

DESIGNING POLYMER/CERAMIC NANOCOMPOSITES OF TAILORED STRUCTURE AND PROPERTIES FOR BIOMEDICAL APPLICATIONS

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[*Engineering of Biomaterials*, 46,(2005),25-27]

Introduction

Nanostructured organic/inorganic composite materials represent modern and advanced systems of specific physico-chemical, mechanical and processing properties. Combining unique properties of the organic component (oligomer or polymer) and the inorganic one (inorganic particles or aggregates, including ceramics), they fulfill the highest requirements of modern materials for electronics, optoelectronics and medicine. One of the modern groups of polymers of unique properties are thermoplastic elastomers (TPE), which have already found numerous applications, including several in the medical field (polymers for tissue reconstruction or drug delivery systems) [1-3]. Their biological properties, in particular related to their bioactivity, are not always as marked as for bioactive ceramics, such as calcium phosphates, Bioglass® or titanium dioxide [4-5]. Therefore, combining the unique properties of organic, polymeric matrix (elasticity and easy of processing) with inorganic highly biocompatible and bioactive inorganic components (micro- and nanoparticles), various composite materials can be prepared especially for biomedical applications. In particular, nanocomposites comprising biocompatible polymer matrices and inorganic nanoparticle fillers represent a new group of composite biomaterials for tissue engineering scaffolds and biomedical implants and devices. Among the polymer matrices, biodegradable polymers such as poly(L-lactic acid) or poly(caprolactone) are commonly used. They are rather stiff materials of limited elongation and rather unsuitable for various applications. Therefore, thermoplastic elastomers, as materials of high flexibility to tailor their structure and properties, represent interesting alternative materials, especially for soft tissue applications. Combining these flexible and degradable materials with bioactive nanoparticles, a new family of biomedical materials can be created. In addition, the superposition of unique features of the two constitute components in these polymers (e.g. variable hard to soft segments ratio) offers a high versatility of design, attainment of specific morphology and excellent mechanical properties. Recently, novel poly(aliphatic/aromatic-ester)s (PED) of segmented (multiblock) structure behaving as thermoplastic elastomers (of hard/soft segments structure) have been synthesized and extensively investigated for biomedical applications [6-8]. PED are composed of semicrystalline poly(butylene terephthalate) (PBT) (hard segments) and unsaturated dilinoleic acid (DLA) (soft segments). PED are synthesized without, often irritant, thermal stabilizers due to excellent oxygen and thermal stability of a component of soft segments (DLA). This feature is especially important if the material is intended for biomedical applications. PED copolymers are biocompatible in vitro and in vivo, and specially modified with active molecules, they show antibacte-

rial properties [9]. It has been demonstrated that addition of ceramic nanoparticles, such as alumina or titania, to polymer matrices greatly influences their mechanical, physical and biological properties [10-13]. The key to good performance is to achieve good homogeneity of the nanoparticle dispersion and uniform microstructure. Thus, these systems require optimized formulation and processing methods. We proposed a solvent-free method, as an excellent tool for nanocomposites preparation. The method involves in-situ polycondensation process of a TPE in a presence of TiO₂ nanoparticles. TiO₂ was selected because its nanoparticles have a higher cytocompatibility than composites made using conventional (micrometer) TiO₂, i.e. the adhesion of osteoblasts and chondrocytes is much higher when nanoparticles are used [11]. These findings imply that TiO₂ nanoparticles may be a potential improved substitution to the micro-sized particulate coatings presently used on bioresorbable polymer scaffolds [14]. Moreover several studies have proved that TiO₂ can act as a bioactive ceramic [15-17] in the sense that some forms of TiO₂ exhibit a strong interfacial bonding to living tissue by means of the formation of a biologically active hydroxyapatite (HA) layer on the material surface. In this work we present results of the influence of different concentrations of TiO₂ on composite properties. In such systems, a PED multiblock thermoplastic elastomer was used as the matrix.

