Reduction of Aging Tendency in *p*-Aramide Fibers Using Ultrasound

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ABSTRACT: The impact of ultrasound pretreatment of *p*-aramide fibers is investigated to reduce negative effects of fiber aging induced by artificial white light (Suntest), as well as by sunlight and weathering. The investigations indicate that such a pretreatment has a beneficial influence in reducing the aging tendency of the fibers. The ultrasound pretreatment reduces strength losses due to aging in a natural environment by up to 40%, and as much as 60% in artificial environment. A positive impact of the duration of ultrasound treatments is also established in assessing the resistance of *p*-aramide fibers to aging. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2340–2345, 2000

Key words: *p*-aramide fibers; ultrasound; aging; tensile strength; breaking load

INTRODUCTION

Since the first application of high-performance fibers in the areas of high safety risk (e.g., plane industry, rocket, and military technique, protection, shipbuilding, etc.) a number of researchers in the field of polymer science and technology have been investigating the phenomenon of aging in these polymers. For the practical application of these and other polymers, it is especially important to find ways to keep them resistant and prolong their useful life; in other words, to find out how to slow down the process of aging.

Regardless of the complexity and variety of the processes taking place in the fiber, aging is always associated with degradation. Polymer degradation means a set of physical and/or chemical changes of polymer molecules, regarding their size, chemical composition, configuration, conformance, and the supramolecular structure of the fiber.

Various influences cause degradation, such as: light, heat, some chemical agents, radiation, mechanical, microbiological influences, etc.

It is well known that all types of aramide fibers are prone to aging when exposed to weathering conditions. The investigations on the impact of various weather parameters on aramide fiber aging indicate that degradation takes place only in the presence of oxygen, and is not accelerated by pollutants, such as SO_2 .[1] Absorption of irradiated energy of particular wavelength (provided it possesses enough power to break chemical bonds in the fiber) precedes fiber degradation under the impact of certain radiation. The absorption spectrum of *p*-aramide fibers and the radiation spectrum of sunlight at the Earth's surface overlap in the area of near ultraviolet and a part of visual spectrum, for example, from 300 to 450 nm, which practically covers the circumstances of the usage of these fibers in the open. Aging tendency of aramide fibers under the impact of sunlight can also be proved by the fact that, although only a minor part of this radiation is present in artificial light sources, this radiation also causes a considerable degree of fiber degradation.[1,2]

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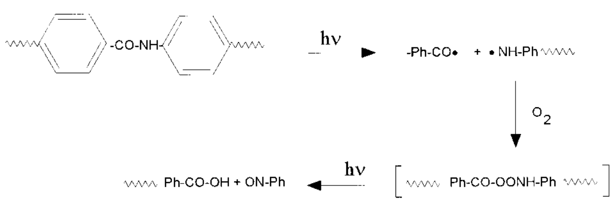
Table I Properties of Tested *p*-Aramide Woven Fabric

Fiber Fineness (dtex)	Yarn Fineness Warp/Weft (tex)	Fabric Thickness (mm)	Weight per Unit Area (g/m^2)	Fabric Weave	Fabric Density Warp/Weft (Yarns/10 cm)	Special Finishing
0.98	93/93	0.30	194	plain	108/104	waterproof

The degradation of *p*-aramide fibers induced by UV radiation is a reaction of random splitting of a polymer molecule, with an intensive reduction of molecular mass. The extent and the rate of the process are augmented by the presence of amide groups and aromatic rings, sensitive to photooxidation. The most pronounced characteristic of oxidative degradation is the creation and degradation of hydroperoxide.

Photooxidative degradation of *p*-aramide starts at the amide group advances by a radical mechanism and can be attributed to the Norrish-I splitting. The radicals created by splitting amide links bind oxygen, giving a peroxide intermediary, which is unstable and is degraded by the absorption of the light.[3]



Even after a short exposure of unprotected aramide fibers to UV radiation, certain signs of aging can be noticed, due to the changes occurring in the fibers. Only a thin surface layer is altered chemically, the thickness of which is limited by the depth of UV ray penetration. The color, luster, and the quality of the surface deteriorate gradually, while the mechanical properties deteriorate at a much faster rate. To protect aramide fibers from the destructive influence of light, it is necessary to prevent the impact of the spectrum in the range from 350 to 450 nm, or otherwise, improve the resistance of the fibers by incorporating certain light absorbers in their structure, or modify them in some other way.

In the course of the investigation described, the authors have tried to slow down *p*-aramide fiber aging by employing ultrasound.

