Toughening Modification of Polylactic Acid by Long-Chain Hyperbranched Polymers Containing Polycaprolactone end Groups

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Abstract
The hyperbranched polyester (HBPEs) were synthesized by the "one-step method" and grafted with caprolactone (ε-Cl) to obtain long-chain hyperbranched polymers (LCHBPs-Cl). In this study, LCHBPs-Cl with Cl long chain end groups were used for the first time to toughen and strengthen polylactic acid (PLA) by melt blending. Compared with pure PLA, the most significant toughening effect was obviously when the addition amount of LCHBPs-Cl was 2.0 phr. The tensile strength increased from 37.00 to 62.61 MPa. The impact strength was increased from 14.88 to 18.50 kJ. The elongation at break increased from 1.80% to 2.50%. The scanning electron microscope (SEM) images showed the impact section of the blends became rough, the brittle-ductile fracture transition occurred, and a large number of white wire drawing phenomena were produced. Due to the formation of topological entanglement and cohesive entanglement between the long-chain substituents of LCHBPs-Cl and PLA molecular chains, the plastic deformation of PLA was successfully improved, and the toughness of polylactic acid was highly improved.

Keywords Long-chain hyperbranched polyester · Polylactic acid · Toughening

Instruction
Recently, the international tension has led to increasingly serious energy shortages and pollution problems in the traditional oil industry. Therefore, as excellent alternatives, bio-based and biodegradable materials attracted expanding interest from both researchers and manufacturers, such as cellulose [1], nutshell powder [2], and so on. PLA is a type of bio-based material polymerized with lactic acid as raw material. Lactic acid can be obtained by microbial fermentation [3]. PLA has many advantages, such as biocompatibility, processability [4], tensile strength, fabricability, and thermal plasticity [5]. It can be made into packaging films, medicine bags, thermal insulating foam materials, preservation bags, shells, disposable tableware (non-temperature resistant, oil resistant), vehicle supplies, vehicle pads, toys, etc.

Unfortunately, its disadvantages, including its brittleness, become an obstacle to its application and constrain its development [6]. To meet the application requirements, Srisuwan et al. [7] investigated the effect of PLA-nature rubber (NR) copolymers on the physical properties of the PLA/NR blends and found that the addition of the copolymers could significantly increase the compatibilization between the two phases, which in turn improved the toughness of blends. Li et al. [8] used a chain-end engineering strategy to toughen PLA via an industry-friendly melt processing method and significantly improved the toughness of the blends. Song et al. [9] prepared a series of flame retardant toughened PLA composites by blending PLA with poly(ethylene glycol) 6000 (PEG6000) and
ammonium polyphosphate (APP). It was found that the flame retardancy and the brittleness of PLA could be significantly improved. Xi et al. [10] prepared the PLA/PBE (propylene-based elastomer) melt-blown nonwovens by blending PLA with PBE. The result showed that the toughness and strength of the PLA/PBE melt-blown nonwovens increased dramatically with the increase of PBE content. Rahman et al. [11] prepared the PLA/TPU melt-blown nonwovens, which exhibited better strength and tensile ductility than pure PLA.

Hyperbranched polymers (HBPs) are considered to be promising novel materials. Because of their hyperbranched architectures, HBPs have a large number of terminal functional groups and therefore have lower viscosity. Moreover, Long-chain Hyperbranched polymers (LCHBPs) also have higher strength and better processability than conventional HBPs with short-branched chains [12]. LCHBPs combine the advantages of linear polymers and hyperbranched polymers. Their unique physicochemical properties, such as a high degree of branching [13], low viscosity [14], and high crystallization [15], have led to an increasing number of studies on their use as modifiers, providing more possibilities for their wide application. Mackay et al. [16] found that the modification of hyperbranched polyester LLDPE (linear low-density polyethylene) membrane with the addition of a small amount of alkane terminated hyperbranched polymers could effectively improve mechanical properties and processability. Jikei et al. [17] synthesized the Long-chain branched poly (t-lactide)s-(LCB-PLLAn) by elf-polycondensation and found that the mechanical properties were improved. Huang et al. [18] found that the physical and thermal properties of polylactic acid (PLA)/cellulose acetate (CA) blends were improved by adding LCHBPs. Zhang et al. [19] synthesized a novel hyperbranched flame-retardant polymer (referred to as ITA-HBP) from itaconic anhydride. Upon the incorporation of ITA-HBP, both the toughness and flame-retarding ability of epoxy resins with low phosphorus contents increased dramatically. Chen et al. [20] found the tensile strength, tensile toughness, flexural strength and flexural modulus, impact strength of the thermosets of resin were improved by [HBP-AMIM][PF$_6$] (a type of novel hyperbranched polymeric ionic liquid).

