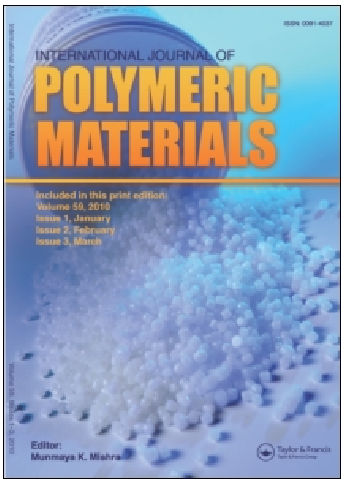

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Chitosan Based Films. Synthesis and Crystalline Properties of Nanocomposites with Amine Propyl Siloxane

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The sol-gel treatment of equal amounts of chitosan and partially hydrolyzed aminopropylsiloxane (APS) leads to the formation of transparent, flexible films indicating high compatibility at the molecular level of the components. X-Ray diffraction and thermal analysis of the products indicate the formation of a new phase with a structure which in light of its FTIR spectrum appears to be similar to that of the form I of the pristine chitosan.

Keywords: Chitosan; aminopropylsiloxane; sol-gel

INTRODUCTION

Nanocomposites are in general a combination of two or more phases where at least one dimension is in the nanometer range. These materials which often result from the combination of different inorganic and organic substrata behave as compounds displaying properties different from those of their components. For the production of such kind of materials sol-gel processes combining organic and inorganic polymers [1–2] appear as useful and versatile methods. The syntheses of organic-inorganic composites containing a biopolymer are of special interest for preparing biomimetic materials [3–5].

Chitosan, poly-β (1–4)-2-amino-2-deoxy-D-glucose, being the partial deacetylated product of the alkali treatment of chitin, an abundant biopolymer contained in the shell of crustaceans, appears to be very suitable for the synthesis of new biomimetic materials [3]. Because of its solubility in organic dilute acids it is also appropriate for preparing membranes.

The presence of groups with Lewis acid-base activity in the polymer is reflected in its capability for absorbing metal ions, that being specially strong because of chelating properties of this class of macromolecules [6]. Nanoporous membranes of Chitosan have been indeed used in reverse osmosis applications [7]. Great interest also exist in the biomedical applications of this polymer. It is hemocompatible and shows bioactivity being indeed successfully applied to problems related with blood vessel surface coating and artificial human skin [8–9].

Although applications above are certainly strongly related to both the molecular and supramolecular structure as well as to the crystalline structure of the membranes, there is relatively few information concerning these subjects [10]. For designing chitosan based materials with predetermined mechanical, physicochemical, and selectivity properties, further knowledge about the relationships between chemical composition, structural features, and chemical recognition ability for such a kind of compounds is still needed. The study of the modification of chitosan membranes by both building organic-inorganic hybrid networks and adding specific metal ions are plausible approaches and they are being indeed researched on in our laboratory.

In this paper the preparation and characterization of hybrid films containing chitosan and poly-(aminopropyl) siloxane is described.

EXPERIMENTAL

Chitosan (CHI), Mw 1.14×10^6 and 86% deacetylation degree (Bioquímica Austral Ltda.) was washed with acetone, then with ethanol, and finally dried in vacuum at about 60°C. 3-Amino-2-propyltriethoxysilane (APS) (Aldrich) was used as received. CHI and APS were used as 2% w/w formic acid solutions.

Hydrolysis of APS. 22.8 ml APS (0.1 mol) were dissolved in 20 ml 0.5M formic acid and maintained at 45°C for about three days letting off the solvent by evaporation until the solution stops flowing at a specific weight of 0.7 g cm^{-3}.

The APS polycondensation process was followed by viscosity determinations using the falling ball method.

Film preparation. Solutions of chitosan and pre-hydrolyzed APS were mixed and maintained under stirring for about 24 h at room temperature. Films were obtained by using the appropriate CHI to APS weight ratios. Occasionally, the aged solutions were pre-concentrated in a rotary evaporator. Thereafter, the solutions were poured on a polypropylene film letting the solvent evaporate at room temperature.

Characterization of films. The crystalline structure of resulting films was examined using both X-ray diffraction (XRD) analysis and FTIR-spectroscopy. Further characterization was accomplished by thermal analysis determinations, DSC (Perkin-Elmer DSC7), and simultaneous DSC/TGA (STA625, Polymer Laboratories).

