Production and Characterization of Polypropylene Fiber upon Addition of Selective Peroxide during Melt Spinning and Comparison with Conventional Polypropylene Fibers

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ABSTRACT: In the present work, effect of selective peroxide on reactor grade polypropylene (PP) (known as V30S) during melt spinning process on the physical and thermal properties of as-spun resultant multifilament yarn was studied. Attempts have also been made to compare this yarn sample with other fiber samples produced from reactor and controlled rheology grades polypropylene. The results show that the multifilament yarn spun from V30S/Peroxide sample shows higher birefringence and tensile strength and also lower modulus, elongation at break, and shrinkage compared with that of spun from pure V30S granule. Density and thermal behavior studies show low variations compared with original sample. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2287–2293, 2007

Key words: polypropylene fiber; melt spinning; organic peroxide; molecular weight; mechanical properties

INTRODUCTION

Polypropylene (PP) is a widely used versatile commodity polymer with a number of desirable properties. PP resins produced in most industrial polymerization process have a high molecular weight and broad molecular weight distribution (MWD). The resulting high melt viscosity and elasticity limit its efficient processing in certain applications exhibiting, for example, draw resonance in fiber spinning.[1–3] For the purpose of improving application and processing characteristics, the molecular weight and MWD of the polymer can be modified under controlled conditions. This is the so-called controlled rheology PP (CR-PP). CR-PP can be prepared in several ways. Controlled degradation of PP through the action of peroxide—known as ''vis-breaking''—is the most widely used approach. In this process, PP and organic peroxide are fed to the extruder where degradation reaction occurs. The degradation reaction produces PP with lower molecular weight and narrower MWD. These modifications are most attractive for improving processing characteristics and end-use properties of PP.[4–8]

The numerous studies have been focused on the production technology and the process of controlled degradation, and also compares the properties of CR and reactor types of PP. Degradation of PP with peroxide is believed to occur through a series of free-radical reactions involving steps such as initiation, scission, transfer, and termination.[9–11]

In the present investigation, peroxide was chosen as an additive to improve processing and mechanical properties of a commercial fiber grade PP granule with broad MWD known as V30S.

EXPERIMENTAL

Materials

Multifilament yarns were spun from three commercial fiber grade isotactic polypropylene granules, known as 512P (Sabic Co., Saudi Arabic) a fiber grade controlled rheology (CR) polymer, V30S and Z30S (Arak Petrochemical Co., Iran). General characteristics of these granules have been shown in Table I.

512P granule is a narrow molecular weight distribution (MWD) polymer whereas V30S and Z30S granules have broad MWDs. These materials are normally considered to be stable against weathering oxidation, since these contain usual synergistic combination of antioxidants that are found in commercial granules. The peroxide used for degradation of PP was 2,5-dimethyl-di(t-butylperoxy)hexane, (DHBP, Trigonox 101 from Akzo Chemie, Amersfoort, The Netherlands).

Preparation of melt-spun filaments

Melt spinning was performed under nitrogen gas on a Fourne-Automatic melt spinning unit (pilot plant).

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TABLE I
Characterization of As-Received Granules

	Molecular weight (g/mol)	Molecular weight distribution	Melt flow index (g/10 min)
512P	186,036	2.59	25
V30S	225,552	4.14	16
Z30S	191,337	3.76	25

The temperature profile of five heating zones of the extruder and spinning head for the production of yarn samples has been shown in Table II.

The prepump pressure was 50 bar. The polymer melts were extruded at approximately a rate of 100 g/min through a spinneret with 36 circular orifices, each of 0.25 mm diameter. The as-spun filaments were collected at a take-up speed of 2000 m/min. The final linear density of multifilament yarns was 140 dtex. For fiber spinning from V30S/Peroxide sample, we first determined the optimum concentration of peroxide. Three peroxide amounts (0.1, 0.3, and 0.5 wt %) were used. Before the reactive extrusion runs, the V30S granule was mixed with a peroxide powder to obtain the desired peroxide concentration. After examining the spinnability of V30S/Peroxide sample with different concentration of peroxide, we choose 0.3 wt % peroxide for mixing with V30S granule. The unstable spinning conditions and capillary break of extruded polymer jet signified that melt spinning of V30S/Peroxide sample at higher peroxide concentrations would not be possible. In addition, melt spinning with peroxide concentrations greater than 0.3 wt % would be difficult because the high degradation rate of PP which can be resulted in melt flow rate becomes so high that the polymer melt flows freely longer. Consequently, we could produce fiber from V30S/Peroxide sample containing up to 0.3 wt % of peroxide. A possible way to increase the peroxide concentration is by using a lower melt flow rate material initially. As can be seen in Table II, in our study the optimum spinning temperature of V30S/Peroxide blend sample was found to be around 240°C, whereas that of V30S polymer was around 260°C. We choose a relatively high extruder barrel temperature to be sure that the degradation reaction is finished upon reaching the

