

# Effect of Dry/Wet Spinning on the Photooxidative Degradation of Acrylic Fibers

A. Aghanouri,<sup>1</sup> A. Zadhoush,<sup>1</sup> M. Haghighat<sup>2</sup>

<sup>1</sup>Textile Engineering Department, Isfahan University of Technology, Isfahan 84156–83111, Iran

<sup>2</sup>Chemical Engineering Department, Isfahan University of Technology, Isfahan 84156, Iran

Received 8 July 2007; accepted 6 July 2008

DOI 10.1002/app.29044

Published online 17 October 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The photooxidative degradation of acrylic fibers was investigated with two different fiber-spinning processes, that is, dry spinning and wet spinning. Several analytical methods were used in this study: viscometry, X-ray diffraction, Fourier transform infrared spectroscopy, optical measurements, and mechanical testing. Viscometry was used to determine the molecular weight as a monitoring factor for degradation. X-ray diagrams showed lower changes in the crystallinity of wet-spun

fibers during a weathering process by irradiation. The results from mechanical testing indicated that the tenacity of dry-spun fibers had less deterioration than that of wet-spun fibers. Degraded wet-spun and dry-spun fibers showed similar trends in optical and spectroscopy analysis. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 945–952, 2009

**Key words:** orientation; photochemistry; radiation

## INTRODUCTION

One of the oldest methods for the preparation of manmade fibers is solution spinning, which was introduced industrially at the end of the 19th century. Solution spinning includes wet spinning and dry spinning. Acrylic fibers can be produced by either dry- or wet-spinning processes.

The dry-spinning process begins with the dissolution of the polymer in an organic solvent. This solution is blended with additives and is filtered to produce a viscous polymer solution, which is called the *dope*, for spinning. The polymer solution is then extruded through a spinneret (die) with numerous holes (one to thousands) as filaments into a zone of heated gas or vapor. As the fibers exit the spinneret, air is used to evaporate the solvent so that the fibers solidify and can be collected on a take-up wheel. Stretching of the fibers provides orientation of the polymer chains along the fiber axis.<sup>1,2</sup> Wet spinning begins by the dissolution of polymer chips in a suitable organic solvent, such as dimethylformamide (DMF), dimethylacetamide (DMAc), or acetone, as in dry spinning, or in a weak inorganic acid, such as zinc chloride or aqueous sodium thiocyanate. In wet spinning, the spinning solution is extruded through spinnerets into a precipitation bath that contains a coagulant (or precipitant) such as aqueous DMAc or water. Precipitation or coagulation occurs by diffu-

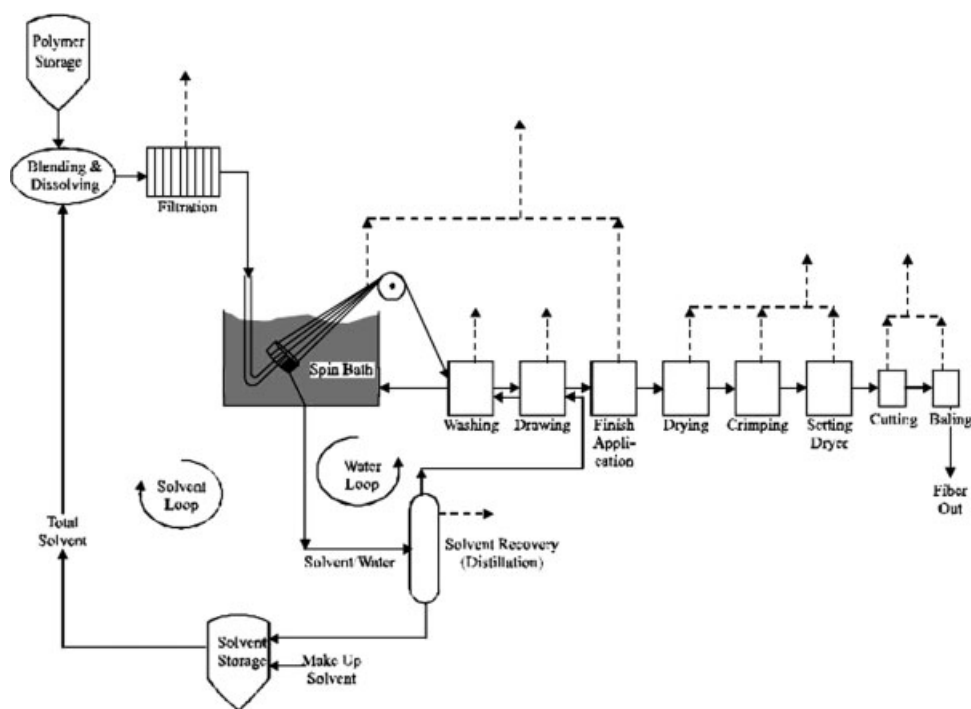
sion of the solvent out of the thread and by diffusion of the coagulant into the thread.<sup>3</sup>

