

Thermal Conductivity of Ramie Fiber Drawn in Water in Low Temperature

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ABSTRACT: To understand the effect of extension of molecular chain in amorphous region in polymer fibers to thermal conductivity, the thermal conductivity, tensile modulus and crystal orientation angle of ramie fibers and those drawn by the stress of 17.4 kg/mm² (water treatment) in the water were investigated. The tensile modulus of ramie fiber in fiber direction increased from 61 to 130 GPa by drawing in the water. The crystal orientation angles of ramie fiber with and without water treatment were measured by X-ray diffraction. The orientation degrees of ramie fibers without and with water treatment were estimated as 92.9 and 93.6%, respectively. Therefore, the tensile modulus increases two times as that of blank ramie by water treatment although crystal orientation angle does not change distinctly. The increasing of tensile modulus of ramie fiber by water treat-

ment was explained by extension of the molecular chains in the amorphous region. Thermal conductivities of ramie fibers with and without water treatment were measured in the fiber direction in the temperature range from 10 to 150 K. Thermal conductivity of ramie fiber in the fiber direction increased by water treatment. The increasing ratio of thermal conductivity by water treatment agreed to that of sound velocity induced by increasing tensile modulus. Those results suggest that thermal conductivity of polymer fiber increase by the extension of molecular chains in the amorphous region. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2196–2202, 2006

Key words: thermal conductivity; ramie; sound velocity; drawing in water; amorphous

INTRODUCTION

In applications of polymeric materials, the thermal conductivity has been an important property, for example, for a cool/warm sensation for clothing fiber or wood products, or in the thermal insulation of plastics, including styro-forms.^{1–4} With the recent development of superconducting and electronic engineering technologies, the thermal conductivity of structural and insulating materials used as composites in cryogenic and heat-releasing materials in electrical equipment has become more important. Furthermore, the desired features vary, depending upon the application, from insulation for use in cryostat⁵ to high-thermal conductivity for use in superconducting coils⁶ and electronic engineering.⁷ Investigation of the factors that affect the thermal conductivity of polymeric materials is essential to enable the formation of technologies for designing polymeric materials that possess the required thermal conductivity.

From previous studies of polymeric materials, it is well-known that the thermal conductivity of amorphous polymers is smaller than that of metals and semiconductors.^{8,9} Therefore, these have principally been used as heat insulators. The thermal conductivity of electrical insulators is considered to be attributable to phonons,^{10,11} and the heat in polymers is conducted in the direction of covalently bonded molecular chains, whereas conduction in the direction to intermolecular chains bonded by van der Waals forces is much less. It is considered that thermal conduction in amorphous polymer is largely contributed by the intermolecular-chains conduction. On the other hand, thermal conductivity of extended molecular chain is expected to be high in chain axis. In fact, it has been reported that polymeric crystals possess a high-thermal conductivity in the direction in which the molecular chains are covalently bonded regularly, polyethylene crystals being an example.^{10–16} Therefore, the thermal conductivity depends on the crystallization, orientation, crystal size, and defects in the polymer crystal material. Thus, high-crystallization and high-orientation polymers exhibit high-thermal conductivity.^{11–16} For example, highly crystallized polymer materials including high-strength polyethylene fiber^{11,17,18,19} and high-strength polypara-phenylene-

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benzo-bisoxazole (PBO) fiber¹⁷ are known to possess high-thermal conductivity similar to that of metals. Therefore, the thermal conductivity depends on the crystal structure or morphology, and it is expected to be possible to control the thermal conductivity.

Ramie fiber is one of the natural cellulose fibers used as the fiber material for clothes as like cotton. It is known that the tensile modulus of ramie fiber increases by drawing in the water (hereinafter water treatment).²⁰ It is reported that the tensile modulus is increased by the increasing of orientation degree of molecular chains in the amorphous region of ramie fiber by water treatment.²⁰ It is also known that the tensile modulus of cotton fiber increases by drawing in the water.²⁰ But, crystal orientation degree also increases by drawing in the water in the case of cotton.²⁰ It is considered that hydrogen bonding inter-chain is cut by water molecules invading into cellulose fiber.²⁰ Thus, the cellulose molecular chains are expected to become easy to move.²⁰ In this state, the cellulose molecular chain is considered to be extended easily by drawing force.²⁰ This increasing of tensile modulus by water treatment is inferred to be caused by orientation of molecular chain by extension in the water.²⁰ In this study, we investigate the thermal conductivity of ramie fibers with water treatment in the fiber direction to effect of orientation of molecular chains in amorphous region on thermal conductivity.