EXPERIMENTAL

Investigations of fiber aging under various conditions have been organized in The Department of Textile Chemistry and Material Testing, Faculty of Textile Technology, University of Zagreb,[4,5] as well as possible ways to solve this problem. Quite interesting results have been obtained employing ultrasound. In the course of current investigations of polyamide fibers, the impact of ultrasound waves on fiber properties has been investigated, and the results have confirmed that after being exposed to ultrasound, the fibers show less tendency of aging under the influence of UV light in natural environment.[6,7] These results served as a basis of further investigations of the impact of ultrasound pretreatment on the aging tendency of *p*-aramide fibers under the influence of light and weather conditions, as the proneness to aging of *p*-aramide fibers under these conditions is one of their most prominent disadvantages.

Samples Tested and Treatments Applied

The investigations described were performed on a *p*-aramide woven fabric [Twaron®-AKZO, High Tenacity Yarn (Type 2000/2040) CT709] with properties presented in Table I. (Detailed data on contained additives was not available.)

Samples were prepared from the fabric described, and then subjected to treatments the impact of which on fiber properties was planned to be tested.

A part of the samples was subjected to ultrasound pretreatment (frequency of ultrasound waves: 30 kHz). Distilled water was used as a medium of propagating the ultrasound waves. The initial water temperature was 40°C; the treatment duration: 10, 20, and 40 min.

Samples treated with ultrasound, and the untreated samples were simultaneously subjected to the influence of light in natural and artificial surroundings. As *p*-aramide fiber aging by influence of light starts after a relatively short exposure time (a few hours), the exposure was limited from a few hours to a few days at most.

In the investigations of natural aging, the yarn taken from the fabric was exposed to atmospheric conditions in a rural environment for the periods of 3, 6, 9, 24, 72, and 168 h. The key factor of aging

Table II Determination of *p*-Aramide Fiber Breaking Load Before and After Weathering

Ultrasound Treatment	Exposure Time (h)	*F* (cN)	σ (cN)	*V* (%)	ΔF (%)
No treatment	0	3.3	0.95	16.0	—
	3	2.97	0.70	21.2	−10
	6	2.78	0.73	21.8	−16
	24	2.53	0.80	21.1	−23
	72	2.18	0.85	19.0	−34
	168	2.04	0.37	24.6	−38
10 min	0	3.48	0.92	17.6	+5
	3	2.96	0.85	22.1	−1
	6	2.73	0.74	25.0	−17
	24	2.61	1.09	23.3	−21
	72	2.51	0.75	21.0	−24
	168	2.28	0.80	20.7	−31
20 min	0	3.50	0.97	15.6	+6
	3	3.28	0.82	20.1	−5
	6	2.90	0.49	17.0	−12
	24	2.86	1.10	18.0	−13
	72	2.59	0.85	23.1	−22
	168	2.40	0.80	20.0	−27

was sunlight, but the presence of weather conditions and pollutants in the atmosphere should not be ignored. Rural environment was chosen specifically because of a minimal atmospheric pollution present there.

Artificial aging was performed by exposing the samples to the influence of UV and visible spectrum of light (λ from 280 nm to 830 nm, Suntest CPS apparatus, Heraeus Industrie Technik), for the duration of 20 min and 1, 3, 18, and 24 h. According to the specifications provided by the manufacturer,[8] the treatment in the Suntest apparatus is around 10 times more intensive compared to natural conditions, meaning that the above duration of the treatment correspond to 3.3, 10, 30, 180, and 240 h of exposure in natural environment.

Aging Process Characterization

Strength reduction was taken as a measure for fiber degradation due to aging. For this purpose the breaking load of single fibers and of fabric samples was measured on a tensile testing machine. The breaking load of fibers was measured according to the single fiber method (DIN 53816, 1976, 50 parallel measurements), and for the fabric the Standard Test Method for Breaking Force and Elongation of Textile Fabrics (strip Force) according to ASTM D 5035-90 (type of specimen: 50 mm cut strip test; type of tensile testing machine: constant-rate-of-extension, CRE) was used. The testing was performed in the warp and weft directions of the fabric samples. For each measuring point for the fabric samples, the average value of five measurements was taken.

The results obtained were statistically processed, and statistical data for the assessment of result dispersion and reliability were also calculated.

RESULTS AND DISCUSSION

The results of measuring the fiber breaking load (F, cN), as well as the breaking load of the fabric (F, N) in warp and from weft direction are given in Tables II and III.

Tables II and III also show the conventional statistical data for the standard deviation (σ) and variation coefficient (V), while the changes in strength are presented as a percentage of fiber and fabric breaking load change after the treatments, in relation to the untreated sample. The results are graphically presented in Figures 1, 2, and 3, where the error bars are also shown.

