

Quantitative Investigation on Structural Evolution of Co-continuous Phase under Shear Flow

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Electronic Supplementary Information

Abstract Components of co-continuous phase can form an interpenetrating network structure, which has great potential to synergistically improve the mechanical properties of the blends, and to impart the functional blends superior electrical conductivity and permeability. In this work, the effects of shear rates ($50\text{--}5000\text{ s}^{-1}$) at different temperatures on the phase morphology, phase size and lamellar crystallites of biodegradable co-continuous polybutylene terephthalate (PBAT)/polybutylene succinate (PBS) blend are quantitatively investigated. The results show that the above features of the PBAT/PBS have a strong dependence on the shear flow and thermal field. The co-continuous phase of the blend is well maintained at $130\text{ }^{\circ}\text{C}$. Interestingly, this phase structure transforms into a “sea-island” structure at $160\text{ }^{\circ}\text{C}$, which gradually recovers to a co-continuous phase when the shear rate increases from 1000 s^{-1} to 5000 s^{-1} . The phase size decreases with the increase of shear rate both at $130\text{ }^{\circ}\text{C}$ and $160\text{ }^{\circ}\text{C}$ due to the refinement and deformation of phase structures caused by strong shear stress. Unexpectedly, a unique phenomenon is observed that the shear-induced lamellar crystallites are oriented perpendicular to shear direction in the range of $500\text{--}5000\text{ s}^{-1}$ at $130\text{ }^{\circ}\text{C}$, while the orientation of lamellar crystallites at $160\text{ }^{\circ}\text{C}$ is along the shear direction within the whole range of shear rates. The degree of orientation for the PBAT/PBS blend crystals increases first and then decreases at both temperatures above. In addition, the range of shear rate has reached the level in the industrial processing. Therefore, this work has important guiding significance for the regulation of the co-continuous phase structure and the performance for the blend in the practical processing.

Keywords Co-continuous phase; Shear rate; Phase size; Crystal orientation

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INTRODUCTION

Development of biodegradable material as a potential substitute for non-biodegradable material is an emerging field of research. In recent years, different types of biodegradable polymers have received an immense amount of attention for the need of developing various new materials and reducing environmental concerns.^[1] As a biodegradable polyester, poly(butylene adipate-co-terephthalate) (PBAT) has excellent toughness,^[2] which is often used to toughen other brittle biodegradable materials, such as poly(lactic acid),^[3] polycarbonate^[4] and poly(hydroxybutyrate-co-valerate).^[5] However, PBAT itself has low mechanical strength and poor crystallization property,^[6,7] resulting in that the performance and dimensional stability of its products could not meet the requirements of related fields. As another biodegradable polyester, poly(buty-

lene succinate) (PBS) is a semi-crystalline polymer with a rapid crystallization rate, a crystallinity usually higher than 35%, good thermal stability, desirable processing properties, better barrier properties, low melting point and high mechanical strength.^[8–10] As noted above, PBS and PBAT are the most promising candidates for future biodegradable materials, and the complementary advantages of the two materials could endow the PBAT/PBS blend with superior mechanical properties over the single component, bringing great potential for various applications.

For a polymeric blend, a co-continuous structure is a special morphology in which two components self-assemble into a mesh-like continuous structure that synergistically improves the mechanical properties of the binary blends, as well as improving the permeability and electrical conductivity for functional blends. There is a growing interest in co-continuous blends as they can effectively combine the characteristics of the two components to obtain excellent processing and mechanical properties. For instance, an electrically conductive poly(vinylidene fluoride) (PVDF)/polyamide 6 (PA6)/carbon nanotubes (CNTs) composite with a unique hierarchical

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morphology has been fabricated by the formation of co-continuous and nano-dispersion structures using high-shear processing.^[11] PVDF and PA6 basically form co-continuous phase and the CNTs are exclusively located in the PA6 phase. The composites prepared show very unique double percolation structures with markedly reduced percolation threshold and significantly improved electrical and mechanical properties. Compared with the "sea-island" structure, the co-continuous structure is more beneficial to the stress transfer and matrix deformation, improving the toughness of the blended system.^[12] The formation of co-continuous phase can be affected by components,^[13–15] temperature,^[16] interfacial compatibility,^[17,18] viscosity ratio^[18,19] and phase inversion.^[19] Besides the prerequisite of component, thermal treatment is currently one of the main factors to affect the phase size and continuity of co-continuous phase. For example, the molecular chains of the blend components in the co-continuous phase have higher mobility at high temperature (above the melting point), which leads to spontaneous phase aggregation and a rapid increase in phase size. The phase size can generally be raised from a few microns to several hundred microns, and the continuity of the blend system will decrease due to the aggregation effect, and may even lose the co-continuity characteristics and transform into a "sea-island" structure.

