Epitaxial Crystallization of Poly(ε-caprolactone) on Reduced Graphene Oxide at a Low Shear Rate by In Situ SAXS/WAXD Methods

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ABSTRACT: The interfacial interaction between polymers and reinforcements has a positive effect on the properties of polymer nanocomposites, and a further study on the evolution of this interfacial interaction under a shear field is conducive to reasonable regulation of the properties of polymer nanocomposites. For this purpose, epitaxial crystallization of poly(ε-caprolactone) (PCL) on reduced graphene oxide (RGO) is investigated by shearing at the shear rate of 3 s⁻¹ by in situ synchrotron radiation. In situ two-dimensional small-angle X-ray scattering (2D SAXS) results suggest that the imposed shear field promotes the orientation of the polymer chains, resulting in the formation of a large periodic structure of PCL on the RGO surface. In addition, higher shear temperatures facilitate the conformational adjustment of the PCL molecular chain on RGO at the shear rate of 3 s⁻¹, resulting in the formation of thicker lamellae. In situ two-dimensional wide-angle X-ray diffraction (2D WAXD) results show that shear enhances the crystallinity of the PCL/RGO nanocomposite and promotes the oriented growth of epitaxial and bulk crystals. The current findings can improve the understanding of the structural evolution behavior of PCL/RGO nanocomposites after shear and especially enhance dramatically our understanding of the underlying mechanism of influence of shear on interfacial epitaxial crystallization in polymer/graphene nanocomposite systems.

INTRODUCTION

In the past few decades, nanoscale reinforcing fillers have attracted great interest in the field of composite materials due to their inherent properties and numerous potential applications.¹⁻³ Polymer nanocomposites represent a new class of materials for their enhanced properties through nanoscale reinforcement,⁴ which provides an efficient way to fabricate special structures with desired properties and/or functionalities of polymeric materials. The mechanical properties of polymer/nanofiller composites depend on not only the mechanical properties of nanofillers but also the interaction between polymers and nanofillers at the interface.⁵⁻⁶ A large number of studies have shown that an effective interfacial interaction promotes the dispersion of the nanoreinforcement in the polymer matrix, which plays a nucleation role in the semicrystalline polymer⁷ and thus improves the mechanical properties of the nanocomposite. Therefore, understanding the interfacial interaction mechanism is beneficial to the property regulation of polymer composites.

Great effort has been devoted to improving the interaction between nanofillers and polymer matrices. Surface-induced polymer epitaxial crystallization offers a simple and effective method to enhance polymer/nanofiller interfacial interactions and has attracted a lot of attention. The occurrence of the epitaxial crystallization of a polymer on a foreign surface is based on certain crystallographic matches according to lots of investigation results.⁸ One-dimensional (1D) or two-dimensional crystallographic matches generate special interactions between the polymer chains and substrate at the contacting interface, forming an interfacial crystalline layer.⁹ The epitaxy can increase the nucleation density, which produces generally a transcristalline layer, and the nucleation time, which accelerates the crystallization process.¹⁰ For instance, Chang et al.¹¹ reported that all of the poly(ε-caprolactone) (PCL) chains can form extremely broad lamellae thickness on the polyethylene (PE) substrate due to the strong interaction between PCL and the oriented PE.

With a two-dimensional, atomically thick sheet composed of sp² carbon atoms arranged in a honeycomb structure, graphene has been the strongest material up to now (ultimate strength is 130 GPa and Young modulus is 1 TPa).¹²⁻¹⁴ Some excellent studies have been carried out since scientists discovered it, which is due to its unique mechanical, thermal, and electrical...
properties. It has been reported that graphene could significantly improve the mechanical properties of polyesters such as poly(ε-caprolactone) (PCL), poly(3-hydroxybutyrate) (PHB), poly(l-lactic acid) (PLLA), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). Incorporating graphene into polyesters has drawn much attention as a route to obtain new materials with excellent properties. In addition, graphene has a high specific surface area, which decreases the surface free energy barrier and facilitates the epitaxial growth of polymers on its surface. The space lattice matching between PE and graphene results in the formation of edge-on lamellae on the graphene surface that are much thicker than those produced by bulk crystallization. In our previous work, we studied the crystallization and mechanical properties of PCL/reduced graphene oxide (RGO) nanocomposites, and the results indicated that the epitaxial interaction between PCL and RGO can enhance the crystallization and orientation of the PCL matrix, which is the major factor for the improvement of mechanical properties.

