Effect of Thermal Treatment on Structure and Properties of Polyester Tire Cords

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ABSTRACT: Polyester and nylon are the mostly used reinforcing textile fibers in many industrial rubber applications. Now-a-days body ply of a passenger car radial is mostly made up of polyester fiber. Because of its thermoplastic nature, it undergoes some kind of thermal shrinkage during processing and vulcanization, which lead to many problems related to shape, dimension, and dimensional stability. To avoid this, polyester is subjected to thermal treatment at higher temperature. Hence, thermomechanical properties of polyester tire cords become very important. During the thermal treatment, there is not only change in shrinkage, shrinkage force, and mechanical properties but also it affects structural and morphological properties. In this work, the changes in thermomechanical properties due to heat setting have been correlated to structural and morphological changes like crystallinity, crystal size, orientation, crystal perfection, etc. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 266–274, 2012

Key words: polyester; heat treatment; X-ray diffraction; differential scanning calorimetry; shrinkage; orientation

INTRODUCTION

Fibers are used as the reinforcing material in most of the industrial and consumer rubber products, which provides strength and dimensional stability. Polyester, nylon cords are the most abundantly used synthetic fibers in rubber products. The intrinsic properties of a fiber are determined by its crystallinity, crystal structure, the degree of orientation, rigidity of molecular chain, and intermolecular forces.¹ The reinforcements take the major share of structural load of a vehicle in case of a tire. To get better performance and durability of a tire, the reinforcing elements should exhibit good strength, fatigue resistance, excellent toughness, dimensional stability, and low-heat generation.²⁻¹⁰ Polyester is the most preferred reinforcing material used as body ply in case of passenger car radial tires; because of their thermal stability, strength, along with cost-effectiveness. Polymeric yarns are processed to form cords prior to their application in tires. Besides the intrinsic properties of the fibers, the external configuration like twist level also has a significant effect on the overall mechanical properties. During running, the temperature of a tire increases due to frictional forces and

hysteresis losses due to viscoelasticity and may reach a temperature as high as 120-130°C.4 Besides this, during rubber product manufacturing the cords may be exposed to vulcanization temperature around 150°C. Hence, the overall performance of a tire gets affected following its processing and operating conditions and adversely affects the dimensional stability of thermoplastic cords like polyester and polyamide, as they undergo shrinkage.^{11,12} Thermal shrinkage affects mechanical as well as creep properties of the cords. So, often these cord materials are subjected to heat treatment at much higher temperature near their melting points and subjected to specified load to reduce residual shrinkage during vulcanization as well as at operating condition. This process is popularly known as heat setting of fiber. Effect of heat setting on physical properties, dye-uptake, viscoelastic behavior, etc., of different thermoplastic cords has been reported in literature.13-18

The present investigation deals with the study on the effect of thermal treatment on different properties of polyester tire cord. The heat treatment was carried out at different temperatures ranging from 150 to 210°C for different time duration. The residual shrinkage was then measured at 150°C for all heat-treated sample. The effect of heat treatment on mechanical properties and shrinkage behavior was studied. The changes in mechanical properties and shrinkage behavior were correlated with the change in crystal structure and fiber orientation.

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EXPERIMENTAL

Materials

Double plied greige (un-dipped) polyester tire cords (polyethylene terephthalate, PET) were obtained through "Birla Tires," India from their commercial supplier. The greige tire cords were of 1500/2 denier and twist of 327–343 (TPM).

The samples are designated either as PETX, where X is the heat treatment temperature without any load or PETXa or PETXb or PETXc, where X represents the heat setting temperature and "a" stands for the case when applied force is less than the shrinkage force, "b" stands for the case when the applied load is equal to the shrinkage force, and "c" stands for the case when applied force is higher than the shrinkage force. PET0 stands for untreated cord.

Shrinkage

Shrinkage force and shrinkage was measured using thermal shrinkage testing machine (S.C. Dey and Co., Kolkata, India) at different temperatures (150, 170, 190, and 210°C). After finding out the shrinkage force at the aforementioned temperatures, thermal treatment was done with and without load at aforementioned temperatures for 2 min. Shrinkage measurement was also carried out during the thermal treatment. For free shrinkage measurement, pretension used was 0.001 g/denier. In case of shrinkage measurement under load, samples were quenched to room temperature under the same load.

