

Unidirectional Pre-stretching and Isothermal Annealing Reinforced Poly(butylene carbonate) Sheets at Room Temperature

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Electronic Supplementary Information

Abstract Semicrystalline polymers usually undergo multilevel microstructural evolutions with annealing and stretching processes, which is essential to tailor the physical properties of the polymer. Here, poly(butylene carbonate) (PBC) sheets were prepared via isothermal annealing and unidirectional pre-stretching processes, then the changes of PBC in crystallinity, mechanical properties, thermal properties and microscopic changes before and after annealing and stretching were measured, as well as the relationship between microstructure and macroscopic properties before and after stretching. The strengthening mechanism of PBC was also described. It was demonstrated that shish-kabab structure emerged under the pre-stretching process. With the increase of the tensile ratio, the crystallinity, structure and mechanical properties are increased differently. Among them, the crystallinity and tensile strength after annealing-stretching treatment increased to 24.45% and 104.5 MPa, respectively, which were about 1.55 times and 3.4 times of those without any treatment.

Keywords Poly(butylene carbonate); Pre-stretching; Isothermal annealing; Mechanical properties; Crystallinity

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INTRODUCTION

In recent years, the increasingly serious environmental issues caused by the non-degradability of petroleum-based polymers, resulting in bio-based degradable polymers, such as polyesters and polycarbonates, have received extensive attention in fundamental research.^[1] Poly(butylene carbonate) (PBC) is a thermoplastic aliphatic polycarbonate with a wide range of sources and low prices.^[2,3] It has the advantages of excellent biocompatibility and biodegradability as well as high elongation at break and processability. Currently, it can be processed according to various specifications. Products such as films and sheets have great application prospects in biomedicine and daily necessities.^[4] Unfortunately, more applications of PBC are limited owing to its inherent tensile strength defects.

To overcome this shortcoming, many methods have been used to improve the strength of PBCs, such as copolymerisation,^[5,6] melt blending, and processing. Copolymerization has been proven to be an effective approach. Unfortunately, the modification process is complicated and cumbersome, limiting its application.^[7]

Stretching is a modification-effective path for increasing

crystallization without additives and meeting the basic requirements of 'green chemistry'.^[8,9] Numerous studies have focused on developing orientation and strain-induced crystallization of polymers during a rubbery state because the pre-stretching process causes crystallization and relaxation of chains above T_g .^[10,11] Wu *et al.* reported that stretching can affect the thermal properties, crystallinity, shrinkage, and mechanical properties, especially in biaxial stretching.^[12] Zheng *et al.* obtained poly(lactic acid) with excellent strength via uniaxial pre-stretching above the T_g , with an increase in the pre-stretching ratio,^[13] for the destruction of the network structure and the formation of orientation, mesophase, and oriented nanocrystalline phase improves the toughness, strength, and heat resistance of the material without sacrificing transparency and biodegradability during pre-stretching. Dong *et al.* illustrated that the tensile strength of poly(lactic acid) can be enhanced via pre-stretching to improve its crystallinity.^[14] Dong's team continues to study pre-stretching with nucleating agents such as SiO_2 to make microporous adjustments and improve the strength of the materials.^[15–17] Ma *et al.*, via a melt-blending and solid-phase sequential multiaxial stretching strategy, studied various bio-degradation materials, which were also illustrated that pre-stretching can improve the mechanical properties and induce other properties.^[18,19] Moreover, through the "biaxial stretching-confined anneal-

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ing” method, Xu *et al.* combined the regulation of the amorphous chain entanglement network of poly(lactic acid) with the construction of highly oriented graphene oxide nanosheets and a clearly defined “double barrier wall” of crystals to enhance the barrier properties and ductility of nanocomposite films.^[20,21] After Subsequently, polycaprolactone was used as a toughening agent to simultaneously improve the strength and toughness of poly(glycolide acid) at the same time at a high pre-stretching rate (300 mm·min⁻¹) by extrusion casting-hot stretching. It was found that with an increase in the pre-stretching temperature, crystallization and T_g increased, but the molecular chain relaxation rate was fast, causing the chain orientation to decrease, resulting in high yield strength and low toughness of the blends, inverse, resulting in higher tensile strength and elongation at break at low pre-stretching temperatures.^[22]

Moreover, Nie *et al.*^[23,24] utilized simulation *via* the Monte Carlo method to analyze the pre-stretching process to enhance the degree of crystallinity and Hu *et al.*^[25] investigated the change in crystallinity and mechanical properties of the polymer after the pre-stretching process. Although many studies have found that the annealing and pre-stretching processes could occur in the crystal transition of polymer,^[26,27] several reports of PBC mention pre-stretching-induced crystallization and isothermal annealing to enhance the mechanical properties.

In this study, PBC sheets were prepared through annealing and unidirectional pre-stretching to modulate crystallinity and internal orientation. We systematically investigated changes in crystallinity, mechanical properties, thermal properties, and microstructure—both before and after processing—across different treatment sequences and stretching parameters (including aging degree, pre-stretching ratio, rate, and maintenance time). Furthermore, we established the relationship between microstructure evolution and macroscopic properties during stretching and elucidated the strengthening mechanism of PBC.

EXPERIMENTAL

Materials

Poly(butylene carbonate) (PBC), laboratory-made *via* melt transesterification method, has a number-average molecular weight of 7.54×10^4 g·mol⁻¹, weight-average molecular weight of 1.22×10^5 g·mol⁻¹, and molecular weight distribution index of 1.62.

Preparation

PBC particles were dried in a vacuum oven at 50 °C for 8 h, and the particles were placed in a flat vulcanization bed machine. The PBC sheets (thickness of 1 mm) were obtained by hot-pressing at 105 °C and 13 MPa for 10 min and cool-pressing at room temperature.

The sheets were annealed in a vacuum oven at 50 °C for 7 h, and after the above PBC was fully crystallized (naturally cooled from the annealing temperature to room temperature and placed for 24 h at room temperature), it was subjected to unidirectional pre-stretching experiments at room temperature using a microcomputer universal tensile machine (NKK 3010D) and stretched to different magnifications with a 20 mm gauge, and the pre-stretching ratio, namely the local

plastic strain, it is still marked at 25%, 50%, 100%, 200%, and 300%. After pre-stretching, the sample was removed from the fixture after it had fully crystallized. Following the same steps, adjust the pre-stretching rates and maintain the times. Here, all the samples named annealing-stretching, shortly called AS, for instance, the sheet has a pre-stretching ratio at 25% with 10 mm·min⁻¹ for 0.5 h called AS-25%-10-0.5. Similarly, the series of SA refers to the first stretching to the goal ratio with a special context and then isothermal annealing in a vacuum oven at 50 °C for 7 h.

Tensile Testing

The static mechanical properties of PBCs with and without pre-stretching were measured using a tensile-testing machine (NKK 3010D) at 50 mm·min⁻¹ at room temperature. The tensile-testing samples with necks of 2.30 mm × 10.00 mm were cut from the sheets along the stretching direction. The sample thickness varies from 0.50 mm to 1.00 mm with various pre-stretching ratios. The average values and standard errors were obtained from five specimens of each sample.