The addition of PCL, both linear and branch structures have been studied for many experts. For example, Martins et al. [21] studied PCL (poly epsilon-caprolactone)/PLA creep and stress relaxation behavior of PLA-PCL fibresand. Liu et al. [22] improved crystallinity, mechanical properties and rheological behavior by introducing a long-chain branched block copolymer (LB-PCLA) of PLA and poly-epsilon-caprolactone (PCL). It could be seen that PCL has obvious toughening effect on PLA. Therefore, it is very important and meaningful to study the effect of LCHBPs-Cl on PLA.

In this study, polyester-type LCHBPs-Cl were synthesized by grafting long-chain polyesters onto the hyperbranched polymers and were introduced into PLA to improve the toughness. The effect of LCHBPs-Cl content on the toughness of PLA was investigated. It was found that the formation of the topological entanglement and cohesive entanglement between the long-chain substituent of LCHBPs-Cl and PLA molecular chain improved the toughness of the blends.

**Materials and Methods**

**Materials**

PLA(REVODE110, $M_w = 3.5 \times 10^5$ g mol$^{-1}$, DI = 2.5) was bought from Zhejiang Haizheng Biomaterials Co., Ltd. Tri-methylolpropane (TMP), P-toluenesulfonic acid (P-TSA) were purchased from Shanghai Macklin Biochemical Co., Ltd. 2,2-Dihydroxymethylpropionic acid (DMPA), Stannous octanoate (Sn(Oct)$_2$) were purchased from Shanghai Aladin Biochemical Co., Ltd. And E-Caprolactone (ε-CL) was purchased from Aladdin Industrial Corporation Polyoxymethylene (POH), Tetrahydrofuran (THF), N, N-Dimethylformamide (DMF) were purchased from Beijing chemical plant. All reagents and solvents were used directly as received without any treatment.

**Synthesis of LCHBPs-Cl**

HBPE was prepared by “one-step” melt polycondensation [23] in our laboratory by ourselves. 2.59g of HBPE (Mn = 3423 g mol$^{-1}$, 7.57 $10^{-4}$ mol) was completely melted in a flask and dried under vacuum conditions at 100 °C for 6 h. 3–4 drops of Sn (OCT)$_2$ were added to the flask and stirred at 140 °C at 120 r min$^{-1}$. Then 54.22g of ε-CL (Mn = 114 g mol$^{-1}$, 0.48mol) was added and stirred for 24 h. The molar ratio of HBPE and ε-CL was 1 : 630. After the reaction was completed, cold formaldehyde was added to precipitate the product. The precipitate was filtered and dried to obtain the target products LCHBPs-Cl as white powders. Fig. 1 shows the process and the detailed chemical structure of the prepared LCHBPs-Cl.

**Preparation of the Blends**

PLA was dried at 80 °C for 6 h. PLA was blended with different contents of LCHBPs-Cl through a twin-screw extruder (XSS-300, Shanghai Kechang Rubber Co., Ltd., China). The temperature of each zone of the twin-screw extruder was set to 160 °C, 165 °C, 170 °C, 170 °C, and 165 °C, respectively. The PLA/LCHBPs-Cl blends were cooled before being cut into granulation using a stock cutter (CTE-35, Cobelon Coya Machinery Co., Ltd). Finally,
standard splines were injection molded by an injection molding machine (TY400, Hangzhou Dayu Machinery Co., Ltd., China). The injection temperature was set to 170 °C, and the injection pressure was 50 bar.

**Characterization**

**Fourier Transform Spectroscopy (FTIR)**

Samples were mixed with KBr in a 1:100 weight ratio and pressed into complete and transparent sheets for testing. The scanning wavelength of FTIR spectroscopy (NicoletiZ10, Thermo scientific, USA) was set in the range of 4000–500 cm⁻¹. The resolution was set to 4 cm⁻¹ and the number of scans was 32.

