ABSTRACT: Petroleum-based polymer materials heavily rely on nonrenewable petrochemical resources, and damping materials are an important category of them. As far as green chemistry, recycling, and damping materials are concerned, there is an urgent need for renewable and recyclable biobased materials with high damping performance. Thus, this study designs and synthesizes a series of polylactic acid-based thermoplastic polyurethanes (PLA-based TPUs) composed of modified polylactic acid polyols, 4,4′-diphenylmethane diisocyanate, and 1,4-butanediol. PLA-based TPUs, as prepared, display excellent mechanical properties, damping performance, and biocompatibility. Otherwise, they can be used for three-dimensional printing (3D printing). Under multiple recycling, the overall performance of PLA-based TPUs is still maintained well. Overall, PLA-based TPUs, as designed in this article, show a potential application in damping materials under room temperature and personalized shoes via 3D printing and could realize resource recycling and material reuse.

1. INTRODUCTION

Polymer materials are ubiquitous in our daily lives and contribute significantly to the development and progress of the society because of their unique properties compared with metals and inorganic materials.7,8 However, petroleum remains a critical source of raw materials for polymer materials, and the unsustainability of petrochemical resources severely limits the development of synthetic materials in the future. Moreover, materials based on petroleum do not degrade easily under natural conditions, causing environmental pollution and ultimately threatening humans.5,6 Therefore, it is critical to develop renewable and degradable polymeric materials.

Recently, the European Union declared that 100% of plastics should either be reusable or recyclable by 2030 in their new plastic strategy.7,8 Similarly, sports equipment manufacturers, such as Adidas and Nike, have long been developing biodegradable and renewable materials for future production.7,8 Thus, there are considerable indications that biodegradable and biobased plastics received much attention recently. Fortunately, polylactic acid (PLA) is a widely known renewable and degradable material.3 Researchers have shown growing interest in PLA because of its excellent degradability and biocompatibility, making it competitive in the biomedical materials field.10,11 Furthermore, lactic acid can come from diverse biomass sources through biological fermentation, significantly enhancing the competitiveness of PLA.12–14 PLA was employed to manufacture several products by injection molding, roll forming, and 3D printing. 3D printing is a new processing method that has received much attention because of its personalized customization and ability to print complicated objects.15,16 However, PLA is predominantly used as a plastic whose application is limited by a lack of toughness.17 In previous studies, physical blending was often used to improve the toughness of PLA composites.

In the polymer family, the polyurethane (PU) elastomer possesses both the flexibility of soft segments (SS) and the
rigidity of hard segments (HS), showing excellent toughness, and is excellent to be used in shoe soles and damping materials. Note that most of the sole materials are cross-linked rubber that cannot be recycled and degraded. A considerable amount of literature has been published on PU damping materials, showing that it is challenging to simultaneously achieve a high loss factor, wide range, and room-temperature damping.20−22 Most of the commercial PUs are derived from petrochemical resources. Taking full advantage of the renewability and degradability of PLA and the toughness of the PU elastomer is a potential strategy to overcome brittleness and maintain the advantages of both PLA and the PU elastomer, respectively.

Thus, general polylactic acid-based polyurethanes (PLA-PUs) that could be derived from biomass have attracted the attention of scientists because of their regenerative properties. Although the toughness of PLA-PU is higher than that of pure PLA plastic, the glass transition temperature (T_g) of PLA-PU is above room temperature, limiting its application in other fields.23−25 Therefore, many efforts, including copolymerization and blending, were made to improve the toughness of PLA-PU. For example, Ali et al. introduced polycaprolactone (PCL) as a chain extender during the preparation of PLA-PU, and the results showed that both the tensile strength and elongation at breaking were significantly improved.26 Zhao et al. synthesized a series of PLA-TPU from modified PLA-polyols, hexamethylene diisocyanate (HDI), and butanediol (BDO).27 The results revealed that the damping performance and toughness were excellent, but the mechanical properties need improvement, especially in tensile strength. Generally, the benzene ring in isocyanates improves mechanical strength and heat resistance.28,29

In this study, we design PLA-based TPUs, with the introduction of benzene improving the heat resistance and damping properties, to reduce the dependence on fossil fuels via the prepolymer polymerization method. The results indicate that PLA-based TPUs show excellent damping performance at room temperature compared with other materials. Their good retention of performance after recycling allows them to be used many times. Moreover, PLA-based TPUs can also be hopefully applied in producing personalized customized products through 3D printing. Overall, our study sheds light on the promotion of sustainable and renewable materials to reduce environmental pollution and reliance on fossil fuels.