Thermal Properties

The thermal properties of PBCs with and without stretching were characterized using differential scanning calorimetry (DSC). The instrument was calibrated using indium standard. Samples weighing 5–8 mg were heated from –60 °C to 100 °C at a rate of 10 °C·min⁻¹ under a N₂ atmosphere using a Model Q20 DSC (TA Instruments Inc., New Castle, DE, USA).

Structural Characterisation

Fourier-transform infrared (FTIR) spectroscopic analysis was performed at room temperature on a Thermo Fisher Nicolet 670 spectrometer. FTIR spectra were obtained by accumulating 16 scans with a resolution of 4 cm⁻¹ in the wavenumber range of 4000–400 cm⁻¹.

X-ray Diffraction (XRD), Small-Angle X-ray Scattering (SAXS) and Grazing-incidence Small-Angle X-ray Scattering (GISAXS) Measures

X-ray diffraction (XRD) was performed with a D8A Advance (Bruker, Germany), employing CuK α radiation ($\lambda = 1.54$ Å) at 40 kV and 40 mA. A scan axis of 2θ (10°–35°) was used to obtain diffraction patterns.^[26]

All SAXS data were corrected based on background, air scattering, and sample absorption. Two-dimensional (2D) SAXS patterns were converted into one-dimensional (1D) data *via* integration. The 1D-SAXS curves were integrated along the stretching direction of the 2D-SAXS patterns.

The orientation degree of the crystals was evaluated using the orientation parameter f proposed by Hermans^[28]

$$f_{hkl} = \frac{3 \langle \cos^2 \varphi_{hkl} \rangle - 1}{2} \quad (1)$$

where φ is the angle between the normal direction of the crystal plane and the reference axis. $3 \langle \cos^2 \varphi_{hkl} \rangle$ is obtained from the azimuthal diffraction intensity distribution by

$$3 \langle \cos^2 \varphi_{hkl} \rangle = \frac{\int_0^{\pi/2} I_{hkl}(\varphi) \cos^2 \varphi \sin \varphi d\varphi}{\int_0^{\pi/2} I_{hkl}(\varphi) \sin \varphi d\varphi}, \text{ where } I \text{ is the diffraction intensity along the azimuthal angle } \varphi, f = -0.5, \text{ when all}$$

crystals are perfectly oriented with their normal perpendicular to the stretching direction and 0 when the crystals are randomly oriented.

Grazing-incidence small-angle X-ray scattering (GISAXS) was performed at the beamline BL16B1 of the Shanghai Synchrotron Radiation Facility (SSRF) in China. The wavelength of the X-ray radiation was 1.24 Å. Two-dimensional (2D) GISAXS patterns were recorded with a resolution of $172\ \mu\text{m} \times 172\ \mu\text{m}$ and an exposure time of 30 s. The sample-to-detector distance was calibrated to 2000 mm for GISAXS using standard samples of silver behenate (AgBe).

Scanning Electron Microscopy (SEM)

To obtain a clear observation of the crystalline morphology, scanning electron microscopy (SEM) (ZEISS Sigma 360, Germany) was employed. The surface and cross-section of the specimen were obtained from the fracture of the spline neck in the mechanical test. All the samples were sputter-coated with a thin layer of gold and observed at an accelerated voltage of 3 kV.

RESULTS AND DISCUSSION

The Pre-stretching of PBC

To determine the optimal pre-stretching ratio, the tensile behavior of PBC was analyzed at ambient temperature, and the corresponding stress-strain curve is illustrated in Fig. 1. The curve can be categorized into three distinct regions based on the observed responses during the tensile testing: the elastic deformation region, characterized by stretching ratio of 5%; the strain softening region, where stress either decreases or remains stable; and the strain hardening region, marked by a significant increase in stress.^[14] PBC with different pre-stretching ratios ranging from 5% to 300% exhibit a correlated increase in stress, indicating the potential formation of different strain-induced structures that may lead to varying mechanical properties. Consequently, the pre-stretching ratios of 25%, 50%, 100%, 200% and 300% were selected for further investigation. Given that the glass transition temperature (T_g) is approximately $-35\ ^\circ\text{C}$,^[7] there is chain mobility at room temperature. Therefore, the selection of various pre-stretching ratios was determined by the stress-strain curve and T_g , focusing on the aforementioned regions. The pre-stretching experiments were conducted at room

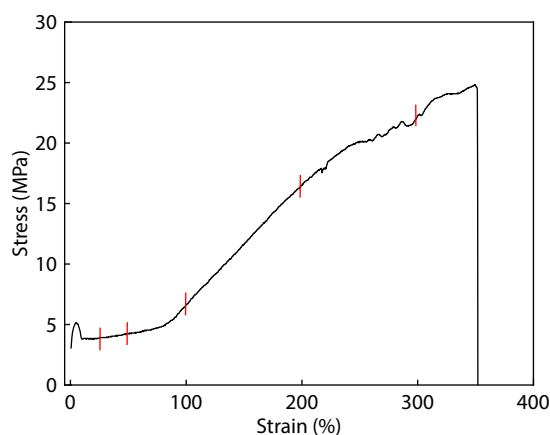


Fig. 1 The stress-strain curve of unannealed PBC at room temperature with $50\ \text{mm}\cdot\text{min}^{-1}$.

temperature to produce the corresponding pre-stretched sheets. This study further examined the influence of the crystallization perfection, stretching speed, and stretching maintenance time on the mechanical, thermal, and crystallization properties of the material. Additionally, a preliminary exploration of the relationship between mechanical properties and microstructure was undertaken.

Mechanical Properties

The solid-phase stretching mechanism of semicrystalline polymers can be activated by the alignment of the amorphous molecular chains. The mechanical characteristics of the PBC, both with and without pre-stretching, were evaluated by tensile testing at ambient temperature. The stress-strain curves corresponding to various, with and without subsequent annealing, are illustrated in Figs. 2(a)–2(c). Figs. 2(d)–2(f) show magnified views of the small deformation regions in Figs. 2(a)–2(c), respectively. For the samples that were not subjected to annealing, the untreated PBC exhibited ductile fracture, characterized by a tensile strength of 30.74 MPa, an elastic modulus of 0.056 GPa, a breaking strength of 25.93 MPa, and an elongation at break of 348.99%. The PBC sheets that underwent pre-stretching exhibited a stress-softening region analogous to that of the untreated samples when the pre-stretching ratio was below 100%. However, when the pre-stretching ratio exceeded 100%, the stress-softening region was no longer present, and the tensile strength increased to 74.79 MPa at a pre-stretching ratio of 200%. Notably, the stress-softening region was absent at a pre-stretching ratio of 100%, with the maximum tensile strength reaching 104.55 MPa at a pre-stretching ratio of 300%, which is 3.4 times greater than that of the unannealed samples and 1.4 times greater than that of the unpre-stretched samples. Furthermore, as the pre-stretching ratio increased, the elongation at break initially increased, before subsequently declining. The peak elongation at break values for the unannealed and annealed samples were 456% and 534%, respectively, at a pre-stretching ratio of 200%. Despite the decline in the elongation at break beyond this maximum, the values remained higher than those of the untreated samples, regardless of annealing. Additionally, this study examined the stress and strain of PBC sheets pre-stretched to 200% under varying tensile rates and holding times post-annealing. As depicted in Fig. S1(a) (in the electronic supplementary information, ESI), the tensile strength increased at higher rates, whereas the elongation at break exhibited a gradual decrease. Conversely, the stress-strain curves remained relatively unchanged across different holding times, as shown in Fig. S2(a) (in ESI), suggesting that the holding time following stretching did not significantly influence the mechanical properties of PBC.

