Improvement of Tensile Properties of Ramie Yarns by Applying a Winding Machine with Heat Treatment

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ABSTRACT: A winding machine with heat treatment was newly developed to strengthen ramie yarns. During the treatment process, ramie yarn in normal or wet state was wound on a winding machine and passed continuously through a heater at 100 and 150°C, respectively, with different winding speeds and tensions. Higher tensile strength and stiffness of ramie yarn was achieved after heat treatment on wet yarn and winding speed had a significant influence on the tensile properties of yarns. However, a little decline in tensile strength was found for ramie yarns after heat treatment in normal state. This implies that the water-swollened structure of ramie yarn during the heat treatment is crucial in strengthening yarns. In the case of heat treatment on wet yarns, the effect of winding tension on the tensile properties of yarns was studied. It was found that the tensile strengths and Young's moduli of ramie yarns first increased and then reached equilibrium as the winding tension was increased. The crystallinity calculated from X-ray diffraction diagrams showed a slight decrease in heat-treated ramie yarns whereas the crystalline orientation factors had no appreciable change. It was considered that the improved effect was related to the more oriented molecular chains in amorphous region and optimized yarn structure. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 685–692, 2010

Key words: fibers; mechanical properties; modification; supramolecular structures

INTRODUCTION

In the last decade, plant-based natural fibers like jute, flax, hemp, sisal, ramie, and so forth have attracted great importance as load bearing constituents in polymer matrix composites.[1–3] The advantages of plant fibers over traditional reinforcing materials such as glass or carbon fibers are abundant, low cost, light weight, and biodegradable. Moreover, when specific strength and modulus are taken into consideration, plant fibers are competitive well with synthetic fibers used in reinforced composites.[4]

Ramie is a perennial plant native to China, Japan, and the Malay Peninsula. The ramie fiber obtained from the outer part of the stem has been used as a textile fiber for centuries due to their advantages of high tenacity, silk-like luster, and resistance to bacteria.[5] In the past, the applications of ramie have been extensive, as seen in the fields of clothing fabrics, carpets, industrial packaging, and decorative articles. With a greater concern for environmental protection, ramie fibers are furthermore considered as a potential alternative to the synthetic fibers currently used as reinforcement in engineering composites. Recently, varieties of ramie fiber-reinforced composites have been successfully developed and tested.[6–9] Despite excellent properties and diverse applications of ramie fibers, in most cases, the overall mechanical properties of ramie/matrix composites have not reached those of glass fiber-reinforced composites.[6]

To gain desirable surface or improved mechanical properties, reinforced plant fibers can be modified by physical and chemical methods. Chemical treatments such as pre-impregnation,[10] esterification,[11,12] and silane coupling,[13] can make strong polarized plant fibers more compatible with hydrophobic thermosetting and thermoplastics polymers by introducing a third material. However, chemical methods often have the inherent problems of poor uniformity and reproducibility. Physical treatment, without altering the chemical composition of fibers, is an environmental-friendly technique. It can change the structural and surface properties of fiber and thereby influence the mechanical bonding to the matrix. Physical techniques of surface oxidation activation (corona,[14] cold plasma,[15] ultraviolet treatment, etc.) are known to be very effective in improving the interfacial bonding between fiber and matrix. Unfortunately, the oxidation of the fiber surface always leads to a decrease in the fiber tenacity.[14] Alkali treatment, called mercerization, has been widely

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TABLE I
Physical and Chemical Properties of Ramie Fibers

Density (mg/m^3)	Microfibril angle (°)	Moisture content (wt %)	Chemical composition (wt %)				
			Cellulose	Lignin	Hemicellulose	Pectin	Wax
1.50	7.5	8.0	68.6–76.2	0.6–0.7	13.1–16.7	1.9	0.3

used on cotton textiles for more than one century. At present, substantive work have been done to use mercerization on plant-based fibers as well.[16–18] The optimized fiber structure and improved fiber tenacity can be achieved by applying alkali treatment under isometric conditions or with tensile load.[19,20] Yet, the challenge of this technique is the difficulty of reclaiming alkali solutions. Several other novel physical modification methods have been suggested to improve mechanical properties of plant fibers. For instance, drawing fiber with tension in water is an effective way to enhance the tensile modulus of fibers.[21] To open up fiber bundles into fibers of lesser diameters, heat treatment can endow plant fibers with improved strength characteristics.[22] In addition, a cyclic load application on ramie yarns was found to improve the tensile strength and modulus of ramie yarns remarkably.[23] However, these modification means are carried out only in small batch, which may limit their industrial application.