RESULTS AND DISCUSSION

Chitosan-APS mixtures form films which, contrasting with those of chitosan alone, are highly flexible and with a great transparency degree. This feature indicates a good compatibility of the components at molecular level similar to that reported for the combination of chitosan with a silica network obtained by hydrolyzing tetraethoxysilane (TEOS) by a typical sol-gel process [11]. Some differences between the films using TEOS and APS as the inorganic constituent, concerning specially solubility properties, are however apparent. Differences as well as similarities of the films obtained with these two siliceous precursors should be related with the properties of the silica-like networks obtained by the corresponding pre-hydrolysis processes. Although precursors obtained from APS hydrolysis are expected to have a structure essentially similar to those generated by the hydrolysis of TEOS, the presence of the propylamino-groups at the silicon atoms could influence the degree of condensation or any other property of the resulting siloxane chain. An answer to this question was attempted studying the hydrolysis of the APS.

APS Hydrolysis

The sequence of hydrolysis and condensation reactions occurring in the APS sol-gel process may be represented by the following equations:

$$Si(OET)_3(C_3H_7NH_2) + H_2O \rightarrow Si(OEt)_2(C_3H_7NH_2)(OH) + EtOH$$

$$Si(OET)_2(C_3H_7NH_2)(OH) + Si(OET)_3(C_3H_7NH_2) \rightarrow$$

$$(OEt)_2(C_3H_7NH_2)Si{-}O{-}Si(OET)_3(C_3H_7NH_2) + EtOH, \text{ etc.}$$

Although the viscosity of the solutions appears to increase with the aging time, this increment is mainly due to concentration changes. Indeed, the viscosity increment after diluting the solutions to the initial volume is minimal. This feature points to formation of oligomer with rather low molecular weight. Accordingly, molecular size exclusion chromatography determinations reveals an average molecular weight of ca. 800. Nevertheless, these oligomers are actually able to generating gels and films in a way similar to that of the siloxanes obtained from the hydrolysis of TEOS. The nature of both types of aggregates should be however different. APS gels and films are indeed, contrary to observations on TEOS derivatives, soluble in water, thus revealing a linking among building blocks weaker than in TEOS products, which is accomplished probably not by silica-like Si—O—Si covalent bonds but by hydrogen bonding. Promoting condensations among APS oligomers for producing silica containing propylamino groups would need temperatures far higher than those used in the experiments described here [12].

According to the discussion above, hybrid chitosan-APS films would be constituted by long chitosan chains linked by small propylaminosiloxane oligomers, thus producing the changes in the crystallinity of the pristine polymers discussed below.

Films Crystallinity

The crystalline structure of chitosan has been studied by several authors using IR spectroscopy as well as X-ray diffraction analysis. Samuels [13] and Muzzarelli [6] have found that there are two classes of crystalline Structures I and II, labelled by other authors as β and α respectively. As illustrated in Figure 1, form I has a lower degree of order than form II.

Structures I and II may be recognized by relatively wide diffraction lines appearing at approximately $2\theta = 8.7$, 11.8, 18.5 and 24 degrees for form I and at $2\theta = 16$, 21, 24 and 28 degrees (the two latter with low intensity) for form II [13–6]. Moreover, from the relative intensities of corresponding lines, the ratio between these two forms may be also estimated. According to Samuels [13] and Urbanczyk [14], these two kinds of structures can be also distinguished by some characteristic bands in their IR spectra. Form I shows a single peak at 1580 cm^{-1}, two peaks at 1380 and 1350 cm^{-1}, and one peak at 760 cm^{-1}. For form II, one doublet at 1580 and 1670 cm^{-1} and multiple peaks