EXPERIMENTAL

Sample

In this work, thermal conductivities of ramie fibers with and without water treatment were measured in the range of low temperature. The sample preparations were described in the following.

Ramie fiber

The ramie fiber samples used in this work were made in China. The ramie fibers were scoured and bleached. The specific gravity and fineness of ramie fibers were 1.5 and 4.3 dtex, respectively.

Ramie fiber drawn in water (water treatment)

Ramie fibers described earlier were dipped into the water and were weighed with 5 g by a single filament (17.4 kg/mm²) in water for 12 h. They were dried by naturally with weighing for 24 h after taking out from water with weighing.

Measurements

First, the tensile modulus of the ramie fibers with and without water treatment were measured to certificate

the extension of the molecular chain by water treatment. And, the crystal orientation angles were measured by X-ray diffraction for estimation of contribution of crystal region to molecular orientation. After those measurements of orientation of molecular chain by water treatment, the thermal conductivities of ramie fibers with and without water treatment were measured. In this section, the measurements are described.

Tensile modulus

The tensile test of a single fiber was carried out on small tensilon TOYO SOKKI UTM-II. The span length was 10 mm, and the cross head speed was 10 mm/min.

Orientation angle

Orientation angle of crystalline phase to fiber axis was estimated by X-ray diffraction. The samples were prepared in the form of a bundle of about 30 filaments in parallel, and they were fixed at the both ends. Rigaku RU-200 (40 kV × 100 mA) was used with X-ray diffraction on Ni-filtered CuK α ($\lambda = 0.1548$ nm). The intensity distribution of (002) diffraction spot was used for estimating orientation angles.

Thermal conductivity

Thermal conductivity (κ) was measured by a steady-state heat flow method.^{17,18,21} The measurements of κ were carried out on the automated measuring system with thermal controller of a Gifford-MacMahon (GM) cycle helium refrigerator as a cryostat.²¹ The fiber samples were prepared by bundling about 6000 monofilaments with length of 25 mm. Both ends of the fiber bundle were fixed by adhesive STYCAST GT. One end of the bundle was attached to the cold stage of a GM refrigerator by mechanical pressing, using indium metal and the adhesive STYCAST GT. A small resistance heater (1 k Ω) was adhered to the other end of the bundle using GE7031 varnish. The intermediate positions where thermocouples were contacted were bound by fine (0.1 mm) Cu wire. Au (Fe: 0.07%)-chromel thermocouples were used as thermometers, which were adhered by GE7031 varnish. The sample space was evacuated to below 10⁻³ Pa by an oil-diffusion pump for heat insulation. The automated measuring system of κ was operated in the temperature range from 10 to 150 K. The measurements were started after keeping the sample space in high vacuum below 10⁻³ Pa for 24 h to dry up the sample. The κ was estimated by the relation $\kappa(\text{mW/cm K}) = (Q/\Delta T)(L/S)$, where Q is the heat flow per second, ΔT the temperature difference between thermometers, L the distance between the thermometers, and S the cross sec-