Residual shrinkage

Rubber compounds are normally cured at around 150°C to have three-dimensional crosslinked structures. Since tire cords are also exposed to the curing temperature, it is important to know the shrinkage of the previously heat set fibers at curing temperature. Hence, previously heat-treated fibers were again subjected to a temperature of 150°C (curing temperature of rubber) for 5 min. The shrinkage measured at this condition is represented as the residual shrinkage. Residual shrinkage is important to give an idea for retention of dimensional stability of a product during curing.

Density

Densities were measured at room temperature in a density gradient column filled with *n*-heptane and carbon tetrachloride.¹⁹ Crystallinity was measured using the following equation²⁰:

$$\chi_c(\%) = \frac{\rho_c}{\rho} \left(\frac{\rho - \rho_a}{\rho_c - \rho_a} \right) \times 100 \tag{1}$$

where χ_c is the crystallinity, ρ is the density of fiber, ρ_c is the crystalline density (1.455 g cm⁻³), and ρ_a is the amorphous density (1.335 g cm⁻³).

Birefringence

A Leica polarized light microscope with a tilting compensator (Berek type) and light with a wavelength of 546 nm was used to determine the birefringence.

X-ray diffraction

X-ray diffraction (XRD) studies were carried out on a Philips-PW 1729 X-ray generator with Ni-filtered with CuK_{α} ($\lambda = 0.154$ nm) radiation used under a 40 kV voltage and 30 mA current. The diffraction patterns show the variation of intensity versus twice the angle of diffraction, 2 θ , where θ is the Bragg angle. The fibers were kept parallel to each other glued to an adhesive tape in the back as shown in the following schematic image.²¹



The scan profile was decomposed to three crystalline peaks and fitted through Gaussian function for symmetrical peaks using Microcal Origin 7.5 software.²² The area under the crystalline and amorphous peaks was determined in arbitrary units and the percent crystallinity was calculated using the following equation.

$$% Crystallinity = \frac{I_c}{I_c + I_a} \times 100$$
 (2)

where I_c and I_a are the integrated area corresponding to the crystalline and amorphous peaks, respectively.

Interchain separation, *R*, was calculated using the following equation²¹:

$$R = \frac{5}{4} d_{\text{Bragg}} \tag{3}$$

This refers to the main amorphous peak correspond to the angle around $23.2^{\circ}.^{21}$

$$d_{\rm Bragg} = \frac{\lambda}{2\sin\theta} \tag{4}$$

Differential scanning calorimetry (DSC)

The differential scanning calorimetry (DSC) studies of the greige cords were performed on TA Instruments DSC-Q100 under nitrogen atmosphere at a heating rate of 10°C/min. Dry nitrogen gas was purged into the DSC cell with a flow rate of 50 mL/min. The reference was an empty aluminum pan and lid with mass matched to that of the sample pan and lid. The reference pan and lid received no thermal treatment. Indium was employed for the temperature and heat flow calibration. The onset of melting for indium is 156.59° and the heat of fusion (ΔH) is 28.45 J g⁻¹.

Heat of fusion (ΔH) calculated from the melting endothermic peaks was used to calculate the crystallinities of the cords (ASTM E-974) using the following equation²³:

$$X_{\text{thermal}}(\%) = \frac{\Delta H}{\Delta H_0} * 100 \tag{4}$$

Heat of fusion for pure polyester crystals (ΔH_0) is 132 J g^{-1.24}

Tensile properties

Tensile properties of cords were measured on a Hounsfield (KS-10) Universal Testing Machine at 25°C with a gauge length of 150 mm and crosshead speed of 200 mm/min. An average of five test results has been reported, as per ASTM D885.

