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Influence of ceria nanoparticles on chemical structure and properties of segmented polyesters

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ABSTRACT

In this work, we present new nanocomposite materials derived from segmented copolyesters, comprising ethylene terephthalate (PET) segments and dimerized linoleic acid (DLA), and nanometric cerium oxide particles (CeO_2). Nanoparticles were incorporated in situ during polycondensation in various concentrations, from 0.1 up to 0.6 wt.%. It was found that preparation of nanocomposites in situ, during polycondensation, had no significant influence on changes in segmental composition as determined from ^1H and ^{13}C, as well as 2D NMR. Thermal analysis and calculated degree of crystallinity showed that increasing concentration of ceria nanoparticles lead to an increase in mass content of PET crystallites in hard segments. The XRD investigations also showed an increased intensity of characteristic signals with increasing ceria concentration. Simultaneously, the incorporation of CeO_2 led to an increase in tensile strength and elongation at break, indicating a reinforcing and plasticizing effect of ceria nanoparticles. However, the modulus at 10% strain decreased with increasing amount of nanoparticles. The in vitro culture of human cardiac progenitor cells (hCPCs) on the new materials indicated a homogenous cell displacement across the samples after 5 days with no signs of cytotoxicity, indicating good biocompatibility in vitro of CeO_2-based nanocomposites and a potential for biomedical applications.

1. Introduction

In the recent decades, significant progress has been made in the area of advanced polymeric materials for biomedical applications. Existing research had been focused primarily on one-phase bulk or porous materials. However, biological systems are most often multiphase systems, either hierarchical (e.g. tendon) or composite (e.g. bone), both built up from constituents differing in size in order of magnitudes. Recently, a biomimetic approach has been proposed for (nano)composite biomaterials design. It has been demonstrated that polymer matrices containing different nanoparticles can provide beneficial properties that are inaccessible for non-filled materials [1]. These properties include enhanced compressive strength, tensile strength or modulus, better cytocompatibility with respect to individual cells, better cell adhesion, more linear drug release profile, and others [1,2]. Thus far, the most thoroughly investigated nanocomposite biomaterials are these with poly(hydroxyacid)s as the polymeric matrices. The suggested applications of these materials are primarily in the area of bone grafting, when filled with nanocrystalline hydroxyapatite, bioactive glass or calcium carbonate [3–5]. Other examples of polymer nanocomposite biomaterials include polycarbohydrates [6,7], polyurethane [8,9], polyester [10,11], and other polymer matrices [12–14]. The majority of these investigated nanocomposite materials are intended for use in hard tissue implants, as the design biomaterials for soft tissue reconstruction remains more challenging [15].

New thermoplastic elastomers (TPEs), poly(aliphatic/aromatic-ester)s (PEDs), have recently attracted attention for biomedical applications [16,17]. These polymers consist of poly(ethylene- or butylene terephthalate) (PET or PBT) units as hard segments and soft segments containing an amorphous fatty acid, such as dimerized linoleic acid (DLA). Commercially available dimerized fatty acids containing C36 are the polymerization products of C18 unsaturated fatty acids or esters such as linoleic and oleic acids derived from vegetable oils [18,19]. PEDs are synthesized with the use of non-toxic monomers (DLA) and, most importantly, without thermal stabilizers, which can act as irritants after the in vivo environment washes them out of the polymer. In previous investigations for soft tissue reconstruction (finger flexor tendon reconstruction), PED polymers exhibited biocompatibility in vitro and in vivo, combined with excellent mechanical properties, especially fatigue resistance [20–23]. Since PEDs are categorized as thermoplastic elastomers, they can be tailor made for a given application: at low concentration of the hard phase these materials have stress–strain curves typical of elastomers, while increasing the hard phase concentration results in a larger toughness typical of thermoplastics.

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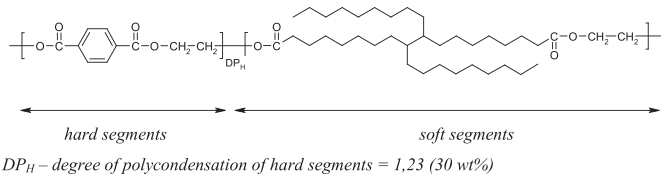

DP_H – degree of polycondensation of hard segments = 1,23 (30 wt%)

Scheme 1. Chemical formula of poly(ethylene terephthalate–ethylene dilinoleate) (PED) multiblock copolymer.

As is well-known, material reinforcement resulting in improved mechanical strength can be realized by preparing composites using different fillers, such as bioactive glass ceramic [24], carbon nanotubes [25], or nanoparticles [26]. Even the addition of a small amount of nanoparticles has been demonstrated to remarkably improve the mechanical strength of the resulting polymer nanocomposite. The specific reinforcing behavior with nanoparticles is due to enhanced filler/matrix and filler/filler interaction in comparison to conventional (i.e. μm-sized) fillers [27]. Importantly, these interactions are strongly correlated with nanoparticle spacing in the polymer matrix.

In order to avoid nanoparticle aggregation, in situ techniques, rather than conventional mixing, are preferred for nanocomposite preparation. In our previous work, we demonstrated successfully the nanoreinforcement of PED materials, composed of polymers with poly(ethylene terephthalate) (PET) hard segments (30 wt.%), with TiO_2 nanofiller [28]. The incorporation of as little as 0.13 vol.% of TiO_2 led to an impressive improvement of fracture strength (by 100%) and increased elongation at fracture by 300%. Further, we observed that the TiO_2 addition increased the surface roughness at the nanometer scale. Finally, adding nanocrystalline TiO_2 can also tune the rate of hydrolytic degradation of the material [29]. Prior studies have also shown that a bioinert surface can be obtained [30], which is crucial for soft tissue implants. It was observed that during 12-week in vivo implantation tests the nanocomposites elicit a very small inflammatory response, similar to that of currently approved and used silicone biomaterials [31]. Additionally, cytocompatibility tests carried out on embryonic myocardial stem cells indicated that the nanocomposites exhibit improved cytocompatibility, as compared to the currently used Polyactive® biomaterials [32].

