

Full Length Research Paper

Characterization of polycaprolactone and starch blends for potential application within the biomaterials field

Jianyu Su , Ling Chen* and Lin Li

Institute of Light Industry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China.

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Thermally blending starch and polycaprolactone with the compatibilizer methylenediphenyl diisocyanate (MDI) distributed in the polyester phase had been previously confirmed to enhance the mechanical properties and interface between the two phases of the blends. In this study, blends of polycaprolactone with various levels of starch and 1.0% MDI were prepared through melt blending using a twin-screw extruder, and an extensive characterization including mechanical properties, microstructure, melting, thermo-mechanical behaviour, hydrophilicity and degradation in Hank's solution were further carried out, aiming at an alternative for orthopaedic applications. The results demonstrated that MDI had improved the mechanical properties of polycaprolactone (PCL) and starch blends, but an optimal ratio of starch level and MDI content was required, which had been found to be 1.0 wt % MDI with 30 wt % starch content. The present study indicated the starch and polycaprolactone blends may present a significant potential for biomedical applications.

Key words: Polycaprolactone, starch blends, biomaterials.

INTRODUCTION

Materials discovery for bone repair and regeneration are one of the leading concerns in the biomaterials field. The particular properties of bone have posed an obstacle for the development of biomaterials, and a satisfactory material is considered to include routine mechanical properties, as well as controlled degradability by human fluids, bone bonding ability, and biocompatibility (Silva et al., 2005). As application is concerned, biodegradable materials are specifically desired, with some currently available biodegradable polymers already under clinical application, including polyglycolic acid (PGA) (Daniels et al., 1994; Adriano et al., 1994), polylactic acid (PLA) (Daniels et al., 1994; Adriano et al., 1994), polyhydroxybutyrate (PHB) (Silva et al., 2005; Koller et al., 1996) and polycaprolactone (PCL) (Wang et al., 2005). Nevertheless, further research may focus on introduction of new materials for new devices to emerge (Reis RL, 1995).

With advantages on mechanical properties, compatibility with many types of polymers, together with great biocompatibility, PCL is considered to be a major biodegradable polyesters and has been commonly used (Wang et al., 2005), which has been used in different biomedical applications (Umekia et al., 2010; Agrawal and Ray, 2001). However, the limitations to the tissue regeneration using PCL scaffolds are the hydrophobic issue, which may affect the cell adhesion and its rate of degradation. A simple way carried out to improve hydrophilicity of PCL is blending with hydrophilic polymers (Thomson et al., 1995). In respect with biodegradable polymers materials, starch is regarded as an ideal alternative, for its high hydrophilicity. The development and biodegradable properties of the blends of starch with PCL (SPCL) has been well documented previously (Gomes et al., 2003; Marques et al., 2003; Azevedo and Reis, 2009; Kweon et al., 2004). Starch improves hydrophilicity of the end products, as well as biodegradable characteristics to PCL. Whereas, hydrophobic aliphatic polyesters and hydrophilic starches are thermodynamically immiscible, this leads to poor adhesion between the two components and

*Corresponding author. E-mail: felchen@scut.edu.cn. Tel: +86-20-87113252. Fax: +86-20-87113252.

irreproducible performances. In a preliminary study (Yu et al., 2007), methylenediphenyl diisocyanate (MDI) had been shown to act as a compatibilizer, improving the interfacial interaction and consequently enhancing the mechanical properties of PCL and starch blends. In particular, when MDI was distributed in the polyester phase first rather than in the starch phase prior to blending proved that the mechanical properties and the interface between starch and PCL had been greatly improved compared to a blend without MDI and a blend with MDI adding in other ways.

Recently, SPCL materials had been applied within the biomaterials field (Reis et al), including tissue engineering scaffolds (Gomes et al., 2003; Marques et al., 2003; Azevedo and Reis, 2009), and for different orthopaedic purposes (Costa and Reis, 2004).

Besides adequate physical properties, this blend exhibited good biocompatibility (Gomes et al., 2003; Pashkuleva et al., 2010) and low inflammatory response (Marques et al., 2003).