As we all know, the external shear field during the processing and shaping operations of semicrystalline polymer materials, such as injection molding, film blowing, and fiber spinning, can strongly impact the crystallization behaviors and mechanical properties of semicrystalline polymers, which eventually affects the product properties and performance. Generally, the processing and shaping operations make polymer chains well oriented in intense shear and/or elongation flow. Therefore, the crystallization kinetics of polymers can be significantly promoted with a shear field to produce highly oriented morphologies. Su et al. investigated the crystallization of injection-molded bars of a high-density polyethylene (HDPE)/isotactic polypropylene (iPP) blend. The results showed that the shear force in injection molding could induce the crystallization of HDPE and iPP, which improved the mechanical properties of the composite. Meanwhile, it is also established that the crystallization process and the resulting structure are strongly related to the shear temperature, shear rate, total strain, and the subsequent crystallization temperature.

The interfacial interaction between polymer and reinforcements has a positive effect on the properties of materials, and a study on the influence of an external shear field on the interfacial interaction is conducive to reasonable regulation of the properties of polymer nanocomposites. In our previous work, we confirmed that the imposed shear field could affect epitaxial crystallization of PCL chains on the RGO surface. Furthermore, a high shear temperature and a low shear rate are the prerequisites for PCL chains to epitaxially crystallize well on RGO by off-line measurements. However, the evolution of molecular chain orientation during shear and its effect on isothermal crystallization need to be further revealed, which can especially enhance dramatically our understanding of the underlying mechanism of influence of shear on interfacial epitaxial crystallization in polymer/graphene nanocomposite systems. For the above research purposes, we deeply study the effects of shear on epitaxial crystallization of PCL on graphene by in situ synchrotron radiation in this work. PCL/0.5 wt % RGO nanocomposite sheets were sheared at the shear rate of 3 s⁻¹ at different shear temperatures of 65, 70, and 75 °C. Two-dimensional wide-angle X-ray diffraction (2D WAXD), two-dimensional small-angle X-ray scattering (2D SAXS), and rheometer measurements were applied to investigate the structural mechanism of the effects of the imposed shear field on epitaxial crystallization of PCL chains on RGO. The conclusions of this article will provide a theoretical reference for the property regulation of polymer nanocomposites.

### EXPERIMENTAL SECTION

**Materials.** PCL was purchased from Shanghai Yizhu Co., Ltd. (Shanghai, China), with average weight 

\[ M_w = 42,500 \text{ g mol}^{-1} \]  

and polydispersity index 

\[ M_w/M_n = 1.5 \]. The melt point of PCL is 62.14 °C, and its crystallization temperature is 29.72 °C. Natural flake graphite was purchased from Qingdao Jiuyi Graphite Co., Ltd. (Shandong, China) with a mean particle size of 50 μm. Hydrochloric acid (HCl) (37%), sulfuric acid (H₂SO₄) (98%), potassium nitrate (KNO₃), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂) (35%), n-hexanol, and chloroform were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were used as received without further purification.

**Preparation of the PCL/RGO Nanocomposite.** Graphene oxide (GO) was exfoliated by ultrasonication from graphite oxide, which was produced by a modified Hummers method. Reduced graphene oxide was prepared by thermal exfoliation and reduction of GO.

The poly(ε-caprolactone)/0.5 wt % reduced graphene oxide (PCL/0.5 wt % RGO) nanocomposite was melt-mixed at 90 °C in a HAKKE Minilab for 3 min to cut it into pieces with the thickness of 0.5 mm.

**Analytical Methods.** Melt Viscosity. PCL/0.5 wt % RGO samples were analyzed by a DHR-3 (TA instrument) rheometer using a 25 mm parallel plate geometry under a N₂ atmosphere. The samples were first melted at 90 °C for 3 min to eliminate previous thermal history, and then they were cooled down at the cooling rate of 30 °C min⁻¹ to 65, 70, and 75 °C. The samples were then sheared isothermally at the shear rate of 3 s⁻¹ for 100 s.

