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Synthesis and characterization of polyurethane sealants containing rosin intended for sealing defect in annulus for disc regeneration

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ABSTRACT

Thermoplastic polyurethanes containing rosin or mixtures of rosin and 1,4 butane diol in the chain extender were proposed as potential sealants for defects in disc regeneration surgery. The polyurethane sealants were prepared by using the prepolymer method and different mixtures of rosin and 1,4 butane diol were used as chain extenders. The existence of one carboxylic moiety in the rosin structure allowed the reaction with the isocyanate end groups in the prepolymer during polyurethane synthesis, creating additional urethane-amide hard segments. The polyurethanes were characterized by ATR-IR spectroscopy, differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMA), thermal gravimetric analysis (TGA), scanning electron microscopy, X-ray diffraction and laser confocal microscopy. The adhesion of the polyurethane sealants were tested by *T*-peel test of leather/polyurethane sealant/leather joints and by single lap-shear tests of aluminium/polyurethane sealant/aluminium joints. Depending on the rosin content in the chain extender the structure of the polyurethanes was different, i.e. more urethane and urethane-amide hard segments were created up to 50 eq% rosin in the chain extender and separation of domains was prevailing in the polyurethanes with higher rosin content. Furthermore, the addition of rosin caused an increase in the length of the polymer chains but a decrease in the storage modulus was produced (particularly in the polyurethane containing 50 eq% rosin), likely due to the bulky structure of the rosin as compared to the linear structure of 1,4 butane diol, allowing the separation of the linear polyurethane chains. On the other hand, the melting of the soft segments in the polyurethanes started at 40–57 °C and the addition of more than 50 eq% rosin in the chain extender decreased the melting enthalpy. Moreover, the crystallinity of the polyurethanes containing up to 50 eq% rosin showed lower number and smaller spherulites. Finally, the peel strength increased in the joints made with the polyurethane sealants containing rosin whereas the adhesive shear strength decreased when the polyurethane sealant contained 50 eq% rosin or less.

1. Introduction

In the framework of the FP7 European project DISC REGENERATION a novel non-invasive surgical approach is currently under development [1]. The project is intended to solve the back pain problems caused by herniated disc proposing the regeneration of the intervertebral disc by means of a new hydrogel injection. Because of the injection of the hydrogel in the disc, the defect made in the annulus pulposus should be effectively seal to avoid hydrogel losses. It has been shown [2,3] that one limitation of the current disc regeneration therapy is the lack of an effective sealing system of the defect in the disc as an efficient sealing system has not been developed yet. In this study, new thermoplastic polyurethane sealants (PU) are proposed as potential sealants for the defect in disc regeneration therapy.

Polyurethanes are among the most versatile materials that can be used for construction of medical devices including hollow fibres membranes for haemodialysis, balloons, drug-eluting stent coatings, and central-venous catheter probe covers, among other. They are tough, biocompatible, and hemocompatible [4,5]. They can be strong elastomers or rigid plastics, and they can be processed by extrusion, injection moulding, film blowing, solution dipping, and two-part liquid moulding.

Melt-processable, or thermoplastic, polyurethanes, are used extensively in medical devices. Thermoplastic polyurethanes are long-chain linear polymers without cross-links. Their linear structure allows the polyurethane to be melted to form parts of devices that can be resolidified. Thermoplastic polyurethanes are often used to produce catheters (over-the-needle catheters,

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central-venous access catheters, multilumen catheters), in asymmetric membranes manufacture for dialysis, and in wound dressings used to make a covering that is impermeable to fluids and bacteria but allows moisture to permeate. Some polyurethane emulsions intended for catheter device were synthesized from urethane prepolymer extended in water using L-lysine, ethylenediamine, and their mixture as chain extenders [6]. These emulsions exhibited satisfactory freeze/thaw stability and the films cast from the emulsions possessed excellent mechanical properties. Although the swelling ratios of the polyurethanes immersed in water for 24 h were different, the polyurethane obtained with L-lysine possessed the smallest weight loss after hydrolysis. On the other hand, all polyurethanes showed antiblood coagulation in-vitro.

Polyurethanes are manufactured by reacting an isocyanate, a macroglycol or polyol, and a chain extender. Thermoplastic polyurethanes are fully reacted materials, i.e. they do not contain unreacted NCO moieties, and they are block copolymers with $-(AB)_n-$ structure where A is the hard segment and B is the soft segment. The hard segments, formed by reaction of the isocyanate groups with the chain extender, have low molecular weight and they are rigid and highly polar; on the other hand, the soft segments correspond to long hydrocarbon chains of macroglycol, and they are flexible and non-polar [7]. The segmented structure of the thermoplastic polyurethanes allows phase separation into hard and soft domains which determines the polyurethane properties. Thermoplastic polyurethane structure is made of long linear chains that interact by physical forces which can be destroyed by heating and/or by solvents.

