CHITOSAN HYDROGELS MODIFIED WITH SILK, GRAPHENE OXIDE OR REDUCED GRAPHENE OXIDE

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[ENGINEERING OF BIOMATERIALS 158 (2020) 44]

Introduction

The aim of the work was to produce and characterize nanocomposite hydrogels based on chitosan, modified with silk powder and carbon nano-additives in the form of graphene oxide or reduced graphene oxide.

The variety of favourable properties of chitosan, such as biocompatibility, biodegradability, antibacterial or antioxidant activity make this polysaccharide a polymer of choice in many medical applications e.g. in tissue engineering, wound healing, and drug delivery systems [1]. Also, silk is increasingly being used in medicine because it consists fibroin which improves collagen deposition and fibroblast proliferation [2]. In recent years, a “cutting edge materials” used in variety fields and applications have been graphene-family nanoparticles. Their unique two-dimensional planar structure vests exceptional properties e.g. super conductivity, chemical and mechanical stability, large surface area and biocompatibility. Graphene and graphene oxides modified composites have a huge potential for regenerative medicine of all types of tissues including nerves, bones, cartilages, skeletal and cardiac muscles, skin and adipose tissue regeneration [3]. Such composites might be used also in gene and small molecular drug delivery, for biofunctionalization of protein, in anticancer therapy, or as an antimicrobial agent carriers for bone and teeth implantation.

Materials and Methods

In this study a natural polymer matrix – hydrogel based on combination of chitosan (CS) and silk (SP) – was reinforced with two types of carbon nanoparticles: graphene oxide (GO) and reduced graphene oxide (rGO) (ITME, Poland) with various weight content.

To obtain composite “a solution-evaporation casting method” was applied and as a result thin foils were acquired. To prepare liquid matrix, a chitosan powder mixed with a silk powder in 4:1 ratio was dissolved in lactic acid. Then, matrix modifiers were introduced in following amounts: 0.5, 1.5, 3wt%. One group of samples was modified with GO and the second one with rGO. Each type of mixture was transferred into a Petri dish and left overnight to dry. When ready, foils were physically crosslinked by neutralization in 1M sodium hydroxide solution. In the end, six types of composites were obtained: CS/SP/0.5GO, CS/SP/1.5GO, CS/SP/ 3GO, CS/SP/0.5rGO, CS/SP/1.5rGO, CS/SP/3rGO. For reference purpose, foils made of pure CS and CS/SP were prepared in the same manner. After rinsing in water, the samples were incubated in distilled water and SBF. Morphology of the materials was examined before and after incubation. The impact of the type and amount of the introduced nanoadditives and the incubation process on the properties of the hydrogels was assessed.

Results and Discussion

Microscopic observations revealed that depending on the composition different morphology was obtained. For CS and CS/SP, crosslinking process had no effect on the flatness and smoothness of the samples surface, whereas for composites modified with GO and rGO high surface development with a mesh of tiny tubular channels was observed. The higher content of GO or rGO, the more distinct effect was present. In all types of tested materials ten-week incubation in water did not change surface characteristics. Sample images of CS, CS/SP, CS/SP/3GO and CS/SP/3rGO after incubation are shown in FIG. 1.

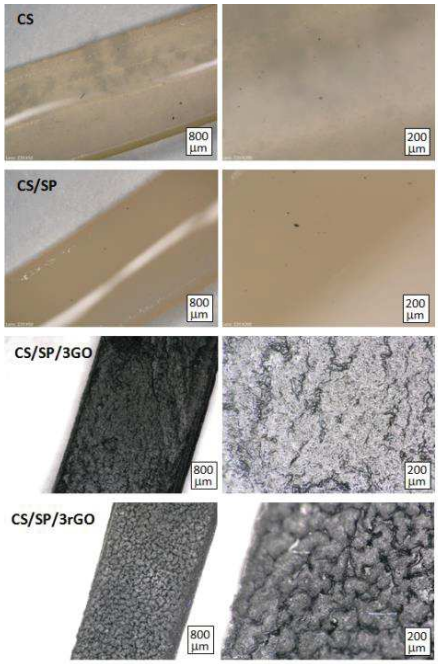

FIG. 1. Microscope images of hydrogels: CS, CS/SP, CS/SP/3GO and CS/SP/3rGO after 10-week incubation in distilled water; (Keyence VHX900, mag. 50x and 200x).

Bioactivity of tested materials was verified in SBF. On flat surface of CS foil there were only few spots of mineralized apatite. Addition of silk (CS/SP) improved this effect a bit, but the best results were observed for GO and rGO modified ones, were many apatite-like structures were observed. The amount of the modifier was irrelevant.

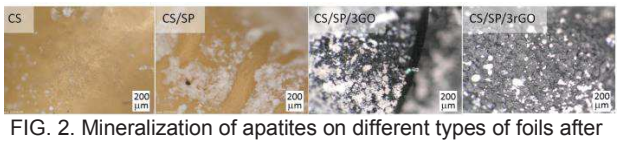

FIG. 2. Mineralization of apatites on different types of foils after 10 weeks incubation in SBF.

This leads to the conclusion that these materials have high bioactivity and potential to use in bone or cartilage regeneration. Such a statement cannot be placed for not modified chitosan.

References

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Acknowledgments

The authors would like to thank the National Centre for Research and Development, Poland for providing financial support to this project (STRATEGMED3/303570/7/NCBR/2017).