**Polarized Optical Microscopy (POM)**

An appropriate amount of samples was cut and placed between two clean slides, and the slides were placed on a hot table, then the samples were heated, melted, and pressed into thin sheets. The heating rate was set to 50 °C/min, and the temperature was increased to 200 °C and kept for 5 min to eliminate the crystalline state of PLA. The crystalline state of the sample was recorded by a POM (CBX51, Olympus, Japan) during natural cooling to room temperature.

**Scanning Electron Microscope (SEM)**

The fractured surfaces of impact specimens were observed under a scanning electron microscope (QuantaFEG, FEI, USA). Before SEM analysis, gold spraying was performed at a working voltage of 15 kV.

**Differential Scanning Calorimetry (DSC)**

The thermal analysis of PLA/LCHBPs-Cl was measured with a differential scanning calorimeter (Q20, TA, USA) under nitrogen protection. Samples (5.0–10.0 mg) were heated from room temperature to 200 °C, kept at 200 °C for 3 min, then cooled from 200 °C to 110 °C at the speed of 20 °C/min, and reheated to 200 °C at 20 °C/min.

The isothermal crystallization of PLA/LCHBPs-Cl was investigated by DSC. Samples were taken into aluminum pans and heated to 200 °C and kept for 3 mins to eliminate thermal history and residual stress. Then the samples were cooled from 200 °C to 110 °C at the speed of 40 °C/min and kept for at least 30 mins. The crystallinity (X_c) of PLA/LCHBPs-Cl blends was calculated according to Eq. (1). The isothermal crystallization kinetic parameters were obtained from Eq. (2).

\[
X_c = \frac{\Delta H}{(1 - \Phi_{LCHBPs-CL}) \times \Delta H_{100\%PLA}}
\]  

(1)

\[
X_t: \text{relative crystallinity, } \Phi_{LCHBPs-CL}: \text{the weight fraction of LCHBPs-Cl, } \Delta H_{100\%PLA}: \text{the melting enthalpy of pure PLA} (\Delta H_{100\%PLA} = 93.6 J\cdot g^{-1}) \text{[24]}
\]

\[
\lg[-\ln(1 - X_t)] = n \lg t + \lg k
\]  

(2)

\(X_t: \text{relative crystallinity of the sample at a certain time, } k: \text{the crystallization rate constant, which is related to the nucleation mode and crystal growth rate related, } n: \text{the Avrami index, which is related to the nucleation mechanism and crystal structure}

**Heat Deflection Temperatures**

Heat deflection temperature was tested via a microcomputer-controlled thermal deformation viaka softening
point testing machine (ZWK1302-B, Metex Industrial, China) under specified load and deformation. The span was 64 mm. The size of the samples was 125.0 × 12.7 × 3.2 mm. The heating rate was 120 °C/h.

**Thermal Stability Analysis**

The thermal stability of PLA/LCHBPs-Cl was analyzed by a thermogravimetric analyzer (Q50, TA, USA). The sample was heated from room temperature to 550 °C at a rate of 10 °C/min to explore its weight change.

**Mechanical Properties**

Tensile strength and elongation at the break of the blends were tested by a computer-controlled electronic universal testing machine (CMT6104, MTS Industry System Co., Ltd., Shenzhen, Guangdong Province, P.R. China) according to ISO527.2. The crosshead speed was 10mm/min and the loading was 10 kN.

The impact energy of the pendulum was 2 J. The size A-type notched spline was determined according to the ISO 180:2000:80 mm × 10 mm × 4 mm. The machine was a combined digital display impact testing machine (XJZ-50, Chengde testing machine Co., Ltd., China).

**Rheological Properties**

The thickness of the samples was 1mm, the temperature was set at 170 °C, and the test was carried out when the sample was melted. The starting value of angular frequency was 0.1 rad s⁻¹ and the final value was 100 rad s⁻¹. The change law was logarithmic.

**Contact Angle**

The contact angle was observed by a contact angle tester (OCA35, Beijing Audrino machine Co., Ltd., China). The samples were placed on a horizontal surface and a drop of water was placed on the sample’s surface. Then a horizontal surface was specified to define the contact angle.

**Ultraviolet Transmittance**

According to AS/NZS4399:1996, PLA/LCHBPs-Cl blends were performed with platinum-sputtering for 1.5 mins under a high vacuum. The ultraviolet protection was measured on a spectrophotometer (Labsphere UV-1000F Transmittance Analyzer).