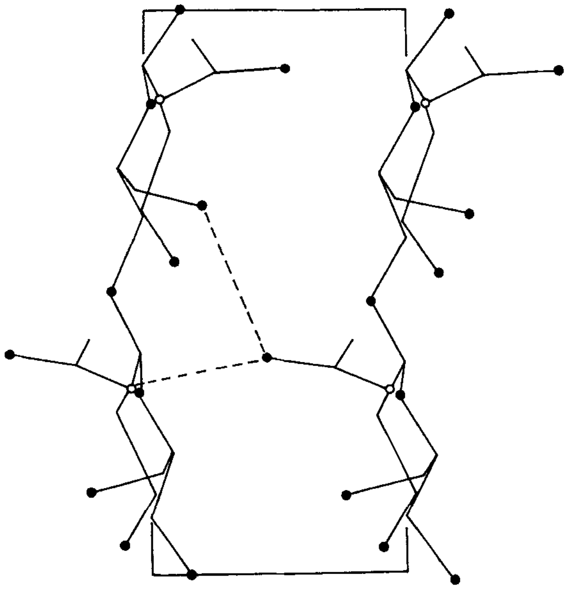

FIGURE 1a

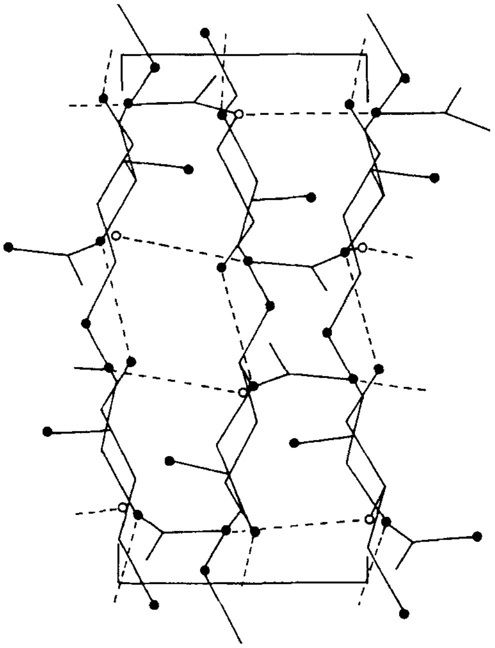

FIGURE 1b

FIGURE 1 Proposed projections for the structures of: (a) β-chitin and (b) α-chitin.

centered at 1475, 1425, 1380 and 1320 cm^{-1} are observed, while the absorptions at 1350 and 760 cm^{-1} are not detected.

The conversion of β-chitin to α-chitin as well as that of chitosan in the form II to the form I occurs by a rearrangement of the intermolecular hydrogen bonds between antiparallel chains.

CHI-APS Hybrid Films

The addition of oligo-aminosiloxanes obtained by hydrolysis of APS to chitosan leads to structural changes which, as observed in Figures 2a–c, may be clearly appreciated in the X-ray diffractograms.

For the hybrid films, a diffraction pattern rather different from those of the components, APS and chitosan (vide infra), is observed.

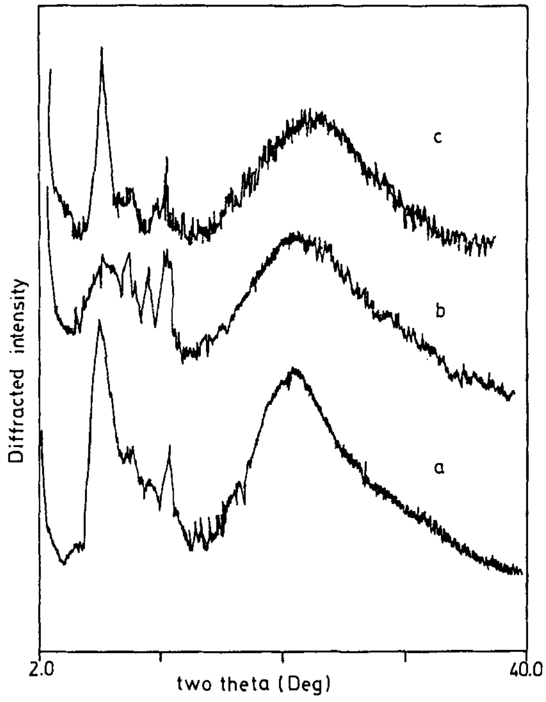

FIGURE 2 X-ray diffraction spectra of films in different CHI-hydrolyzed APS rations. (a) 1:1; (b) 2:1; (c) 1:2.

In the XRD spectra of films obtained from solutions of the pristine chitosan (Figs. 3a–b) it could be observed that the films of CHI is essentially amorphous by the presence of unneutralized species [15]; the film obtained from hydrolyzed APS shows good definite peaks at $2\theta = 6.7$, 8.5, 22.2, exhibiting a relatively high degree order. Comparing these features with those observed for the CHI-APS composites, the compatibility at molecular level in the latter may be inferred. Surprisingly, no changes indicative of shifting of the equilibrium between chitosan forms I and II are apparent in the FTIR spectra of the samples. Spectra always show the absorption pattern corresponding to a preponderance of the form I similar to that observed in the pristine chitosan.