Acrylic fibers are based on acrylonitrile monomer, which is derived from propylene and ammonia. Acrylics are defined as those fibers that are at least 85% acrylonitrile. The remaining composition of the fiber typically includes at least one of the following: methyl methacrylate, methyl acrylate, vinyl acetate, vinyl chloride, and vinylidene chloride.

As shown in Figures 1 and 2, the polymer is dissolved in a suitable solvent, such as DMF or DMAc. Additives and delusterants are added, and the solution is filtered in plate and frame presses. The solution is then pumped through a manifold to the spinnerets (usually a bank of 30–50 per machine). At this point in the process, either wet or dry spinning can be used to form the acrylic fibers. The spinnerets are in a spinning bath for wet-spun fibers or at the top of an enclosed column for dry spinning. The wet-spun filaments are pulled from the bath on take-up wheels and then washed to remove more solvent. After being washed, the filaments are gathered into a tow band, stretched to improve strength, dried, crimped, heat-set, and then cut into staples. The dry-spun filaments are gathered into a tow band, stretched, dried, crimped, and cut into staples.

Photodegradation is the chemical transformation of a compound into smaller compounds caused by the absorption of ultraviolet, visible, or infrared radiation (light). In many cases, photodegradation is an oxidation process.<sup>4–7</sup> Many compounds, when exposed to sunlight, degrade into smaller compounds.

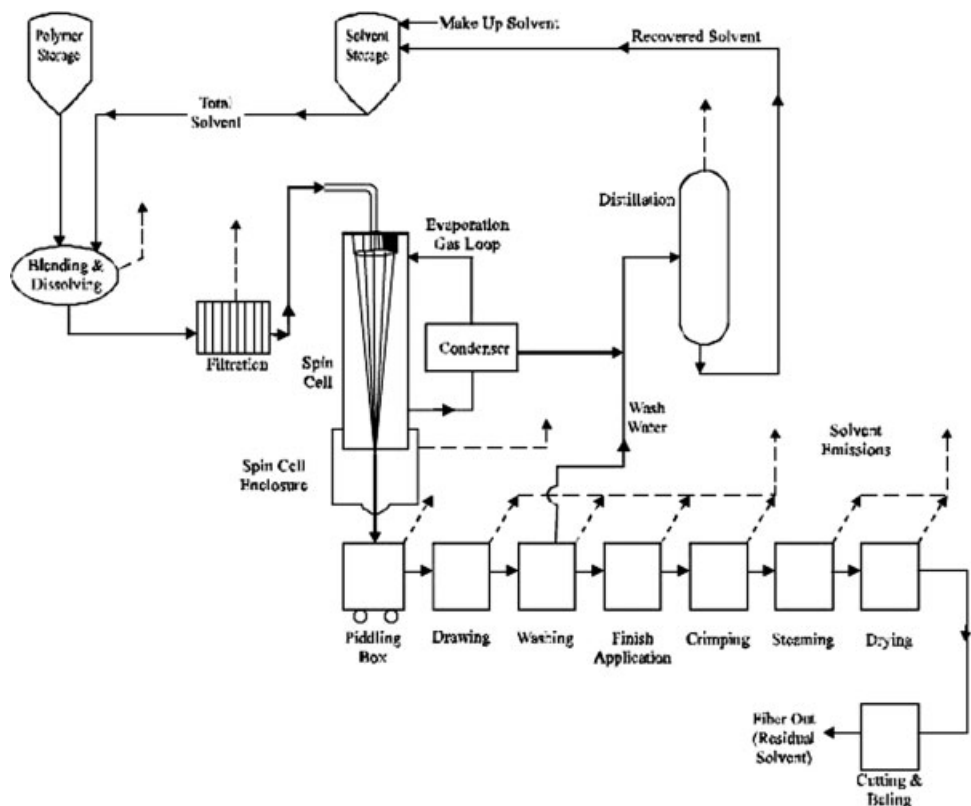
Correspondence to: A. Zadhoush (zadhoush@cc.iut.ac.ir).



