Shrinkage of Short PP and PAN Fibers Under Hot-Stage Microscope

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SYNOPSIS

Marked shrinkage behavior when heated is typical of semicrystalline polymer fibers such as polypropylene (PP) and polyacrylonitrile (PAN). Shrinkage of PP and PAN fibers may give the possibility to control the spalling tendency of fiber concrete under the heat exposure of fire. Cut staple fibers are normally delivered for concrete reinforcement. Modern methods for continuous fibers cannot be used by the end-user for shrinkage determination of commercial staple fiber grades. The shrinkage of five different commercial staple fibers specially designed for concrete reinforcement was studied under a hot-stage microscope. Significant differences in cumulative shrinkages of the various PP and PAN fibers were detected, shrinkages being 3–15% with PP fibers and 6–7% with PAN fibers at a temperature of 150–170°C. At about 160–165°C, PP fibers melt, whereas PAN fibers continue shrinking. Hot-stage microscopy provides a simple and a relatively accurate method for estimating thermal shrinkage of staple PP and PAN fibers, the deviations from measured average values remaining typically at 10–15%. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is generally accepted that the presence of water is the main cause of spalling of traditional concrete during heating.[1,2] If heating is slow, the evaporable water will be expelled at 105°C in a controlled manner. If heat exposure is intense and sudden, as in most fire situations, not all the water is expelled fast enough. This results in vaporization at higher temperatures, leading to high pressures, and microcracking and spalling of concrete.[3] It seems reasonable to anticipate that the behavior of concrete structures under fire can be improved by adding fibers to the concrete mortar, reducing spalling caused by a sudden rise in temperature. However, details of the potential beneficial features of the fiber addition are poorly understood and require further research. Few studies to date have broached the question.[4-7] Shrinkage of polypropylene and polyacrylonitrile fibers may give the possibility of controlling the spalling tendency of fiber concrete under the heat exposure of fire. Fiber shrinkage creates free space in the concrete material, allowing more possibilities for the evaporating water to find an exit.

Polypropylene (PP) and polyacrylonitrile (PAN) are semicrystalline polymers with flexible chains. Details of the fiber morphology, in the form of an interplay between crystalline and amorphous regions of PP and PAN, have an essential effect on the thermomechanical properties of these polymers.[8] Both thermal and mechanical properties of semicrystalline polymers are dependent on thermal history, orientation, and morphology.

Ibhadon discussed different studies of PP: The morphology of isotactic PP has been investigated by electron microscopy and wide- and small-angle X-ray scattering. The crystallinity of drawn isotactic PP samples has also been investigated and the melting behavior of melt and solution-crystallized samples studied.[9] Ibhadon reported on the effect of orientation on the melting point of PP. Orientation progressively shifts the onset of, and the observed, melting point to higher temperatures and increases the peak heights of differential scanning calorimetric (DSC) endotherms. The melting point of PP fibers may vary between 143 and 185°C. The increase in melting point with orientation has been attributed to the increase in configurational entropy of the ex-

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Table I Physical Properties of PP Fibers and PAN Fibers Used in the Study

Fiber Type	Fiber Length (mm)	Density (g/cm^3)	Modulus of Elasticity (GPa)	Tensile Strength (MPa)	Linear Density (dtex)	Remarks
PP7 (Krenit Standard)	12	0.91	12.5	450	140	Fiber from film
PP11 (Krenit Special)	12	1.01	13	420	130	Fiber from film, $CaCO_3$ filler
PP15 (Crackstop)	12	0.91	4	300	2.8	Melt spun fiber
PAN4 (Dolanit 11)	12	1.18	15–18	400–500	100	Spun fiber
PAN5 (Dolanit 10)	12	1.18	17–19.5	900–1000	3.0	Spun fiber

tended melt into which the polymer crystallites melt.[9]

Thermal reactions of PAN fibers have been studied extensively. Turner and Johnson studied the pyrolysis of PAN fibers up to 400°C in an inert atmosphere by thermogravimetric and differential thermal analysis.[10] The pyrolysis of PAN has also been studied up to 1000°C by Grassie and McGuchan using thermogravimetry, differential thermal analysis, and thermal volatilization analysis.[11] Instead of an endothermic melting process, as with PP, an exothermic reaction at a temperature between 200 and 350°C in an inert atmosphere is typical of PAN. This has been explained in terms of nitrile group polymerization, although many side reactions such as formation of ammonia and depolymerization also occur in the same temperature region.[11]