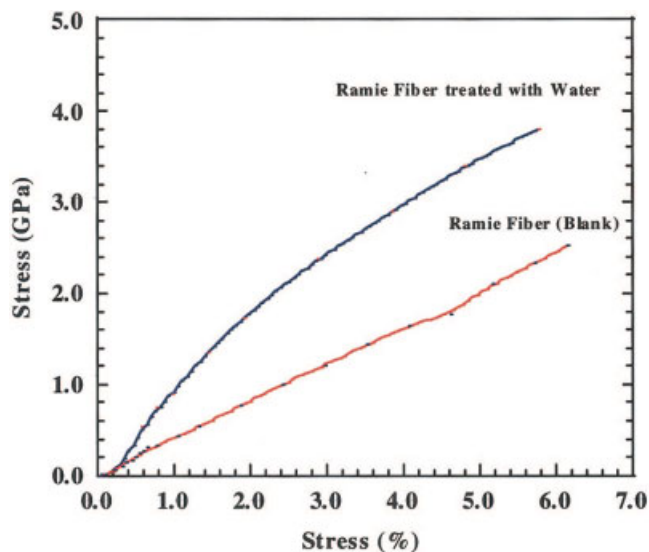


Figure 1 Stress–strain curves of ramie fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion of the bundle. Details of the determination of κ are described elsewhere.^{17,18}

RESULTS AND DISCUSSION

Tensile modulus

The stress–strain (*s–s*) curves of ramie fibers with and without water treatment observed by the tensile test are shown in Figure 1. This figure shows that the tensile modulus and strength of ramie fiber increase by drawing in the water very much. The tensile modulus of those ramie fibers are estimated by the inclinations of the *s–s* curves. The estimated tensile modulus of ramie fiber is 61 GPa and that of water-treated one is 130 GPa. To clear the change of tensile property by water treatment, the tensile modulus of the ramie fibers with and without water treatment are shown in Figure 2. The tensile modulus of blank ramie fiber shown in Figure 2 is almost equal to that reported in previous papers.^{22,23} On the other hand, the tensile modulus of the ramie fiber with water treatment is twice as high as that of blank ramie fiber. This increasing of tensile modulus suggests that the molecular chains are extended and that the contribution of molecular chain to tensile modulus in fiber direction increases by the water treatment. The tensile modulus of ramie fiber with water treatment is almost equal to that of crystal of natural cellulose in chain axis.^{24–26} It is also reported by Abe et al. that the tensile modulus of ramie fiber with water treatment is almost equal to crystal tensile modulus of natural cellulose.²⁰ This result is inferred to be caused by full extension of molecular chain of ramie cellulose by drawing in the

water.²⁰ From those results, the tensile modulus of ramie fiber increases to twice by water treatment, and it suggests the extension of molecular chains of ramie fibers.

To investigate the contribution of crystal orientation to molecular orientation by water treatment, crystal orientation angles and degrees of ramie fibers with and without water treatment are measured by X-ray diffraction in the following section.

Orientation angle

The X-ray diffraction photographs of ramie fibers with and without water treatment are shown in Figure 3. The orientation angles of crystals were estimated by azimuthal intensity distribution of the (002) diffraction spot. X-ray diffraction profiles of (002) spot of the ramie fibers are shown in Figure 4. The half-width of diffraction peak changes not so much by water treatments. The orientation angles are estimated by the half-width of diffraction peak, and the orientation degrees are estimated by using orientation angles in the following formula (1).^{20,27}

$$\phi = [(180 - \beta) / 180] \times 100 \quad (1)$$

In this formula (1), ϕ is defined as orientation degree, and β as orientation angle.

The estimated orientation angles and orientation degrees of ramie fibers with and without water treatment are shown in Figures 5 and 6, respectively. The orientation angle of ramie fiber without water treatment is 12.7°, and that with water treatment 11.5°, respectively. The orientation degrees of ramie fibers

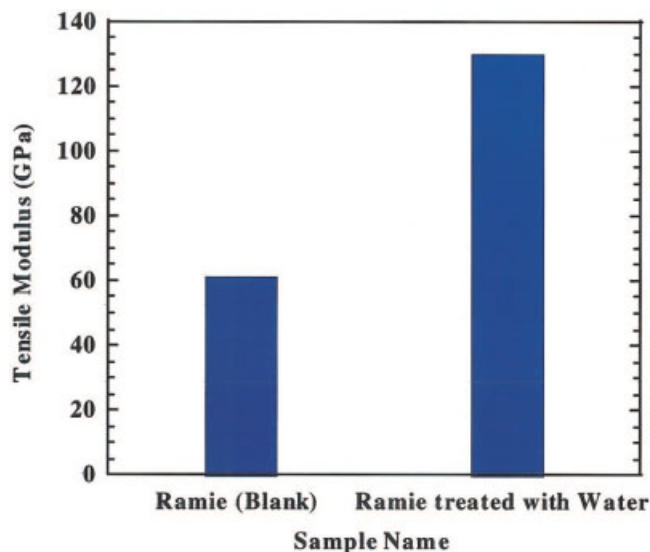


Figure 2 Tensile modulus of ramie fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