**Figure 1** Schematic representation for the wet-spinning process of the acrylic fibers.

Most of the studies on the photooxidation of acrylic polymers have been concerned with the mechanism of degradation, polymer structure, and effects of fillers and pigments on the degradation.<sup>8-15</sup>

At present, a literature search shows no publications on the effect of the spinning process type on the degradation of synthetic fibers, especially acrylic fibers. In this study, the photooxidation of acrylic



**Figure 2** Schematic representation for the dry-spinning process of the acrylic fibers.

TABLE I  
Acrylic Fiber Characteristics

Sample	Acrylonitrile	Methyl acrylate	SAS	SAMPS	Solution	Spinneret whole cross section	Draw ratio	Spin finish	Crimping
Dry-spun	94%	5.5%	0.3%	—	DMF	Circular	5	Yes	Stuffer box
Wet-spun	94%	5.5%	—	0.4%	DMF	Circular	5	Yes	Stuffer box

SAS, sodium allylsulfonate; SAMPS, sodium 2-methyl-2-acrylamidopropane sulfonate.

fibers manufactured by a dry/wet-spinning process was investigated.

Photooxidation of acrylic fibers over a period of time can cause discoloration and a reduction of physical properties. In actual environmental exposure, a fiber is subjected to the effects of actinic radiation (ultraviolet and visible light), oxygen, heat, moisture, and airborne pollutants. The magnitude of these effects can vary from location to location. Acrylics are among the fibers most resistant to the effects of weathering, and this has led to their applications in awnings, tents, outdoor furniture, and sandbags.

Acrylic fiber is the most stable of fibers against tensile strength degradation. Although acrylic yarn is the least affected by dry ultraviolet exposure, it is the most affected by wet/dry cycles.<sup>16</sup>

## EXPERIMENTAL

The investigated dry/wet-spun acrylic fibers were provided by Polyacryl Co. (Isfahan, Iran), and their characteristics are shown in Tables I and II.

Acrylic fibers were conditioned for 2 months in a standard environment in the absence of light.

Irradiation was carried out with a Heraeus (Hanau, Germany) Xenotest 150S in accordance with ISO 105 B04. The xenon-arc weatherometer used a long-arc, air-cooled xenon lamp equipped with inner and outer filters as the light source. The test conditions were specified as much as possible to find the highest possible level of reproducibility. The test parameters are given in Tables III and IV.

The test methods used for the evaluation of the effects of weathering are given in Table V.

Tensile tests were performed under a standard atmosphere with a Fafegraph HR (Mönchengladbach, Germany) fiber test machine with a constant

rate of crosshead speed of 20 mm/min. The tests were performed in accordance with ISO 527.

Color differences caused by weathering were measured with a Data Color (Zurich, Switzerland) Texflash. Results are expressed in terms of the Commission Internationale de l'Eclairage  $L^*a^*b^*$  system. Color differences are also expressed with respect to unweathered test pieces.

The effects of weathering were investigated by infrared measurements with a Bomem MB100 (Vannier, Quebec, Canada) Fourier transform infrared apparatus, and samples were exposed to infrared radiation in the range of 400–4000  $\text{cm}^{-1}$ . Infrared spectra from the exposed surfaces were obtained for all materials before and after exposure.

To investigate the evolution of the crystalline order in these samples, a Philips X'Pert-MPD (Amsterdam, the Netherlands) X-ray diffraction apparatus was used. The start angle, end angle, and step size were 10, 50, and 0.04°, respectively.

