**ABSTRACT:** Poly(glycolic acid) (PGA) is a semicrystalline biodegradable polyester with high gas barrier properties. However, due to its poor processability and low ductility, PGA could hardly find applications in the packaging field. Here, a strategy was adopted for *in situ* generation of high-aspect-ratio flexible microfibres with strong interface affinity for the PGA matrix. Because poly(butylene adipate-co-terephthalate) (PBAT) possesses impressive ductility, it was selected as the "fibrillar toughening phase" to enhance the ductility of PGA. Moreover, a chain extender was used to enhance the interfacial adhesion between the two polymers. The extrusion blown film technique was then used to develop fully biodegradable PGA/PBAT films with a superior combination of excellent barrier performance and robust mechanical properties. The PBAT phase can *in situ* form microfibres under the influence of extensional flow. Simultaneously, the synergetic function of the extensional flow field could effectively promote the motion of the PGA molecular chain to develop an oriented crystalline microstructure. Because of the aligned oriented lamellar crystal of PGA and oriented PBAT fibril structures serving as robust "barrier walls" 60PGA/ADR blown films demonstrated dramatically improved resistance to oxygen and water vapor, with 59 and 44 times lower oxygen permeability and water vapor permeability, respectively, when compared to the neat PBAT blown film. As a result, PGA/PBAT blown films offer a variety of benefits, including superior ductility, toughness, and a strong gas barrier property. The potential of these films to degrade makes them a viable contender for replacing classical nondegradable packaging films.

1. **INTRODUCTION**

The high gas barrier packaging materials are important for extending the shelf life of food, beverage, dairy, pharmaceutical, and cosmetic items, as well as any other products that need lower oxidative reaction rates and moisture control. 1,2 Currently, biodegradable packing material films such as polymers made up of butylene succinate (PBS), poly(butylene adipate-co-terephthalate) (PBAT), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and poly(lactic acid) (PLA) are extensively investigated. 3−6 Among these, PLA has been extensively investigated to enhance its barrier performance to gas, ranging from compounding with other biodegradable polymers, impermeable nanoclays, or graphene oxide (GO) to controlling microstructures. 7,8 Previously, Zhou et al. successfully fabricated PLA/PBAT composite films with outstanding barrier and mechanical properties using "slit die extrusion stretching thermal treatment" methods. The PLA/PBAT (85/15) film showed about an 89% reduction in O₂ permeability compared to the neat PLA film. 9 In addition, the dispersion of organically modified montmorillonite and GO into the PLA matrix also is an effective way of enhancing gas barrier performance. 10,11 However, when adding nanofillers to a polymer matrix, the improvement in barrier performance is not
obvious when the addition amount is small; however, when the addition amount is large, the nanofillers agglomerate and cannot be dispersed in the matrix.2,8,12 Furthermore, nanofillers have a limited ability to increase the ductility of PLA films.13 Consequently, it is nevertheless an incredible challenge to develop an approach that might afford robust PLA-based packaging films that correspond to metalized packaging films with high-quality barrier properties and ductility. Therefore, developing a degradable polymer with good barrier properties can fundamentally solve this problem.

Poly(glycolic acid) (PGA) is a semicrystalline biodegradable polyester with good mechanical strength and barrier properties. The gas barrier performance of PGA is 1000 times that of PLA and 100 times that of PET.14,15 Due to the poor processability and low ductility, PGA is hardly used in packaging as compared to PLA.15–19 Recently, several studies have reported the preparation and gas barrier properties of PBAT/PBA composite films with PGA as a minor component (<50%).20–22 However, if PGA is the minor component, its excellent gas barrier performance has not been well developed and applied. As a result of the poor barrier properties of PBAT, it is essential to make PBAT a minor component. At present, there is no research report on the preparation of a PGA/PBAT composite film with PGA as the main component by the continuous method, such as using extrusion casting or extrusion blowing methods. This is mainly because the inherent brittle nature and poor melt strength of PGA severely limit its processing. The difference between the melting temperature Tm (220 °C) and crystallization temperature (Tc = 192–198 °C) of PGA is relatively small.23 For the extrusion and blown films, the rapid crystallization of melt after cooling will make it difficult to obtain the film with an oriented crystalline microstructure.

In this study, an in situ strategy for the generation of high-aspect-ratio flexible sub-micron scale fibrils with strong interface affinity with the PGA matrix was adopted to overcome the brittle nature of PGA. Previously, Kowalczuk et al.24 confirmed that the degradation products of the PBAT are harmless to the plants. Moreover, a food-grade chain extender with epoxy groups, styrene-glycidyl methacrylate oligomer (ADR 4468), was used to reactively compatibilized PGA and PBAT during the blending process.25 It has been widely used as a reactive compatibilizer in immiscible polyester blends, and can forms copolymers at the interface of the blends during the extrusion process. This work aims to tailor a dispersed PBAT droplet phase for in situ microfibril formation by manipulating the rheological properties of the melts and employing extensional flow. Simultaneously, to develop an oriented crystalline microstructure, the motion of the PGA molecular chain could be effectively promoted by the synergistic function of the extensional flow field. Usually, under specific processing conditions, the microfibrillar structure would be formed mainly depending on the rheological and thermal conditions of the melts.26,27 The different processing conditions, including hot-pressing and extrusion blowing processes, under the influence of the in situ PBAT fibril generation, crystalline structure, and mechanical properties of the resulting films were completely investigated. Ultimately, biodegradable PGA/PBAT films, with PGA as the main component, combining excellent ductility, proper strength, and superior gas barrier performance were successfully prepared.

