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A Comparison between the Thermomechanical and Structural Changes in Textured PET Yarns after Superheated Steam and Dry Heat Treatment

Hale Canbaz Karakaş*

Textile Engineering Department, Istanbul Technical University, Istanbul 34437, Turkey
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Abstract: PET yarns textured at different texturing conditions were treated with superheated steam or dry heat at different temperatures for different times. The effects of the treatment conditions on the thermomechanical and structural changes of the yarn were examined by shrinkage, X-ray diffraction and birefringence measurements. With increase in superheated steam temperature, the crystalline orientation factor and birefringence decreased, whereas crystal size increased. Dry heat treatment had a smaller effect on shrinkage and structural properties in comparison with superheated steam treatment. The additional shrinkage after texturing process was investigated. The effect of heat-setting in both media was more significant at 200 °C. The time dependence of the properties was not linear.

Keywords: Heat-setting, Superheated steam, Dry heat, Polyester, False-twist texturing

Introduction

Superheated steam is used more commonly in textile drying and steaming processes recently [1-3]. Its advantages in comparison with drying with air have been investigated and published in the literature [4-7]. As superheated steaming is used in textile dyeing and finishing industry for heat-setting, dye-fixation and finishing, its effects on the structural properties of fibers need special attention. These effects are also very important in industrial practice. Heat treatment conditions must be adapted to the nature of the polymer and the type of fiber. An effective temperature is defined, which is a function of residence time and presence of molecular lubricants like water or other solvents [8].

The effects of a small amounts of water vapor in superheated steam on the fine structure and dyeing behaviour of nylon 6, nylon 66 and poly(ethylene terephthalate) fibers have been examined at various steaming temperatures and were compared with those of dry heat treatment [9]. In our study, the structural changes in false-twist textured PET fibers subjected to superheated steam at various temperatures and treatment times are investigated and compared to those of the dry heat treatment. The thermally activated structural changes are characterized by shrinkage measurements, x-ray analysis and birefringence measurements. Information about the pretreatment that altered the structure of the fibers and about the behaviour of these fibers in subsequent processes is achieved by the shrinkage of the fiber.

Materials and Methods

304 dtex/30 f PET yarn was textured on a laboratory-type stacked-disc false twist-texturing machine with a single heater and the resultant yarn fineness was 167 dtex/30 f. The texturing speed was kept at 1000 m/min and as the length of the high-temperature heater was only 1 meter, the residence time of the yarn at the heater was 0.06 seconds. Texturing temperatures of 160, 170, 180, and 190 °C were used in order to obtain textured yarns with different mechanical and structural properties [10]. The temperature of the yarn just after the heater was measured with a Luxtron-Transmet temperature measurement system in order to consider the actual temperature of the yarn. The mechanical and microstructural properties of the textured yarns are given in Table 1. The differently textured yarns were treated under unrestrained conditions with superheated steam and dry heat in a laboratory-type HT steamer at a temperature range between 120-200 °C for 4 minutes. The effect of the treatment times were also studied at 2, 4, 6, and 8 minutes. Heat treatment under an unrestrained condition was made as a preliminary study and minimal stress can be applied in the actual manufacture of the polyester fibers.

The shrinkage of the yarn samples was determined according to ASTMN D2259 [11]. The crystalline orientation index and the crystal size was measured using Rigaku Dmax III X-ray diffractometer. CuKα radiation was used along with a Nickel filter for monochromation of x-rays and an alternating voltage of 35 kV with an anode current of 20 mA. The scanning range was $2\theta = 13^{\circ} - 32^{\circ}$ in 0.05° steps for the equatorial scan and the 100 plane was used for azimuthal scanning.

