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Structure and blood compatibility of highly oriented poly(lactic acid)/ thermoplastic polyurethane blends produced by solid hot stretching

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Abstract: Highly-oriented poly(lactic acid) (PLA)/thermoplastic polyurethane (TPU) blends were fabricated through solid hot stretching technology in an effort to improve the mechanical properties and blood biocompatibility of PLA as blood-contacting medical devices. It was found that the tensile strength and modulus of the blends can be improved dramatically by stretching. With the increase of draw ratio, the cold crystallization peak became smaller, and the glass transition and the melting peak moved to high temperature, while the crystallinity increased, and the grain size of PLA decreased, indicating of the stress-induced crystallization during drawing. The oriented blends exhibited structures with longitudinal striations which indicate the presence of micro-fibers. TPU phase was finely and homogeneously dispersed in the PLA, and after drawing, TPU domains were elongated to ellipsoid. The introduction of TPU and orientation could enhance the blood compatibility of PLA by prolonging kinetic clotting time, and decreasing hemolysis ratio and platelet activation.

Keywords: poly(lactic acid) (PLA); thermoplastic polyurethane (TPU); solid hot stretching; orientation; mechanical properties; blood compatibility

1. Introduction

Intense effort has been being made on preparing biomedical materials through centuries because of their extensive and significant importance in biology and medicine science [1]. PLA has been considered to be a good candidate for biomedical materials due to its favorable physical properties, ease of handling and processing, and its biodegradable and biocompatible nature, which have been approved by the Food and Drug Administration (FDA) for numerous clinical applications, such as sutures, bone plates, abdominal mesh, and extended-release pharmaceuticals [2~4].

For biomedical materials, two fundamental requirements are proposed. First,

their physical properties such as flexibility or rigidity, mechanical strength, etc., must fulfill the purposes for multiple practices relating with biological preference. In addition, for a biomedical implant material to be in contact with blood, the blood compatibility is another one of the most important properties in order to ensure the security of clinical practice [5]. Although extensive efforts have been devoted to modifying the mechanical properties of PLA by copolymerization with other monomers or blending PLA with other polymers, limited studies have been reported on the blood compatibility of PLA and PLA based blends [6~8].

Solid hot stretching technology presents the advantages of high production rates, high orientation, and significant enhancements in the properties without complex processing apparatus [9~11]. Through solid hot stretching technology, first of all, PLA with sufficient initial strength and sufficient strength retention over a period of time could be prepared to meet the requirement of desirable physical properties for biomedical use. Meanwhile, the surface properties of PLA may be influenced by processing and thus affect the interaction with the biological elements of the organism.

Thermoplastic polyurethane (TPU) elastomers have a unique combination of toughness, durability, flexibility, biocompatibility and bio-stability, which makes them suitable materials for use in a diverse range of implantable medical devices [12~15]. The soft segments of PU elastomers are mainly polyester or polyether, which are expected to have good compatibility with PLA because PLA has been reported to be miscible with some polyesters and polyethers [16~17]. In view of its favorable mechanical properties, good biocompatibility, as well as the possible compatibility with PLA, TPU elastomer was considered to be a good candidate for blending with PLA.

In this paper, TPU based on polyethylene glycol (PEG) as the soft segments and hard segment percentage of 60%, was synthesized by bulk polymerization, and PLA/TPU blends were prepared. Because a significant longitudinal orientation and fibrous structure have been observed in the innermost layer of the blood vessel, design of ordered fibrillar structure in polymer is one of the favorable biomimetic strategies to improve the blood compatibility. In this work, highly oriented PLA and PLA/TPU blends were fabricated through solid hot stretching technology in order to improve the mechanical properties and blood biocompatibility of PLA as blood-contacting medical devices by promoting the formation of ordered fibrillar structure in the materials, and the structure and properties of the oriented samples were studied.

2. Experimental

2.1 Materials

PLA used in this study was a commercial grade granular product without any additives, supplied by Cargill Dow Co. (USA). The molecular weight (\overline{M}_n) was about 1×10^5 ; Diphenylmethane diisocyanate (MDI) from Wanhua Polyurethane Co. Ltd (Yantai, China) was used as received; 1,4-butanediol (BDO) was supplied by Bodi Chemical Co. Ltd. (Tianjin, China); polyethylene glycol (PEG) (\overline{M}_n , 6000) was purchased from Kelong Chemical Engineering Co. Ltd (Chengdu, China).

