Chinese Journal of Polymer Science Vol. 34, No. 7, (2016), 901–909

Chinese Journal of Polymer Science

High Performance Bio-based Polyurethane Elastomers: Effect of Different Soft and Hard Segments*

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Abstract In this work, a series of high performance bio-based polyurethanes (bio-PUs) were synthesized from polylactide (PLA)-based diols, different diisocyanates (TDI, MDI, HDI, IPDI) and chain extender 1,4-butanediol, in which different soft and hard segments are used to adjust their transition temperatures and mechanical properties. Poly(lactide-*co*-caprolactone) copolymer diols (*co*-PLAols) instead of PLA diols as the soft segment improved the thermal stability and mechanical properties of the synthesized bio-PUs. Among them, MDI-based bio-PUs have the highest T_g (43.8 °C), tensile strength (23.5 MPa) and modulus (380.8 MPa), while HDI-based bio-PUs have the lowest T_g (21.4 °C) and highest elongation at break (580%). Especially, the bio-PUs synthesized from *co*-PLAols and MDI demonstrate better mechanical properties, closed to petroleum-based commodities. Furthermore, the obtained bio-PUs display good shape memory properties at body temperature and cytocompatibility. Therefore, these bio-PUs are promising for applications in biomedical fields.

Keywords: Polylactide diols; Bio-based polyurethane; Shape memory; Biocompatibility.

INTRODUCTION

Currently, a great number of disposable medical devices, such as infusion apparatus, catheters, and blood bag are used to avoid the inflection from medical devices[1]. Most of these single-use medical devices are made from phthalate plasticized poly(vinyl chloride) (PVC), but the plasticizers often cause troubles, especially upon contact with body fluids or tissues[2, 3]. Some polyolefin alloys or thermoplastic elastomers have been reported to partially replace soft PVC in medical devices[1, 2, 4]. However, the above-mentioned materials are not biodegradable, which would result in environmental pollution over a long period of time. Therefore, it is desired to develop a green material as an alternative to PVC in medical devices.

On the other hand, significant interest has been paid to biodegradable polymers due to serious environment pollution and their biomedical applications[5–8]. Among them, polylactide (PLA), produced from bio-based lactic acid, is known to be one of the promising polymers because of its good biodegradability and

* The research is financially supported by the National Natural Science Foundation of China (No. 21404112), Ningbo Key Scientific and Technological Project (No. 2014B10023), Ningbo Natural Science Foundation (No. 2015A610016), Open Project of Key Laboratory of Marine Materials and Related Technologies (No. 2016K07) and Ningbo Science and Technology Innovation Team (No. 2015B11003).

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Received January 29, 2016; Revised February 23, 2016; Accepted February 29, 2016
doi: 10.1007/s10118-016-1811-7

biocompatibility[9–11]. It can be degraded into small molecules in the body, and then further broken down into CO_2 and water, which can be excreted through metabolism. However, the brittle nature, poor ductility and impact toughness of PLA limit some applications where mechanical toughness is required[12, 13]. Recently, a series of PLA-based polyurethanes (PUs) with shape memory properties have been reported[14–17]. For example, Jing *et al*. reported PLA-based PUs with glass transition temperature (T_g) in the range of 33−63 °C were synthesized from PLA diols, diisocyanate compounds and 1,4-butanediol (BDO)[15, 16]. However, these PLA-based PUs showed high Young's modulus and hardness, which makes them unsuitable to replace PVC in medical devices.

In the present work, a series of high performance bio-based polyurethanes (bio-PUs) were synthesized from PLA-based diols, different diisocyanates and chain extender 1,4-butanediol, in which different soft and hard segments are used to adjust their transition temperatures and mechanical properties. Poly(lactide-*co*-caprolactone) copolymer diols instead of PLA diols as the soft segment improved the thermal stability and mechanical properties of the synthesized bio-PUs. Among them, MDI-based bio-PUs exhibit better mechanical properties than soft PVC, closed to petroleum-based commodities. Furthermore, the obtained bio-PUs display good shape memory properties at body temperature and cytocompatibility. Therefore, these bio-PUs are promising for applications in biomedical fields, which are especially expected to replace PVC in medical devices.