The crystal size was measured using the Scherrer equation [12] using the 100 and 010 peak;

$$C.S. = K \cdot \lambda / \beta \cdot \cos\theta \quad (1)$$

Where;

$C.S.$: Crystal Size
K = Scherrer constant (0.9)
λ = Wavelength of CuKα X-ray (1.54 Å)
β = Width at half maximum
θ = Bragg angle

*Corresponding author: karakashal@itu.edu.tr

Table 1. The mechanical and microstructural properties of the textured yarns

Sample code	Texturing temperature* (°C)	Tenacity (cN/tex)	Crimp contraction (%)	Crystalline orientation index	Crystal size, Angstrom (100)	Birefringence ($\Delta n \times 10^{-3}$)	Boiling Water Shrinkage (%)
T1	160	38.76	24.33	0.829	26.24	0.1580	3,60
T2	170	38.95	28.10	0.837	27.87	0.1609	3,25
T3	180	39.90	34.01	0.848	28.86	0.1630	2,80
T4	190	42.19	34.88	0.885	29.02	0.1672	2,72

*Texturing temperature is the actual temperature of the yarn measured at the exit of the heater.

Crystalline orientation index was calculated from the width at half maximum intensity of the 100 peak, $W_{1/2}$, using the equation:

$$Ico = (180^\circ - W_{1/2})/180^\circ \quad (2)$$

The birefringence measurements were made by using a Leitz polarizing microscope and a Berek compensator.

Results and Discussion

An increase in the draw-texturing temperature of polyester leads to reduction of thermal shrinkage as can be seen in Table 1. This is probably due to reduced residual stress and molecular mobility. The increasing temperature interrupts more and more intermolecular interactions and softens the material; as a consequence yarn stress is reduced. The crystalline orientation index of the yarn increases with increase in the yarn exit temperature. With increase in temperature for any contact time in the heater, the heat input in the yarn increases and the mobility of the macromolecular chains is faciliated. As the temperature increases, the mobility of the polymer segments increase and this allows easier alignment of the polymer segments to the crystals. Therefore, the flexibility of the macromolecules and the motion of structural elements increase. As the stiffness of the filaments will be lower due to the enhanced mobility of the polymer chains, the crystallites will align more easily. It is observed that crystal size increases with increasing heater exit temperature. Smaller and imperfect crystals melt and the growth of bigger crystals is faciliated at higher temperatures.

The boiling water shrinkage of draw-textured PET after treatment with superheated steam is shown in Figures 1, 2, 3, and 4. The boiling shrinkage of textured PET yarns after superheated steam treatment represents the residual shrinkage in the yarn, so it is a measure of the effectiveness of the heat-setting of the final yarn.

A comparison of the initial boiling water shrinkage of textured yarns and yarns treated with superheated steam at 120 °C do not show a significant change for yarns textured at 180 °C or 190 °C at treatment times of 2 or 4 minutes. However, the change is significant at treatment times of 6 and 8 minutes. The effect of the treatment at 140 °C is also

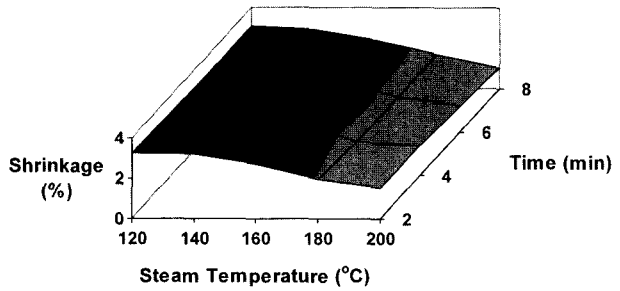

Figure 1. The changes in the shrinkage values of 160 °C textured PET yarns with treatment temperature and time in subsequent superheated steam treatment.

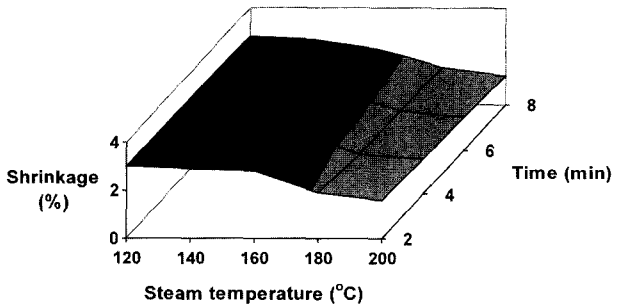

Figure 2. The changes in the shrinkage values of 170 °C textured PET yarns with treatment temperature and time in subsequent superheated steam treatment.