die exit due to the very short half-life time of peroxide at this temperature.

Characterization techniques

The fringe shift inside the fibers was measured by a cross-polarized optical microscope (Carl Zeiss, Jena, Germany) and birefringence was calculated using the following equation:[12]

$$\Delta n = \frac{dz\lambda}{zd} \tag{1}$$

where dz is a fringe shift inside the fiber, z is an interfringe spacing, λ is the wavelength of the monochromatic light used (in our case, $\lambda = 550$ nm), and d is the fiber thickness. Hermans orientation factor (f) is related to the refractive index difference by the relation:[13]

$$f = \frac{\Delta n}{\Delta n^*} \tag{2}$$

where Δn^* is the intrinsic maximum birefringence that corresponds to the case where all the molecule are perfectly aligned. The value of Δn^* for PP fiber was taken to be 0.045.[14]

Densities of fibers were determined by a floatation method. A binary medium prepared from various ratios of distilled water and ethyl alcohol was used at 23°C. The crystalline fraction (X) of the yarn samples was then estimated using the following expression:

$$X = \frac{(\rho - \rho_a)}{(\rho_c - \rho_a)} \times \frac{\rho_c}{\rho} \tag{3}$$

where ρ is sample density and ρ_c and ρ_a are densities of crystalline and amorphous PP and were taken to be 0.9363 g/cm^3 and 0.8576 g/cm^3, respectively.[15]

Infra-red spectra were obtained with a Nicolet Fourier Transform Spectrophotometer with a resolution of 4 cm^{-1} (30 scans average) to measure isotacticity of as-spun fibers. Stress–strain curves were obtained using an Instron tensile tester model 5566 H1730. A gauge length of 100 mm and cross-head

TABLE II
Temperature Profile of Heating Zones in Melt Spinning Machine
for Production of As-Spun Yarns

	Feeding section (°C)	Metering section (°C)	Melt-blending section (°C)	Die section (°C)	Spinneret block (°C)
512P	200	220	230	240	240
V30S	220	240	250	260	260
Z30S	200	220	230	240	240
V30S/Peroxide	200	220	230	240	240

TABLE III
Characterization of Multifilament Yarns Spun from
Different Polypropylene Granules

	Density (g/cm³)	Crystallinity (by density, %)	Birefringence (×10³)	Orientation factor	Isotacticity (by FTIR, %)
512P	0.8987	54.40	22.71	0.50	86.30
V30S/Peroxide	0.9009	57.18	21.67	0.48	89.20
V30S	0.9008	57.05	20.22	0.45	91.94
Z30S	0.9025	59.18	19.17	0.43	91.73

speed of 500 mm/min were employed. From stress–strain plots, the modulus, tenacity, and percentage extension at break were evaluated. The reported values of all the mechanical properties have been averaged over at least 10 independent measurements.

Differential scanning calorimetry (DSC) measurements were carried out on DSC 2010 machine (TA Instruments, New Castle, DE) to examine the melting behavior of multifilament yarns. Samples of 10 mg, which were cut from the fibers, were heated from room temperature to 210°C at a scanning rate of 10°C/min under nitrogen atmosphere. The equipment was calibrated with indium. From the heat of fusion, an apparent crystallinity (X) was determined by following equation:

$$X(\%) = (\Delta H / \Delta H^*) \times 100 \qquad (4)$$

where ΔH is the measured melting enthalpy and ΔH^* is the enthalpy of fusion of a 100% crystalline PP, that is 190 J/g.[16]

The yarn shrinkages were measured after heating a free hanged length of yarns in an oven at 120°C for 15 min. The initial and final lengths were measured at room temperature, with the shrinkage calculated as percent change in length relative to the initial length. The average of five measurements was reported as shrinkage.

