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Controlled Chemical modifications of chitosan. Characterisation and investigation of original properties"

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Chitosan is the most important derivative obtained from chitin; chitin being the second more important natural polymer after cellulose is especially interesting due to the presence in the repeat unit of a $–NH_2$ group in C-2 position which may be specifically modified by controlled chemical reactions.

In addition, the second advantage of chitosan is that it becomes water-soluble in acidic conditions (pH<6) allowing to prepare biocompatible and often biodegradable polymer with optimized properties, in homogeneous conditions; the solubility also allows to cover the domain of applications in solution and in gel (after crosslinking by chemical or physical bonds).

In this view, a first series of derivatives was obtained by alkylation on the C-2 position of the repeat unit. The introduction of a hydrophobic entity gives a random copolymer in which hydrophobic attractions counterbalance the electrostatic repulsion between the $–NH_3^+$ groups. Depending on the pH and ionic strength of the solution and on the temperature, on the degree of alkylation and on the length of the alkyl chains introduced, the physical properties of the dispersed polymer varies from a thickener to a gelling system. The mild conditions for alkylation do not modify the molecular weight of the polysaccharide; it is important because the alkylated polysaccharides usually present aggregates which perturb the mass determination. The degree of substitution is obtained by NMR.[1, 2]. In this paper, we will describe the main properties obtained for these amphiphilic systems. Bulk properties are important but also interfacial characteristics. The surface tension of alkylchitosan solutions and the mechanism of electrostatic complex formed in presence of surfactant was investigated and will be presented [3,4].

The more recent modifications concern the obtention of two series of derivatives with complementary characteristics: a β-cyclodextrin (CD) derivative is grafted randomly along the chitosan backbone up to 10% molar ratio based on repeat unit. It is demonstrated that the specific complexation properties of CD are not modified by grafting on the polymer; for that purpose, different techniques were used such as NMR and microcalorimetric titration to determine the association constant with some hydrophobic small molecules among which adamantane derivatives. A chitosan grafted with adamantane was prepared and characterized. The two derivatized polysaccharides were mixed and a large increase of viscosity was observed due to specific recognition between the two grafted entities. The evolution of the physical properties of the systems obtained as a function of different parameters were

examined and the main results will be presented. The stability of the reversible crosslink point is related to the stability constant of the CD-Adamantane complex formed [5,6]. The self assembly of the modified polymer is specific and new systems are now developed to enter the domain of adaptative materials.

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