**Results and Discussion**

**FTIR**

Comparing the FTIR spectra of PLA and PLA/LCHBPs-Cl blends from Fig. 2a, the absorption peak around the 3500 cm⁻¹ was assigned to the –OH stretching vibration of LCHBPs-Cl. With the addition of LCHBPs-Cl, the hydroxyl vibration peak moved to the high wave number, and the intensity of the peak was weakened, indicating that hydrogen bonds were formed between the hydroxyl of LCHBPs-Cl and polylactic acid. Because the hydroxyl end groups of LCHBPs-Cl were relatively dispersed, LCHBPs-Cl cannot form hydrogen bonds through their interaction by itself alone [25]. The peak of PLA displayed at 2995–2946 cm⁻¹ was the stretching vibrations of –CH (–CH₂–, –CH₃) [26]. The peak around 1730 cm⁻¹ corresponded to –C=O stretching vibration. With the increase of LCHBPs-Cl content, the hydroxyl peak moved to the high wavenumber region. The

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![Fig. 2](image-url) **Fig. 2** FTIR of PLA/LCHBPs-Cl blends (a); Sketch for the formation of hydrogen bonding interaction and evolution of polymer aggregation structure and crystal structure in the PLA/LCHBPs-Cl blends (b)
stretching vibrations of $-\text{C}=\text{O}$ became stronger due to the increase of $-\text{C}=$O concentration caused by the addition of LCHBPs-Cl. The hydroxyl group of LCHBPs-Cl interacted with the carbonyl groups in PLA to form hydrogen bonds. The sketch for the formation of hydrogen bonding and evolution of polymer aggregation structure and crystal structure in the PLA/LCHBPs-Cl blends was shown in Fig. 2b

**Crystallization Behavior**

Fig. 3 shows the polarizing optical microscope images of the PLA/LCHBPs-Cl blends. As can be seen from Fig. 3a, the crystal of polylactic acid was spherulite and the Maltese black cross patterns appeared. The average size of neat polylactic acid spherulites was 86 $\mu$m, which was shown in Fig. S1. When the content of LCHBP-CL was less than 2.0 phr, the spherulite size and the spherulite number increased with the addition of LCHBP-CL, as shown in Fig. 3b–e. It indicated that the addition of LCHBPs-Cl could promote the formation of the PLA crystallization nucleus. The average size of PLA spherulites increased to 124 $\mu$m when containing 2.0 phr LCHBPs-Cl. As the number of spherical crystallization nuclei of PLA gradually increased, the spherulite size became larger, indicating that the addition of LCHBPs-Cl promoted the formation of PLA crystallization nucleus and the growth of PLA grains. LCHBPs-Cl was a three-dimensional spherical structure, which lubricated the molecular chain and accelerated the movement ability of the molecular chain segment. LCHBPs-Cl promoted the crystallization nucleation and growth of PLA spherulite in the blends as heterogeneous nucleating agents.

However, when the LCHBPs-Cl content was greater than 2.0 phr, the crystallization spherulite size and the spherulite number decreased, as illustrated in Fig. 3f. This phenomenon indicated that the agglomeration of LCHBPs-Cl occurred due to the long-chain structure of LCHBPs-Cl with the increasing of LCHBPs-Cl content. The size of agglomeration became larger, which hindered the orderly arrangement of PLA and may lead to difficulties in PLA crystallization.

**Morphology Analysis**

The impact surface morphology of the PLA/LCHBPs-Cl blends was shown in Fig. 4. PLA exhibited brittle fracture with relatively smooth and neat surfaces as shown in Fig. 4a. In Fig. 4b, when the LCHBPs-Cl content was 0.5 phr, the appearance of the pull-out phenomenon occurred at the fracture surface. In Fig. 4b–f, with the increase of LCHBPs-Cl, a large amount of ligament fibrillation and fiber pulling out phenomenon was generated, indicating that productive toughness fracture occurred for PLA/LCHBPs-Cl blends, and the toughness was highly improved. In addition, it could be observed that with the addition of LCHBPs-Cl, PLA/LCHBPs-Cl blends underwent the brittle-tough fracture transformation, while some small holes were formed between PLA and LCHBPs-Cl and debonding occurred on the surface, indicating that the interfacial adhesion and compatibility between LPLA and LCHBPs-Cl were improved, and LCHBPs-Cl were dispersed uniformly in PLA matrix.
When the content of LCHBPs-Cl was greater than 2.0 phr, with the content of LCHBPs-Cl increased, the small holes became larger. This phenomenon indicated that LCHBPs-Cl agglomerated on the surface of PLA and the dispersion uniformity became poor, which in turn led to lowered interfacial compatibility between PLA and LCHBPs-Cl and may adversely affect the performance of PLA.