2.2 Preparation of the oriented PLA/TPU blends

Synthesis of TPU

A one-step procedure was adopted to prepare TPU via bulk polymerization. The stoichiometric amounts of the PEG were dried under vacuum at 120 °C for 2 h. Then an appropriate amount of BDO was added into this bulk by vigorously stirring. At a

chosen temperature, the calculated amount of reactant (MDI) was added to give a final NCO/OH ratio of 0.98, resulting in a polymer with a linear chain. Finally the product was cast in a mold at a chosen temperature for 12 h. The hard-segments of this product were composed of diisocyanate and the chain extender, and the soft-segments originated from the PEG. The reaction equation for PEG-TPU synthesized in this study was shown in Scheme 1.

The composition of synthesised TPU was analyzed by FTIR. As shown in Figure 1, there was a $\text{-CH}_2\text{-}$ stretching vibration absorption peak at 2890.0 cm^{-1} ; a C=O stretching peak was observed at 1725.9 cm^{-1} ; the peak at 1533.8 cm^{-1} was assigned to N-H bending vibration absorption or the stretching vibration of the phenyl framework; the stretching vibration peak of C-O-C was in the range of $1100.0\sim 1258.6\text{ cm}^{-1}$; and especially, the strong absorption peak at 1103.3 cm^{-1} was attributed to the stretching vibration of C-O-C on the PEG molecular chain. The absorption peak of diisocyanate (-N=C=O) band at $2250.0\sim 2275\text{ cm}^{-1}$ was absent in the spectra of the TPU, indicating that this group was completely consumed in the reaction.

Preparation of PLA/TPU blends

Samples of PLA/TPU blend with weight ratio of 80/20 were prepared by melt mixing using a TSSJ-25/03 twin-screw extruder at a rotational speed of 45 rpm, and the temperatures of the barrel were in the range of $180\text{ }^\circ\text{C} \sim 220\text{ }^\circ\text{C}$. The extrudate was pelletized and dried, and then moulded to tensile specimens by using injection moulding machine.

Preparation of the oriented PLA/TPU blends

The oriented samples of PLA and PLA/TPU blends were prepared by being heated at $90\text{ }^\circ\text{C}$ and mechanically stretched through a converging die. After the desired draw

ratio was obtained, the sample was cooled down to room temperature, and then the load was released.

2.3 Measurements

Mechanical properties

The mechanical properties of the samples were measured with a 4302 material testing machine from Instron Co. (U.S.A.) according to ISO527/1-1993 (E). The test speed was 50 mm/min, and the sample length between benchmarks was 25 mm.

Non-isothermal crystallization analysis

The non-isothermal crystallization was performed with a Netzsch 204 Phoenix differential scanning calorimetry (DSC) of Germany. The temperature scale of DSC was calibrated with indium. Granulated samples of about 10 mg were heated from ambient temperature to 200°C at a constant rate of 10 K/min under nitrogen atmosphere. X_c can be calculated with the following equation:

$$X_c = (\Delta H_m / \Delta H_0) * 100\% \quad (1)$$

where ΔH_m is the melting enthalpy of the samples and ΔH_0 is the balance melting enthalpy, i.e., the melting enthalpy of 100% crystallizing polymer.

Wide-angle X-ray diffraction analysis (WAXD)

WAXD analysis was performed with a Rigaku D/max IIIB X-ray diffractometer (Japan) at room temperature. XRD data were collected from 5 to 35°.

Scanning electron microscope analysis

The fractured surface morphology analysis of the samples was performed with JEOL JSM-5900LV scanning electron microscope (SEM) with an acceleration voltage of 20 kV. The samples were sputter-coated with gold for 2~3 min.

Contact angle measurement

The contact angles of water as testing liquids on the samples were measured by an ErmaG-1 contact angle test apparatus (Japan) at room temperature using the sessile drop method. Five measurements were made on each sample to obtain the values of contact angle.

