NOTE

A Study on the Further Acetylation of SPA Cotton

INTRODUCTION

In a previous publication[1] we described a new process for the decrystallization of cellulosic materials such as cotton, viscose, ramie, jute, and paper. This process involves two steps, namely, swelling of cellulose in alkali and an interaction of the resulting alkali cellulose with acetic anhydride. The products obtained are swollen and partially acetylated and hence designated as SPA products. It was shown that the SPA cotton has an acetyl content of 16% and has greater accessibility and breaking strength than untreated cotton. SPA cotton consequently appears to be a better starting material for fibrous acetylation of cellulose than raw, or even mercerized, cotton. The present communication describes the results of experimental work undertaken to verify this hypothesis.

EXPERIMENTAL

Materials

The cotton (Egyptian Karnak) used in this work was purified by Soxhlet extraction for 24 hr in a mixture of ethanol and benzene.

Methods of Treatment

Mercerized cotton was prepared by swelling raw cotton in 24% NaOH for 15 min at 27°C, followed by washing with water and air drying. SPA cotton was prepared by swelling raw cotton in 24% NaOH for 15 min at 27°C, centrifuging the swollen cotton to remove excess NaOH, and immersing it in an excess of acetic anhydride for 30 min. The sample was washed with water and dried in air under ambient conditions.

The recipe used in the partial acetylation was as follows: benzene, 50 ml; acetic anhydride, 35 ml; glacial acetic acid, 15 ml; and perchloric acid, 0.5 ml. The acetylation reaction was carried out at room temperature for a period of 30 min. Heat treatment of acetylated SPA cotton was carried out at 240°C for 10 min in air.

Characterization of Product

The acetyl content for the various acetylated cotton samples was determined using a standard procedure.[2] Moisture content was calculated from the difference between the weight of a sample conditioned at 65% R.H. and the dry weight of the sample. Equatorial x-ray diffractograms were obtained on a vertical, Philips x-ray diffractometer employing a curved crystal focalizer in the transmission setup. Diffracted intensities were monitored using a scintillation counter and a pulse height discriminator. All intensity data were recorded employing x-rays from a tube with a Cu target operated at 35 kV and 15 mA.

RESULTS AND DISCUSSION

The results of the acetylation experiments on raw cotton, mercerized cotton, and SPA cotton using the normal recipe for partial acetylation are compared in Table I. The acetylated product prepared from the SPA cotton has an acetyl value of 31%, which is high in comparison with the products prepared from raw and mercerized cottons which have acetyl contents of 4.3% and 2.2%, respectively.

The acetylated SPA cotton retains its fibrous character, and the fibers are not brittle. Equatorial x-ray diffraction from a bundle of combed and parallelized acetylated SPA cotton fibers has been

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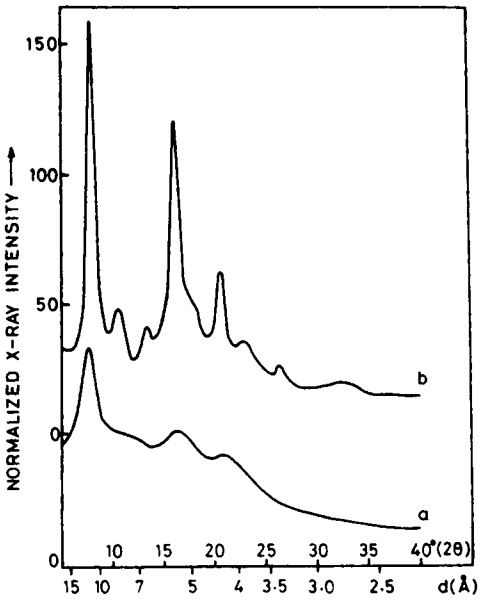

Fig. 1. Equatorial x-ray diffractograms of acetylated SPA cotton (a) before and (b) after annealing at 240°C for 10 min.

TABLE I
Results of Partial Acetylation of Raw Cotton, Mercerized Cotton, and SPA Cotton[a]

Acetylated Sample	Acetyl content (%)	Moisture content (%)
Raw Cotton	4.3	5.3
Mercerized Cotton	2.2	7.7
SPA Cotton	31.2	4.3

[a] Egyptian Karnak.

recorded, and the diffractogram shows three broad peaks at 7.75°, 16.5° and 21° (2θ), respectively (Fig. 1, curve a). This diffractogram is similar[3-5] to that of amorphous cellulose triacetate I. Consequently, we have assumed that these samples contain predominantly cellulose triacetate I. This assumption was made because the spacings of the strong reflections observed corresponded more closely[5] to those of the cellulose triacetate I form, rather than the triacetate II form. When the acetylated SPA cotton sample is heated at 240°C for 10 min in air, there is a considerable sharpening of the x-ray diffraction peaks (Fig. 1, curve b) on account of crystallization of the macromolecules into a lattice which is predominantly that of cellulose triacetate I. In addition to the strong peaks at 8°, 16°, and 20.7° (2θ) corresponding to the 11.1, 5.5, and 4.3 Å (d) characteristic of the triacetate I form, the diffractogram also shows peaks at 10.5° and 13.25° (2θ) corresponding to the 8.4 and 6.7 Å (d) which can be attributed[5,6] to a small fraction of the cellulose triacetate II form (Fig. 1, curve b). If cellulose triacetate II alone had been present, the ratio of the intensities of the peaks would have been slightly different from those actually observed. This method of fibrous acetylation can be employed for yarns and fabrics as well.

TABLE II
Effect of Catalyst Concentration on the Acetyl Content of Acetylated SPA Cotton

Concentration of $HClO_4$ catalyst in bath	Acetyl content of product (%)
0.01%	29.0
0.10%	37.6
0.50%	31.2

The recipe for partial acetylation used to obtain the data in Table I was in fact formulated for raw and mercerized cottons and may not be an optimum formulation for the further acetylation of SPA cotton. Keeping this in mind, the effect of varying the concentration of catalyst ($HClO_4$) in the recipe on the acetyl value of the product was studied. The results obtained are summarized in Table II and show that a catalyst concentration of about 0.1% in the recipe of partial acetylation is nearly optimum for obtaining the highest degree of acetylation (acetyl value $\simeq$ 38%) starting from SPA cotton.

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