2. EXPERIMENTAL SECTION

2.1. Materials. PBAT (Ecoworld) was kindly supplied by Jinhui Zhaolong High Tech Co., Ltd (Shanxi, China), with a density of 1.23 g/cm³ and MFR of 21.7 g/10 min (230 °C, 2.16 kg). PGA was provided by Shanghai Pujing Chemical Industry Co., Ltd (Shanghai, China), with a density of 1.51 g/cm³ and MFR of 31.6 g/10 min (230 °C, 2.16 kg). Styrene-glycidyl methacrylate oligomer (ADR 4468) was purchased from BASF (German), with an epoxy equivalent weight of 285 g/mol. Dichloromethane (DCM) was purchased by Honeywell Trading Co., Ltd. (Shanghai, China).

2.2. Preparation of Blend Pellets. PBAT and PGA were dried under vacuum at 80 °C for 12 h before use. The formulations of PGA/PBAT composites with and without chain extender are listed in Table 1. All of the formulations were compounded in a twin-screw extruder with a screw diameter of 30 mm and an L/D ratio of 32. The melt compounding temperature from zone one to zone eight was independently controlled to achieve a temperature profile in the range of 180–230 °C. The screw speed was set at 50 rpm.

2.3. Hot-Pressed Films. First, all of the compositions and neat polymers were made into hot-pressed films. The pellets were pressed under vacuum at 2 tons and 220 °C for 300s between two nonstick metal sheets using a ZG-20T press. The hot-pressed films were then cooled at room temperature and pressed films were obtained. The thickness of the pressed films is about 80 ± 5 μm.

2.4. Blown Films. Then, the compositions of 60PGA/ADR formulations were further made into blown films. The blown films were prepared by a single screw extruder (Kechuang, China, LSJ20), with a 25 mm-diameter screw and an L/D ratio of 22. The processing temperature in different zones was set in the range from 215 to 220 °C. The screw speed was set at 25 RPM and the blow-up speed was set to 1.5 m/min. The thickness of the blown films is about 40 ± 5 μm.

2.5. Characterizations. Before tensile testing, the film samples were placed at room temperature for 24 h and then the samples were tested with an electronic universal testing machine (Mester Industrial Systems Limited Corporation, CMT6104) controlled by a microcomputer. The distance of the clamp was set to 50 mm, and the stretching speed was 10 mm/min. Each group of samples was tested at least 5 times and the average value was calculated along with the standard deviation.

Table 1. Formulations of PGA/PBAT Composites Prepared in this Work

| Samples       | PGA (wt %) | PBAT (wt %) | ADR (phr) |
|---------------|------------|-------------|-----------|
| PBAT          | 0          | 100         |           |
| PGA           | 100        | 0           |           |
| 80PGA         | 80         | 20          |           |
| 20PGA         | 20         | 80          |           |
| 40PGA         | 40         | 60          |           |
| 40PGA/0.5ADR  | 40         | 60          | 0.5       |
| 40PGA/1.0ADR  | 40         | 60          | 1.0       |
| 40PGA/1.5ADR  | 40         | 60          | 1.5       |
| 60PGA         | 60         | 40          |           |
| 60PGA/0.5ADR  | 60         | 40          | 0.5       |
| 60PGA/1.0ADR  | 60         | 40          | 1.0       |
| 60PGA/1.5ADR  | 60         | 40          | 1.5       |
The rheological characteristics of the composites were determined using a plate rheometer (Anton Paar, MCR-502, Austria). As a function of angular frequency, the viscosity, storage modulus, and loss modulus of the blend materials were measured at 240 °C in the dynamic mode, using parallel plate geometry (50 mm in diameter) with a gap between the two plates of 1 mm. The strain amplitude was selected to be within the linear viscoelastic range. Chain extension reactions between the chain extender and the polymers were characterized using a PerkinElmer 782 Fourier transform spectrometer.

The crystallization behavior of samples was determined on a differential scanning calorimetry (DSC) analyzer (TA2500). Under a N2 atmosphere (flow rate: 50 mL/min) at a heating rate of 10 °C/min from −50 to 250, the scans were performed. The degree of crystallinity (χc) was determined using the first heating cycle. The χc of PGA was calculated by

\[ \chi_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \]  

where \( \Delta H_m \) is the melting enthalpy (J/g), and \( \Delta H_m^0 \) is the melting enthalpy of completely crystalline PGA (\( \Delta H_m^0 = 183.2 \) J/g), and w% is the weight ratio of PGA within the composites.

The cryo-fractured surfaces of pressed films and blown films were observed using a scanning electron microscope (FEI Company, Quanta 250 FEG). To better observe and research the micromorphology and dispersion of two phases, the cryo-fractured surfaces of the samples were etched with DCM at room temperature for 30 min to selectively resolve and remove the PBAT phase. Then, these etched surfaces were sputter-coated with a thin layer of gold prior to scanning electron microscopy (SEM) observation.

The wide-angle X-ray diffractometry (WAXD) was performed on a Bruker D8 Advance X-ray diffractometer between 3 and 40°, with 5° min⁻¹ scanning rate and 1.54 Å Cu Kα radiation wavelength. Small-angle X-ray scattering (SAXS) was conducted at the SAXSess mc² (Bruker-AXS Nanostar) with a 30 W microfocus Incoatec IμS Cu source and 1.54 Å of Cu Kα radiation wavelength. The generator was operated at 50 kV and 600 μA, and the detector-sample distance was 1070 mm.