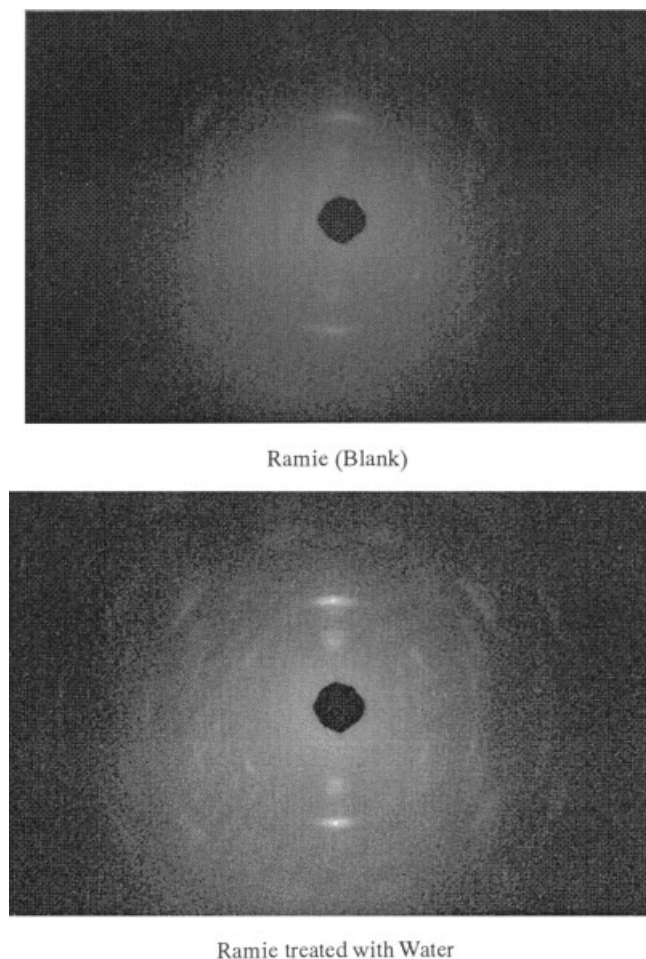


Figure 3 X-ray diffraction photographs of ramie fibers.

without and with water treatment estimated by the formula (1) are 92.9 and 93.6%, respectively. Those results agree to that by Abe et al., which are reported in previous article.²⁰ It is shown that the crystal orientation angle and degree do not change by water treatment. On the other hand, it is reported that the orientation degree of crystal increases by water treatment in the case of cotton fiber.²⁰ In the case of ramie fiber, the crystal is highly oriented in blank fiber. Therefore, it is considered that the orientation degree of crystal region increases not so much by drawing in the water.²⁰

With above-mentioned tensile test and X-ray diffraction, the tensile modulus increases two times as that of blank ramie by water treatment although crystal orientation angle does not change distinctly. Those results agree to the report by Abe et al.²⁰ In this study,²⁰ it is considered that the molecular chains in the amorphous region are extended by water treatment and that those extended chains contribute to the increasing tensile modulus. In the case of cotton fiber, which is natural cellulose fiber composed of Cellulose-I type crystal as like ramie fiber, it is known that