RESULTS AND DISCUSSION

Birefringence

Several characteristics of multifilament yarns are shown in Table III. The birefringence values and orientation factors of the as-spun fibers are shown in Figure 1.

Five specimens were chosen for this test and the reported data are statistical average of these specimens. As it can be seen in Figure 1 and Table III, the fiber spun from 512P granule has highest birefringence and orientation factor followed by the fibers spun from V30S/Peroxide, V30S, and Z30S granules.

Nadella et al.[17] and Lu and Spruiell[18] have reported that the development of molecular orientation in spin line is closely related to spinning stress, which becomes higher for spinning conditions of lower spinning temperature and higher molecular weight due to higher elongation viscosity. By broadening MWD, the spin line stress increases due to higher chain entanglement and as a result the final orientation is higher. But, the broader MWD polymer would develop lower final birefringence than the narrower MWD polymer, as is the case in our presented results.

A possible reason for lower birefringence of fiber spun from V30S granule is the formation of bimodal orientation distribution due to higher stress-induced crystallization in broader MWD polymer.[19] These findings support that, as expected, the peroxide narrows the MWD and decreases the presence of the higher molecular weight species. As a result, chain mobility increases and birefringence of fiber spun from V30/Peroxide sample is higher than that of spun from V30S granule.

The delay in crystallization of narrow MWD polymer allows greater amorphous orientation to develop before crystallization begins. Achieving the highest orientation value in fiber spun from 512P granule may be attributed to this reason.

FTIR analysis

The FTIR tacticity are shown for the fiber samples in Table III, indicating the isotacticity is approximately the same for the fibers spun from V30S and Z30S granules while the fiber spun from 512P granule has
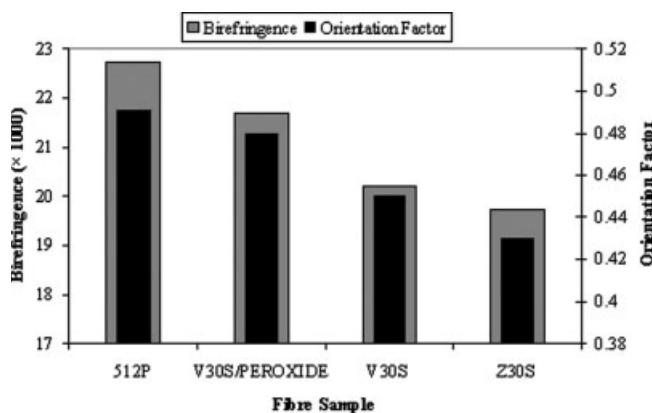

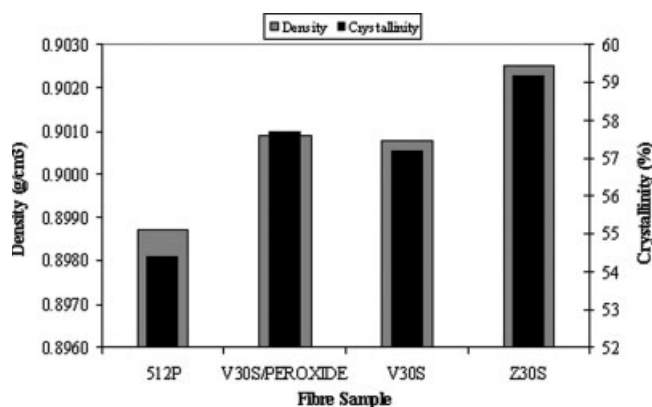**Figure 1** The birefringences and orientation factors of As-spun yarns.

Figure 2 The density and crystallinity calculated from density of As-spun filaments.

lowest isotacticity. The isotacticity of fiber spun from V30S/Peroxide sample is slightly lower than that spun from V30S granule. This suggests that in the fiber spun from V30S/Peroxide sample the molecules in the helical conformation are lower compared with that spun from V30S granule.

Density

The densities of the as-spun fibers and calculated crystalline fraction from density measurements are shown in Figure 2. It can be seen from this figure, the fiber spun from 512P granule has lowest density values of all the polymers studied whereas the Z30S polymer exhibited highest mentioned values. It should be noted that the density and calculated crystallinity of fiber spun from V30S granule are very slightly lower than that of spun from V30S/Peroxide granule.