**Experimental Process.** A Linkam heating instrument equipped with a temperature controller (Linkam CSS-450, Linkam Scientific Instruments Ltd, U.K.) was used to adjust the gap between two platforms, temperature, heating/cooling rate, and shear rate.

A synchronous experimental protocol was used in the shear studies consisting of the following discrete steps: The sample was heated from room temperature to 90 °C at the rate of 30 °C·min⁻¹, and the temperature was held at 90 °C for 3 min to eliminate thermal history. The sample was cooled to 65, 70, and 75 °C at the rate of 30 °C·min⁻¹, and then the sample was sheared at 3 s⁻¹ for 100 s. After shear, it was cooled to 30 °C at the rate of 15 °C·min⁻¹ (Figure 1).

**In situ SAXS and WAXD measurements.** WAXD and SAXS measurements were carried out at the BL16B1 beamline in the Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of X-ray radiation was 0.1239 nm. Two-dimensional (2D) WAXD and SAXS patterns were collected using a Mar CCD X-ray detector (MAR165), having a 18 mm rotation range.
resolution of 2048 × 2048 pixels. The beam intensity monitor before sample adsorption was a N2 gas ionization chamber, and the monitor after sample adsorption was a photodiode in the beam stop. Two scatterless slits (Xenocs) were used to depress parasitic scattering. The sample holder was mounted onto an optical table.37 The sample-to-detector distance was 2020 mm for SAXS and 109 mm for WAXD. The collection time for each image was 14 s, followed by 20 s for the next image collection.

**SAXS and WAXD Data Analysis.** The analysis of SAXS and WAXD measurement data was carried out through a small-angle arc integral from 170 to 190° for the meridian and 80 to 100° for the equator by the Fit2d software package.38 The thickness of lamellae ($L_v$) of the PCL/0.5 wt % RGO nanocomposite was calculated by a one-dimensional electron cloud density function.39 In WAXD analysis, the orientation degree of crystals was obtained by the Herman’s method.40 In particular, the orientation degree of $f_{110}$ was calculated from the azimuthal intensity distribution, $I(\Phi)$, of the (110) crystal reflection. The crystallinity was calculated according to the diffraction intensity of crystalline and amorphous phases, and the diffraction intensity was obtained through the integration from azimuthal angles of 0–180°.

**RESULTS AND DISCUSSION**

**Rheology Analysis.** Figure 12 shows the viscosities of PCL/0.5 wt % RGO nanocomposites during shear at the shear rate of 3 s⁻¹ for 100 s with different shear temperatures of 65, 70, and 75 °C. Figure 2. Viscosities of PCL/0.5 wt % RGO nanocomposites during shear at the shear rate of 3 s⁻¹ for 100 s with different shear temperatures of 65, 70, and 75 °C.

patterns change from circles to ellipses, further forming classical rhombi, which indicates that there exist oriented structures with long periods. Combining our previous results,35 the scattering signals of the ellipse and even the rhombus at the central part of 2D SAXS patterns indicate that the PCL chains epitaxially crystallize on the RGO surface after shear for 160 s, resulting in a long period composed of irregular periodic structures. We can find that the 2D SAXS pattern along the shear direction of 160 s with the shear temperature of 75 °C is sharper than those of shear temperatures of 65 and 70 °C. This suggests that the higher shear temperature makes PCL chains more highly oriented and much better adhered to the RGO surface along the shear direction. As the temperature decreases, the collected data gradually enters into the isothermal crystallization region, namely, the 2D SAXS patterns after 200 s in Figure 3. In the 2D SAXS patterns from 200 to 480 s in Figure 3, the outermost ellipsoidal scattering pattern gradually transforms into a larger elliptical scattering pattern, while the central ellipsoidal scattering pattern gradually transforms into a circle at 280 s. This central circular scattering pattern is similar in shape to that before shear and within 120 s of the shear time, but their molecular orientation and crystal structures are completely different. The above results show that as the temperature decreases and the crystallization time increases, more non-epitaxial crystals are formed, and a large number of signals of nonepitaxial crystals cover the signals of the epitaxial crystals formed at the early stage. Along the shear direction, 2D SAXS patterns show a pair of distinct scattering points along the shear direction at 200 s after shear. As the crystallization time increases, the scattering points gradually become scattering arcs, and the distance from the scattering arc to the center seems to be getting gradually long. According to the above analysis, the
Figure 4. Lorentz-corrected SAXS intensity profiles taken perpendicular to the shear direction as a function of time after shear at the shear rate of 3 s$^{-1}$ with three shear temperatures: (a) 65 °C, (b) 70 °C, and (c) 75 °C. In each panel, the time range from 40 to 160 s represents the cooling process of PCL/RGO nanocomposites after shear. The time range from 200 to 480 s represents the isothermal crystallization at the crystallization temperature of 30 °C of PCL/RGO nanocomposites after shear.

