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Abstract : The demand for paper yarn has increased as a textile fabric because of its light weight and low static electricity. However, paper yarn wrinkles easily and its softness and stretching properties are low. So we attempted to improve the stretching property of paper yarn by the high-pressure steam method which could provide a shape memorization to cellulosic materials. The most suitable condition based on our finding was steaming at 170℃ for 2 min after soaking in 0.28 % NH_3 aqueous solution. By this treatment, over 84 % of the number of twists of paper yarn was maintained while the strength decreased to 78 %. For the paper yarn twisted together with viscose rayon filament, the number of twists was maintained at 94 % at 120℃ for 2 min of steaming without pre-treatment while the strength decreased to 85 %. The most desirable stretching property was achieved by the multi-twisting at 400 r/m of ten paper yarns, followed by high-pressure steaming. X-ray diffraction and CP/MAS ^{13}C-NMR revealed that the crystallinity was increased 2 %, and the width of cellulose micelle was much larger by high-pressure steaming. I_β type rich crystals of Manila hemp cellulose were stable at the steaming condition, so little transformation of the crystal type was observed. However, the orientation of the crystal was slightly improved by high-pressure steaming. It was considered that the mechanism of permanent shape memorization was derived from some recombination of the hydrogen bonds in the crystal region. High-pressure steaming was effective in the shape memorization of cellulosic fabrics and then the method improved the stretching property of textile made of multi-twisted paper yarns.

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1. Introduction

The use of environmentally-friendly materials is considered to be an important factor in the creation of a harmonious global environment. Cellulose materials such as cotton and linen are widely utilized as natural textile fabrics.

Recently, “paper yarn” has received attention as a new cellulosic textile material. Paper yarn is made from Manila hemp whose physical strength is 1.2 times that of ordinary hemp and has good anti-weather ability [1]. The paper for yarn is made by pulping, beating and paper manufacturing. The paper is then cut into 1-2 mm width and twisted to form yarn. Paper yarn has several advantages, such as lightweight and low static electricity, which are suitable for textile fabrics.

However, the textile fabrics wove by paper yarn wrinkles easily and the softness and stretching properties are low. We attempted to improve the stretching property of paper yarn by high-pressure steaming and to clarify the mechanism of shape memorization. The high-pressure steam method was developed in our laboratory, and has been applied to some materials, e.g., woody materials, cotton, rayon, wool and silk, for the purpose of permanently stabilizing their shapes [2-5]. This method employs only water and heat, which is also in accord with environmentally-friendly method.

It is expected that the shape memorization will contribute to inducing the stretching property of paper yarn. However, the degradation will supervene by high-pressure steaming due to high temperature. Therefore, the present work investigated the prevention of degradation with pre-treatments by soaking in water or NH_3 aqueous solution before steaming. It is thought that the improvement of stretching property was difficult to make only by increasing the number of twists for one string of paper yarn. Thus, the effect of multi-twisting and the following shape memorization induced by high-pressure steaming was investigated in this report. Furthermore, the mechanism of shape memorization was investigated by searching for changes of the crystallinity, the crystal form and the width of cellulose micelle.

2. Experimental

2.1 Materials

Two types of paper yarn were supplied from KAWABO Co., Ltd. One was 264 denier paper yarn produced by 800 r/m of twisting Manila hemp paper in the S-direction. The other was 290 denier produced by 700 r/m of twisting Manila hemp paper and about 20 % of 70 denier rayon filament in the Z-direction, hereby referred to as paper/rayon yarn. 28 % NH_3 aqueous solution was purchased from Nacalai Tesque, Ltd.

2.2 High-pressure steam treatment

Post-treatment for shape memorization was conducted in a high-pressure steam apparatus HTP 40/60 manufactured by Hisaka Works, Ltd. and our laboratory. The paper yarns were treated by high-pressure saturated steam at 130-180℃ (0.38-1.12 MPa) for 2 min. Out of these, two kinds of pretreatments were applied ; one soaking in water, and the other soaking in 0.28 % NH_3 aqueous solution. The paper/rayon yarn was treated by high-pressure saturated steam at 110-160℃ (0.23-0.73 MPa) for 2 min without pre-treatment.

