Enhanced Rheological Properties of PLLA with a Purpose-Designed PDLA-b-PEG-b-PDLA Triblock Copolymer and the Application in the Film Blowing Process to Acquire Biodegradable PLLA Films

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Supporting Information

ABSTRACT: The inadequate rheological properties limit the film blowing process of biodegradable polylactic acid (PLA), thus hindering its potential application in environmentally friendly packaging films and mulch films. Herein, biodegradable polyethylene glycol (PEG) and d-lactide were used to synthesize three kinds of poly-d-lactic acid (PDLA)-b-PEG-b-PDLA (DPD) triblock copolymers, and their effects on stereocomplex (sc) structure formation and rheological properties of the composites were studied. The results showed that the poly l-lactic acid (PLLA)/DPD4k sample introduced the highest sc content, storage modulus, and complex viscosity value compared with PLLA/DPD2k and PLLA/DPD10k at the same loading condition, indicating that the PEG4k chains can better accelerate the formation of a sc network between DPD4k and the PLLA matrix. The introduction of 10 wt % DPD4k also resulted in about 38 times longer relaxation time and a strain-hardening behavior during the steady biaxial extension of PLLA. At last, the continuous film blowing process was successfully conducted in the PLLA/DPD4k composites, which acquired a stable blow-up ratio of 3.07. On the basis of the above results, the soft chain-grafted PDLA copolymer may provide a novel method for film blowing of biodegradable PLA.

INTRODUCTION

Renewable biobased polylactic acid (PLA) possesses good biocompatibility, transparency, and tensile strength, which makes it one of the most promising biodegradable materials, especially in plastic packaging and biomedical fields. The most commonly used plastics are packaging film and mulch film, which are almost produced by the film blowing process that requires stretching and orientation. However, PLA fails to support the stable growth of membrane bubbles in the common film blowing production because of its poor viscoelastic response behavior. The rigid molecular structure of the PLA chain makes it difficult to form effective molecular entanglements in the melt state, resulting in the bad rheological performance of PLA.

Film blowing of PLA became a research focus because of environmental protection and sustainable development. It is a widely used approach to introduce nanofillers with physical cross-link points to improve the melt rheological properties of PLA. However, the aggregation of nanoparticles and poor compatibility with PLA are a big challenge to achieve good mechanical performance and transparency. Attempts have also been made to blend poly l-lactic acid (PLLA) with other polymers and chain extenders or branched polymers, while the poor interface compatibility and low efficiency limit the material’s performance. Furthermore, PLA-blown films were also manufactured by controlling the processing strategies without melt strength enhancers, but the low production efficiency and strict processing window may hinder their large-scale application.

PLA’s raw material lactide has two chiral carbon atoms, so it is possible to prepare PLLA, poly d-lactic acid (PDLA), and meso-PLA. A unique stereocomplex (sc) structure can be formed when blending PLLA with PDLA, which has almost 50 °C higher melting point compared with pure PLA. The PLA’s stereocrystallites (sc-PLA) and homocrystallites (hc-PLA) are two competing crystallizations in the composites of PLLA/PDLA. The formation of sc-PLA is preferred when the $M_n$ of either PLLA or PDLA is below 5000 g/mol, and the formation of hc-PLA is preferred if the $M_n$ of PLLA and PDLA is higher than 100 000 g/mol. The sc structure was proven to have strong ability in enhancing the crystallization ability and viscosity of the PLA matrix. However, research studies on the film blowing process of PLLA with sc-PLA are seldom reported yet.