RESULTS AND DISCUSSION

Thermal shrinkage

During manufacturing, polymeric fibers are formed into molecular structures having highly crystalline and oriented chains in the fiber direction, which is accomplished through series of thermomechanical processes.¹ Orientation results in compact packing of molecules. Although polymeric fibers are highly oriented and crystallized, amorphous regions still exist in the yarns, and these regions significantly influence the cord's material properties. Thermoplastic cords like nylon and polyester when subjected to high temperature exhibit some tendency to shrink. This is because, polymer chains in a fiber yarn are highly crystalline and oriented and the orientation is in the direction of fiber axis making the fiber anisotropic in nature. However, this state of fiber is a state of low entropy.²⁵ The molecular orientation will be stable if the consequent decrease in energy compensates for the drop in entropy. So, whenever yarns are subjected to thermal treatment, a tendency will be to go toward the state of higher entropy. In amorphous regions, the state of molecular orientation is not stable and this is the reason for fiber shrinkage due to thermal disturbance during heat treatment.



Figure 1 Shrinkage force versus time at different temperatures.

The thermal force is acting against the intermolecular force of attraction holding the oriented polymer molecules present in the fiber. The magnitude of this force is substantially higher in fiber form of the polymer compared with that in ordinary polymer form. With the increase in heat treatment temperature, the shrinkage force increases for a fixed time of exposure. The variation of shrinkage force against exposure time in isothermal condition at different temperatures of heat treatment is presented in Figure 1. It was also observed from this figure that at all temperatures of thermal treatment initially the shrinkage force increases with exposure time almost linearly and then attains a plateau value within 30-50 s similar to nylon 6, as observed in our earlier studies.²⁶ However at very high temperature $(\geq 170^{\circ}C)$ of exposure, small drop in shrinkage force beyond 30-50 s is not observed in case of polyester as that of nylon 6. This may be due to difference in the melting point of nylon 6 which is close to 215°C than that of polyester which is around 260°C.

Mostly, the shrinking process is almost complete within 90 s. It is observed that 95% of the total shrinkage takes place within this time period. At all temperatures of thermal treatment the free shrinkage of a cord increases with the exposure time initially at a much faster rate, then assume a steady state value on prolonged exposure. The free shrinkage also increases with heat treatment temperature at any particular time of exposure (Fig. 2). The initial fast shrinkage may be attributed to mostly fiber disorientation in the amorphous phase and the later on slow shrinkage is due to chain folding.²⁷

However, when shrinkage is carried out under controlled conditions; that is, when cords are exposed to heat treatment at different temperatures under some applied load (called as taut fiber), then depending upon the situation there may be



Figure 2 Shrinkage versus time at different temperatures.

expansion (when applied stress is greater than shrinkage stress) or contraction (if applied stress is less than shrinkage stress). These two situations are known as heat setting and relaxation.²⁸ So, depending on the exposure temperature the shrinkage force varies, as shown in Figure 1 and applied stress at different temperatures has to be adjusted accordingly to get the heat setting and relaxation situation as required to control fiber properties and residual shrinkage. The effect of different applied stress at different thermal treatment temperatures are presented in Table I. When applied stress is less than the shrinkage force the amount of shrinkage increases with any particular temperature initially at faster rate, then slowly against the exposure time. It

TABLE I Shrinkage at Different Load and Temperature

		Shr	Shrinkage % at different		
			times		
Temperature (°C)	Load (N)	30 s	60 s	120 s	300 s
150	0	5.6	6.6	7.3	7.7
	2.0	2.2	2.7	3.0	3.1
	2.7	0.3	0.4	0.5	0.6
	8.2	-1.3	-1.5	-1.6	-1.6
170	0	10.2	11.0	11.5	11.9
	2.0	4.1	4.7	5.0	5.1
	3.9	0.4	0.5	0.6	0.7
	8.2	-1.3	-1.4	-1.5	-1.5
190	0	14.3	15.6	16.2	16.7
	2.0	6.4	6.8	7.1	7.2
	4.7	0.5	0.6	0.7	0.7
	8.2	-1.2	-1.1	-1.1	-1.1
210	0	21.4	23.0	23.5	23.7
	2.0	6.9	9.7	9.9	10.0
	4.9	0.4	0.6	0.7	0.7
	8.2	-0.8	-0.7	-0.7	-0.7

Negative shrinkage represents the expansion.