The mechanical properties associated with tensile elongation are illustrated in Fig. 3, encompassing metrics such as the elongation at break, tensile strength, breaking strength, and elastic modulus. An increase in the pre-stretching ratio correlates with an enhancement in the tensile strength of the PBC. Notably, when pre-stretching ratios exceeded 100%, the tensile strength values obtained through the annealing-stretching method surpassed those achieved *via* stretching-annealing and the untreated condition, with a peak tensile strength of 92.9 MPa observed at a pre-stretching ratio of 300%. This phenomenon can be attributed to several factors: (1) The

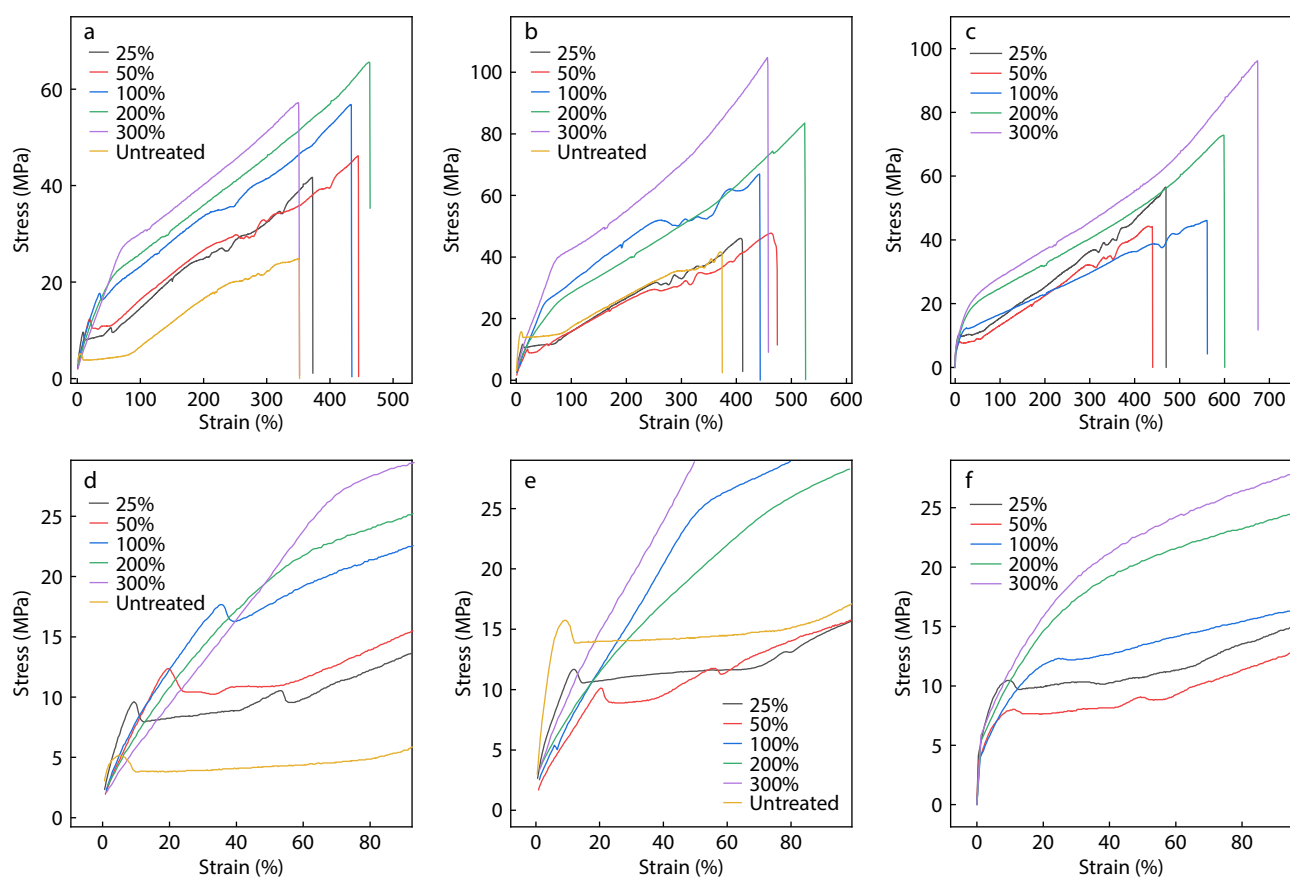


Fig. 2 The stress-strain curves of PBC pre-stretching with various ratios: (a) unannealed; (b) annealing-stretching; (c) stretching-annealing, (d), (e) and (f) are the enlarged images of small deformation region of (a), (b) and (c), respectively.

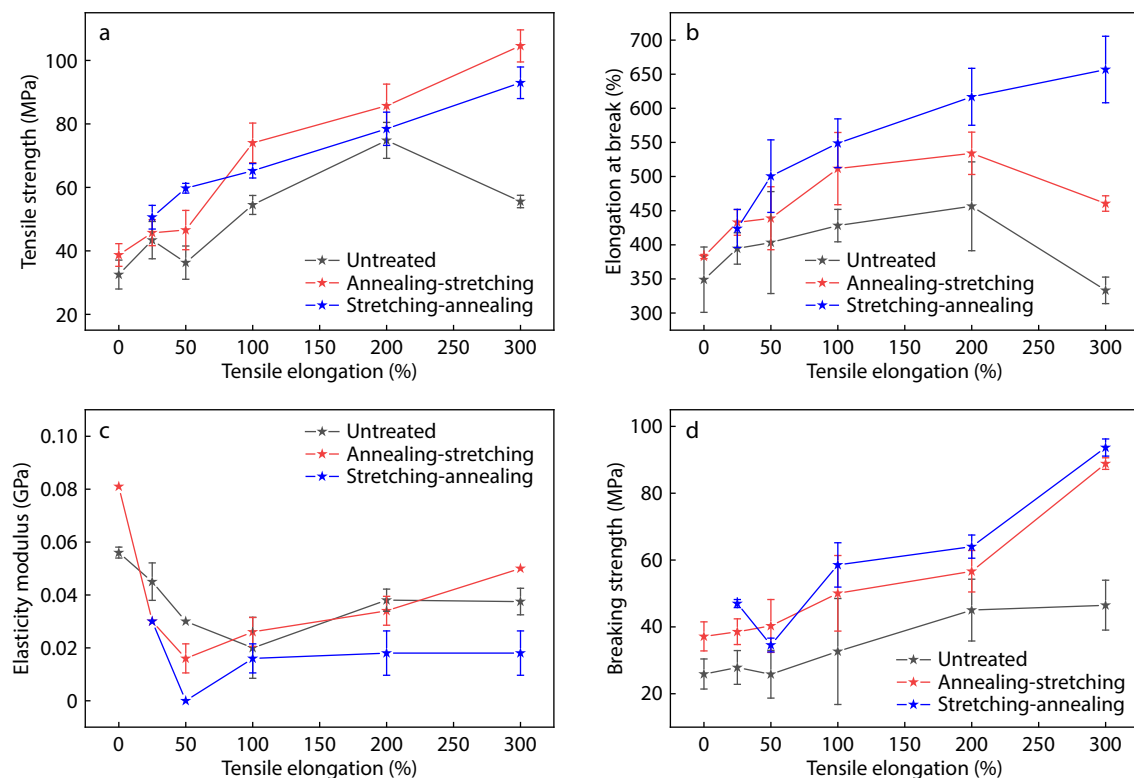


Fig. 3 The mechanical properties of PBC with untreated, annealing-stretching and stretching-annealing treatment: (a) tensile strength, (b) elongation at break, (c) elastic modulus and (d) breaking strength in the various pre-stretching ratios.