Polymers from the developed PED family of TPE have also been modified with nanocrystalline hydroxyapatites (HAps) of different types. Both in vitro and in vivo testing indicates that these nanocomposites possess good cyto- and tissue compatibility [33,34]. Further, submicron fibers have been electrospun from the nanocomposites, demonstrating the potential application of such materials for bone tissue engineering scaffolds. A model has been proposed, utilizing the HAp-modified TPEs to built a hybrid biomaterial for meniscus replacement [35].

Recently, cerium oxide (CeO_2) nanoparticles are emerging as interesting nanofillers for potential biomedical applications [36]. Undoped ceria and doped ceria are promising materials for many applications, including solid oxide fuel cells [37], catalysis [38], and even photovoltaics [39]. The key properties of ceria are imparted by the presence of Ce ions in both Ce^{4+} and Ce^{3+} oxidation states, giving ceria the ability to quench free radicals and opening new applications in the biomedical field. In fact, nanocrystalline ceria has been recently proposed for the therapeutic treatment of various diseases induced by reactive oxygen

Table 1
Inherent viscosity (IV) of the synthesized materials.

Material	c [g/100 cm^3]	IV [dL/g]
PED	0.5042	0.552
PED + 0.1% CeO_2	0.5000	0.661
PED + 0.2% CeO_2	0.5004	0.599
PED + 0.4% CeO_2	0.5004	0.925
PED + 0.6% CeO_2	0.5000	0.919

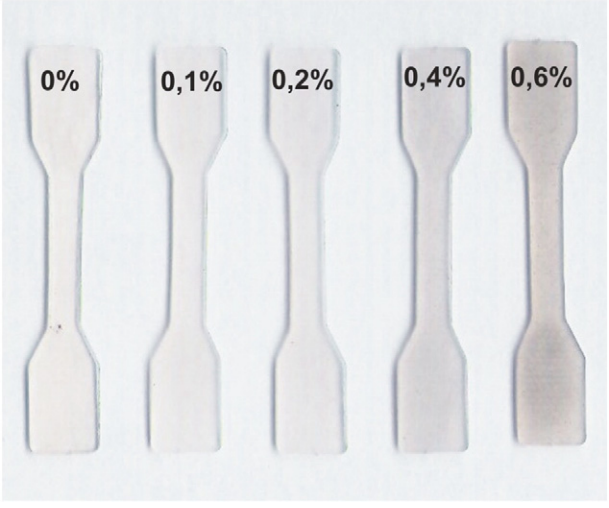

Fig. 1. The appearance of the synthesized materials. The weight percentages of ceria nanoparticles content are shown in the figure.

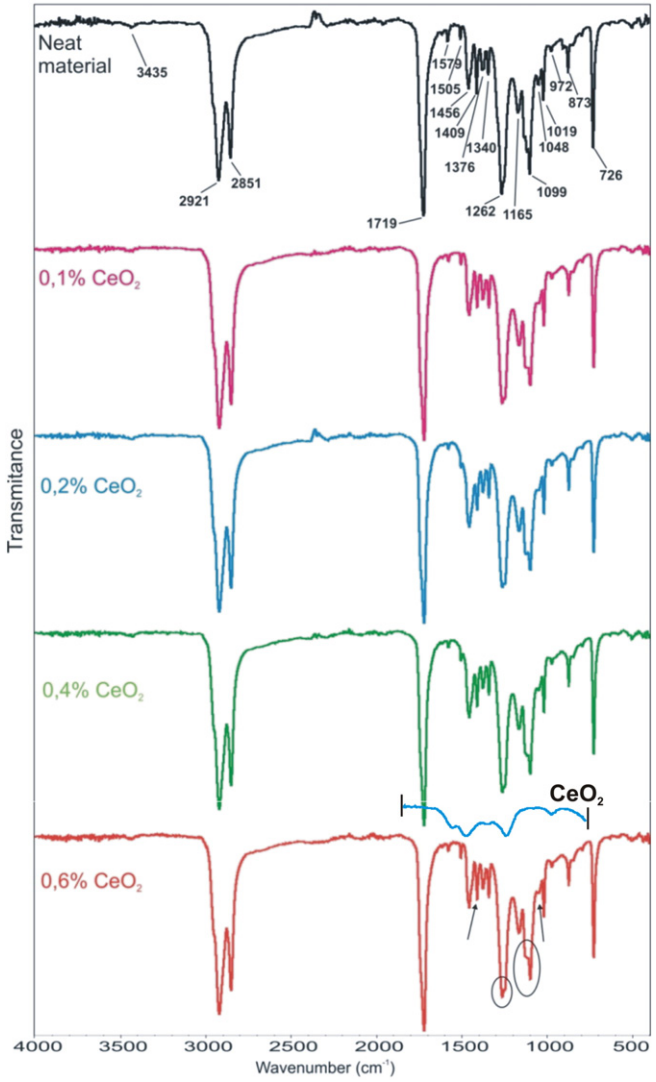

Fig. 2. ATR FT-IR spectra of the synthesized materials.