However, the reported blends were acquired from Novamont company with 10 wt % of natural plasticisers (Wang et al., 2005; Gomes et al., 2003; Marques et al., 2003; Azevedo and Reis, 2009; Kweon et al., 2004; Costa and Reis, 2004; Pashkuleva et al., 2010) and the preparation and characterization of SPCL blends had barely been discussed. In fact, properties and processibility of a polymer blend containing starch may be adversely affected by the starch content, constituted a major concern on its application.

The objective of this article was to study the effects of various starch levels on mechanical properties, microstructure, melting, thermo-mechanical behaviour, hydrophilicity and degradation in Hank's solution of the PCL/starch blend in the presence of 1.0 wt % MDI, aiming at orthopaedic applications. The present study may aid in the preparation and application of SPCL blends in the field of tissue engineering strategy.

MATERIALS AND METHODS

Materials and compounding

Cornstarch, supplied by Penford, Australia, with moisture content 13.1% was used in the experimental work. Commercial biodegradable aliphatic polyester polycaprolactone (PCL, commercial name CAPA, grade 650) was supplied by Solvay caprolactones, with an Mw of 50,000. The preparation of the blends involved (1) gelatinization of starch; (2) premixing of the compatibilizer and polyester; and (3) compounding gelatinized starch with polyester.

Initially 70 wt % cornstarch (dry based) was pregelatinized with 30% water using a twin-screw extruder (HAAKE Reomex 24/40p, Germany) with the highest temperature reaching 170°C (60, 100, 150, 170, 170, 170, 170, and 150°C for zone 1 to 9 and 130°C for the die). Then 1.0% compatibilizer MDI was premixed with PCL in the high speed commingler. Finally the pellets of gelatinized starch were premixed with polyester in various ratios of starch/polyester than compounded using the extruder with the highest temperature of 110°C (Yu et al., 2007).

Characterization of the compounds

Mechanical testing

Tensile properties were evaluated in accordance with ASTM D5938 standard on an Instron tensile testing apparatus (5566). Tensile strength and elongation were measured at a crosshead speed of 50 mm/min. An external extensometer was used for independent modulus measurement at a crosshead speed of 0.5 mm/min. Impact testing was carried out according to ASTM 256 on a Radmana IRT 2000 instrumented impact tester in Izod mode with impact strain rate 3.5 m/s.

SEM analysis

A LEO 1530VP SEM was used to investigate the fracture surfaces and morphologies of the blends. The un-deformed fracture surface was obtained from the breaking pellets in liquid nitrogen and then coated with gold.

FTIR analysis

The FTIR spectra were recorded on a Bruker Tensor 37 FTIR with an attenuated total reflectance (ATR) device from SPECAC. Spectra were recorded from 4000 to 400 cm⁻¹. Samples were thoroughly ground with KBr and pellets were prepared by compression under vacuum.

DSC analysis

A PerkinElmer Diamond-1 DSC apparatus was used to study the effect of adding starch on the melting properties of the polyesters. Samples were cut from specimens and a heating rate of 10°C/min was used in the experimental work. Temperature was ranged from 40 to 80°C.

Dynamic contact angle measurements

The dynamic contact angle measurements were performed using an OCA15 produced by Dataphysics Ltd. in Germany. The measurements were performed with the aid of an image analysis system installed in the apparatus. Duplicate measurements were recorded for each drop deposition. The values were recorded at interval 1 s after 5 s of the drop deposition. All the measurements were made at room temperature and the probe liquids were water.

Degradation studies

The degradation of the materials was studied on pellet samples with 1.5 g weight, over a period of 90 days. They were conditioned to minimum weight at 37±1°C in an oven containing desiccant prior to being immersed into 100 ml of a Hank's Balanced Salt Solution (HBSS) (pH 7.4) (Reis, 1995). The specimens were removed at regular 5 days intervals, being taken out of the solution, blotted on filter paper to remove surface solution and dried in an oven to 40°C to constant weight in order to determine eventual weight loss. The degradation was calculated by:

$$\% \text{ weight loss} = (M_i - M_f) / M_i \times 100.$$

' M_i ' is the initial weight of the sample and ' M_f ' is the weight obtained after drying of the samples at 40°C to constant weight.