EXPERIMENTAL

Materials

Hexamethylene diisocyanate (HDI), 4,4′-diphenyl methane diisocyanate (MDI), 1,4-butanediol (BDO) and stannous octoate ($SnOct_2$) are analytically pure, and were obtained from Aladdin (Shanghai, China). Toluene diisocyanate (TDI), tetrahydrofuran (THF) and *N*,*N*-dimethyl formamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. *ε*-Caprolactone (CL) and *L*-lactide (LA) were provided from Shenzhen Esun Industrial Co., Ltd.

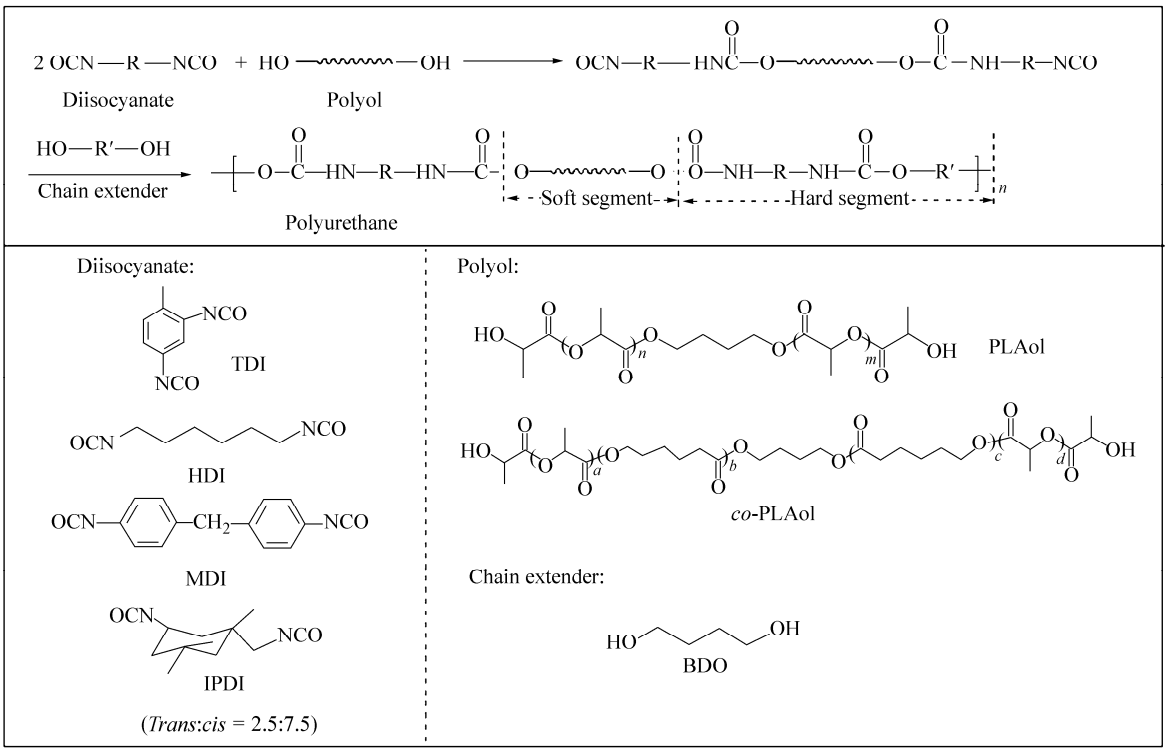
Synthesis of Bio-based PLA and Copolymer Diols

A series of PLA diols (PLAols) were synthesized by ring opening polymerization of LA using $SnOct_2$ and BDO as the catalyst and chain transferring agent, respectively. In a N_2 atmosphere, LA, BDO and $SnOct_2$ were added to a 1-L flask free of oxygen and water, where the catalyst amount was 0.1% with respect to LA, wt/wt. The reaction was performed at 160 °C for 6 h. The molecular weight of PLAols was tuned to be 1000 and 2000 g/mol by changing the feed molar ratio of BDO and LA (1/6.0, 1/13.3), which were denoted as PLAol-1000 and PLAol-2000, respectively.

The poly(LA-*co*-CL) diols (*co*-PLAols) were prepared in a similar way, where the feed molar ratio of LA and CL was 3.17. The *co*-PLAols with molecular weight of 1000, 2000 and 3000 g/mol were nominated as *co*-PLAol-1000, *co*-PLAol-2000 and *co*-PLAol-3000, respectively.

