image)

Fig. 8 Hot-stage POM photographs of PCL with different layer numbers: (a) Pure PCL, (b) PEO/PCL-2layer, (c) PEO/PCL-16layer, (d) PEO/PCL-128layer, isothermal crystallized at 40°C.

### 3.3 Interfacial interaction of PEO and PCL layers
From the results mentioned above, it was clear that the crystallization morphology and kinetics of the PEO and PCL layers was significantly influenced by the interfacial interaction and the spatial confinement of the layers. In order to further understand the interfacial interaction between the PEO and PCL layers and its effects on the crystallization behavior of the composites, micro-FTIR measurement was performed (Fig. 9). Compared with regular FTIR, the micro-FTIR technique allows for the in-situ analysis of the samples, with a spatial resolution of about 20 μm. For PEO and PCL layers, the analysis positions were located in the middle and at the interface of a single layer to investigate the interfacial interaction of these two layers (Fig. 9c).

![Micro-FTIR spectra](image)

**Fig. 9** Micro-FTIR spectra of (a): PEO layers, (b): PCL layers in the 16-layer sample, and (c): Schematic of positions of micro-FTIR measurements in the sample.

The FTIR results of PEO layers are shown in Fig. 9a, with the layer numbers being 16. The FTIR spectra from the middle region of the PEO layers exhibited typical PEO absorption peaks, no new peaks were observed. Noticeably, a weak peak at 1724 cm⁻¹ was observed at the interface of PEO layers, which was
corresponding to the stretching vibrations of C=O from PCL.\textsuperscript{32} This result confirmed the invasion of PCL lamella into PEO layers.

The FTIR results of PCL layers are shown in Fig. 9b, with the layer numbers being 16. When the testing spot was shifted from the middle region to the interface, the peaks at 1724 cm\(^{-1}\) and 1192 cm\(^{-1}\), which were attributed to the stretching vibrations of C=O and C-O-C groups from the crystalline conformation of PCL,\textsuperscript{32, 33} decreased apparently. Thus the crystallization of PCL was suppressed near the interface, which was also in accordance with our hot-stage POM results.

3.4 Lamellae orientation of PEO and PCL

The two-dimensional WAXD (2D-WAXD) measurements were utilized to investigate the lamellae orientation of PEO and PCL in the multilayered composites. A series of 2D-WAXD patterns for 2-, 16- and 128-layer as well as the conventional blend samples are shown in Fig. 10. From inner to outer, the three isotropic reflection circles of the conventional blend were belonged to PEO (120), PCL (110), PEO (032) and PCL (200) planes (Fig. 10a).\textsuperscript{34, 35} The scattering angle of PEO (032) (2\(\theta\)=23.2\(^{\circ}\)) and PCL (200) (2\(\theta\)=23.5\(^{\circ}\)) were similar, so they had the same reflection circle. The multilayered composites with lower layer numbers (2- and 16-layer) also exhibited isotropic rings (Fig. 10b and c), indicating the random orientation of PEO and PCL lamellae. Two arcs located on the equator were observed for the 128-layer sample (Fig. 10d), which was indexed as the PEO (120) reflection located at 2\(\theta\)=19.0\(^{\circ}\).\textsuperscript{34, 35} The weak but distinct four off-axis arcs (at the outer layer line) were regarded as the PEO (032) plane. These results exhibited a partially orientation of PEO in the 128-layer sample, which was resulted from the spatial confinement of the layers. It was noticeable that these arcs were broad and weak, which might be due to the defective structure of PEO crystals. No orientation of the PCL crystal lamellae was observed in the multilayered samples, indicating that the spatial confinement of the layers had little effect on the crystalline of PCL.
Fig. 10 Two-dimensional WAXD patterns of specimens: (a): conventional blend, (b): PEO/PCL-2layer, (c): PEO/PCL-16layer and (d): PEO/PCL-128layer. The arrows denote the diffraction rings representing of different crystal planes.

4. Conclusions

Alternating multilayered polyethylene oxide (PEO)/poly(ε-caprolactone) (PCL) composites were fabricated through the layer-multiplying coextrusion, and the layer number was easily adjusted. The effects of the interfacial interaction and the spatial confinement on the crystallization behavior of the PEO and PCL layers were investigated. For the crystallization of PEO, the melted PCL layers promoted the crystallization rate of PEO, while the spatial confinement suppressed the crystallization rate of PEO as the layer number became higher. Because of the small crystal size of PCL, the effect of spatial
confinement on the crystallization of PCL was negligible, while the interfacial interaction between PEO layers and PCL layers significantly suppressed the crystallization rate of PCL in the layer interfaces.

Acknowledgments

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References and Notes

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Due to the effects of the interfacial interaction between PEO and PCL layers and the spatial confinement. The crystallization behaviors of PEO and PCL in multilayered structure varied distinguishably as the layer number became higher.