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Polyethylene glycol (PEG) is also a biodegradable polymer and has good compatibility with PLA. The sc crystallization can be accelerated by the PEG soft chain in PLLA/PDLA composites.\textsuperscript{39} However, the low efficiency and easy precipitation make the addition of PEG a double-edged sword.\textsuperscript{30–33}

In this study, the triblock copolymer PDLA-PEG-PDLA (DPD) with specified PEG and PLLA chain length was prepared and mixed with PLLA. The $M_n$ of the PLLA segment was designed to be about 4000 g/mol to result in better formation of sc-PLA. First, the chemical bonds between PEG and PLLA chains can result in better compatibility of PEG and PLLA and eliminate the PEG’s precipitation. Second, flexible PEG chains in the middle of DPD copolymers can theoretically promote the chain movement of PLLA chains to form sc crystallites, as well as chemically tie up two or more sc crystallites together to build a particular physical network in the matrix. Furthermore, because of its unique network and filler effects, the sc crystallites can efficiently enhance the viscosity and elastic response of PLLA in the melt.\textsuperscript{34–36} In this work, three kinds of DPD copolymers with different PEG chains were prepared and mixed with PLLA to improve the thermal and rheological performance of the PLLA matrix, thus finding application in the PLA film blowing process.

## EXPERIMENTAL SECTION

### Materials

The PLLA matrix (REVODE110, Zhejiang Hisun Biomaterials Co., Ltd. China, $M_n = 5.0 \times 10^4$ g/mol, PDI = 1.9), L-lactide and d-lactide (>99%, Jinan Daigang Co., Ltd. China), PEG2k ($M_n = 2000$ g/mol), PEG4k ($M_n = 4000$ g/mol), and PEG10k ($M_n = 10 000$ g/mol) (Aladdin Inc, China) were dried at 60 °C in a vacuum oven for 24 h before use. Stannous octoate (AG, Sigma-Aldrich Co., Ltd. China) was diluted to 0.05 mol/L with dry redistilled toluene (Chengdu Haihong Experimental Instrument Co. Ltd. China).

### Synthesis of DPD

The triblock copolymer DPD was prepared through ring-opening polymerization (ROP) of d-lactide with PEG as the macroinitiator and stannous octoate as the catalyst. PEG2k, PEG4k, and PEG10k were used to produce three kinds of DPD (DPD2k, DPD4k, and DPD10k) with different PEG lengths. The required amounts of the d-lactide monomer, PEG ($\eta_{\text{nuc}}/\eta_{\text{PEG}} = 55.6:1$), and stannous octoate were mixed in a three-necked flask under the nitrogen atmosphere. The obtained products were dissolved in pure chloroform and then precipitated in ethanol after the ROP reaction for 15 h at 150 °C. After that, the products were vacuum-filtered, washed several times with deionized water, and then dried in a vacuum oven for 2 days at 60 °C. By contrast, PLLA-b-PEG4k-b-PLLA (LPL4k) was also synthesized under the same condition.

### Preparation of PLLA/DPD Composites

The PLLA/DPD composites were melt-blended by an XSS-300 Haake torque rheometer (Shanghai Kechuang Rubber Plastics Machinery Co., Ltd. China). The composites were mixed at 175 °C and 50 rpm for 5 min. The samples with 5 wt % of DPD2k, DPD4k, DPD10k, and LPL4k were obtained at the same condition and labeled as PLLA/DPD2k-5%, PLLA/DPD4k-5%, PLLA/DPD10k-5%, and PLLA/LPL4k-5%, respectively. The samples with 2, 10, and 15 wt % of DPD4k were also prepared and labeled as PLLA/DPD4k-2%, PLLA/DPD4k-10%, and PLLA/DPD4k-15%, respectively.

### Extrusion-Blown PLA Films

PLLA and PLLA/DPD4k were melt-compounded by an SHJ-20 co-rotating twin-screw extruder (Giant-China Mechanical and Electrical Co., Ltd. Nanjing, China) at 60 rpm. The temperature was set between 170 and 195 °C. Then, PLLA and PLLA/DPD4k films were blown using an LSJ-10 single screw extruder (screw diameter 20 mm, $L/D = 25$) and an LF-250 film blowing machine (Labtech Engineering Co., Ltd. Thailand). The film blowing temperature of the extruder was fixed at 150–180–180–170 °C from the hopper to the die.