**Thermal Analysis**

The DSC curves of PLA/LCHBPs-Cl blends were shown in Fig. 5a. It showed that the glass transition temperature ($T_g$) of the PLA/LCHBPs-Cl blends remained almost constant at about 60 °C with the increase of LCHBPs-Cl. The deviation of $T_g$ was less than 1.4 °C. $T_g$ is the inherent property of amorphous polymer materials and the macroscopic transformation of polymer movement form which directly affects the service performance and process performance of materials. The variation of $T_g$ for PLA-LCHBPs-Cl was not significant, indicating that LCHBPs-Cl had little impact on the processability of PLA materials.

Table 1 shows that the crystallinity ($\chi_c$) of PLA increased with the addition of LCHBPs-Cl when the LCHBPs-Cl content was not exceeded 1.5 phr. The lubrication effect of LCHBPs-Cl accelerated the mobility of molecular chains of PLA, which increased the crystallinity of PLA. With the increase of LCHBPs-Cl content, the physical micro-crosslinks were formed due to the entanglement between...
flexible PCL chains and PLA molecular chains. At the same time, the hydrogen bonds between the hydroxyl groups at the end of the flexible long chain of LCHBPs-Cl and the PLA ester group restricted the movement of its molecular chain and reduced the crystallinity.

The heat deflection temperature of the PLA/LCHBPs-Cl blends was shown in Fig. 5b. With increasing the LCHBPs-Cl content, the heat deflection temperature of PLA slightly increased. The results showed that the addition of LCHBPs-Cl improved the heat resistance of the blends, which was due to the physical entanglement between PLA and LCHBPs-Cl, and crystallization had little effect.

**Table 1. Thermal parameters of the PLA/LCHBPs blends**

| LCHBPs-Cl content (phr) | \( T_g (^\circ C) \) | \( \Delta H_{cc} (\text{J/g}) \) | \( \Delta H_m (\text{J/g}) \) | \( \chi_c (\%) \) | \( T_{d5\%} (^\circ C) \) |
|-------------------------|----------------|----------------|----------------|-------------|----------------|
| 0.0                     | 60.05          | 22.21          | 23.66          | 1.50        | 348.22         |
| 0.5                     | 60.28          | 26.07          | 27.93          | 1.90        | 350.66         |
| 1.0                     | 60.27          | 25.31          | 27.23          | 2.00        | 351.25         |
| 1.5                     | 61.43          | 26.48          | 27.49          | 1.00        | 349.38         |
| 2.0                     | 60.34          | 27.41          | 28.40          | 1.00        | 349.76         |
| 2.5                     | 60.06          | 28.05          | 29.21          | 1.20        | 352.62         |

As shown in Fig. 6a, the crystallinity vs t curves for PLA/LCHBPs-Cl blends changed from steep to slow and the slope decreased with the increase of LCHBPs-Cl content. The crystallization rate reached the lowest value when the addition of LCHBPs-Cl was 2.0 phr. The results indicated that the introduction of LCHBPs-Cl improved the crystallization process of PLA and promoted the crystallization of PLA.

Fig. 6b shows the Avrami equation fitting lines for PLA/LCHBPs-Cl blends. Avrami index (n) and crystallization rate constant (k) could be obtained from the slope and intercept of the straight lines. The corresponding isothermal crystallization kinetic parameters were summarized in Table 2.

Table 2 revealed that the semi-crystallization time (\( t_{1/2} \)) of pure PLA was 7.44 min and the crystallization rate constant was only 0.0125 at 110 °C, which indicated a short crystallization time and fast crystallization rate of PLA. When the LCHBPs-Cl content was less than 2.0 phr, the introduction of LCHBPs-Cl significantly reduced the crystallization rate and prolonged the crystallization time of PLA. With the increase of LCHBPs-Cl content, \( t_{1/2} \) of the PLA/LCHBPs-Cl blends first increased and then decreased. When the addition of LCHBPs-Cl was 2.0 phr,
t_{1/2} was 13.78 min, which was nearly twice longer than that of pure PLA, and the crystallization rate constant was more than three times that of pure PLA. In addition, the Avrami index (n) that related to the nucleation mechanism and growth dimension of the crystallization process increased and the physical entanglement of PLA/LCHBPs-Cl led to a decrease in crystallinity.