presence of numerous imperfect crystals in the untreated sheets results in a lower degree of crystallinity; (2) Pre-stretching disrupts the existing perfect crystals, leading to the formation of finer crystals, which enhances the number of crystalline sites and promotes crystal orientation, thereby increasing the crystallization potential of PBC during the annealing-stretching process. As the stretching ratio increases, the highly oriented amorphous chains are more susceptible to a disorder-order transition, which facilitates an earlier onset of strain hardening and a notable increase in the slope of the stress-strain curves;^[29,30] (3) While the formation of finer crystals enhances crystallinity, the annealing process approaches the melting point, which inhibits the formation of crystal nuclei, thereby hindering the crystallization process and resulting in a reduction in crystallinity. Consequently, the tensile strength of the stretching-annealing samples is marginally lower than that of the annealing-stretching samples,^[31] and the increase in the crystal content in the film after heat treatment significantly increases the mechanical strength and modulus. However, the heat treatment process also consumes a large number of movable amorphous chains, which destroys part of the chain entanglement, resulting in a decrease in elongation at break;^[20,22] (4) Once the stretching-annealing process achieves a certain level of perfect crystallization, the percentages of crystallinity and crystal integrity within the material remain relatively stable.^[32]

As the pre-stretching ratio continued to increase, the elongation at break initially increased before subsequently declining, whereas the elastic modulus exhibited the opposite trend, decreasing initially and then increasing. However, the breaking strength increased consistently. In contrast to the tensile strength, the stretching-annealed samples demonstrated superior elongation at break and breaking strength, which may be attributed to a reduction in the degree of crystal orientation and the reversion of free chains in PBC to a less-ordered state following the annealing process.

Furthermore, an increase in the pre-stretching rate or the duration of pre-stretching maintenance at 200% pre-stretching resulted in observable upward trends in the stress-strain curves of PBC, as illustrated in Figs. S1 and S2 (in ESI). This is accompanied by corresponding increases in the tensile strength, elongation at break, yield strength, and elastic modulus, as depicted in Figs. S3 and S4 (in ESI). As the pre-stretching rate increased, the tensile strengths of the annealed and stretched samples exhibited a significant enhancement, although this was accompanied by a reduction in the elongation at break. Notably, although the tensile strength remained stable, there was a consistent decrease in the elongation at break. Similarly, the relationship between tensile strength and elongation at break demonstrated a gradual decline with increasing pre-stretching rates. However, the mechanical properties of PBC subjected to 200% pre-stretching at a rate of 10 mm·min⁻¹ exhibit a stable trend despite variations in the maintenance time of the pre-stretching process.

To avoid excellent mechanical properties owing to the thin-film thickness, the mechanical properties of PBC sheets with similar thicknesses (approximately 0.4 mm) were tested, and the results are shown in Fig. S5 (in ESI). This result illustrates that the mechanical properties are closely related to

the crystal orientation, and a high orientation can improve mechanical properties.

In conclusion, the elongation at break, tensile strength, breaking strength, and elastic modulus increased under optimal pre-stretching ratios and rates. Furthermore, these properties were more effectively demonstrated by isothermal annealing. This suggests that pre-stretching can improve the performance of PBC under specific conditions.

Thermal Properties

The initial heating process is related to the inherent properties of the PBC as well as its thermal and force history. Consequently, PBC was subjected to a preliminary heating DSC test to investigate the effects of the pre-stretching and isothermal annealing processes on its thermodynamic behavior and crystallization characteristics. Figs. 4 and S6 (in ESI) illustrate the first heating curves of PBC under the conditions of pre-stretching, annealing, and the absence of both treatments, while the relevant thermodynamic data are summarized in Table S1 (in ESI). The T_g of PBC was approximately $-34\text{ }^{\circ}\text{C}$, and a distinct double melting peak was observed at approximately $55\text{ }^{\circ}\text{C}$ in the absence of annealing and pre-stretching.

Isothermal annealing and pre-stretching processes can refine the degree of crystallization of PBC. While the thermal behavior of pre-stretched PBC is similar to that of unstretched PBC, a comparative analysis of the primary heating curves before and after annealing, as illustrated by the DSC curves, reveals that the area corresponding to the melting peak of imperfect crystals varies in size across the stretching-annealing, unannealed, and annealing-stretching conditions, progressing from smaller to larger areas.^[33,34] Notably, as the pre-stretching ratio increased in both the unannealed and annealing-stretching conditions, as depicted in Figs. 4(a)–4(c), the strength of the melting peak associated with imperfect crystals gradually intensified in both the pre-annealed and post-annealed PBC. This phenomenon may be attributed to the disruption of the crystal structure (perfect or imperfect crystals) or the emergence of an intermediate phase within the perfect crystal lattice. The proportion of the imperfect crystal area within the melting peak of the stretching-annealing process is minimal, indicating that the annealing process effectively refines the crystal size and morphology. Furthermore, the ordered chain entanglement network and new phase established in the stretched film restrict the movement and relaxation of the amorphous chains, necessitating higher temperatures to achieve the glass transition and melting.^[34–36] In comparison to the untreated film, the T_g of the annealing-stretching and stretching-annealing films is significantly elevated, as the perfect crystal structure imposes substantial limitations on the mobility of the amorphous chains.^[37] This alteration corresponds to the derivative peak observed at $22.6\text{ }^{\circ}\text{C}$ in the XRD analysis, and the changes in the melting peak of the imperfect crystals align with the variations in the XRD data. As the pre-stretching rate increased, the presence of imperfect crystals also exhibited a gradual upward trend, although the changes in the diffraction peak remained subtle across different time intervals, regardless of the annealing and stretching sequence. This peak serves as an indicator of the thermal stability of imperfect crystals.