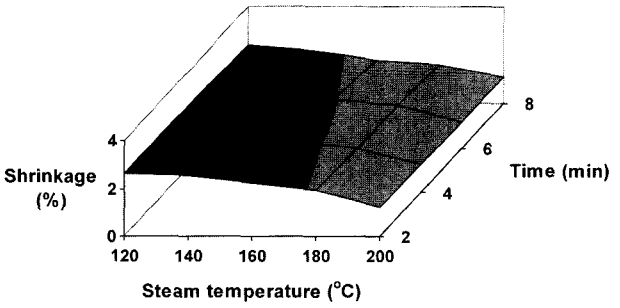

Figure 3. The changes in the shrinkage values of 180 °C textured PET yarns with treatment temperature and time in subsequent superheated steam treatment.

minor at 2 minutes for the same samples T3 and T4, however, it becomes significant at 4, 6, and 8 minutes. This is due to the

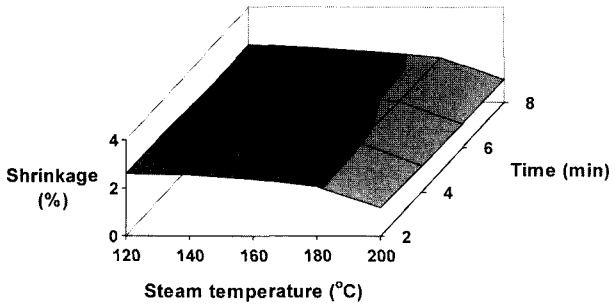

Figure 4. The changes in the shrinkage values of 190 °C textured PET yarns with treatment temperature and time in subsequent superheated steam treatment.

fact that texturing at those temperatures is a much more severe heat-treatment than the treatment at 120 °C and the additional shrinkage after these treatments is small. Therefore, the shrinkage in boiling water does not alter significantly in the case of these samples. The treatment at 160 °C changes the boiling water shrinkage value for T1 (textured at 160 °C) at all treatment times, but its effect is minor for T2, T3, T4 samples textured at higher temperatures (textured at 170 °C, 180 °C, 190 °C) for 2 minutes treatment.

The decrease in residual shrinkage is very clear at 180 °C and 200 °C at all treatment times. As the heat treatment becomes more drastic, the residual shrinkage of the heat-treated fibers decreases. A comparison between the shrinkage values of textured yarns and shrinkage values after heat-treatment shows the need for higher temperatures in subsequent heating in order to obtain a lower shrinkage value. However, it has to be stated that the boiling water shrinkage of the final samples show decrease at all treatment temperatures and times for the conducted experiments, even though minor for lower temperatures and times. The change of shrinkage with time is reflected and it can be observed that the change of shrinkage with superheated steam treatment time is not linear.

Figure 5 and Figure 6 reflect the comparison of shrinkage of PET yarn textured at 160 °C (T1) and the shrinkage of PET yarn textured at 180 °C (T3) after superheated steam

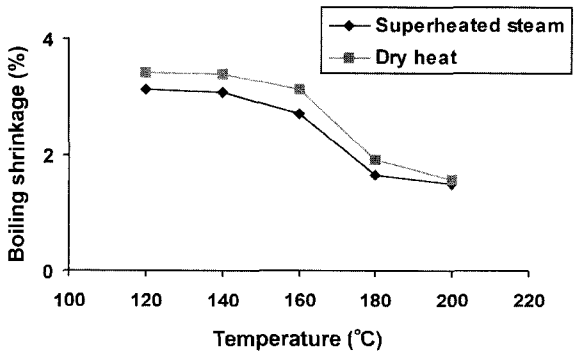

Figure 5. Shrinkage of PET yarn textured at 160 °C (T1) after superheated steam and dry heat treatment for 4 minutes.