### Characterizations

#### Fourier-Transform Infrared Spectrometry

The DPD molecular structure was characterized using a Nicolet 6700 FTIR (Nicolet Instrument Company, USA). Samples of PEG and DPD4k were mixed with KBr powder and pressed into sheets for Fourier-transform infrared (FTIR) scanning in the 650–4000 cm$^{-1}$ wavelength range.

#### $^{1}$H Nuclear Magnetic Resonance

The content of the grafted PLLA segment in the DPD4k triblock copolymer was characterized by $^{1}$H NMR (AV II-600 MHz, Bruker Company, Switzerland) in deuterated chloroform (CDCl$_3$) as the solvent with tetramethylsilane as the internal standard.

#### Differential Scanning Calorimetry

Thermal analysis of PLLA and PLLA/DPD composites was performed with differential scanning calorimetry (DSC) (Q20, TA Instruments Inc., USA) under the nitrogen atmosphere. Each sample of 5–8 mg was heated from 30 to 160 °C at 10 °C/min and kept isothermally for 5 min to partly eliminate thermal history and then cooled to 20 °C at the rate of 10 °C/min and kept isothermally for 3 min, and then the sample was reheated to 250 °C at the rate of 10 °C/min. The PLLA-blown films were heated from 30 to 250 °C at the rate of 10 °C/min to study the crystallinity of the films.

#### X-ray Diffraction Measurement

The sc crystallinity of the PLLA/DPD composites was also tested by a Siemens-D5000 XRD (Siemens AG, Berlin, Germany) with a Cu Kz radiation source ($\lambda = 0.154056$ nm, 40 kV, 30 mA), and the scattering angle range 20 was set between 5 and 80° at 2°/min.

#### Dynamic Rheology

Testing sheets of all samples were compression-molded into thick disks of 25 mm diameter and 1.5 mm thickness at 170 °C and 10 MPa pressure. The dynamic rheological properties of PLA samples were measured using an AR2000ex rheometer (TA Instruments, USA) at 170 °C. Each sample disk was placed in a parallel-plate geometry, and the gap value was set as 250 μm. The frequency sweep test was conducted from 0.0628 to 628 rad/s at 170 °C with a strain rate of 0.1%, which was in the linear viscoelastic region of the composite melts.\textsuperscript{37} All the tests were conducted under the nitrogen atmosphere.

#### Extensional Rheology

The PLA composite samples were compression-molded into 17 mm × 10 mm × 1 mm under the above conditions. The uniaxial extensional rheological properties of PLLA/DPD composites were measured using an ARES extensional rheometer (EVF, TA Instruments, USA) with the extensional viscosity fixture at 158.5 °C under the extensional strain rate of 0.05 s$^{-1}$. The tests were also conducted under the nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of DPD Triblock Copolymers

DPD was obtained through the ROP reaction of PEG and d-lactide as shown in Scheme 1. The structure of DPD4k was characterized by FTIR, and the curves are presented in Figure 1a. The absorption band located at about 1750 cm$^{-1}$ in DPD4k belongs to the carbonyl group of PDLA segments. The methyl asymmetric deformation in PDLA segments was observed at about 1475 cm$^{-1}$, and the peak at
Scheme 1. Illustration of the Synthesis Method of DPD

Around 1200 cm⁻¹ belongs to the symmetric C=O−C stretching vibration in ester groups. The FTIR results indicated that PDLA chains were grafted onto PEG and DPD was synthesized as expected. The ¹H NMR spectra of DPD4k are shown in Figure S1; only PEG and PDLA resonances were found, consistent with the previous report.⁹ The average lengths of each PDLA segment in DPD2k, DPD4k, and DPD10k calculated by NMR results were 4029, 4135, and 3946 g/mol, respectively, which were approximately the same length and close to our designing purpose and feeding ratio (Table S1).