PBC is a semi-crystalline polymer with a slow crystallization

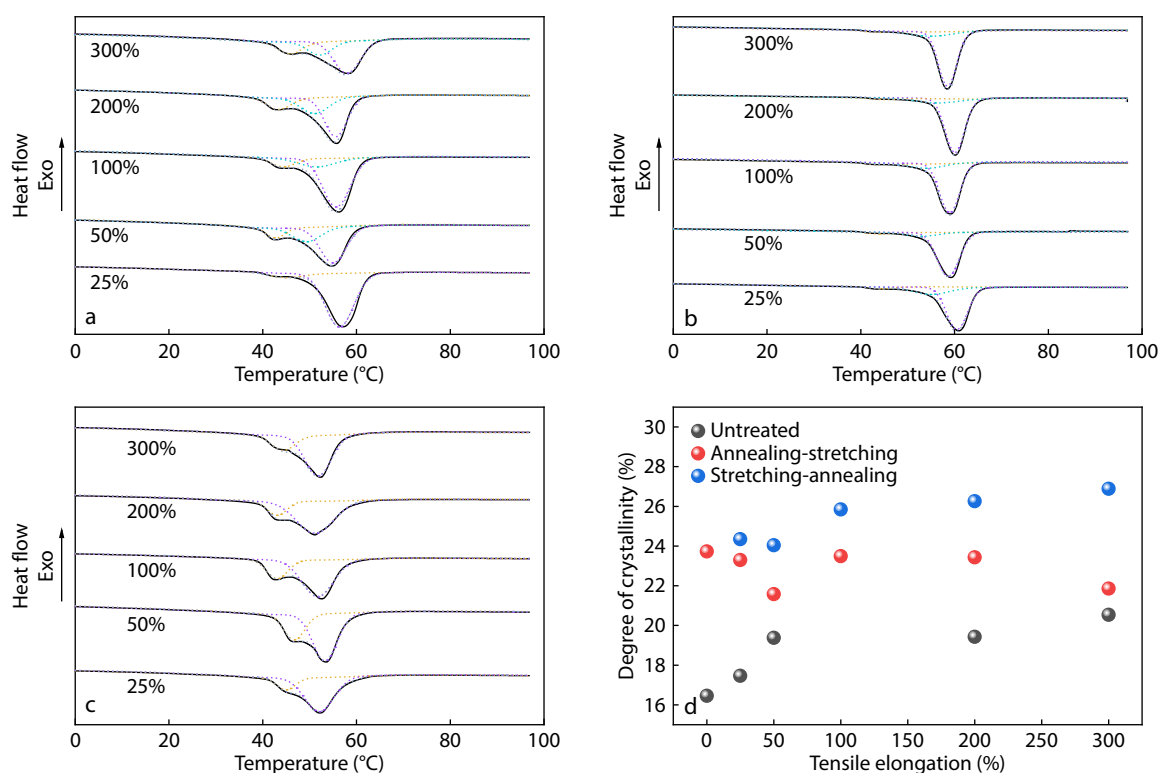


Fig. 4 (a-c) The first heating curves of PBC with (a) annealing-stretching, (b) stretching-annealing and (c) untreated, respectively; (d) the degree of crystallinity of PBC with various processes.

rate, and its crystallinity increases with annealing temperature or time. The degree of crystallinity from DSC (X_{c-DSC}) was calculated using the following formula:

$$X_{c-DSC} = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (2)$$

where ΔH_m^0 is the melting enthalpy of 100% crystalline PBC with a value of $137.1 \text{ J} \cdot \text{g}^{-1}$,^[7] which can be compared to the crystallinity of PBC after the annealing process.^[38] The relationship between the crystallinity and pre-stretching ratio via various processes is shown in Fig. 4(d). The degree of crystallinity of PBC without annealing and pre-stretching was only 15.70%. With the pre-stretching increase, the degree of crystallinity increased slowly and reached a maximum value (20.53%) at ratio of 300%, and underwent isothermal annealing; the crystallinities were above the unannealed whether annealing-stretching or stretching-annealing processes, and the stretching-annealing process had a higher crystallinity for the imperfect crystals produced in pre-stretching, transforming perfect crystals during the annealing process. The crystallinity in annealing-stretching and stretching-annealing reached 24.45% and 26.89%, respectively, and the crystallinity is 1.56 and 1.71 times that of untreated.

XRD Analysis

Fig. S8 (in ESI) displays the XRD pattern of PBC without pre-stretching, revealing diffraction peaks at 16.4° , 20.9° , 21.4° , and 24.1° , which are consistent with previously reported data.^[3] Notably, Crystalline reflections were observed at approximately $2\theta = 21.4^\circ$. In the case of PBC subjected to pre-stretching, it was found that there were no significant changes at a pre-stretching ratio of 25%, regardless of whether stretching or annealing was

applied. However, as the pre-stretching ratio increased, a new diffraction peak emerged at $2\theta = 22.6^\circ$ and its intensity gradually increased. The stretching-annealing condition exhibited a slower rate of intensity increase compared to the other conditions, leading to lower relative intensities for the 22.6° peak. A similar trend was observed across various pre-stretching rates and durations, as shown in Figs. S8 and S9 (in ESI). Furthermore, the intensity of the new peak increased with higher pre-stretching rates, particularly under 200% pre-stretching; however, the degree of crystallinity remained stable beyond a stretching rate of $10 \text{ mm} \cdot \text{min}^{-1}$.

To explore the order structure generated, XRD analyses were conducted on the PBC with and without pre-stretching. The PBC content was determined by evaluating the relative intensities of the diffraction peaks associated with amorphous and crystalline regions. (There is a large error in the crystallinity calculated by XRD, so the peaks at 22.6° and 21.4° are rough compared to the relative content.)

The specific formula utilized for this calculation is as follows

$$\text{Contents} = \frac{I_c}{I_a + I_c} \times 100\% \quad (3)$$

where I_a and I_c represent the areas of the diffraction peaks in amorphous and crystalline regions, respectively. The XRD patterns, along with the corresponding contents for PBC subjected to various pre-stretching ratios, are illustrated in Fig. 5, encompassing the conditions of un-annealing, annealing-stretching, and stretching-annealing. To further explore the correlation between the microstructure and the pre-stretching process under different annealing treatments, the XRD patterns were analyzed, and the contents of the various diffraction peaks were calculated.