The results agree with current theory, in that the higher MW and broader MWD polymer should develop the higher density due to the higher amount of stress in the spin line.[20] The fiber spun from V30S granule has higher MW and broader MWD comparison to that of spun from Z30S granule, but it seems that both these factors have negative effects on measured density and reduces the V30S granule chain mobility. This can be explained as the lower density of fiber spun from V30S granule comparison to that of spun from Z30S granule. The greater density of fiber spun from Z30S granule compared with that of spun from 512P granule is consistent with a lower tacticity of filaments spun from 512P granule, as shown in Table III.

Mechanical properties

The tensile strength (tenacity), percent elongation at break, and modulus for as-spun fibers are plotted in Figures 3–5, respectively. As can be seen in Figure 3

the fiber spun from 512P granule has the highest tensile strength followed by the fibers spun from V30S/Peroxide sample, V30S, and Z30S granules. The tenacities of the fibers spun from V30S and Z30S granules did not show significant difference. The tenacity values show that the addition of peroxide to V30S granule increases that value around 10% for the fiber spun from V30S/Peroxide sample in relation to that of spun from V30S granule.

Lu and Spruiell[18] showed that the tenacity of PP fibers has a strong relationship to the MW and MWD of granules. It is pointed out that tenacity is dependent on the percentage crystallinity and overall orientation of fiber. The differences in the tensile strength among the fibers spun from the granules tend to reflect the differences in overall molecular orientation as measured by the birefringence data. By comparing the crystalline fractions and birefringences of multifilament yarns, as shown in Table III, it can be concluded that the reduction in overall orientation has a more negative effect on the tenacity of multifilament yarns than the possible positive effect of the increase crystallinity. On the other hand, Samules[21] has shown that the tenacity of drawn PP filaments is controlled primarily by the orientation of the amorphous (noncrystalline) fraction of the sample and has little relationship to the crystallinity or crystalline orientation.

The orientation of the amorphous phase is more difficult to establish. From the literature[22] it is known that the narrow band at 1155 cm^{-1} in FTIR plot of PP is most suitable to study the orientation of the amorphous phase. However, in our experimental results the peak at 1155 cm^{-1} was strongly overlapped, hence difficult to separate. But it seems that peroxide decreases the presence of the high molecular weight species and increases mobility of molecular chains, which would facilitate the orientation in amorphous phase. This finding can be explained has the higher tenacity of fiber spun from V30S/Peroxide sample as compared with that of spun from V30S granule.
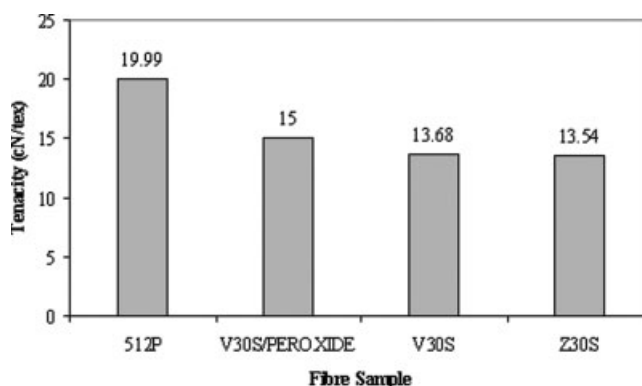

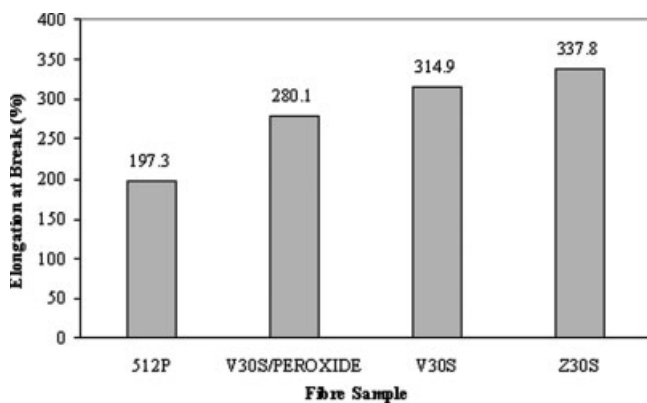**Figure 3** The tenacities of As-spun filaments.

Figure 4 The elongation at break values of As-spun filaments.