Table 1. Mechanical properties of PCL and PCL/starch blends with different weight ratio of starch*.

Formulation	Tensile strength (MPa)	Elongation (%)	Modulus (MPa)	Moisture content (%)
PCL	10.3	9.91	503.9	0.6
90%PCL /10%starch	12.6	57.49	340.4	2.1
70%PCL/30%starch	14.2	69.23	398.3	5.2
50%PCL /50%starch	9.6	16.57	387.2	7.6

*Triplicate samples were used for every measurement.

RESULTS AND DISCUSSION

Materials characterization

Table 1 shows the mechanical properties and moisture content for a series of PCL/starch, in which the ratio of starch to polyester changed incrementally. The modulus of the blends were increased initially with the addition of starch, but at 30 wt % starch content reached a maximum, followed by an increase in the starch content and a further reduction of the modulus value. Yield strength and impact strength were decreased with increasing addition of the incompatible starch. Especially at high starch loadings (the data see my other article). In a binary system of PCL and starch without MDI, as reported by Avella (Avella et al., 2000), the yield strength of blends decreased significantly as starch content increased. In their study, the yield strength decreased from 10.7 to 4.0 MPa at 10 to 50% wt starch in the blends. The present work showed that the addition of MDI improved the mechanical properties of the PCL/starch blend at appropriate proportion. It was possible that adhesion at the interface between PCL and starch might exist.

Fracture toughness is usually associated with fracture energy. For high toughness, the fracture energy must be at least equal to or larger than the surface energy at the interface of cracking. The blends with MDI had higher fracture energy than that without MDI. MDI has two highly reactive isocyanate groups that might react with both carboxyl and hydroxyl groups on PCL and with the hydroxyl groups on starch. It could be explained that when the MDI was first extruded with the polyester, it may react with the hydroxyl groups present at the end of the polyester chains producing an MDI grafted polyester to extend the chain length or it may also remain unreacted, but well dispersed within the polyester matrix. The isocyanate groups on the MDI grafted polyester could react with the hydroxyl groups in the starch, producing the compatibilized starch/polyester block copolymer. It was also possible that the free dispersed isocyanate could also react with the hydroxyl groups in the starch and the polyester during the second extrusion. The second extrusion of MDI/polyester with gelatinized starch may result in further hydrolysis of the ester groups of the

polyester via the water bound in the gelatinized starch producing more hydroxyl end groups for the isocyanate to react with. Some of these reactions probably resulted in primary chemical bonds between the surface of starch granules and PCL, leading to high interface adhesion, and consequently high fracture energy. Figure 1 shows the FTIR spectra of PCL and SPCL blends. As shown in the figure, the spectra of different weight ratio starch of SPCL blends were accompanied with pure PCL and starch. The signals of the most characteristic bands at 3600 to 3000 cm^{-1} ($\nu_{\text{O-H}}$) of the carboxylic acid groups from PCL and hydroxyl from starch were larger as the weight ratio of starch increased. It was because starch was rich in hydroxyl groups and as a consequence this part of the spectrum was very informative as the weight ratio of starch increased. Some other typical bands such as anhydride bands at about 1860 and 1780 cm^{-1} could not be detected because of over lapping of very intense ester band of PCL at 1736 cm^{-1} . The above results did not give a clear experimental evidence of the formation of grafted starch/PCL molecules, for the over lapping of very intense bands in PCL and starch.

Generally, the tensile properties of a blend are associated with its microstructure. Figure 2 shows the fracture surfaces of PCL and SPCL blends after breaking in liquid nitrogen observed by SEM. Figure 2A shows that pure PCL was a continuous phase with a smooth surface. While the surface of PCL/starch blends with 1.0 wt % MDI (Figure 2B to D) was rough, this was typical of a compatibilized structure. At starch levels at and below 30 wt %, there was not any starch spherical particle being seen from the figures, and the interface between starch and PCL was unclear. Most of the starch granules were well enveloped by the PCL matrix and fractures occurred through the PCL matrix. At 50 wt % starch content, starch granule aggregations were observed, and the fracture occurred through the interface at some locations probably due to the high concentration of starch.