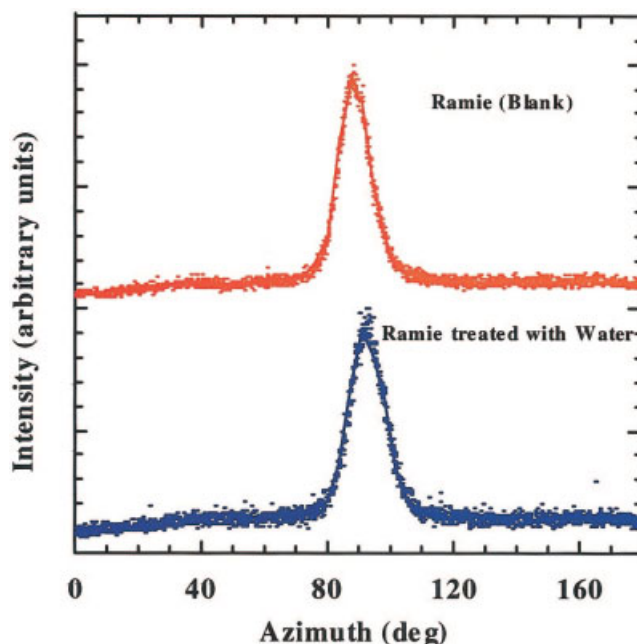


Figure 4 X-ray diffraction profile of ramie fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

spin-lattice relaxation time of ^{13}C of amorphous peak in C4 resonance in solid-state NMR spectrum becomes longer by water treatment.²⁰ It suggested the decrease of molecular motion of amorphous region in cotton fiber.²⁰ And, it was reported as an evidence of orientation of molecular chains in amorphous region.²⁰

In the next section, the thermal conductivities of ramie fibers with and without water treatment are investigated in the range of low temperature.

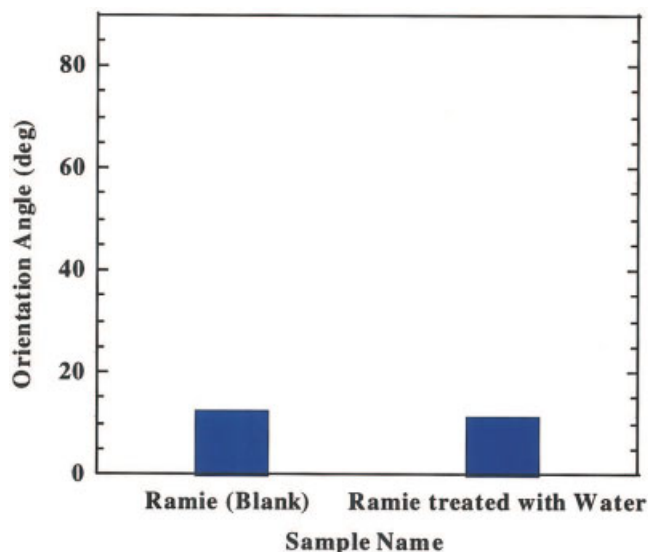


Figure 5 Orientation angles of ramie fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

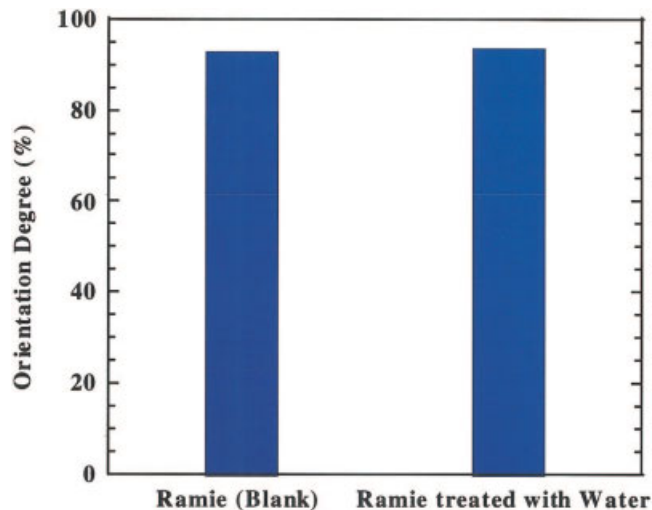


Figure 6 Orientation degree of ramie fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Thermal conductivity

The temperature dependence of thermal conductivities of ramie fibers with and without water treatment in fiber direction from 10 to 150 K is shown in Figure 7. The thermal conductivities of both samples decrease with decreasing temperature. Ramie is an electrical insulator. Therefore, it is considered that thermal conduction of ramie fibers is caused by phonon conduction as like most of polymeric materials.

