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NOVEL MATERIALS BASED ON CHITOSAN: CICECO AVEIRO'S CONTRIBUTION

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The purpose of this lecture is to provide a succinct outline about the recent research carried out in the CICECO Laboratory of Aveiro University in the realm of the exploitation of chitosan as a source of novel materials. This update purports to show that our preliminary results reported at the last SIAQ, when we were just beginning research on this extraordinary polymer, have now grown into what we consider as valuable contributions to the field.
Two different topics are discussed, namely (i) the preparation and characterization of physical blends of chitosan with cellulose fibers using a variety of actual systems, and (ii) the chemical modification of chitosan in view of preparing novel materials with specific properties.
Prior to this discussion, it is important to emphasize the relevance of a preliminary consideration. This has to do with the contradictory results and interpretations regarding the absurdly low surface energy values for chitosan (a key parameter, particularly in considerations related with the formation of interfaces with other substrates) reported in numerous publications, without any discussion. This situation was shown to arise from an inadequate purification of the chitosan samples, which translated into the classical artifact of low-polarity impurities migrating at the surface of the chitosan films [1].
The chitosan samples used in these investigations were provided by Mahtani Chitosan Pvt., India (high DP, DDA > 95%), and Norwegian Chitosan AS (medium DP, DDA = 67-79%).

1. Chitosan and Cellulose

The interaction of chitosan with cellulose fibers has been assessed in three different contexts, which are briefly expounded below.

A. Chitosan and Paper

A study is presented on the distribution of chitosans (as such, chemically modified for water solubility, chemically modified for fluorescence) *onto* and *within* paper sheets. Layer-by-layer depositions showed that the penetration of chitosan within the fiber mat ceased after the third layer, with further deposition contributing to the chitosan film formation at the paper surface. The properties associated with these materials are provided and discussed [2].

B. Chitosan and Bacterial Cellulose

The introduction of different proportion of bacterial cellulose (BC) into chitosan films gave rise to composites with excellent interfacial adhesion and improved mechanical properties. Given the nanometric morphology of the reinforcing BC web, these films were transparent, with ~80% transmission in the whole of the visible range, at 10% of BC incorporation [3].

C. Chitosan and Nanofibrillated Cellulose

Chitosan nanocomposited were also prepared using nanofibrillated (NF) cellulose as reinforcing element. Again, the ensuing films were transparent and the mechanical properties positively affected by the inclusion of the nanofibers. Quantitative comparisons are provided regarding the differences in effects between BC and NF [4].

2. Chitosan Chemical Modification

A number of specific modifications are discussed, including (i) the oxypropylation of both chitin and chitosan residues to produce viscous polyol macromonomers [5]; (ii) the incorporation of perfluorinated grafts to generate highly hydrophobic chitosan surfaces; (iii) the incorporation of furan-bearing grafts and the thermally reversible crosslinking of the ensuing functionalized chitosan macromolecules with a bismaleimide, through the application of the Diels-Alder and retro-Diels-Alder reactions.

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