The results given in Tables II and III indicate a positive impact of ultrasound pretreatment on the strength of the tested fibers and fabric. After the ultrasound pretreatment, all the samples exhibit

Table III Determination of *p*-Aramide Fiber-Breaking Load Before and After the Treatment with Artificial Light

			Warp				Weft			
Ultrasound Treatment	[a]Suntest (h)	[b]Et (h)	*F* (N)	σ (N)	*V* (%)	Δ*F* (%)	*F* (N)	σ (N)	*V* (%)	Δ*F* (%)
No treatment	0	0	7750	286	3.7	—	7259	335	5.0	—
	0.33	3.3	6932	290	4.1	−11	6638	333	5.0	−9
	1	10	6278	292	4.6	−19	5886	376	6.4	−19
	3	30	6148	274	4.5	−20	5526	391	7.0	−24
	18	180	5821	284	4.9	−25	5330	408	7.4	−27
	24	240	5592	295	5.2	−29	5019	374	7.4	−31
20 min	0	0	8535	189	2.2	+10	8371	326	3.9	+15
	0.33	3.3	7848	242	3.1	+1	7783	337	4.3	+7
	1	10	7161	272	3.8	−8	6769	394	5.8	−7
	3	30	6802	291	4.3	−12	6409	285	4.4	−12
	18	180	6507	314	4.8	−16	6246	335	5.3	−14
	24	240	6311	293	4.6	−19	6115	315	5.1	−16
40 min	0	0	8488	247	2.9	+10	8339	312	3.7	+15
	0.33	3.3	7521	271	3.6	−3	7423	344	4.6	+2
	1	10	7227	292	4.0	−7	6965	300	4.3	−4
	3	30	6932	328	4.7	−11	6736	295	4.4	−7
	18	180	6671	307	4.6	−14	6540	265	4.0	−10
	24	240	6605	317	4.8	−15	6311	284	4.5	−13

[a] Duration of the artificial aging in Suntest apparatus.
[b] Equivalent time to natural weathering.

a higher breaking load, 10 to 15% for the fabric (Table III) and 5 to 6% for fibers (Table II). Similar results are obtained by the investigations of B. C. Pai et al.,[8] dealing with enhancing carbon fiber strength by ultrasound treatment.

Beneficial impact of ultrasound pretreatment is especially prominent in the field of the aging tendency of the fibers by the influence of light. The exposure of the fibers to sunlight and weather conditions for 168 h (7 days), without ultrasound pretreatment, results in a breaking load loss of 38% (Table II). On the other hand, the samples treated with ultrasound exhibit a higher resistance to aging, with a lower loss of breaking load (31% after a 10 min ultrasound treatment and 27% after a 20 min treatment).

The results of fiber testing (Table II and Fig. 1) indicate a somewhat higher degree of dispersion

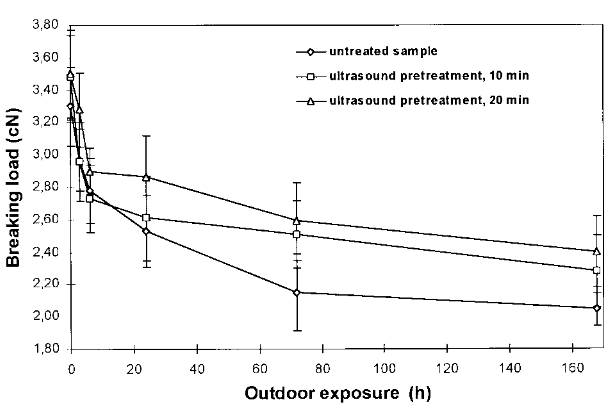


Figure 1 The impact of ultrasound pretreatment on the aging of *p*-aramide fibers in a natural environment.

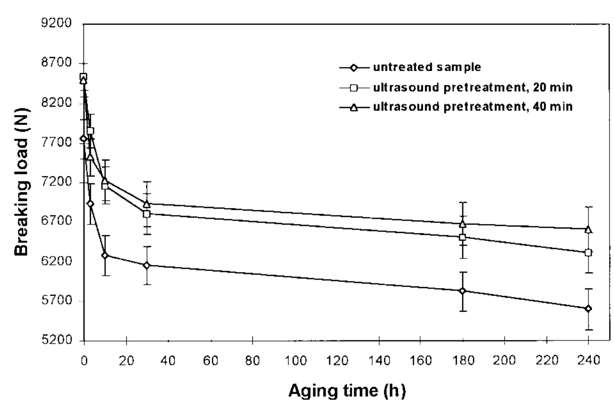


Figure 2 The impact of ultrasound pretreatment on the aging of *p*-aramide fabrics (warp direction) in Suntest.