The thermal properties of the starch and PCL during blending might play an important role in the wetting of the starch granules surface. At low starch levels in a blend, it was observed that the time needed to reach the set temperature was shorter, because PCL has a higher thermal conductivity than the dried starch (Yu et al., 2007). PCL undergoes de-polymerization during the hot

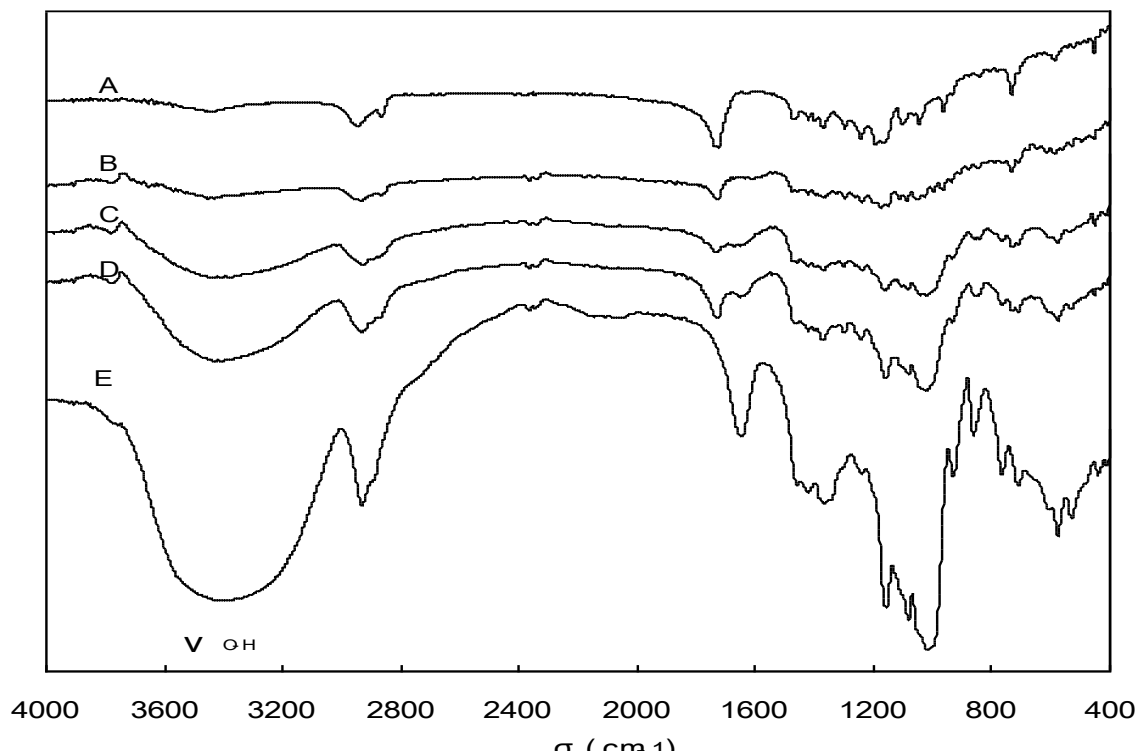


Figure 1. FTIR spectra of the sample. A: PCL; B: 90%PCL/10%starch; C: 70%PCL/30%starch; D: 50%PCL/50%starch; E: starch.

mixing step. An increased portion of PCL short chains would increase the levels of hydroxyl and carboxyl groups in the matrix, which would compete with starch hydroxyls for MDI. In addition, even if the bonding layer at the interface between PCL and starch was achieved, it might be degraded to some degree because of the larger shearing at the set mixing temperature. At higher starch levels, additional mixing time was required for the blend to reach the set temperature. In this situation, less PCL was degraded and more MDI was available for starch. However, the amount of MDI was fixed at 1.0 wt % which probably was insufficient to wet all the starch. It seemed that 30% starch and 1.0 wt % MDI was a preferable combination. This data suggested that starch level and MDI content may be added at an optimum ratio to gain an optimum product.

