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DIFFERENT METHODS OF CHITOSAN GRAFTING WITH QUERCETINE AND DETERMINING THE ANTIOXIDANT ACTIVITY OF SYNTHESIZED COPOLYMERS

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Introduction

Chitosan has become one of the most interesting polymers in different fields due to a rare combination of biological, mechanical and physical activities. It is one of the main products of chitin, which is commercially obtained by chitin deacetylation produced by crustaceans.

Reducing the molecular weight and thus decreasing the crystallinity, it is improved its solubility in diluted acids at pH = 5 where the free amine groups are protonated. In the synthesis of chitosan derivatives, three methods have been developed to produce chitosan compounds functionalized with polyphenols: ester-mediated modification; enzyme-mediated strategy; grafting induced by free radicals. The main purpose of experimental studies is the synthesis of chitosan derivatives by grafting it with certain compounds that exhibit antioxidant properties and represent part of the flavonoid class and studying, comparing the antioxidant properties of the obtained copolymers.

Materials and methods

In the experimental studies two modalities of functionalization of chitosan with quercetin were investigated. One of them includes the functionalization of chitosan with maleic anhydride (MA), and subsequent functionalization of the quercetin to the obtained copolymer (copolymer I). In the second method, grafting of chitosan macromolecule with the same flavonoid was performed (copolymer II).

Results and conclusions

The solubility of chitosan derivatives with Que in different organic and inorganic solvents was determined. It has been determined that both derivatives of this polymer are soluble in DMF and that the copolymer II (low molecular weight) is soluble in ethanol.

Both of the copolymers were obtained from chitosan at low temperatures (0-5°C). The prolongation effect of the copolymers I and II was determined and it was found to be 6-8 times higher than the molecular quercetin. In the second grafting method, lower molecular weight chitosan was used by oxidation with hydrogen peroxide which then was functionalized with quercetin. Using UV-VIS spectroscopy, the antioxidant activity of low molecular weight chitosan with quercetin (copolymer II) and the maleic anhydride chitosan-copolymer functionalized with the same flavonoid (copolymer I) was determined.

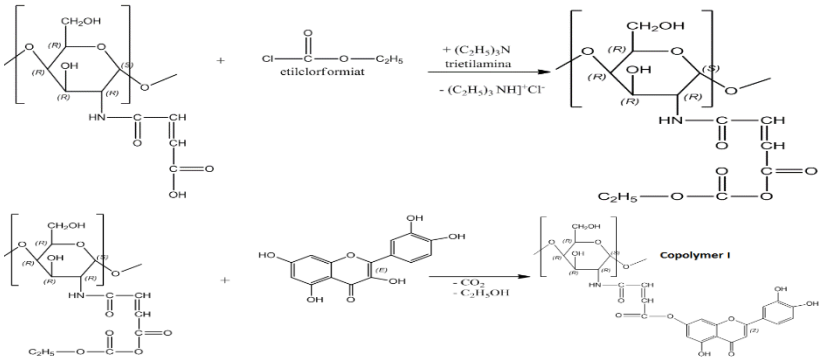

Figure 1. The covalent grafting of chitosan with quercetin via AM.

Determination of the antioxidant activity (AAO) of chitosan synthesized copolymers was performed using the DPPH free radical method. A DPPH solution of 1x10-4 M concentration was prepared and the concentration of chitosan derivatives varied in the range of $1x10^{-5}$ M to $2x10^{-4}$ M. The influence of the concentration of the copolymers on DPPH consumption over time was measured by studying the variation in the absorbance of the mixture at λmax=517 nm. The antioxidant activity of the functionalized copolymers and EC50 was determined, representing the amount of antioxidant required to reduce the DPPH concentration by 50%. Concentrations (%) at DPPH equilibrium were then determined in all the modeled systems. The [Antiox.]/[DPPH] molar ratio was determined and Wech (DPPH) = f ([Inh.]/[DPPH]) dependence was constructed for both copolymers.

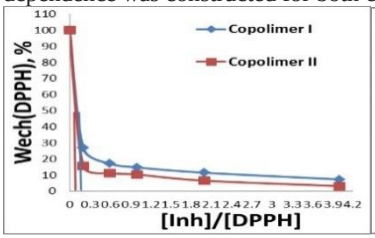

Figure 2. Dependence of [DPPH] of [Antiox.]/[DPPH].

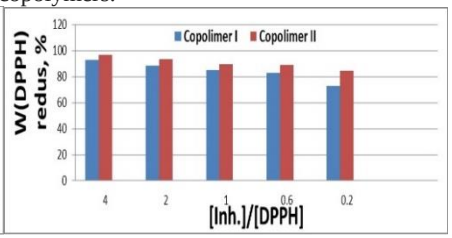

Figure 3. The amount of reduced [DPPH] of [Antiox.]/[DPPH].

Significant antiradical activity was documented in the study of the antioxidant activity of lower molecular mass quitosan grafted with quercetine. The compound obtained in the functionalization has a lower effective concentration (EC_{50}=0.2) than the compound obtained by maleic anhydride (EC_{50}=0.25), indicating that the decrease in the molecular weight of chitosan improves not only the solubility of the derivatives of the given polymer but also favors the antioxidant activity of the chitosan functionalizing product. The prolongation effect of both synthesized copolymers was determined and this effect was found to increase 6-8 times, being greater for the copolymer nr. II.