Preparation of PLA-based Polyurethanes

PLA-based polyurethanes were synthesized *via* a two-step polymerization process, where the molar ratio of polyol, diisocyanate and chain extender is 1:2:1, as shown in Scheme 1. First, the polyol was dissolved in THF at 60 °C and then diisocyanate and $SnOct_2$ were added to the THF solution. Second, when the remaining NCO content was closed to the theoretical value, the chain extender was added to the above reaction system. The reaction was carried out until the FTIR absorption peak of NCO group (2270 cm^{-1}) disappeared. The detailed information of the obtained bio-PUs are listed in Table 1.



Scheme 1 Synthetic route of the bio-PUs

Table 1. Detail information of the obtained bio-PUs

Samples	Polyols	Diisocyanates	HS [a] (wt%)	M_w [b]	M_w/M_n [b]
T1K	PLAol-1000	TDI	29.2	1.7×10^4	2.1
T2K	PLAol-2000	TDI	18.1	2.0×10^4	2.1
co-T1K	*co*-PLAol-1000	TDI	30.5	1.7×10^4	2.0
co-T2K	*co*-PLAol-2000	TDI	18.0	2.2×10^4	2.0
co-T3K	*co*-PLAol-3000	TDI	12.7	2.3×10^4	2.2
co-H2K	*co*-PLAol-2000	HDI	17.5	2.2×10^4	2.0
co-M2K	*co*-PLAol-2000	MDI	22.8	3.5×10^4	2.3
co-I2K	*co*-PLAol-2000	IPDI	21.1	2.7×10^4	2.1

[a] The hard segment weight percent (HS, wt%), which is defined as the percent by weight of BDO and diisocyanates in the polyurethane; [b] Measured by GPC

Characterization Methods

FTIR spectra were performed on a Thermo Nicolet 6700 spectrometer under an attenuated total reflection (ATR) mode. ^{1}H-NMR spectra were measured at room temperature on a Bruker AV-400 NMR apparatus in deuterated chloroform ($CDCl_3$). The molecular weights (M_n, M_w) of the resulted polyurethanes were obtained on a HLC-8320 gel permeation chromatography (GPC) according to polystyrene (PS) standard using THF as eluent.

Differential scanning calorimetry (DSC) analysis was recorded using a DSC 214 of Polyma (Netisch) Instruments. The samples were initially heated from −30 °C to 180 °C, then cooled to −30 °C, and finally heated up to 180 °C at a rate of 10 K/min in a nitrogen atmosphere. The glass transition temperature (T_g) was determined from the second heating scan to reduce the influence of thermal history. Thermo gravimetric analysis (TGA) was performed using a TGA-Q50 system from TA Instruments at a heating rate of 20 K/min in a nitrogen atmosphere. Atomic force microscopy (AFM) was conducted on a Dimension 3100 V scanning probe microscope in tapping mode. The AFM sample was prepared by casting the bio-PUs solution (5 wt%) on a silicon wafer.

Tensile tests were conducted on a tensile instrument (Instron 5567) with a speed of 100 mm/min at 25 °C. The mean value of five replicated measurements was taken for each sample. The shape memory test of bio-PUs was performed as follows: Firstly, the specimens were bent to a given angle at 37 °C. Subsequently, they were quenched below T_g using liquid nitrogen. Then the samples were allowed for free recovery at 37 °C.

Cytotoxicity of bio-PUs was examined by Alamar blue assay. After sterilization *via* sonication for 30 min in DI water and 75% ethanol respectively, the specimens were immersed in Eagle's minimum essential medium, Alpha modification (α-MEM; Gibco) supplemented with 10% fetal bovine serum (FBS; Gibco), 1% penicillin and 1% streptomycin, and incubated for 72 h under the cell culture conditions (95% humidity, 5% CO_2, 20% O_2 37 °C). 2×10^5 of human mesenchymal stem cells (hMSCs) were seeded in each well of a 24-well plate. The cell viability was examined by Alamar blue assay at several time points after incubation in the extracts (days 1 and 3) and compared with the viability in the pure cell culture medium. Briefly, 50 μL of Alamar blue assay reagent were added into each well of the culture plate and the absorbance at 562 nm was measured after incubation for 4 h in dark. Each group consisted of 4 independent samples.