The elongations at break data in Figure 4 are basically the inverse of the tensile strength data. It is noted that the addition of peroxide to V30S granule decreases this parameter around 35% in fiber spun from V30S/Peroxide sample compared with that of spun from V30S granule. As expected, the highest and lowest elongation at break observed in fibers spun from Z30S and 512P granules, respectively. These results reflect the observed differences in orientation of the filaments as measured by the birefringence values (see Table III).

It is observed from Figure 5 the fiber spun from Z30S granule has the highest initial modulus values followed by the fibers spun from V30S, V30S/Peroxide, and 512P granules. Generally, initial modulus is highly related to the crystallinity, crystal size, and somewhat to the orientation.[23] Initial modulus of multifilament yarns are confirmed by their crystallinity values (see Table III).

Figure 6 presents the specific stress–strain curves of the as-spun fibers. It is clear that the fiber spun from the 512P granule has the most tenacity and of least extensible among all fiber samples. The addition of peroxide to V30S granule resulted in achieving higher stress at the same percent of extension for
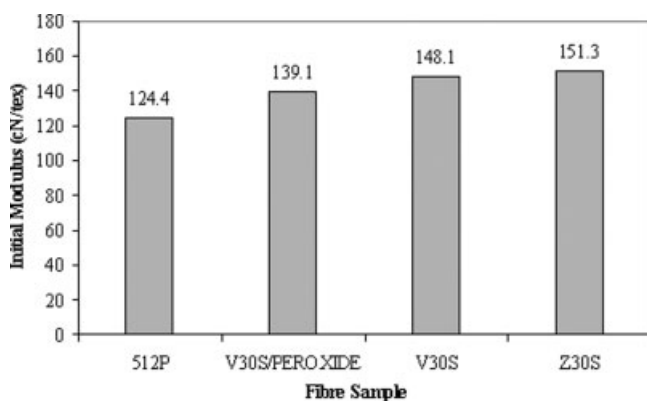

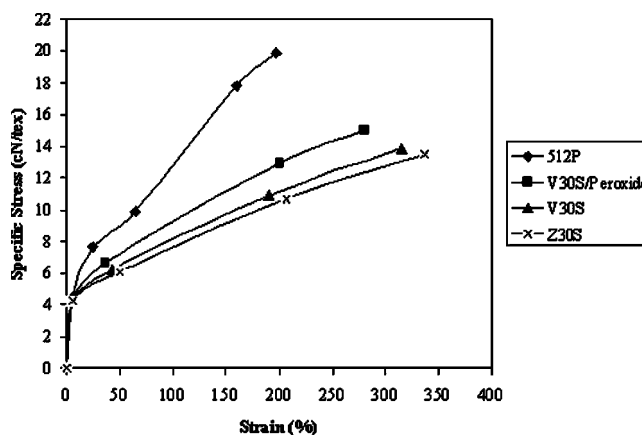**Figure 5** The modulus values of As-spun filaments.

Figure 6 Specific stress–strain curves of As-spun polypropylene yarns.

the fiber spun from the V30S/Peroxide than that of spun from V30S granule. From Figure 6, it can be seen that the stress–strain curve of fiber spun from V30S/Peroxide sample has been to some extent different from original sample (fiber spun from V30S granule). Also the stress–strain curve of fiber spun from V30S/Peroxide sample is moving towards that of spun from 512P granule.

DSC studies

The results of DSC analysis of as-spun fibers are summarized in Table IV. As can be seen in this table, no pronounced differences were observed in either the melt enthalpy or melting point of samples. Moreover, the differences in the temperatures of the onset of melting between the four fiber samples were not so significant.

Although the absolute values of crystallinity obtained from calorimetry are different from crystallinity calculated from density, trends in Table III and IV are similar. The difference indicates that different structural parameters are involved in the two different methods of measurements.