Experimental

Preparation method

The organic-inorganic nanocomposites were prepared by in situ polycondensation of polyester and TiO₂ nanoparticles. Commercially available TiO₂ nanopowder (Aeroxide® P25, Degussa, Frankfurt a. M., Germany) with a mean primary size of 21 nm and a specific surface area of 50 m²/g was used. The nanoparticles consist of approximately 80% anatase and 20% rutile [18]. In situ polycondensation included two steps carried out in separate cascade reactors. First, transesterification process between dimethyl terephthalate (DMT, ZWCh Elana, Torun, Poland) and ethylene glycol (EG, Aldrich, 99%) has been carried out at elevated temperature in presence of Zn(Ac)₂ and Sb₂O₃ (Aldrich, 99.99%) catalyst. During the second stage of the reaction, a hydrogenated dilinoleic acid (DLA) (Uniqema - ICI, The Netherlands; acid value 196mg KOH/g), and the variable concentration of TiO₂ nanoparticles (0.2; 0.4 and 0.6 wt%) were added. The polycondensation was carried out at 245-250°C and 0.5-0.6 mm Hg of vacuum. The process was considered complete on the basis of the observed power consumption of the stirrer motor when the product of highest melt viscosity was obtained, up to a constant value of power consumption by the reactor stirrer was

Sample	soft segments		hard segments			
	T _{g1} (°C)	ΔC _p J/g°C	T _{g2} (°C)	T _{m2} (°C)	ΔH _{m2} J/g	T _{c2} (°C)
PET-D	-28.4	0.271	70.4	185.0	15.1	96.9
PET-D – 0.2% TiO ₂	-27.2	0.229	72.3	180.1	10.3	106.4
PET-D – 0.4% TiO ₂	-26.8	0.245	76.4	173.1	37.9	113.6
PET-D – 0.6% TiO ₂	-36.6 -83.6*	0.198 0.423	-	193.1	13.2	119.6

T_{g1} – glass transition temperature of soft segments, ΔC_p – heat capacity; T_{g2}, T_{m2}, T_{c2} – glass transition, melting and crystallization temperature of hard segments, respectively; ΔH_{m2} – melting enthalpy of hard segments, * - second glass transition temperature

TABLE 1. Thermal properties of nanocomposites.

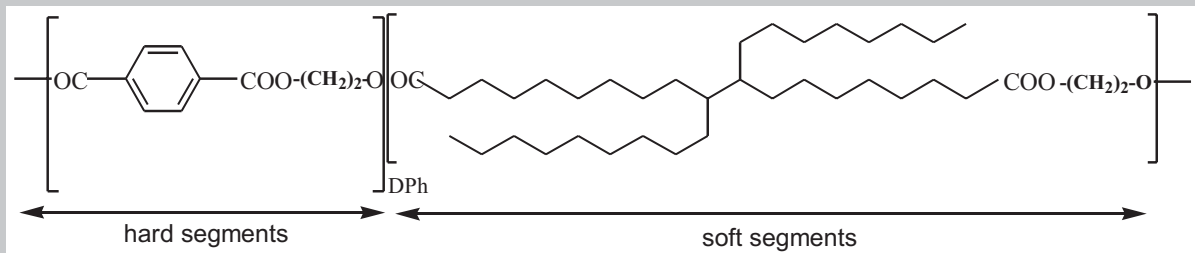


FIG. 1. Chemical formula of poly(aliphatic/aromatic-ester) containing a 70:30 (wt%) soft to hard segments (ratio DPh - degree of polycondensation of hard segments equal 1.2).

achieved. The neat (PET/DLA) copolymer (hard to soft segments ratio - 30:70 wt%) was prepared in a similar way, without TiO_2 nanopowder.