**Thermal Stability**

The thermogravimetric (TG) curves and derivative thermogravimetric (DTG) curves of PLA/LCHBPs-Cl blends were shown in Fig. 6c, d. According to the TG and DTG curves, the initial decomposition temperatures of PLA/LCHBPs-Cl blends were about 350 °C, and the temperatures at the maximum decomposition rate of PLA/LCHBPs-Cl blends were also approximately the same, which were about 355 °C. Table 1 shows the initial decomposition temperature (T_{d5%}) of PLA blends with different content of LCHBPs-Cl. With the increase of LCHBPs-Cl content, the thermal decomposition temperature of the PLA/LCHBPs-Cl blends increased only slightly, which showed that the addition of LCHBPs-Cl had little effect on the thermal decomposition temperature of the PLA/LCHBPs-Cl blends and the effect of hydrogen bonding between LCHBPs-Cl, and PLA on the thermal decomposition temperature was not very obvious. It indicated that the thermal stability and processing decomposition temperature of PLA were hardly affected by the addition of LCHBPs-Cl.

The reason for this phenomenon could be attributed to the lower LCHBPs-Cl molecular weight than that of PLA. The decomposition temperature of LCHBPs-Cl was much lower than that of PLA, thus the addition of LCHBPs-Cl during melt blending can affect the thermal stability of the PLA/LCHBPs blends to some extent. However, due to the strong hydrogen bonding between LCHBPs and PLA and the low addition of LCHBPs-CL in the PLA matrix, the decrease of T_{55%} in PLA/LCHBPs-Cl blends was not obvious.

### Table 2: Isothermal crystallization kinetic parameters for PLA/LCHBPs-Cl blends

| LCHBPs-Cl content (phr) | n   | k       | t_{1/2} / min |
|-------------------------|-----|---------|--------------|
| 0.0                     | 2.20| 0.0125  | 7.44         |
| 0.5                     | 2.55| 0.0056  | 11.12        |
| 1.0                     | 2.60| 0.0045  | 12.47        |
| 1.5                     | 2.40| 0.0060  | 10.73        |
| 2.0                     | 2.62| 0.0037  | 13.78        |
| 2.5                     | 2.65| 0.0040  | 13.17        |

**Rheological Properties**

Composite viscosity (a); storage modulus (b); Loss modulus (c); tan δ (d)

As shown in Fig. 7a, when LCHBPs-Cl was added, the storage modulus of the blends at the low-frequency region was lower than that of pure PLA. At the high-frequency region, the storage modulus of the PLA/LCHBPs-Cl blends containing 2.5 phr LCHBPs-Cl was higher than that of pure PLA. The storage modulus represented rigidity, and the rigidity was the lowest when LCHBPs-Cl content was 2 phr, which may be due to physical entanglement [27, 28]. The entanglement became more obvious when the frequency increased.

As shown in Fig. 7b, the loss modulus of the blends at low frequencies was lower than that of pure PLA after the addition of LCHBPs-Cl. The loss modulus of the blends at high frequency was higher than pure PLA. The loss modulus represented the viscosity of the blends. The increase in viscosity might be because LCHBPs-Cl had enough time to disentangle at low frequency, resulting in a low modulus. At high frequencies, the entangled polymer chain did not have enough relaxation time, so the loss modulus was high.

Fig. 7c shows the variation of the composite viscosities of the blends with the angular frequencies. The complex viscosities of the blends were extremely closely related to the dispersion of LCHBPs-Cl in PLA. When the LCHBPs-Cl content was low, the lubrication effect of LCHBPs-Cl was not conducive to the physical entanglement effects in PLA. When the content of LCHBPs-Cl was 2.5 phr, the physical entanglements between LCHBPs-Cl and PLA became more obvious, which increased the complex viscosities of the blends.

As shown in Fig. 7d, tan δ gradually increased with LCHBPs-Cl content when LCHBPs-Cl was less than 2.0 phr, and then decreased when the content of LCHBPs-Cl was 2.5 phr. When the Tan δ increased, the energy loss increased and the processibility became worse. Compared with pure PLA, the overall energy loss increased, the viscosity slightly increased and the processibility improved. The increase in viscosity may be due to the physical entanglement between LCHBPs-Cl and PLA and the polarity of the LCHBPs-Cl end group. The increase in viscosity was also a manifestation of the improved toughness.

