

Characterisation of Ramie Yarn Treated with Sodium Hydroxide and Crosslinked by 1,2,3,4-Butanetetracarboxylic Acid

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Abstract

The microstructure and tensile properties of ramie treated with NaOH and crosslinked with 1,2,3,4-butanetetracarboxylic acid were characterised. X-ray diffraction and FTIR were used to study the crystalline structure of the resultant ramie yarns. Results showed that the maximum change in the structure of the modified ramie took place at 16% NaOH, which would completely transform Cellulose I to Cellulose II. Also, the crystallinity index and fibre orientation decreased to the minimum value while the absorption properties were enhanced. The average degree of polymerization of the treated ramie yarns slightly decreased after NaOH treatment.

Introduction

Considerable work has been done to modify the morphology and molecular structure of the ramie fibre. Alkali treatment was widely studied and used as a normal means to study microstructure of ramie fibre. Because the crystal structures of cellulose have already been identified [1], it is time to use the same crystallographic conventions in crystallinity analyses as are used in fibre diffraction studies. Chemical crosslinking can improve the wrinkle resistance of cellulose. Polycarboxylic acid has been used to develop non-formaldehyde wrinkle-free cotton goods [2-4]. The most effective polycarboxylic acid is 1,2,3,4-butanetetracarboxylic acid (BTCA). In this study, the microstructure and tensile properties of ramie yarns treated with various concentrations of NaOH were characterised. The response of the NaOH treatment with respect to the subsequent BTCA treatment was also investigated.

Experimental

Several analytical techniques were used to obtain information concerning the microstructure of the

treated samples and the resulting changes in fibre structure. Transmission infrared spectra were obtained with 96 scans for each of the samples. Scanning electron microscope was used to analyse fibre samples taken from both the treated and control ramie yarns. X-ray diffractometer was used to collect the X-ray diffraction diagram of the samples. For investigation of the crystallinity and crystallite dimension, powder diffraction was adopted. For the determination of the crystallite orientation, the meridional [040] reflection was selected. The orientation scans were obtained by keeping the 2θ fixed and rotating the sample through 360° in a plane perpendicular to the radiation direction. Values of Hermans crystallite orientation factors and the average angle of orientation were determined. Birefringence of fibre taken from the treated yarn was determined by means of a compensation method combined with a polarising microscope, and it was used to estimate the average orientation of the fibre. The average degree of polymerization of the treated yarn was determined by the method of viscosity using copper diethylene-amine as the cellulose solvent.

Results

X-ray Diffraction Investigation

X-ray diffraction diagram of control ramie exhibits a sharp high peak at 2θ 23 degree, which is assigned to the [002] lattice plane of Cellulose I. Ramie yarns treated with 4% and 8% NaOH solution show similar diffraction diagrams as the control. When the NaOH concentration is increased to 12%, the two additional diffraction peaks appears at 12.0 and 19.9 degree which are assigned to be the [101] and $[10\bar{1}]$ lattice planes of Cellulose II. 16% and 20% NaOH treated ramie show the diffraction diagram of the characteristic

of the Cellulose II. X-ray diffraction shows little change before and after being crosslinked with BTCA, indicating that the crosslinking treatment has little effect on the crystallite structure of the ramie. Since the crosslinking agent cannot penetrate into the crystalline regions, thus the crosslinking reaction mainly occurs in the accessible regions of the fibre. The control ramie has the crystallinity index of 75.0%. 4% and 8% NaOH slightly increased the crystallinity index by about 5%. When the NaOH concentration was increased to 12% or higher, the crystallinity index decrease to the value below 65%, and the minimum crystallinity index was obtained at 16% NaOH. 12% NaOH solution led to partial transformation of ramie cellulose from Cellulose I to Cellulose II. 16% and 20% NaOH treatment resulted in a complete transformation of Cellulose I to Cellulose II.

FTIR Investigation

FTIR spectra show that there is only a little change in the absorbance at 1432 cm^{-1} which is assigned to be CH_2 symmetrical deformation when the NaOH concentration is lower than 16%. However, it shifts towards the low frequency side along with a sharp decline in intensity at 16% NaOH. The change in intensity and position of this band is correlated with the change in the environment of the C_6 carbon atom due to the formation or breakage of the hydrogen bond involving the atom O_6 , which indicates the transition of lattice between Cellulose I and Cellulose II. The intensity at 895 cm^{-1} , which is the characteristic of β -linkage assigned to the C_1 group frequency and is sensitive to the change in chain conformation, increases with higher NaOH concentration. The change in this band becomes most significant at 16% NaOH. FTIR spectra show two additional absorption peaks appear after BTCA treatment which correspond to ester bond and carboxylate respectively indicating the successful esterification of the ramie yarn.

Fibre Orientation

There is a slight reduction in the orientation index of the crystalline regions with an increase in NaOH concentration as determined by the [040] diffraction. However, the orientation index of the amorphous regions show a steady decrease in value at higher NaOH concentration, especially when the NaOH concentration is higher than 8%.

Average Degree of Polymerisation (DP)

The DP of the control ramie and NaOH treated ramie ranges from 1686 to 1768. It is obvious that alkali treatment only slightly reduced the DP of the treated ramie yarns. This may be due to the oxidative degradation of the ramie cellulose in the presence of oxygen gas.

Tensile Properties

There was a little increase in the tenacity of the treated yarn when the concentration of NaOH was less than 12%. It seemed that higher concentration of NaOH caused a progressive decrease in the tenacity of ramie yarn. The decrease in tenacity of the slack mercerised ramie was probably attributed to the decrease in crystalline orientation as a result of the unrestrained lateral swelling of the fibrils. Warwicker [4] noted that the differential response of ramie and cotton to the slack swelling with NaOH was a function of fibre morphology rather than differences in fine structure. He demonstrated that ramie had a simple structure with no primary wall to exert restraint on lateral swelling and consequent disorientation of the swollen fibrils.

Conclusions

The biostructure of ramie yarn treated with NaOH was characterised. Results showed that NaOH with concentration lower than 8% caused no transformation of Cellulose I to Cellulose II with a slight increase in the crystallinity index. When the NaOH concentration was higher than 16%, all the Cellulose I were transferred to Cellulose II. FTIR investigation further confirmed the phase change and decrystallisation of the treated ramie yarns. Fibre orientation of both crystalline and amorphous regions decreased with higher NaOH concentration. There was a slight decrease of DP with NaOH treatment with a corresponding increase in breaking elongation and tremendous decrease in modulus resulting in higher elasticity and softer hand. Crosslinking treatment with BTCA would result in an obvious drop in the tenacity of the ramie yarn.

References

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