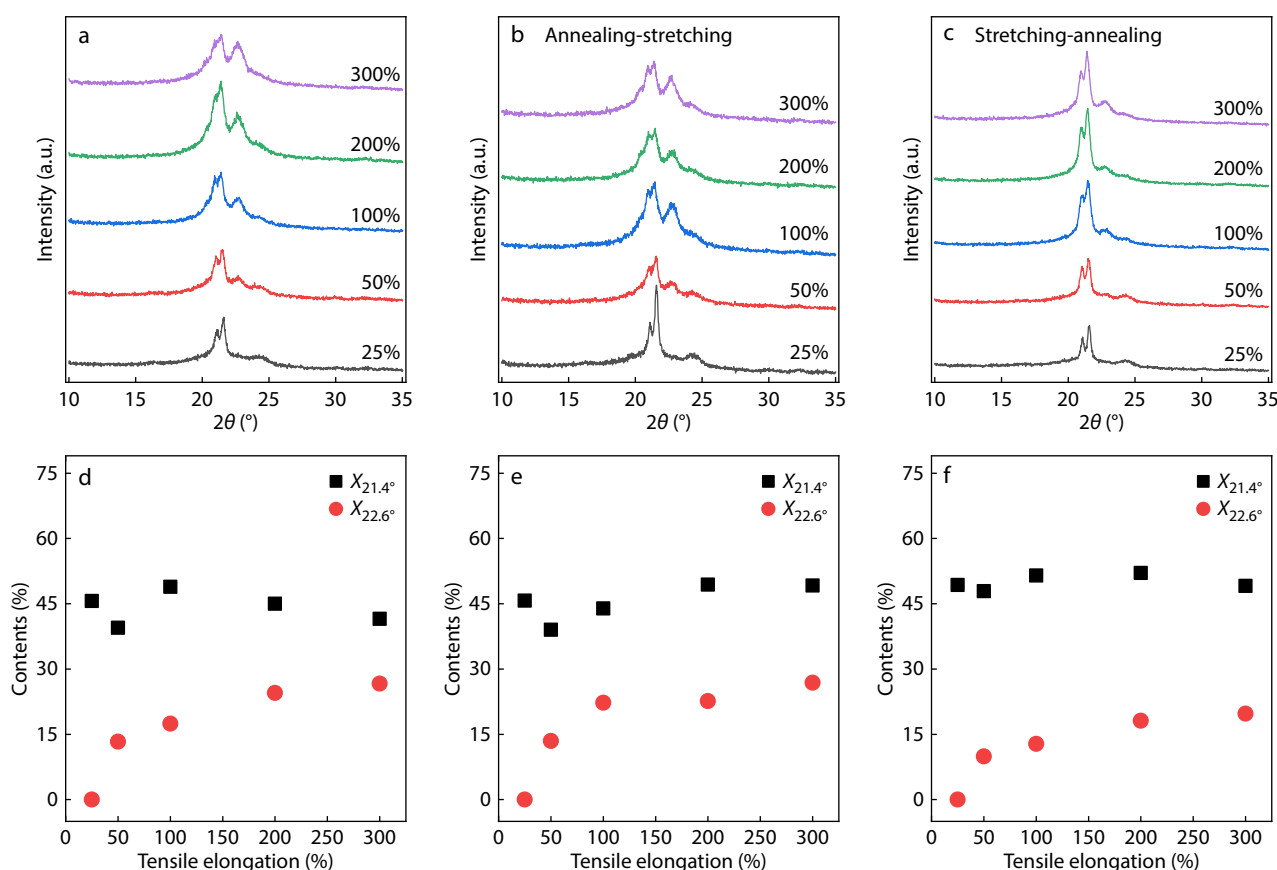


Fig. 5 The XRD patterns with various pre-stretching ratios: (a) un-annealing, (b) annealing-stretching and (c) stretching-annealing, and the corresponding contents of PBC: (d) un-annealing, (e) annealing-stretching and (f) stretching-annealing.

ed. This analysis facilitated the establishment of a relationship between the contents and crystal diffraction peaks, considering the perfection of the crystal, pre-stretching ratios, pre-stretching rates, and pre-stretching maintenance durations, as illustrated in Figs. 5, S8 and S9 (in ESI). The findings indicate that as the pre-stretching ratio increased, the contents of the peak at 22.6° progressively increased. While the content associated with the original diffraction peak at 21.4° remained constant. This suggests that the intensity of the peak at 22.6° following pre-stretching increases with the stretching ratio, regardless of whether stretching or annealing is applied. However, the enhancement observed during the stretching-annealing process was gradual, with the contents stabilizing around 20%. This phenomenon may be attributed to the finer crystallization induced by pre-stretching, which can promote crystallization within the amorphous regions and facilitate the ordering of polymer chains, resulting in a lower crystallinity at 22.6° compared to other peaks, while simultaneously enhancing the crystallinity at 21.4° . Compared with the degree of crystallinity in DSC (in Fig. 4d), the increasing trend of the peak at 22.6° is similar in untreated and stretching-annealed parts, where the degree of crystallinity and content of the peak at 22.6° is up with the increasing pre-stretching elongation. However, a different phenomenon occurs in the stretching-annealing part, in that the crystallinity remains constant at 24% with the stretching elongation changes, which can reveal that the degree of crystallinity is mainly affected by the degree of annealing, followed

by the contents of the peak at 22.6° . Therefore, the anomaly value of the pre-stretching ratio at 50%, especially in the annealing-stretching process, can demonstrate that some crystals are broken and the crystal core (belonging to peak at 22.6°) is not enough to form perfect crystalline without isothermal annealing treatment.

The XRD patterns and contents of PBC subjected to various pre-stretching rates and maintenance time are presented in Figs. S8 and S9 (in ESI). It was observed that the content also increased with higher pre-stretching rates, although the degree of change appeared to stabilize over time.

SAXS and GISAXS Analysis

To examine alterations in the internal structure during the pre-stretching process, the crystal orientation was initially analyzed using SAXS, as shown in Fig. 6. Figs. 6(a) and 6(b) illustrate the 2D-SAXS patterns of PBC both with and without pre-stretching process at 200% after annealing, respectively. The results indicate that the pattern of the unstretched PBC exhibits uniform amorphous halos, which suggests isotropy and no or lower orientation within the internal microstructure of the PBC. Conversely, for the pre-stretching at 200%, four symmetrical small diffraction spots appear at positions away from the equatorial direction, revealing that some crystals have broken or tilted.^[39] Additionally, there is a markedly distinct X-ray diffraction pattern along the equatorial line compared to that of the untreated sample, thereby indicating the formation of a highly oriented crystalline structure in the pre-stretched PBC, resulting in the

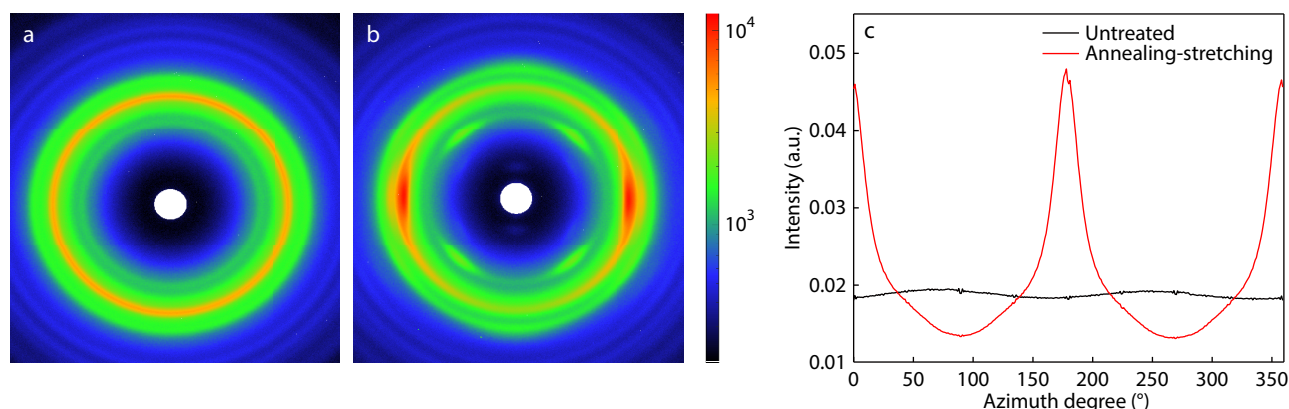


Fig. 6 The SAXS patterns of PBC: (a) untreated and (b) pre-stretching at 200% in annealing-stretching, (c) the intensity distribution of 2D-SAXS patterns for PBC along the azimuthal angle with and without pre-stretching (pre-stretching ratio at 200%).

emergence of a pair of pronounced diffraction spots in the SAXS pattern. The amorphous halo contracted towards the equatorial region, and a slight reduction in intensity was observed in the meridian direction. This indicates that the polymer chains of PBC become oriented in alignment with the stretching. In addition, after pre-stretching, the 2D-SAXS of pre-stretching showed a new diffraction signal along the stretching direction. Combined with XRD and 1D-SAXS results (Fig. S7 in ESI), this indicates that the material has a structural transformation or new phase formation after stretching, and the diffraction peak signal is consistent with the structure corresponding to 22.6° in XRD.^[40] To assess the degree of orientation during the pre-stretching process, the intensity distribution of the 2D-SAXS patterns for PBC was analyzed along the azimuth angle, both with and without pre-stretching (pre-stretching ratio at 200%) in Fig. 6(c). The degree of orientation was calculated using the formula proposed by Hermans, revealing that the untreated PBC exhibited negligible orientation, while the orientation of the pre-stretched sample increased significantly from 0.025 to 0.821. This finding confirms the formation of a highly oriented crystalline structure, due to the stress-induced crystallization phenomenon occurring during pre-stretching above the glass transition temperature (T_g), which is consistent with observations made in poly(*p*-dioxanone).^[26]

GISAXS tests were performed on samples with different stretching ratios to further study the structural changes in the polymer film under different stretching ratios and confirm the crystal phase transition or new phase formation during the stretching process. The experimental results are shown in Figs. 7 and S10 (in ESI).