**Mechanical Properties**

The tensile strength, elongation at break, and impact strength curves of the PLA/LCHBPs-Cl blends with different content of LCHBPs-Cl were shown in Fig. 8a and b. Upon addition of LCHBPs-Cl, the impact strength, elongation at break and tensile strength of the blends were all greater than those of pure PLA. When the content of LCHBPs-Cl was 2.0 phr, the
impact strength, elongation at break, and tensile strength of the blends reached the maximum values. The tensile strength increased from 37.00 to 62.61 MPa. The impact strength was increased from 14.88 to 18.50 kJ. When the content of LCHBPs-Cl was 2.0 phr, the elongation at break increased from 1.80% to 2.50%. The reason for this phenomenon was ascribed to the formation of micro-crosslinks between PLA and LCHBPs-Cl and the promotion of LCHBPs-Cl on PLA crystallization. However, when the content of LCHBPs-Cl was more than 2.0 phr, the toughness of the blends decreased due to the poor dispersion and the agglomeration of LCHBPs-Cl in the PLA matrix and the decrease of PLA crystallinity.

Contact Angle

The liquid contact angle reflects the hydrophilicity and hydrophobicity of the materials. The increase in contact angle indicates that the hydrophobicity of the material is improved [29]. Fig. 8c shows the contact angle of PLA/LCHBPs-Cl blends with different LCHBPs-Cl content. The hydrophobicity of PLA could be enhanced by introducing LCHBPs-CL into PLA. The contact angle of PLA/ LCHBPs-CL blends gradually increased with the increase of LCHBPs-CL content. LCHBPs-CL contains a large number of long-chain structures with strong hydrophobicity. The uniform distribution of LCHBPs-CL in the PLA matrix could improve its hydrophobicity. Due to the hydrogen bond between the ester group of PLA and the hydroxyl group of LCHBPs-Cl, some hydroxyl groups of LCHBPs-Cl could be shielded, thus the number of free hydroxyl groups interacting with water on the film surface was reduced [30]. As a result, the contact angle of PLA/ LCHBPs-Cl was increased and the water resistance of the material was enhanced.

Optical Properties

As shown in Fig. 8d, compared to that of pure PLA, the transmittance of the PLA/LCHBPs-Cl blends was improved. The introduction of LCHBPs-CL promoted the crystallization of PLA and produced a large number of small crystals with small grain size, which was conducive to light transmission. At the same time, with the addition of LCHBPs-CL, the crystallinity of PLA decreased, the crystalline area decreased, and the amorphous area increased, resulting in the improvement of transparency. In addition, the aggregation of excess LCHBPs-CL resulted in PLA crystallinity
decreased, which was conducive to light transmission and increased the transmittance.

**Conclusion**

In the text, LCHBPs-Cl containing Cl long chain terminal group was successfully synthesized and the PLA/LCHBPs-Cl blends were prepared by melt blending to strengthen and toughen poly(lactic acid). The tensile strength, the elongation at break, and impact strength all improved upon with the addition of LCHBPs-Cl. The impact surface morphology of the blends was changed from smooth to rough and the brittle-ductile fracture transition occurred with the increasing of LCHBPs-Cl content. With the introduction of LCHBPs-Cl, the spherulite size of PLA was reduced, and the optical transmittance was improved. It could be used as a heterogeneous nucleation agent to promote the crystallization nucleation and growth of PLA. The contact angle analysis showed that with the increasing of the LCHBPs-Cl content, the water-resistance of the material was enhanced. The optimal properties of PLA/LCHBPs-Cl were achieved when the content of LCHBPs-Cl was 2.0 phr.

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**Author Contributions** RT are mainly responsible for writing papers, YH guide the experiment as a whole, SJ prepared figures, XL and GL are responsible for the consulting data. SM are responsible for the final examination and revision of the paper. YJ and HT are corresponding authors. All authors reviewed the manuscript.
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Conflict of interest  We confirm that neither the entire paper nor any part of its content has been published or has been accepted elsewhere. It is not being submitted to any other journal. It has been approved by all co-authors and Beijing Technology and Business University.

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