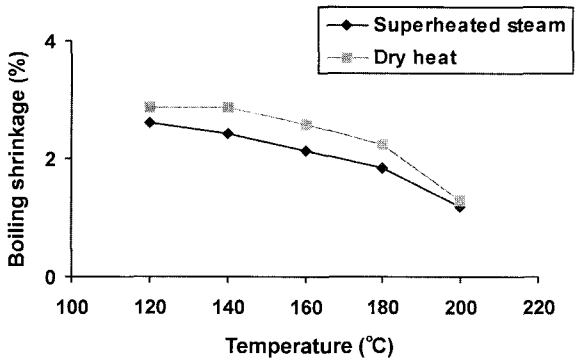

Figure 6. Shrinkage of PET textured at 180 °C (T3) after superheated steam and dry heat treatment for 4 minutes.

and dry heat treatment for 4 minutes. There is a sharp decrease at 180 °C for PET yarn textured at 160 °C for both dry heat and superheated steam treatment. This decrease is seen in PET textured at 180 °C at 200 °C only. These are higher temperatures than the texturing temperatues and the shrinkage difference is smaller for the lower temperatures. Statton *et al.* have shown that the tension in the heat-treatment process affect the extent of microstructural rearrangement [13]. The magnitude of thermal shrinkage increased when an external tension was applied to a fiber during heat treatment as is the case during false-twist draw-texturing process. The same co-workers suggested that allowing crystal reorganization during annealing would decrease the potential for subsequent shrinkage and therefore higher temperatures in subsequent reheating would be required to activate any additional shrinkage [14]. The shrinkage of textured yarn after heat-setting at temperatures above the texturing temperature of the sample cause an additional shrinkage. This will decrease the residual stress and hence the boiling water shrinkage of the heat-set fiber decreases. So, higher heat-setting temperature is required for decreasing the residual shrinkage in textured yarns. Heat-setting at lower temperatures cause less significant decrease in shrinkage. The treatment below texturing temperature, i.e. 120 °C-140 °C, causes a decrease in shrinkage only at longer treatment times. Thermal treatment at lower temperatures can still change the set at longer treatment times. As PET has a rigid chain structure, the short treatment time in texturing is not enough for the fiber to take an equilibrium position. Therefore, a thermal treatment after texturing introduces some mobility and allows the structure to move to equilibrium at longer treatment times. It is also worthy to note that the boiling water shrinkage of samples treated with dry heat and superheated steam became similar at 200 °C. The difference between them is significant at 140 °C, 160 °C, and 180 °C. At 120 °C, the difference is not significant as the effect at that temperature is less.

Fujimoto and Yamashita compared the free thermal shrinkage of drawn nylon 6 filaments treated in super-heated steam and in dry heat and found that thermal shrinkage increased with

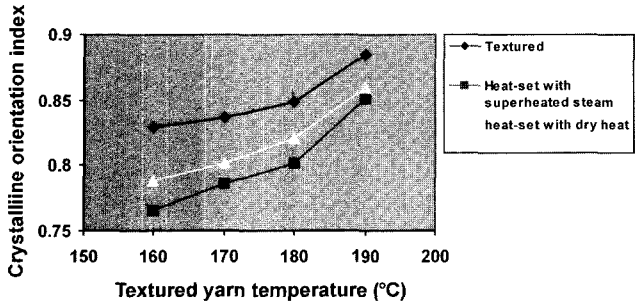

Figure 7. Effect of superheated-steam and dry heat treatment at 200 °C for 4 minutes on crystalline orientation factor of textured PET yarns.