Hemolysis analysis

Hemolytic activity was assessed by determining hemoglobin release under static conditions using the two phase hemolysis test (according to ASTM F 756-00). Blood testing solution was prepared by using 4 mL fresh blood with an acid citrate dextrose anticoagulant (ACD medium) and was diluted with 5 ml of physiological saline. In the first phase, each sample (1 cm × 1 cm) was incubated in 10 ml pure saline for 30 min at 37 °C. Then, diluted fresh blood (0.2 mL) was added and incubation went on for another 60 min in a shaker at the constant temperature of 37 °C. Positive and negative controls were produced by adding 0.2 mL of diluted fresh blood to 10 ml of purified water and saline, respectively. After incubation, samples were centrifuged at 2500 r/min for 5 min. Optical density of the supernatant was measured at 545 nm by a spectrophotometer. The hemolysis ratio was calculated according to Equation 2:

$$Z=100%*(D_t-D_{nc})/(D_{pc}-D_{nc}) \quad (2)$$

Where Z represented the hemolysis ratio, D_t represented the absorbance of test samples, D_{nc} and D_{pc} represented the negative samples and positive samples, respectively (ASTM F 756-00).

Kinetic clotting time

Kinetic clotting time was measured as follows: 100 μL of anticoagulant blood was carefully added on the test samples (1 cm × 1 cm) surface, followed by the addition of 10 μL of calcium chloride solution (0.2 mol/L) simultaneously. Thereafter, time was

recorded. After the preset, 10, 20 30, 40 and 50 min, the surface of the test sample with blood was flowed slowly by the distilled water separately and the flowed liquid was collected and then measured with a spectrophotometer at a wavelength of 545 nm. Glass silicide and glass were used as a negative control and a positive control, respectively.

Platelet adhesion measurement

To test the platelet adhesion, samples in square shape (1cm×1cm) were incubated with the platelet rich plasma (PRP) for 1 h at 37°C under static conditions. After 1h incubation, the samples were rinsed carefully three times with phosphate-buffered saline (PBS, pH=7.3) buffer. The adherent platelets were fixed using 2.5% glutaraldehyde in PBS for at least 1 h, dehydrated in a graded series (50%, 60%, 70%, 80%, 90%, 95%, and 100%, v/v) of ethanol, and dried under vacuum at -50°C overnight. The samples were then sputter coated with a thin layer of gold and observed using a scanning electron microscopy (JEOL JSM-5900LV).

3. Results and Discussion

3.1 Mechanical properties of drawn PLA/TPU blends

The mechanical properties of isotropic and drawn PLA/TPU blends in comparison with neat PLA were shown in Figure 2. Compared to the neat PLA, the addition of the TPU brought about some increase in elongation at break and decrease in tensile strength and modulus, which could be attributed to the toughing effect of TPU on PLA. With increasing draw ratio, the tensile strength and modulus increased, while the elongation at break decreased for both PLA and PLA/TPU blends. The downward trend of elongation at break for the blends was more obvious than that of pure PLA.

For Figure 2(a), the variation of the gap between PLA and PLA/TPU blend during drawing in tensile strength and modulus can be explained as below: In the initial isotropic specimen, the addition of the TPU brought about some increase in elongation at break without a significant drop in the tensile strength and modulus due to the effective toughening effect of TPU on PLA. During stretching, the interaction between PLA and TPU hindered the crystallization and orientation movement of molecules of PLA which may lead to bigger gap between pure PLA and the blends at draw ratio of 280% and 340% in tensile strength and modulus. With a further increase of draw ratio, joint orientation may be formed for PLA matrix and TPU resulting in smaller gap in strength and modulus between them.

3.2 Structure and morphology of drawn PLA/TPU blends

3.2.1 Crystallization property

DSC measurements were performed in order to evaluate the influence of processing conditions on the crystallization properties of PLA and PLA/TPU blends. The DSC thermograms of isotropic and drawn samples were shown in Figure 3, from which the melting temperature (T_m), the heat of melting (ΔH_m) and the crystallinity (X_c) can be obtained, as listed in Table 1. All samples exhibited three distinct peaks corresponding to glass transition at around 60 °C, cold crystallization peaks at about 80 °C, and melting peaks at around 169 °C respectively. Compared with the neat PLA, an additional endothermic peak at around 65 °C can be observed for PLA/TPU blends corresponding to the melting peak of TPU, which became bigger after drawing.

