



Thermal and hydrolytic stability of silver nanoparticle polyurethane biocomposites for medical applications



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ABSTRACT

Polyurethane-extracellular matrix bionanocomposites containing in situ generated silver nanoparticles and biocompatible polymers such as hydrolyzed collagen, elastin, hyaluronic acid or chondroitin sulfate, were obtained by solvent casting method in order to achieve improved antibacterial biomaterials for medical devices. Using thermal analyses the stabilizing effect of polymeric components on the incorporated silver nanoparticles (metallic silver and/or silver in oxidized state) was evidenced. The non-isothermal kinetic parameters of the thermal degradation of studied bionanocomposites are evaluated in terms of integral methods. The variation of kinetic parameters in function of conversion was determined. By means of FTIR spectroscopy analysis the hydrolytic stability in PBS solutions (pH 4.6 and 7.4) of the studied silver bionanocomposites was investigated. It was found that the hydrolytic degradation occurred at the ester and urethane bonds in the poly(ester urethanes). The incorporated extracellular matrix components increased the hydrophilicity and favoured the hydrolysis. During hydrolysis increased hydrogen bonding and crystallinity principally for AgNPs stabilized polyurethane matrices which indicate a "chemicrystallization" effect.

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1. Introduction

The nanoscale materials have been appeared as new antimicrobial products due to their high surface area to volume ratio and unique chemical and physical properties [1]. Silver nanoparticles have found applications in different fields such as optics [2], electronics [3], medicine [4], nanomedicine [5], and pharmacy [6]. Especially the use of silver nanoparticles (AgNPs) was investigated as a constituent of coatings on medical devices and implants [7], due to their very strong bactericidal activity against both Gram-positive and Gram-negative bacteria, including multiresistant strains; however the concentration of silver is an important factor. The release of silver depends on the nature and concentration of the silver and the polymer matrix. Therefore studies regarding mechanisms of binding and interaction between the silver and polymer matrix to obtain biocide materials would be also straightforwardly necessary. Silver-impregnated coatings can be more effective than direct surface coating alone. Stabilizing of AgNPs with polymeric systems is important in improving

antimicrobial activity in comparison to unstabilized AgNPs. The AgNPs protected by synthetic and natural polymer composites [8–10] decrease their potential to aggregate and thus increase their biocompatibility. The biological characteristics in contact with blood and tissues for long periods, in particular good antithrombogenic properties, recommend the use of extracellular matrix components such as collagen, elastin and glycosaminoglycans (GAG) for obtaining biomaterials.

The applications of thermal analysis to the fields of biochemistry and biology have expanded noticeably and made important contributions to structural and conformational determinations of biological compounds. Polyurethane catheters are the most chosen biomaterials for implantable devices [11]. In literature are reported several techniques for impregnation of polyurethanes catheters with silver nanoparticles [12,13] that are able to release bactericidal concentrations of silver ions from the medical device.

In this work new type of silver bionanocomposite membranes based on polyurethane (PU) and extracellular matrix (EM) components was prepared by employing solvent casting method. The as-prepared biomembranes possess good antibacterial qualities [14] and non-cytotoxicity necessary for biomedical device applications. The study of interaction between silver nanoparticles and polymer matrix is important in assessing the functional properties

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and behaviour of the antibacterial material. The investigation of thermal transitions is used to gain insight into the structures of the nanobiocomposites.

The purpose of this work is to perform thermal analysis of these nanobiocomposites by employing differential scanning calorimetry (DSC), thermogravimetry and derivative thermogravimetry under dynamic conditions of temperature and investigation by means of FTIR spectroscopy of hydrolytic degradation of these biocomposites in slightly alkaline and very strong acid media (pH conditions of urine).

2. Experimental part

2.1. Materials

Polyurethane (PU) employed in the biocomposites preparation was synthesized using a two-step polyaddition reaction, as previously described for other polyurethane preparation [15,16]. The composition of PU is as follows: PEA (poly(ethylene adipate)diol)/MDI (4,4'-diphenyl methane diisocyanate)/EG (ethylene glycol) (wt %) 55.56/37.50/6.94. Weight-average molecular weight is 109613 and polydispersity index is 1.287. Glass transition temperature (DSC, second heating run, 10 °C/min) $T_g = -27$ °C.

2.1.1. Preparation of biomembranes

Two kinds of polyurethane (PU)- extracellular matrix polymer (hydrolyzed collagen (HC), k-elasticin (KEL), chondroitin sulfate (CS), hyaluronic acid (HA)) biomembranes with the following compositions: PU/HC/KEL/HA (100:10:1:0.1, w/w) (PU-HA) and PU/HC/KEL/CS (100:10:1:0.1, w/w) (PU-CS) were obtained by solvent casting method [14].

