Effect of thermoplastic polyurethane (TPU) on the thermal and mechanical properties of polylactic acid (PLA)/curcumin blends

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Abstract. Polylactic acid (PLA) is known to be brittle by nature and thus limits the flexibility of the polymer. A possible solution to enhance the flexibility of PLA is to add a flexible polymeric based material such as thermoplastic polyurethane (TPU). In this study, 30-50 wt% of TPU was added into PLA/curcumin blends to improve its flexibility. Thermal analysis using differential scanning calorimetry shows that further additions of TPU at the expense of PLA did not affect the glass transition temperature, crystallisation temperature and melting temperature of the blends. Fibers of PLA/curcumin/TPU were successfully drawn and Single Fiber Tensile Test (SFTT) showed vast improvement in elongation at break. The initial addition of 30 wt% of TPU to the brittle PLA/curcumin composition causes a significant increase in elongation at break by 39 times and further additions at 50 wt%, the elongation at break increases by 105 times. However, with the increase in elongation, a decrease in strength and Young’s modulus was observed.

1. Introduction

Currently there is an increasing demand for polymeric based materials that are being made from renewable starting materials and are biocompatible as well as biodegradable. Amongst the most studied biocompatible polymers are polylactic acid (PLA) and thermoplastic polyurethane (TPU). Generally, PLA has a high strength but its brittleness with a very low impact resistance and flexibility, restricts its application as a general-purpose plastic [1]. Nevertheless, PLA has been proposed for biomedical application due to its ability to fulfill complex requirements on biocompatibility, complete biodegradability, non-toxic degradation products and thermoplastic processability [2]. Whilst TPU, an effective flexibilizer has attracted wide attention in many fields due to its excellent mechanical properties such as high elasticity, great flexibility and toughness, and high resistance to tear, oxidation, and humidity [3]. Thus the combination of PLA and TPU in various ratios would lead to tailored properties suitable for a wide variety of tissue engineering scaffold applications [4, 5]. Degradation tests in phosphate buffered saline of PLA/TPU scaffolds showed a balanced degradation behavior in-between the more easily degraded PLA and the more stable TPU as well as good biocompatibility [6].

Curcumin is a polyphenolic compound derived from Curcuma domestica (Zingiberaceae) that possesses diverse pharmacological effects including anti-inflammatory, antioxidant, antimicrobial, and anticarcinogenic activities [7]. In vivo and in vitro studies have uncovered many important
bioactivities of curcumin such as inducing cell apoptosis, inhibiting cell proliferation, anti-cell adhesion and motility, anti-angiogenesis and anti-microbe properties [8]. The blend of curcumin and PLA have been produced in the form of nanofiber mat and have been observed to generate faster wound closure at treated animals [9, 10].

The present study investigates the effect of TPU on PLA/curcumin blends. Different weight percentages of TPU was added at the expense of PLA whilst curcumin amount was maintained at 5 wt%. The blends were thermally characterized prior to being processed via melt drawing process into fibers. The fibers were then mechanically tested to obtain their strength, modulus and elongation at break.

2. Experimental procedures

PLA (Natureworks IngeoTM Biopolymer 3052D grade) and chloroform (R&M Chemicals, United Kingdom) were of analytical grade hence they were used without further purification. The curcumin used in this study with Bioperine extract was manufactured by Pahang Pharmacy Sdn. Bhd., Malaysia. The TPU used in this study is TPU Desmopan 8785A from Bayer Material Science.

2.1 Sample preparation

A weight amount of PLA was dissolved in the following ratio of 1g PLA: 10 ml chloroform. Curcumin powder (5 wt%) was then mixed in PLA solution. The mixture was stirred for 2 days to achieve a homogenous solution using magnetic stirrer at room temperature. The mixture was then poured into a Teflon covered tray and was left to dry in the fume cupboard. The dried PLA/curcumin mixtures were then crushed prior to melt blending with TPU via the internal mixer (Thermo Scientific Haake Rheomix). The mixer was set at temperature of 170°C, speed of 50 rpm and duration of 15 minutes. The PLA/curcumin/TPU blend was then crushed prior to the melt spinning process into fibers. The fibers were spun at the speed of 115 rpm and at a temperature range between 160-180°C to accommodate the change in viscosity as more TPU was added to the PLA.

2.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed employing a Sapphire DSC (Perkin Elmer Instruments, USA) within the temperature range 30 °C to 320 °C at a constant heating rate of 10°C/min under nitrogen gas flow 50mL/min.