RESULTS AND DISCUSSION

Synthesis and Characterization of Bio-based PLA Diols and Polyurethanes

Five bio-based PLA and copolymer diols (PLAol-1000, 2000 and *co*-PLAol-1000, 2000, 3000) were synthesized by the above-mentioned method. The structures of PLAol and *co*-PLAol were confirmed by ^{1}H-NMR, as shown in Fig. 1. The signals at $\delta = 5.17$ are ascribed to the —CH— connected to C=O in PLAol and *co*-PLAol, while the signals at δ = 2.32, 1.64, 1.29, 1.62 and 4.08 are assigned to protons on —C=O—C<u>H$_2$</u>—C<u>H$_2$</u>—C<u>H$_2$</u>—C<u>H$_2$</u>—C<u>H$_2$</u>—O— in *co*-PLAol, respectively[18]. Figure 2 shows the DSC curves of the synthesized PLAol and *co*-PLAol. PLAols with M_n of above 2000 have multi-melting peaks, and their T_g values increase with the increase of M_n. In comparison, *co*-PLAols are amorphous and have relatively low T_gs. Instead of an elastomer, the bio-PUs synthesized from PLAols and TDI were rigid solid at room temperature. To obtain high performance bio-PUs, *co*-PLAols were therefore chosen to be used as the soft segments.