Except for the aforementioned thermal field, shear flow field, which inevitably exists during polymer processing, also affects the co-continuous phase.^[20] At shear rate of 60 s^{-1} , it is found that the co-continuous phase of the polyamide 6 (PA6)-poly(styrene-ethylene-butadiene-styrene) (SEBS)-polypropylene (PP) ternary blends is oriented along the shear direction and has a small phase size. However, the phase morphology gradually aggregates and subsequently the phase size increases with the shear rate from 60 s^{-1} to 2.5 s^{-1} .^[21] Rotella et al.^[22] applied shear flow field to the blend of polyamide and polyethylene with isotropic co-continuous phase above the melting point and the co-continuous blend are oriented along the flow direction and form an anisotropic phase morphology at various velocities ranging from $1\text{ }\mu\text{m}\cdot\text{s}^{-1}$ to $1\text{ mm}\cdot\text{s}^{-1}$. Therefore, the synergistic effect of mechano-thermal field could affect the phase morphology, the phase size and the orientation of molecular chains of polymer, which is of great significance to control the co-continuous phase during processing.

However, to the best of our knowledge, the above research on the co-continuous structure only stays in the qualitative evaluations, and the shear rate range resulting in the occurrence of the above phenomenon is relatively small and narrow. There is little quantitative investigation on the multiscale structure evolution of the co-continuous phase in a wide range of shear rate.^[23] Quantitative research allows for precise design of co-continuous structures under mechano-thermal field, and structural quantification can also regulate the mechanical properties and functionality of products, which is beneficial to guide the actual production more precisely. Based on the above considerations, this work quantitatively investigates the phase morphology, phase size and lamellar crystals of co-continuous phase at a wide shear rate range of $50\text{--}5000\text{ s}^{-1}$ (this range has reached the level of

shear rate in conventional processing) through the coupling effect of shear flow field and thermal field. In our work, the PBAT/PBS biodegradable material with co-continuous structure is prepared by melt extrusion. To quantitatively investigate the effect of shear flow and thermal fields on the phase structure and crystal structure of PBAT/PBS co-continuous phase during processing, a high-pressure capillary rheometer is used to provide precise shear rate to the co-continuous PBAT/PBS blends at different temperatures. Subsequently the phase morphology, phase size and crystal structure of the blends are characterized by field emission scanning electron microscopy (FE-SEM) and synchrotron radiation X-ray scattering/diffraction. The effect of mechano-thermal field on the multiscale structure of the co-continuous phase is then analyzed.

EXPERIMENTAL

Materials

Poly(butylene adipate-co-terephthalate) (PBAT) was purchased from Xinjiang Lanshan Tunhe Chemical Co., Ltd. ($M_w=7.50\times 10^4\text{ g/mol}$, MFI= 15.1 g/10min at $190\text{ }^\circ\text{C}/2.16\text{ kg}$ according to the ASTM D1238). Poly(butylene succinate)(PBS) was purchased from SHOWA Highpolymer, Japan (MFI= 25.8 g/10min at $190\text{ }^\circ\text{C}/2.16\text{ kg}$ according to the ASTM D1238). Sodium hydroxide (NaOH), methanol and tetrahydrofuran (THF) were purchased from Chengdu Kelong Chemical Reagent Factory (Chengdu, China).

Sample Preparation

To avoid the degradation of PBAT and PBS due to hydrolysis during processing, the raw materials of PBAT and PBS pellets were vacuum dried at $80\text{ }^\circ\text{C}$ for 8 h before melt compounding. The PBAT/PBS blends with mass ratio of 60/40 (named as PBAT-60 for short) were fabricated in a co-rotating twin-screw extruder with a ratio of screw length to its diameter (L/D) of 40. Temperatures in seven zones were set at 130, 140, 150, 150, 150 and $130\text{ }^\circ\text{C}$ from the feed section to the die section, respectively. The screw speed was held constantly at 150 r/min . The obtained PBAT-60 presents a typical co-continuous morphology, as shown in Fig. S1 (in the electronic supplementary information, ESI), and the thickness of the two continuous phases was about $1.1\text{ }\mu\text{m}$. In addition, both the PBS phase and the PBAT phase had a very high degree of continuity, which provided a prerequisite for studying the effect of mechano-thermal field on the evolution of the co-continuous phase. The obtained PBAT-60 samples were also vacuum dried at $80\text{ }^\circ\text{C}$ for 8 h to prevent hydrolysis during following processing. The dried samples were preheated at 130 and $160\text{ }^\circ\text{C}$ for 5 min in the tube of high-pressure capillary rheometer (RHEOGRAPH 120, Germany, the length and diameter of the capillary are 20 mm and 1 mm, respectively) and then different shear rates were applied at 130 and $160\text{ }^\circ\text{C}$, which correspond to the lower and upper limits of the processing temperature for PBAT and PBS products in the literature and actual processing,^[12,24] respectively. In addition, the application of shear rate was accurately set by adjusting the compression rate. Seven shear rates of 50, 100, 200, 500, 1000, 2000, 5000 s^{-1} that span a wide range were selected for analysis. The relation between the compression velocities and shear rates is shown in

Table 1 The relation between velocities and shear rates.

Velocities (mm·s ⁻¹)	Shear rates (s ⁻¹)
0.027	50
0.055	100
0.111	200
0.278	500
0.555	1000
1.111	2000
2.778	5000

Table 1. This range fully covers injection molding, tape casting, blow molding and other conventional processing methods. As shown in Fig. S2 (in ESI), the viscosity of PBAT is higher than that of PBS under various shear rates at both 130 and 160 °C. Both the storage modulus and loss modulus of PBAT and PBS also have large differences.^[25] The viscoelasticity asymmetry of PBAT and PBS under the shear flow condition is important for the formation of PBAT/PBS co-continuous morphology.^[26]

The relation between the compression velocities and shear rates is obtained according to the following equation:

$$\dot{\gamma} = \frac{4R_b^2 S_p}{R_c^3} \quad (1)$$

where $\dot{\gamma}$ is shear rate, S_p is speed of the plunger, $R_b=7.5$ mm and $R_c=0.5$ mm, are radius of the barrel and the capillary (die), respectively.

