

Degradation of Respirable Fibrils of Poly(*p*-phenylene terephthalamide) by Solar Ultraviolet Radiation

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SYNOPSIS

After ~ 160 days in the environment, the polymer in a respirable-size poly(*p*-phenylene terephthalamide) fibril (diameter = $0.3 \mu\text{m}$) is expected to degrade, due to solar ultraviolet radiation, from an initial molecular weight of $\sim 20,000$ to less than 400. This estimate is based on ultraviolet absorption characteristics, photolytic degradation kinetics, and judgments regarding how these translate into actual time in the environment. Degradation to this molecular weight level will cause the fibril tensile strength and modulus to decrease to $\sim 1\%$ of their initial values. Mechanically, such a degraded fibril will be weak and brittle with properties similar to those of uncooked spaghetti. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The purpose of this article was to estimate the rate and extent of polymer degradation and decrease in mechanical properties of respirable size fibrils of poly(*p*-phenylene terephthalamide) (PPTA) in the environment due to solar ultraviolet radiation.

The fibrils of specific interest in this report are those which when respirated are retained in the lungs. Studies have shown that the dimensions of such fibrils are approximately $12 \mu\text{m}$ long with a diameter of $0.3 \mu\text{m}$.¹ Shorter fibrils ($\leq 5 \mu\text{m}$), although respirated, are cleared by the natural defense mechanisms of the lung. With the increasing use of such aramid products in industrial applications, it is important to estimate if there will be any significant buildup potential of such fibrils in the environment. If the rate of chemical degradation and subsequent size reduction through mechanical breakdown of these fibrils in the environment is rapid compared to the rate at which they are released, there will be little opportunity for significant buildup. A potential important mechanism of breakdown is by solar ultraviolet degradation, the topic addressed in this article.

The strength loss of PPTA yarns and cables due to ultraviolet degradation has been extensively studied and previously reported.² These data, how-

ever, are of minimal value for the purposes of this study because the diameter of these bundles is $> 10,000$ times larger than that of interest here. The often-mentioned self-screening property of aramid yarns is a result of the very high extinction (absorption) coefficient. The data referenced reflect the impact of degradation of only a fraction of the outer filaments, often less than 1% of the total material. In this case, the observed strength loss is a result of a complex stress concentration and subsequent failure initiation process.

EXPERIMENTAL

Ultraviolet Solar Radiation

The ultraviolet portion of the electromagnetic spectrum comprises wavelengths between ~ 10 and 400 nm . Ultraviolet radiation from the sun reaching the earth's surface extends down to a minimum wavelength of $\sim 290 \text{ nm}$, higher energy radiation being screened out by the atmosphere. The spectral energy distribution of this radiation is shown in Figure 1.³ The total radiant flux from wavelengths $< 400 \text{ nm}$ is approximately $7 \times 10^{15} \text{ quanta}/(\text{cm}^2\text{-s})$.⁴

PPTA

PPTA is a fully aromatic polyamide that is synthesized by a condensation polymerization of *p*-phenylene diamine and terephthaloyl chloride.⁵

Ultraviolet Absorption Properties

PPTA absorbs ultraviolet radiation strongly. As can be seen in Figure 1, there is a strong absorption band with a maximum at about 330 nm. The extinction coefficient of this maximum, which has been determined from thin solvent cast films, is $\sim 40 \text{ L}/(\text{g}\cdot\text{cm})$.² There is significant overlap in the absorption spectrum of PPTA and the solar spectrum at the surface of the earth.

The result of this high extinction coefficient is that penetration of ultraviolet radiation in this wavelength range is such that most of the energy is absorbed by the polymer within the first μm of the exposed surface. Figure 2 shows the approximate intensity profile within the polymer computed for extinction coefficients from $5 \text{ L}/(\text{g}\cdot\text{cm})$ to $40 \text{ L}/(\text{g}\cdot\text{cm})$ using the Beer-Lambert absorption law.