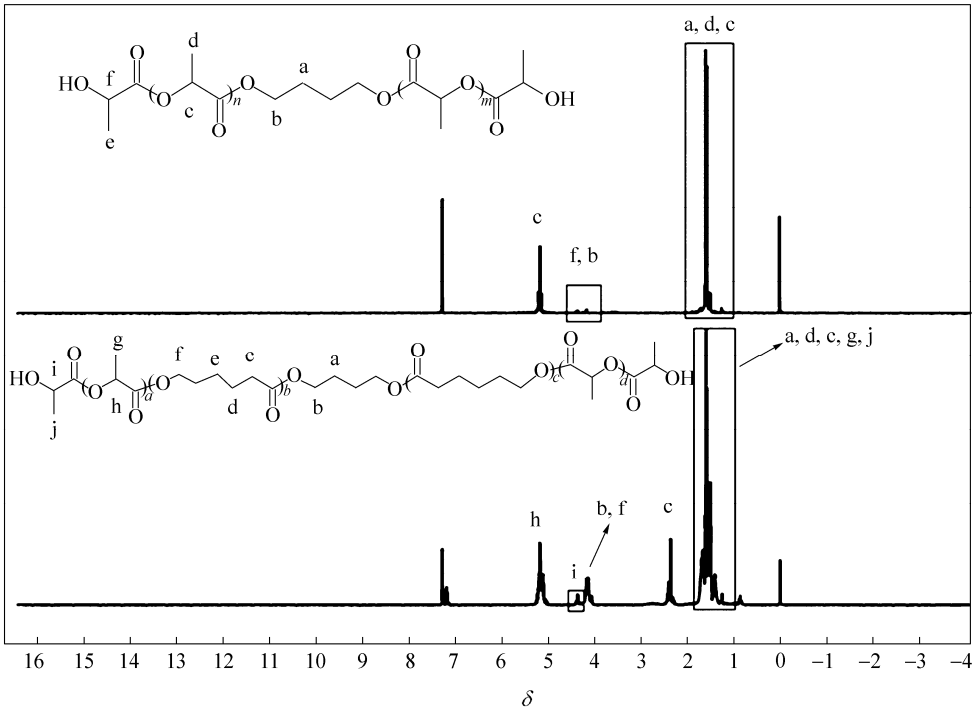


Fig. 1 ^{1}H-NMR spectra of PLAol-2000 and *co*-PLAol-2000

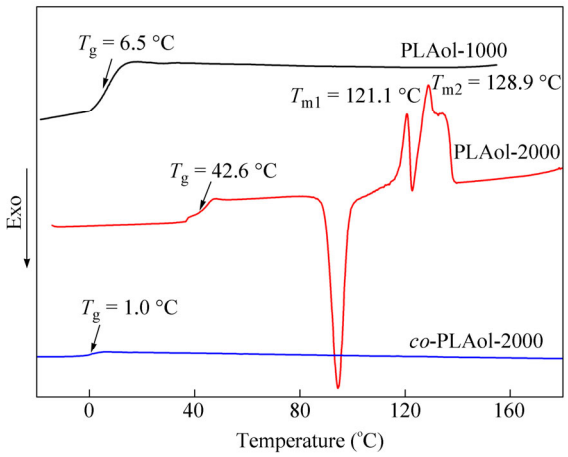


Fig. 2 DSC curves of PLAol-1000, 2000 and *co*-PLAol-2000

As shown in Scheme 1, the bio-PUs were prepared from different diisocyantes *via* a two-step polymerization process, whose structure was characterized by FTIR spectra. The spectra (Fig. 3) exhibit absorption peaks at about 3360 and 1530 cm^{-1}, which are assigned to the stretching vibrations of NH and amide II in the urethane groups, and they do not display the stretching vibration bands of N=C=O groups at about 2270 cm^{-1} and OH groups at about 3500 cm^{-1}. Moreover, the strong absorptions at about 1750 and 1200 cm^{-1} correspond to the stretching vibrations of C=O and C—O—C in the ester groups of polyols, respectively. These results demonstrate that the bio-PUs from different diisocyanates were successfully synthesized. In the following sections, the thermal, mechanical, shape memory properties and phase separation behavior of the synthesized bio-PUs with different hard segments would be discussed.

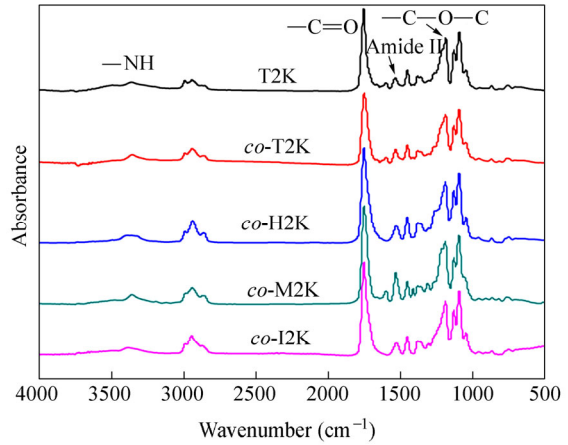


Fig. 3 FTIR spectra of the obtained bio-PUs

Properties of Bio-PUs

Figure 4 shows the DSC curves of the synthesized bio-PUs with different soft and hard segments, and their T_g values are summarized in Table 2. All obtained bio-PUs display only one T_g and no crystallization or melting peaks in the DSC curves, indicating that the obtained PUs were amorphous[19]. As the molecular weight of soft segments PLAols increased from 1000 to 2000, the T_g values of TDI-based PUs increased from 28.9 °C to 42.7 °C. While *co*-PLAols were used to be the soft segments, the T_g values of TDI-based PUs were very closed. The PU synthesized from MDI has a higher T_g than the TDI-based one, and the reason lies in that MDI has more symmetrical structure than TDI, which may help to enhance the intermolecular interaction, leading to higher T_g.

Moreover, the T_g values of the synthesized bio-PUs are closed to body temperature. Hence, as shape memory polymers, these obtained bio-PUs are expected to have many applications in medical devices.