2.1.2. Preparation of silver nanoparticle bionanocomposites PU-EM-Ag

The silver nanoparticles were obtained in the PU solution (in situ) by reducing silver nitrate (AgNO_3) with dimethylformamide (DMF) at room temperature [14]. For hydrolytic degradation study PBS solutions (pH 4.6 and 7.4) were employed.

2.2. Methods

DSC measurements were conducted on a DSC 200 F3 Maia (Netzsch, Germany). A mass of 5 mg of each sample was heated in pressed and pierced aluminum crucibles at a heating rate of 10 °C min^{-1} . Nitrogen was used as inert atmosphere at a flow rate of 50 mL min^{-1} .

Thermogravimetric measurements were conducted on a STA F1 449 Jupiter device (Netzsch, Germany). 10 mg of each sample was heated in alumina crucibles at a heating rate of 10 °C min^{-1} . Nitrogen was used as inert atmosphere at a flow rate of 50 mL min^{-1} .

ATR-FTIR spectra were recorded using a FTIR Bruker Vertex 70 spectrometer equipped with ZnSe crystal. The spectra were recorded in attenuated total reflection in the 600–4000 cm^{-1} wavenumber range at room temperature with 32 scans per spectrum at a resolution of 4 cm^{-1} . ATR-FTIR spectra were collected before and after 2, 4, 8 and 12 weeks of hydrolytic degradation. All biocomposite samples were immersed individually in separate glass flasks filled with 10 mL phosphate buffer solutions (pH 4.6 and 7.4) at room temperature. The biocomposite samples were removed from the solution after the required period of immersion and afterwards they were washed with distilled water and vacuum dried at 30 °C for 48 h prior to analyze. After 4 and 8 weeks of immersion the solutions were replaced with fresh media.

3. Results and discussion

3.1. DSC analysis

In Fig. 1 the DSC thermograms of PU, PU-EM with and without AgNPs (first and second heating runs) are presented.

Thermal analysis of the PU and PU-EM matrices with and without incorporated AgNPs was performed in order to provide insights into the morphological structure of the investigated biomaterials and the structural modification of the polymer matrices with the introduction of the AgNPs. The transition temperature values and the corresponding melting enthalpy values are listed in Table 1. The thermal history during polymer processing as well as the incorporation of AgNPs influence the arrangement of amorphous/crystalline phase and consequently influence the physico-mechanical properties of the biomaterials. It can be seen that the incorporation of AgNPs affects transition temperatures and melting enthalpies. The homogeneous dispersion of AgNPs into PU matrix determined small change (up to 1 °C) of T_g (h2-second heating) and increase of melting enthalpy (h1-first heating) because AgNPs facilitate the crystallization of PU. For PU sample a cold crystallization peak (Table 1) is observed at second heating due to rapid cooling during processing which vanishes for PU-1.5% AgNPs.

In general, in case of nanocomposites, mass crystallization kinetics depends on nucleation, interaction between polymer chains and Ag nanoparticle surfaces, distortion of spherulite growth, co-existence of several crystalline phases with different nucleation and crystal growth rates. As to samples PU-CS and PU-HA, they evidence only small changes (up to 1 °C) of T_g s (h2-second heating) and decreases of melting enthalpies (h1-first heating runs). These results are explained by the presence of both metallic silver and in oxidized state for PU sample and silver only in oxidized state for PU-CS and PU-HA samples (as determined previously by XRD and XPS analyses) [14]. Silver ions interact specifically with protein molecules, such as hydrolyzed collagen in PU-CS and PU-HA samples and therefore influence amorphous/crystalline phase of the polymer matrices and also do not fabricate nucleation sites. Interactions with proteins as ligands favour smaller particle size and increase the dissolution of AgNPs by formation of Ag^+ complexes [17].

3.2. Thermogravimetric analysis

The non-isothermal kinetic parameters of the thermal degradation of studied bionanocomposites are evaluated in terms of the Coats–Redfern [18], Flynn–Wall [19], for constant heating rate [20], van Krevelen [21], Urbanovici–Segal [22], integral methods. The Reich-Levi method [23] was also employed in evaluation of variation of the kinetic parameters with conversion. In Fig. 2 the thermogravimetric and derivative thermogravimetric curves of the polyurethane and polyurethane biocomposites are presented, respectively. The thermal characteristics obtained from TG and DTG curves are tabulated in Table 2.

DTG thermograms clearly show at least three decomposition peaks for the parent polyurethane, and the polyurethane silver nanobiocomposites. The multi-stage decomposition process in nitrogen is a complex mass loss process with several mechanisms.

From TG and DTG curves it is observed that AgNPs influence significantly the degradation mechanisms of the PU, PU-CS and PU-HA samples by changing the number of thermal degradation steps. It is very well-known the catalytic effect of AgNPs on thermodegradation on different chemical reactions [24]. PU is slightly less stable than its silver nanobiocomposite, because its initial decomposition temperature (T_{onset}) is lower (see also Table 2). The well-homogenized AgNPs in polymer matrix restrict the polymer chain

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