central scattering results indicate that the imposed shear field induces certain orientation of the PCL chains, which promotes the epitaxial growth of PCL on the RGO surface and formation of lamellae. In addition to the periodic structure formed by PCL epitaxial crystallization, the results of the scattering arc along the shear direction and its variation indicate that the PCL/RGO nanocomposite has an obvious oriented periodic structure after shear. Unfortunately, it is not possible to distinguish the effects of different shear temperatures on the crystallization of the PCL/RGO nanocomposite just from 2D SAXS patterns.

For the purpose of showing the effects of shear temperature on epitaxial crystallization of PCL chains on the RGO surface, Lorentz-corrected SAXS intensity profiles taken along and perpendicular to the shear direction as a function of time are calculated through a small-angle arc integral by the Fit2d software package. As we all know, the intensity of SAXS is dependent on the electron density difference between the phases of the system. Lorentz-corrected intensity $I_q^2$ is a function of the scatter vector $q$ under different shear temperatures along and perpendicular to the shear direction. Figure 4 shows Lorentz-corrected SAXS intensity profiles taken perpendicular to the shear direction of the PCL/RGO nanocomposite after shear as a function of time. From Figure 4, it can be seen that Lorentz-corrected SAXS intensity profiles in the time interval from 40 to 120 s of PCL/RGO nanocomposites after shear, and we cannot find any difference among the SAXS curves. It further illustrates that the temperatures of PCL/RGO nanocomposites are high, resulting in no perfect structures in the time range of 40–120 s. From Figure 4, we can see that very small scattering peaks appear after shear for 160 s and they become more and more sharp from 200 to 480 s. All of the sharp peaks shift to increasing $q$ values, which is due to the fact that relatively complete crystals are formed gradually in the PCL phase at this time with the decrease in the temperature, resulting in a great difference in the electron density of the system. The above results suggest that the imposed shear field leads to differently oriented structures in PCL chains.

The Lorentz-corrected SAXS intensity profiles along the shear direction are shown in Figure 5. There are no obvious differences existing in these SAXS intensity profiles in the time range from 40 to 120 s, as in the case of data perpendicular to the shear direction shown in Figure 4, also suggesting no perfect structures. From Figure 5c, we can see a sharp peak existing in the Lorentz-corrected SAXS intensity profiles of the PCL/RGO nanocomposite after shear for 160 s at the shear temperature of 75 °C, which is not the same as that at 60 and 65 °C. This is because the high shear temperature of 75 °C makes PCL chains easily stretched to form thick lamellae. It is also different from that in the profiles taken perpendicular to the shear direction of the PCL/RGO nanocomposite after shear at the temperature of 75 °C at 160 s, which also suggests that the PCL chains are more likely to undergo conformation transition and form thicker lamellae along the shear direction. However, with the temperature of the PCL/RGO nanocomposite after shear decreasing, there exists an obvious sharp peak in each Lorentz-corrected SAXS intensity profile in the time range from 200 to 480 s. All of the sharp peaks of PCL/RGO nanocomposites at three shear temperatures shift to high $q$ values with the increase of isothermal crystallization time. After the formation of epitaxial crystals and bulk oriented crystals in the early shear stage, the remaining molecular chains in the isothermal process also begin to crystallize, resulting in the formation of crystals with different structures and components in the PCL/RGO nanocomposites eventually. Therefore, there is a great difference in the electron
density of the system as the isothermal time increases, which is
the main reason for the increase of the \( q \) value.