2.3 Tensile strength and elongation

The tensile strength was determined by a multi-strength testing machine (Imada Seisakusho Co., Ltd. SV-55) and Data Logger (Tokyo Sokki Co., Ltd. TDS-601). Tensile strength was measured by the modified method of JIS L 1096, 8.12.1.-A [6]. The sample length and the elongation rate were 20 mm and 20 mm/min, respectively, and the average of five measurements was obtained. The elongation was obtained by the equation.

$$\text{Elongation} = [(L - L_0) / L_0] \times 100\ (\%)$$

Where L_0 and L were the initial and the breaking lengths of yarn, respectively.

2.4 Degree of fixation

The degree of fixation was defined as follows. The paper yarn was cut to 15 cm length, and the number of twists (T_0) was counted. Next, after soaking in water at 24℃ for 3 min under free tension followed by drying on a Teflon sheet, the number of twists (T) was counted. The average number of twists of five different samples were compared, and the degree of twist fixation was obtained as (T / T_0) × 100 (%).

2.5 Production of multi-twisted paper yarn

Ten strings of paper yarn were twisted together by 150 r/m or 400 r/m in the S-direction. To fix the twist, the paper yarn was treated by high-pressure steaming and the shape of twist was fixed at 170℃ for 2 min after soaking

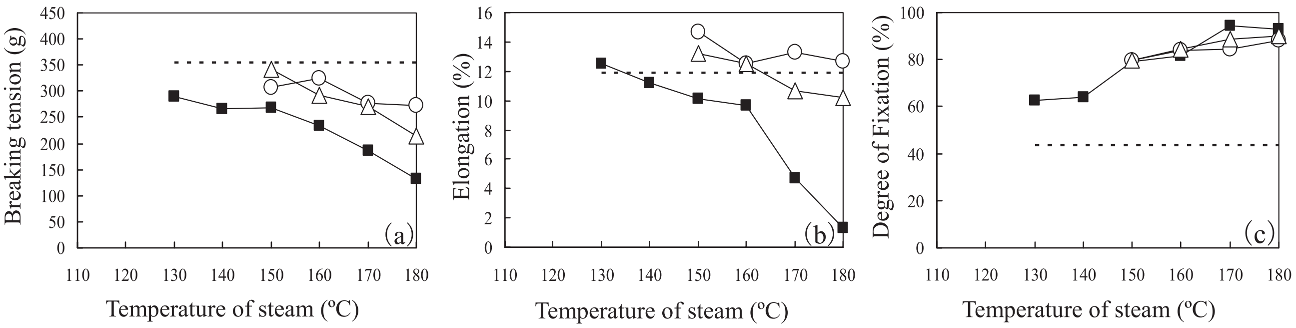

Fig. 1 Physical property of 264 denier paper yarn treated by high-pressure steaming for 2 min. (a) strength, (b) elongation, and (c) degree of twisted fixation (■ : in dry condition, △ : in wet condition, ○ : in wet condition after soaking into 0.28 % NH_3 aqueous solution, --- : value before steaming).

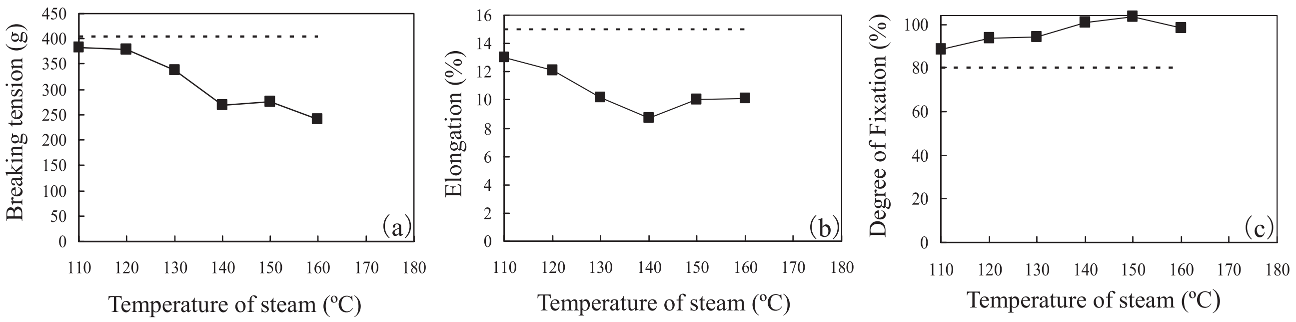

Fig. 2 Physical property of paper/rayon yarn treated by high-pressure steaming for 2 min. (a) strength, (b) elongation, and (c) degree of twisted fixation (--- : value before steaming).