Characterization

Field emission scanning electron microscope (FE-SEM)

A field-emission SEM (Nova NanoSEM450, FEI, USA) with an accelerating voltage of 5 kV was used to observe the phase morphology and phase size of PBAT-60 sample extruded from high-pressure capillary tubes. Before measurement, the sample was immersed in liquid nitrogen for 1 h for quenching and the cryo-fracture of the sample was conducted perpendicular to the flow field direction. Then the amorphous phase in the sample was etched by water-methanol (volume ratio 1:1) solution with 0.1 mol/L of sodium hydroxide at 25 °C for 48 h. Finally, the etched sample surface was sprayed with gold for subsequent SEM observation.

Two-dimensional small-angle X-ray scattering (2D-SAXS)

Two-dimensional small-angle X-ray scattering (2D-SAXS) was used to characterize the lamellar crystallites at the BL16B1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The X-ray wavelength was 0.124 nm, and the distance between the sample and the detector was 2192.5 mm. In addition, the intensity integration of 2D-SAXS pattern was performed with the Xpolar software at 0°–180° to obtain the 1D-SAXS curve. Through the 1D-SAXS pattern and correlation function analysis, the average long period (d_{ac}), lamellar thickness (d_c) and amorphous thickness (d_a) of the sample can be calculated, respectively. The data processing process was as follows, and the intensity $I(q)$ - q curve was obtained by intensity integration. According to the one-dimensional electron density correlation function $K(z)$ (Eq. 2), the d_{ac} , d_c and d_a in the film were obtained:

$$K(z) = \frac{\int_0^\infty I(q) q^2 \cos(qz) dq}{\int_0^\infty I(q) q^2 dq} \quad (2)$$

Because the crystallinity of PBAT is usually less than 10% in

blending system, and the crystallinity of PBS is also lower than 50%. Therefore, the smaller value obtained by the electron density correlation function is regarded as the average lamellar thickness, and the amorphous thickness is calculated by $d_a = d_{ac} - d_c$.

Two-dimensional wide-angle X-ray diffraction (2D-WAXD)

To characterize the crystal structure at the molecular scale, two-dimensional wide-angle X-ray diffraction (2D-WAXD) was utilized at the BL16B1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The X-ray wavelength was 0.124 nm, and the distance between the sample and the detector was 175.5 mm. The intensity integration of the 2D-WAXD patterns was performed with the Xpolar software at 0°–180° to obtain the 1D-WAXD curve.

RESULTS AND DISCUSSION

Effect of Shear Flow on Co-continuous Phase at Various Temperatures

To investigate the effect of shear flow field on the co-continuous phase at various temperatures, the phase morphology of PBAT-60 is characterized by SEM and shown in Figs. 1 and 2. Under the thermal treatment temperature of 130 °C, the co-continuous

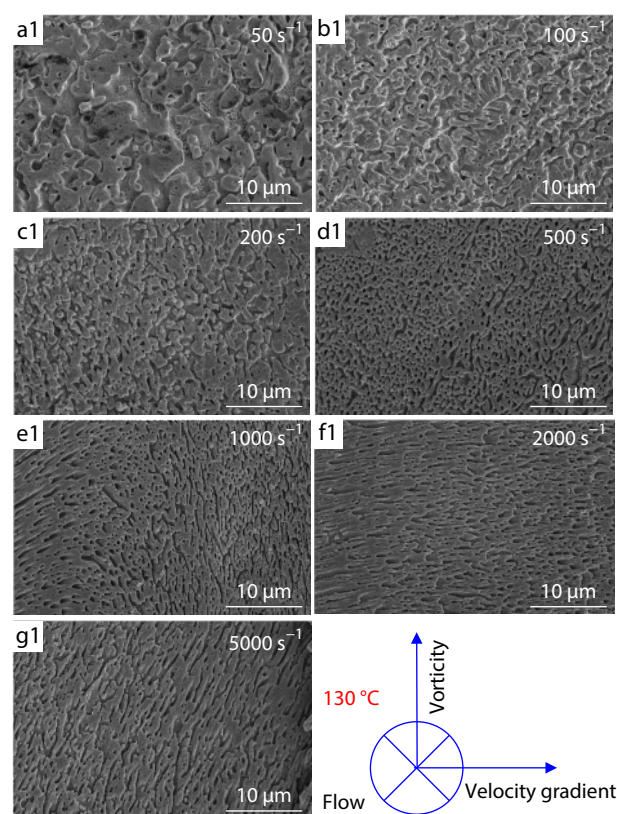


Fig. 1 SEM micrographs of PBAT-60 at 130 °C with various shear rates of (a1) 50 s⁻¹, (b1) 100 s⁻¹, (c1) 200 s⁻¹, (d1) 500 s⁻¹, (e1) 1000 s⁻¹, (f1) 2000 s⁻¹, and (g1) 5000 s⁻¹ under the viewpoint perpendicular to the shear direction after etching the amorphous phase using a water-methanol (1:1 by volume) solution containing 0.1 mol·L⁻¹ of sodium hydroxide. The shear flow direction (FD) is pointed into the page, the velocity gradient direction is horizontal and the vorticity direction is vertical, as indicated by the marking.