Figure 3 Stress-strain plot of different heat-treated polyester (freely shrunk).

is also observed that at any particular temperature with the increase in load the degree of shrinkage decreases. However, with the increase in applied stress beyond shrinkage stress at any temperature, there is an overall expansion of the cord that is expressed as negative shrinkage. This expansion increases when applied stress increases further beyond the shrinkage force at any temperature of heat treatment. This expansion is found to decrease with the increase in exposure temperatures at a fixed load and increase with time of exposure at a fixed temperature (Table I). That is, when difference between shrinkage force and applied stress decreases, the degree of shrinkage decreases. When heat set is done at constant length, the entropic forces of contraction are balanced by the reaction of external constraints. This leads the whole molecular system to be under load and hinders further shrinkage and increases the possibility of relaxation processes through breakage of physical links leading to intermolecular slippage.²⁹

Stress-strain properties

The effect of heat treatment temperatures on stressstrain properties of the cords (under free shrinkage condition) is presented in Figure 3 and Table II. It is observed that due to heat treatment under free condition, there is drop in tenacity and initial modulus but increase in the elongation at break (Fig. 4) and energy of rupture as compared with original untreated yarn. This is due to chain-folding during heat treatment.^{30,31} The drop in tenacity over the whole temperature range (150-210°C) of heat treatment is gradual. However, in our earlier work, we observed that there was a drastic drop in tenacity as well as elongation at break for nylon 6 tire cord at

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Mechanical Properties of Different Heat-Treated Samples					
Sample	Breaking load (N)	E.B. (%)	Tenacity (cN/Tex)	Initial modulus (cN/Tex)	Work of rupture (N m)
PET0	247.0	17.8	74.4	433	4.392
PET150	243.2	26.2	73.0	332	5.502
PET150a	245.8	21.8	73.7	410	5.210
PET150b	248.5	19.6	74.1	445	4.658
PET150c	252.1	14.6	74.7	543	3.623
PET170	237.1	30.7	71.1	320	6.063
PET170a	242.3	23.8	70.2	413	5.427
PET170b	247.8	19.7	72.2	471	4.484
PET170c	251.0	15.3	74.1	555	3.985
PET190	226.5	36.6	69.1	285	7.337
PET190a	234.3	24.6	70.3	399	5.452
PET190b	236.5	17.4	71.2	483	4.340
PET190c	243.4	15.5	73.5	562	4.076
PET210	216.6	44.8	67.4	249	9.163
PET210a	227.2	27.4	68.6	368	5.823
PET210b	236.7	18.6	71.0	486	4.656
PET210c	241.2	16.0	72.4	573	4.306

TABLE II

210°C.²⁶ This may be due to the difference in the melting point of both the fibers. The maximum heat treatment temperature of 210°C is not as drastic for polyester as it is for nylon 6 as the melting point of nylon 6 is around 215°C, but the same for polyester is around 260°C. There is some internal change in the crystal structure and morphology of the cord and the degree of change depends on heat treatment temperature³² and this will be discussed later.

At any particular heat treatment temperature, there is some change in stress-strain properties with the change in applied stress. A representative plot of stress-strain properties at any particular temperature under load is shown in Figure 5. It is interesting to note that at higher applied stress there is increase in tenacity and initial modulus but with a decrease in elongation at break. At any particular temperature, say at 210°C when applied load changes the variation of initial modulus and elongation at break is presented in Figure 6. Elongation at break continuously decreases with increase in applied load whereas initial modulus continuously increases. This is also found to be true for other temperatures of heat treatment.

Effect of heat setting on crystal structure

It is interesting to note that due to heat treatment, there is also some change in the nature of DSC thermogram (Fig. 7). It is clearly seen from the figure that there is increase in the sharpness of the DSC thermogram when the fiber is subjected to higher



Figure 4 Elongation at break and initial modulus of free shrunk polyester.



Figure 5 Stress-strain plot of polyester heat treated at 210°C at different load.