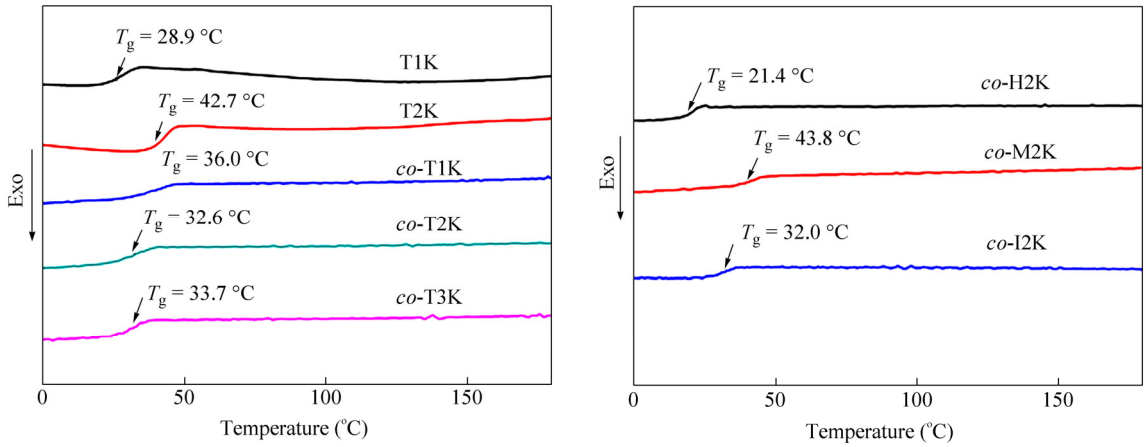


Fig. 4 DSC curves of the obtained bio-PUs

Table 2. Thermal and mechanical properties of bio-PUs samples

	T_g (°C)	$T_{5\%}$ (°C)	T_{max} [a] (°C)	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
T1K	28.9	182.7	281.5	–	–	–
T2K	42.7	239.7	288.0	–	–	–
co-T1K	36.0	214.9	293.6	–	–	–
co-T2K	32.6	256.3	319.0	8.8	460	217.3
co-T3K	33.7	255.4	307.3	5.6	440	84.1
co-H2K	21.4	270.8	329.4	2.2	580	22.0
co-M2K	43.8	274.1	302.2	23.5	430	380.8
co-I2K	32.0	261.9	306.4	3.5	350	137.5

[a] T_{max} is the temperature of the maximum rate of weight-loss of the samples.

The effect of different soft and hard segments on the thermal stability of the obtained bio-PUs was investigated by TGA, as shown in Fig. 5. Their weight loss temperatures ($T_{5\%}$, T_{max}) are listed in Table 2. Instead of PLAols as the soft segment, *co*-PLAols improved the thermal stability of the synthesized PUs. In comparison, the type of diisocyanates has a little impact on the thermal stability of the obtained PUs. Furthermore, the $T_{5\%}$ and T_{max} of the bio-PUs synthesized from *co*-PLAols are above 200 and 300 °C, respectively, indicating the good thermal stability of these bio-PUs.