in 0.28 % NH_3 aqueous solution. Untwisted ten-bound paper yarns were also prepared and compared with ten-twisted paper yarns. The tensile strength and degree of elongation of these paper yarns were measured by method 2-3. The stretching property was confirmed also by sensory examination manually.

2.6 X-ray diffraction

X-ray diffraction was measured by X-ray diffractometer (Rigaku Rint 2000/PC) with a vertical goniometer. The wavelength of X-ray was 0.154 nm (Cu $K_{\alpha 1}$ line), and the range of scanning angle (2θ) was 5 to 40 degrees. The degree of crystallinity index (CrI) was calculated by Segal's equation [7].

$$CrI = (I_{020} - I_{am}) / I_{020} \times 100\ (\%)$$

I_{020} : the intensity of (020) cellulose crystal plane

I_{am} : the intensity of amorphous region of cellulose

The width of micelle was calculated by Scherrer's equation [8].

$$D = (K \times \alpha) / (B \times \cos\theta)\ (\text{Å})$$

K : constant = 0.9

α : wave length of X-ray = 1.542 Å

B : half width (rad)

2θ : angle of the peak for (020) plane

2.7 CP/MAS ^{13}C-NMR

The solid state CP/MAS ^{13}C-NMR spectra of paper yarns were obtained by a JEOL JNM-ECA500 spectrometer using a NM-93030CPM probe. Samples were contained in a cylindrical rotor made of zirconia and spun as fast as 1.2 kHz. The contact time was 2 ms, and the repetition time was 5 s.

3. Results and discussion

3.1 Physical properties of paper yarn

Effect of steaming temperature on the physical properties of paper yarn is shown in Fig. 1. Both the tensile strength and the elongation gradually decreased with increasing temperature of high-pressure steaming. On the contrary, the degree of fixation increased. The high temperature is effective for the fixation of shape memorization, but induces a partial hydrolysis of amorphous region of cellulose.

Consequently, performing the pre-treatments by soaking in water or 0.28 % NH_3 aqueous solution inhibited tensile strength and elongation from decrease. In this way, the high degree of fixation was maintained at the highest steam temperature. It was found that the pretreatment by soaking in 0.28 % NH_3 aqueous solution is more effective than in water for avoiding the hydrolysis of cellulose, because cellulose is stable in mild alkali conditions. The elongation of steam treated yarn was higher than the untreated one. These results showed that the high-pressure steam treatment of paper yarn is preferable for textile fabric.

The result of the physical properties of the paper/rayon yarn is shown in Fig. 2. The tendency of steaming was similar to paper yarn. However, the fixation effect for paper/rayon yarn appeared at a lower temperature than that of paper yarn, i.e., 94 % of fixing of paper/rayon yarn achieved by steaming at 120℃ for 2 min. This means that rayon filament in paper/rayon yarn was effective for shape fixation at low temperature without soaking in 0.28 % NH_3 aqueous solution which suggests that the rayon assisted the memorization of overall paper yarn.

3.2 Stretching property of paper yarn

To improve the stretching property of paper yarn, some procedures were examined : (1) increasing the number of twists (for example 400 r/m) and fixing the shape, (2) converting to coiled shape by winding around a stainless wire (for example 1 mm diameter) and fixing the shape, (3) twisting two strings of paper yarn together and fixing the shape, and (4) twisting ten strings of paper yarn together and fixing the shape. Their stretching properties were observed by sensory examination manually. As a result, method (1) and (3) brought about the hardening of yarn and decrease of the stretching property. The stretching property of coiled yarn produced by method (2) was weak. Finally, method (4) resulted in improvement of stretching property of yarn. Next, method (4) was confirmed by applying three different methods of twisting ten paper yarns : without twisting, and with twisting at 150 r/m or 400 r/m. The results of the tensile strength and degree of elongation are shown in Fig. 3. The

