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ORIGINAL PAPER

Preparation of ductile PLA materials by modification with trimethyl hexamethylene diisocyanate

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Abstract Polylactide (PLA) is biodegradable and has been useful in various biomedical applications. Since the majority of the biodegradable polymers in clinical use are rather stiff materials that exhibit limited extendibility with low elongation at break values, the physical and mechanical properties of PLA must be improved to allow for more biomedical applications. Poly(ester-urethane) structure polymer materials were prepared; PLA was reacted with a small amount of trimethyl hexamethylene diisocyanate to obtain ductile PLA with markedly improved mechanical properties. Elongation at break was increased by more than 20 times while maintaining relatively high tensile stress when compared to pristine PLA. Impact resistance (notched) improved 1.6 times. Thus, the modified PLA biodegradable polymers presented here may have greater application as a biomedical material due to its enhanced mechanical properties.

Keywords Biodegradable polymer · PLA · Ductile · Mechanical properties

Introduction

Poly(lactide) (PLA) has attracted significant attention due to its renewable resource, biodegradation, and biocompatibility [1, 2]. It has been used in medical applications, such as surgical sutures, implants, tissue culture [3], and controlled drug delivery [4]. While PLA has been successfully utilized in a variety of applications, implementation of PLA on a broader scale has been somewhat thwarted. Two property issues that have

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limited PLA to some extent are its relatively low glass transition temperature and low impact strength [5]. To expand the applicability of biodegradable PLA, materials with better mechanical and thermal properties should be engineered [6]. In recent years, many researchers have copolymerized PLA with other organic compounds, such as polyethylene oxide (PEO), polypropylene oxide (PPO), 4,4-methylene diphenyl diisocyanate (MDI), or ε-caprolactone, to improve the physical, chemical, and mechanical properties of PLA [7–11]. Cohn and Salomon [8] synthesized a series of multiblock PEO/PLA thermoplastic elastomers. The first step of synthesis consisted of ring-opening polymerization of L-lactide, followed by the chain extension of these PLA–PEO–PLA triblocks using hexamethylene diisocyanate (HDI). The synthesized multiblock copolymers exhibited superior mechanical properties, with ultimate tensile strength values around 30 MPa and high elongation at break values. Xiong et al. [9] grafted PLA to both ends of Pluronic F87 block copolymer (PEO–PPO–PEO) to obtain amphiphilic P(LA-*b*-EO-*b*-PO-*b*-EO-*b*-LA) block copolymers, and used these temperature-sensitive copolymers in drug release studies. High stiffness and brittleness at ambient temperatures associated with PLA can be improved by blending PLA with biodegradable plasticizer such as poly(ethylene glycol) (PEG) [12–15] or by quenching treatment applied on heated cast sheet extruded films of PLA [16]. Martin and Averous [14] plasticized PLA with several biocompatible plasticizers, such as PEG and oligomeric lactic acid, which have shown significant decrease in glass transition temperature (T_g) and rise in elongation at break. McCarthy and Song [15] investigated the effect of biodegradable plasticizer on PLA properties and found that adding plasticizers resulted in increased toughness and improved performance. While the above approaches were utilized to improve the mechanical properties of PLA, they often involved tedious processes or achieved less than desired performance.

We have found that the addition of 2-methacryloyloxyethyl isocyanate (MOI) significantly improved the ductility of PLA and provided superior mechanical properties with much higher elongation compared to PLA alone [17]. However, due to the limited supply of commercially available MOI, we investigated another alternative, trimethyl hexamethylene diisocyanate (TMDI), in this study. By reacting PLA with small amount of TMDI, a ductile PLA with poly(ester-urethane) structure polymer material was prepared. The novel material exhibited markedly improved mechanical properties; elongation at break increased by more than 20 times while relatively high tensile stress was maintained, and impact strength improved 1.6 times when compared to pristine PLA.

The synthesized TMDI-modified PLA polymers were characterized by Fourier transform infrared (FTIR) and NMR to identify the chemical structures. The mechanical and thermal properties of ductile PLA were investigated.

Experimental

Materials

PLA (product NCP0003) was purchased from NatureWorks. A mixture of 2,2,4- and 2,4,4-TMDI was obtained from Evonik, Germany. Dibutyltin dilaurate was purchased from Acros. High purity toluene (HPLC grade) was purchased from Tedia. Common reagents were used as received without further purification.