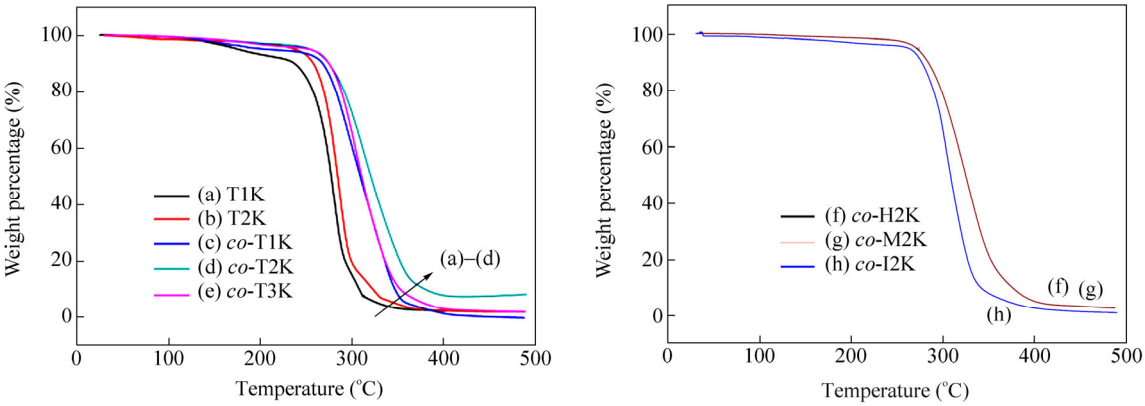


Fig. 5 TGA curves of the obtained bio-PUs

Figure 6 displays the typical stress-strain curves of the obtained bio-PUs from *co*-PLAols, and their tensile strength, elongation and Young's modulus are summarized in Table 2. Obvious yielding was observed before break. From Table 2, the tensile strength and modulus of the samples decreased with the molecular weight of soft segment increasing, from 8.8 MPa and 217.3 MPa for *co*-T2K to 5.6 MPa and 84.1 MPa of *co*-T3K, respectively. Compared with TDI, MDI and IPDI-based PUs, HDI-based PUs have the highest elongation at break, possibly due to the long aliphatic carbon chains of HDI, resulting in good flexibility of the PU chains. From Fig. 6 and Table 2, we can conclude that the mechanical properties of the obtained bio-PUs could be adjusted in a wide range. The tensile strength and elongation of *co*-M2K synthesized from *co*-PLAol-2000 and MDI were 23.5 MPa and 430%, respectively, which are comparable to commercial petroleum-based polyester PUs (Desmopan® 400 serials) from Bayer Corporation[20]. The superior mechanical properties are mainly attributed to the well-defined phase separation morphology, as shown in Fig. 7. Compared with TDI, HDI and IPDI-based PUs, the micro-phase of MDI-based PUs becomes more developed.

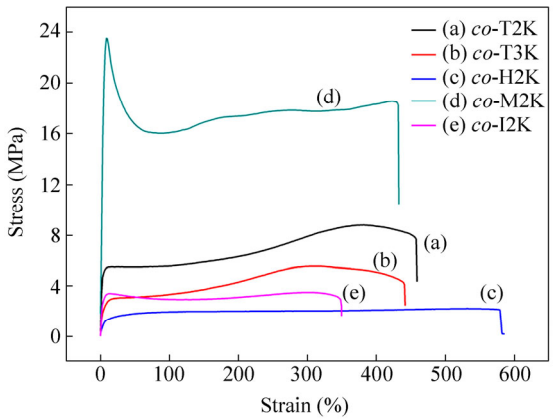


Fig. 6 Stress-strain curves of the obtained bio-PUs from *co*-PLAols

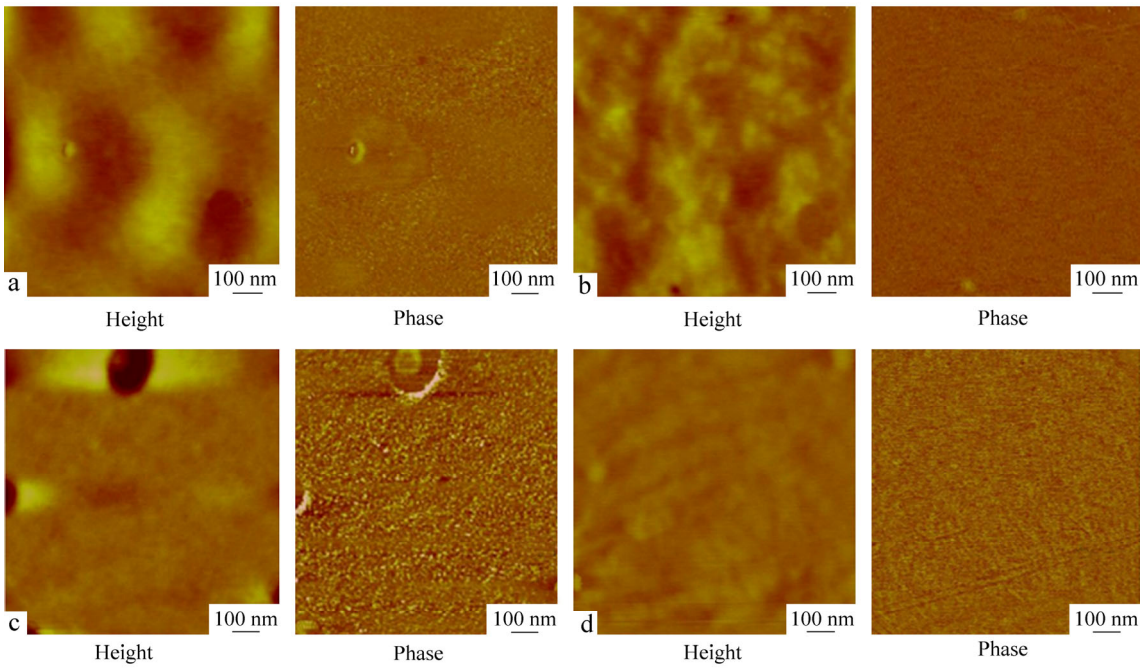


Fig. 7 AFM height and phase images of the bio-PUs: (a) *co*-T2K, (b) *co*-H2K, (c) *co*-M2K and (d) *co*-I2K

The shape memory properties of the obtained bio-PUs at body temperature are also measured. Figure 8 shows the shape recovery process of *co*-I2K at body temperature (37 °C). The sample was changed into a bending shape at 37 °C and then cooled rapidly below T_g using liquid nitrogen and it reached the original shape state in about 2 min at 37 °C.