Figure 6 Elongation at break and initial modulus for heat treated at 210°C under different load.

heat treatment temperature. There is also increase in the area under endotherm, which represents heat of fusion and is proportional to crystallinity (Table III) or some ordering taking place in the fiber structure. Broad endotherm with two peaks for untreated yarn reveals that there exist crystals of different sizes in the polyester fiber. With heat treatment, there may be change in crystal breadth along with its length. Besides, there is also some reorganization of some amorphous region within two crystalline regions present in the polyester fiber. This reorganization of amorphous region is reflected in the change in the elongation at break. However, the process of reorganization of crystalline and amorphous region is temperature dependent. The rise in temperature affects this organization process. Again with the increase in heat treatment temperature that leads to some kind of thermal organization in the crystal size distribution leading to melting of some small size crystals thus increasing the density of bigger size crystals. This can also be supported by the increase in density with heat treatment temperature (Table III).

XRD pattern of polyester fibers subject to heat treatment at different temperatures are presented in Figure 8. For the ease of distinguishing each individual, X-ray plots have been shifted by a constant factor along *y*-axis. From the graph, it can be seen that



Figure 7 DSC thermogram of different heat-treated polyester fiber (freely shrunk).

three major peaks are observed within 2 θ values ranging from 17 to 27° and details of different crystal parameters like half width, *d*-spacing and crystal size as calculated is presented in Table IV. The three major peaks are observed at an angle of 17.8, 22.9, and 25.9° for the planes 010, 110, and 100, respectively.³³ For the three intense reflections, crystallite size has been calculated by using Scherrer equation without considering instrumental broadening.²¹

The crystallite size for all the three planes is found to increase with the increase in heat treatment temperature. Again half width for all the three major peaks, show a decreasing trend with increase in heat treatment temperature. The decrease in the half width represents sharpness of the peak, which may be due to increase in crystallinity or perfection of crystal structures, which is also supported by the sharp DSC thermograms and increased density values.

It has been reported that there exists some relation between crystal perfection measured from X-ray analysis and fiber density.³⁴ The density of the polymer again increases with the increase in crystallinity. It is important to note that even in fiber where there is high degree of crystallinity due to orientation, there may exist some kind of crystal defects. In fact

TABLE III Crystallinity by Different Methods

	DSC		Den	XRD	
Sample	Heat of fusion (J g^{-1})	Crystallinity (%)	Density (g cm ⁻³)	Crystallinity (%)	Crystallinity (%)
PET0	47.5	36	1.3740	34	37
PET150	50.8	38	1.3764	36	39
PET170	54.2	41	1.3789	39	53
PET190	59.3	45	1.3850	44	60
PET210	66.5	50	1.3910	49	65

Figure 8 XRD of different heat-treated polyester fiber (free shrunk).

in a crystalline fiber, polymer chains run through successively crystalline and amorphous region. However, this amorphous region present in the fiber is much more oriented and parallelized compared with undrawn crystalline polymer.^{35,36} Heat setting under load often organizes this amorphous region as well as modifies the crystalline regions already present. Perhaps there may be some modification of crystallites.³⁷ There is also possibility during heat setting, that bigger crystallites can become more perfect by expelling the defects out of the crystals.³¹

In general, XRD gives better representation of crystallinity and crystalline structure for semicrystalline or highly crystalline polymers. However, it is worth mentioning here, the crystallinity measured for nylon 6 or polyester fiber in the usual procedure may not be perfect.³⁴ It is mainly because the amorphous halo is buried inside the crystalline peaks and is not perfectly detectable. In such situation besides crystallinity other parameters like crystal size, full width at half maxima (FWHM), interchain separation (*R*), etc., should also be checked. Crystallinity is also measured from DSC and density is also given in Table III. It can be observed that crystallinity



PET150 PET170 PET190 PET210

0.49

0.48

PETO

nterchain Separation, nm

measured by all three methods show increasing trend with the increase in the heat treatment temperature. The interchain separation, R, is measured from the position of the maxima of the major halo at around 23.2° by using the relation given by Klug and Alexander²¹ and is plotted in the Figure 9. It can be observed that the interchain separation increases with heat treatment temperature. This parameter may be correlated to orientation of the amorphous region. This means the orientation of the amorphous region decreases with increase in heat treatment temperature. This may be the reason for reduction in tenacity and initial modulus for free shrunk fiber, though the crystallinity of the same increases. To further reinforce this birefringence study of the heat-treated samples were done. The birefringence index (Δn) with the heat set temperature is also plotted in Figure 10. This shows reduction of Δn which means, the orientation of the fiber decreases with the increase in the heat treatment temperature. However, heat setting under load often organizes this amorphous region as well as modifies the crystalline regions, already present which is supported by increase in Δn for taut fiber compared with free shrunk fiber. Hence tenacity and initial modulus also increase for taut fiber. Again, it is also observed that crystallinity measured by X-ray method

