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Influence of e-beam irradiation on the dynamic creep and fatigue properties of poly(aliphatic/aromatic-ester) copolymers for biomedical applications

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ABSTRACT

Biomaterials must meet special medical prerequisites like biocompatibility and resistance to degradation and fracture, especially under cyclic loading. Promising candidates are poly(aliphatic/aromatic-ester) (PED) multiblock copolymers, which belong to the class of thermoplastic elastomers (TPEs), characterized by a physical network of semi-crystalline hard segments. Here we focus on the dynamic creep and fatigue performance of these TPEs and compare their behaviour with commercial benchmark materials. The PEDs were e-beam cured, to enhance their fatigue behaviour by the formation of an additional network structure. All materials were evaluated using quasi-static tensile tests and dynamic hysteresis measurements. Their mechanical properties were related to the network structure. E-beam irradiation increased the tensile strength and decreased the dynamic creep rate of PEDs. This effect can be explained by the formation of chemical cross-links, which are located in the hard phase segments. In conclusion, these novel biomaterials are a comparable alternative to their commercial counterparts like silicones and thermoplastic polyurethanes.

1. Introduction

Thermoplastic elastomers (TPE) constitute a relatively new group of polymeric materials which can be classified as a separate category of rubbers. TPEs do not need to be vulcanized and therefore offer many advantages in comparison to chemically cross-linked elastomers, while being processible as conventional thermoplastics. High performance TPEs with a good solvent resistance, elasticity, tear strength and flex fatigue properties are used in a wide range of medical applications such as medical tubing or equipment parts [1].

Because of their chemical structure and the matrix-domain morphology, characterized by the presence of hard and soft segments, selected TPEs like poly(ether–urethanes) or poly(ester–ether)s have unique physiochemical and mechanical properties and show a high degree of biocompatibility [2]. These TPEs are commonly used for medical implant applications as well as silicone and thermoplastic urethanes [1,3,4].

The mechanical behaviour of biomaterials like implants or rubbery medical parts is as important as their biocompatibility since an inadequate performance or even premature failure can let to health issues for patients. Therefore the durability or long-term mechanical behaviour of new biomaterials has become a prime concern in their adoption for medical devices. In addition, most of the loadings during the use as a body implant are dynamical in nature and polymers are known to creep or relax under sustained loadings. Implants should remain in the body for a long time [5], such that the number of surgical operations on patients is reduced, In order to evaluate the long-term dynamic properties of potential biomaterials a dynamic sinusoidal loading can be applied to the material specimen at various step-wise increasing load intervals. This step-wise increasing load test (SILT) induces a progressive deterioration of dynamic properties of the materials [6,7].

Recently novel poly(aliphatic/aromatic-ester)s (PEDs) have been synthesized as an alternative biomaterials for temporary flexor tendon prosthesis [8]. These PEDs contain discrete (nanometric) hard segments of semi-crystalline poly(butylene terephthalate) (PBT) embedded in a matrix of soft segments containing aliphatic dimer fatty acid, here dilinoleic acid (DLA) that impart the elastomeric character to the copolymer. The DLA component has a good oxygen and thermal stability and is suitable for biomedical applications due to its nontoxicity. In addition, the use of thermal stabilizers for the synthesis is not required [9–13].

In a previous work [2] these nano-structured PEDs already showed a much more improved dynamic mechanical behaviour than the medical-grade polyurethane (Pellethane®) at high number of cyclic loadings. In order to enhance the short- and long-term

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mechanical behaviour of PEDs through stiffening of the material, an additional cross-linked network structure was introduced. The cross-linking can be achieved by using e-beam irradiation which promotes cross-linking among polymer chains [10]. The use of e-beam irradiation improves the static mechanical behaviour of polymers, but can also yield better dynamic creep and fatigue resistance [14].

This work focuses on the dynamic creep and fatigue behaviour of these novel nano-structured PEDs modified with various dosages of e-beam irradiation. Differential scanning calorimetry (DSC) was used to evaluate the thermal behaviour of the materials, and to identify any detrimental onset of material degradation. This method allows one to predict the extent of cross-linking that can be introduced to the material. Quasi-static tensile testing was performed to determine the ultimate strength of the PEDs, which is necessary for the dynamic SILT methodology and the evaluation of the dynamic creep behaviour measured by single load tests. In addition, atomic force microscopy (AFM) was carried out to highlight the micro-structure of the materials. The impact of e-beam irradiation on the mechanical properties of PEDs is discussed.