With the increase of draw ratio, the cold crystallization peak became smaller, while the glass transition and the melting peak moved to high temperature for both PLA and PLA/TPU blends. As shown in Table 1, the melting enthalpy and crystallinity of PLA

increased with the draw ratio, indicating of the stress-induced crystallization of PLA during drawing.

Wide-angle X-ray diffraction (WAXD) measurements were taken to further confirm the crystallization behavior of PLA and PLA/TPU blends during solid hot drawing. Figure 4 displayed the WAXD patterns in the range of $2\theta=5\sim 35^\circ$ for the neat PLA and the PLA/TPU blends. The samples before drawing exhibited a diffraction peak at $2\theta = 16.7^\circ$, which belonged to α crystal form of PLA as reported previously[18]. Moreover, compared with neat PLA, a relatively broad peak for PLA/TPU blends at this position can be observed, resulting from low crystallinity of TPU. A very diffused diffraction peak near $2\theta=23.4^\circ$ appeared for all PLA/TPU blends with different draw ratios, which was attributed to a short-range-order arrangement of chain segments of TPU molecules [19].

Moreover, it can be seen that the diffraction peak position of oriented PLA and PLA/TPU blends with different draw ratios had no change, however, there were significant differences in intensity. Because the intensity of the diffraction peak represented the degree of the order in the material, including crystallization and orientation, the results indicated that stretching did not affect the crystal type, but it could significantly affect the crystallization and orientation of PLA.

The crystallinity of PLA can be calculated by the peak area of crystal and amorphous region from the WAXD curves obtained by PeakFit software. The calculated data were summarized in Table 2.

When the grain size is below $10\mu\text{m}$, the polycrystal X-ray diffraction peak broaden remarkably. Based on the widen amount of diffraction peak, the grain size can be calculated with the following equation:

$$L_{hkl} = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

Where L_{hkl} is the grain size of normal direction of (hkl) crystal plane; θ is the Bragg angle; β is the widening amount of diffraction peak attributed to the decrease of the grain size; λ is the wave length of entrance X-ray; k is a constant.

As shown in Table 2, with the increase of the draw ratio, the crystallinity increased, while the grain size decreased for both pure PLA and PLA/TPU blends, indicating that slipping and rupture of the lamellar in the spherulite occurred during the stretching of samples and a clear orientation of molecules formed. Compared with the pure PLA at the same draw ratio, the crystallinity and the grain size of the blends was lower, indicating that the interaction between PLA and TPU hindered the crystallization and orientation movement of PLA molecules in the blends during stretching.

3.2.2 Orientation morphology

The section morphology of PLA and PLA/TPU blends drawn at different draw ratios was shown in Figure 5.

It can be seen that the sections of all samples with different draw ratio were fairly smooth, except for longitudinal striations which indicate the possible presence of micro-fibers, as reported in a previous publication [20]. These micro-fibers were mainly composed of highly oriented folded lamellar crystals of PLA and noncrystal parts oriented along the drawing direction which alternately and periodically arranged [21]. The formation of these high oriented micro-fibers contributed to the significantly high tensile strength and modulus of the sample.

Moreover, as a whole, the dispersed TPU phase was finely and homogeneously

dispersed in the PLA matrix for the blends and the interface of PLA and TPU was not so clear as shown in Figure 5(e~g), indicating some compatibility of PLA and TPU. From the high magnified images, it can be seen that, after stretching, the TPU domains were elongated along the stress direction and their shape became ellipsoid, as shown in Figure 5(h).

3.3 Surface properties of drawn PLA/TPU blends

Surface properties such as availability of certain functional groups, domain structure, electrical charge, hydrophilicity/hydrophobicity, interfacial adaptability and surface roughness are considered to determine the fate of blood proteins, enzymes and cells interacting with the materials which, in turn, can induce several cascade reactions and activation phenomena [22]. In particular, the surface wettability is expected to play a significant role in terms of blood compatibility.

Water contact angles of the PLA and PLA/TPU blends as determined by the sessile drop method were listed in Table 3. All PLA/TPU blends had lower contact angles than neat PLA at the same draw ratio and the low contact angle may be due to hydrophilicity of the PEG segments on the TPU chain. Moreover, the water contact angle of PLA and PLA/TPU blends increased slightly with the increase of draw ratio, which indicated that the surface properties of PLA were significantly influenced by the introduction of TPU and the alignment of PLA and TPU molecules. Therefore, for drawn PLA and PLA/TPU blends, it was thought that the different blood compatibility may be due to their different surface properties.