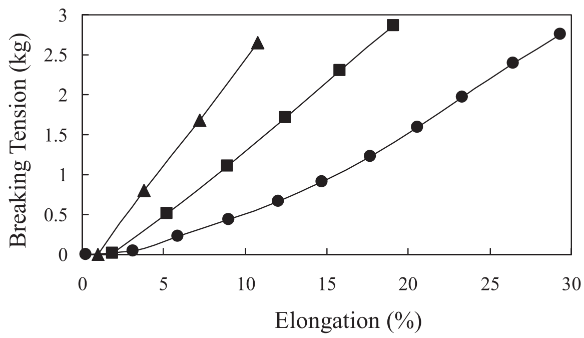

Fig. 3 The strength and degree of elongation of ten-twisted paper yarns (▲ : without twist, ■ : twisted at 150 r/m, ● : twisted at 400 r/m).

improvement of stretching property was achieved by multi-twisting of ten paper yarns at 400 r/m. It was found that both the multi-yarns and the number of twists were a major factor for improvement of the stretching property, and the fixing of twists by high-pressure steaming was a necessary treatment.

3.3 The mechanism of shape memorization

There are four crystal types of cellulose, i.e. I, II, III and IV, and type I is further classified into cellulose I_α and I_β. Native cellulose is constructed of type I crystalline and amorphous regions. The existence ratio between crystalline and amorphous regions, and between I_α and I_β, are each different by natural sources [9]. For example, the cellulose crystal in the integument of Ascidian (*Protochordate*) is mostly cellulose I_β [10]. The cellulose of *Glaucocystis* and *Valonia macrophysa* consisted of a majority of I_α and a minority of I_β [11, 12].

The investigation of crystal region of paper yarn was determined by X-ray diffraction and CP/MAS ^{13}C-NMR spectra. X-ray diffraction of untreated and steamed paper yarns are shown in Fig. 4. It was found that the crystal type of paper yarn was I type crystalline and the crystallinity was increased 2 % and the width of cellulose micelle was much larger after high-pressure steaming as shown in Table 1.

Furthermore, the CP/MAS ^{13}C-NMR spectra indicated that the crystal types of untreated and steamed paper yarns were almost constructed of I_β as shown in their C1 peaks in Fig. 5 [9, 13]. The width of each peak sharpened after high-pressure steaming. Consequently, the shape memorization of paper yarn was induced by high-pressure steam treatment in spite of the unchanged crystal type. In this process, it is thought that the hydrogen bonds are reconstructed in both crystal and amorphous regions.

In common polymer materials, shape memorization occurs owing to the proper cross linkage and crystallinity as observed in the rubber elasticity above the glass transition temperature [14]. Their shapes can be fixed by heating to above the glass transition temperature and subsequently cooling down into a desired mold.

However, the aforementioned mechanism cannot be used to explain the fixing of cellulose in paper yarn because the glass transition is not observed in cellulose. We presume the mechanism of shape memorization of cellulose as follows. The hydrogen bonds in the crystal region are temporarily broken. Thus, the strains in the cellulose are left out [15-17]. After cooling, the new hydrogen bonds are reconstructed to I_β. If there is I_α form in the sample, it is transformed to I_β by breaking and

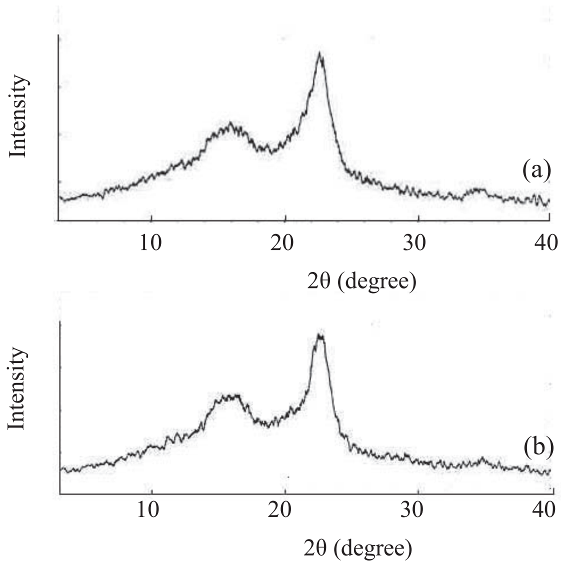

Fig. 4 X-ray diffraction of paper yarn (a) untreated, and (b) high-pressure steamed at 180℃ for 2 min.