The filler effects of the sc crystallites would help improve the melt viscosity of the composite. As flexible PEG can lead to the movement of PLA chains in PLLA/PDLA blends and help in the formation of sc-PLA, we hope that the PEG chain movement can directly result in better mobility of PDLA segments through chemical bonds in our DPD structure, thus promoting the sc arrangement of PDLA and PLLA chains. Furthermore, sc crystals that chemically cross-link with PEG segments and physically cross-link with PLLA chains can effectively form more effective networks in the matrix as shown in Figure 1b. PLAG chains around the sc crystals can not only improve particle dispersion but also tangle with the matrix molecules and form a widely distributed network in the matrix to achieve the goal of melt strengthening.

**sc Structure between PLLA and DPD Composites.**

The melting behavior and nonisothermal crystallization of different PLLA/DPD composites were investigated through the second heating runs by DSC, and the results are presented in Figure 2a. The exothermal peak at 115 °C belongs to the cold crystallization temperature (Tc) of the PLLA chain. It is shown from the curves that the Tc shifts to the higher temperature after the addition of DPD, which indicates a restriction effect of sc crystals to the PLLA chain movement. The endothermic peaks around 153 °C corresponding to homocrystallites (Tm-hc) can be observed in neat PLLA, PLLA/LPLA4k-5%, and PLLA/DPD composites. The endothermic peaks at about 200 °C (Tm-sc) appeared only in PLLA/DPD composites, which can be assigned to the PLLA and DPD’s PLDA segments formed by the sc structure. Among the three PLLA/DPD samples with 5% addition, the Tm-sc of PLLA/DPD4k-5% has the highest melt temperature and peak value, followed by the PLLA/DPD2k-5% and PLLA/DPD10k-5% samples. The reason can be inferred that the PEG2k chain is not flexible enough to help acquire much sc crystals under this condition and that the PEG10k chain is long enough but has a smaller proportion of PDLA segments, which can form few sc crystals. In the PLLA/DPD4k-5% sample, the chain of PEG4k is flexible enough to promote the PLLA chain movement, and the proportion of the PDLA segment is enough to acquire sc crystals, which contributes to numerous stable sc structures with higher melting temperature.

Because DPD4k can help in better formation of stable sc structures, the detailed information about the thermal properties of PLLA/DPD4k composites in different addition amounts were also studied through the second heating runs of DSC, and the results are shown in Figure 2b and Table 1. The Tm of the homocrystallite shifts from 115 °C to about 125 °C after DPD4k addition, indicating that the homocrystallites are suppressed by sc crystallization. The melting peaks of sc crystallites occurred at about 200 °C when adding DPD4k to the PLLA matrix. With the DPD4k copolymer addition increased from 2 to 15%, the crystallinity of sc (Xc-sc) increases from 1.19 to 10.57%. The Xc-sc was also calculated by X-ray diffraction (XRD, Figure S2), and the results were listed below. The sc crystallinity of PLA samples was calculated by the following equation:

\[
X_c = \frac{\Delta H_m - \Delta H_m^0}{100}\%;
\]

\[
sc-PLA: \Delta H_m^0 = 142 \text{ J/g}
\]

(1)

**Relaxation Behavior of the PLLA/DPD Composites.**

The interfacial interaction between polymer chains can be evaluated with the variation of rheological parameters such as storage modulus, loss modulus, and complex viscosity.³¹ As shown in previous studies, the melt temperature of the sc crystallite is about 50 °C higher than that of pure PLA. In melt processing at suitable temperature, the sc crystallites introduced to PLLA can act as an effective rheological enhancer to enhance the elastic response and viscosity because of the filler effects and cross-linking effects of the sc network.²²–⁴⁴

To study the impact of DPD on the rheological behaviors of the PLLA matrix, the frequency sweep experiments of PLLA/DPD composites were carried out at 170 °C. Figure 3 demonstrates the storage modulus (Figure 3a), loss modulus (Figure 3b), and complex viscosity (Figure 3c) change of