Synthesis of TMDI-modified PLA polymer

15 g of PLA was dissolved in 90 g of toluene while stirring at 85 °C in a 500 mL round-bottom flask purged with nitrogen. When all of the PLA was dissolved in toluene, the temperature was increased to 105 °C. Then, dibutyltin dilaurate (0.15 g) was added as catalyst. Various amount of TMDI (0.45 or 0.75 g) was then charged. The mixture was stirred for 8 h and the temperature was maintained at 105 °C.

The final mixture was spread onto glass plates to obtain modified PLA films. The films were vacuum dried at 60 °C for 2 h to remove solvent in a pre-heated oven. Then, the films were fixed in a film casting apparatus to prevent the film from curving and were heated in a forced air oven at 60 °C for 12–24 h. The films (with a thickness of 50–60 μm) were cooled and stripped from the plates. To measure impact strength, these films were hot pressed to make Izod-type test specimen according to ASTM D256.

Chemical characterization

FTIR measurements were carried out on a Bio-Rad Digilab FTS-40 IR spectrometer under N_2 purging. Both the transmission and the attenuated total reflectance (ATR) FTIR spectra were recorded at a resolution of 8 cm^{-1} and accumulation of 16 scans. ^1H spectra were performed on a Bruker AV-400 spectrometer with $CDCl_3$ as the solvent. Molecular weight was determined by a gel permeation chromatography (GPC) with polystyrene calibration using a Perkin-Elmer series 200 HPLC system equipped with Jordi Gel DVB column at 35 °C in THF. Since the modified material was insoluble in THF, we dissolved the material in chloroform first and then mixed it with THF, prior to filtration and injection into GPC.

Mechanical properties measurement

An Instron universal tester model 3369 was used to study the stress–strain behavior at room temperature. The load cell used was 5 kg and the crosshead rate was 5 mm min^{-1}. Measurements were performed with film specimens (1.35-cm wide, 6-cm long, and 50–60-μm thick). Impact strength was measured by an Izod impact tester according to ASTM D256.

Thermal properties measurement

Thermogravimetric analyses were performed with a Perkin-Elmer Pyris 1 TGA instrument at a heating rate of 20 °C min^{-1} in nitrogen atmosphere to determine the thermal decomposition temperature. Differential scanning calorimetry (DSC) data were obtained from a Perkin-Elmer Pyris Diamond DSC. The samples (about 8 mg) were pre-sealed into an aluminum pan, heated to 200 °C, held for 2 min, and then cooled to the desired temperature with cooling rate of 10 °C min^{-1}. Samples were scanned at a heating rate of 10 °C min^{-1} under N_2. The value of the midpoint of the transition in the second heating process was taken as the T_g. The heat deformation temperature (HDT) was determined by the following test procedure as ASTM D648. The test specimen (127 × 3 × 11 mm) was loaded in three-point bending in the edgewise direction. A load of 3.1 MPa was placed on each specimen. The specimens were then lowered into a silicone oil bath where the temperature was increased at 2 °C min^{-1} until the specimen deflected 0.25 mm. The melt index (MI) was measured by a melt flow indexer GT-7100-MIB manufactured by GOTECH. Test procedures followed ASTM D1238 and the load was 2.16 kg with a time interval of 5 s.

