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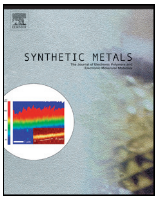

Polyaniline as potential radical scavenger for ultra-high molecular weight polyethylene

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ABSTRACT

Novel ultra-high molecular weight polyethylene (UHMWPE) composites were processed by micro-extrusion with polyaniline (PANI) as potential reinforcing and radical scavenging agent and with lauryl gallate (LG) as coupling agent. By means of UV–vis spectroscopy, it was found that the presence of PANI reduced at maximum by 27.3% the concentration in free radicals of a 2,2-dimethyl-1-picrylhydrazyl (DPPH) solution in which was immersed the composite. This result was obtained with the UHMWPE/LG/PANI weight composition 89/1/10, which also demonstrated to retain the viscoelastic and tensile properties of neat UHMWPE. The dispersion of PANI micro-particles within the UHMWPE matrix may be an alternative to the stabilization step of crosslinked UHMWPE used in joint prosthesis.

1. Introduction

Crosslinked ultra-high molecular weight polyethylene (UHMWPE) has replaced conventional UHMWPE in total hip and knee arthroplasty due to a higher wear resistance [1]. In particular, during the joint motion the surface deformation of the crosslinked UHMWPE network was significantly reduced compared to the reference non-crosslinked network, resulting in a less fibrils induced by large plastic deformation, and hence, less release of debris [1,2]. However, crosslinking that is generally conducted by gamma-irradiation has two major issues: (i) a reduced molecular mobility resulting in a lower toughness and fatigue resistance compared to conventional UHMWPE and (ii) a low chemical stability due to the presence of excess free-radicals and trapped free-radicals in the crystalline domains that react with oxygen and induce oxidation [1,3]. Gamma-sterilization of UHMWPE also led to the presence of excess free-radicals [4]. To quench free-radicals, different treatments have been developed: (i) annealing below the melting temperature after crosslinking [1], (ii) melting after crosslinking [1,5], (iii) sequential crosslinking/annealing procedures [6], and (iv) diffusion of vitamin E to the polymer matrix [1,7,8]. The two last treatments appear to be the most effective ones concerning UHMWPE implant longevity [1]. In particular, vitamin E-blended UHMWPE resins are commercially available since 2009 with proven post-irradiation chemical stability [1].

We propose in this paper an alternative treatment to the diffusion of vitamin E to UHMWPE. A radical scavenger agent could be distributed and dispersed within the UHMWPE matrix from the processing step of the polymer. An agent of interest could be polyaniline (PANI) that was proved to have a radical scavenging activity [9–12]. In particular, it was shown that solid sample of PANI immersed in a stable 2,2-dimethyl-1-picrylhydrazyl (DPPH) radical solution enabled to reduce by a factor of 5.8 the content in DPPH radicals [9]. It was also demonstrated that the scavenging activity increased when considering the more reduced PANI type [12]. Although some authors prepared some UHMWPE/PANI composites from solution [13,14] or from in-situ polymerization of PANI in the presence of UHMWPE [15], the potential radical scavenging activity of the obtained composite has never been investigated. At the same time, it is of high importance to verify that the presence of PANI inclusions is not detrimental to the mechanical properties of UHMWPE. However, the use of composites for joint replacement may present issues concerning the biocompatibility of the composite itself and of its wear debris. Some proof of concepts proved the possible biocompatibility of PANI [16,17], which is obviously suitable for joint replacement application. Biocompatibility is crucial in the case of hip or knee arthroplasty and would require further investigation in the case of these composites.

The objective of the paper is to elaborate composites of UHMWPE with PANI inclusions and to study the potential scavenging activity of the composites by means of the DPPH assay, as a pilot study. The distribution and dispersion of rigid inclusions within the UHMWPE matrix represents a challenge due

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to the high intrinsic viscosity of the matrix and is addressed by using a micro-extruder with specific conditions. The structure of the composite is studied by scanning electron microscopy (SEM) and wide-angle X-ray scattering (WAXS), while its mechanical properties are investigated by dynamical mechanical analysis (DMA) and tensile testing.

2. Experimental

2.1. Materials

Aniline (An, Sigma–Aldrich) and 2,2-diphenyl-1-picrylhydrazyl (DPPH, Sigma–Aldrich) were stored in the dark at 5 °C prior to use. Hydrochloric acid (HCl, Sigma–Aldrich), ammonium persulfate (APS, Sigma–Aldrich), and methanol (MeOH, Sigma–Aldrich) were used as received. Ultra high molecular weight polyethylene (UHMWPE) GUR 1020 ($M_w = 5.0 \times 10^6$ g/mol) was supplied by Ticona GmbH (Oberhausen, Germany). Lauryl gallate (LG, Sigma–Aldrich, $M_w = 338.44$ g/mol) was used as coupling agent between UHMWPE and PANI. Ultra pure water (simplicity system from Millipore, $\rho = 18.2$ MΩ cm) was used through all the processes.