Viscometry analysis was performed with a KPG Cannon–Fenske viscometer (type 51320), State College, PA. Samples (0.5, 0.7, and 0.9 g) were dissolved in 100 mL of DMF at 25°C. The procedure was carried out according to ASTM D 4603-96.<sup>17</sup> The molecular weight was usually expressed in terms of its equivalent intrinsic viscosity ( $[\eta]$ ). The viscosity-average molecular weight ( $M_v$ ) of samples was calculated on the basis of  $[\eta]$  data with the Mark–Houwink relationship:<sup>18</sup>

$$[\eta] = K[M_v]^a$$

The following equation was used for the determination of the number-average molecular weight:<sup>19</sup>

$$[\eta] = 3.10 \times 10^{-4} [M_n]^{0.79}$$

TABLE III  
Prescribed Test Conditions

Test condition	Requirement
Irradiance in the band pass of 300–400 nm	105–140 W/m <sup>2</sup>
Rain and dry cycles	1/29 min/min
Relative humidity	7.3–30%
Chamber temperature	18–31.5°C
Black standard temperature	50°C
White standard temperature	40°C

TABLE II  
Acrylic Fiber Characteristics

Sample	Fiber number (dtex)	$M_n$	Tenacity (cN/dtex)	Elongation (%)
Dry-spun	7.9	35,900	3.16	32.28
Wet-spun	8.5	35,300	2.65	42.55

**TABLE IV**  
Prescribed Ultraviolet Exposure Times

Material designation		Exposure time (h)
Wet-spun	Dry-spun	
W	D	0
W75	D75	75
W150	D150	150
W225	D225	225
W300	D300	300

## RESULTS AND DISCUSSION

### Viscometry

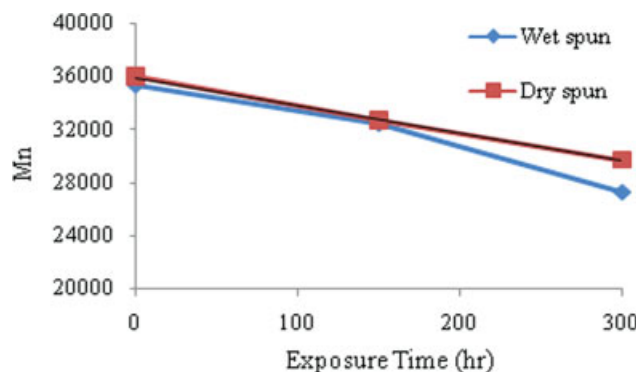
The extent of degradation of the acrylic fibers has been measured by the monitoring of changes in the molecular weight. The extent of photodegradation (reduction of the molecular weight) increases with increasing time because of molecular chain breakdown caused by the irradiation, and this is illustrated by the data shown in Figure 3. From Figure 3, it can also be observed that the average variation in the molecular weight in the wet-spun fibers is higher than that in the dry-spun fibers. This shows that the degradation and chain scission in the wet-spun fibers are higher.

### Yellowness index

As shown in Figure 4, at high energy levels ( $\lambda > 250$  nm), the formation of intermediate diradicals from  $-\text{C}^\bullet=\text{N}^\bullet$  groups and subsequent ring closure account for the yellowish-brown color (corresponding to the yellowness index). The extent of such reactions occurring under lower energy conditions of exposure to longer wavelength, natural sun light remains to be determined. Hence, the yellowness index can show the magnitude of the degradation.<sup>8,16</sup>

**TABLE V**  
Test Methods Used for the Evaluation of Weathering Effects

Property	Method of evaluation
Mechanical	
Tensile strength	ISO 527
Elongation at break	ISO 527
Optical	
Color ( $L^*$ , $a^*$ , $b^*$ )	ISO 2579
Chemical	
Functional groups	Fourier transform infrared
Physical	
Molecular weight	Viscometry
Crystallinity	X-ray diffraction



