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Luísa Zagalo, Gonçalo Pereira, Pedro Oliveira, Maria João Oliveira, Luísa Gonçalves, Carlos Zagalo & José Brito

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Chemically crosslinked PVA hydrogels for cartilage substitution

Inês Patacho[a,b], Andreia S. Oliveira[a,c], Pedro Nolasco[a,b,c], Rogério Colaço[c] and Ana P. Serro[a,b]

[a]CQE, Instituto Superior Técnico – Universidade de Lisboa, Lisbon, Portugal; [b]Centro de Investigação Interdisciplinar Egas Moniz (CiiEM), Egas Moniz Cooperativa de Ensino Superior, Caparica, Portugal; [c]IDMEC and DEM, Instituto Superior Técnico – Universidade de Lisboa, Lisbon, Portugal

ABSTRACT

Introduction: In recent decades, hydrogels have gained increasing interest as potential cartilage replacement materials. Among these, polyvinyl alcohol (PVA) hydrogels have shown to be very promising candidates due to their biocompatibility, high degree of swelling, and elastic and rubbery nature, which allows them to mimic the natural tissues [1]. The properties of PVA-based hydrogels can be tailored by adding different compounds. The main objective of this study is to investigate the effect of adding two distinct crosslinking agents to the polymeric mixture, on the microstructure, water content, hydrophilicity, and mechanical behaviour of PVA hydrogels.

Materials and Methods: Four types of materials were prepared using a PVA aqueous solution (7.75% w/w) containing two different crosslinking agents: glyoxal at 0.2% and 1%, and glutaraldehyde at 5.95% and 11.9% (where the percentages indicated refer to the mass of the crosslinker relative to that of the PVA). The mixtures were poured into Petri dishes and dried at 37 °C (4 days) and then at 60 °C (2 days). The surface morphology of the samples was analysed by scanning electron microscopy (SEM) after they had been lyophilised for 48 h and coated with an Au/Pd layer. To determine the equilibrium water content (EWC), samples hydrated in pure water were weighed, dried at 60 °C until reached a constant weight, and weighed again. The water contact angles were determined in hydrated samples by the captive bubble method. To evaluate the mechanical properties, compression tests were performed with a texturometer on samples placed in an aqueous medium, using a test speed of 0.1 mm/s until a force of 5 kg was reached.

Results: The results showed that all materials are non-porous and have a similar surface morphology. The hydrogels crosslinked with glyoxal present higher EWC values (69.1% and 69.7% for 0.2% and 1% of glyoxal, respectively), while those with glutaraldehyde have an EWC of 52.8% and 41.5% for 5.95% and 11.9% of glutaraldehyde, correspondingly. Concerning wettability, all samples are hydrophilic and exhibit a water contact angle $<55°$. The modulus of elasticity of materials prepared with glyoxal is lower ($1.1 - 1.4$ MPa) than that of those done with glutaraldehyde ($6.2 - 9.3$ MPa), but their toughness is higher ($0.67 - 0.45$ MJ/m^3 *vs* $0.22 - 0.27$ MJ/m^3). For gels crosslinked with glyoxal, the dissipated energy assumes values between $17 - 22$% and for samples prepared with glutaraldehyde, it is negligible.

Discussion and conclusions: In conclusion, the nature and amount of crosslinking can determine the properties of PVA hydrogels. Glyoxal-containing materials have a greater water absorption capacity, are less stiff, absorb more energy, and exhibit a lower elastic recovery than glutaraldehyde-containing gels. Overall, glyoxal-crosslinked hydrogels have EWC values and mechanical properties closer to those of the natural cartilage, and therefore should be preferred as potential substitutes of this tissue.