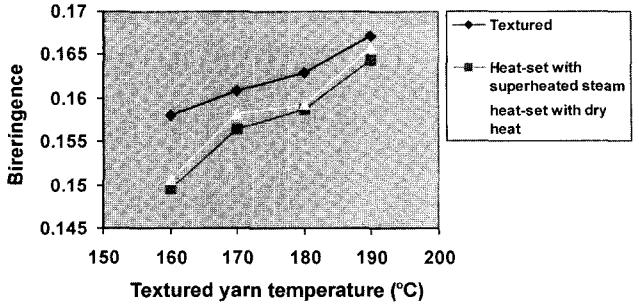

Figure 8. Effect of superheated-steam and dry heat treatment at 200 °C for 4 minutes on birefringence ($\Delta n \times 10^{-3}$) of textured PET yarns.

increasing temperature in dry heat and that it decreased in superheated-steam with a minimum at about 150 °C though the two treatments were similar above 160 °C [15]. The samples treated with dry heat have higher boiling water shrinkage values than the superheated steam treatment. It becomes evident that superheated steam was more efficient in reducing the residual stress. The presence of a small amount of water vapor in superheated steam affects the structure of the fibers compared to dry heat and structural differences are enhanced [9]. It is known that heat-treatment in a free state leads to positive shrinkage (i.e., contraction), more rapid and going further at higher temperatures [16]. Our study also reflects this, however treatment temperatures below the texturing temperature do not cause rapid shrinkage changes.

The effect of superheated-steam and dry heat treatment at 200 °C for 4 minutes on the crystalline orientation index of textured PET yarns is shown in Figure 7. The crytals in textured yarn exhibit higher orientation as a result of the tension during the false-twisting. However, during heat-setting in a free state, deorientation results especially for PET yarns textured at lower temperatures. Therefore, the crystalline orientation values show a greater decrease after setting at 200 °C. The effect of both treatments are similar at texturing temperature of 190 °C, which is close to the heat-setting temperature. Texturing is a very rapid process and the time that the fiber is subjected to mecahnical stresses at high temperatures is usually in the region of 1 second or less. In our study, the residence time of the yarn at the heater is only 0.06 seconds. As PET has a rigid molecular chain, its half-time for crystallization is relatively high. A subsequent heat-treatment releases the locked-in stresses. Therefore, the crystal orientation index is lower after heat treatment.

Effect of superheated-steam and dry heat treatment at 200 °C for 4 minutes on the birefringence of textured PET yarns are seen in Figure 8. Birefringence of treated PET is lower than the textured sample. The observed birefringence in oriented fibers depends on the orientation in crystalline and amorphous regions as well as on the degree of crystallinity. Reduction of birefringence with heating in a free state is a net result of partial disorientation of original crystallites and amorphous regions, possibly accompanied by recrystallization [17]. This is expected as heat treatment results in relaxation of the residual stress and decrease in the overall birefringence. Another factor is incorporation of the non-crystalline chains into the crystals. Authors agree that two mechanisms of molecular change exist, occurring at two distinct kinetic levels. One stage involves rapid processes relating to crystallite reorganization, i.e. the formation of new, more stable crystalline structures by crystallite thickening (regularization of chain folds) and perfection processes. The second level relates to slower processes, involving stress relaxation in the amorphous and intercrystalline regions [18,19]. It can be seen that the birefringence is much lower for yarns textured at lower temperatures. Both dry heat and superheated steam treatments at 200 °C result in similar birefringence values. In superheated steam the yarn will lose moisture to the atmosphere and the effect attained will then tend towards that given by dry-heat setting [20]. Superheated steam contains much less water vapor than high-pressure steam. There is less water vapor present at superheated steaming done at higher temperature and superheated steam at a high temperature behaves the same as dry air [9]. The amount of water vapor contained in superheated steam decreases with increasing temperature.

Effect of superheated steam and dry-heat treatment at 200 °C for 4 minutes on crystal size (Å) calculated based on the 010 and 100 planes of textured PET yarns are seen in Figures 9 and 10. The crystal sizes increase after heat-treatment and the increase is greater for superheated-steaming.

