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# Hydrogels based on poly(vinyl alcohol) for cartilage substitution

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#### 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.

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### Hydrogels based on poly(vinyl alcohol) for cartilage substitution

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#### 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  $FT_{NaCI}$ ) were prepared with 5 cycles of 10 h at

-20 °C and 2 h at room temperature. For FT<sub>NaCI</sub> samples, an aqueous solution of NaCI (25% w/w) was pre-added to the initial polymer solution in a proportion of 1:10 (v/v) relative to PVA. The hydrogels were characterised concerning equilibrium water content (EWC), surface morphology (analysed by Scanning Electron Microscopy (SEM, JEOL JSM-7001F)), thermotropic behaviour (studied by differential scanning calorimeter (NETZSCH 200 F3 Maia) with thermograms being recorded over the range of 20–280 °C at a heating rate of 10 °C/min), mechanical performance (evaluated by uniaxial tensile and unconfined compression tests carried out in a TA.XT Express Texture Analyzer) and friction behaviour (pin-ondisc tests done in linear reciprocal oscillation mode using stainless steel 316 L balls as counter-bodies, with loads of 10 and 20 N, in phosphate buffered saline (PBS) solution and simulated synovial fluid (SSF) solution with hyaluronic acid and bovine serum albumin).

**Results:**  $CD_4$  and  $CD_{30}$  showed an EWC in the range of 63–66% while that of  $FT_0$  and  $FT_{NaCl}$  varied between 87–89%. SEM micrographs revealed different structures for CD and FT samples. The surface of CD gels was smoother with no evident porosity, while FT materials exhibited holes in different porosity patterns.  $FT_{NaCl}$  presented smaller pores than  $FT_0$ , although a minor number of large pores coexist. The degree of crystallinity (35–36%), glass transition temperature (43–44 °C), and melting transition temperature (214–216 °C) were similar for all samples. Regarding mechanical performance, the elastic modulus in both compression and tensile, was inferior for the FT materials, in particular for  $FT_{NaCl}$ . In tensile experiments, CD gels had the highest ultimate tensile strength and toughness. Concerning tribology behaviour, the friction coefficients (CoF) of all samples were low and similar in PBS solution when 10 N of force was applied. For 20 N, the CoF values of the CD materials decreased. In SSF solution, CD samples presented higher CoF with both tested forces.

**Discussion and conclusions:** The properties of the PVA hydrogels were strongly influenced by the preparation conditions. CD method proved to be more suitable for producing PVA cartilage substitutes. It led to more compact, rigid, and resistant materials with adequate values of EWC and CoF.

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## Influence of the liquid phase content and presence of hydroxypropyl methyl cellulose on the properties of a calcium phosphate bone cement

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#### ABSTRACT

**Introduction:** Calcium phosphate cements (CPCs) have been widely used for bone defects filling given their excellent biocompatibility, osteoconduction ability and ease of manipulation [1]. Nevertheless, their mechanical properties and handling performance still need to be improved to satisfy clinical requirements. Indeed, enhancing their injectability can widen its application to minimally invasive surgical procedures [2]. This work aims to investigate the effect of the liquid phase amount and presence of hydroxypropyl methyl cellulose (HPMC) on the basic properties of a commercial CPC containing a polymeric adjuvant, chitosan (Chi).

**Materials and methods:** Starting from the original formulation containing Chi, samples with different amounts of liquid phase (LP 30%, 38%, 42%, 50%) were prepared. Additionally, for LP 38% and 42% formulations, Chi was replaced by HPMC polymer. Setting times were measured using the Vicat apparatus. After 6 days of setting, mechanical properties were studied through compression assays and Vickers hardness was measured. Injectability experiments were done and