Marked shrinkage behavior prior to melting is very characteristic of PP fibers. PP fibers decrease in linear length when exposed to boiling water, steam, or hot air for a specified period of time under relaxed conditions. This entropy shrinkage is a function of molecular heat relaxation.[12]

PAN fibers also shrink lengthwise when heated. Depending on the PAN type, cumulative shrinkage by up to about 30% may be observed. This involves a primary entropy shrinkage due to molecular relaxation and a secondary chemical-reaction shrinkage attributed to cyclization and hydrogenation reactions. Entropy shrinkage starts below 100°C and ends below 200°C, followed by chemical-reaction shrinkage.[13] Entropy shrinkage is strongly influenced by prestretch treatment of the fiber.[14] Chemical-reaction shrinkage is thought to be independent of such treatment, especially if measured without load on the fibers. However, the amount of chemical shrinkage above 200°C is strongly influenced by comonomers. A higher copolymer content causes greater chemical shrinkage, and a faster heating rate increases its total amount.[15]

Thermal shrinkage of continuous fibers may be determined by standard textile methods.[16,17] Dynamic-mechanical thermal analysis (DMTA) with strain deformation may provide valuable information about molecular-relaxation processes in fibers. This experimental technique determines the relation

Table II Cumulative Shrinkage at 140 and 155°C and Melting Temperature of PP7 Fibers

Sample	Sample Length (mm)	Shrinkage at 140°C (%)	Shrinkage at 155°C (%)	Melting Temperature (°C)
PP7 No. 1	0.557	3.4	5.2	158–160
PP7 No. 2	0.629	2.3	5.3	158–160
PP7 No. 3	0.672	2.9	6.4	159–160
PP7 No. 4	0.922	3.1	6.8	158–160
PP7 No. 5	0.931	3.1	7.2	158–160
	Average	3.0 ± 0.4	6.2 ± 0.9	158–160

Table III Cumulative Shrinkage at 150 and 160°C and Melting Temperature of PP11 Fibers

Sample	Sample Length (mm)	Shrinkage at 150°C (%)	Shrinkage at 160°C (%)	Melting Temperature (°C)
PP11 No. 1	0.499	1.0	2.9	164–167
PP11 No. 2	0.619	2.3	3.1	164–167
PP11 No. 3	0.643	1.5	3.0	164–167
PP11 No. 4	0.864	2.8	3.9	164–166
	Average	1.9 ± 0.8	3.2 ± 0.5	164–167

between dynamic load and dynamic deformation of a test sample as a function of temperature.[8] In practice, however, continuous fiber is not always available. For example, cut staple fibers (8–12 mm) are typically delivered for concrete reinforcement. Methods for continuous fibers cannot be used for shrinkage determination of commercial staple fiber grades. In this article, thermal shrinkages of commercial PP and PAN staple fibers, especially designed for concrete, are reported using hot-stage microscopy.

EXPERIMENTAL

Materials

Commercial grades of PP fibers (Krenit and Crackstop) and PAN (Dolanit) fibers specially developed for concrete reinforcement were studied. The PP fibers were made from film (Krenit) or by melt-spinning (Crackstop), and the PAN fibers, by spinning. The fiber properties as given by the manufacturers are given in Table I. The fibers are coded PP7, PP11, PP15, PAN4, and PAN5. A boiling water shrinkage value of 7–8% and hot-air shrinkage values of 5.5–6.5% at 150°C and 9–10% at 200°C were reported for PAN fibers by the manufacturer.

Method

A hot-stage microscope is used to observe the thermal behavior of a sample at the microscopic level. A Mettler FP800 thermal analysis system with an FP82 hot-stage measuring cell coupled to a Nikon Optihot-2 microscope was used in this study. A Nikon FX-35DX camera was connected to the microscope. The measurement cell was interfaced with a control instrument (Mettler FP80 central processor) and the temperature program was entered over the central processor keyboard. The selected program consisted of a starting temperature (80°C), a heating rate (10°C/min), and an end temperature (180°C for PP and 230°C for PAN).

The samples were prepared by cutting the fibers on a thin glass using a laboratory knife. The measurement scale limit of the microscope was 1 mm, which was also the maximum sample limit. The samples were placed on microslides (26 × 76 mm^2), covered with a cover glass 18 × 18 mm^2), and studied under the hot-stage microscope. Four to five measurements per fiber type were carried out.