The pole figures of the samples were tested by the Schulz back-reflection method on an X-ray diffractometer (Panalytical Xpert MRD, Cu target voltage, 40 kV, current 40 mA). Three incomplete pole figures (\( 0^\circ \leq \alpha \leq 70^\circ, 0^\circ \leq \beta \leq 360^\circ \)) were measured for each diffraction plane: (110) and (020) for PGA (diffraction angle 2θ = 22.06 and 28.7°). According to the polar figures of (110) and (020), the polar figure of (002) can be calculated from the orientation distribution function (ODF) using MulTex software.

According to ASTM D3985, the PGA/PBAT film with an area of 10 cm² was tested by an oxygen permeability tester (VAC-V1, Jinan Languang Electromechanical Technology Co., Ltd.) under the experimental conditions of 23 °C and 30% relative humidity. Each test was performed three times and the average value was calculated. The water vapor barrier properties of PBAT/PGA films were tested by water vapor permeometer (C360M, Jinan Languang Electromechanical Technology Co., Ltd.) according to GB/T 1037 at 38 °C and 90% relative humidity (RH). Individual groups of samples were tested three times, and the average value was taken according to the effective value.

3. RESULTS AND DISCUSSION

The branching and chain extension reactions between PGA/PBAT and ADR were determined by Fourier transform infrared (FTIR) spectra. As shown in Figure 1, the characteristic absorption peaks of the epoxy group in the ADR are approximately 843 and 907 cm⁻¹. These two peaks cannot be observed in the spectrum of the 60PGA/1.0ADR sample, which suggests the successful ring-opening reaction between the epoxy groups of ADR and the carboxyl or hydroxyl end groups of PGA and PBAT. The reaction mechanism between PGA, PBAT, and ADR is illustrated in Figure 2.

3.1. Tensile Properties of Hot-Pressed Films. Thanks to its easy molding method, hot-pressed films with varying ratios of PGA and PBAT were prepared first. The tensile properties of neat PGA, neat PBAT, and variable-ratio PGA/PBAT pressed films are shown in Table 2. Lower flexibility and excellent strength properties were observed for PGA. It can also be seen that the tensile strength (TS) and the tensile modulus (TM) of the PGA/PBAT blends decreased significantly, while the elongation at break (EB) increased less significantly with increasing PBAT content from 20 to 80 wt %. As calculated by the group contribution method, the solubility parameters of PGA and PBAT are 23.8 and 22.2 MPa⁻¹/², respectively. Although there is little difference between solubility parameters of PGA and PBAT, the PGA/PBAT blend shows less interaction and poor compatibility due to the strong chain interaction and high crystallization ability of PGA molecular chains. Hence, interfacial compatibility of PGA and PBAT could be increased by the addition of the reactive compatibilizer. PGA/PBAT blends prepared at a ratio of 60/40 and 40/60 were selected to fabricate pressed films in the presence of ADR compatibilizer. The mechanism of the reaction between ADR, PGA, and PBAT is shown in Figure S1.

The tensile properties of PGA/PBAT hot-pressed films with different ratios of compatibilizer are presented in Table 3. In the case of the PGA/PBAT blend with a ratio of 40/60 and 60/40, it is observed that the EB is gradually increased with increasing addition amount of ADR. TS is also improved compared to PGA/PBAT blends with ratios of 40/60 and 60/40, in formulations without the chain extender. These improvements in tensile properties demonstrate the improved interfacial adhesion between PGA and PBAT due to the formation of an ester bond at the interface with the addition of
ADR. Next, these 60PGA/ADR blends were used to fabricate blown films.

3.2. Tensile Properties of the Blown Films. As a comparison with hot-pressed films, the mechanical properties of 60PGA/ADR blown films were studied and the results are listed in Table 4, as well as shown in Figure 3. The results presented a decrease in TS and an increase in EB with the increase of ADR content in both machine direction (MD) and transverse direction (TD). With the increase in ADR content, some unreacted ADR molecules play a role in the lubrication and plasticizing effect, so the EB increased, while TS decreased. When under the same component, the EB of blowing films in the MD was about 10−15 times and was about 3−4 times higher in the TD than that of hot-pressed films. These remarkable differences in EB imply that the two different hot-pressing and extrusion blowing methods will significantly influence the microstructure of the films.

3.4. Rheological Properties of the Blends. The rheological properties of neat PGA, neat PBAT, 60PGA, and 60PGA/ADR blends were characterized to investigate the effect of compatibilizer and its amount on the complex viscosity, storage modulus, and loss modulus of blends. Viscoelastic behavior of PGA, PBAT, and their blend melts is a combination of irreversible viscous flow due to polymer chain slippage and reversible elastic deformation due to molecular entanglement.