We investigated the effect of water treatment to thermal conductivity in the following. Thermal conductivity of ramie fiber increases by water treatment

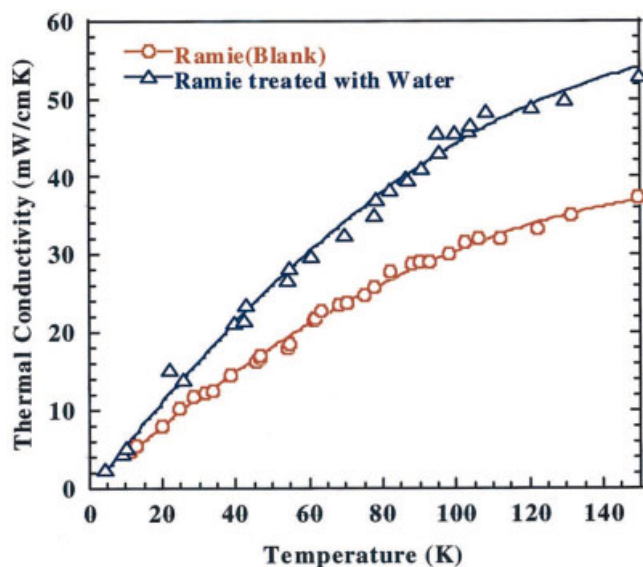


Figure 7 Temperature dependence of thermal conductivities of ramie fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

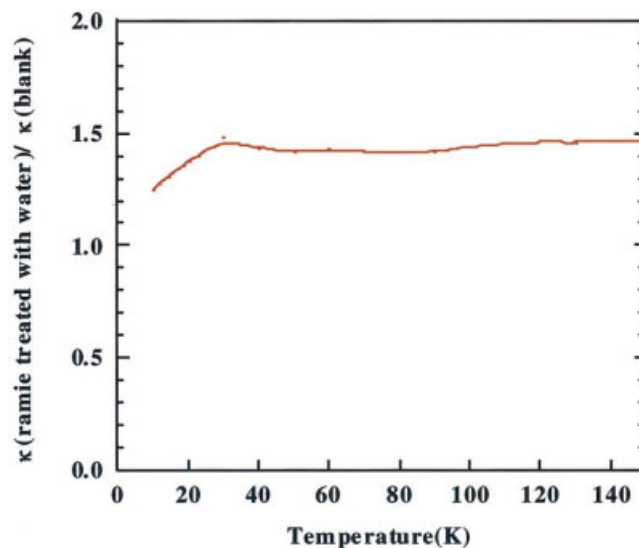


Figure 8 Temperature dependence of the ratio of thermal conductivity of ramie treated with water to that of blank. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

very much. It is inferred to be caused by the extension of molecular chain in the fiber direction with drawing in the water. The increasing of the thermal conductivity of ramie fiber by water treatment is caused by the orientation of molecular chains in the amorphous region since the molecular chains are extended by water treatment in the amorphous region as described earlier.

To compare the thermal conductivity between the ramie fibers without and with water treatment, the ratio of thermal conductivity of ramie treated with water to that of blank is estimated by the curves in Figure 7. Temperature dependence of the estimated results is shown in Figure 8. From this figure, the increasing ratio of thermal conductivity of ramie fiber by water treatment is the range from 1.25 to 1.46. Especially, the increasing ratio is almost constant in the range from 1.40 to 1.46 in the temperature range from 40 to 150 K. The cause of increasing thermal conductivity by water treatment is discussed in the following.

The thermal conductivity is shown in the following formula (2) in the case that thermal conduction is caused by phonon.^{15,17-19,28}

$$\kappa = (1/3)C_p\rho vl \quad (2)$$

In this formula, the parameters are defined as follows: κ , thermal conductivity; C_p , heat capacity at constant pressure; ρ , density of ramie fiber; v , sound velocity in fiber direction; l , mean free path of phonon in the fiber direction.