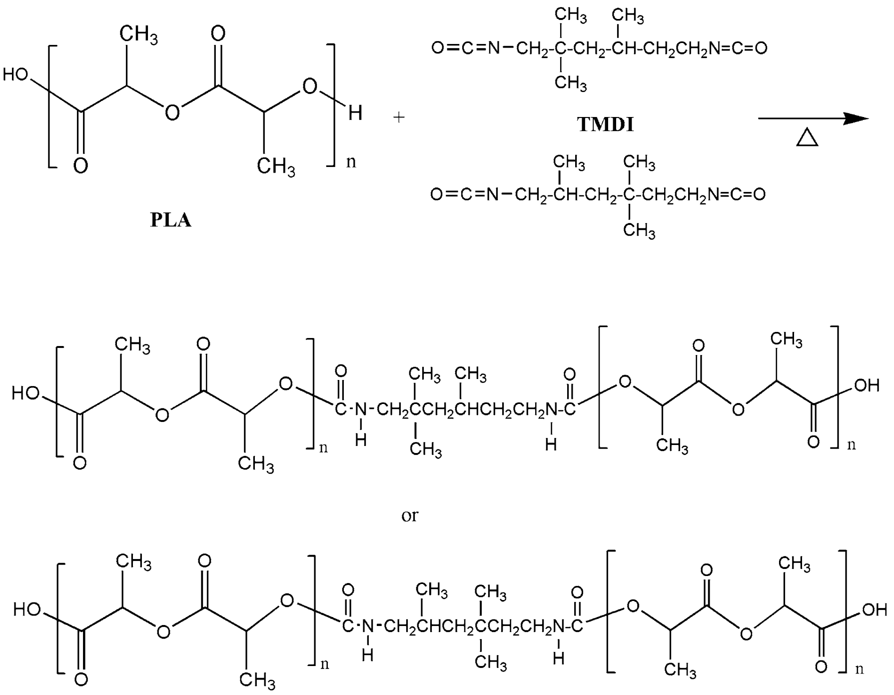
Results and discussion

Structure characterization

Based on the chemical structures of PLA and TMDI, a reaction scheme with poly(ester-urethane) structure was proposed as shown in Scheme 1. The FTIR spectra of PLA and TMDI-modified polymers are shown in Fig. 1. For PLA, it shows two main intense absorption bands at 1,758 and 1,186 cm^{-1} corresponding to C=O and C–O stretching groups, respectively. PLA modified with TMDI exhibits characteristic amide group absorptions at 3,350 cm^{-1} (N–H stretching), 1,576 and 1,638 cm^{-1} (NH bending, amide II band), also at 1,218 cm^{-1} (C–N stretching). ^{1}H NMR analyses demonstrated that upon synthesis, TMDI [$\delta = 0.88$–0.96 (t, 9H, CH_3)] reacted with PLA [$\delta = 1.58$ (m, CH_3), 5.17 (m, CH)] and formed a modified PLA with NH at 7.18–7.26 ppm. Spectroscopic data obtained were in good agreement with the proposed structure (shown in Scheme 1). GPC analyses showed that molecular weights of TMDI-modified PLA increased with the amount of TMDI added (see Table 1). This indicated that the molecular weight of the modified polymer increased by the chemical structure of TMDI linked with PLA.

PLA mechanical properties improvement

PLA materials are stiff, brittle, and exhibit limited extendibility [18, 19], with tensile stress of pure PLA at 50–64 MPa and strain at break at 2–5 %. In previous studies, we showed that adding MOI to PLA substantially improved the mechanical properties of PLA [17]. This MOI-modified ductile material was shown to have a very high elongation at break ($\sim$20 times when compared to pristine PLA), but demonstrated lower tensile strength around 25 MPa (down from 49.2 MPa). In this study, we replaced MOI with TMDI and found that TMDI-modified PLA materials markedly improved tensile strength in addition to producing a more ductile and tougher material in comparison with MOI-modified materials. Table 2 lists the mechanical properties of the novel materials, and Fig. 2 depicted the comparison of stress–strain relationship for three materials (PLA, MOI-, and TMDI-modified materials). The experimental results showed that the tensile strength improved



Scheme 1 Reaction scheme of TMDI-modified PLA

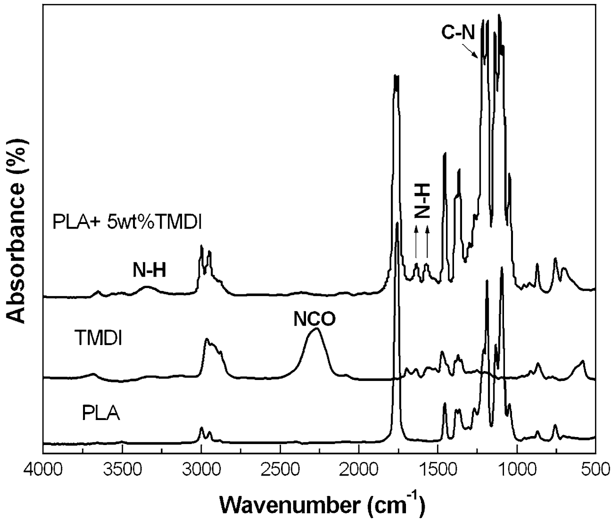


Fig. 1 FTIR spectra of PLA, TMDI, and modified polymer

substantially with TMDI-modified material while maintaining similar elongation at break. The ultimate strain in samples increased with the amount of TMDI added. This can be attributed to the poly(ester-urethane) structure and the increased

Table 1 Molecular weight of PLA and TMDI-modified polymers

Sample	Mw	Mn	PDI
PLA	15×10^4	7.4×10^4	2.06
PLA + TMDI (3 %)	17×10^4	8.2×10^4	2.07
PLA + TMDI (5 %)	23×10^4	10.7×10^4	2.14