Table 2. Tensile Properties of PGA/PBAT Hot-Pressed Films with Different Mass Ratios of PGA and PBAT

| samples          | tensile strength (MPa) | elongation at break (%) | tensile modulus (GPa) |
|------------------|------------------------|-------------------------|-----------------------|
| PBAT             | 18.8 ± 1.3             | 822 ± 48                | 0.05 ± 0.005          |
| PGA              | 102.2 ± 11.5            | 0.51 ± 0.07             | 10.3 ± 2.1            |
| 20PGA            | 11.5 ± 3.2              | 75.4 ± 5.5              | 0.15 ± 0.04           |
| 40PGA            | 14.1 ± 2.5              | 5.04 ± 0.8              | 0.68 ± 0.12           |
| 60PGA            | 38.0 ± 2.2              | 1.7 ± 0.2               | 3.5 ± 0.3             |
| 80PGA            | 68.6 ± 5.6              | 0.58 ± 0.05             | 11.2 ± 2.7            |

Table 3. Tensile Properties of PGA/PBAT Hot-Pressed Films with ADR

| samples          | tensile strength (MPa) | elongation at break (%) | tensile modulus (GPa) |
|------------------|------------------------|-------------------------|-----------------------|
| 40PGA/0.5ADR     | 28.4 ± 1.6             | 8.2 ± 1.6               | 1.19 ± 0.11           |
| 40PGA/1.0ADR     | 28.9 ± 1.4             | 24.0 ± 2.1              | 0.86 ± 0.04           |
| 40PGA/1.5ADR     | 30.6 ± 1.3             | 56.0 ± 3.6              | 0.79 ± 0.06           |
| 60PGA/0.5ADR     | 47.5 ± 2.7             | 8.7 ± 0.5               | 4.8 ± 0.5             |
| 60PGA/1.0ADR     | 47.7 ± 3.3             | 11.0 ± 1.7              | 3.9 ± 0.2             |
| 60PGA/1.5ADR     | 46.5 ± 1.5             | 16.4 ± 0.9              | 3.7 ± 0.3             |

ADR. Next, these 60PGA/ADR blends were used to fabricate blown films.

3.2. Tensile Properties of the Blown Films. As a comparison with hot-pressed films, the mechanical properties of 60PGA/ADR blown films were studied and the results are listed in Table 4, as well as shown in Figure 3. The results presented a decrease in TS and an increase in EB with the increase of ADR content in both machine direction (MD) and transverse direction (TD). With the increase in ADR content, some unreacted ADR molecules play a role in the lubrication and plasticizing effect, so the EB increased, while TS decreased. When under the same component, the EB of blowing films in the MD was about 10−15 times and was about 3−4 times higher in the TD than that of hot-pressed films. These remarkable differences in EB imply that the two different hot-pressing and extrusion blowing methods will significantly influence the microstructure of the films.

3.4. Rheological Properties of the Blends. The rheological properties of neat PGA, neat PBAT, 60PGA, and 60PGA/ADR blends were characterized to investigate the effect of compatibilizer and its amount on the complex viscosity, storage modulus, and loss modulus of blends. Viscoelastic behavior of PGA, PBAT, and their blend melts is a combination of irreversible viscous flow due to polymer chain slippage and reversible elastic deformation due to molecular entanglement.

Table 4. Mechanical Properties of Neat PBAT and 60PGA/ADR Blown Films

| samples          | MD          | TD          | MD          | TD          |
|------------------|-------------|-------------|-------------|-------------|
| PBAT             | 17.7 ± 0.43 | 15.9 ± 0.31 | 637.6 ± 8.58| 547.4 ± 13.57|
| 60PGA/0.5ADR     | 47.76 ± 0.78| 31.43 ± 0.69| 71.81 ± 4.71| 35.38 ± 0.91 |
| 60PGA/1.0ADR     | 40.87 ± 0.51| 29.48 ± 1.90| 240.07 ± 7.59| 42.95 ± 0.71 |
| 60PGA/1.5ADR     | 37.19 ± 0.81| 23.57 ± 1.41| 281.71 ± 7.84| 43.68 ± 2.65 |

Table 5 shows terminal zone slopes of PBAT, PGA, and PGA/PBAT melts from the master curves for $G'$ and $G''$ (Figure 4a,b) at lower frequencies ($\omega < 10$ rad/s). In the terminal region of the curves, the slopes of $G'$ and $G''$ of neat
PGA melt are 0.86 and 0.84, respectively. For neat PBAT, the slopes of $G'$ and $G''$ are 1.35 and 0.96, respectively. PBAT melt curves show higher slopes than that of PGA. PBAT is a known copolymer of butylene, terephthalate, and adipate. It has a more flexible molecular chain than PGA and can easily entangle.33 Because the entanglement density is higher than that of PGA, the melts exhibit high reversible elastic deformation ($G'$). For the PGA/PBAT blend, the incorporation of 40 wt % PBAT into PGA will decrease the slopes of PGA. This is mainly because the relaxation of PBAT structures with high entanglement density is partially prevented by the PGA molecular chain. As a result, the terminal slopes of 60PGA decrease with the addition of PBAT. While for PGA/PBAT blends with ADR, these two values are considerably lower, and for 60PGA/1.0ADR they are the lowest among all blends with ADR. The formation of more entanglement structures in blend melts is indicated by lower slope values and higher absolute values of dynamic moduli.33 This indicates that the most entanglement structures were formed in the 60PGA/1.0ADR structure. The results showed that the addition of ADR caused chain extension or branching reaction and increased the density of entanglement in the PGA/PBAT blends.34,35 However, when the amount of ADR was 1.5 phr, the slopes increased. This may be because some unreacted ADR played a role in lubrication and a plasticizing effect in the melt structure.