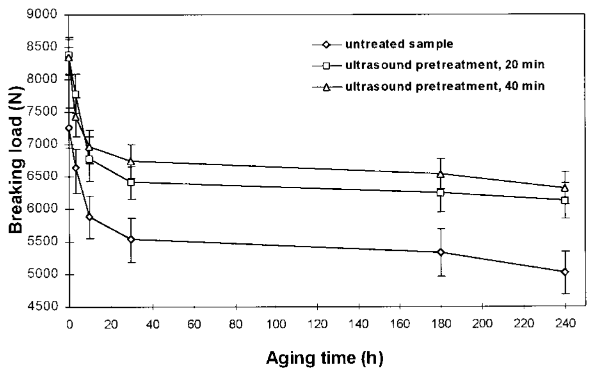


Figure 3 The impact of ultrasound pretreatment on the aging of *p*-aramide fabrics (weft direction) in Suntest.

in measuring breaking force, and consequently, overlapping of error bars (Fig. 1) for individual testing points. Higher deviations from the average values can be explained by the irregularity and diversity of natural conditions (different irradiation, changes of daytime and nighttime conditions, pollutants, weather conditions) compared to regular conditions in the Sunset apparatus. The results of the investigation of the impact of ultrasound on the fabric exposed to artificial aging in the Sunset apparatus indicate considerably lower dispersions (Fig. 2 and 3).

Even a higher level of impact of ultrasound pretreatment has been established on the samples exposed to aging in an artificial environment, such as created by the Suntest apparatus. The breaking load measured on the samples previously treated by ultrasound is doubled compared to those not subjected to the treatment, where both sample groups were identically aged.

The breaking load loss of the samples treated by ultrasound and subjected to aging, compared to the untreated samples is as much as 50% lower. For the samples untreated by ultrasound, the loss of breaking load amounts to 30%, and in the ultrasound-treated samples not more than 13 to 19%.

Slower degradation processes on the samples treated with ultrasound can be connected with the probable ordering of fiber structure and establishing new crosslinks, resulting from vibrations on the level of molecular segments. According to Patrick,[9] ultrasound waves with the frequency of 10 to 100 kHz cause rotation of macromolecule segments, changes in conformation, and vibration of polymer system, which can obviously have a considerable impact on the changes in the fiber structure. Ultrasound waves used in the investigations described were in the above range (30 kHz); thus, the influence described is quite probable. It may be supposed that structural defects,[1] which, despite the high technology level used in *p*-aramide fiber production, cannot be avoided in real polymer systems such as commercial fibers, are somewhat reduced by ultrasound.

The results obtained indicate that there is no significant difference in the aging tendency between the samples treated with ultrasound for 20 and 40 min; however, the untreated samples show much lower resistance to aging.

Measurements performed reveal the extent of *p*-aramide fiber sensitivity to the initial exposure to light. The load loss is the highest in the short initial period of the time exposure to light (first 30 h) as presented in Figures 1, 2, and 3. The strength is continuously, but only gradually, reduced afterwards.

The comparison of degradation processes occurring in natural aging and in Sunset apparatus (Tables II and III) shows higher intensities of the aging process in a natural environment compared to the equivalent time in the Suntest apparatus. This means that the Sunset manufacturer statement, saying that 24 h in a Suntest apparatus equals 10 days of aging in natural environment, is not confirmed. The breaking strength reduction in the course of aging in natural and man-made environment show that the multiplying factor of 10, claimed be the manufacturer, is too high. This should be taken into account when estimating artificial aging.

CONCLUSION

The results obtained by the investigations described indicate that ultrasound pretreatment considerably reduces the aging tendency of *p*-aramide fibers under the influence of light, both in natural and artificial environment, although the problem cannot be eliminated completely by this means.

The ultrasound treatment reduces strength losses due to aging in a natural environment by 10 to 40%, and as much as 60% in artificial environment.

The aging tendency is reduced by the ultrasound pretreatment, whereas the duration of the treatment showed no significant influence.

The ultrasound treatment also results in certain improvements in fiber and fabric strength, which also should not be neglected.

There is a fair chance of implementing the obtained results in practice.

REFERENCES

1. Yang, H. H. Kevlar Aramid Fiber; John Wiley & Sons Ltd.: London, UK, 1993.
2. Davis, A.; Sims, D. Weathering of Polymers; Elsevier Applied Science Publishers: London, 1986.
3. Batzer, H. Polymere Werkstoffe, Band I; Georg Thieme Verlag: Stuttgart, 1984.
4. Pezelj, E. Doctoral dissertation, Zagreb (October, 1997).
5. Čunko, R.; Gambiroža, M.; Pezelj, E. J Appl Polym Sci 1999, 71, 2337.
6. Čunko, R.; Pezelj, E.; Andrassy, M. Tekstil 1997, 46, 667.
7. Andrassy, M.; Čunko, R.; Pezelj, E. International Conference & Exhibition, American Association of Textile Chemists and Colorist, September 22–25, 1998, Philadelphia Marriott, Philadelphia, PA.
8. Pai, B. C., et al. J Mater Sci Lett 1992, 11, 779.
9. Patrick, R. A. Adv Sonochem 1991, 2, 65.