Table 2 Mechanical properties of PLA and modified polymer materials

Material	Tensile strength (MPa)	Elongation at break (%)	Young modulus (GPa)	Impact resistance (J m^{-1})
PLA	49.2 ± 2.6	2.5 ± 0.5	3.3 ± 0.06	46.3 ± 0.3
PLA + TMDI (3 %)	43.8 ± 1.7	21.9 ± 2.1	2.9 ± 0.03	48.0 ± 0.2
PLA + TMDI (5 %)	37.7 ± 2.0	52.8 ± 2.5	2.2 ± 0.03	73.2 ± 1.5
PLA + MOI (5 %)[a]	25.8 ± 1.8	51.5 ± 2.6	1.6 ± 0.05	71.2 ± 1.0

[a] Ref. [17]

molecular weight of TMDI-modified materials. Previous studies by other researchers have demonstrated that molecular weight has a positive effect on the tensile strength of polymer materials [20]. For the 5 % TMDI-modified PLA, elongation at break increased from 2.5 to 52.8 % (increased by ~21 times when compared to pristine PLA), tensile stress decreased slightly to 38 MPa, and impact resistance (notched) improved from 46.3 to 73.2 J m^{-1}.

Thermal properties of modified PLA

In a previous study of ductile PLA, we found that MOI markedly improved the mechanical properties of PLA, but reduced the thermal properties of PLA [17]. The thermal properties of TMDI-modified PLA are tabulated in Table 3. For the thermal decomposition of PLA materials, the thermal decomposition temperatures at 10 % weight loss ($T_{\mathrm{d,\ 10\ \%}}$) decreased from 357 °C (PLA) to 325 °C for PLA modified with 5 % TMDI. Figure 3 depicts TGA curves of the modified PLA materials. The TGA data demonstrated lower thermal stability of modified ductile materials than pristine PLA.

DSC has been a vital technique to study melting and crystallization behavior of polymers [21]. Figure 4 shows the DSC melting scans of PLA and modified materials after a second scan. The corresponding thermal data, glass transition, and melting temperatures are listed in Table 3. Double melting peaks were observed for all samples. Multiple melting behavior of a polymer is usually linked to either the process of partial melting and recrystallization and remelting, or to melting of crystals with different lamellar thickness and/or different crystal structures [22]. The area of the secondary crystal melting peak is higher than the primary crystal melting peak, suggesting a large degree of recrystallization [21]. From Fig. 4, the T_g decreased from 60.6 °C for PLA to around 50 °C for TDMI-modified materials. The

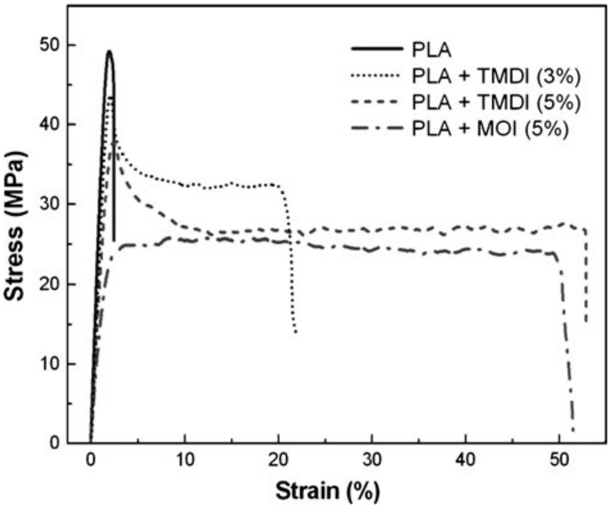


Fig. 2 Stress–strain relationship for various modified PLA materials

Table 3 Thermal properties of PLA and modified polymer materials

Material	Glass transition T_g (°C)	Melting peak	Decomposition temperature $T_{d,10\ \%}$ (°C)	Deformation temperature HDT (°C)	Crystallinity χ_c (%)
PLA	60.6	164.2	357	56	40.8
PLA + TMDI (3 %)	56.4	163.9	346	52	38.5
PLA + TMDI (5 %)	47.2	163.3	325	51	35.7
PLA + MOI (5 %)[a]	59.2	163.2	344	53	37.6

[a] Ref. [17]

data also show that T_m of modified PLA materials decreased slightly with the addition of various amount of TMDI. This might be due to the effect of increased molecular weight on T_m to compromise the decreased T_g for modified PLA materials [23].