Table IV Cumulative Shrinkage at 150, 155, and 157°C and Melting Temperature of PP15 Fibers

Sample	Sample Length (mm)	Shrinkage at 150°C (%)	Shrinkage at 155°C (%)	Shrinkage at 157°C (%)	Melting Temperature (°C)
PP15 No. 1	0.278	3.4	10.3	17.2	158–161
PP15 No. 2	0.403	8.3	10.7	(28.6)	158–160
PP15 No. 3	0.662	7.2	10.1	15.9	158–160
PP15 No. 4	0.682	4.2	10.6	15.5	160–161
PP15 No. 5	0.739	5.2	10.4	15.6	160–162
	Average	5.7 ± 2.0	10.4 ± 0.2	16.0 ± 0.8	159–161

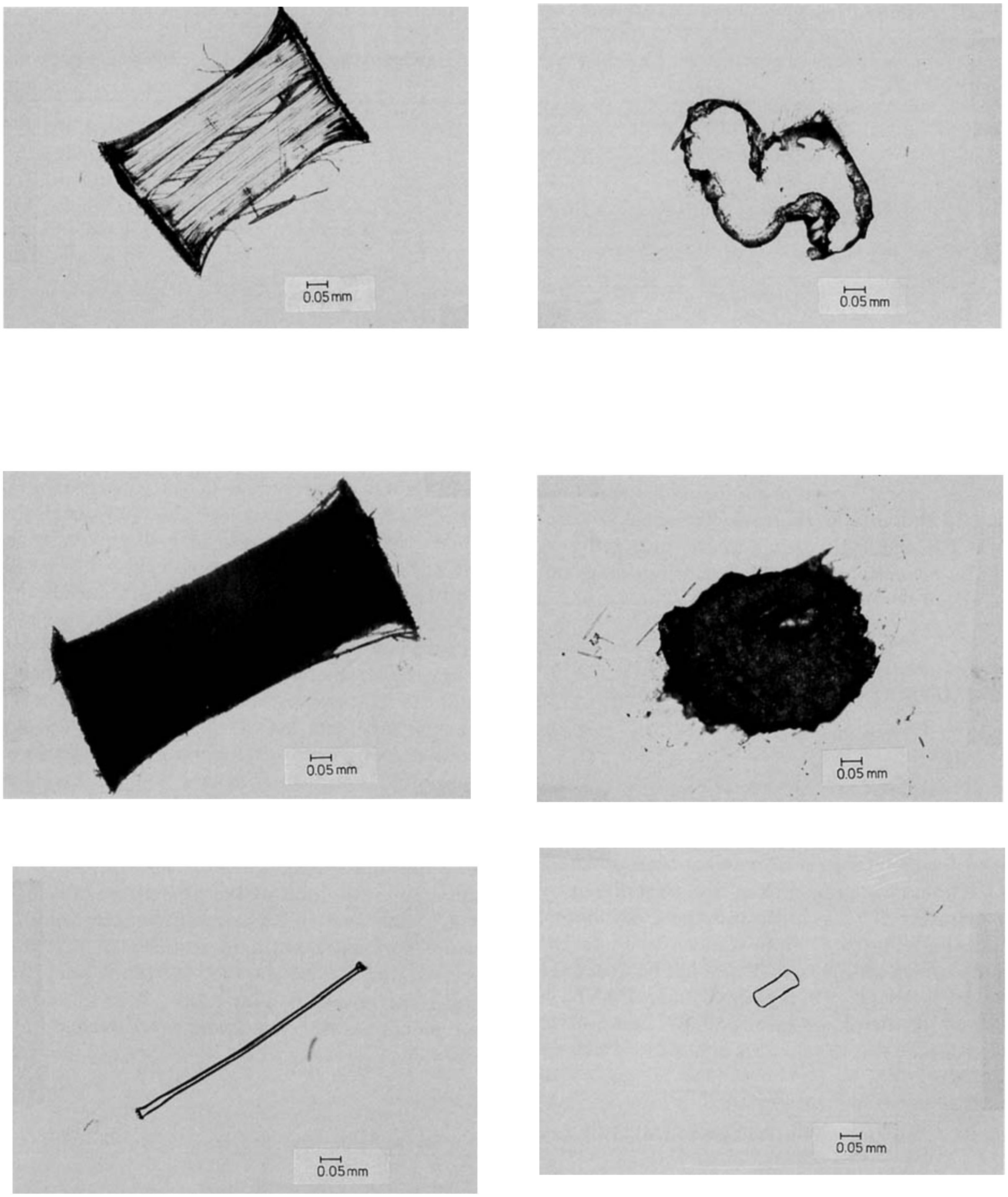

Figure 1 Fiber samples of (upper) PP7, (middle) PP11, and (lower) PP15 under a hot-stage microscope at (left) 80°C and (right) 165–168°C.