The overall aim of the work is to explore the possibility of improving tensile properties of ramie yarns by a mechanical and mass-productive method. In this work, a winding machine equipped with a cylindrical heater was prepared, where the yarns could be heated under a proper tension in the continuous movement. The tensile properties of ramie yarns applied by heat treatment in different conditions were investigated. In addition, the inner microstructural changes in ramie yarns by heat treatment were interpreted by X-ray diffraction measurements.

EXPERIMENTAL

Materials

Ramie yarns used in this study, having a fineness of 66.7 tex, were supplied by TOSCO (Type No. 25). The physical and chemical properties of ramie fibers are listed in Table I, which were reported in literature.[20] It was found that the percentage of lignin is very low in the ramie fiber, which is different from other natural fibers.

Heat treatment using a winding machine

The heat treatment on ramie yarns was carried out on a winding machine. A sketch of the winding

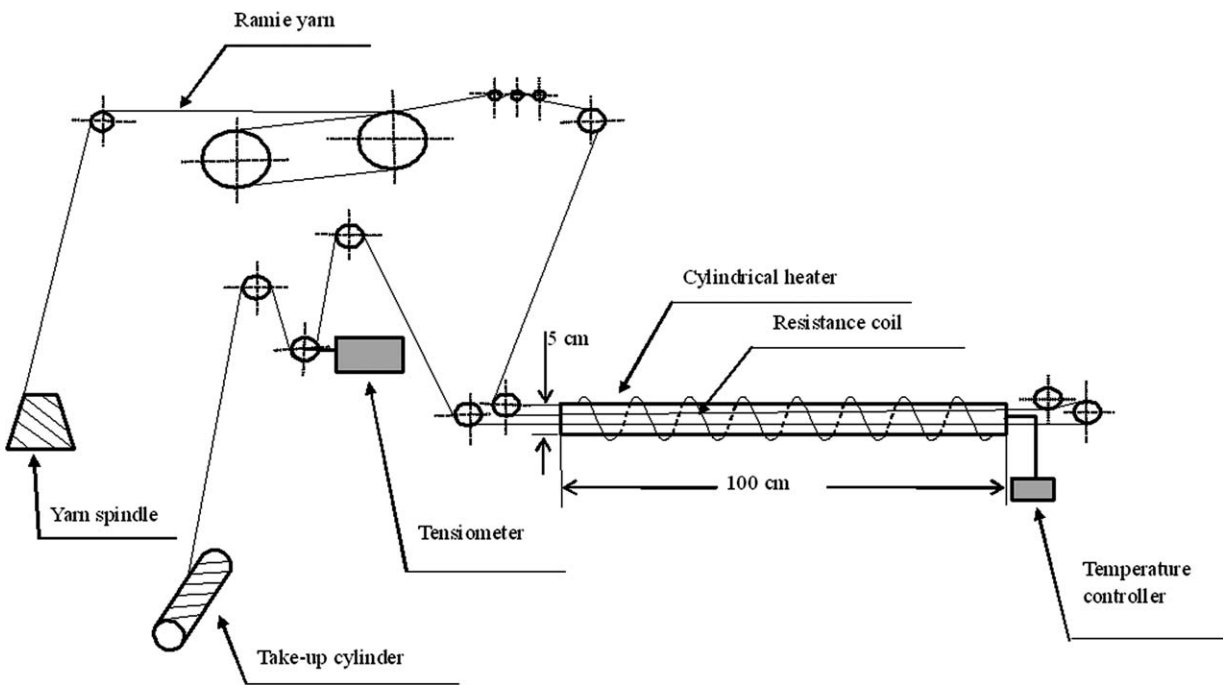

Figure 1 Sketch of winding machine equipped with a heater.