The fibers in continuous filament PPTA yarns typically have a diameter of about $12 \mu\text{m}$ and, therefore, solar ultraviolet radiation penetrates only a fraction of such fibers. In cords and cables that normally contain many thousands of fibers, the outer layer of fibers provide an effective and durable shield for the bulk of the fibers. The small fibrils of interest here (diameter = $0.3 \mu\text{m}$), however, are essentially completely penetrated by such ultraviolet radiation. This is clear from the intensity profiles shown in Figure 2.

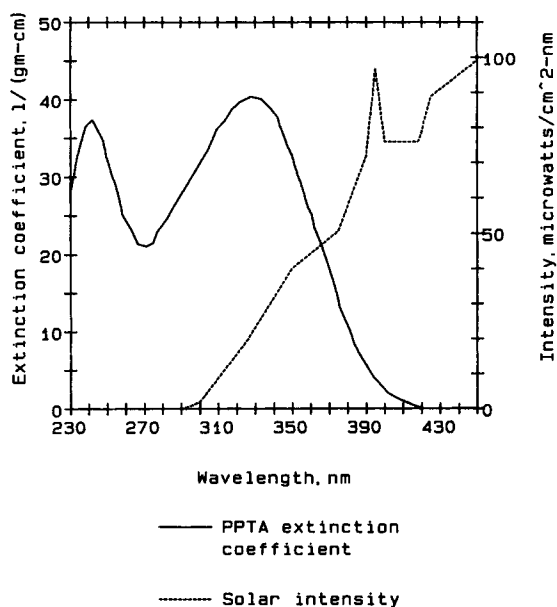


Figure 1 Optical absorption of PPTA film and solar spectral intensity.

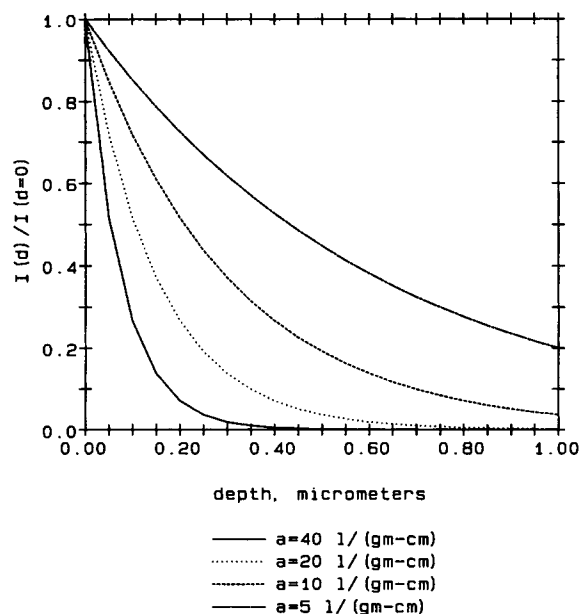


Figure 2 Intensity vs. penetration depth in PPTA using the Beer-Lambert law.

Photolytic Degradation of PPTA

Aromatic polyamides, in general, undergo significant photolytic-initiated chemistry as a result of exposure to ultraviolet radiation. In the absence of oxygen, the major reaction is a photo-Fries rearrangement that produces 2- and 4-aminobenzophenone units along the backbone.^{6,7} In the presence of oxygen, the predominant reaction involves oxygen interception of the primary radical, resulting in a peroxide intermediate and subsequent rearrangement to give carboxylic acid and nitroso end groups.⁸ The formation of end groups decrease the polymer molecular weight.

The product quantum yield* of the ultraviolet degradation of aramid polymers in the presence of oxygen can be estimated by monitoring the formation of carboxylic end groups using infrared spectroscopy. This has been reported for a number of aramid polymers.⁸ Although the quantum yield for PPTA has not been specifically determined, the value for poly(*p*-benzamide)[†] has been estimated to be $1.0 \pm 0.3 \times 10^{-5} \text{ mol/einstein}$. Because of the similarities of their chemical structure, it is expected

* The product quantum yield of a photolytic reaction is the fraction of absorbed quanta that result in the product species.