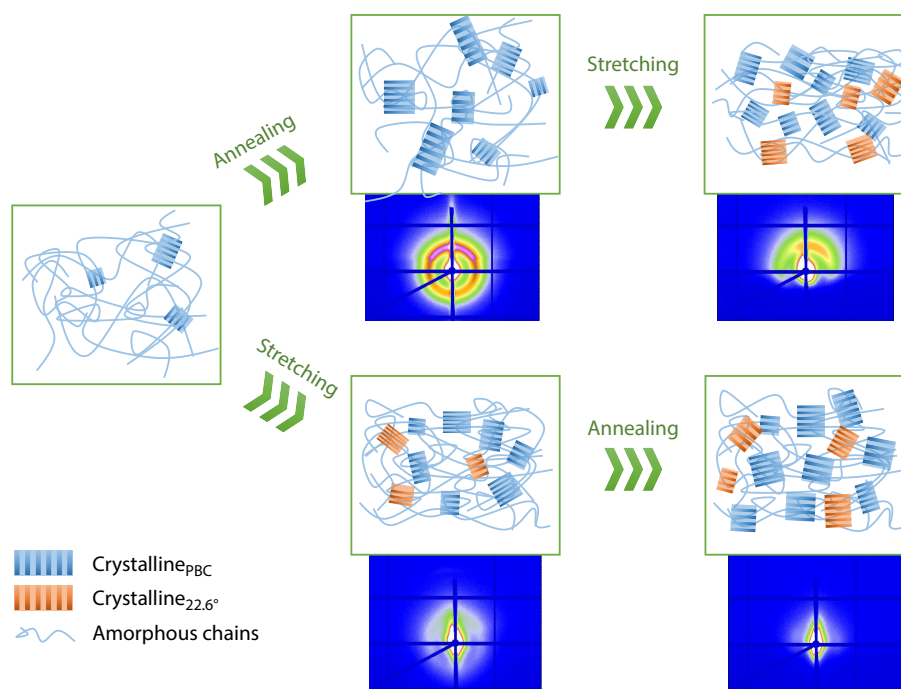
Before stretching, PBC was mainly isotropic. Although there is a high signal for some arcs, it is still dominated by diffraction rings, indicating that there is a slight crystal orientation in the polymer during the unstretched stage.^[41] Although it is different from 2D-SAXS, it is consistent with the conclusion of the orientation degree obtained in Fig. 6(c) that there is a partial crystallization orientation at this stage. With an increase in the pre-stretching ratio of the annealed polymer film, the polymer is mainly based on the diffraction rings and some arcs in the early stage of stretching (<50%), and scattering signal shows that the dispersion circle shifts to the spindle, indicating that the crystal has a slight orientation along the stretching direction. This is similar to the phenomenon of

shish-kabab for chain stretching, which is a necessary condition for its formation. This is similar to the shish-kabab phenomenon, and chain stretching is a necessary condition for the formation of shish-kababs.^[39,42] In the middle of stretching (50%–200%), the diffraction signal changes from a diffraction arc to a short arc and gradually becomes a spindle, and a weak fringe scattering signal appears on both sides and near the beam aperture. This indicates that some new shish-kabab formations were induced by the stretching and orientation nucleation of the stretching segments of the entangled network; under stretching, many crystals were arranged along the stretching direction. Combined with the XRD pattern, the peak at 22.6° corresponds to the shish-kabab generated from the pre-stretching process; therefore, the shish is also namely crystalline_{22.6°}. In the later stage of stretching (> 200%), the halo gradually changed from spindle to stripe information, and the maximum scattering appeared in the stretching direction, which is similar to the reported type III shish information,^[43] indicating that the crystal becomes more regular along the stretching direction, forming a more clearer layered structure, and the layered normal is oriented along the stretching direction. According to Cui's report, the lamellar structure that appears is embedded in a shish structure, different from the common kebab structure, which is generated from the lateral growth of shish nuclei.^[43]

Internal Mechanism

The results showed that the mechanical properties, thermal behaviors, and strain-induced structural evolution of PBC depend on the pre-stretching ratio and rate. Based on the above-mentioned results and previous reports, the relationship between the microstructure and mechanical properties of polymers with and without pre-stretching is discussed herein. The microstructural variation of PBC with pre-stretching and isothermal annealing is depicted in Scheme 1, and the SAXS pattern is shown in Fig. S11 (in ESI).

First, the crystallinity of the sample was analyzed from the XRD and DSC data without being stretched and unannealed. There is already an ordered arrangement inside the PBC, in which the PBC exhibits ductile fracture. According to Qian^[44] and Pan^[45], during the physical aging process, the polymer chains are rearranged from disordered to more ordered in the amorphous phase, resulting in cohesive entanglement. Cohe-



Scheme 1 The internal microstructure changes with the annealing and pre-stretching process.

sive entanglement is due to the anisotropy of the van der Waals force, which is formed in the amorphous phase (isotropy and lower orientation)^[13] of the polymer during physical aging, and is derived from the local nematic interaction between a few unit segments of two or three nearest neighbor chains. Therefore, the mechanical properties and thermal behavior of the untreated PBC were poor.

Then, by pre-stretching the unannealed PBC spline, the ordered structure of some internal tangles is destroyed owing to the unidirectional force applied, and the molecular chain is oriented along the uniaxial pre-stretching direction, which may inhibit the chain recombination of the unentangled part. Therefore, the fracture form of PBC was ductile at a ratio of 100%. With a gradual increase in the pre-stretching ratio, the orientation degree of the chain is enhanced, and more cohesive structures- shish) are formed, and corresponding peak ($X_{22.6^\circ}$) in XRD (see in Fig. 6) pattern. From the XRD spectra, it can be observed that the larger the stretching ratio, the higher the content of the intermediate phase. Therefore, the mechanical properties of PBC after pre-stretching, especially the breaking strength and T_g , were significantly increased; elongation at break first increased and then declined, and the elastic modulus increased abruptly first after reaching the minimum value in Fig. 3, where the yield point disappeared when the pre-stretching ratio was greater than 100%, regardless of the order of annealing and pre-stretching in Fig. 2, suggesting that with the increase in internal order or tangles, the mechanical properties also refined, especially in tensile strength. Although the degree of crystallinity and scattering intensity of the samples without pre-stretching after annealing was improved, the internal structure was almost isotropic and had a low orientation, and the mechanical properties were not significantly improved compared to the samples without annealing after pre-stretching. The annealing PBC

just reaches 42.6 MPa for internal tangles during the aging process.