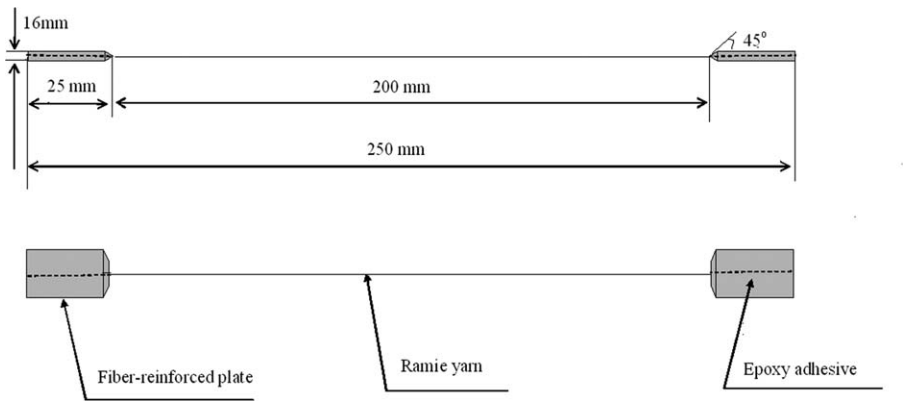

Figure 2 Shape and dimensions of ramie specimen for tensile test.

machine (Kamitsu Seisakusho, Japan) equipped with a cylindrical heater is illustrated in Figure 1. The ramie yarns were wound on the winding machine with a certain tension and passed through the cylindrical heater. The external diameter and length of the heater were 5 cm and 100 cm, respectively. The temperature of the heater was adjusted by the temperature controller. The processing time of the heat treatment could be regulated by adjusting the winding speed. The winding tension of yarn, controlled by the tension spring, was recorded by a tensiometer.

The heat treatment was performed on the normal and wet ramie yarns, respectively. In normal state, the ramie yarns were conditioned in ambient environment. The wet ramie yarns were achieved by winding the yarns without tension on a plastic tube and immersing them in water for 1 day. To avoid the water evaporation during winding process, the wet state was maintained by spraying water into the yarns. The temperature in heat treatment was set at 100 and 150°C, respectively. The winding speed was chosen as 20, 28, 56, 74, and 92 cm/min, respectively, and winding tension was varied from 33 to 167 MPa. For clarification, the normal and wet yarns treated in 100 and 150°C were denoted as NHT100, NHT150, WHT100, and WHT150 samples, respectively.

Oven-drying method was used to test the moisture content of ramie yarns by considering the mass of dried yarns conditioned in the vacuum containers (W_d) and the mass of moisture-absorbed yarns (W_m) as follows:

$$\text{Moisture content } (\%) = \frac{W_m - W_d}{W_d} \times 100 \qquad (1)$$

It was calculated that the moisture content of a ramie yarn sample in ambient environment was 6.66%, whereas a totally wet sample has a moisture content of 96.6%.

After treatment, the samples were put into a desiccator for 1 day and then the tensile properties and structure of ramie yarns were measured.

Tensile test

Tensile tests of ramie single yarns were performed using a tensile testing machine (Shimadzu model EHF-EB10). Before tensile test, both ends of specimens were fixed on fiber-reinforced plates with epoxy adhesive, as given in Figure 2. The cross-head speed used in tensile test was 6 mm/min and the initial gage length for each specimen was 200 mm. The fracture load and strain were measured from the load-displacement curve. At least 10 specimens were tested for each set of samples and the mean values were reported.

Yarn fineness measurement

The yarn fineness was determined by weighing method, in which a single yarn randomly selected from the ramie specimen was cut to a length of 50 mm at a relaxant state and then weighed on a sensitive microbalance.[24] In each case, the average of 30 readings was reported and tex was calculated. The cross-sectional area was then determined from the tex and the density of fiber, and the tensile strength and Young's modulus of a single yarns were calculated from the measured load-displacement curve.

