Organic-inorganic nanocomposites for biomedical applications

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Introduction

Polyurethane (PU) and PU nanocomposites with good biocompatibility and mechanical properties can be used as the biomedical matrix and tissue engineering biomaterials. Magnetic nanoparticles, especially ferrite nanoparticles have attracted much interest due to their specific physicochemical properties in various areas including magnetic recording, biosensing, catalyst, drug delivery systems, magnetic resonance imaging (MRI) and cancer therapy. Despite all these advantages, the nanoparticle agglomeration reduces the efficiency of the nanoparticles, so the nanoparticle incorporation into an appropriate polymeric matrix to prepare organic-inorganic nanocomposites is a right direction in the current scenario of biomedical nanotechnology. In this study, organic- inorganic PU nanocomposites based on zinc and copper ferrites and with the same composition of PU were prepared. The properties of PU nanocomposites were evaluated by nanoindentation, water contact angle and water absorption measurements.

Synthesis and characterization

PU/ferrite nanocomposites with 60 wt% of soft PDMS segments were prepared by addition of different types of ferrite nanoparticles and by using in situ polymerization in a solution of NMP/THF (9/1, v/v). The starting reactants were α,ω-dihydroxy-ethoxypropyl-PDMS, MDI, and Boltorn hydroxy-functional hyperbranched polyester of the second pseudogeneration (BH-20) as the crosslinking agent. For nanocomposite preparation, different types of ferrite nanoparticles were used in small amounts (1 wt%). Throughout the preparation, MDI was in slight excess (the ratio of NCO groups to the total OH groups was 1.05). All syntheses were carried out in a four-neck, round bottom flask equipped with a mechanical stirrer, a nitrogen inlet, a dropping funnel and a reflux condenser. Calculated amounts of PDMS macrodiol and MDI were weighed into reaction flasks at room temperature, dissolved in the mixture of NMP/THF (9/1, v/v) and then heated up to 65 °C under a nitrogen atmosphere. The reaction was started by introducing a solution of Sn(Oct)2 in NMP/THF (0.02 wt%). The reaction mixture was stirred for 40 min at 65 °C to prepare the NCO-terminated prepolymer. The NCO content in the prepolymer was 4.9 %, which was determined by the dibutylamine back-titration method. In the second stage of the reaction, a dilute solution of BH-20 in NMP was added dropwise to the NCO-terminated prepolymer, and the reaction mixture was stirred and kept at 65 °C for 10 min. The ferrite nanoparticle dispersion was added dropwise to the reaction mixture at the end of the first phase of polyaddition reaction. Afterwards, the mixture was transferred into Teflon moulds, and solvent removal as well as crosslinking reaction was continued in a force-draft oven at 40 °C for 2 h, at 60 °C for 2 h and at 80 °C for 24 h.

Nanoindentation measurements of pure PU and PU/ferrite were performed on an Agilent G200 instrument. The applied load force was 30 nM, with depth control mode set at 45 μm and Poisson ratio of 0.49. For each sample, 100 measurements were taken, in a 10 × 10 rectangular array on different spots on the surface of the investigated samples.

Water uptake measurements of pure PU and PU/ferrite were carried out by immersing the dry films in distilled water for 48 h at 24 °C. After this time, the hydrated films were removed and blotted with filter paper to remove excess water. The average value of three measurements for each film was used. The weight percent of water uptake was calculated taking into account the weight of the fully hydrated sample (ww) and the weight of the dried sample (wW_0)

Cell adhesion on the surface of PU and PU/ferrite films was examined by a computer-based Carl Zeiss Axiovision microscope. Cells were seeded onto PU and PU/ferrite films placed in 96-well plates (Sarstedt, Germany) at a density 15000 cells/well. 96 h after seeding, attached cells were fixed with glutaraldehyde solution, stained with nigrosin solution and photographed using the Carl Zeiss Axiovision microscope. The number of attached cells was calculated by counting the cells in eight different sections per sample and expressed as number of cells/mm^2 ± SD.

Contact angles were measured using the method suggested by Zisman, i.e., by an optical goniometer with a digital camera installed in the axial extension of its lens. The results were the mean value of three replicates. The Owens-Wendt method was then used to calculate the surface free energy of the materials