Effect of superheated steam and dry heat temperature on crystalline orientation index (PET yarn textured at 180 °C and heat-set for 4 minutes) is seen in Figure 11. The decrease in the crystalline orientation index on dry heat and superheated steam treatment is greater at elevated temperatures. The decrease at 120 °C is not significant. This is expected as this temperature is far less than the texturing temperature of the yarns.

The change in birefringence and crystal size after heat-setting can be seen in Figures 12, 13, and 14. The birefringence values after both dry heat and superheated steam treatment at 120 °C show very little change when compared with the value

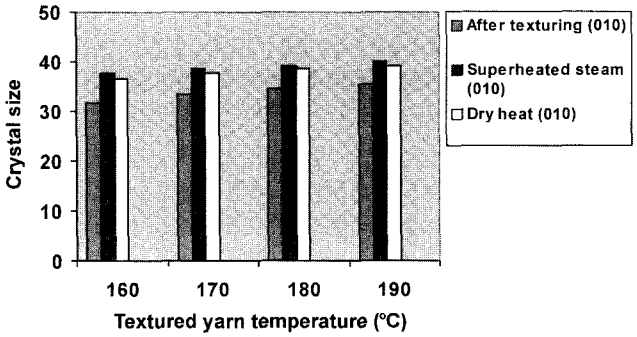

Figure 9. Effect of superheated steam and dry-heat treatment at 200 °C for 4 minutes on crystal size (Å) at (010) plane of textured PET yarns.

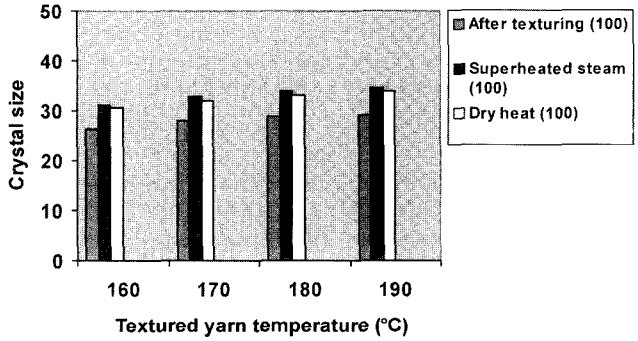

Figure 10. Effect of superheated steam and dry-heat treatment at 200 °C for 4 minutes on crystal size (Å) at (100) plane of textured PET yarns.

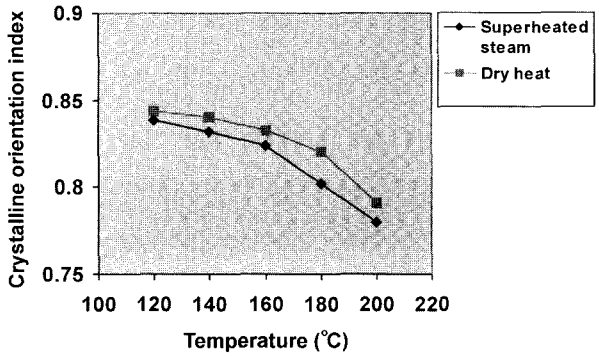

Figure 11. Effect of superheated steam and dry heat temperature on crystalline orientation factor (PET yarn yextured at 180 °C- heat-setting time: 4 minutes).

of the yarn textured at 180 °C. At 120 °C the structure is not affected as it is far below the texturing temperature of the yarns. The difference between dry air and superheated steam is noticeable at 160 °C and 180 °C. However, this difference is very small at 200 °C. This also shows that at these temperatures dry heat and superheated steam acts similarly and their influence is very similar. The change in crystal size of

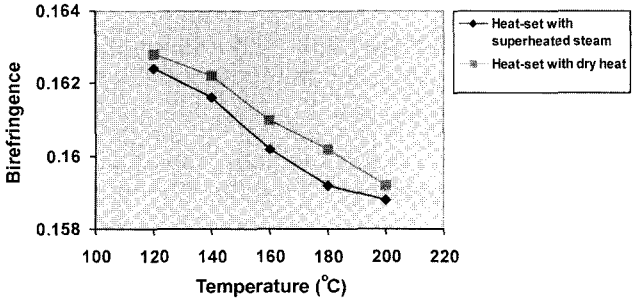

Figure 12. Effect of superheated steam and dry heat temperature on birefringence, $\Delta n \times 10^{-3}$ (PET yarn yextured at 180 °C- heat-setting time: 4 minutes).