X-ray diffraction measurement

A D/Max-3D diffractometer (Rigaku Corporation, Japan) was used to collect the X-ray diffraction (XRD) diagram of ramie yarn samples with the following components involved: Ni-filtered Cu Ka radiation, 40 kV accelerating voltage, 200 mA anode current intensity. For investigation of the crystallinity, powder diffraction was adopted. Yarn samples were ground in a Wiley mill and then pressed into pellets

of about 1 mm diameter. A 2θ scan was started from 6 to 40°, with a 68/min scanning speed.

The crystallinity index was calculated by the ratio between the crystalline scatter of the (002) reflection, *Crh*, with the height of the "amorphous reflection", *Amh*, as follows[25]:

$$\text{Crystallinity}(\%) = \left(1 - \frac{Amh}{Crh}\right) \times 100 \qquad (2)$$

For investigation of crystalline orientation, the yarn was untwisted and the parallel filament sample was prepared. The crystalline orientation factor was determined from the azimuthal intensity distribution of the equatorial reflections at 22.9° according to the following equation[26]:

$$\text{Crystalline orientation factor}(\%) = \left(1 - \frac{W_{1/2}}{180}\right) \times 100 \qquad (3)$$

where $W_{1/2}$ is the half width of the azimuthal intensity distribution for the meridional reflection at the (002) plane.

RESULTS AND DISCUSSION

Effect of winding speed on tensile properties of yarns by heat treatment

In this work, ramie yarns were heat-treated and kept at a constant winding tension of 122 MPa with different winding speeds and temperatures. As the winding speed was varied from 20 to 92 cm/min, the corresponding processing time was shortened from 600 to 120 s. The curves of the tensile strength as a function of winding speed for ramie yarns untreated and treated in different conditions were illustrated in Figure 3. It was found that the tensile strengths of NHT100 and NHT150 yarns were ~ 1–6% lower than the initial values and had no obvious change with the increase of winding speed. The tensile strength of NHT150 was decreased more than that of NHT100, which is possibly due to the domination of oxidation and chain degradation at higher temperature.

In comparison, the tensile strengths of WHT100 and WHT150 samples have a significant increase of ~ 5–18%. This implies that the water-swollened structure in ramie yarns during heat treatment plays an important role in improving the tensile properties of yarns. As winding speed was increased, the increment of tensile strength of WHT100 samples rose up to 18% at 74 cm/min and then fell slightly. In WHT150 samples, the tensile strength was slightly

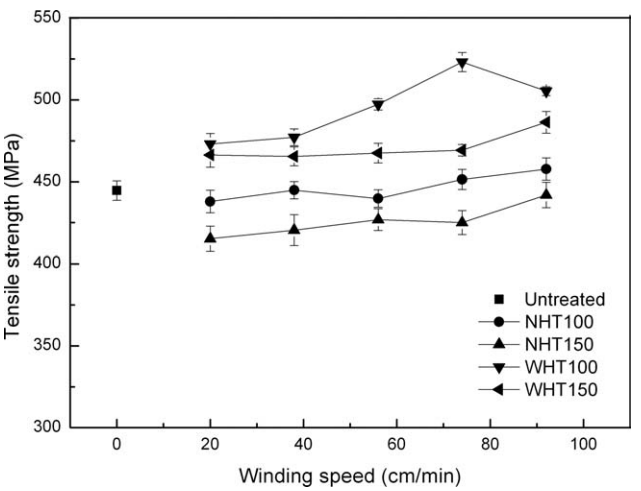

Figure 3 Tensile strength as a function of winding speed for ramie yarns untreated and treated in different conditions.