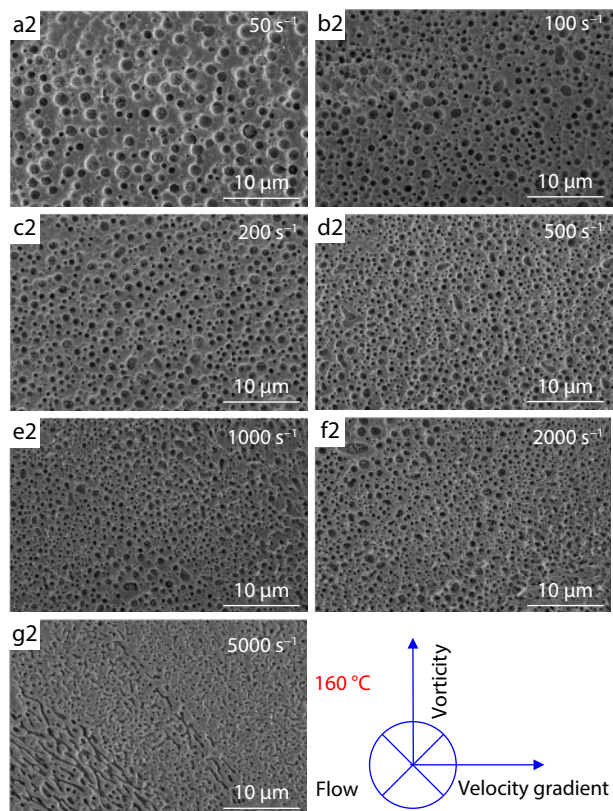


Fig. 2 SEM micrographs of PBAT-60 at 160 °C with various shear rates of (a2) 50 s⁻¹, (b2) 100 s⁻¹, (c2) 200 s⁻¹, (d2) 500 s⁻¹, (e2) 1000 s⁻¹, (f2) 2000 s⁻¹, and (g2) 5000 s⁻¹ under the viewpoint perpendicular to shear direction after etching the amorphous phase using a water–methanol (1:1 by volume) solution containing 0.1 mol·L⁻¹ of sodium hydroxide. The shear flow direction (FD) is pointed into the page, the velocity gradient direction is horizontal and the vorticity direction is vertical, as indicated by the marking.

phase morphology is well maintained with the improvement of the shear rate induced shear stress (as shown in Fig. S3a in ESI) and the average phase size decreases from ~4.7 μm at 50 s⁻¹ to ~0.68 μm at 500 s⁻¹ because the co-continuous phase is deformed and refined under shear stress action. Continue to increase the shear rate, unexpectedly, the oriented morphology perpendicular to the shear flow direction is observed. This interesting phenomenon is similar to the case of the droplets-cluster transition in polymer blends.^[21,27] In the weak shear field, the droplets tend to align along the shear direction, whereas for strong shear field, the droplet alignment is perpendicular to the flow direction.^[28,29] The phenomenon results from the existence of negative shear normal stresses (N1). As we can see, a single polymer coil can deform because of shear flow, and Brownian motion could randomize the chain and restore it to an initial undeformed coil which generates tension along streamlines. Meanwhile, it can also create shear normal stress, which increases with the increase of the degree of orientation. When N1>0, the cluster is tensioned in the flow direction and compressed in the gradient direction, which makes the cluster elongate along the shear direction. However, the cluster can only extend to the vorticity direction if the cluster is subjected to

compression in both flow and gradient directions, i.e., N1<0.^[29] Based on the above points, it is supposed that the co-continuous phase morphology aligned perpendicular to shear direction in this study is attributed to the negative normal stresses caused by high shear stress. In comparison with our case, Rotella *et al.* applied shear stress at 240 °C to the co-continuous blends at various velocities ranging from 1 μm·s⁻¹ to 1 mm·s⁻¹. The microdomains tend to align along the flow direction over the entire velocity range and the degree of alignment decreases with the increase of squeezing velocity. The micrograph exhibits an anisotropic morphology at the lowest velocity, however, resembles the initial isotropic morphology at the highest velocity.^[22] The alignment direction and orientation of co-continuous phase are different from those of our work, indicating that the processing temperature and shear rate have great influence on the co-continuous phase structure of blends.