2. Experimental

2.1. Materials

The materials were segmented poly(aliphatic/aromatic-ester) (PED) multiblock copolymers containing poly(butylene terephthalate) (PBT) sequences which are extended with butylene ester of dilinoleic acid (DLA). DLA belongs to the group of dimer fatty acids. The semi-crystalline PBT is the hard segment phase while DLA is an amorphous diacid, which imparts the elastomeric characteristic to the polymer and therefore represents the soft phase segments. The biocompatibility of PBT and DLA has been well established and both can be used as a biomaterial or as blend components [8]. The chemical structure of the segmented PED is shown in Fig. 1.

In this study, two hard/soft segment ratios of PED were investigated (PBT-26 and PBT-30). PBT-26 contains 26 wt.% PBT and 74 wt.% DLA. PBT-30 respectively contains 30 wt.% PBT and 70 wt.% DLA, respectively. Pellethane®, which belongs to the thermoplastic polyurethanes (TPU) and a chemically cross-linked medical-grade silicone were used as benchmark materials for comparison of the PED copolymers with commercial products.

2.2. Sample preparation

Segmented multiblock copolymers (PED) were obtained in a two-stage process of transesterification and polycondensation in the melt as described elsewhere [15]. Briefly, dimethyl terephthalate (DMT) and 1,4-butanediol (1,4-BD) were subjected to transesterfication process to produce oligomer of butylene terephthalate (PBT) and using tetrabutoxy titanate as a catalyst. Then, oligomers of PBT were reacted with dimer fatty acid (here a dilinoleic acid, DLA) and a catalyst to initiate the polycondensation process at 250 °C. Hot reaction mass was extruded into water using compressed nitrogen, granulated and then purified by Soxhlet extraction from methanol [9,16].

In the next step, the materials were compression-moulded and e-beam irradiated. A linear electron accelerator Elektronika 10/10 was used to generate a 10 MeV electron beam for different dosages. The samples did not show any water uptake at standard laboratory conditions. Finally, micro dumbbells were produced from the material with a cutting tool according to DIN 53504 [17]. Puskas et al. [18] showed that the use of micro dumbbells is sufficient to monitor the fatigue performance of TPEs. Table 1 shows the materials of this study and the weight and number average molecular weight (M_n and M_W), the polydispersity index P_i, the intrinsic viscosity number η and the hardness.

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) scans of PED copolymers were performed using a DSC-Q1000 (TA Instruments, USA), with a triple cycle of heating–cooling–heating over the temperature range of −150 to 250 °C at a heating/cooling rate of 10 °C/min. The first heating cycle started at 23 °C and is intended to remove the thermal history. All DSC measurements were conducted in a nitrogen environment at a flow rate of 50 ml/min.

The glass transition temperature T_g of soft segments was determined from the upper inflection point of the received DSC thermogram. The crystallization temperature T_c was determined using the exothermic peak during the cooling cycle, while the melting temperature T_{m2} corresponds to the endothermic peak shown in the second heating cycle. In addition, the melting enthalpy ΔH_{m2} of PBT and the mass content of PBT crystallites $w_{c,h}$ were calculated [19–21].

2.4. Quasi-static testing

Tensile tests were carried out using a Zwick Z2.5 universal test equipment with a 0.5 kN load cell, a cross-head speed of 100 mm/min and a grip distance of 20 mm. The measurements were performed using sandpaper which was attached to the clamps in order to prevent slippage of the soft tensile bars from the clamps.

Tensile tests were performed with the benchmark materials as received under the standard laboratory conditions. The ultimate tensile stress σ_{max}, the elongation at break ε_{max} and Young's modulus E_{mod} were evaluated according to DIN 53504 [17]. The modulus of elasticity E_{mod} was calculated at 10% strain and all tensile results were averaged from 5 samples.

2.5. Fatigue testing

In order to conduct the hysteresis measurements, a servo-hydraulic test machine with a 20 kN servo cylinder, a 50 N load cell, a proper digital controller (Instron 8400/8800) and a special software package were used for the evaluation of the hysteresis loops. The resulting strain was measured using the real-time displacement between the specimen fixtures.

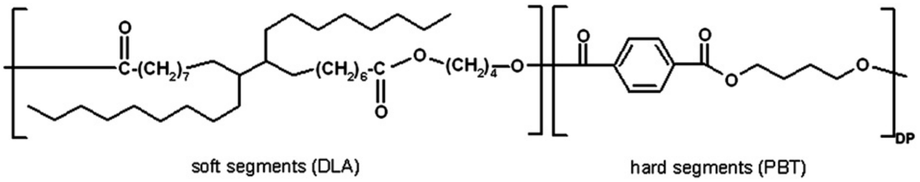

Fig. 1. Chemical structure of poly(aliphatic/aromatic-ester) (PED) multiblock copolymers, composed of dilinoleic acid (DLA) as the soft segments and poly(butylene terephthalate) (PBT) representing the hard segments.