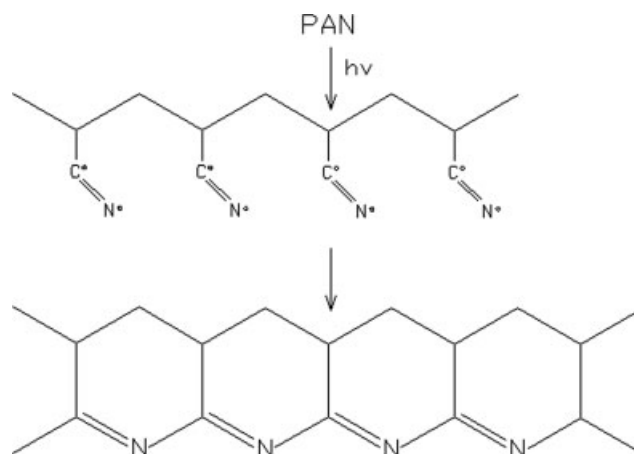
**Figure 3** Changes in  $M_n$  of the acrylic fibers as a function of the irradiation exposure time. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Figure 5 shows that the dry- and wet-spun acrylic fibers change with respect to the yellowness index with the exposure time. The yellowness index increases as a function of the exposure time for both fibers. In the wet-spun fibers, the yellowness index is more pronounced than in the dry-spun fibers, and this indicates that the extent of degradation in the wet-spun fibers is higher and is in accordance with the viscometry results.

### X-ray diffraction and orientation

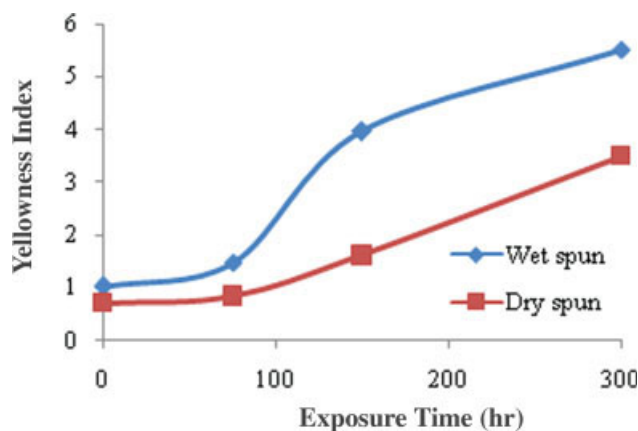
In crystalline regions, it is assumed that the distance between the chains is very small; therefore, the access of other compounds to this molecular fragment is very difficult.

Parts of the chain, which are not structurally aligned, participate in the formation of an amorphous region, which differs from that of the crystalline regions. One difference between these regions is



**Figure 4** Formation of intermediate diradicals and a subsequent ring structure as a function of irradiation.



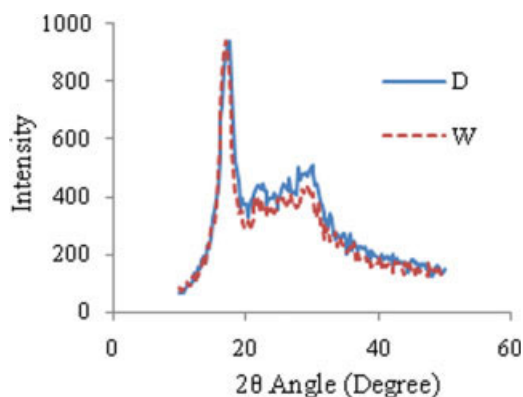


**Figure 5** Yellowness index (D65) of the acrylic fibers as function of the exposure time. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the freedom of chain movement, which is restricted in the crystalline area and more free in the amorphous area; therefore, differences between crystalline and amorphous areas result in different reactions in each area.

If gases, liquids, radicals, stabilizers, and so forth are expected to react in a particular system, they will react at sites that they are able to penetrate, namely, fold surfaces or amorphous regions. Wypych<sup>20</sup> studied the photochemistry of polyolefins and the effect of radiation exposure on elongation and crystallinity. He too found that specimen irradiation results in increasing crystallinity after a sufficient amount of chain scission has occurred. Also, the oxidation rate is roughly proportional to the amount of the amorphous fraction present.