The long period of the PCL/RGO nanocomposite after shear
is calculated through a small-angle arc integral from 170 to 190°
along the shear direction using the Fit2d software to study the
effect of shear on the periodic structure in the nanocomposite.
According to the above analysis, there exist two kinds of long
periods in the PCL/RGO nanocomposite after shear. One is the
RGO-induced epitaxial crystallization at the initial shearing
stage, and the other is the bulk crystallization of PCL after shear.
2D SAXS patterns corresponding to epitaxial crystals, namely,
the central ring around the beam stop as shown in Figure 3,
manifest that their long periods are much larger than that of the
PCL bulk crystals. It is a pity that the long period of epitaxial
crystals cannot be distinguished, because of which are covered
by the beam stop and beyond the limit of size that can be
calculated.

Figure 6 shows the long period and the thickness of lamellae in
the PCL/RGO nanocomposite in the time range from 200 to
480 s after shear. The long period is calculated by the Lorentz-
corrected SAXS intensity profiles taken along the shear direction
as a function of time after shear, which is used to figure out clearly how the imposed shear field affects the epitaxial
crystallization and bulk crystallization of PCL chains apart
from the RGO surface. As shown in Figure 6, the long period
and the thickness of lamellae of PCL/RGO nanocomposites
decrease with the increase of isothermal crystallization time.

This is because that the influence of the early epitaxial crystals on
the formation of PCL bulk crystals gradually decreases with the
increase of crystallization time, resulting in the decrease of the
thickness and long period of the later formed crystals. The long
period from 200 to 480 s of the PCL/RGO nanocomposite after
shear decreases as the crystallization temperature increases. This
is due to the fact that the high temperature is more conducive to
the conformational adjustment of the molecular chain in the
initial 160 s shear, which also affects the subsequent isothermal
crystallization of the bulk to form thicker lamellae from 200 to
480 s after shear. However, the high crystallinity of the crystals
formed after shear at the high shear temperature results in a
slightly lower long period.
**WAXD Analysis.** Figure 7 shows 2D WAXD patterns of PCL/RGO nanocomposites before, during, and after shear. Only one scattering ring appears in 2D WAXD patterns of PCL/RGO nanocomposites before shear, which indicates that holding at 90 °C for 3 min can completely eliminate the thermal history of the PCL/RGO nanocomposite and there is no crystal existing in the PCL melts before shear. No complete crystal was produced during the 65–75 °C shear process, which is shown as a torus in the 2D WAXD patterns of Figure 7. This is also consistent with the 2D SAXS results. Due to the high temperature, no complete crystal appeared in the PCL/RGO nanocomposites during the 40–120 s cooling process. The 2D WAXD patterns at 160 s after shear change significantly, evolving from tori into the diffraction rings as shown in Figure 7. This proves that the PCL/RGO nanocomposite after shear at all crystallization temperatures completes epitaxial crystallization of PCL chains on the RGO surface to form a surface crystalline layer. Two diffraction rings can be clearly seen in the 2D WAXD patterns of the isothermal crystallization process at 30 °C, and the inner circle of these 2D WAXD patterns is much wider than the outer ring, suggesting that PCL crystals gradually form at the stage of isothermal crystallization. Considering the effect of shear temperature on 2D WAXD patterns after shear, no significant difference is found in all 2D WAXD patterns of the PCL/RGO nanocomposites.

WAXD curves are calculated by circular integration to distinguish the effects of shear temperatures on the crystal structures of PCL/RGO nanocomposites. The WAXD curves in Figure 8 show a significant difference in the cooling process of PCL/RGO nanocomposites after shear. 1D WAXD curves from 40 to 120 s after shear show no sharp peak, suggesting that no PCL crystals exist in this process. As the melt temperature of PCL/RGO nanomaterials decreases, the PCL chains begin to attach to the RGO surface and form a more regular crystal structure, and subsequently three diffraction peaks appear at 160 s in the WAXD curve of Figure 8. In the isothermal crystallization process at 30 °C, PCL bulk crystals with a periodic structure were formed and gradually improved with the increase of the isothermal time. Notably, three diffraction peaks are supposed to reflect three diffraction rings in 2D WAXD patterns; thus, the inner wide rings shown in Figure 7 are indeed two close diffraction rings that cannot be distinguished clearly from 2D WAXD patterns. The three distinct diffraction peaks of WAXD curves in the time range from 160 to 480 s of PCL/0.5 wt % RGO nanocomposites after shear were located at 17.2, 17.7, and 19.1 °C, which are designated to the (110), (111), and (200) planes of PCL crystals.