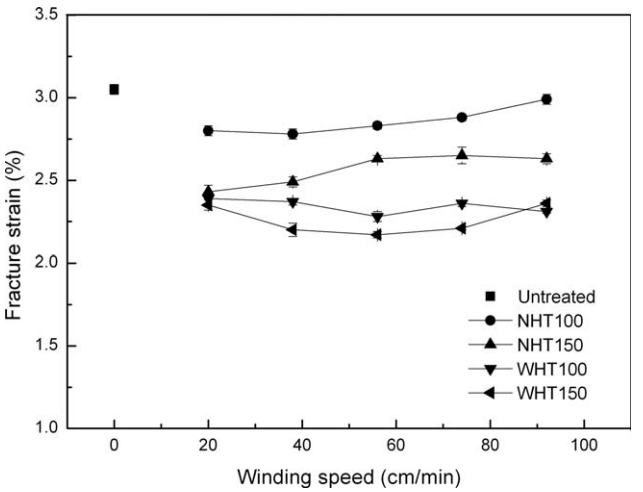

Figure 4 Fracture strain as a function of winding speed for ramie yarns untreated and treated in different conditions.

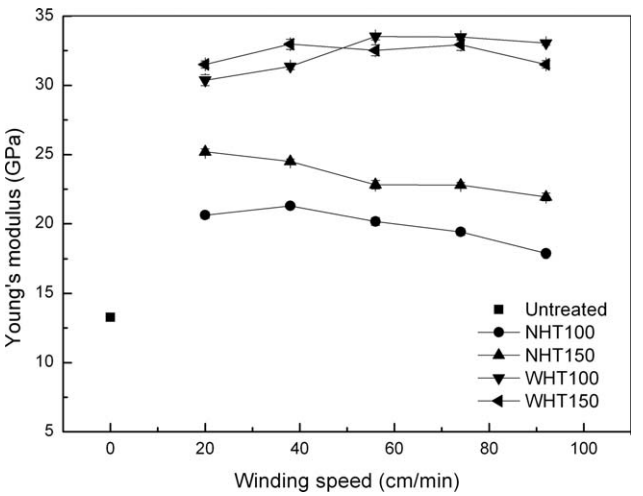

Figure 5 Young's modulus as a function of winding speed for ramie yarns untreated and treated in different conditions.

TABLE II
Data of Tensile Properties of Untreated and WHT100 Ramie Yarns with Different Winding Tensions

Specimen type	Winding tension (MPa)	Cross-sectional area (mm^2)	Fracture load (N) ± SD[a]	Tensile strength (MPa) ± SD	Fracture strain (%) ± SD	Young's modulus (GPa) ± SD
Untreated	0	0.044	19.8 ± 1.6	444.6 ± 37.7	3.05 ± 0.21	13.3 ± 1.7
WHT100	33	0.044	22.0 ± 1.4	498.4 ± 32.6	2.79 ± 0.14	25.5 ± 1.6
	78	0.044	23.2 ± 1.8	524.6 ± 41.2	2.47 ± 0.16	33.6 ± 1.7
	122	0.044	23.0 ± 1.8	521.5 ± 40.5	2.16 ± 0.11	33.8 ± 2.3
	167	0.044	23.3 ± 2.1	529.7 ± 48.1	1.73 ± 0.31	34.0 ± 2.7

[a] Standard deviation.

increased with increasing winding speed. This is probably related to the change of water content at different winding speed because at lower winding speed, namely, longer duration of ramie yarns passed through the heater, water in ramie yarn is evaporated completely and cannot be added conveniently inside the heater immediately.

Figure 4 shows that the fracture strains of all heat-treated samples were decreased slightly. This could be related to the enhanced molecular orientation caused by heat treatment. When a tensile test is performed on such a treated yarn, more microfibrils along the fiber axis would bear the force. However, the molecules would become difficult to move and extend, which could result in a decreased fracture strain. Young's modulus was calculated from the slope of the linear part of the stress–strain diagrams. It can be seen from Figure 5 that the Young's modulus has a remarkable increase for all heat-treated samples. An increase of about 34–89% in Young's moduli was obtained for NHT100 and NHT150 samples. And the increase in their Young's moduli was declined as increasing winding speed. The Young's modulus of WHT samples increased more than that of NHT samples, having an increase of about 129–152%.