Figure 6 presents the results of X-ray diffraction for the initial exposure time of the acrylic fibers. Both spinning methods have almost equal amorphous and crystalline regions. It is therefore



**Figure 6** Crystallinity of the dry/wet-spun fibers at the end of exposure. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 7** Cross section of the wet-spun fibers (1000× zoom).

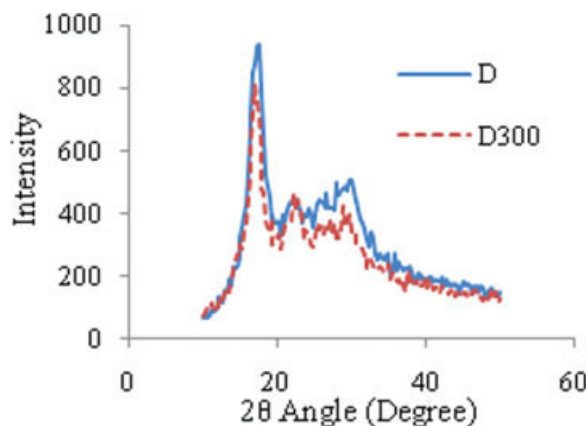
expected that the two spinning methods will have the same extent of degradation, but the viscometry and yellowness index show different results.

This discrepancy can be explained by the cross-sectional area of the fibers shown in Figures 7 and 8. The micrographs show an almost bicomponent sheath–core status with a typical two-zone morphology cross section. The sheath percentage of the dry-spun fibers is much higher than the sheath section of the wet-spun fibers. This thicker sheath prevents water and gas penetration and acts as an oxygen barrier, resulting in a lower extent of degradation for the dry-spun fibers.

Figures 9 and 10 show the results of changes in the crystallinity of dry- and wet-spun acrylic fibers at the start and end of the exposure time. In both

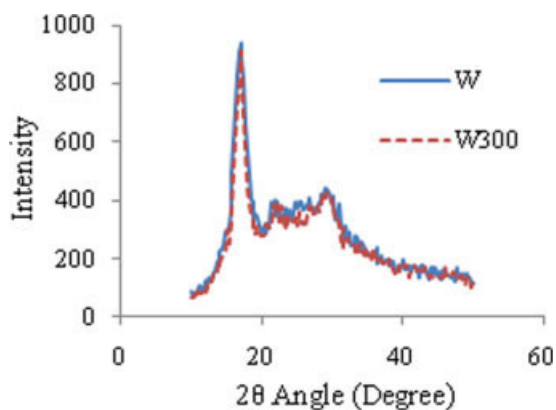


**Figure 8** Cross section of the dry-spun fibers (1000× zoom).



**Figure 9** Crystallinity changes in the dry-spun acrylic fibers. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

spinning methods, no significant change has been seen in the crystallinity of the acrylic fibers. In the wet-spun acrylic fibers, the exposure time has led to no changes in the crystallinity, but in the dry-spun fibers, the crystallinity has decreased. This is due to the higher chain scission occurring in the wet-spun fibers, which results in a shortening of the molecular chains in the interface and amorphous regions. Hence, the tension on the molecules is released, and this enables the rearrangement of the molecules, causing higher crystallinity. On the other hand, degradation at the surface of the crystalline region will cause a reduction in the amount of crystallinity; the net result of these phenomena will dictate the overall increase or decrease in the degree of crystallinity. In addition, water acts as a plasticizer and accelerates the recrystallization of the shortened chain molecules.<sup>20</sup>



**Figure 10** Crystallinity variations in the wet-spun acrylic fibers. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

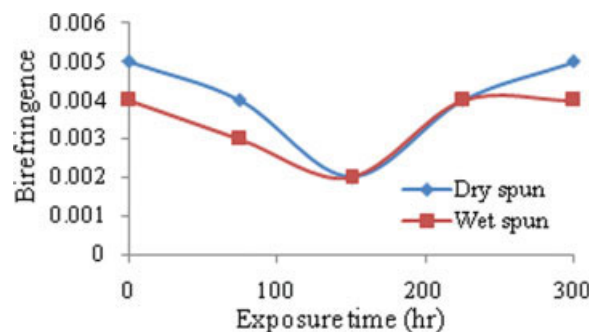
Birefringence is a measure of molecular orientation. In Figure 11, the results of the birefringence variation of acrylic fibers as a function of the exposure time are shown. The orientation decreases up to 150 h and increases with a longer exposure time. This can be explained as follows: in the first stage, changes in the molecular chain lengths and crystallinity facilitate the release of the solvent from the amorphous region, and this can cause higher orientation.