Figure 3 shows the DSC thermo-grams of the SPCL blends. The addition of starch to PCL appeared to decrease the melting temperature and melting enthalpy of PCL, possibly due to a reduction in molecular weight of the PCL and hydrolysis of the ester groups by the water in the gelatinized starch similar to previously reported work (Averous et al., 2000). Table 2 summarizes the characteristic data for melting behaviour of PCL and SPCL. For the PCL and SPCL, the melting temperature and the enthalpy decreased as the weight ratio of starch was added. The values of melting enthalpy could be compared with $139.5 \text{ J}\cdot\text{g}^{-1}$, corresponding to a 100%

crystalline PCL (Sarazina et al., 2008). Follow this, the crystallinity of PCL could be easily estimated. The crystallinity was 32.9% and 33.5~38.8% for PCL and for PCL within SPCL, respectively. The results may be because the urethane linkage between starch and PCL restricted the interface slippage and resulted in an increase in PCL molecular fragmentation during mechanical shearing, which would accelerate the crystallization and increase the crystallinity.

Dynamic contact angle measurements

The testing methods for contact angle can be divided into two categories; one is the static drop micro-observation, while the other is the dynamic testing method. However, the first method has many disadvantages as it can only acquire static contact angles. As a smooth transition area exists between the solid and a liquid, it is difficult to precisely measure contact angles by the static approach. The dynamic contact angle measurement, known as the Wilhelmy technique (Huang et al., 2006), is specially designed to explore the dynamic process of wetting. When a solid is dipped into a liquid, the liquid will ascend (hydrophilic) or descend (hydrophobic) along the vertical side of the solid.

Dynamic contact angle measurements for the PCL and SPCL blends were showed as Figure 4. As expected, a