The phase morphology is distinct in the case of thermal treatment at 160 °C. The phase morphology from the point of view perpendicular to the shear direction has evolved into a typical "sea-island" structure, with the PBS phase randomly distributed in the PBAT matrix as an island phase. Because the molecular chains of PBS in PBAT-60 have lower viscosity at high temperature (Fig. S3b in ESI) and thus possess high mobility, which produces rapid aggregation and leads to a sharp decrease in the continuity. The phase morphology thus subsequently evolves into a "sea-island" structure, suggesting that higher temperature is not beneficial to the maintenance of the co-continuous phase. Notably, there exist a large of spherical domains in Fig. 2. Since the sample is hard to be cryogenically fractured along the shear direction due to its small diameter (about 0.5 mm), it is difficult to justify whether it is a spherical island phase or an elongated domain. Presumably, it is possible that PBAT-60 can be extended along the shear direction and forms an elongated domain due to high shear forces, resulting in the alignment of phase structure along the shear direction. Namely, the PBAT/PBS blend may form a discrete phase structure under shear at 160 °C. The variation tendency of phase size at 160 °C for the PBS dispersed phase is analogous to that at 130 °C. Interestingly, for sample with the thermal treatment of 160 °C, the phase morphology gradually transforms back into a co-continuous phase structure from a "sea-island" structure at high shear rate ranging from 1000 s⁻¹ to 5000 s⁻¹, especially at 5000 s⁻¹, which has been rarely reported in other work. According to Eq. (3), the shear strain is proportional to the shear rate under the same time. Namely, the total strain increases with the increase of shear rate and the relaxation time of elongated domain is basically the same due to the equivalent cooling rate from the capillary tube outlet to air. Therefore, the higher shear rate improves the total strain under the condition of largely immobilized relaxation time for the elongated domain, resulting in larger deformation and connection of the dispersed phase. The phase morphology transition is attributed to the breakup and deformation of the formed aggregation caused by strong shear stress.

The exponential law equation reflecting the rheological properties of viscous liquids is as follows:

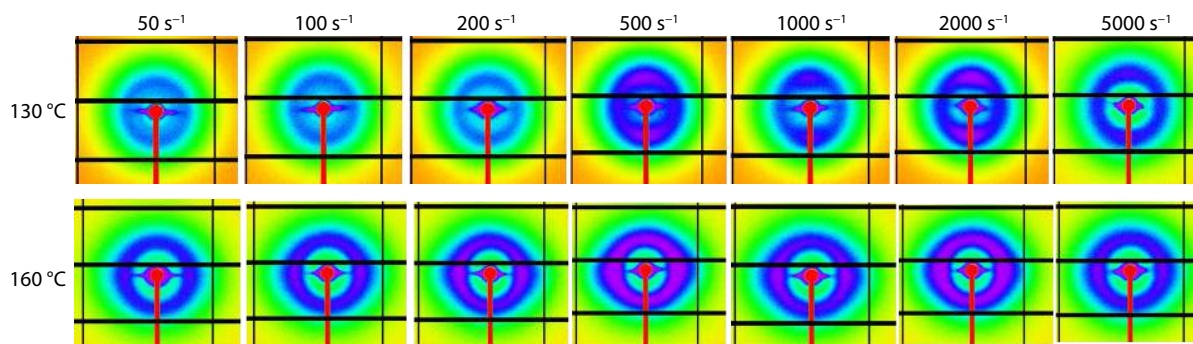


Fig. 3 Two-dimensional SAXS patterns of PBAT-60 at 130 °C and 160 °C with various shear rates of 50, 100, 200, 500, 1000, 2000, and 5000 s^{-1} . The shear flow direction is horizontal.

$$\tau = K \left(\frac{dv}{dr} \right)^n = K \left(\frac{dy}{dt} \right)^n = K \dot{\gamma}^n \quad (3)$$

where τ , γ , $\dot{\gamma}$ and dv/dr are the shear stress, the shear strain, the shear rate and the velocity gradient, respectively, and K and n represent the viscosity coefficient and flow index, respectively.

The above SEM results only qualitatively describe the phase morphology of PBAT-60 under the mechano-thermal field. Herein, the continuity of PBAT phase in PBAT-60 is quantitatively characterized. The samples cut from extruded threads at different mechano-thermal fields were immersed in tetrahydrofuran (THF) solvent to selectively remove the PBAT phase, and then the result is shown in Fig. S4 (in ESI). In agreement with the SEM, the PBAT shows 100% continuity within the whole shear rate range at 160 °C and accordingly, the PBAT is considered as matrix. It is also calculated that the continuity of PBAT gradually increases from 66.1% at 50 s^{-1} to 100% at 2000 s^{-1} at 130 °C, indicating that the shear flow induces the orientation and deformation of the PBAT phase, which promotes the dispersion of aggregated phase zone and thus improves the continuity of PBAT. To sum up, it is considered that under the condition of low-temperature thermal treatment, the co-continuous phase morphology is well maintained within the whole shear rate range and is oriented perpendicular to the flow field direction at high shear rate. Whereas the high-temperature thermal treatment causes aggregation of the PBS to form clusters with certain aspect ratios, which can evolve into a continuous phase again as the shear rate further increases. Meanwhile, the phase size of PBAT-60 at both 130 and 160 °C gradually decreased with the increase of shear rate due to the refinement and deformation of phase morphology.