CONTACT Inês Patacho mariana.patacho@tecnico.ulisboa.pt

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Discrimination by X-ray fluorescence analysis of elemental concentrations in healthy and diseased rat tissues

Luísa Zagalo[a], Gonçalo Pereira[a], Pedro Oliveira[a], Maria João Oliveira[b], Luísa Gonçalves[a], Carlos Zagalo[a] and José Brito[a]

[a]Centro de Investigação Interdisciplinar Egas Moniz (CiiEM), Egas Moniz Cooperativa de Ensino Superior, Caparica, Portugal; [b]Instituto de Ciências Biomédicas Abel Salazar, Porto, Portugal

ABSTRACT

Introduction: Elements such as Ca and P are involved in important physiological processes and their concentrations may differ significantly between healthy and diseased individuals [1]. Investigation of the role of single elements has been questioned because it ignores important interactions amongst various elements [2]. Often, when concentrations of various elements are obtained in the same study, comparisons between healthy and diseased tissues, or correlations between those elements, both intrinsically multivariate, are implemented with univariate methods, which may result in inflated or unobserved existing effects [3,4]. The methodologies in here complement multielement determinations by X-ray fluorescence spectroscopy (XRF) with multivariate data analysis methodologies, and offer an important contribute to fill existing gaps in current knowledge of the role elements in such metabolic pathways.

Materials and methods: Here, the XRF technique is applied to assess the concentration profile of Ca and P, in samples of 4 groups of Wistar rat tibiae, aiming at assessing the musculoskeletal impact of the synergy effects of an environmental factor and a disease with recognised systemic effects. Each group contained 12 animals: exposed to low-frequency noise (yes/no) and diabetic/hyperglycaemic rats (yes/no). Animals from each group were randomly divided into three timepoints and sacrificed after 1, 6 and 12 weeks of exposure. In view of this experimental design, Two-Way ANOVA has been used to assess the effect of main factors and interaction of those factors on the dependent variables, after validation of model assumptions.

Results: For bone Ca concentration, there was no interaction between the two main factors, with no effect due to noise exposure ($p = .501$) but with a significant effect due to diabetes ($p = .038$), with observed power of 68%. A similar outcome was observed for bone P concentration ($p = .456$), with no interaction between factors, no effect due to noise, but with significant impact due to diabetes ($p = .003$), with observed power of 69.2%. In both cases, the concentrations of Ca and P were decreased in the group of diabetic animals. For the ratio Ca/P no significant effects or interactions were detected ($p = .140$).

Discussion and conclusions: XRF spectrometry is clearly a highly promising technique to be used in the discrimination of elemental concentrations in healthy and diseased rat tissues. As this is a pioneer investigative work and the number of animals included is limited in this first approach, it is early to anticipate definite results. However, we can, in the meantime, observe the presence of diabetic-induced osteopenia, with no effects resulting from exposure to noise.

CONTACT Luísa Zagalo analuisazagalo@gmail.com

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Hydrogels based on poly(vinyl alcohol) for cartilage substitution

A. S. Oliveira[a,b,c], R. Colaço[b] and A. P. Serro[a,c]

[a]CQE, IST – Universidade de Lisboa, Lisboa, Portugal; [b]IDMEC, IST – Universidade de Lisboa, Lisboa, Portugal; [c]Centro de Investigação Interdisciplinar Egas Moniz (CiiEM), Egas Moniz Cooperativa de Ensino Superior, Caparica, Portugal

ABSTRACT

Introduction: Cartilage damage is an important concern because of the tissue's limited ability to repair itself [1,2]. Among the existing strategies to replace cartilage, hydrogels have been widely considered due to their ability to easily mimic the natural tissue [1,2]. Poly(vinyl alcohol) (PVA) based hydrogels have been the focus of a large number of studies as they are easy to produce, have excellent biocompatibility, low toxicity, high water content, and stability [2]. The aim of this study was to evaluate the effect of different preparation conditions of PVA hydrogels on the properties of the materials.

Materials and methods: PVA (MW 145000 Da) aqueous solutions (15% w/v) were prepared at 95 °C for 6 h, poured into flat moulds and cooled down to room temperature. Cast drying samples (CD_4 and CD_{30}) samples were dried at 4 and 30 °C until they reach a constant weight. Freeze-thawing samples (FT_0 and FT_{NaCl}) were prepared with 5 cycles of 10 h at