Effect of winding tension on tensile properties of yarns by heat treatment

From the above study, the tensile strength of WHT100 ramie samples reached a maximum with the winding speed of 74 cm/min. In this case, the effect of different winding tensions on the tensile properties of WHT100 samples was investigated and the results were shown in Table II. It was found that tensile strengths and Young's moduli of WHT100 samples were increased with increasing winding tension and then leveled off, whereas their fracture strains experienced some decrease.

The mechanical properties data after 3 months of storage were added in Table III. It can be seen that compared to the yarns treated immediately, the tensile strength and Young's modulus of treated yarns after 3 months of storage had decreased a little. However, the mechanical properties data were still higher than those of untreated yarns.

Figure 6 shows the typical stress–strain diagrams of the untreated and WHT100 samples with different winding tensions. As seen in the figure, the slopes of the stress–strain relation for ramie yarns after heat treatment with tension were obviously raised. Higher winding tension leads to a steeper slope but the high tensions of 78, 122, and 167 MPa resulted in almost overlapped stress–strain curves.

Structural change

The X-ray diffraction diagrams of untreated and WHT100 ramie yarns with different winding tensions are shown in Figure 7. Similar crystalline forms can be seen for ramie yarns untreated and treated, all of which have three characteristic diffraction peaks at $2\theta = 14.9°$, $16.7°$, and $22.9°$, corresponding to the (101), ($10\bar{1}$), and (002) planes of cellulose. However, the (002) peaks for WHT100 samples became weaker than that of untreated samples.

The crystallinity index reported in Table III shows that compared to untreated yarns, the crystallinity of

TABLE III
Data of Tensile Properties of WHT100 Ramie Yarns with Different Winding Tensions After 3 Months of Storage

Winding tension (MPa)	Cross-sectional area (mm^2)	Fracture load (N) ± SD[a]	Tensile strength (MPa) ± SD	Fracture strain (%) ± SD	Young's modulus (GPa) ± SD
33	0.044	21.0 ± 1.7	477.3 ± 38.6	2.81 ± 0.12	22.1 ± 1.4
78	0.044	22.1 ± 1.6	502.3 ± 36.4	2.54 ± 0.15	30.4 ± 2.1
122	0.044	22.3 ± 1.2	506.8 ± 27.3	2.19 ± 0.11	29.6 ± 1.5
167	0.044	22.4 ± 1.3	509.1 ± 29.5	2.03 ± 0.20	27.3 ± 1.8

[a] Standard deviation.

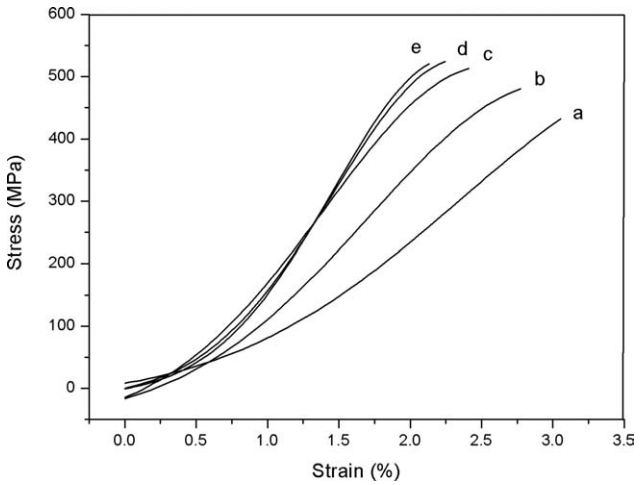

Figure 6 Typical stress–strain diagrams of untreated and WHT100 ramie yarns with different winding tensions: (a) untreated; (b) tension of 33 MPa; (c) tension of 78 MPa; (d) tension of 122 MPa; (e) tension of 167 MPa.