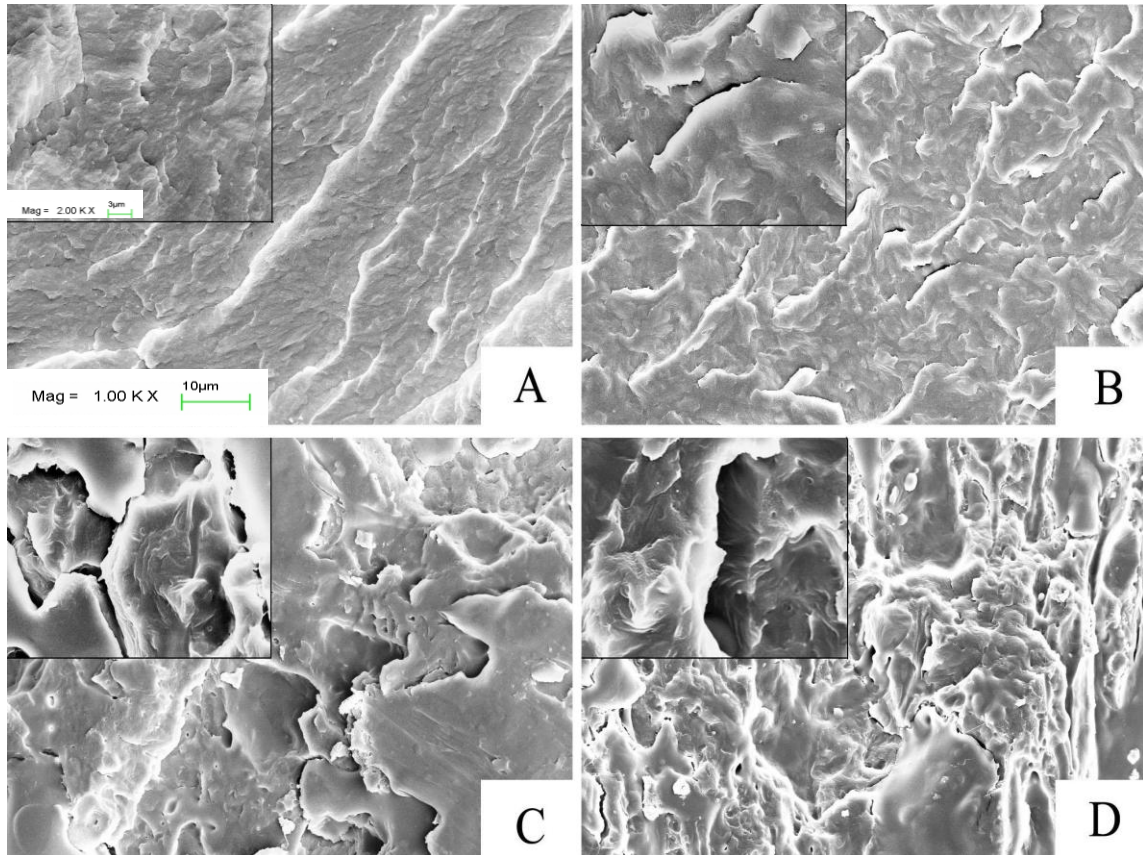


Figure 2. SEM photographs of PCL and SPCL blends. A: PCL; B: 90%PCL/10%starch; C: 70%PCL/30%starch; D: 50%PCL/50% starch.

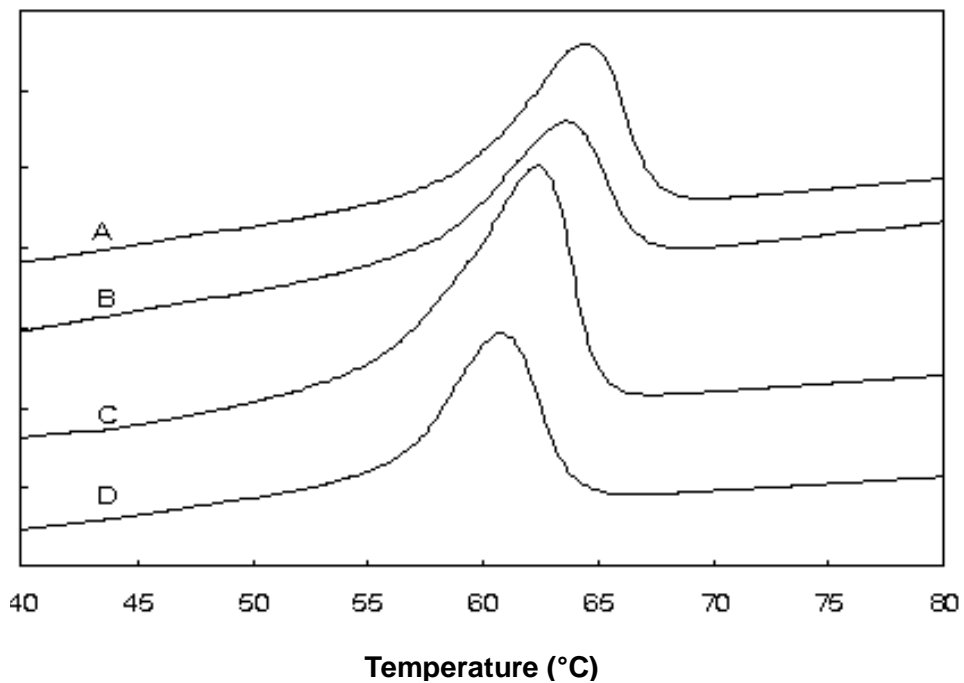
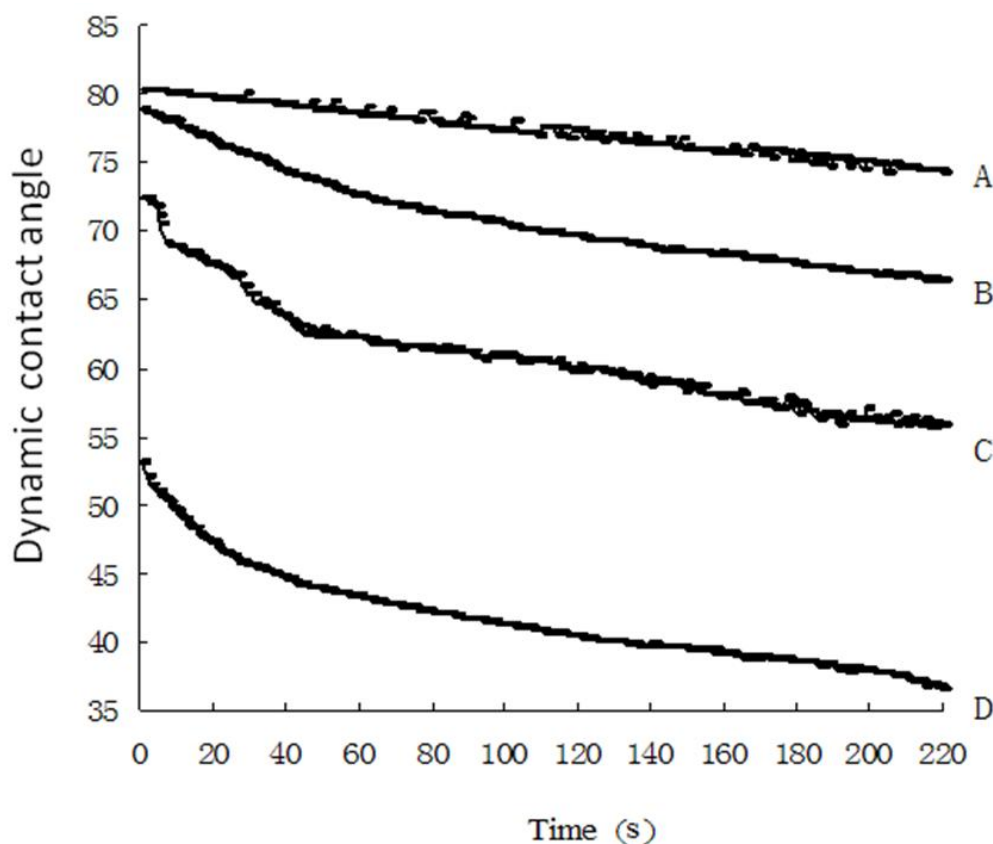