3.4 Blood compatibility of drawn PLA/TPU blends

3.4.1 Hemolysis ratio

Hemolysis of the blood is an extremely serious problem associated with the

bio-incompatibility of materials faced by biomaterials researchers. Red blood cells may hemolyze when contacting with implant materials and thus cause eventually failure [23~24]. Therefore, in evaluating blood compatibility and biocompatibility, it is of vital importance to investigate the hemolysis ratio of the material. Here, PLA and PLA/blends at different drawing stages were selectively chosen to explore their hemolytic activity.

Results obtained from hemolysis test of ACD blood with PLA and PLA/TPU blends were shown in Table 4. According to the related standard (ASTM F 756-00), permissible hemolysis ratio of biomaterials should be at least lower than 5%. Therefore, first, the hemolysis ratio of 2.83% for pristine PLA makes it suitable as the substrate material. As to the surface of PLA/TPU blends before drawing, an obviously less hemolysis rate was obtained indicating that the TPU would improve the compatibility of the blends to a certain extent when contacting with biofluids. More importantly and promisingly, a key finding here was the fact that the surface of the sample after drawing with different draw ratios was much less hemolytic than the isotropic one. Therefore, leading to less damage of red blood cells, the oriented PLA and oriented PLA/TPU blends exhibited desirable blood compatibility.

3.4.2 Kinetic clotting time

Figure 6 showed the kinetic clotting time curves of the PLA and PLA/TPU blends with different draw ratio. The clotting time measurement was to test the activated degree of intrinsic coagulation factors. The higher absorbance, the better thromboresistance was. A similar change tendency in the O.D value of the all samples was observed: decreasing with the increase of the contact time. Compared with neat PLA, PLA/TPU blends had higher absorbance at the same clotting time, indicating that the

blends possessed better blood compatibility than that of neat PLA. Moreover, the clotting trend of the drawn sample was much lower than that of the sample before drawing, which indicated that the blood compatibility of the PLA and PLA/TPU blends was improved by orientation.

Generally, the time when O.D value is equal to 0.1 is defined as initial clotting time. From Figure 6, it can be seen that, the initial clotting time of the oriented samples was longer than those of isotropic samples, and compared with neat PLA before drawing, the initial clotting time of PLA/TPU blends with draw ratio of 480% increased by almost 17 min.

3.5.3 Platelet adhesion

When platelets are activated, they will deform and crosslink to promote aggregation of further platelets. Platelet adhesion and activation on the surface of a biomaterial is the most essential character in determining the blood compatibility of a biomaterial. Low platelet adhesion and activation denotes good blood compatibility, while a higher degree of platelet adhesion and activation could result in a thrombus.

The platelet adhesion densities on the polymers were evaluated, as shown in Figure 7. After contacting with the PRP for 60 min, a large number of platelets aggregating together were observed on the surface of isotropic PLA samples, however, the platelet adherent density on oriented PLA with different draw ratios was significantly lower than that on PLA before drawing. Although the number of platelets on oriented PLA became fewer, there was still a certain degree of activation.

In the case of PLA/TPU blends, however, the surface seemed prone to prevent platelets from adhering, since much less platelets were observed, especially in the case of PLA/TPU with draw ratio of 480%, indicating that the activation of platelets

on PLA/TPU blends was limited.

4. Conclusions

Highly-oriented PLA/TPU blends with enhanced mechanical properties and blood compatibility were fabricated through solid hot stretching technology. The tensile strength and modulus of the blends increased significantly by stretching for both PLA and PLA/TPU blends. With the increase of draw ratio, the cold crystallization peak became smaller, and the glass transition and the melting peak moved to high temperature, while the crystallinity increased, and the grain size of PLA decreased, indicating of the stress-induced crystallization during drawing. The section of all drawn PLA and PLA/TPU blends exhibited structures with longitudinal striations which indicate the presence of micro-fibers, and for the blends, the TPU domains were elongated along the stress direction and their shape became ellipsoid after stretching. Results obtained from hemolysis test showed that, before drawing, an obviously less hemolysis rate than neat PLA was obtained for the blends, and after drawing, the oriented surface was much less hemolytic than the isotropic one. The clotting trend of the drawn sample was much lower than that of the sample before drawing, and compared with neat PLA, PLA/TPU blends had higher absorbance at the same clotting time, indicating that the blends possessed better blood compatibility. After contacting with the PRP for 60 min, the platelet adherent density on oriented PLA was lower than that on PLA before drawing. In the case of PLA/TPU blends, much less platelets were observed, especially in the case of PLA/TPU with draw ratio of 480%, indicating that the activation of platelets on PLA/TPU blends was limited.