Hierarchical Crystal Structure of Co-continuous Phase

To investigate the effect of mechano-thermal field on the hierarchical crystal structure of PBAT-60, the X-ray scattering/diffraction technique is used to analyze the lamellar crystallites and crystal structure at molecular scale. The 2D-SAXS patterns of samples with different shear rates at 130 and 160 °C are shown in Fig. 3. The PBS is difficult to form oriented lamellae due to a low molecular weight, leading to faster relaxation of molecular chains,^[12] so the oriented signal from the 2D-SAXS patterns represents the PBAT phase. Intriguingly, the SAXS patterns show two bulb-shaped lobes in the meridional direction, indicating that the formed lamellae are oriented perpendicular to the

shear direction at 130 °C within the shear rate range of 500–5000 s^{-1} , which is consistent with the observation by SEM. To the best of our knowledge, this lamellar orientation is completely different from the commonly observed shear-induced orientation of lamellar crystallites which is generally along the flow direction.^[30,31] At 160 °C, the lamellar crystallites are oriented along the shear flow direction and relatively uniform.

To quantitatively characterize the lamellar crystallites of PBAT-60, the electron density correlation function $K(z)$, the variation of the long period (d_{ac}), the lamellar thickness (d_c) and the amorphous thickness (d_a) of the samples with different shear rates at 130 and 160 °C are calculated, as exhibited in Fig. 4, respectively. As seen from Fig. 4(b), the d_{ac} at 130 °C decreases gradually with the increasing shear rate, but the d_{ac} at 160 °C is scarcely affected by the shear rate. Meanwhile, the former is consistently higher than the latter under the same shear rates. It is also found in Fig. 4(c) that the d_c of the sample prepared at different shear rates from 50 s^{-1} to 5000 s^{-1} at both 130 and 160 °C is in the range of 2.8–3.0 nm and has little difference, indicating that mechano-thermal field has a slight effect on lamellar thickness of PBAT-60. However, the d_a under various shear rates in Fig. 4(d) shows large differences between 130 and 160 °C. The d_a of the samples prepared at 130 °C gradually decreases from 7.5 nm to 6.1 nm. The variation of amorphous thickness at 160 °C, however, is relatively not obvious in the range of 5.7–6.3 nm with the increase of shear rate. Meantime, it is observed that the d_a at 130 °C is higher than that at 160 °C. In the case of little difference in lamellar thickness, the discrepancy of long period is mainly attributed to the difference of amorphous thickness at both temperatures. The possible reason for the difference is that the higher shear stress induced from shear action at 130 °C makes the molecular chains of the amorphous layer become straighter, resulting in the increase of the distance between the lamellar crystals (*i.e.*, the long period), but the lamellar thickness has little variation. On the other hand, shear-induced molecular chain orientation after the extrusion at 160 °C has enough time to relax and consequently the distance between the lamellar crystals is not as high as that at 130 °C.^[32]

The crystal structure information of PBAT-60 at the molecular scale under mechano-thermal field is further investigated