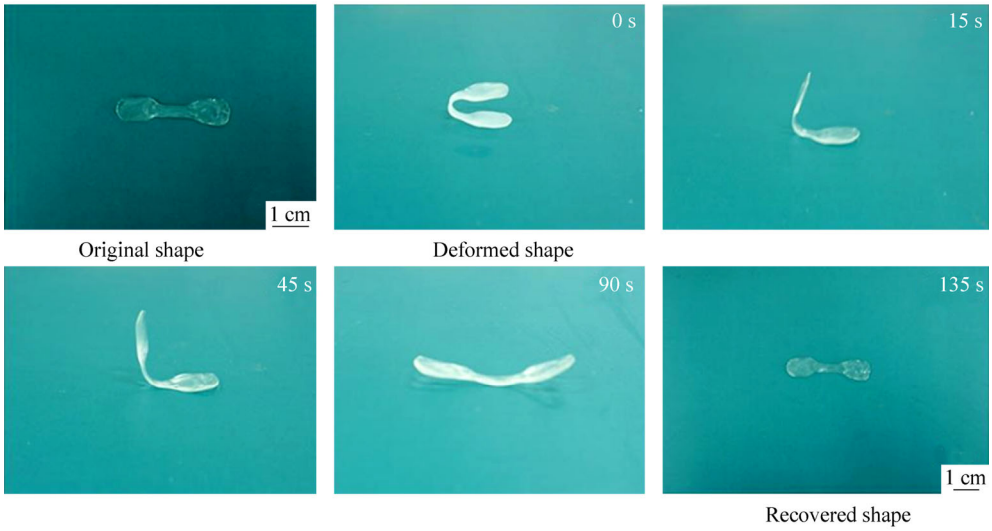


Fig. 8 Recovery process of shape memory *co*-I2K at 37 °C

The above-mentioned results indicate that the synthesized bio-PUs display better mechanical properties and good shape memory properties at body temperature, which are promising for applications in medical devices.

Cytotoxicity of Bio-PUs

To determine the cytotoxicity of the synthesized bio-PUs, the Alamar blue assay by hMSCs was used, as shown in Fig. 9. It can be clearly seen that *co*-H2K and *co*-I2K showed no cytotoxicity, and their cell vibabilities were nearly closed to 100% after incubation for 1 and 3 days. This result indicates that the synthesized bio-PUs are cytocompatible to hMSCs[21].

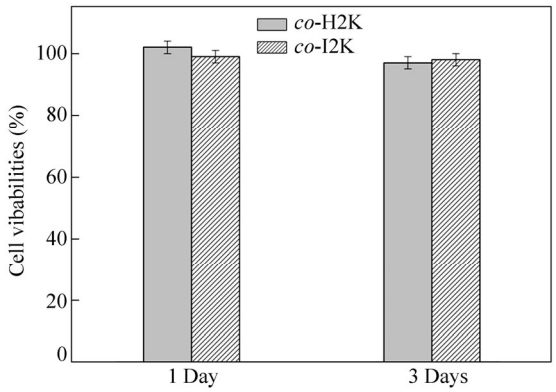


Fig. 9 Cytotoxicity of *co*-H2K and *co*-I2K to hMSCs

CONCLUSIONS

A series of high performance bio-PUs elastomers from PLA-based diols and different diisocyanates were successfully prepared and characterized. Instead of PLAols as the soft segment, *co*-PLAols improved the thermal stability and mechanical properties of the synthesized PUs. Among them, *co*-M2K from MDI demonstrates

better mechanical properties, closed to the petroleum-based polyester polyurethane (Bayer Desmopan® 400 series). Moreover, the obtained bio-PUs display good shape memory properties at body temperature and biocompatibility, which are hence promising for applications in biomedical fields and especially expected to replace PVC for medical devices.

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