As shown in Figure 4c, the compatibilized blends have a higher complex viscosity than the uncompatibilized blends due to the restriction of molecular mobility and the decrease in free volume caused by the interfacial interaction.36 Additionally, all of the curves in Figure 4c exhibited shear-thinning behavior. Moreover, the viscosities of compatibilized blends tended to be lower than that of neat PBAT with the increase of shearing frequency. This is primarily because the complex viscosity of PGA/PBAT blends is caused by two factors: (1) the interfacial adhesion of PGA and PBAT and (2) the entanglement density of the molecular chain itself. The interfacial adhesion between PGA and PBAT played a significant role in the viscosity at low frequencies. However, the entanglement density of neat PBAT is more obvious than blends with the further increase in frequency. Therefore, neat PBAT shows higher viscosity than compatibilized blends.

3.5. Morphologies of the Pressed Films and Blown Films. Figure 5 depicts the etched cryo-fractured surface morphologies of both pressed films and blown films (along the MD). The PBAT phase was etched away in DCM and the residual phase is the crystalize and amorphous region of PGA. Obviously, in the case of 60PGA/ADR pressed films (Figure 5a−c), the morphology of PBAT is droplets in the PGA matrix.

Table 5. Rheology Characteristics of Neat PBAT, Neat PGA, and 60PGA Blends (with and without ADR)

|                 | PBAT | PGA | 60PGA | 60PGA/0.5ADR | 60PGA/1.0ADR | 60PGA/1.5ADR |
|-----------------|------|-----|-------|--------------|--------------|--------------|
| terminal region slope of $G'$ | 1.35 | 0.86 | 0.83  | 0.41         | 0.30         | 0.37         |
| terminal region slope of $G''$  | 0.96 | 0.84 | 0.75  | 0.58         | 0.49         | 0.66         |

Figure 4. (a) Storage modulus, (b) loss modulus, and (c) complex viscosities ($\eta^*$) of PGA/PBAT (60/40) blends, neat PGA, and neat PBAT.
Figure 5. SEM images of the etched cryo-fractured surface of 60PGA/ADR pressed films: (a) 60PGA/0.5ADR, (b) 60PGA/1.0ADR, and (c) 60PGA/1.5ADR. SEM images of the etched cryo-fractured surface along the MD of 60PGA/ADR blown films: (d) 60PGA/0.5ADR, (e) 60PGA/1.0ADR, and (f) 60PGA/1.5ADR.

Figure 6. WAXD (a, b) and SAXS (c, d) of blown films (a, c) and pressed films (b, d).
Table 6. Structural Parameters of 60PGA/ADR Blown Films and Pressed Films

|          | $q_{\text{max}}$ ($\text{Å}^{-1}$) | $X_{\text{c-PGA}}$ (%) | $d_{\text{ac}}$ (Å) | $d_{\text{a}}$ (Å) | $d_{\text{c}}$ (Å) |
|----------|-----------------------------------|------------------------|----------------------|---------------------|-------------------|
| blown films |                                   |                        |                      |                     |                   |
| 60PGA/0.5ADR | 0.058                            | 52.3                   | 107.6                | 56.3                | 51.3              |
| 60PGA/1.0ADR | 0.058                            | 49.4                   | 107.6                | 53.1                | 54.4              |
| 60PGA/1.5ADR | 0.064                            | 45.5                   | 98.0                 | 44.6                | 53.4              |
| pressed films |                                  |                        |                      |                     |                   |
| 60PGA/0.5ADR | 0.057                            | 58.7                   | 110.3                | 64.7                | 45.5              |
| 60PGA/1.0ADR | 0.057                            | 57.6                   | 110.3                | 63.5                | 46.8              |
| 60PGA/1.5ADR | 0.051                            | 56.8                   | 122.5                | 69.6                | 52.9              |

\[ d_{\text{c}} = d_{\text{ac}} \times X_{\text{c-PGA}} \]  
(3)

\[ d_{\text{a}} = d_{\text{ac}} - d_{\text{c}} \]  
(4)

In the case of blown films, however, the elongated and fibrillar structure of PBAT appears to have been established (Figure 5d–f). Only oriented fibrillar embossment can be seen in blown films, which appears to be distinct from typical sea island phase morphology in pressed films, resulting in favorable interfacial interaction between PGA and PBAT. Therefore, the morphology changes from droplets in pressed films to elongated and fibrillar structures in blown films explain the increase in the EB of the machine direction. In addition, with the increase of the ADR content, the length and number of pores decrease significantly, and the decrease of the PBAT phase indicates that more PBAT and PGA are connected by ADR.

As mentioned above, debonding and internal cavitation are the proposed mechanism for toughening 60PGA/ADR blends. Because of the elongated and fibrillar structure of PBAT, the interfacial adhesion between the PGA matrix and PBAT fibrillar phases was enhanced in blown films. Thus, stress and strain can be more efficiently transferred from the PGA matrix to the PBAT phase, resulting in increasing ductility of the films. In the following section, the crystalline structure and barrier performance of 60PGA/ADR blown films and pressed films were made for comparison.

