CHITOSAN-BASED NANOCOMPOSITES MODIFIED WITH REDUCED GRAPHENE OXIDE PREPARED VIA GREEN SYNTHESIS

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Introduction

Nanocarbon materials, such as graphene, graphene oxide (GO) and reduced graphene oxide (rGO) have shown great potential in biomedical applications [1]. Recently, particularly graphene modified nanocomposites became the subject of intensive research [2,3]. In this paper, we report simple method of GO reduction using green reducing agent – L-ascorbic acid and fabrication of chitosan based nanocomposites modified with GO, green-synthesized rGO and hydroxyapatite.

Materials and Methods

Graphene oxide was prepared from graphite by the modified Marcano method (ITME, Poland). Green synthesis of rGO was performed as follows: known amount of L-ascorbic acid (Avantor Performance Materials Poland S.A.) was added to 300 ml of aqueous GO dispersion (0.1 mg/ml) under vigorous stirring. Next, sodium hydroxide solution (1 M NaOH) was added drop-wise to adjust the pH of the suspension to 9-11. The whole system was then sonicated for 0.5 h and kept for 2h at 70 ^{0}C. To produce nanocomposites, dispersion of GO or rGO was added to 4.7% (w/v) solution of chitosan (Acros Organics, M=600000-800000) in 5% acetic acid and sonicated for 1h at RT. Homogeneous chitosan solutions modified with GO (1.5%), rGO (1.5%) or rGO and hydroxyapatite (6%; HA, Chema-Elektromet, Poland) were cast into Teflon dishes and left for 96h at RT.
Structural properties of the prepared nanocomposites were investigated by attenuated total reflection spectroscopy (ATR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). In addition, wettability and degradation behavior were investigated.

Results and Discussion

X-ray diffraction pattern of GO showed sharp peaks at 11.51^0 (d-spacing ~0.77 nm), which completely disappeared after the GO reduction and a new wide peak showed up at 22.83^0 (~0.39 nm). Reduction of functional groups in GO was confirmed by ATR spectroscopy - intensity of the oxygen groups peaks decreased significantly.
When added to chitosan matrix, GO flakes stacked together, while exfoliated rGO nanosheets aligned parallel to the film surface (FIG. 1). Chitosan/GO sample surface was relatively smooth (FIG. 1A). In comparison, chitosan/rGO (FIG. 1C) and chitosan/rGO/HA (FIG. 1D) samples had higher surface roughness with plenty of graphene flakes and hydroxyapatite particles visible. Modification of chitosan with GO and rGO resulted in decrease of water contact angle value (FIG. 2). In the case of GO modification, it can be mainly attributed to hydrophilic groups attached to nanosheets. Significantly reduction of contact angle was observed for both types of rGO-modified nanocomposites (i.e. chitosan/rGO and chitosan/rGO/HA), despite the smaller number of hydrophilic functional groups attached to rGO. It can be assumed that the surface roughness has a decisive influence on the wettability.

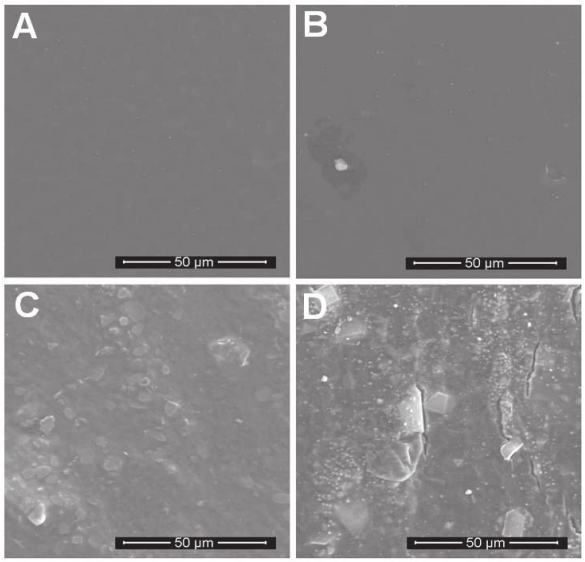

FIG. 1. SEM images of pure chitosan (A), chitosan/GO (B), chitosan/rGO (C), chitosan/rGO/HA (D).

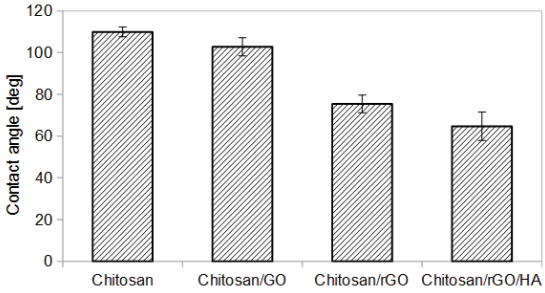

FIG. 2. Effect of nanofillers and HAP on contact angle.

Degradation behaviour of chitosan and its nanocomposites was investigated at 37^{o}C in three types of aqueous media: distilled water, PBS and Ringer's solution. Chitosan and chitosan/GO samples dissolved completely after only one day. The pH value decreased due to acetic acid residues and degradation products presence. Composites modified with rGO or rGO and HA were stable for weeks.

Conclusions

Reduced graphene oxide was successfully prepared via green synthesis using L-ascorbic acid as a reducing agent. Alkaline conditions provided colloidal stability of graphene oxide through electrostatic repulsion of the layers. Further, we have successfully prepared chitosan-based composites modified with GO, rGO and HA. Addition of green-synthesized rGO improved wettability and stability in PBS and Ringer's solution of the nanocomposite films. Both, chitosan/rGO and chitosan/rGO/HA are promising materials for biomedical applications, e.g. bone tissue engineering.

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