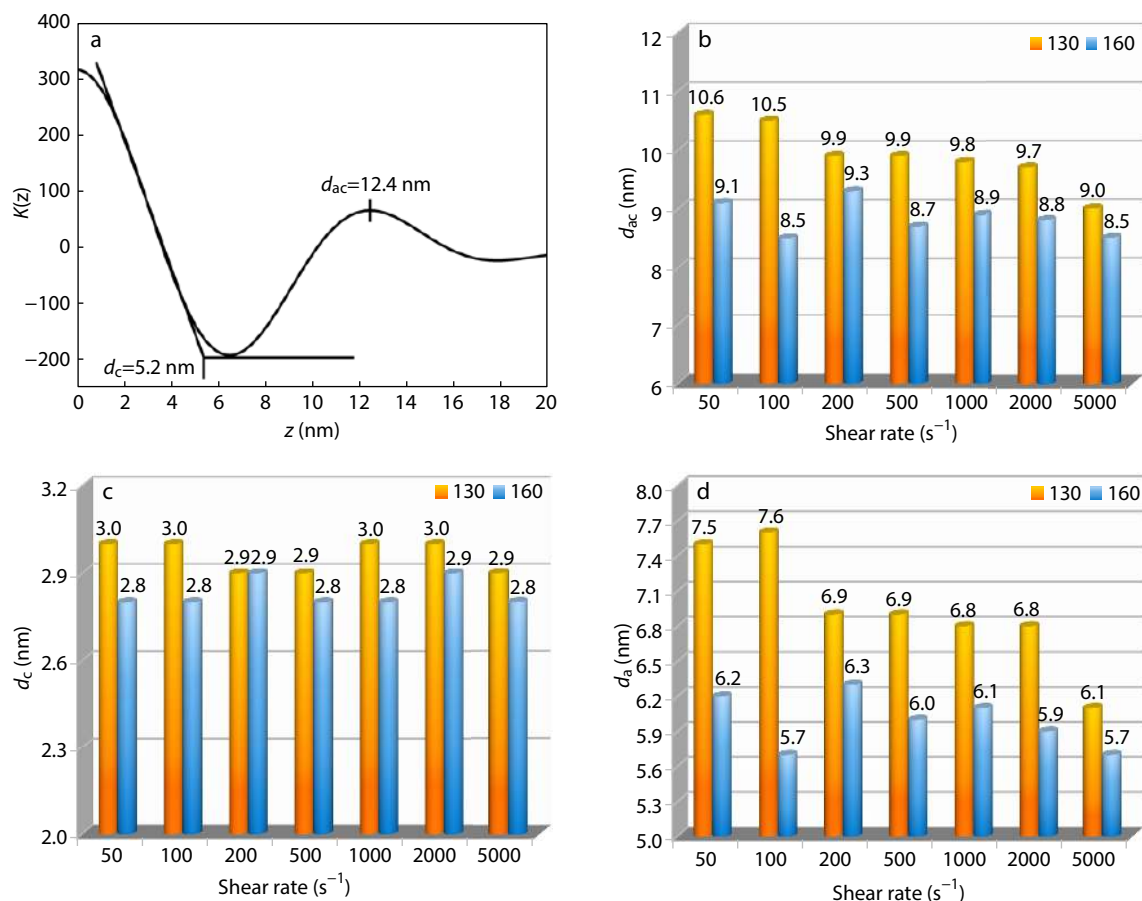


Fig. 4 Analysis of SAXS data: (a) example showing the analysis of lamellar crystallites using electron density correlation analysis; (b) long period (d_{ac}); (c) lamellar thickness (d_c) and (d) amorphous thickness (d_a) of PBAT-60 at 130 and 160 °C with various shear rates of 50, 100, 200, 500, 1000, 2000, and 5000 s⁻¹.

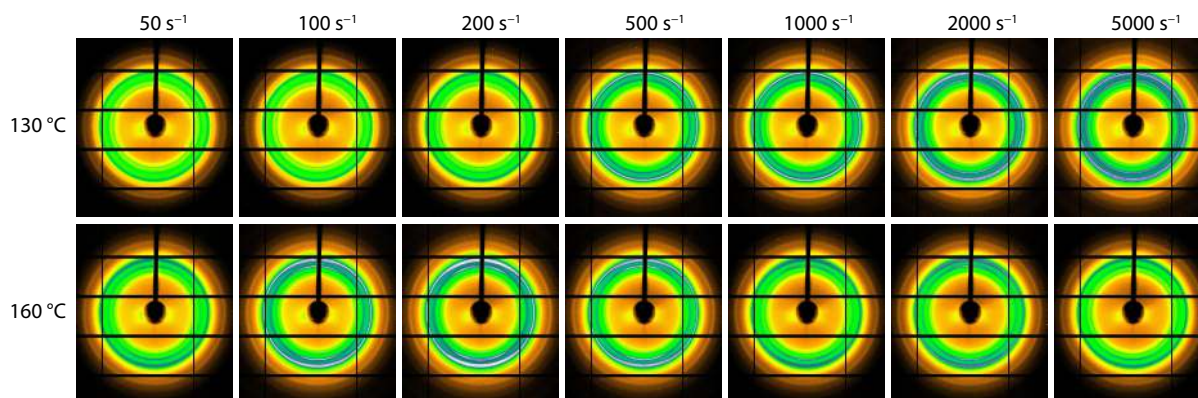


Fig. 5 Two-dimensional WAXD patterns of PBAT-60 at 130 and 160 °C with various shear rates of 50, 100, 200, 500, 1000, 2000, and 5000 s⁻¹. The shear flow direction is horizontal.

by 2D-WAXD, and the results are displayed in Fig. 5. And the 1D-WAXD intensity curves are shown in Fig. S5 (in ESI). Five distinct Bragg reflections can be observed in the 1D WAXD pattern of PBAT-60, which are assigned to the (011), (010), (102), (100) and (111) planes of PBAT α -form crystal, respectively. Three main characteristic diffraction peaks are assigned to (020), (021) and (110) planes of PBS α -form crystal, where

the (020) and (110) crystalline planes of PBS are close to the (102) and (110) planes of PBAT, respectively.^[12] After when shear flow field is applied at both 130 and 160 °C, arc-like Bragg reflections appear in the meridional direction whose strength increase first and subsequently decrease with the increase of shear rate both at 130 and 160 °C (Fig. S6 in ESI), indicating that the orientation of PBAT-60 crystals increases first