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Figure 1. FTIR spectra of PEG4k and DPD4k (a) and illustration of the sc network formed in PLA/DPD composites (b).
PLLA with 5% different triblock copolymers. The results of PLLA/LPL4k-5% are almost the same as that of neat PLLA, while the storage, loss modulus, and complex viscosity values increased a lot by the addition of 5% DPD copolymers. Among these samples, PLLA/DPD4k-5% shows the largest increase, followed by PLLA/DPD10k-5% and PLLA/DPD2k-5%. The order of improvement degree is consistent with the order of \( X_{c-sc} \) amount in each group. The main difference between DPD4k and LPL4k is that DPD can form sc with PLLA chains. Thus, the sc structure is the key factor that resulted in melt viscosity improvement. The higher storage, loss modulus, and viscosity value can be mainly ascribed to the strong interaction of the sc network between the DPD chains and the PLLA matrix.

The low-viscosity character of PLA has a negative impact on its processing such as extrusion processing and blow molding.

**Figure 2.** DSC heating curves of PLLA with 5% different additives (a) and PLLA with different DPD4k addition amounts (b).

**Table 1.** sc Crystallinity of PLLA with Different DPD4k Contents

|           | PLLA    | PLLA/DPD4k-2% | PLLA/DPD4k-5% | PLLA/DPD4k-10% | PLLA/DPD4k-15% |
|-----------|---------|---------------|---------------|----------------|----------------|
| \( T_m-sc \) (°C) | 196.2   | 197.6         | 198.8         | 200.4          |                |
| \( X_{c-sc} \) (%)   | 1.19    | 3.15          | 7.20          | 10.57          |                |
| \( X_{sc-XRD} \) (%) | 1.08    | 2.59          | 6.96          | 9.58           |                |

**Figure 3.** Dependence of storage modulus (a), loss modulus (b), and complex viscosity (c) of PLLA with 5% different copolymers and storage modulus (a'), loss modulus (b'), and the dependence complex viscosity (c') of PLLA with different contents of the DPD4k copolymer at 170 °C as a function of frequency.

**Table 2.** \( G' \), \( G'' \), and Complex Viscosity Value of PLLA/DPD4k Composites at Low Shear Frequency (0.01 Hz) and High Shear Frequency (100 Hz)

| sample                | \( G' \) (Pa) | \( G'' \) (Pa) | complex viscosity (Pa s) |
|-----------------------|---------------|----------------|--------------------------|
|                       | 0.01 Hz     | 100 Hz        | 0.01 Hz      | 100 Hz                  | 0.01 Hz       | 100 Hz |
| PLLA                  | 6.67         | 155 500       | 87.73        | 106 700                 | 1400          | 300.2   |
| PLLA/DPD4k-2%         | 10.45        | 253 300       | 199.4        | 177 000                 | 3178          | 491.8   |
| PLLA/DPD4k-5%         | 61.29        | 400 900       | 506.9        | 254 100                 | 8126          | 755.4   |
| PLLA/DPD4k-10%        | 1343         | 552 900       | 1726         | 362 500                 | 34 810        | 1052    |
| PLLA/DPD4k-15%        | 15 600       | 909 900       | 9378         | 517 600                 | 289 700       | 1666    |
DPD4k can better enhance the rheological viscosity of the PLLA melt, thus the PLLA/DPD4k composites with different addition amounts were studied. The storage (Figure 3a'), loss modulus (Figure 3b'), and complex viscosity (Figure 3c') have been enhanced significantly with an increase in the DPD4k copolymer addition. When the addition amount of DPD4k increases to 10 wt %, it can be seen that the \( G' \) of the system is less dependent on the change at low frequency from 0.01 to 0.1 Hz, which deviates greatly from the behavior of PLA, indicating that the material shows a solidlike behavior. The storage modulus increases about 2 orders of magnitude under both low shear frequency and about 4 times under high shear frequency as shown in Table 2, indicating a strong and stable sc network existing in the composites, which helps to increase the melt stability of the material. Complex viscosity of the polymer is also an important parameter to characterize its rheological properties. PLA has a low shear viscosity because of its low entanglement density; the formation of the sc network also increased the complex viscosity of the polymer from low shear frequency to high shear frequency with the addition of DPD4k, which will help to increase the stability of PLA’s melt processing.