Figure 3. DSC melting thermograms of PCL and SPCL blends. A: PCL; B: 90%PCL/10%starch; C: 70%PCL/30%starch; D: 50%PCL/50%starch.

Table 2. Melting behaviour of PCL and SPCL probed by DSC.

Material	Melting temperature (°C)	Melting enthalpy(J.g ⁻¹)	Relative crystallization (%)
PCL	64.43	45.872	32.9
90%PCL/10%starch	63.75	42.051	33.5
70%PCL/30%starch	62.40	37.233	38.1
50%PCL/50%starch	61.31	27.082	38.8

**Figure 4.** Dynamic contact angle of PCL and SPCL blends. A: PCL; B: 90%PCL/10%starch; C: 70%PCL/30%starch; D: 50%PCL/50%starch.

decrease of average water contact angle was observed for the addition of starch. This meant that the surfaces of the hydrophilicity of the SPCL blends were increased by the addition weight ratio of starch. It may be justified by the higher amounts of hydroxyl groups by the introduction of starch. These groups were easily solvated by water molecules, the testing liquid used during these measurements. The results were confirmed by the FTIR, where the bands at 3600 to 3000 cm^{-1} were increased as the weight ratio of starch added.

Degradation studies

Immersion studies at $37\pm 1^\circ\text{C}$ in Hank's solution provide evidence of the *in vitro* biodegradability of the PCL and

SPCL blends. Figure 5 showed the degradation curves (percentage weight loss against time) for the materials studied. The extent of the degradation in the starch based polymers was highly dependent on the weight ratio of starch. For the 50% wt SPCL, the weight loss was more obviously and faster, without attaining a plateau during the testing period. This phenomenon may be related to a hydrolytic surface dissolution of the original sample and the materials may be bulk degraded in the HBSS, due to the strong water-permeability of the starch (Heller, 1980).