2. RESULTS AND DISCUSSION

2.1. Synthesis of PLA-Based TPUs. FTIR was used to analyze the chemical structure and the formation of hydrogen bonding in TPUs. Figure 1 shows the FTIR spectra of PLA-based TPUs. There is no absorption peak at 2270 cm⁻¹, related to the stretching vibration of NCO groups, whereas the characteristic broad absorption band of N−H groups at 3300−3400 cm⁻¹ can be observed. The absorption peak of C=O between 1650 and 1850 cm⁻¹ changes simultaneously compared to the FTIR spectra of PLA-polyols (Figure S1). Thus, it is confirmed that the NCO groups of MDI fully reacted during polymerization, which turned into urethane groups, and the bonding changes proved that polyurethane was successfully synthesized.30,31

Generally, hydrogen atoms of N−H and oxygen atoms of C=O were proton donors and proton acceptors, respectively, easily forming hydrogen bonds, which are vital for the final properties of TPU.32,33 Based on the consideration of quantitatively analyzing the proportion of hydrogen-bonded carbonyl groups under different states, the FTIR spectrum of the carbonyl stretching region could be curve-fitted to two (Gaussian) bands at approximately 1700 and 1737 cm⁻¹, which could be attributed to hydrogen-bonded carbonyl groups and free (nonhydrogen-bonded) carbonyl groups, respectively.34,35 Hydrogen bonding predominantly exists in the hard segment and the two-phase interface. Table S2 lists the curve-fitting results, and the results indicated that the proportion of hydrogen-bonded carbonyl groups obviously increases as the HS content increases. Based on the same HS content, PLA1K-32 has a lower proportion of hydrogen-bonded carbonyl groups than PLA2K-32 and PLA3K-32.

Figure 1. FTIR spectra of PLA-based TPUs with (a) different HS contents and (b) different SS lengths.
2.2. Thermodynamic Testing. DSC was used to analyze the thermal properties of PLA-based TPUs, and the results are shown in Figure 2. All samples exhibit a glass transition temperature ($T_g$) related to the segment motion of SS. In Figure 2a, the $T_g$ value does not significantly increase upon increasing the HS content when the $M_n$ of the polyol is the same. The result is consistent with previous articles.27−29 In Figure 2b, the graph shows that $T_g$ decreases as the $M_n$ of polyol increases when the HS content is the same. This could be associated with the HS size (the average molecular weight of a single HS unit) because a larger HS size reduces the contact area of the two phases, and the HS content dissolved in SS decreases. PLA3K-32 has the biggest individual HS particles, and PLA1K-32 has the smallest HS particles. Thus, PLA3K-32 has a lower $T_g$ value than PLA1K-32 because of a higher degree of separation of the two phases.

2.3. Thermomechanical Testing. The poor heat resistance of PU significantly limits its commercial application at high temperatures. TMA curves reflect the heat resistance of polymers by detecting the degree of deformation at different temperatures. Thus, TMA is effective for characterizing the heat resistance of polymers.

As Figure 3 and Table S3 show, the softening temperature increases rapidly with a higher HS content, whereas the $M_n$ of the PLA-polyol is the same. The softening temperature is related to the size of individual HS particles when the HS content is consistent. The larger HS particles lead to a higher softening temperature (Figure 3b) because the concentration of the hydrogen bond affects the aggregation of the HS domain, and the dissociation of the hydrogen bond will make materials soften under high temperatures. To illustrate this, a variable-temperature infrared test was used to study the changes in the HS hydrogen bonding. During the heating process, the proportion of hydrogen-bonded carbonyl groups continues to decrease, which is related to the dissociation of the hydrogen bond (Figure 4). It exhibits the absorption peak of C═O and N−H belonging to PLA1K-32, PLA2K-32, and PLA3K-32 at 150 °C in Figure S2. Therefore, PLA3K-32 has a high proportion of hydrogen-bonded C═O and N−H, whereas PLA1K-32 is the opposite.

2.4. Static and Dynamic Mechanical Properties. The static mechanical properties of PLA-based TPUs were investigated by tensile testing. Figure 5 shows the strain−stress curves of PLA-based TPUs, and Table S4 summarizes the results. The HS functions as cross-linking points and reinforcement units that are related to tensile strength and breaking elongation. A larger HS domain with an ordered interior can undertake larger stress but also restrict the motion of the molecular chain to a higher degree.

Figure 5a shows that the tensile strength increases because the average size of the HS domain grows, whereas the breaking elongation decreases because of the physical cross-linking and reinforcing effects of HS, as mentioned in previous studies.27−29,33 As mentioned above, the HS content depends on both individual HS particles and the number of HS particles. Therefore, the tensile strength is predominantly determined by the HS size, and bigger HS particles will undertake larger stress. Breaking elongation depends on HS restriction and the flexibility of the SS.39 Hence, PLA2K-32 displays a balanced breaking elongation based on these two factors. Furthermore, PLA3K-32 displays a stretching orientation effect that shows potential application on spinning and could be used for making biodegradable clothing to which major sports brand companies pay great attention.

