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Preparation of cellulose-chitosan polymer blends

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Films of cellulose and chitosan blends were prepared using trifluoroacetic acid (TFA) as a co-solvent for the two polysaccharides. Analyses of X-ray diffractograms, scanning electron micrographs, and the mechanical properties of the films suggest that cellulose and chitosan are intimately blended in the films. This behavior is consistent with the similarity of both the primary and secondary structures of the two linear polysaccharides.

INTRODUCTION

Cellulose is the beta-1,4-linked polymer of anhydroglucose, and chitosan is the similarly linked polymer of 2-deoxy 2-amino ahydroglucose; the two polymers differ only in that the latter has the deoxyamino group instead of the hydroxyl group at C-2 of the pyranose ring. This similarity in primary structures suggests that the secondary structures and patterns of aggregation may also be sufficiently similar to facilitate the formation of homogeneous blends of the two polymers. Preliminary observations using X-ray diffractometry and Raman spectroscopy (Atalla, R.H. & Whitmore, R., unpublished) are consistent with this expectation.

Introduction of some amino groups into a cellulosic system is important to facilitate chemical modification. However, it is generally difficult to introduce sufficient amounts of amino groups into cellulose by simple and efficient reactions without significant degradation of the cellulose chains. Chitosan has received considerable attention as an amine-containing polymer (*Proc. 2nd Internat. Conf. on Chitin and Chitosan*, 1982), and Noguchi *et al.* (1973) have reported on cellulose–chitin blends prepared using xanthate (NaOH and CS_2) as a co-solvent for the two polysaccharides.

In this communication we report on an exploration of the use of cellulose–chitosan blends as an alternative approach to development of an amino group containing cellulosic system. Blends of cellulose with chitosan appear more promising for chemical derivatization because the amino group in chitosan is much more reactive than the acetamide group in chitin. We describe the preparation procedure and the compatibility of the polymers in co-solvents, the appearance of films of the blend, their crystallinity, and physical strength. Sufficient physical strength and chemical functionality are expected to be derived from cellulose and chitosan, respectively, in films of well-mixed blends.

EXPERIMENTAL

The celluloses used included Whatman (Maidstone, UK) CF1 microcrystalline powder, linters, cotton, and bleached kraft pulp; all were subjected to conventional purification procedures. Commercial chitosan was further deacetylated with 50% NaOH at 120°C for 2 h (Araki & Ito, 1975). Acidic solvents such as trifluoroacetic acid (TFA) (Patel & Gilbert, 1981), 85% phosphoric acid, 72% sulfuric acid, and formic acid dissolved both cellulose and chitosan, whereas some of the new cellulose solvent systems such as LiCl-dimethylacetamide (Turbak *et al.*, 1981), SO_2-amine systems (Isogai *et al.*, 1987) and paraformaldehyde-dimethylsulfoxide (Johnson *et al.*, 1976) did not dissolve chitosan.

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However, since the acids, with the exception of TFA, brought about severe depolymerization of cellulose during the dissolution process, the regenerated polymer blends could not retain their film or fiber forms. Thus, TFA was used as the co-solvent for cellulose and chitosan for preparation of the polymer blends. Patel and Gilbert had used dichloromethane as a diluent for TFA. In the present work TFA alone was found more effective.

The sequence for dissolution in TFA and preparation of the films was the following. To a total of 1 g of cellulose and chitosan, TFA is added to prepare 1–7 wt% solution, the concentration selected depending upon the molecular weight of the cellulose. For CF1 cellulose, 3–7 wt% solution can be obtained without difficulty. However, the concentration for linter and cotton celluloses needs to be less than 1·5% in order to avoid too high a viscosity, and to reduce time for dissolution. As shown in Table 1, it took approximately 2, 6, and 9 days for CF1, linters, and cotton, respectively, for complete dissolution in TFA at room temperature without stirring. The solution was then diluted with acetic acid or formic acid to control the viscosity for casting and to avoid the formation of foam in the film during evaporation of the solvents. In this case, these acids can be added freely without any precipitation of cellulose, once cellulose has been dissolved in pure TFA.

After casting the solution on a glass plate, the solvents were removed by natural evaporation at room temperature. Transparent films can be obtained by peeling them off from the glass plate. Films prepared in this manner have the amino groups protonated and incorporate the acids as the corresponding salts. In order to obtain the films with free amino groups, the films were soaked in 1 N NaOH at room temperature for 1 day while still on the glass plate to remove the acids. The films separated spontaneously from the plate during this procedure. They were then washed with water, and dried by being placed between a metal plate and a filter paper at room temperature, for approximately 16 h (TAPPI Test Methods, 1988).

RESULTS AND DISCUSSION

Although almost all cellulose films prepared from cellulose solvents by regeneration into aqueous media are brittle in the absence of plasticizing agents, the cellulose and cellulose–chitosan blend films prepared in the present work were all transparent and sufficiently flexible without plasticizers. Furthermore, little shrinkage of the films occurred during evaporation and drying after they were treated with alkali and washed with water. The surface of the film in contact with the glass plate was quite smooth, whereas the other side was slightly uneven, perhaps due to factors associated with the evaporation of solvents. While it is expected that the two surfaces are equally uniform in composition, because of the differences in surface texture no attempt was made to confirm this by spectral measurements. Figure 1 shows scanning electron micrographs of a blend film (cellulose: chitosan = 7:3, alkali-treated), and suggests that the two components are mixed well in the film.