Conclusion

Various blends of gelatinized corn starch and biodegradable polyesters PCL were prepared through melt blending

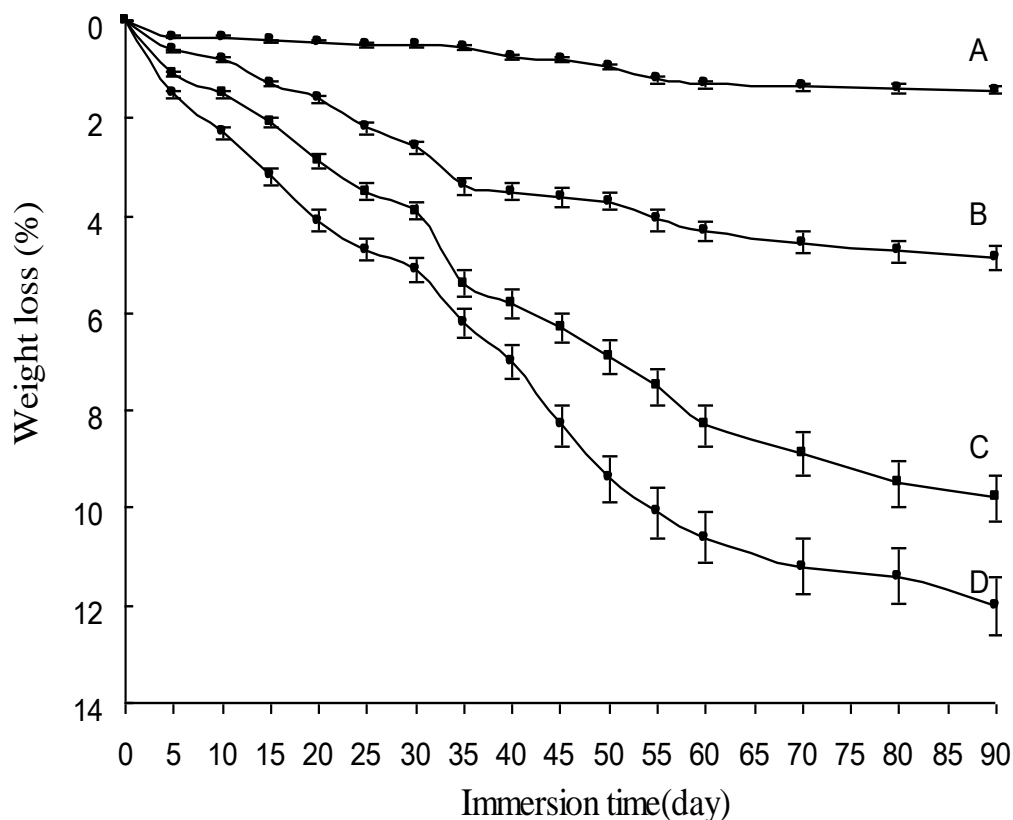


Figure 5. Degradation behavior of PCL and SPCL blends. A: PCL; B: 90%PCL/10%starch; C: 70%PCL/30%starch; D: 50%PCL/50%starch.

using a twin-screw extruder, with 1.0 wt % compatibilizer MDI previously distributed in the polyester phase. A comparative study on the mechanical properties, microstructure, melting, thermo-mechanical behaviour, hydrophilicity and degradation in Hank's solution for typical commercial available PCL and various weight ratio blends of starch and PCL were reported by using many modernization analysis apparatuses.

The results indicated that MDI had significantly improved the phases of PCL and starch. However, the increase of starch content affected the mechanical properties, crystallization, melting peak temperature, melting enthalpy and the dynamic mechanical at the scale of body temperature for SPCL blends compared with pure PCL. Satisfied end products had been obtained with starch level and MDI content at an optimal proportion, which was found to be 1.0 wt % MDI with 30 wt % starch content. At this proportion, the complex had a relatively smooth microstructure with proper mechanical properties, and high dynamic mechanical at the scale of body temperature. At 37°C, all materials exhibited interesting damping properties, which may be relevant in orthopaedic applications and further aid in the dissipation of the mechanical energy generated by the patient movements.

As expected, the hydrophilicity and degraded in HBSS

were correlatively changed with the weight ratio of starch and PCL.

The materials may be bulk degradation in the HBSS, due to the strong water-permeability of the starch. In this study, SPCL presented a great potential for biomedical applications, and the research provided preliminary data on the preparation and application of SPCL blends in the field of tissue engineering strategy. Nevertheless, better knowledge of the degradation mechanisms and their effect on the performance of the materials, as well as the possibilities of improving mechanical properties are required in further research.

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