The melt strength of a polymer is strongly related to its polymer entanglements and relaxation. Increasing the polymer entanglement density and the maximum relaxation time of polymer molecular chains can improve the tensile viscosity of the polymer. Polymer’s relaxation behavior can be obtained from the weighted relaxation spectrum (eqs 2a and 2b). The continuous relaxation time spectrum of the materials can be obtained using the relaxation time, \( \tau \). The relaxation time spectra of the samples obtained based on the frequency sweep results are shown in Figure 4a. The values of the largest relaxation time and peak intensity are listed in Table 3. The longest relaxation time of PLLA assigned to free PLLA molecular segments or chain movement is found within the range of 0.026 s, which indicates that pure PLLA chains lack entanglements and relax quickly. After the introduction of DPD4k chains, the intensity of the relaxation spectrum was improved remarkably and the longest relaxation peak extends to longer time with the increasing DPD4k content. The longest relaxation time of PLLA/DPD4k-10% extends about 27 times from 0.026 to 0.695 s, and the intensity under the largest relaxation time increases about 37 times from 300 to 11 176 Pa s compared with pure PLLA sample.

Meanwhile, the range of the relaxation peak is much larger with the addition of DPD4k, indicating a broader processing window of the composites. A solidlike phenomenon is observed in the PLLA/DPD4k-15% sample, and a relaxation peak is not observed because of a large number of sc network structures. Sc crystallites that chemically cross-link with PEG chain segments and physically cross-link with PLLA chains can effectively form an effective network in the matrix. The sc network between PLLA and DPD4k chains, along with the interaction between the sc particles and the PLLA matrix, inhibits the PLLA chain movement, thus resulting in better melt stability and broadening the processing window of the composites.

In the film blowing process, the effect of stretching field is of significant importance, and the tensile rheological properties are instructive for the film blowing process of PLLA. Therefore, the extensional rheological properties of PLLA and PLLA/DPD4k composites were studied by the extensional rheology, and the results are displayed in Figure 4b and Table 3. The elongation viscosity of the composites is markedly improved with the addition of DPD4k. The elongation viscosity of pure PLLA melt increases a little with the increase of tensile time and becomes steady after a short time. However, the elongational viscosity was significantly enhanced with the increasing addition of DPD4k. A strain-hardening behavior can be observed when the DPD content exceeds 5%, which can be attributed to the entanglement of sc structures between

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Table 3. Largest Relaxation Time, \( \lambda H(\lambda) \), and Elongation Viscosity Values of PLLA/DPD4k Composites

| Sample                  | PLLA       | PLLA/DPD4k-2% | PLLA/DPD4k-5% | PLLA/DPD4k-10% | PLLA/DPD4k-15% |
|-------------------------|------------|---------------|---------------|----------------|----------------|
| Relaxation time (s)     | 0.026      | 0.031         | 0.036         | 0.695          |                |
| \( \lambda H(\lambda) \) (Pa s) | 300        | 1038          | 1428          | 11 176         |                |
| Elongation viscosity (Pa s) | 22 054    | 41 497        | 94 071        | 146 546        | 29 766         |

\[ G'(\omega) = \int_{-\infty}^{+\infty} H(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \, d\ln \tau \] (2a)

\[ G''(\omega) = \int_{-\infty}^{+\infty} H(\tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} \, d\ln \tau \] (2b)
DPD4k and PLLA. This has a good effect on improving the biaxial tensile stability of the melt in the film blowing process.

