



The effect of plasma surface modification on the biodegradation rate and biocompatibility of a poly(butylene succinate)-based copolymer



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ABSTRACT

In this contribution, a poly(butylene succinate)-based copolymer containing thioether linkages (P(BS85BTGD15)) has been synthesized and characterized from the molecular, thermal and mechanical point of view. The results have been compared to the parent homopolymer. Films obtained both by PBS and P(BS85BTGD15) have been subjected to surface modification by means of non-thermal plasma surface treatment and the effect on physic/mechanical properties has been considered. Hydrolytic degradation rate under physiological conditions and *in vitro* biocompatibility of treated and non-treated polymeric films have been also investigated.

The introduction of thioether linkages and the plasma etching enhanced the polymer surface wettability, thus resulting in an increased hydrolytic degradation rate. On the other hand, bulk properties were not significantly affected.

Biocompatibility assays highlighted the absence of potentially cytotoxic products into the culture medium and proved that the investigated polymeric films can support cell adhesion and proliferation.

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1. Introduction

The use of biodegradable polymers in regenerative medicine has attracted considerable attention as they are capable to undergo hydrolysis in the human body. The implant removal through surgery is therefore no longer needed.

However, to be employed as biomaterials, they need to show excellent biocompatibility, their degradation products must be nontoxic to the organism and the degradation rate has to respect the requirements of the intended application [1].

Various classes of biodegradable polymers have been synthesized, but aliphatic polyesters (APs) have so far risen as the most

successful, thanks to their ease of synthesis, excellent properties and moderate costs [2]. Poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(caprolactone) (PCL) and their copolymers are undoubtedly the most well-known and used APs, as their commercialization dates back to the 70 s and 90 s [3,4]. Since then, they have been employed for the realization of sutures, implants, screws as well as for controlled drug release applications [4].

In recent years, another member of the APs class, namely poly(butylene succinate) (PBS), has been extensively studied, because its use can overcome some of the problems related to the other aliphatic polyesters. It is commercially available, it can be easily processed into various forms and structures and it possesses mechanical properties resembling those of PE and PP [5]. In addition, the raw materials employed in the PBS synthesis can be obtained not only from fossil resources, but from renewable ones as well [6,7]. Different companies have focused on the development of large scale production of biobased succinic acid [8].

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Unfortunately, the hydrophobicity and low surface energy of PBS and other APs lead to inefficient cell attachment, spreading and proliferation [9,10]. Moreover, the mechanical properties of the currently available biopolymers do not fulfill the requirements for all the different applications.

As a result, chemical and/or surface modification is usually necessary to improve the properties and the biocompatibility of the polymers used in biomedicine.

As to the chemical modification, our group recently focused on the realization of new aliphatic polyesters containing ether and thioether linkages, whose presence significantly affects both wettability and crystallinity degree, thus mechanical properties, biodegradation rate and biocompatibility of the material [11–15]. In particular, thioether containing aliphatic polyesters displayed an increased surface wettability with respect to the parent homopolymer, due to the electronegative sulphur atoms, and a reduced crystallinity degree and a less perfect crystalline phase, caused by the presence of a second comonomeric unit, acting as a defect during chain folding [16].

The reduced crystallinity degree and the enhanced wettability significantly improved the biodegradation rate of the copolyesters [12]. On the other hand, as far as the biocompatibility is concerned, no adverse effect was observed [17].

Finally, lower elastic modulus and higher elongation to break not only with respect to the parent homopolymer, but also as compared to copolyesters containing ether linkages of similar block length and crystallinity degree were highlighted. This effect has been explained on the basis of longer distance of the C–S bonds with respect to C–O bonds and of the weaker interchain interactions due to the lower electronegativity of sulfur atoms as compared to oxygen ones [16].

Increased wettability can be also achieved through surface modification, e.g. with the insertion of functional groups. Common techniques, such as surface hydrolysis (with the use of a NaOH solution) or surface aminolysis (for example in 1,6-hexanediamine), are too aggressive when applied to some sensitive materials, possibly influencing their bulk properties as well [9]. Moreover, such methods are known to produce hazardous chemical waste and possibly irregular surface etching. Plasma treatment is a very convenient strategy, since it can be used to incorporate functional groups on a polymer surface without affecting any bulk properties. Plasma surface treatments can also be effective with big, complex 3D geometries [18], produce a negligible amount of waste material and are potentially very cheap processes [9,19].