WHT100 samples were lowered slightly. This is reasonable because water and heat at 100°C would not have any impact on crystalline phase in the microstructure of fiber. Water goes to amorphous phase only. Because of swelling of surrounding amorphous phase, the crystallinity of WHT100 samples could have a slight decrease. In addition, no obvious change in crystalline orientation factor between untreated and treated samples can be seen from Table IV. This could be attributed to the highly oriented structure and nonthermoplastic characteristic of ramie yarns.

From the results of the aforementioned tensile test and X-ray diffraction measurement, both tensile strength and Young's modulus of WHT100 samples were improved significantly compared to untreated

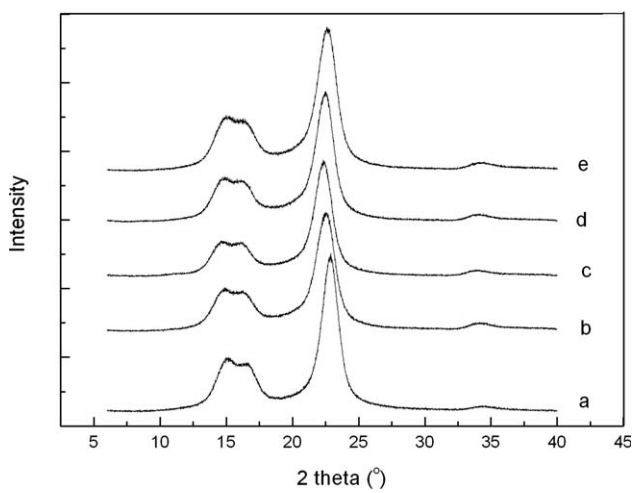

Figure 7 X-ray diffraction patterns for untreated and WHT100 ramie yarns with different winding tensions: (a) untreated; (b) tension of 33 MPa; (c) tension of 78 MPa; (d) tension of 122 MPa; (e) tension of 167 MPa.

TABLE IV
Crystallinity and Orientation of Untreated and WHT100 Ramie Yarns with Different Winding Tensions

Specimen type	Winding tension (MPa)	Crystallinity (%)	Crystalline orientation factor (%)
Untreated	0	87.7	97.7
WHT100	33	84.6	97.7
	78	87.0	97.8
	122	86.1	97.8
	167	85.7	97.9

yarns while their crystallinity and crystalline orientation factor had no distinct change. Those results agree to our previous report when ramie yarns were treated by cyclic load application[23] and work of other researchers.[21,26] In the study of Zhang et al.,[26] it was considered that the improved amorphous orientation resulted in the increase of tensile strength and initial modulus of heat-treated Lyocell fibers which is a kind of regenerated cellulose fiber. Yamanaka et al.[21] also reported that the tensile modulus increased two times as that of blank ramie fibers by water treatment and suggested that this increase could be explained by extension of the molecular chains in amorphous region.

The main components, crystalline microfibrils based on cellulose, are connected to a complete layer by amorphous lignin and hemicellulose, where the angle between microfibril and fiber axis is regarded as microfibrillar angle. When a ramie fiber is heated, the thermal movement of molecular chains can be accelerated. Meanwhile, the concomitant degradation of lignin and softness of wax can take place, leading to the reduced bonding agents in cellulose structure, although their percentage is very low in chemical composition (Table I) and their influence on crystallinity of ramie fiber is negligible (Table IV). This ensures that microfibrils could be stretched more easily under tension. On the other hand, in a water-swollened fiber, because hydrogen bond is broken by water molecules invading into cellulose, the original regular orderly cellulose structure is destroyed and cellulose molecules are permitted to move more freely. Consequently, the mass of cellulose is softened and can change shape more easily with an application of force. In this way, through applying a tension along the fiber axis on wet fiber at high temperature, the molecular chains can be rearranged more uniform and microfibrils can be extended and tilted to the fiber axis. Accordingly, a decreased microfibrillar angle and more oriented cellulose chains in amorphous region could be achieved, accounting for the enhanced tensile results.