Since TFA is a strong acid, depolymerization of cellulose is inevitable during the dissolution procedure (Albersheim *et al.*, 1967; Fengel *et al.*, 1977). The blend films prepared from CF1 were too weak to maintain the film form. However, all alkali-treated or untreated cellulose and cellulose–chitosan blends prepared from linters, cotton, or kraft pulp had tensile strength of *c.* 50–80 MPa. These values are quite high and exceed those of commercial cellophane. Table 1 shows the degrees of polymerization (DPv) of the original and regenerated celluloses. Clearly, acid hydrolysis occurred in all the cellulose samples upon dissolution in TFA. However, a DPv higher than 500 was found to be sufficient for the films to have adequate physical strength. TFA is a volatile cellulose solvent, and this unique property may be the key to formation of strong films.

Figure 2 shows X-ray diffraction patterns of untreated and alkali-treated cellulose and cellulose–chitosan blend films. The alkali-treated films are of higher crystallinity than the corresponding untreated ones.

Table 1. Degrees of polymerization (DPv) of celluloses regenerated from cellulose/ trifluoroacetic acid solution

Sample	Time for complete dissolution in TFA at room temperature	DPv[a]	
		Original	Regenerated
CF1	2 days	252	205
Linter	6 days	1185	561
Cotton	9 days	1936	693
Kraft pulp	10 days	1077	603
Groundwood pulp	Insoluble	—	—

[a] Cupriethylenediamine method (0·5 Mol), 1·75 × $[\eta]$ = DPv (Smith *et al.*, 1963).

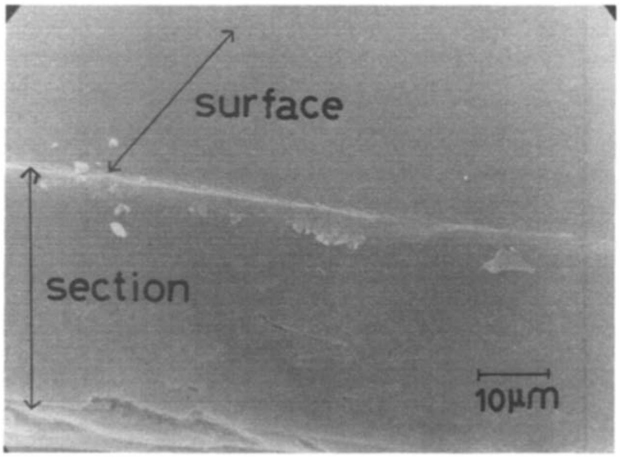

Fig. 1. Scanning electron micrograph of cellulose–chitosan blend film (7:3 by weight, alkali-treated).

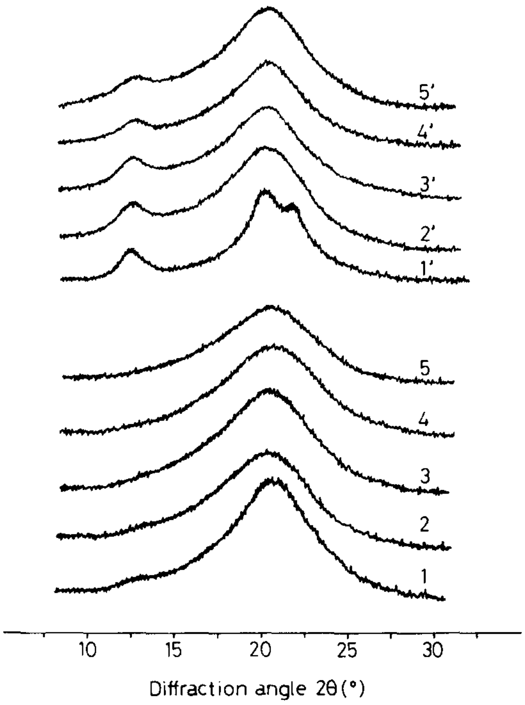

Fig. 2. X-ray diffraction patterns of cellulose–chitosan blend films. Weight ratios between cellulose and chitosan were: 1 and 1', 10:0; 2 and 2', 9:1; 3 and 3', 8:2; 4 and 4', 7:3; and 5 and 5', 5:5. 1–5: Before 1 N NaOH treatment. 1'–5': After 1 N NaOH treatment followed by washing with water.

Molecular rearrangement of cellulose and chitosan and/or the removal of acid at the amino group of chitosan by the alkali treatment may facilitate the increase in crystallinity. Yet it is also clear that the presence of the chitosan limits the crystallinity of the cellulose. It is interesting that the tensile strengths were almost equal for the original and alkali-treated films. The results, including X-ray diffraction data, SEM photographs, and mechanical properties, suggest that cellulose and chitosan are very well mixed in these films, reflecting the high degree of similarity of both primary and secondary structures in these two linear polysaccharides. Since many factors contribute to development of the patterns of aggregation of the beta-1,4-linked polysaccharides, it is difficult to identify a particular element of the structure of chitosan as the dominant factor in its interaction with cellulose.

CONCLUSIONS

We have observed that well-mixed blends of cellulose and chitosan, which have sufficient physical strength, can be prepared by using TFA as the co-solvent. Some of the special characteristics and uses of chitosan, such as its use in separations, adsorption, immobilized enzyme systems, and polymer catalysis, are clearly worthy of exploration in the context of the blends of cellulose and chitosan reported here.

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