### 3.6. Crystalline Structures

As discussed above, an imbalance in the mechanical properties in MD and TD of the blown film is observed (Figure 3). When stretched in TD, the film ruptures relatively brittlely, whereas in MD, the film ruptures in a ductile manner. This behavior indicates that the films have an imbalanced oriented crystalline structure in two directions. To illustrate the crystalline morphology, WAXD and SAXS were performed to analyze the crystal structure and macrostructure of 60PGA/ADR blown films and pressed films, as demonstrated in Figure 6. Comparing Figure 6a,b, it is found that there is the absence of the (002) crystal plane diffraction peak in the WAXD diagram of the blown film samples, while it can be observed in the pressed film samples. Based on the reported crystal lattice of PGA, the 002 planes of PGA can only be detected on meridional X-ray diffraction profiles. This indicates that PGA crystals in blown films were more oriented than in pressed films.

Figure 6c,d shows the SAXS intensity profiles of blown films and pressed films, which can be used to quantitatively analyze the feature of the oriented lamellar crystalline superstructure. From the $q$ value of the peak in Figure 6c,d, the long period can be obtained. The long period $d_{\text{ac}}$ (Å), defined as the thickness of the crystal layer along with one interlamellar amorphous layer, was calculated using Bragg’s eq 2

\[ d_{\text{ac}} = \frac{2\pi}{q_{\text{max}}} \]  
(2)

Eqs. 3 and 4 can be used to calculate the crystal layer thickness $d_{\text{c}}$ (Å) and the amorphous layer thickness $d_{\text{a}}$ (Å) as summarized in Table 6.

### 3.7. Barrier Properties

Table 7 summarizes the oxygen and water vapor transport performance of 60PGA/ADR blown films and pressed films. Compared with the oxygen permeability ($P_{\text{O}_2}$) of pressed films, the $P_{\text{O}_2}$ of blown films is almost one order of magnitude lower than that of the former. In particular, the 60PGA/1.5ADR blown film exhibited a low permeability value of 0.016 Barrer, which was about 59 times lower than that of the neat PBAT films. The $P_{\text{O}_2}$ of both blown films and pressed films decreases with the increase of the ADR content in the 60PGA/ADR composite. This is due to the improved interfacial adhesion between the PGA matrix and PBAT segments in the amorphous phase and compatibility improved in the formed blends. Moreover, with the increase in the ADR content, the crystallinity and enthalpy of crystallization were decreased. It indicates that the chain extension reaction led to the increase of molecular weight, which resulted in the impeding mobility of the entangled chain, and an inhibited crystal growth process. It is interesting to point out that according to the structural data in Table 6, the crystallinity and crystal layer thickness of PGA in blown films are lower than those of pressed films. This may be because the crystallization rate slows down under the action of the elongational flow field.
to the improved interfacial adhesion between the PGA matrix and the PBAT phases, which effectively reduces the diffusion path of gas molecules due to the blocking effect. Figure 6 depicts the different mechanisms of gas penetration through pressed films and blown films. The gas molecules would take a lesser and more tortuous path through blown films with PGA oriented lamellar crystal and oriented PBAT fibril structures, whereas in pressed films it takes a more direct and less tortuous path due to dispersed PGA spherulites and granular PBAT.

Further, a comprehensive performance comparison of 60PGA/ADR blown films in this work with other reported blown films containing PGA was studied. Shen et al.20 used a chain extender ADR 4370s to compatibilize different ratios of PGA and PBAT. For 65/35/0.9 PBAT/PGA/ADR 4370s pressed film, the oxygen permeability was 0.437 Barrer. Very recently, Sanantaray et al.21 used glycidyl methacrylate (GMA) as a compatibilizer and prepared a blown film. For the PBAT/PGA/GMA (80/20/2) film, the oxygen permeability was 1.081 Barrer. After post-modification by electron beam treatment, the oxygen permeability of this film was reduced to 0.866 Barrer. Ellingford et al.22 used a terpolymer of ethylene, methyl acrylate, and glycidyl methacrylate (EMA-GMA) (commercially Lotader AX8900) to compatibilize 50/50 PGA/PBAT blends. For 50/50/20PGA/PBAT/AX8900 pressed film, the oxygen permeability was 1.581 Barrer. Based on the result of these works, the relatively lower gas barrier performance of PBAT/PGA/chain extender films mainly due to PGA as the minor component.

In addition, we also studied a comprehensive performance comparison of 60PGA/ADR blown films of this work with current commercially used packing films, such as low-density polyethylene (LDPE), biaxial-oriented polypropylene (BOPP), polystyrene (PS), poly(ethylene terephthalate) (PET), aluminum foil, etc. As illustrated in Figure 9, due to the outstanding ductility, high gas barrier performance, and appropriate tensile strength, the 60PGA/ADR blown film shows superiorly comprehensive properties to those of petroleum-based

Table 7. Oxygen and Water Vapor Transport Performance of 60PGA/ADR Blown Films and Pressed Films

| samples      | OTR (cm³/m²·24 h) | O₂ permeability (Barrer) | WVTR g/(m²·day) | WVP (10⁻¹⁴ g·cm²/cm²·s·Pa) |
|--------------|-------------------|-------------------------|-----------------|---------------------------|
| blown films  |                   |                         |                 |                           |
| PBAT         | 375.2             | 0.941                   | 884.08          | 52.8                      |
| 60PGA/0.5ADR | 35.52             | 0.032                   | 14.57           | 1.19                      |
| 60PGA/1.0ADR | 27.83             | 0.021                   | 23.86           | 1.72                      |
| 60PGA/1.5ADR | 22.52             | 0.016                   | 17.83           | 2.39                      |
| pressed films|                   |                         |                 |                           |
| 60PGA/0.5ADR | 59.91             | 0.129                   | 19.74           | 5.19                      |
| 60PGA/1.0ADR | 59.00             | 0.120                   | 15.07           | 6.99                      |
| 60PGA/1.5ADR | 46.05             | 0.077                   | 28.36           | 8.53                      |