Results

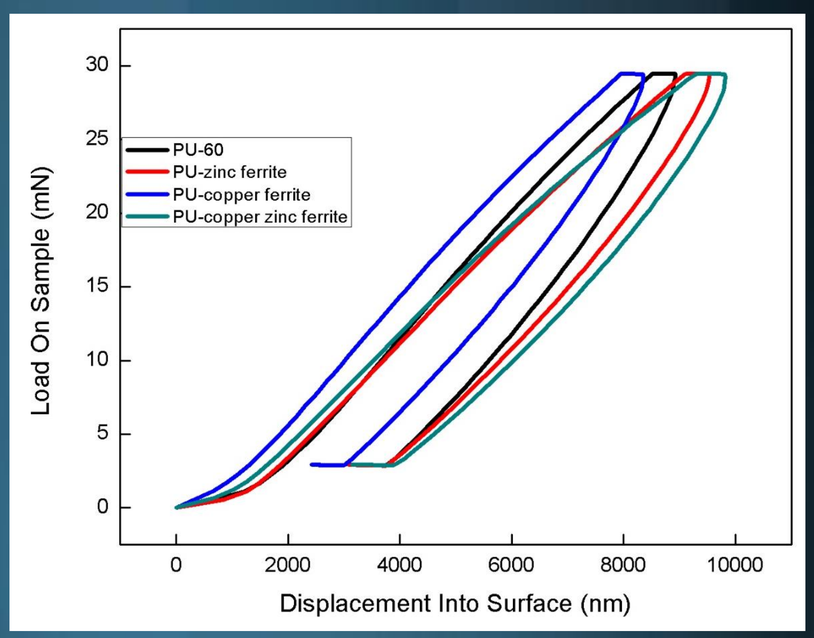

Fig. 1. Nanoindentation measurements of the prepared PU nanocomposites

Table 1. Results of nanoindentation analysis of the prepared materials

Material	Elastic modulus, MPa	Hardness, MPa
PU-zinc ferrite	**152**	**31**
PU-copper ferrite	**184**	**41**
PU-copper zinc ferrite	**142**	**27**
PU-60	**170**	**31**

Table 2. Results of water contact angle and water absorption of the prepared materials

Material	Water contact angle, °	Water absorption, wt.%
PU-zinc ferrite	**86**	**2.10**
PU-copper ferrite	**93**	**1.05**
PU-copper zinc ferrite	**89**	**1.41**
PU-60	**99**	**0.82**

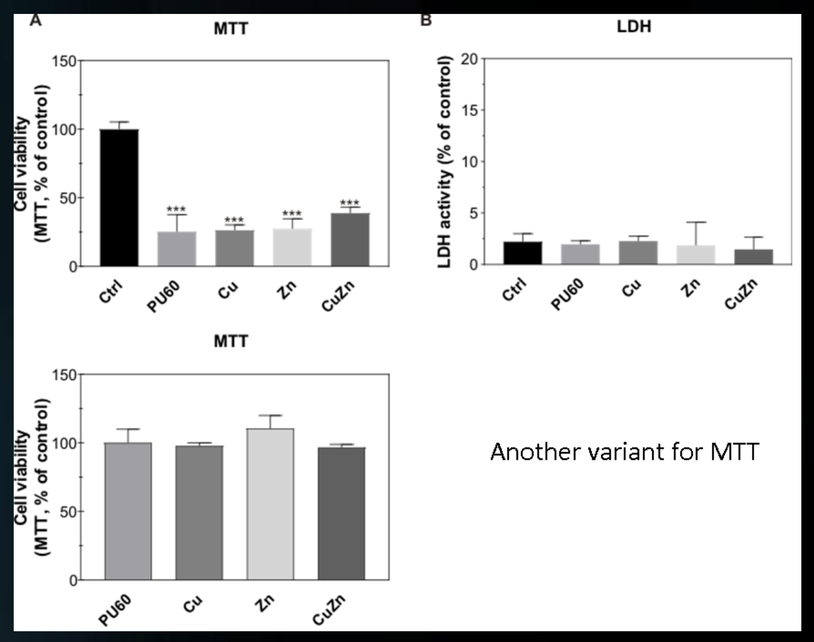

Fig. 2. MTT and LDH tests of the prepared materials

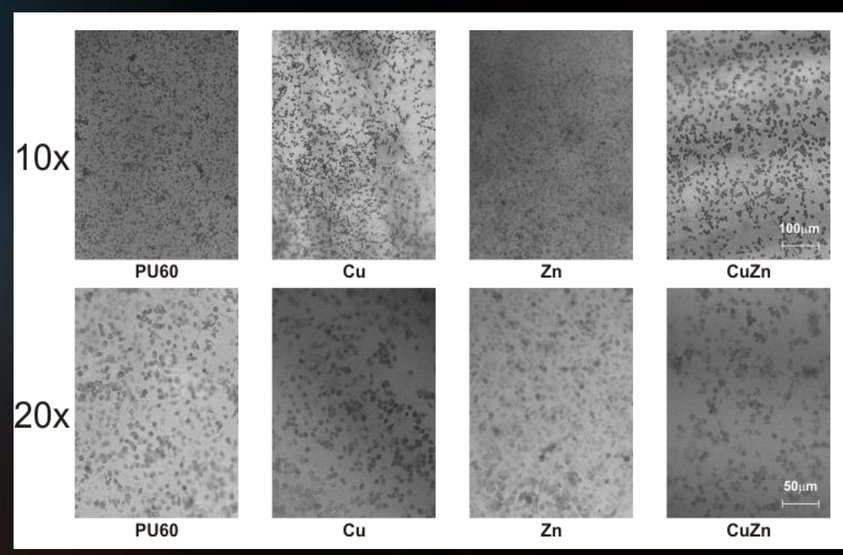

Fig. 3. Adhesion of endothelial cells on the surfaces of the prepared materials.

Conclusions

Novel polyurethane nanocomposite (PUN) materials containing different type of ferrite nanoparticles were prepared by in situ polymerization methodology. Polyurethane network was formed from poly(dimethylsiloxane)-based macrodiol (PDMS), 4,4′-methylenediphenyldiisocyanate (MDI), and hyperbranched polyester of the second pseudo-generation (BH-20; used as crosslinking agent).Pure PU and PU nanocomposites contained 60 wt. % of the soft PDMS segments. The presence of the nanoferrite nanoparticles affects properties of PU nanocomposites such as bulk morphology, mechanical, and biological properties. The biocompatibility of PU nanocomposites was investigated by MTT assay and cell attachment using endothelial cells. According to the results, the prepared PU nanocomposites with noncytotoxic chemistry could be a potential choice for vascular implants development.

References

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