The HDT for these PLA materials reduced slightly from 56 °C of PLA to 51 °C of 5 % TMDI-modified material. These results indicated that the improvements in mechanical properties of PLA were achieved, but some thermal stability was sacrificed. The MI of modified PLA showed significant improvement as depicted in Fig. 5. At 200 °C, the MI for PLA modified with 5 % TMDI was 244 versus 99.6 for pristine PLA. This result demonstrates that the modified PLA material is suitable for textile processing to make biomedical materials.

Our test results clearly demonstrate that reacting TMDI with PLA is highly effective for significant improvement in mechanical properties while thermal stability is slightly sacrificed. Based on the data presented, we suggest that 5 wt% of TMDI be added to improve the properties of PLA.

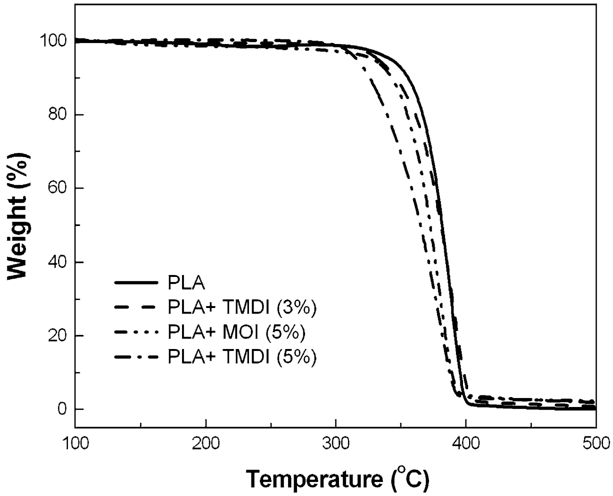


Fig. 3 TGA scan of modified PLA materials

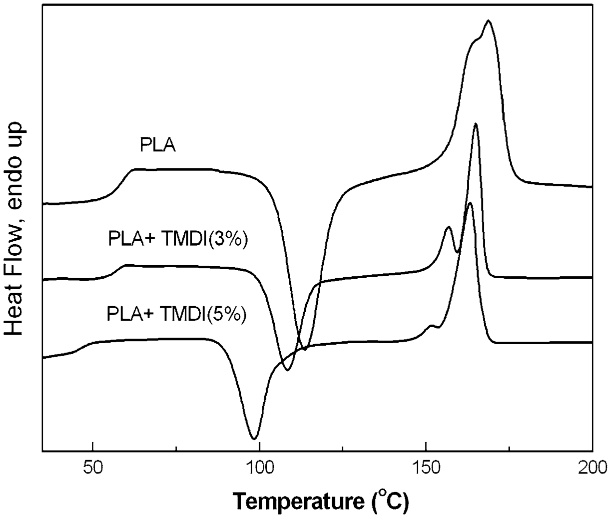


Fig. 4 DSC scans of PLA and TMD-modified polymers at second scan

Conclusions

A novel synthesized TMDI-modified PLA polymer material demonstrated markedly improved mechanical properties. The formation of poly(ester-urethane) structure between the terminal hydroxyl groups of PLA and the NCO end of TMDI contributed to the improvement of ductility. The prepared ductile PLA material showed elongation at break more than 20 times higher than that of pristine PLA. The 5 % TMDI-modified material had impact strengths 1.6 times higher than that of

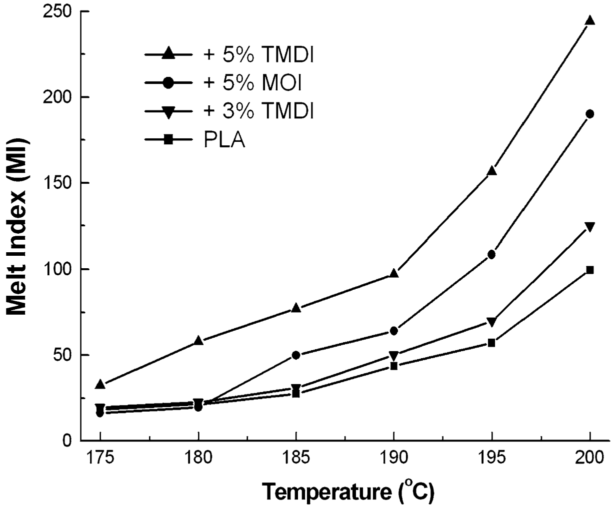


Fig. 5 MI of PLA and modified material at various temperatures

original PLA. Further studies will investigate the biocompatibility of the modified PLA material under physiological conditions to evaluate biomedical applications of this ductile polymer material.

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