Characterization of composite microstructure, thermal and mechanical properties

Surface morphology and sample homogeneity of neat polymer and polymer/ TiO_2 composites (uniformity of TiO_2 nanoparticles in the matrix) were characterised using scanning electron microscopy (SEM) (JEOL JSM). Small pieces of samples were mounted onto stubs using adhesive tapes and sputtered with a gold layer. Accelerating voltages in the range of 6-18 kV were used for the observation of surface topography. Differential scanning calorimetry (DSC) scans were performed with a DuPont apparatus. The samples were dried in vacuum at 70°C , and then kept in a desiccator. The process was carried out in a triple cycle: first heating, subsequent cooling and second heating, in the temperature range from -120°C to 300°C , which is higher than the melting point of the investigated material. The rate of heating and cooling was $10^\circ\text{C min}^{-1}$. The glass transition temperature (T_g) was determined from the temperature diagrams as the mid point of the curve. Samples in the shape of micro-dumbbells (0.5 mm thick) were prepared by press compaction according to ASTM D 1897-77 and then stamped for mechanical testing. Stress-strain curves were collected at room temperature with an Instron TM-M tensile testing machine equipped with a 500 N load cell at a cross-head speed of 200 mm/min. The stress data were calculated as the ratio of force to initial cross-section area. The strain was measured by the clamp displacement, where the starting clamp distance was 25 mm. The stress at failure point, the yield stress and elongation values were averaged over 4 to 6 measurements for each sample.

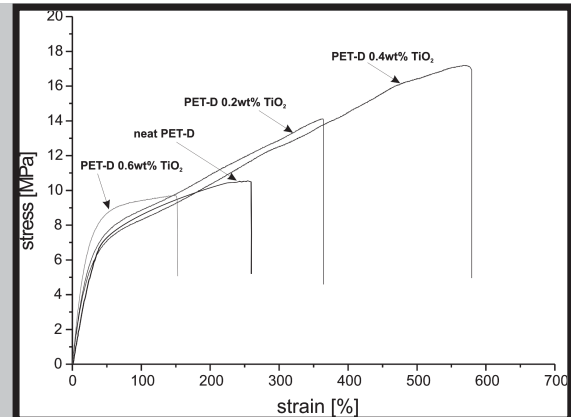


FIG. 3. Static tensile properties of PET-D neat copolymer and composites with variable TiO_2 concentration.

Results and discussion

PET/DLA copolymers containing different concentration of TiO_2 nanoparticles (0.2, 0.4 and 0.6 wt%) were synthesised using a PET/DLA weight ratio of 30/70. Homogenous, opaque materials were produced after 2 h reaction at 290°C . Their properties were compared to neat polymer (without TiO_2) as depicted in FIG. 1.

The thermal properties of the nanocomposites were studied by differential scanning calorimetry (DSC) at a standard heating rate of 10°C/min . Characteristic temperature transitions are presented in TABLE 1. PET/DFA copolymers show two characteristic temperature transitions ascribed to: melting of copolymers (rigid phthalic segments) and low temperature glass transition from dilinoleic acid. It was observed that the melting point (T_m) and the crystallization temperature (T_c) of polymers containing TiO_2 particles increases with increasing nanoparticles concentration. The glass transition temperature increases up to 0.4 wt% TiO_2 , while for

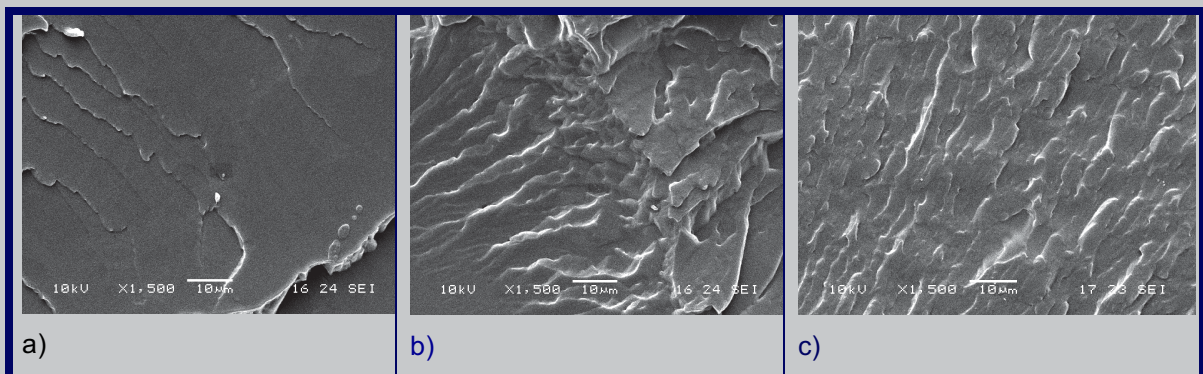


FIG. 2. Fracture surfaces of PET-D copolymer fractured in LN2 (a), sample containing 0.4 wt% TiO_2 (b) and (c) sample containing 0.6 wt% TiO_2 .

system containing 0.6 wt% TiO_2 , the glass transition temperature dramatically decreases, and moreover, the second transition at about 83°C appears. This rather unusual behaviour of the soft matrix at high concentration of TiO_2 nanoparticles will be studied in detail in the future using

additional methods such as DMTA.