The mechanical properties of a yarn are governed not only by the individual fibers made available by the frictional hold but also by its bulk and twist. In

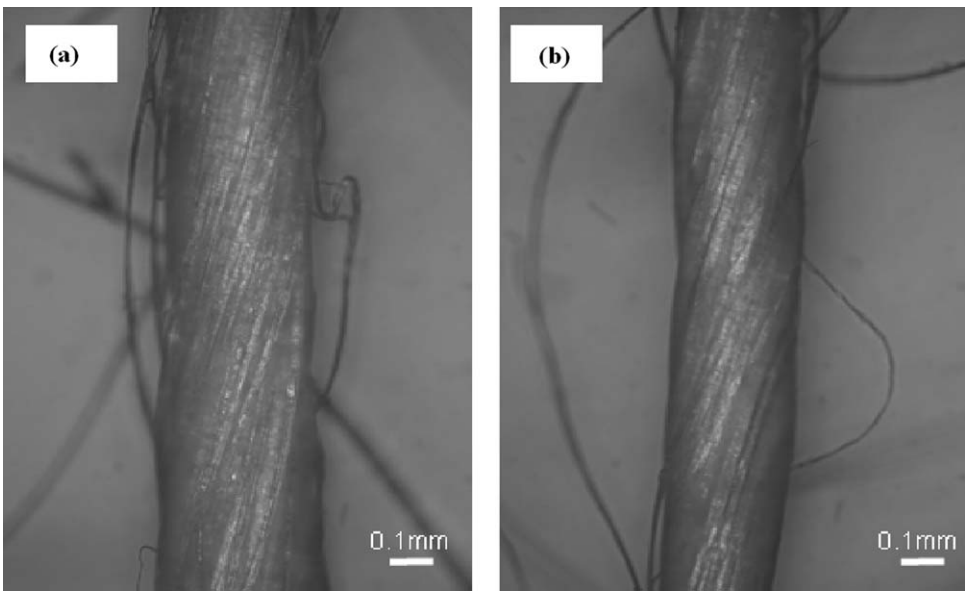

Figure 8 Microphotographs of ramie yarns under the magnification of 10×: (a) untreated and (b) WHT100 sample with winding tension of 74 cm/min and winding tension of 122 MPa.

this study, ramie yarn is composed of hundreds of monofilaments twisted together. The twist angle, namely, the angle between fiber and yarn axis, is expected to decrease resulting from the extension of yarn under the axial tension in the same way as constituent fiber. This is confirmed by microphotographs using an optical microscope (Nikon Eclipse ME 600, Japan) taken for untreated and WHT100 samples, as shown in Figure 8. It was also found that after heat treatment with tension, ramie yarn became slightly thinner and more even in density. Therefore, if such a yarn is placed between the grips of tensile testing machine, a smaller twist angle ensures more monofilaments along the yarn axis to bear the force and a higher degree of regularity present in the yarn lowers the chances of the weakest points to occur.

CONCLUSIONS

A winding machine equipped with a heater was fabricated in this study with an aim of improving tensile properties of ramie yarns. Heat treatments at 100 and 150°C with different winding speeds and winding tensions were carried out, respectively, on normal and wet yarns.

Tensile results showed that compared to untreated ramie yarns, the tensile strength of yarn treated in wet state at high temperature had an increase of ~ 5–18%. After the same heat treatment was performed on the yarns in normal state, however, their tensile strengths were even worse than initial values of untreated yarns. This indicates that the water-swollened structure in ramie yarns during heat treatment plays an important role in improving the tensile properties of yarns. Young's moduli of all heat-treated yarns were enhanced remarkably, with an increase of ~ 33–152%. Ramie yarns heat-treated in wet state had evidently higher modulus values than those treated in normal state. Winding speed had a significant influence on the tensile properties of heat-treated ramie yarns. In the case of ramie yarns treated in wet state at 100°C, as increasing the winding tension, the tensile strengths and Young's moduli of yarns were first raised and then leveled off. XRD results revealed that the crystallinity of heat-treated ramie yarns is decreased slightly whereas their crystalline orientation factors have little been affected. It could be explained that the improved tensile properties were correlated to more oriented cellulose chains in amorphous region, smaller microfibrillar angle, and more uniform yarn structure.

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