Fourier transform infrared results, shown in Figures 12 and 13, indicate the presence of the solvent (DMF) as a carbonyl amide group peak ( $\sim 1670 \text{ cm}^{-1}$ ). The amount of the solvent in the dry-spun fibers seems to be higher as a result of the thicker sheath section. The gradual departure of the solvent during the test time is clearly shown by the changes in the peak intensity.

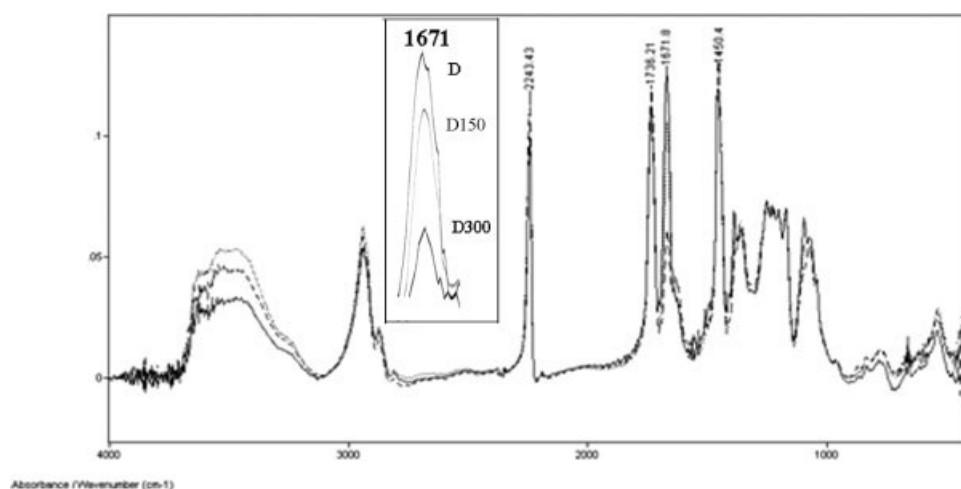
The incomplete exit of the solvent from the fibers and existence of the solvent in the fiber center prevent full orientation in the central section of the fibers and can cause disorder in the molecular arrangements;<sup>1</sup> therefore, with the gradual exit of the solvent from the fibers, the orientation of the amorphous areas increase.

### Mechanical properties

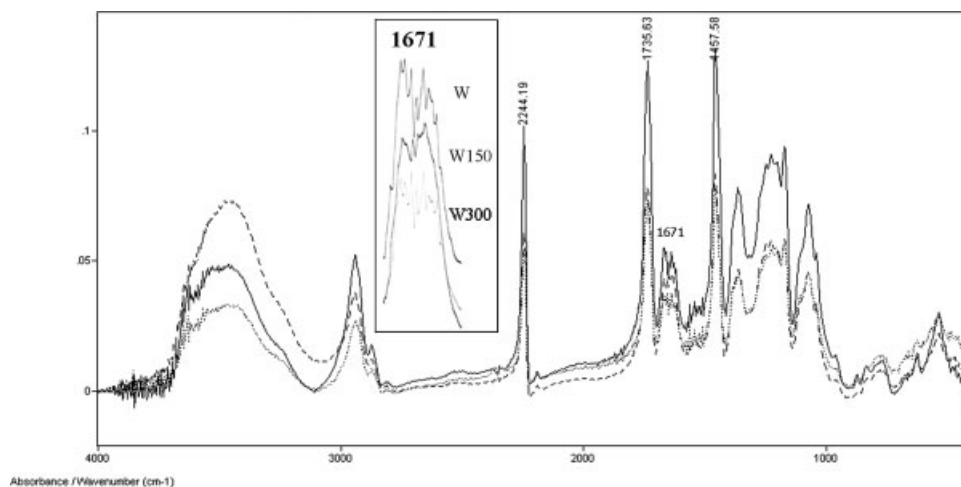
Figures 14 and 15 show the tenacity and elongation at break of degraded dry-spun fibers at different exposure times, respectively. The results show that the tenacity and elongation at break decrease sharply with the exposure time increasing up to 150 h, whereas after this time, the changes for the wet-spun fibers are not significant, but a gradual increase for the dry-spun fibers can be observed. The lower extent of the degradation and higher amount of solvent departure (its departure causing higher orientation) in the dry-spun fibers cause the increase in the tenacity and elongation at break after the initial decrease.