Finally, the internal structure diagram of PBC for both annealing and pre-stretching processes with different orders are shown in Scheme 1. It shows a shish structure (crystalline_{22.6°}) after pre-stretching with apparent content and the detailed information, as shown in Figs. 4–7. Moreover, the cross images of PBC at various pre-stretching ratios, as shown in Fig. S12 (in ESI), show that the number of crystalline upped and the orientation were more evident with the increase in the ratio, which indicates that the annealing-stretching process could improve the internal structure of PBC. Therefore, the mechanical properties of PBC clearly improved during both the annealing and stretching processes. The effects of the pre-stretching ratio, pre-stretching rate, and pre-stretching holding time on the microdeformation mechanism of PBC during room-temperature stretching were studied. Figs. 2, S1 and S2 (in ESI), it can be seen that the tensile strength, elongation at break, breaking strength, and elasticity modulus increased with an increase in the pre-stretching ratio. As shown in Scheme 1, as the pre-stretching ratio increased, more crystal orientations and new phases were generated during the pre-stretching process, and these orientations and phases may have become stress concentration points during the tensile test. Therefore, a higher modulus and strength were obtained.

The microscopic mechanism of tensile deformation at room temperature is also described based on the analysis of the microstructural evolution before and after pre-stretching. During the pre-stretching process, all the PBCs exhibited ductile fracture behavior owing to the destruction of the internal entangled network structure. The PBC obtained two types of stress-strain curves after pre-stretching: one showed obvious yield, short necking, and typical strain hardening, and the

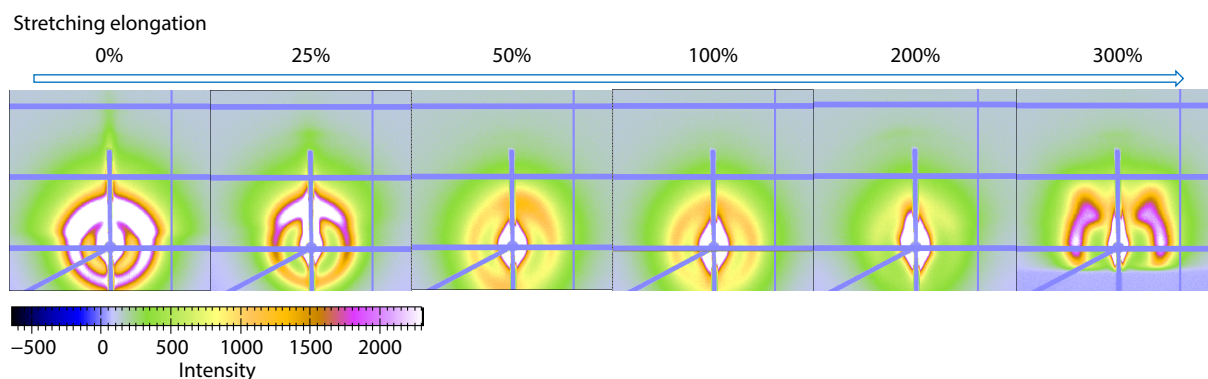


Fig. 7 The GISAXS patterns of PBC with various pre-stretching elongations.

other showed only steep strain hardening. Therefore, the unstretched and 200% stretched splines were selected for small-angle scattering. Most of the unstretched splines were amorphous. When the sample was stretched, a crystal orientation was generated. Studies have shown that with a further increase in tension, under the action of orientation and a new phase, the stress-strain curve is transformed into a strain-hardening zone. At the same time, the movement of the frozen molecular chain is limited, and stress is concentrated in the new phase, resulting in crazing. The spline broke after the phase was destroyed. When the orientation is parallel to the stretching direction, the oriented molecular chain slips more easily during the stretching process, thereby inhibiting the crazing mechanism. Therefore, the elongation at break increased further, and the modulus and strength gradually increased with an increase in the ratio.

In summary, the comprehensive performance of PBC depicted in Fig. 8 shows that the improved mechanical properties are correlated with the degree of crystallinity, orientation, and the content of shish (peak at 22.6°); interestingly, the change trend of tensile strength, degree of crystallinity, and the contents of shish were similar to the increase in the pre-stretching and stretching-annealing parts, and showed an obvious trend with the change in refined steps, such as pre-stretching ratio, pre-stretching rate, and maintaining time. Although the crystallinity remained constant in the annealing-stretching part, the mechanical properties were similar to

those of the shish. Therefore, isothermal annealing and pre-stretching are both excellent paths to enhance the tensile strength *via* comprehensive analysis, and the better value in mechanical properties obtained under both annealing and stretching processes, compared with the one for higher crystallinity and the existence of shish. Combined with the major factor, the PBC prepared *via* the annealing-stretching method obtained the best comprehensive performance, followed by stretching annealing.

CONCLUSIONS

With isothermal annealing and unidirectional pre-stretching, the comprehensive performance of PBC sheets shows a significant improvement. PBC with high orientation was prepared *via* annealing-stretching process, the strength at tensile and break as well as the modulus of the drawn blend were improved by increasing the pre-stretching ratio, where the tensile strength and elongation at break reached maximum values amounting to 104.5 MPa and 534%, respectively, suggesting that the process has an excellent toughening effect. With increased pre-stretching ratios, T_g and T_m shifted to higher temperatures, and the crystallinity of the drawn blend increased. In contrast, the melting peak of the imperfect crystalline structure increased with the pre-stretching ratio during annealing-stretching and maintained a trace during stretching-annealing. XRD and XASX analyses revealed that the shish structure and orientation that emerged *via* strain-reduced crystallization proceeded after the pre-stretching process. Moreover, combined with information on the mechanical properties and degree of crystallinity, the contents of the new phase or orientation are determined by the tensile strength and crystallinity. The relationship between the microstructure and macroscopic properties before and after the stretching process and the strengthening mechanism of PBC are described. Subsequently, the degree of orientation and crystallinity increased along with the occurrence of the new phase; therefore, the strength increased. These results indicate that the orientation and strain-induced crystallization grew during pre-stretching, suggesting that these were the key aspects for strengthening. Consequently, pre-stretching toughened PBC blends enables fabrication of materials suitable for specialized applications such as agricultural preservation films and woven bags.

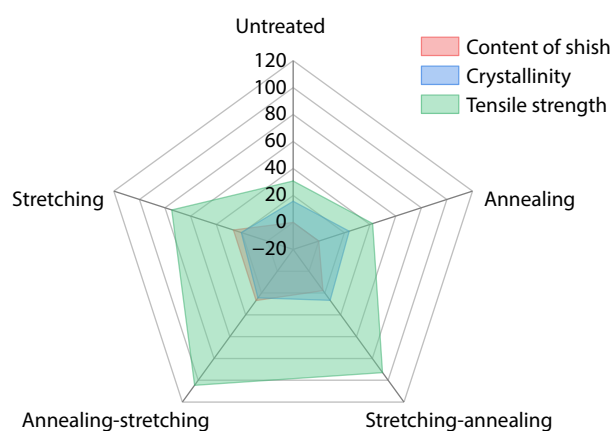


Fig. 8 The comprehensive performance of PBC with various refine methods.

Conflict of Interests

The authors declare no interest conflict.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3410-y>.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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