RESULTS

The PP fibers were studied under the hot-stage microscope up to 180°C, i.e., until the fibers had melted. The results of the shrinkage measurements are given in Tables II–IV. Photographs of some fiber samples are shown in Figure 1.

The PAN fibers were studied under the hot-stage microscope up to 230°C. The results of the shrinkage measurements are given in Tables V and

Table V Cumulative Shrinkage of PAN4 Fibers at 150, 170, 200, and 220°C

Sample	Sample Length (mm)	Shrinkage at 150°C (%)	Shrinkage at 170°C (%)	Shrinkage at 200°C (%)	Shrinkage at 220°C (%)
PAN4 No. 1	0.470	7.1	7.1	8.2	8.2
PAN4 No. 2	0.566	4.2	5.1	5.9	7.6
PAN4 No. 3	0.595	6.5	6.5	8.1	8.1
PAN4 No. 4	0.662	5.8	7.2	8.7	9.4
PAN4 No. 5	0.662	6.5	6.5	8.7	8.7
	Average	6.0 ± 1.1	6.5 ± 0.8	7.9 ± 1.2	8.4 ± 0.7

VI. Photoraphs of some fiber samples are shown in Figure 2.

The PP fibers had different melting temperatures: PP7 and PP15 around 160°C and PP11 around 165°C. The average cumulative shrinkage prior to melting was 6% for PP7, 3% for PP11, and 10–15% for PP15. The higher melting temperature and smaller shrinkage of PP11 is possibly due to the inorganic $CaCO_3$ filler component in its fibers. PP15 fibers shrank significantly more than did the other PP fibers. This suggests that the degree of orientation was originally higher in the melt-spun PP15 than in PP7 or PP11 fibers from film. The cumulative shrinkages of PP7 and PP11 were slightly dependent on the sample length; shrinkage increased with increasing sample length, as can be seen from Tables II and III.

The polyacrylonitrile fibers shrank throughout the heating period without melting. The average cumulative shrinkages for PAN4 fibers at 150, 170, 200, and 220°C were 6, 6.5, 8, and 8.5%, and for PAN5 fibers, 6, 7, 8, and 9.5%, respectively. The differences in shrinkage of the two PAN fiber types were relatively small. Again, however, the measured shrinkage was slightly dependent on sample length, as seen from Tables V and VI. On the whole, shrinkage values measured with the hot-stage microscope agree well with the boiling water and hot-air shrinkage values given by the fiber manufacturer. The shrinkage of PAN fibers was studied only up to 230°C. The measured shrinkage values were relatively small as they mainly represent the primary shrinkage due to molecular relaxation.

The measured shrinkage values seem to have a slight correlation with the basic mechanical properties of the PP fibers—increased shrinkage is obtained with PP15 having the weakest mechanical properties. With PAN fibers, however, no such correlation is found.

The appearance of some fiber samples at different temperatures is seen in Figures 1 and 2. The melting of PP fibers is clearly observed around 160–170°C, whereas PAN fibers retain their shape during the heating process.

DISCUSSION AND CONCLUSIONS

Heating rates of PAN fibers up to 10°C/min have been suggested for technical application.[14] Increasing the heating rate increases the total amount of chemical shrinkage of PAN.[15] A heating rate 10°C/min was chosen in this study for PP and PAN fibers.

Table VI Cumulative Shrinkage of PAN5 Fibers at 150, 170, 200, and 200°C

Sample	Sample Length (mm)	Shrinkage at 150°C (%)	Shrinkage at 170°C (%)	Shrinkage at 200°C (%)	Shrinkage at 220°C (%)
PAN5 No. 1	0.504	5.7	7.6	7.6	8.6
PAN5 No. 2	0.782	5.5	6.7	8.0	9.2
PAN5 No. 3	0.874	6.0	7.1	8.8	9.9
PAN5 No. 4	0.922	6.6	7.7	8.7	9.7
	Average	6.0 ± 0.5	7.3 ± 0.5	8.3 ± 0.6	9.4 ± 0.6