2.2. Synthesis of PANI

Emeraldine salt was synthesized by chemical oxidative polymerization of aniline, using ammonium persulfate as oxidant. Aniline polymerization was carried out without stirring in the presence of hydrochloric acid as dopant and the temperature of the reaction medium was kept at 0 °C. Aniline (0.1 ml) was dissolved in 1.5 M HCl solution (22 ml), and ammonium persulfate (0.22 g) was dissolved separately in water (3 ml). The aniline hydrochloride and oxidant solutions were kept at 0 °C before being mixed. The two solutions were then mixed in the reaction vessel placed into an ice bath. The reaction mixture was left to react for 12 h. The obtained precipitate was first filtered and washed, and then dried at 80 °C in an oven. Reduction of the size of PANI particles prior extrusion was achieved by using a ball milling technique in a Fritsch pulverisette at room temperature for 1 h. The milling speed was about 6 rpm. For melt-blending procedures with UHMWPE, PANI powder was used in the doped form since processing conditions were expected to transform PANI in its emeraldine base form [18]. In particular, thermogravimetric analysis (TGA) was performed on the PANI used in the present study (the curve was not shown here). The weight–temperature curves exhibited a three step weight loss process in the temperature ranges: 25–150 °C, 150–290 °C, and 290–800 °C, resulting in a carbonized residue of 48%. The first weight loss of PANI for temperatures up to 150 °C was attributed to the evaporation of moisture, unreacted monomer, free HCl and/or low molecular weight polymer segments formed during the polymerization. The main component of the volatiles was water molecules. The second weight loss of PANI in the temperature range 150–290 °C was attributed to considerable structure transformations caused by the loss of acid bound (the protonating dopant) from the polymer chain, characterized by the release of hydrochloride acid, and hence, the formation of the emeraldine base form of the PANI. At the extrusion temperature of 220 °C and at the hot-pressing temperature of 240 °C (see Section 2.3), the weight loss was 15% and 17%, respectively. Other changes as chain scission and cross-linking can occur during this second step. Lastly, for temperatures higher than 290 °C, a carbonization process of PANI occurred.

2.3. Composite processing

For the melt-blending procedures, powders of PANI, LG, and UHMWPE were first individually ball milled. Then, powder mixtures of UHMWPE/LG/PANI with different compositions were prepared, ball milled and finally extruded in a 15 cc twin-screw micro-extruder (DSM). The following UHMWPE/LG/PANI materials were considered: 100/0/0, 99/1/0, 98/1/1, and 89/1/10 (in wt%). The extrusion was done at 220 °C under inert atmosphere (use of nitrogen) with co-rotating screws at a speed of 5 rpm, without recirculation, and without the use of a swelling agent as paraffin oil. The resulting extrudates, with a diameter of about 5 mm, were cooled down to room temperature in ambient air. Then, they were cut into 3–5 mm-long sections and hot-pressed at 6.2 MPa and 240 °C during 45 min to form 2 mm-thick plates using a laboratory hydraulic press (model Carver 11T). To investigate the impact of PANI size on the radical scavenging activity of the composite, the material composition 98/1/1 was processed as described above but without the ball-milling procedure to have PANI coarse inclusions. This material is referenced as UHMWPE/LG/PANI 98/1/1c.

2.4. Characterization

The structure of the composites was studied by X-ray diffraction with a Panalytical X'Pert Pro MPD diffractometer using the CuKα radiation (wavelength $\lambda = 1.54$ Å) emitted at 45 kV and 40 mA. This equipment was configured with the transmission configuration (wide-angle X-ray scattering, WAXS) to assess the weight crystallinity X_c of the materials in the 2θ range 5–45°. The diffractograms were analysed with the software PeakFit (Systat) for the deconvolution of crystalline and amorphous peaks by using Gaussian functions. X_c was calculated as the ratio of the crystalline peak areas to the total crystalline and amorphous peak areas.

The distribution and size of PANI inclusions within the composites was characterized by means of a scanning electron microscope (SEM) Quanta FEG 200 from FEI. To this end, the composite specimens were carefully polished to get a mirror-like surface. Backscattered-electron images were recorded with the low-vacuum mode of the SEM using a water pressure of 150 Pa. Energy-dispersive X-ray spectroscopy (EDS) measurements were performed at 15 kV to quantify Cl element within large PANI particles prior and after extrusion and hot-pressing. EDS measurements were repeated on five PANI inclusions from 5 × 5 μm areas.

Viscoelastic properties of the composites were evaluated by dynamic mechanical analysis (DMA) using a Netzsch equipment model DMA 242C at 2 K/min and with the double cantilever mode at 1 Hz. Three rectangular specimens (with the dimensions of 60 × 13 × 2 mm) were tested for each formulation and representative elastic modulus E' – temperature T and loss modulus E'' – temperature T curves were reported here.

Tensile testing was done by means of a universal electromechanical testing machine Instron model 5967 at 22 °C and 1 mm/min. To this end, miniature dog-bone tensile specimens were fabricated by means of a punching procedure from the 2 mm-thick plates. The overall dimensions of a specimen were 30 × 4 × 2 mm, while its gauge length and width were 10 mm and 2 mm, respectively. The yield stress σ_y, ultimate strain ε_u and ultimate stress σ_u of the materials were measured. Tests were repeated on five specimens for each formulation.

2.5. Radical scavenging assay

The DPPH assay for radical scavenging activity was based on the methodology of Hsu et al. [11,19] with some modifications. Briefly, 20 ml of a 64 μM methanolic DPPH freshly prepared solution was added to 1.00 ± 0.05 mg of test samples measured using a five digit balance. The samples were left to react at room temperature for 24 h, after which the absorbance of the supernatant at 516 nm was measured using a PerkinElmer lambda 35 spectrophotometer in the wavelength range comprised between 400 nm and 700 nm