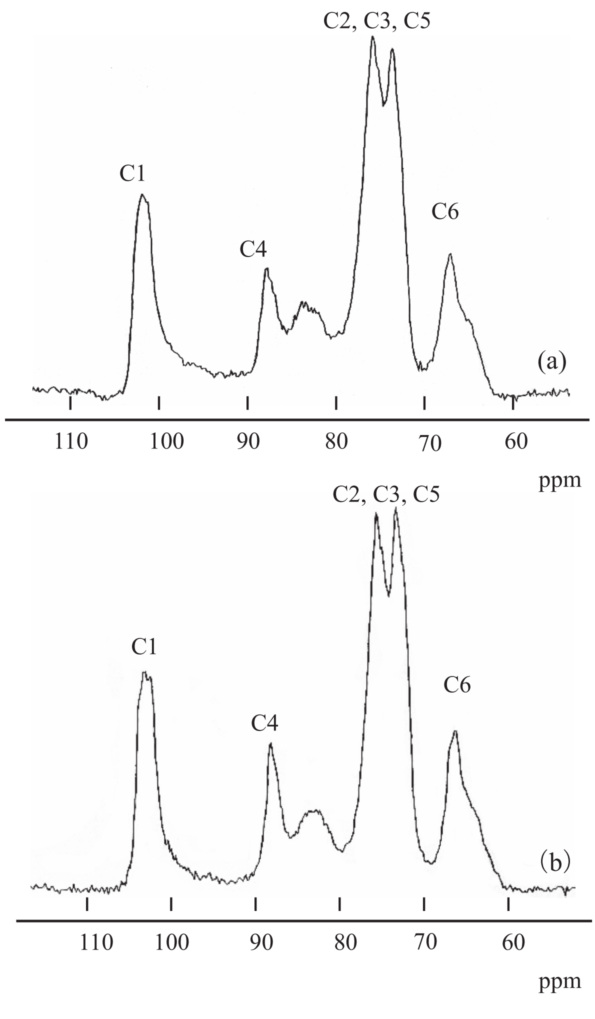

Fig. 5 CP/MAS ^{13}C-NMR spectrum of paper yarn (a) untreated, and (b) high-pressure steamed at 180℃ for 2 min. Letters show the carbon numbers of glucose unit.

Table 1 The crystallinity and micelle width of cellulose in paper yarn determined by X-ray diffraction.

	Crystallinity	Micelle width
Untreated	74 %	6.8 nm
Steamed at 180 ºC for 2 min	76 %	8.0 nm

reconstructing the hydrogen bonds because I_β are more stable form than I_α [10, 13]. On the other hand, a part of amorphous region of cellulose translates to the crystal region through the high-pressure steam [18]. Also for paper yarn, the aforementioned mechanism may cause the shape memorization.

4. Conclusions

It was revealed that the high-pressure steam method induced the permanent shape memorization of paper yarn and improved the stretching property to multi-twisted paper yarn. 84 % degree of shape memorization was achieved for paper yarn by high-pressure steaming at 170℃ for 2 min with pretreatment by soaking in 0.28 % of NH_3 aqueous solution. For paper yarn twisted with rayon filament, 94 % degree of shape memorization was achieved at 120℃ for 2 min steaming without pretreatment. The method of combining the ten-twisting at 400 r/m followed by steaming was suitable to improve the stretching property of paper yarn. It was revealed that the crystallinity of cellulose increased 2 %, the crystal structure of paper yarn was classified as mostly I_β type and the width of micelle was much larger after high-pressure steaming. The mechanism of shape memorization by high-pressure steaming was considered as the reconstruction of the hydrogen bonds in the crystal region and the amorphous regions.

Accordingly, the high-pressure steam treatment was established as a technology for improving the stretching property of paper yarn. When this technique is successfully used to produce clothes made of paper yarn, it will be possible to obtain desirable features, such as shrinkage reduction after washing, improvement in dimensional stability, comfortableness, etc.

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