DSC thermographs of as-spun yarns are illustrated in Figure 7. Only multifilament yarn spun from 512P granule shows a double endotherm peaks while those of spun from other granules show a single peak. This phenomenon depends on the heating rate: at low heating rate, it is more pronounced than at high rates. The first peak is characteristic of the melting of crystals formed during the crystallization, and the second one is due to the melting of crystals formed by recrystallization or reorganization of the original crystals during heating cycle.[24,25]

As can be seen in Figure 7, the endotherm peak forms of yarns spun from V30S, V30S/Peroxide, and Z30S are similar. Peroxide initiated PP degradation has known as a random chain scission reaction, to

	First melting point (°C)	Second melting point (°C)	Melting enthalpy (J/g)	Crystallinity (%)
512P	159.57	164.40	98.94	52.07
V30S/Peroxide	162.66	–	102.90	54.15
V30S	163.69	–	101.50	53.42
Z30S	163.83	–	106.30	55.94

reduce the number of long chains, and to result in less entanglement and higher mobility of molecules. But it seems that peroxide leads to a degradation of the starting granule (V30S) without significant formation of low molecular weight parts. Therefore, recrystallization or reorganization of lower molecular weight species cannot occur considerably. This can be explained that why during DSC test of the fiber spun from V30S/Peroxide double melting peaks were not observed.

Shrinkage

The results of shrinkage experiment in hot-air are given in Figure 8. As can be seen in this figure, the shrinkages of fibers spun from V30S/Peroxide sample and Z30S granule have no significant difference. The fibers spun from V30S and 512P granules have the highest and least shrinkage, respectively. Gupta et al.[26,27] reported that increase in crystallinity and reduction in birefringence (lower overall orientation) lead to a lower thermal shrinkage. Moreover, smaller crystal size and unrelaxed stress took place during orientation causes the shrinkage to be increased. However, this hypothesis cannot be perfectly applied in the result of this study. It seems that due to presence of shorter molecular chains in 512P granule structure, more stress was relieved during melt spin-

ning and this may be responsible for the lower shrinkage of fiber spun from this granule.

The hot air shrinkage of the as-spun yarn spun from V30S/Peroxide sample is around 13% lower than that of spun from V30S granule. This obviously related to the lower residual stress in former and provides supporting evidence for the lower spin line tension in this sample.

CONCLUSION

The results of this study showed that the addition of peroxide during melt spinning of V30S granule has been found to influence the behavior of the system right from the extrusion stage, wherein the peroxide is known to reduce the melt spinning temperature of V30S granule from 260°C to 240°C. This might be beneficial to V30S granule processing from energy saving and decreasing in thermal degradation point of views. The fiber spun from V30S/Peroxide sample has superior mechanical properties compared with that of spun from V30S granule. Birefringence, tensile strength, elongation at break, modulus, and shrinkage variations of as-spun filaments spun from V30S/Peroxide sample are tending to behavior of fiber spun from controlled rheology grade PP known as 512P. The present results provide us an alternative method to produce a multifilament yarn with better properties from granules with broad MWD.
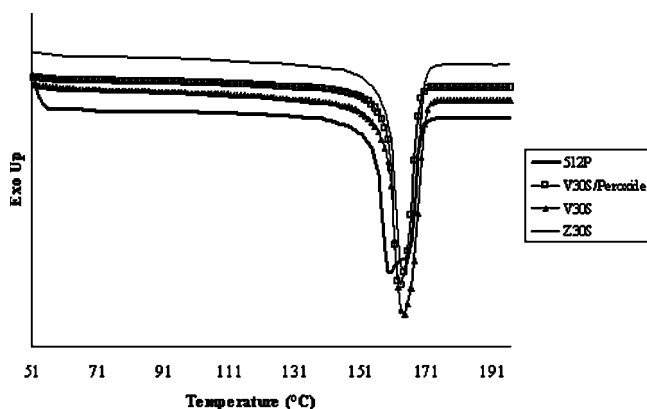

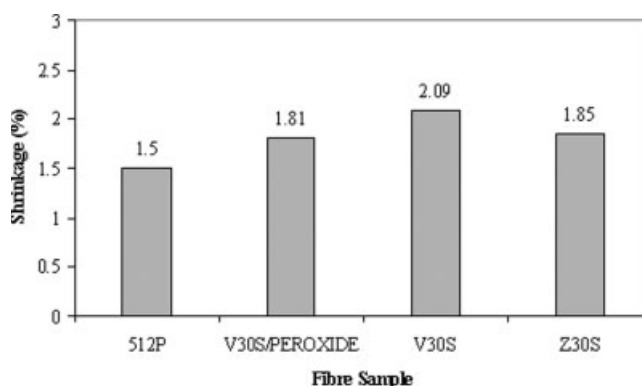Figure 7 Heating cycles of DSC thermograms for As-spun fibers.

Figure 8 The shrinkage values of As-spun filaments.

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