2.3 Single Fiber Tensile Test

The single fiber tensile test (SFTT) was performed according to ASTM D 3882 (Standard Test Method for Tensile Properties of Single Textile Fibers). Essentially, 10 fibers randomly chosen from the fiber bundle were individually mounted on a custom-made sample holder made from paper. A slot with a gage length of 25 mm is cut out in the middle of the tab as shown in Figure 1. The ends of each fibers were bonded to the plastic tab with an epoxy adhesive, Devcon Flow-Mix (USA). The diameter of the fiber was measured individually via Celestron Handheld Digital Microscope PRO (USA). The specimen was then mounted on a Shimadzu Tensile Tester (Japan). Without disturbing the setup, both sides of the paper tab were cut at the middle of the gage length. SFTT was then performed at room temperature with a load capacity of 50 N and a chart speed of 10 mm/min.
3. Results and Discussion

The followings in Table 1 are the abbreviations used for the composites/blends in this study. DSC results in Table 1 shows that initial addition of 30 wt% of TPU in the PLA/curcumin blend did not affect the glass transition (T_g) of the blend. The range of glass transition temperatures (T_g) obtained were in the range of 57 – 60 °C. It is also observed that there is no difference between the crystallization temperatures (T_c) as TPU was incrementally added from 30 to 50 wt% into the mixture at the expense of PLA. The thermal stability of the PLA/Curcumin blends initially dropped as 30 wt% of TPU was added. However further additions of TPU did not affect the thermal stability of the PLA/Curcumin/TPU blends. Lack of improvement in thermal stability with increased amount of TPU suggests that there is a lack of chemical bonding between TPU and PLA. The addition of TPU into the blends created a second melting point at approximately 157°C which suggests the presence of two crystal phases in the blends (see Figure 2).

Table 1. Sample composition (wt%) and thermal properties via DSC.

| Sample       | PLA (wt %) | Curcumin (wt %) | TPU (wt %) | T_g (°C) | T_c (°C) | T_m1 (°C) | T_m2 (°C) | Thermal stability (°C) |
|--------------|------------|-----------------|------------|----------|----------|-----------|-----------|------------------------|
| PLA_Cur_0TPU | 95         | 5               | 0          | 57.1     | 128.0    | 158.5     | -         | 70.9                   |
| PLA_Cur_30TPU| 65         | 5               | 30         | 58.3     | 117.5    | 151.1     | 156.8     | 59.2                   |
| PLA_Cur_40TPU| 55         | 5               | 40         | 59.6     | 116.2    | 151.8     | 157.2     | 56.6                   |
| PLA_Cur_50TPU| 45         | 5               | 50         | 60.3     | 116.5    | 152.1     | 156.6     | 56.2                   |
Fibers with diameters in the range between 100 to 200 µm as shown in Figure 3 were successfully melt drawn using an in house built fiber drawing tower. Initial addition of 30 wt % of TPU caused an obvious decrease in strength and modulus of more than 90% (see Figure 4 and Figure 5). Further addition of TPU only causes a slight drop in both strength and modulus of the fibers. However, initial addition of 30 wt% of TPU to the brittle PLA/curcumin composition causes a significant increase in elongation at break by 39 times and further addition at 50 wt %, the elongation at break increases by 105 times (see Figure 6).
Figure 4. Tensile strength properties of PLA/Curcumin/TPU blends

Figure 5. Tensile modulus properties of PLA/Curcumin/TPU blends

Figure 6. Elongation properties of PLA/Curcumin/TPU blends
TPU is a block co-polymer consisting of alternating sequences of hard and soft segments. The soft block, consists of a polyol and an isocyanate, gives the flexibility and elastomeric property of a TPU. Therefore, when TPU was added into PLA/curcumin blends, the flexibility of the composite blend increases and the brittle characteristics of PLA decreases. Feng and Ye [1] observed the transition of PLA from brittle fracture to ductile fracture with the addition of TPU into PLA and suggested a partially miscible system due to the hydrogen bonding between the molecules of TPU and PLA. The increase in flexibility seen in this study with the addition of TPU can also be achieved if a plasticizer is added instead. Similar effect as seen in a plasticized blend was also observed in this study in which some tensile strength would be lost, but higher elongation characteristics would be achieved [11]. In a study by Jia et al. [12] also found that the addition of TPU by 40% in blends of Polylactic acid (PLA)/organo-montmorillonite (OMMT) increased the elongation at break by 30 times. From the view of manufacturing process, elongation is important in manufacturing as it determines the maximum bending and shaping a material can withstand without breaking. Therefore there is high potential to tailor the strength, modulus and elongation of PLA/curcumin/TPU blends to be used in biomedical application such internal wound suture or as filaments for rapid prototyping.

4. Conclusion
This study was carried out to study the effect of TPU on PLA/curcumin blend. DSC results showed that the thermal stability, Tg and Tm of the blends was not affected significantly with further addition of TPU. PLA/curcumin fiber produced in a previous study by the author was found to be brittle. The brittleness nature of these fibers was found to have improved with the addition of TPU. It was found that the elongation at break increased significantly at the expense of strength and modulus up to 105 times with 50 wt% of TPU.

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