The thermal conductivities of ramie fiber without and with water treatment are defined as $\kappa(b)$ and $\kappa(w)$, respectively. Figure 8 shows that $\kappa(w)/\kappa(b)$ is almost equal to 1.4 ($\kappa(w)/\kappa(b) \cong 1.4$). The effect of increasing the tensile modulus by water treatment on the thermal conductivity is investigated in this section. In the formula (2), the sound velocity v is contributed by tensile modulus. The relation between sound velocity and tensile modulus is shown in the following formula (3).

$$v = (E/\rho)^{1/2} \quad (3)$$

In this formula, v is defined as sound velocity as like formula (2), E as tensile modulus, and ρ as density of ramie. The ratio of sound velocity of ramie fiber with water treatment to that of blank ramie fiber is shown in the following formula (4) introduced by formula (3).

$$\begin{aligned} v(w)/v(b) &= (E(w)/\rho)^{1/2}/(E(b)/\rho)^{1/2} \\ &= (E(w)/E(b))^{1/2} \quad (4) \end{aligned}$$

In this formula (4), the parameters are defined as follows: $v(b)$ and $v(w)$, sound velocities of blank ramie fiber and ramie fiber with water treatment; $E(b)$ and $E(w)$, tensile modulus of blank ramie fiber and ramie fiber with water treatment; respectively.

The ratio $v(w)/v(b)$ is estimated as 1.46 by substitution of the numerical values of $E(b)$ and $E(w)$ into the formula (4). The numerical value of $E(b)$ and $E(w)$ were used 61 and 130 GPa, respectively. Those values were measured by the tensile test in the front section. The numerical value of $v(w)/v(b)$ ($= 1.46$) is almost equal to the increasing ratio of thermal conductivity by water treatment ($\kappa(w)/\kappa(b) \cong 1.4$). Therefore, the increasing of thermal conductivity by water treatment is inferred to be caused by the increasing of sound velocity.

That is to say, the heat capacity C_p and mean free path of phonon l do not change by water treatment since the crystal size, crystallinity, and crystal orientation angle do not change by water treatment. The increasing of thermal conductivity by water treatment is inferred to be caused by the following. By the water treatment, the molecular chains in the amorphous region are extended in the fiber direction. The extension of molecular chains in the amorphous region induces the increase of the tensile modulus in the fiber direction. And, the thermal conductivity increases by only the increasing the sound velocity induced by the increasing of tensile modulus on the fiber direction.

CONCLUSIONS

Thermal conductivity, tensile modulus, and crystal orientation angles were measured for ramie fibers and those drawn in the water by the stress of 17.4 kg/mm²

(water treatment). And, the effects of thermal conductivity by drawing in the water were investigated. The following conclusions were drawn.

1. The tensile modulus of ramie fiber in fiber direction increased from 61 to 130 GPa by drawing in the water.
2. The orientation angle of ramie fiber did not change by drawing in the water.
3. The increasing of tensile modulus of ramie fiber by water treatment was explained by extension of the molecular chains in the amorphous region.
4. Thermal conductivities of ramie fibers with and without water treatment decreased by decreasing temperature.
5. Thermal conductivity of ramie fiber in the fiber direction increased by water treatment. Therefore, thermal conductivity increases by extension of molecular chains in the amorphous region.
6. The increasing ratio of thermal conductivity by water treatment range from 1.25 to 1.46 in the temperature range from 10 to 150 K, especially, almost constant from 1.40 to 1.46 in the temperature range from 40 to 150 K.
7. The increasing ratio of thermal conductivity by water treatment agreed to that of sound velocity induced by increasing tensile modulus. Therefore, the increasing of thermal conductivity of ramie fiber by water treatment was explained by the increasing of sound velocity with increasing of tensile modulus.

With the above-mentioned, it was found that the thermal conductivity of ramie fiber increased by water treatment. Those results suggest that thermal conductivity of polymer fiber increase by the extension of molecular chains in the amorphous region.

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