Plasma is a highly ionized gas consisting of neutral and charged particles including free electrons, ions, chemical radicals and excited molecules. Plasmas can be divided into two main categories: thermal and non-thermal plasmas. In a non-thermal plasma, electrons and heavy particles' temperatures always differ by orders of magnitude. In fact, while the electronic temperature is usually very high, heavy particles' one is not, often being close to room temperature. Non-thermal plasmas' global temperature is therefore usually suitable for polymeric surfaces treatments, since they can provide a highly reactive environment (rich in free electrons, ions and radicals) with little to no thermal drawbacks, depending on materials and conditions.

Non-thermal plasmas can be generated by the application of an electromagnetic field in a gaseous gap. It can be done using different power sources (DC, AC, Radio Frequency and microwaves) with different powers, gases, pressures and electrodic geometries (superficial or volumetric discharges) [19–21]. Such plasma parameters deeply influence plasma treatments' chemical dynamics, consequently varying efficiency and quality [22].

By the impact with energetic particles within the plasma volume, chemical bonds are broken, producing several different

reactive species (ions, radicals, excited atoms) the nature of which strongly depends on the type of gas that is being used. Such reactive species will in turn react with the polymeric surface, possibly introducing new functional groups. Additionally, a portion of accelerated electrons can directly impact the polymeric surface, breaking the chemical bonds inside polymeric chains. Non-thermal plasmas can therefore influence the chemistry of a superficial polymeric layer, changing its properties, depending on the dynamics involved in each treatment.

The effects of a plasma treatment are also time-dependant, since they are influenced both by the treatment time, and by the ageing effect. It is known that after a plasma treatment, polymeric surfaces will show an incomplete recovery of their initial properties, due to migrations and oxidation reactions. Stable conditions are usually met after a week from the original treatment, and can be paused storing the sample under its glass transition temperature [9].

With the aim of improving PBS mechanical properties and biocompatibility, in this contribution a novel PBS-based copolymer containing thioether linkages (P(BS85TDGS15)) is presented. Synthetic strategy, molecular, thermal and mechanical properties are described. Both PBS and P(BS85TDGS15) have been subsequently subjected to a non-thermal plasma surface treatment and its effect on physic/mechanical properties, biodegradation rate and biocompatibility has been considered.

2. Experimental

2.1. Materials

Dimethylsuccinate (DMS), 1,4-butanediol (BD), thiodiglycolic acid (TDGA), and titanium tetrabutoxide (TBT) (Sigma–Aldrich, Milan, Italy) were reagent grade products. All the reagents were used as supplied with the exception of TBT which was distilled before use. Chloroform and methanol were purchased from Sigma–Aldrich and were used without any further purification.

2.2. Synthesis of PBS and P(BS85BTDG15)

Poly(butylene succinate) (PBS) and poly(butylene succinate/thiodiglycolate) (P(BS85BTDG15)), a random copolymer containing 85 mol% of butylene succinate co-units and 15 mol% of butylene thiodiglycolate co-units, were synthesized in bulk by the usual two step melt polycondensation, by employing DMS and BD or DMS, TDGA and BD for PBS and P(BS85BTDG15), respectively.

The reactions have been carried out in a 250-mL stirred glass reactor, with a thermostatted silicon oil bath; temperature and torque were continuously recorded during the polymerization.

In both cases, 20 mol% excess of diol with respect to dimethylester (or dimethylester/dicarboxylic acid mixture) and $\text{Ti}(\text{O}i\text{Bu})_4$ as catalyst (about 150 ppm of Ti/g of polymer) were used.

In the first stage, under pure nitrogen flow, the temperature was risen to 180 °C and kept constant until more than 90% of the theoretical amount of methanol was distilled off (about 90 min). In the second stage, the pressure was reduced to about 0.08 mbar to facilitate the removal of the glycol in excess, and the temperature was gradually risen to 250 °C (10 °C every 30 min); the polymerizations were carried out until a constant torque value was measured.

Polymer purification has been carried out through dissolution in chloroform and subsequent precipitation in methanol.

The chemical structure of P(BS85BTDG15) is reported in Fig. 1.

2.3. Film preparation

Films of PBS and P(BS85BTDG15) were obtained by hot pressing

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