Figure 8. WAXD curves of PCL/0.5 wt % RGO nanocomposites after shear at the shear rate of 3 s⁻¹ with different shear temperatures: (a) 65 °C, (b) 70 °C, and (c) 75 °C.

Figure 9. Crystallinity (a) and the orientation degree of the (110) plane (b) of PCL/0.5 wt % RGO nanocomposites after shear at the shear rate of 3 s⁻¹ with shear temperatures of 65, 70, and 75 °C.

calculated from 1D WAXD curves to study the effects of shear temperature on crystallization. In general, shear imposes some orientation on the polymer chains, which is an important factor affecting the epitaxial crystallization of PCL on the RGO surface. The crystallinity after shear increases with increasing cooling time because it enables PCL to complete the epitaxial crystallization and promote conventional bulk crystallization of PCL chains. The crystallinity increases rapidly after 120 s as...
shown in Figure 9. The reasons for this phenomenon are as follows. First of all, the epitaxial crystals begin to form gradually as the temperature decreases. At the same time, there are imperfect bulk crystal components in the system, which have not yet formed a complete periodic structure at 160 s according to the SAXS results in Figure 3. Finally, both the epitaxial crystals and the imperfect bulk crystals contributed to a significant increase in crystallinity at 160 s. At the 30 °C isothermal crystallization stage (after 200 s in Figure 9a), the crystallinity of PCL/RGO nanocomposites increases gradually. Shear temperatures have a small effect on the crystallinity of PCL/RGO nanocomposites since the crystallinity of bulk crystallization at 75 °C is slightly higher than that at other temperatures, which is related to the decreased long period and increased lamellar thickness with crystallization temperature in SAXS results. On the contrary, the orientation degree of the (110) plane of PCL/RGO nanocomposites after shear decreased slightly with time as shown in Figure 9b. The large-scale epitaxial crystals formed in the early stage further affected the subsequent bulk crystallization of PCL and formed an ordered structure. However, as the cooling and isothermal time continued, the influence of epitaxial crystals becomes weaker and weaker, resulting in a reduced overall orientation degree. With the increase of shear temperature from 65 to 75 °C, the orientation degree of the (110) plane after shear of PCL/RGO nanocomposites slightly increases. This is because the higher shear temperature allows the PCL chains to adhere to the RGO surface much better and form surface crystal layers, which in turn affect the orientation of the molecular chains during the bulk crystallization of PCL chains.

CONCLUSIONS

Effects of shear on epitaxial crystallization of PCL chains on the RGO surface have been investigated by in situ SAXS, WAXD, and rheology measurements. The experimental results show that after shear of the molten PCL/RGO nanocomposite, the PCL molecular chain is oriented along the shear direction, which promotes the epitaxial crystallization of PCL on the RGO surface, which eventually forms a thicker interfacial crystal layer. The higher shear temperature facilitates the conformation adjustment of the PCL molecular chain, which better promotes its epitaxial crystallization on the RGO surface. There are two processes during the shear of PCL at high temperatures, namely, molecular chain elongation and molecular chain relaxation. After shear, RGO first immobilizes the oriented PCL molecular chains to form epitaxial crystals, which subsequently induce crystallization of the relaxed PCL chains in the isothermal crystallization process. Finally, crystal components with different thicknesses and orientation degrees exist in the nanocomposite system. This research is not only important for the study of a shear field on epitaxial crystallization but also expected to be helpful to manipulate the properties of polymer/RGO nanocomposites by adjusting the processing conditions.

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Notes

The authors declare no competing financial interest.

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