1 Barrer = 1 × 10⁻¹⁰ cm³ (STP) cm²/s cm Hg.
Table 8. Water Vapor Permeability and Oxygen Permeability of Packaging Films

| samples                        | OTR (cm²/m²·24 h) | O₂ permeability (Barrer) | WVTR (g/(m²·day)) | WVP (10⁻¹⁵g·cm²/ Pa) | TS (MPa) | EB (%) |
|--------------------------------|-------------------|--------------------------|-------------------|----------------------|----------|-------|
| PBAT/PGA/ADR (65/35/0.9)²⁰     | 0.437             | 703                      | 240               | 19.25                | 10.3     | 498.1 |
| PBAT/PGA/GMA (80/20/2)²¹       | 1.081             | 504                      | 237               | 18.1                 | 541.2    |       |
| PBAT/PGA/GMA (80/20/20-250 Kgs²¹ | 0.866             | 300                      | 145.0             | 29.9                 | 797      |       |
| PBAT/Ag₂O₃                   | 0.51              | 145.0                    | 19.4              | 19.0                 | 600      |       |
| PBAT/mTiO₂                   | 0.29              | 230                      | 253.0             | 25.9                 | 981      |       |
| PBAT/M9S₂·ST0.7²¹            | 2.13              | 57.4                     | 32.0               | 105                  |          |       |
| PBAT/GONS                    | 1.086             | 21280                    | 94.0               | 254                  |          |       |
| PBAT/zeolite SA³³            | 0.008             | 300                      | 28.5               | 1150                 |          |       |

polymers. We also compared the comprehensive performance of 60PGA/ADR blown films with other nanosheets or nanoparticle-modified PBAT films, as summarized in Table 8. Apparently, 60PGA/ADR blown films show outstanding oxygen and water vapor barrier performance than other films reported in refs 39–45.

### CONCLUSIONS

In this study, fully biodegradable PGA/PBAT films with a remarkable combination of excellent barrier property and robust mechanical properties were obtained using the extrusion blown film process. The PBAT phase can in situ form microfibrils under the influence of extensional flow. Simultaneously, the synergistic function of the extensional flow field could effectively promote the motion of the PGA molecular chain to develop an oriented crystalline microstructure. Because of the aligned oriented lamellar crystal of PGA and oriented PBAT fibril structures serving as robust “barrier walls,” 60PGA/ADR blown films demonstrated dramatically improved resistance to oxygen and water vapor, showing 59 and 44 times lower oxygen permeability and water vapor permeability, respectively, when compared to the neat PBAT blown film. Therefore, 60PGA/ADR blown films offer several advantages, including better ductility compared to HDPE or BOPP, robustness, and a high gas barrier. More importantly, the biodegradability of these films makes them a promising candidate for replacing traditional nondegradable packing films. These results provide an innovative methodology for readily regulating and controlling the gas barrier property of polymer films. In future projects, the effect of varying PGA and ADR contents on biodegradation properties of PGA/PBAT composite films in soil and in simulated seawater will be investigated in detail.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02484.

Thermal properties and DSC curves of 60PGA/ADR blown films and pressed films (PDF)

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**Notes**

The authors declare no competing financial interest.

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### REFERENCES

1. Cichello, S. A. Oxygen absorbers in food preservation: a review. J. Food Sci. Technol. 2015, 52, 1889–1895.

2. Tyagi, P.; Salem, K. S.; Hubbe, M. A.; Pal, L. Advances in barrier coatings and film technologies for achieving sustainable packaging of food products – A review. Trends Food Sci. Technol. 2021, 115, 461–485.

3. Montoille, L.; Vicencio, C. M.; Fontalba, D.; Ortiz, J. A.; Moreno-Serna, V.; Peponi, L.; Matiacevich, S.; Zapata, P. A. Study of the effect of the addition of plasticizers on the physical properties of biodegradable films based on kefiran for potential application as food packaging. Food Chem. 2021, 360, No. 129966.

4. Mele, G.; Bloise, E.; Cosentino, F.; Lomonaco, C.; Avelino, F.; Marciano, T.; Massaro, C.; Avelino, F.; Schioppa, M.; Terzi, R. Influence of Cardanol Oil on the Properties of Poly(lactic acid) Films Produced by Melt Extrusion. ACS Omega 2019, 4, 718–726.
Properties of PLA/OMMT Films by Regulating the Interlayer

Biodegradable blends of poly(butylene adipate-co-terephthalate) and polylactic acid) blend with maleated poe/attapulgite hybrid compatibilizer: Evaluation of mechanical, thermal, rheological, and morphological properties. *RSC Adv.* **2015**, *5*, 202−212.

(31) Dil, E. J.; Carreau, P. J.; Favis, B. D. Morphology, miscibility and continuity development in poly(lactic acid)/poly(butylene adipate-co-terephthalate) blends. *Polymer* **2015**, *56*, 65−69.