Dynamic mechanical analysis (DMA) was conducted to investigate the dynamic performance of the as-prepared PLA-based TPUs. Figure 6 shows the evolution of $E'$ (storage modulus) and tan δ (loss factor) as the temperature changes, and Table S5 summarizes the results.

$T_g$ slightly increases with the incremental HS content because the average HS size is larger and the restriction of the chain segment motion is stronger, as discussed in the DSC analysis. Hence, both the tan δ peak value and $\Delta T$ (the
temperature range for tan δ > 0.3) decrease because of the reduction in chain friction, meaning that the ability of energy dissipation is reduced. The $E'$ decreases during the transition from the glassy state to the rubber state, and the larger-size HS enhances the stiffness because of the reinforcing effect of HS that lifts the $E'$ from PLA2K-23 to PLA2K-39 in the rubber state (Figure 6a).

PLA3K-32 has the lowest $T_g$ value because of the well phase separation as discussed in the DSC analysis. The $T_g$ value in DMA and DSC shows a difference that is common in previous studies.28,29,33 The large HS has a strong restriction on the motion of the chain segment. Thus, PLA1K-32 has a high tan δ peak value and damping performance.

Figure 4. FTIR spectra at various temperatures. Characteristics of N−H and C=O for (a,b) PLA1K-32, (c,d) PLA2K-32, and (e,f) PLA3K-32.

Figure 5. Representative strain−stress curves of PLA-based TPs with (a) different HS contents and (b) different SS lengths.
Energy is dissipated through motion within the material, and the external energy is converted into heat energy called damping performance. The unique viscoelasticity of polymers makes them popular as vibration damping materials in many fields, especially in earthquake protection. Therefore, PLA-based TPUs show an excellent damping performance at room temperature, and the methyl pendant on the molecular chain can effectively enhance the damping performance while its mechanical properties are well-maintained. A simple comparison between our work and previous studies on $T_g$ and $\tan \delta_{\text{max}}$ was made and is shown in Figure 6d, showing the unique superiority of damping performance at room temperature.

2.5. Recycling of PLA-Based TPUs. The greatest advantage of TPUs is that it can be recycled and reprocessed many times compared to traditional cross-linked rubber and castable PU, which can reduce environmental pollution and waste. Consequently, the samples were cut into small chips and remolded three times. Table S6 shows the corresponding data of PLA2K-32 during reprocessing. After multiple reprocessing cycles, the tensile strength, breaking elongation, and damping performance of recycling samples were maintained well, proving their reprocessing ability (Figure 7). The rigid benzene in MDI improved the heat resistance of PLA-based TPU and reduced the thermal degradation in reprocessing compared to a previous study.

2.6. Cytotoxicity Testing. Figure 8 demonstrates the results of the in vitro cytotoxicity testing to verify the biotoxicity of PLA-based TPUs. As illustrated in Figure 8, the L929 cells cultured for 72 h in the extracted substrates of the TPUs with or without a catalyst displayed a fusiform morphology, indicating that the cells were in a healthy growth state. When the L929 cells were cultured for 24, 48, and 72 h, the relative growth rate value was higher than 100% and even higher than the tissue culture plate, indicating that the PLA-based TPUs show no cytotoxicity to L929 mouse cells (Figure 8d). The results show the potential application in long-term contact with the body, specifically in shoe soles and clothing.

2.7. Potential Application. PLA-based TPUs perform well on damping, mechanical properties, processability, and recycling. Figure 9 shows potential applications of PLA-based
TPUs. Their excellent damping performance and nontoxicity make them hopefully useful for noise-reducing earphone products that may be in contact with the human body for a long time besides damping gaskets for engineering. Furthermore, molding and 3D printing of PLA-based TPUs were tried separately, and the details are shown in Figures S3 and S4. The combination of their great processability and 3D printing reveals the feasibility and the potential application on personalized product customization. They can also be potentially used as biodegradable products because of their outstanding mechanical performance and the presence of PLA. In addition, the repetitive processing performance of PLA-based TPUs is also very remarkable. All those show that PLA-based TPUs are a kind of green material with great potential and may be expected to be widely used.

3. CONCLUSIONS

This study reported a family of PLA-based TPUs tailored by altering the HS content and SS molecular weight, composed of PLA-derived polyols, BDO, and MDI. The hydrogen-bond interaction, static and dynamic mechanical properties, heat resistance, recycling performance, and cytotoxicity tests were demonstrated. PLA-based TPUs, as reported in this study, show excellent damping performance, advantageous for use as green damping materials, and fill a gap in room-temperature damping. A combination of 3D printing, excellent mechanical properties, and biocompatibility is promising for the personalized customization of shoes and clothing in the future. Furthermore, it is easy to reprocess and recycle, solving the white pollution and resource waste caused by nondegradable or thermosetting materials. After multiple reprocessing, the comprehensive properties of cycling samples were maintained well. In general, our work proposes a green and circular economy and provides a strategy to reduce our dependence on fossil resources.