 TABLE IV

 Crystal size, FWHM, and *d*-Spacing of Different Heat-Treated Samples

				1 0			-		
	<i>d</i> -spacing (Å)		FWHM (°)			Crystal size (Å)			
	010	110	100	010	110	100	010	110	100
PET0	4.989	3.867	3.440	2.49	1.79	1.71	32.3	45.3	47.7
PET150	4.982	3.878	3.427	1.56	1.43	1.24	51.6	56.7	65.8
PET170	4.980	3.879	3.421	1.49	1.3	1.17	54.0	62.4	69.7
PET190	4.979	4.026	3.412	1.43	1.26	1.16	56.2	64.2	70.3
PET210	4.939	4.083	3.403	1.29	1.19	1.12	62.4	68.0	72.8

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Figure 10 Birefringence of free shrunk and taut polyester fiber.

(result not presented) for taut fiber is also quite close to that of free shrunk fiber at any particular heat treatment temperature. A schematic diagram of the PET fiber, before and after heat treatment, is proposed (Fig. 11) considering all these behaviors. The figure illustrates that with heat treatment some of the oriented amorphous region or imperfect crystals get converted to crystalline regions leading to increased overall crystallinity. However, the remaining amorphous region loses orientation along the fiber axis.

Effect of heat setting on residual shrinkage

The residual heat shrinkage plays a very important role in determining the processing conditions of



Figure 11 A schematic model for the arrangement of crystalline and amorphous region in polyester fiber.

	Samples	
Heat-set temperature (°C)	Tension (N)	Residual shrinkage at 150°C (%)
150	0.0 2.0 2.7 8.8	0.9 2.0 2.4 2.7
170	0.0 2.0 3.9 8.8	0.7 1.8 2.1 2.5
190	0.0 2.0 4.7 8.8	0.5 1.4 1.6 1.9
210	0.0 2.0 4.9 8.8	0.4 1.1 1.3 1.7

TABLE V Residual Shrinkage at 150°C for Different Heat-Treated Samples

products like tire, conveyor belt, which use polyester as the reinforcement. The residual heat shrinkage is to be controlled for attainment of perfect size and shape of the product derived from polyester. Hence, it is important to know the residual shrinkage of polyester cord especially at vulcanization temperature, when it is going to be used as rubber reinforcement. So, residual shrinkage, measured at 150°C for both untreated and different heat-treated samples is given in Table V. Compared with untreated samples heat-treated samples always exhibit much low residual shrinkage at 150°C. Cords undergone free thermal shrinkage shows minimum residual shrinkage and cords subjected to higher stress during heat treatment exhibit higher residual shrinkage in latter stage of processing that is during curing. The residual shrinkage generally reduces with increase in heat setting temperatures. This can be explained in terms of change in chain folding and crystal imperfection present in the cord with the change in heat treatment temperature.^{30,31} Higher the heat-set temperature, more the chances of relaxation in locked-in stress generated during manufacturing that leads to more stable structure and hence less residual shrinkage. This change in crystal structure due to heat treatment may be more significant in changing the mechanical properties as well as residual heat shrinkage.

CONCLUSIONS

Shrinkage force and extent of shrinkage at different temperature initially increase sharply with heat treatment time and then attain some plateau within 90 s. In case of free shrinkage, initial modulus and tenacity decrease whereas elongation at break and work of rupture increase steadily with the increase in heat treatment temperature. However, the reverse can be observed for taut fiber. Residual shrinkage increases with the increase in load at any particular heat treatment temperature. All these changes can be correlated with change in crystal structure of polyester fiber. There is an increase in percentage crystallinity, average crystal size with the increase in heat set temperature both for free shrinkage and taut fiber. However, orientation decreases only on free shrinkage and in taut fiber orientation is not affected much.

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