(32) Muiruri, J. K.; Liu, S.; Yeo, J. C. C.; Koh, J. J.; Kong, J.; Thitsartarn, W.; Teo, W. S.; He, C. Synergistic Toughening of Poly(lactic acid)−Cellulose Nanocrystal Composites through Cooperative Effect of Cavitation and Crazing Deformation Mechanisms. *ACS Appl. Polym. Mater.* **2019**, *1*, 509−518.

(33) Gu, S.-Y.; Zhang, K.; Ren, J.; Zhan, H. Melt rheology of polylactide/poly(butylene adipate-co-terephthalate) blends. *Carbohydr. Polym.* **2008**, *74*, 79−85.

(34) Wang, R.; Sun, X.; Chen, L.; Liang, W. Morphological and mechanical properties of biodegradable poly(glycolic acid)/poly(butylene adipate-co-terephthalate) blends with in situ compatibilization. *RSC Adv.* **2021**, *11*, 1241−1249.

(35) Pan, H.; Li, Z.; Yang, J.; Li, X.; Ai, X.; Hao, Y.; Zhang, H.; Dong, L. The effect of MDI on the structure and mechanical properties of poly(lactic acid) and poly(butylene adipate-co-terephthalate) blends. *RSC Adv.* **2018**, *8*, 4610−4623.

(36) Yang, H.; Cai, Z.; Liu, H.; Cao, Z.; Xia, Y.; Ma, W.; Gong, F.; Tao, G.; Liu, C. Compatibilization of polypropylene/poly(glycolic acid) blend with maleated poyl/caprolactone hybrid compatibilizer: Evaluation of mechanical, thermal, rheological, and morphological characteristics. *J. Polym. Sci. B* **2020**, *58*, 903−913.

(37) de Oca, H. M.; Ward, I. M. Structure and mechanical properties of PGA crystals and fibres. *Polym. Sci., Part B* **2006**, *45*, 7070−7077.

(38) Tabbataei, S. H.; Carreau, P. J.; Ajji, A. Structure and properties of MDO stretched polypropylene. *Polymer* **2009**, *50*, 3981−3989.

(39) Venkatesan, R.; Rajeswari, N.; Tamilselvi, A. Antimicrobial, mechanical, barrier, and thermal properties of bio-based poly(butylene adipate-co-terephthalate) (PBAT)/Ag2O nanocomposite films for packaging application. *Polym. Adv. Technol.* **2018**, *29*, 61−68.

(40) Luo, S.; Zhang, P.; Gao, D. Preparation and Properties of Antimicrobial Poly(butylene adipate-co-terephthalate)/TiO2 Nano-composites Films. *J. Macromol. Sci., Part B* **2020**, *59*, 248−261.

(41) Calderaro, M. P.; Sarantopoulos, C. I. G.; Sanchez, E. M. S.; Morales, A. R. PBAT/hybrid nanofillers composites—Part 1: Oxygen and water vapor permeabilities, UV barrier and mechanical properties. *J. Appl. Polym. Sci.* **2020**, *137*, No. 49522.
(42) Ren, P.-G.; Liu, X.-H.; Ren, F.; Zhong, G.-J.; Ji, X.; Xu, L. Biodegradable graphene oxide nanosheets/poly-(butylene adipate-co-terephthalate) nanocomposite film with enhanced gas and water vapor barrier properties. Polym. Test. 2017, 58, 173–180.

(43) Threepopnatkul, P.; Wongsuton, K.; Jiaue, C.; Rakkitwinai, N.; Stittatrakul, A.; Kulsetthanchalee, C. Effect of Zeolite on Mechanical and Barrier Properties of PBAT Films for Life Extension of Agricultural Products. Key Eng. Mater. 2020, 861, 176–181.

(44) Li, J.; Wang, S.; Lai, L.; Liu, P.; Wu, H.; Xu, J.; Severtson, S. J.; Wang, W.-J. Synergistic enhancement of gas barrier and aging resistance for biodegradable films with aligned graphene nanosheets. Carbon 2021, 172, 31–40.

(45) Xie, J.; Wang, Z.; Zhao, Q.; Yang, Y.; Xu, J.; Waterhouse, G. I. N.; Zhang, K.; Li, S.; Jin, P.; Jin, G. Scale-Up Fabrication of Biodegradable Poly(butylene adipate-co-terephthalate)/Organophilic-Clay Nanocomposite Films for Potential Packaging Applications. ACS Omega 2018, 3, 1187–1196.

(46) Park, S. I.; Marsh, K. S.; Dawson, P. Application of chitosan-incorporated LDPE film to sliced fresh red meats for shelf life extension. Meat Sci. 2010, 85, 493–499.

(47) Reesha, K. V.; Panda, S. K.; Bindu, J.; Varghese, T. O. Development and characterization of an LDPE/chitosan composite antimicrobial film for chilled fish storage. Int. J. Biol. Macromol. 2015, 79, 934–942.

(48) Huang, W.; Zeng, S.; Liu, J.; Sun, L. Bi-axially oriented polystyrene/montmorillonite nanocomposite films. RSC Adv. 2015, 5, 58191–58198.

(49) Lange, J.; Wyser, Y. Recent innovations in barrier technologies for plastic packaging? a review. Packag. Technol. Sci. 2003, 16, 149–158.

(50) Hogarth, C. Moulded-Pulp Packaging. In Paper and Paperboard Technology, Kirwan, M. J., Ed.; Blackwell Publishing: London, 2005.

(51) Breil, J. Oriented Film Technology. In Multilayer Flexible Packaging; Elsevier, 2016; pp 153–172.