**Film Blowing Process of PLLA and PLLA/DPD4k-10% Composites.** PLA can be potentially applied in the fields of biodegradable packaging and mulch films, which are mainly manufactured through the film blowing process. The bubble stability affected by the melt strength is very important to conduct continuous production of the film blowing process. The low melt strength of pure PLA can hardly meet the requirements, thus many previous studies have chosen to add some nanocomposites or plasticizers to help in the film blowing of PLA. In this study, we found that the purpose-designed DPD chains can form sc networks with PLLA chains, resulting in enhanced rheological properties of the PLLA/DPD composites.

To test the film blowing effect of our DPD products, 10 wt % DPD4k was introduced to improve the film blowing properties of the PLLA matrix. Figures 5 and S3 show the film blowing bubbles of neat PLLA (Figure 5a) and PLLA/DPD4k-10% (Figure 5b). The bubble of neat PLLA is unstable in shape, uneven in thickness at about 80–100 μm, and easy to burst, leading to production interruption and high cost of film production. However, the bubble of PLLA/DPD4k-10% composites is very stable and of uniform thickness, which achieves the continuous film blowing production and reduces the production cost. At the same time, the blow-up ratio of the PLLA/DPD4k-10% bubble reaches 3.07 with a film thickness of about 50 μm, which meets the demand of industrial production. Both PLLA and PLLA/DPD4k films were highly transparent, which can potentially be used as packaging and mulch films.

**Thermal and Morphological Features of PLLA and PLLA/DPD4k-10% Blown Films.** The DSC heating scans of two blown films are shown in Figure 6a. The specific sc melting temperature at about 190 °C shows the biggest difference between the PLLA film and the PLLA/DPD4k-10% film. The crystallinity of hc-PLA increases from 0.65 to 2.33%, indicating that during the processing a significant amount of crystals was formed in the presence of DPD4k. Figure 6b,c shows that the transparency of PLLA is not damaged with the introduction of DPD4k. The morphology of brittle fracture face of blown films was also studied using SEM (as shown in Figure 6d,e). In general, both the PLLA and PLLA/DPD4k-10% films show a smooth surface, which indicates that DPD4k can be well dispersed in PLLA and has good compatibility with the matrix.

**CONCLUSIONS**

In this work, a comparative study was carried out in PLLA/DPD2k, PLLA/DPD4k, PLLA/DPD10k, and PLLA/LPL4k samples to investigate the effect of PEG length and sc crystallites on the melt strength of the PLLA matrix. The DPD4k products can better form more sc networks with the PLLA matrix and also has the best ability in improving the viscosity and relaxation time of the composite. The unique network generated among the PEG segments, PDLA segments, and PLLA chains demonstrated an obvious effect in improving the melt strength of PLLA.

The improvement in melt strength in the PLLA/DPD composites is associated with the entanglement of sc networks with the PLLA matrix. Such a significant increase in melt viscosity and relaxation time facilitated the PLLA film blowing, which requires high viscosity and molecular entanglements to maintain the shape of blown bubbles. In the film blowing process, the PLLA/DPD4k-10% composites can acquire stable blown bubbles and meet the requirement of the continuous film blowing process. The resulted materials have great potential in green packaging materials such as disposable containers, agricultural films, and so forth.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01470.

$^1$H NMR spectrum of synthesized DPD2k, DPD4k, and DPD10k; $M_n$ of PDLA segments of DPD2k, DPD4k, and DPD10k calculated with the integration ratio of resonances because of PEG blocks and PLA blocks in the $^1$H NMR results; and XRD spectrum of synthesized PLLA/DPD composites (PDF)

Figure 5. Film blowing bubbles of neat PLLA (a) and PLLA/DPD4k-10% composites (b).

Figure 6. DSC heating curves of PLLA films and PLLA/DPD4k films (a); transparent pictures of the PLLA (b) and PLLA/DPD4k-10% films (c); and brittle fracture face morphology of the PLLA (d) and PLLA/DPD4k-10% films (e).
Pictures of film blowing bubbles of PLLA and PLLA/DPD4k-10\% composites (MP4)

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**Notes**

The authors declare no competing financial interest.

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