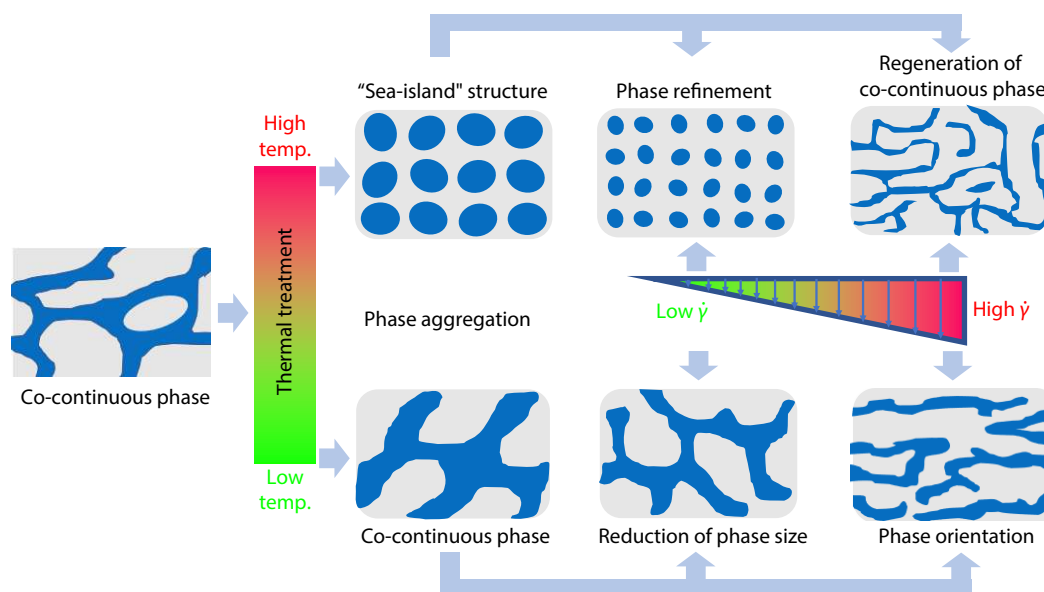


Fig. 6 Illustrations of the evolution of PBAT-60 with an initial co-continuous structure under mechano-thermal field.

and then decreases. As it is well known, the orientation of samples is more obvious at higher shear rate due to the larger shear stress. However, the degree of orientation of PBAT-60 crystals can be higher near the intermediate shear rate instead of high shear rate in the present work. The possible explanation for this phenomenon is the occurrence of shear heat and phase perturbations caused by normal stress at high shear rate, where the former promotes relaxation of the orientation and the latter disrupts the orientation. Noteworthy, the degrees of orientation at both temperatures of thermal treatment, however, are so low that it is not accurately calculated. Combining the aforementioned phase morphology with the information of the hierarchical crystal structures obtained by WAXS/SAXS, it is clear that the phase morphology is oriented perpendicular to the shear direction at higher shear rate, causing the orientation of the lamellar crystallites and the orientation of the molecular chains in crystallites.

Phenomenological Mechanism of the Evolution of the Co-continuous Phase

On the basis of the above discussion, a phenomenological mechanism is proposed as shown in Fig. 6. For a co-continuous phase structure of PBAT/PBS blend, when thermal annealing at high temperature, the molecular chains of the lower viscosity PBS are more mobile and can aggregate rapidly and form a coarsening structure, resulting in a dramatic decline of continuity and consequently evolving from co-continuous phase into a "sea-island" structure. This structure is maintained at low shear rate and the phase size is decreased due to the refinement effect caused by shear stress. However, the phase morphology gradually evolves from the "sea-island" structure back into the co-continuous phase structure at high shear rate due to large deformation of the phases induced by strong shear stress and recombination. As for thermal annealing at low temperature, the weaker molecular motility of PBS with higher viscosity does not induce rapid aggregation, and thus PBAT-60 maintains a co-continuous phase throughout the shear rate

range. At low shear rate, the phase size is also reduced due to the refinement effect. Deformation and orientation of the co-continuous phase occur along the direction parallel to the shear flow. At high shear rate, however, the co-continuous phase is oriented perpendicular to the shear direction due to negative shear normal stresses caused by strong shear force. The above evolution of phase morphology is a dynamic and continuous process within a wide shear rate range at different temperatures, indicating that the synergistic effect of mechano-thermal field could have a significant effect on the co-continuous phase structure.

CONCLUSIONS

In this work, the structural evolution of co-continuous phase of biodegradable PBAT/PBS blend induced by shear flow and thermal field is quantitatively investigated. The co-continuous phase structure is retained throughout a wide shear rate range at a thermal annealing temperature of 130 °C. However, this co-continuous phase transforms into a "sea-island" structure under low shear rates at 160 °C and gradually returns to co-continuous phase again in the shear rate range from 1000 s⁻¹ to 5000 s⁻¹. Furthermore, the phase size decreases with the increase of shear rate at both 130 and 160 °C. Interestingly, the co-continuous phase is oriented perpendicular to the shear flow direction in the shear rate range of 500–5000 s⁻¹ at 130 °C and only under the shear rate of 5000 s⁻¹ at 160 °C. Meanwhile, the hierarchical crystal structures of co-continuous phase are formed under mechano-thermal field. It is found that the PBAT/PBS can form oriented lamellar crystallites under mechano-thermal field. At 160 °C, the lamellar orientation is parallel to the shear direction at the whole shear rate range. Unexpectedly, a novel phenomenon occurs that the lamellar orientation is perpendicular to the shear direction in the shear rate range of 500–5000 s⁻¹ at 130 °C. Both the long period and amorphous thickness of the lamellar crystallites at 130 °C are much larger than those at 160 °C under the same

shear rate due to the fact that the higher shear stress at 130 °C makes the molecular chains of the amorphous layer straighter resulting in the increase of the long period and the amorphous thickness, but the lamellar thickness has little variation. On the other hand, shear-induced molecular chain orientation after the extrusion at 160 °C has enough time to relax and consequently the distance between the lamellar crystals is not as high as that at 130 °C. The crystal structure of PBAT/PBS blend at the molecular scale is also obtained. Degree of molecular orientation in crystallites can be higher near the middle shear rate instead of under high shear rates due to the occurrence of shear heat and phase perturbations caused by normal stress at high shear action, where the former promotes relaxation of the orientation and the latter disrupts the orientation. These understandings have great academic significance for the regulation of crystal structure orientation of other co-continuous systems and also provide guidance for the preparation of high performance PBAT/PBS blend.

NOTES

The authors declare no competing financial interest.



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/s10118-022-2690-8>.

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