The structural features detected for the nanocomposites reported here are further corroborated by thermal analysis, corresponding

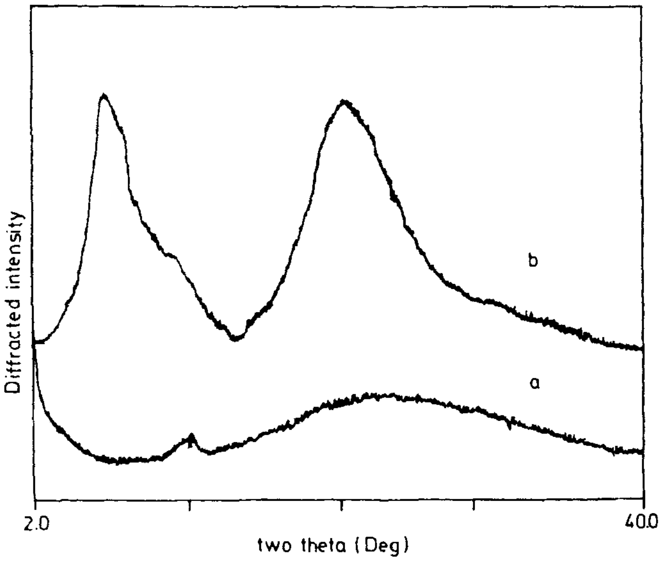

FIGURE 3 X-ray diffraction spectra of films. (a) Chitosan; (b) hydrolyzed APS.

results are illustrated in Figures 4a–d. No peak is observed in the DSC diagram of the polyaminosiloxane until 550°C; The corresponding TG analysis shows only a small, gradual loss of mass. Chitosan shows, in turn, one peak corresponding to its decomposition at a temperature of about 300°C. The same decomposition process is however observed at about 360°C in the mixture chitosan-APS 1:1, thus indicating the formation of a new phase. Accordingly, the DSC diagram of a sample obtained from a film with a composition CHI-APS 2:1 shows two peaks at 294 and 360°C thus pointing to the presence of two phases, chitosan and the new molecularly compatibilized CHI-APS complex system.

From the IR pattern commented above, which remains unchanged with respect to that of the pristine chitosan, it may be further inferred that the hydrogen bonding network in the new phase of chitosan-aminopropylsiloxane is similar to that existing in the low ordered form I of the chitosan.

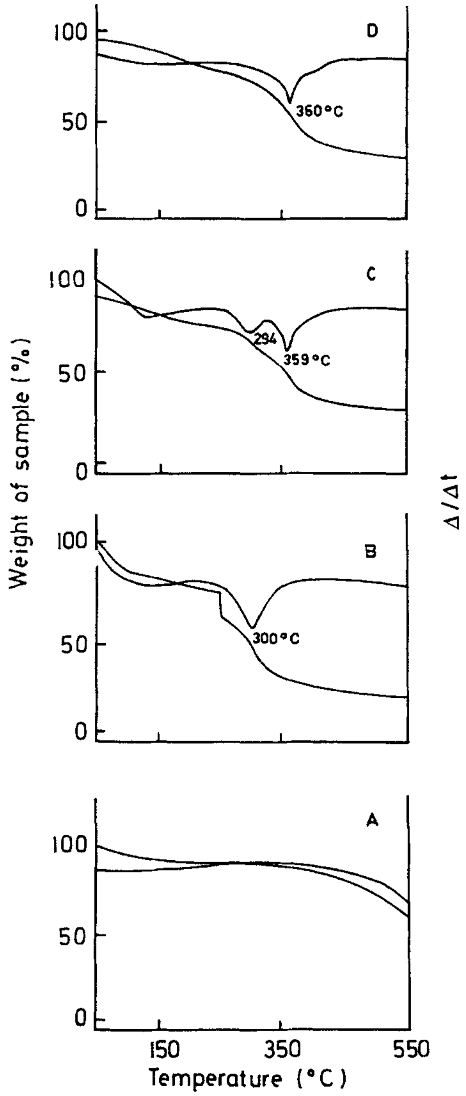

FIGURE 4 DSC/TG of samples obtained from films of (a) hydrolyzed APS; (b) Chitosan; (c) CHI-hydrolyzed APS 2:1; (d) CHI-hydrolyzed APS 1:1.

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