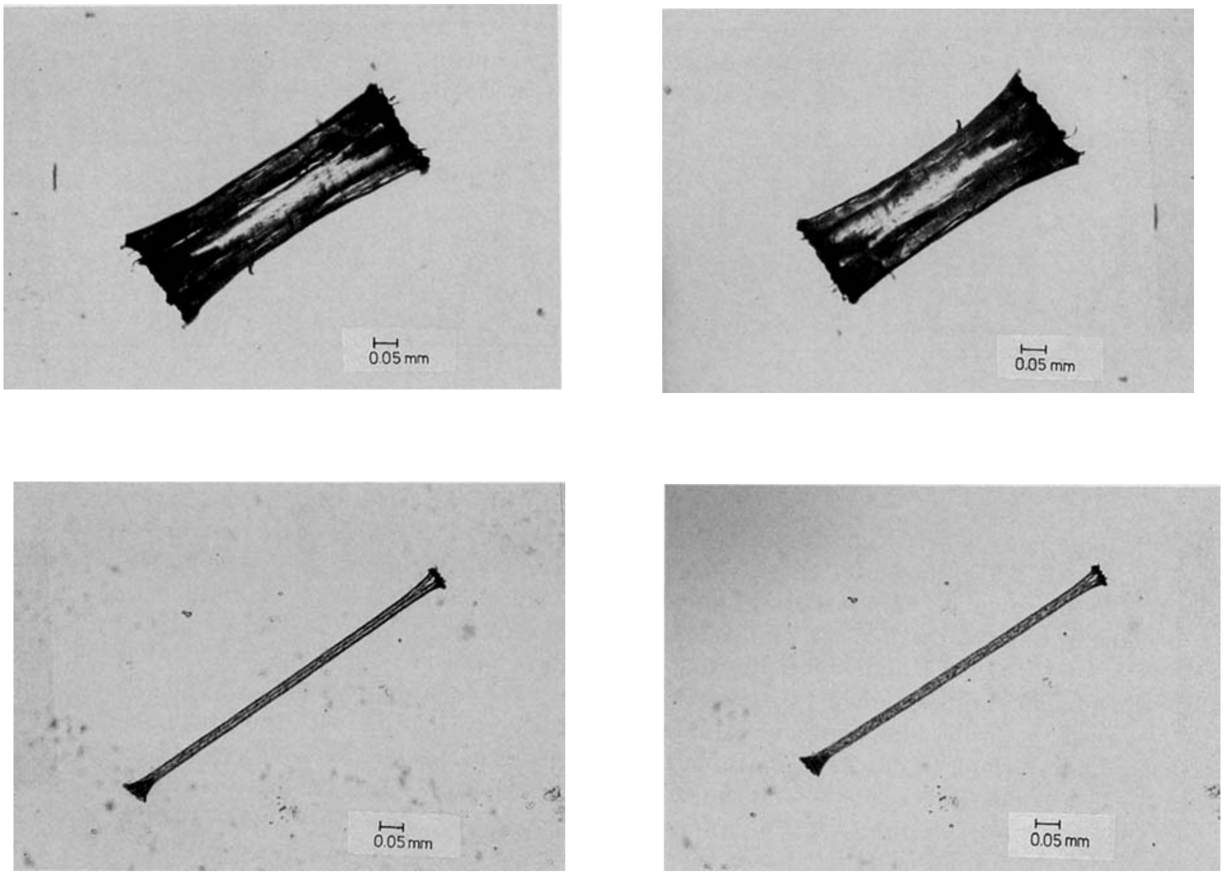

Figure 2 Fiber samples of (upper) PAN4 and (lower) PAN5 under a hot-stage microscope at (left) 80°C and (right) 166–170°C.

Moisture evaporation from concrete takes place at a temperature between 100 and 200°C. This temperature range was chosen for the study of the fibers (80–180°C for PP, 80–230°C for PAN). It was possible to detect significant differences in the cumulative shrinkages of various PP fibers under the hot-stage microscope. With the two PAN fiber types, the differences were smaller. Only primary shrinkage of PAN was measured. Deviations from the measured average shrinkage values were between 2 and 42%, but most typically around 7–15%.

Measured shrinkage values for some fibers seem to increase with sample length. A possible explanation is that distortions in the sample ends had a different shrinkage tendency from that of the bulk fiber structure. The sample preparation technique of cutting with a knife had disrupted the fiber structure at the sample ends. The shorter the sample, the smaller was the proportion of normal bulk fiber structure. Thus, for 12 mm staple fibers, actual relative thermal shrinkage values could be expected to be higher than indicated by hot-stage microscopy.

Hot-stage microscopy provides a simple, inexpensive, and relatively accurate method for estimating thermal shrinkage of staple PP and PAN fibers. In addition, the melting point of a PP fiber is easily determined.

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