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Figure captions

Scheme 1 Synthesis of PEG-TPU via one-step bulk polymerization

Figure 1 FTIR spectrum of synthesized TPU

Figure 2 The mechanical properties of PLA and PLA/TPU blends

Figure 3 DSC curves of PLA and PLA/TPU blends

Figure 4 WAXD curves of PLA and PLA/TPU blends

Figure 5 SEM images of the oriented PLA and PLA/TPU blends

Figure 6 Curves of kinetic clotting time of PLA and PLA/TPU blends

Figure 7 Platelet adsorption of PLA and PLA/TPU blends (Magnification: 5000×)

Tables

Table 1 DSC parameters of PLA and PLA/TPU blends

| Samples | T_m (°C) | ΔH (J/g) | X_c (%) |
|----------------------------|------------|------------------|-----------|
| PLA(Draw ratio: 0) | 168.5 | 25.7 | 27.7 |
| PLA (Draw ratio: 280%) | 169.2 | 28.0 | 30.1 |
| PLA (Draw ratio: 340%) | 170.6 | 30.9 | 33.3 |
| PLA (Draw ratio: 480%) | 170.9 | 32.6 | 35.1 |
| PLA/TPU(Draw ratio: 0) | 166.1 | 20.45 | 22.0 |
| PLA/TPU (Draw ratio: 280%) | 168.9 | 23.13 | 24.9 |
| PLA/TPU (Draw ratio: 340%) | 169.3 | 25.88 | 27.9 |
| PLA/TPU (Draw ratio: 480%) | 169.8 | 28.92 | 31.2 |

Table 2 Crystallinity and grain size of PLA and PLA/TPU blends

| Samples | Crystallinity (%) | Grain size (Å) |
|----------------------------|-------------------|----------------|
| PLA(Draw ratio: 0) | 30.2 | 284 |
| PLA (Draw ratio: 280%) | 38.9 | 164 |
| PLA (Draw ratio: 340%) | 41.2 | 92 |
| PLA (Draw ratio: 480%) | 44.3 | 65 |
| PLA/TPU(Draw ratio: 0) | 16.4 | 112 |
| PLA/TPU (Draw ratio: 280%) | 22.7 | 85 |
| PLA/TPU (Draw ratio: 340%) | 26.3 | 62 |
| PLA/TPU (Draw ratio: 480%) | 33.8 | 54 |

Table 3 Water contact angles of PLA and PLA/TPU blends

| Samples | Water contact angle (°) |
|----------------------------|-------------------------|
| PLA(Draw ratio: 0) | 74 |
| PLA (Draw ratio: 280%) | 76 |
| PLA (Draw ratio: 340%) | 77 |
| PLA (Draw ratio: 480%) | 78 |
| PLA/TPU(Draw ratio: 0) | 66 |
| PLA/TPU (Draw ratio: 280%) | 68 |
| PLA/TPU (Draw ratio: 340%) | 72 |
| PLA/TPU (Draw ratio: 480%) | 74 |

Table 4 Hemolytic activity of PLA and PLA/TPU blends

| Samples | Hemolysis ratio ^(a) (%) |
|----------------------------|------------------------------------|
| PLA(Draw ratio: 0) | 2.837684±0.60 |
| PLA (Draw ratio: 280%) | 0±0.20 |
| PLA (Draw ratio: 340%) | 0.214823±0.07 |
| PLA (Draw ratio: 480%) | 0±0.15 |
| PLA/TPU(Draw ratio: 0) | 1.475596±0.4 |
| PLA/TPU (Draw ratio: 280%) | 1.248581±0.4 |
| PLA/TPU (Draw ratio: 340%) | 0.681044±0.05 |
| PLA/TPU (Draw ratio: 480%) | 0.537057±0.06 |

(a) Each represents the value (mean ± SD) of three determinations.