4. MATERIALS AND METHODS

4.1. Materials. PLA-derived difunctional polyols ($M_n = 1000, 2000,$ and $3000$ g/mol) were purchased from Bright China Industrial Co., Ltd. (Shenzhen, China). Table S1 shows more detailed parameters. MDI, BDO, and dibutyltin dilaurate (DBTDL) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. BDO was treated using a molecular sieve to remove the water before use. Other raw materials were used as received.

4.2. Synthesis of PLA-Based TPUs. Table 1 shows more detailed information about the compositions, and Scheme 1 displays the synthesis diagram of PLA-based TPUs. All PLA-based TPUs in this article were prepared using PLA-derived polyol, BDO, and MDI. The molar ratio of the OH group (from PLA-derived polyol and BDO) to the NCO group (from MDI) is fixed to be 1.0. The prepolymer method was used to synthesize PLA-based TPUs. First, PLA-derived polyols were reacted with MDI at 80 °C for 1 h to prepare the prepolymer after removing the water in the PLA-derived polyol. Second, BDO as a chain extender...
Table 1. Compositions of the Samples

| sample code | $M_n$ of PLA-polyol | molar ratio of PLA-polyol:MDI:BDO | HS content (%) | average HS molecular weight |
|-------------|----------------------|----------------------------------|----------------|----------------------------|
| PLA2K-23    | 2000                 | 1.0:2.0:1.0                      | 23             | 591                        |
| PLA2K-32    | 2000                 | 1.0:3.0:2.0                      | 32             | 931                        |
| PLA2K-39    | 2000                 | 1.0:4.0:3.0                      | 39             | 1272                       |
| PLA1K-32    | 1000                 | 1.0:1.7:0.7                      | 32             | 489                        |
| PLA3K-32    | 3000                 | 1.0:4.3:3.3                      | 32             | 1375                       |

and DBTL (0.03 wt %) were added to the prepolymer at a stirring rate of 400 rpm. Finally, the obtained products were placed in an oven for 12 h at 100 °C. The as-prepared PLA-based TPUs were processed by hot pressing and then used for the following characterizations and evaluations.

4.3. Instrumentation and Measurements. Fourier transform infrared spectra (FTIR) were evaluated in attenuated total reflection mode on a Tensor 27 FTIR spectrophotometer (Bruker, Germany). Scanning was performed 32 times at a resolution of 4 cm⁻¹ in the wavenumber range of 4000–600 cm⁻¹. The variable temperature infrared spectra were measured using the same instrument in absorption mode with a temperature control unit.

Differential scanning calorimetry measurements were recorded on a STArE system DSC instrument (Mettler Toledo International, Inc., Switzerland). Experiments were conducted with ~8 mg samples under a N₂ atmosphere (50 mL/min). The test program was set as follows. First, the samples were heated to 180 °C at a rate of 10 °C/min and maintained for 5 min. The samples were cooled to ~60 °C and maintained at ~60 °C for 5 min. Finally, samples were scanned from ~60 to 180 °C at a rate of 10 °C/min. The DSC curves were obtained from the reheating curves.

Dynamic mechanical properties were investigated using a dynamic mechanical thermal analyzer (Metravib, France) from −20 to 80 °C at a rate of 3 °C/min, with a testing frequency of 10 Hz and an amplitude $\varepsilon$ of 0.1%.

The static mechanical properties of PLA-based TPUs were measured at a rate of 500 mm/min using a CMT4104 electrical tensile tester (SANS Testing Machine Co., Shenzhen, China). The Shore A hardness of PLA-based TPUs was measured using a Shore A durometer (XY-1, No.4 Chemical Machinery Plant of Shanghai Chemical Equipment Co., Ltd., China).

Thermomechanical properties were investigated using a TA Instrument Q400 from 30 to 240 °C at a rate of 5 °C/min.

The PLA-based TPU was cut into small pieces and transformed into uniform wires with a diameter of ~1.75 mm by controlling the speed at 25 mm/min at 170 °C using a micro extruder. The PLA-based TPU was printed at 170 °C using a 3D printer (Wiiboox Technology Co., Ltd., Nanjing, China).

An MTT assay was used to evaluate the cytotoxicity of the prepared polyurethane to L929 cells.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04650.

Detailed information on PLA-polyols, summarized data corresponding to graphs in the manuscript, and detailed photos for 3D printing and molding shoes (PDF)

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