The analysis of SEM micrographs of the neat PET-D copolymer (FIG.2a) and of systems containing 0.4 and 0.6 wt% TiO₂ (Fig.2 b,c) indicates differences in the topography of fracture surfaces: the neat copolymer sample shows features typical for elastomeric material (smooth fracture surface which indicates ductile deformation behaviour) while addition of TiO₂ leads to a surface topography typical for plastic deformation (b,c).

The analysis of static tensile properties indicates that the polymer-nanofiller system achieves the highest values of stress-strain characteristics at 0.4 wt% TiO₂ (FIG.3). The stress at break increased by 160% and the at break by 220%, comparing with the neat polymer, respectively. At higher concentrations of TiO₂ (0.6 wt%) tensile properties dramatically decreased, probably as the result of agglomerates formation (FIG.2c).

Conclusions

It has been demonstrated that the in situ polycondensation method in the presence of TiO₂ nanoparticles is a very interesting method for production of PET-D/TiO₂ nanocomposites. The in situ polycondensation method is a versatile and solvent-free technique to produce materials of interesting properties. Combination of a soft, elastomeric polymer matrix with crystalline ceramic nanoparticles gives an interesting material of enhanced mechanical properties as compared to the neat polymer. It is also expected that incorporation of TiO₂ nanoparticles will influence the degradation rate and bioactivity of these novel nanocomposites.

Acknowledgements

This work was financially supported by the Royal Society Grant (M. El Fray) and research project 3T08E03628. Dr. U. Janssen (Imperial College London) is greatly appreciated for his help with tensile testing.

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PRODUCTION OF TITANIUM AND HYDROXYAPATITE COMPOSITE BIOMATERIAL FOR USE AS BIOMEDICAL IMPLANT BY MECHANICAL ALLOYING PROCESS

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Abstract

Mechanical alloying is a ball milling process where a powder mixture placed in the ball mill is subjected to high energy collision form the balls. As the power particles in the vial are continuously impacted by the balls, cold welding between the particles and fracturing of the particles take place repeatedly during the ball milling process. In this article you will be presented with the case of mechanically alloying a metal such as titanium with hydroxyapatite, a ceramic consisting of calcium, phosphate and hydroxyls. The composite material will be used as a biomaterial used for implants. The starting powders were weighted, mechanically alloyed in an inert atmosphere, pressed and then thermally treated up to 1150°C in a thermal cycle. The samples were then analyzed by TGA-TG, optical microscope, XRD, and SEM.

After the thermal treatment, the samples had an outer shell that was composed of hydroxyapatite, and an inner core that consisted of titanium. Mechanical alloying of titanium and hydroxyapatite did not give a uniform distribution of the powders, but titanium particles were covered by hydroxyapatite fragments only on the surface of the specimens.

Keywords: Titanium, hydroxyapatite, mechanical alloying, biocompatibility
[Engineering of Biomaterials, 46,(2005),27-30]

Introduction

Mechanical alloying was invented in the 1970's as a method to develop dispersion-strengthened high temperature alloys with unique properties [1]. With the discovery of formation of amorphous alloys using this technique, it has received new research interest in developing different material systems.

Mechanical alloying is a ball milling process where a powder mixture placed in the ball mill is subjected to high energy collision form the balls. The process is usually carried out in an inert atmosphere [2]. The two most important events involved in mechanical alloying are the repeated welding and fracturing of the powder mixture. The alloying process is successful only when the rate of welding balances that of fracturing and the average particle size of the powders remains relatively coarse [3]. Alloys with different combination of elements have been synthesized, including at least one ductile metal to act as a host or binder to hold together the other ingredients [4]. The mechanical alloying process is a solid state process where the powder particles are subjected to high energetic impact by the balls in a vial.