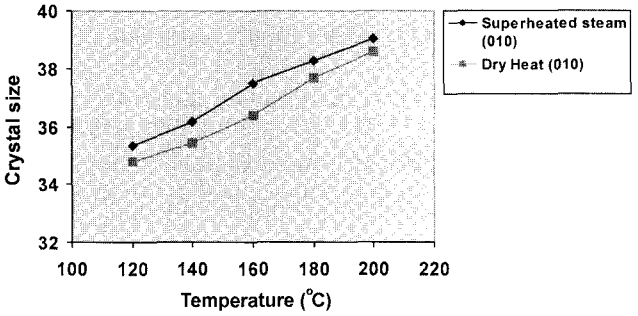

Figure 13. Effect of superheated steam and dry heat temperature on crystal size (Å) at (010) plane (PET yarn yextured at 180 °C- heat-setting time: 4 minutes).

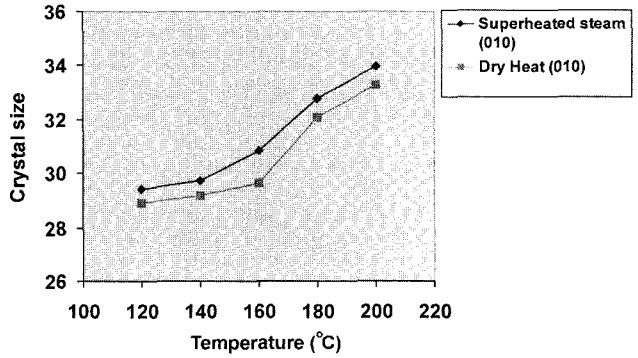

Figure 14. Effect of superheated steam and dry heat temperature on crystal size (Å) at (100) plane (PET yarn yextured at 180 °C- heat-setting time: 4 minutes).

both planes is very little at 120 °C and the difference between the treatments is maximum at 160 °C. The increase in treatment temperature causes increase in crystal size. A very sharp increase is observed at 180 °C. As polyester has a compact and hydrophobic structure, its susceptibility to water in superheated steam is not great. Therefore, greater morphological differences due to superheated steaming could be expected for nylon, where the intermolecular forces between the polymer segments are hydrogen bonding and are more susceptible to the presence of water.

Conclusion

Textured PET yarns were treated with superheated steam at various temperatures for different times. The shrinkage and structural changes were compared with those of the dry heat treatment. It was concluded that higher heat-setting temperature is required to decrease the residual shrinkage in textured yarns at treatment of 2 minutes. Also, higher heat-treatment temperatures than texturing temperature were necessary in order to obtain significantly lower shrinkage value. The boiling water shrinkage of the final samples showed decrease at all treatment temperatures and times for the conducted experiments, even though minor for lower temperatures and times. The dry heat and saturated steam treatment resulted in similar shrinkage values at 200 °C. At this temperature, both treatments behaved in the same way. The crystalline orientation factor and birefringence decreased at higher treatment temperature whereas crystal size increased. Both dry heat and superheated steam treatments at 200 °C resulted in similar birefringence values. The decrease in the crystalline orientation index was not significant at 120 °C, which is far less than the texturing temperatures of the yarn. At elevated temperatures the decrease of crystalline orientation index after dry heat and superheated steam treatment was greater. Investigation of the structural changes in textured yarns after heat treatment with dry heat and superheated steam under a restrained process is thought to be necessary as a further study.

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