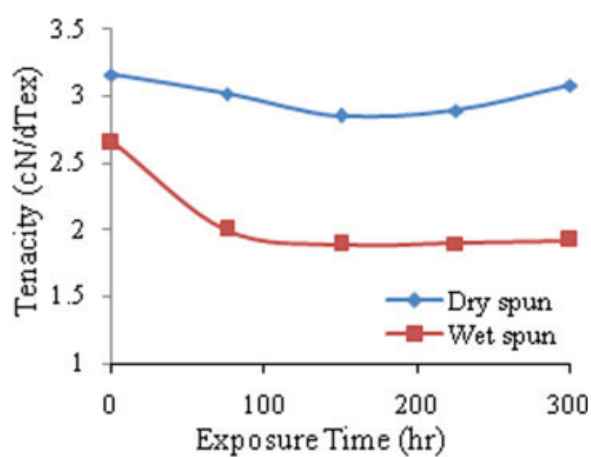
**Figure 11** Orientation changes in the dry/wet-spun acrylic fibers. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



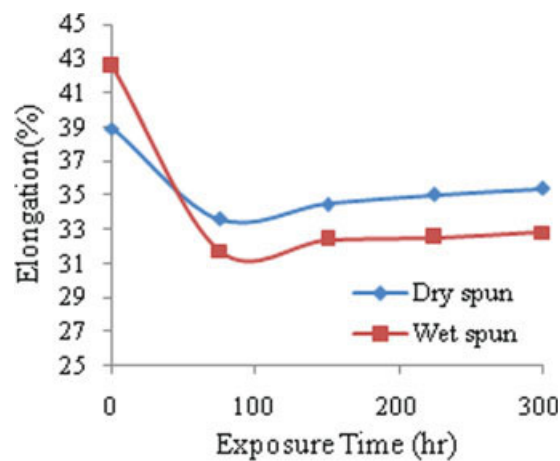
**Figure 12** Decrease in the residual DMF of the dry-spun samples: (—) D, (---) D300, and (· · ·) D150.



**Figure 13** Decrease in the residual DMF of the wet-spun samples: (—) W, (---) W150, and (· · ·) W300.



**Figure 14** Tenacity of the dry/wet-spun acrylic fibers. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 15** Elongation at break of the dry/wet-spun acrylic fibers. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

An important result of this investigation is that the decrease in the tenacity of wet-spun fibers is greater than that in dry-spun fibers. The maximum decrease in the tenacity of wet-spun fibers is 23%, and for the dry-spun fibers, it is 9%; after 300 h of exposure, the decrease in the tenacity of wet-spun fibers is 21%, and for dry-spun fibers, it is 4%. The results for the elongation at break confirm the tenacity results.

### CONCLUSIONS

Under the test conditions used in this study, it can be concluded that the extent of the acrylic fiber degradation is dependent on the type of spinning. The results obtained from photodegradation are as follows:

1. The average variation of the molecular weight in the wet-spun fibers is higher than that in the dry-spun fibers.
2. The extent of the yellowness of the wet-spun fibers is higher than the yellowness of the dry-spun fibers.
3. X-ray analysis shows that the wet-spun fibers have greater resistance to crystallinity changes caused by weathering in comparison with the dry-spun fibers.
4. The orientation changes due to degradation have similar trends for both kinds of fibers.
5. Mechanical testing results for the degraded fibers indicate that the wet-spun fibers have higher potential for degradation.

6. The cross-sectional area of the two kinds of fibers, as well as its characteristics, plays an important role in the extent of fiber degradation.

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