Although thermoplastic polyurethanes have excellent properties, in general, they lack of sufficient immediate adhesion at body temperature, i.e. 37 °C, to allow immediate attach of the sealant into the defect and maintain it in the location of application. Immediate adhesion can be reached in thermoplastic polyurethanes by heating at temperature higher than 50 °C which is not feasible in the sealing of the disc defect [8]. In this study, the addition of rosin into the thermoplastic polyurethane sealant structure is proposed, to impart immediate adhesion at body temperature.

Rosin is a natural tackifier obtained from pine exudates that is commonly added in the formulation of surgical tapes to impart high initial adhesion and tack, and it is also used as an additive in glazing food applications. It has been shown elsewhere [9] that the addition of rosin to formulated thermoplastic polyurethane adhesive was not successful due to poor miscibility causing phase separation. Therefore, rosin has to be incorporated within the polyurethane structure during thermoplastic polyurethane synthesis. Chemical composition of rosin consists in terpene structure based on abietic, neoabietic and palustric acids, all of them having one carboxylic functionality (Fig. 1). The existence of one carboxylic moiety in the rosin structure allows the reaction with the isocyanate moieties in the prepolymer during polyurethane synthesis, anchoring the rosin molecules at the extreme of the polyurethane chains.

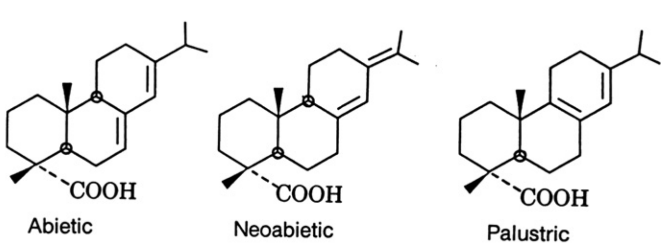

Fig. 1. Chemical composition of rosin.

The synthesis of polyurethane foams containing rosin for medical applications has been reported earlier [10]. Rosin-based polyester polyols were synthesized by reacting rosin–maleic anhydride adduct, diethylene glycol, and ethylene glycol with and without adding adipic acid and phthalic anhydride, in the presence of catalyst. Rigid polyurethane foams were prepared with these rosin-based polyols and it was shown that they had higher compression strength, and similar dimensional stability at 100 °C than those prepared with polyols without rosin derivative. Furthermore, the rosin-modified polyurethane foams exhibited even lower thermal conductivity and much higher activation energies during pyrolysis.

There is little literature [11,12] dealing with the addition of rosin during the synthesis of thermoplastic polyurethanes. Aran-Aís et al. [11] reported the characterization of thermoplastic polyurethanes (TPUs) prepared with the prepolymer method by using chain extenders containing different mixtures (0–50 eq%) of rosin and 1,4 butane diol. The TPUs were used as raw materials to prepare solvent-based polyurethane adhesives. The addition of rosin contributed to the production of two types of hard segments, producing an increase in the average molecular weight, an increase in the viscosity, and improved rheological properties. On the other hand, the immediate adhesion to plasticized PVC in all joints was improved if the TPU contained rosin. Aran-Aís et al. [12] also reported the synthesis and characterization of TPUs containing different hard/soft segment ratios (1.05–1.4) and synthesized with a mixture of 50 eq% rosin and 50 eq% 1,4 butane diol as chain extender. The addition of rosin increased the average molecular weight, more markedly in the TPUs containing higher hard/soft segment ratios, but the elastic and viscous moduli decreased. An increase in the hard/soft segment ratio of the TPUs retarded the kinetics of crystallization and increased the immediate adhesion to PVC but the final adhesion decreased.

The structure of polyurethane elastomers containing rosin was studied by Sánchez-Adsuar et al. [13]. Rosin was used either as an additive, mixed in the TPU solutions, or as a reactant in the chain-extension step of polymer synthesis. Rosin as an additive did not markedly change the polymer properties. On the contrary, the use of rosin in the chain-extension step lead to sharp increase of viscosity and molar mass as well as improved rheological properties and changes in morphology as the crystalline regions were more affected than the amorphous ones. It was concluded that rosin modified the organization of both the hard and the soft segments of the polymers. However, addition of rosin did not improve the low tack of TPU, although as chain extender or co-chain extender (together with 1,4 butane diol) rosin allowed development of significant initial adhesive strength.

Therefore, in this study thermoplastic polyurethanes containing different amounts of rosin were prepared for potential use as disc defect sealant. The synthesis procedure was modified from the previous methods existing in the literature and much wider range of rosin–1,4 butane diol mixtures was tested in order to provide an adequate performance at 37 °C. The TPUs prepared were characterized by using several experimental techniques, including adhesion measurements.

2. Experimental

2.1. Materials

The synthesis of the polyurethane sealants was carried out by using the prepolymer method (Fig. 2). The hard to soft segment ratio (NCO/OH) used was 1.05. The prepolymer was prepared by reacting the polyol and the isocyanate in a 500 ml glass flask under inert atmosphere, with continuous mechanical stirring.