† This is aromatic polyamide prepared by the condensation polymerization of *p*-aminobenzoyl chloride hydrochloride, a close analog of PPTA.

that the quantum yield for the degradation of PPTA will be close to this value.⁸

It is expected that the ultraviolet absorption and photolytic degradation characteristics will change as the polymer molecular weight decreases due to the degradation reaction. This is based on experiments done on low molecular weight aromatic amides.⁹ Included in this work was the amide produced by reacting *p*-phenylene diamine with an excess of benzoyl chloride (1,4-diaminobenzene *N,N'*-dibenzoyl). It contains three phenyl rings and is a model compound of the PPTA trimer. The ultraviolet absorption spectrum of this compound has an absorption maximum at ~ 300 nm with no significant absorption above ~ 360 nm. It experiences little or no photolytic degradation due to ultraviolet radiation in the 300–450 nm range. It was assumed here that the extinction coefficient and quantum yield remain constant and equal to that of the starting high molecular weight material down to the trimer, at which point they change to those of the trimer. Experimental clarification of this assumption is an important item for future work (Recommendations for Future Work section).

Degradation Kinetics and Molecular Weight Decrease

Using the PPTA polymer absorption data, the solar energy spectrum and the Beer–Lambert absorption law discussed above, the solar ultraviolet energy absorption rate for a circular cross-section PPTA fiber has been computed as a function of the fiber diameter. This was accomplished through numerical integration of the following expression for the energy absorption rate per unit volume[‡]:

$$(1/\pi R^2) \int_{-R}^{+R} \int_{250}^{450} I(\lambda) \times [1 - \exp(-ca(\lambda)2\sqrt{R^2 - x^2})] d\lambda dx$$

in which $I(\lambda)$ is the solar spectral intensity as a function of wavelength (Fig. 1); $a(\lambda)$, the wavelength-dependent extinction coefficient (Fig. 1); R , the fibril radius; and c , the polymer concentration.

The results of this calculation show that as diameter decreases the energy absorption rate per unit volume of polymer increases dramatically (Fig. 3). This increase is a result of the transition from es-

[‡] This is for radiation incident normal to the fiber axis in which only transmission and absorption occur. It has been estimated that ignoring reflection and refraction results in $\leq 5\%$ error in the computation for $0.3 \mu\text{m}$ diameter fibrils.

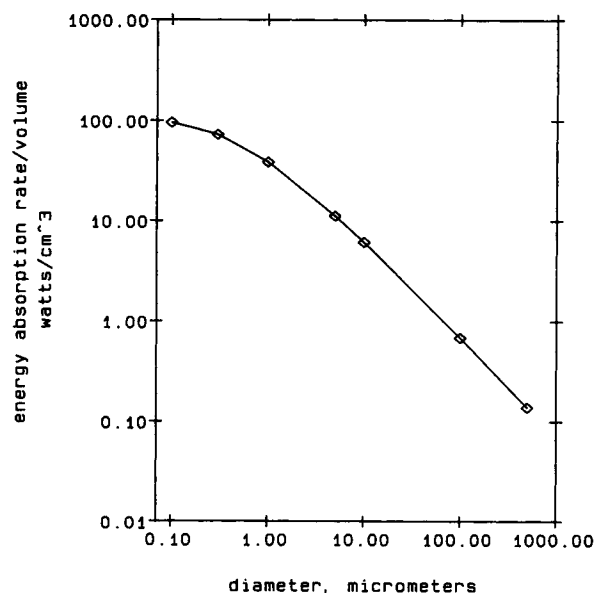


Figure 3 Solar ultraviolet energy absorption rate per unit volume of a PPTA fibril vs. fiber diameter.

entially surface absorption at the larger diameters to more uniform penetration and absorption for the smaller diameters. Fibrils with the $0.3 \mu\text{m}$ diameter of interest absorb 1.3×10^{20} quanta/($\text{cm}^3\text{-s}$) ($\sim 70 \text{ W}/\text{cm}^3$) of solar ultraviolet radiation, a significant energy absorption rate density.

The number of end groups produced as a result of photolytic degradation caused by the absorbed energy has been also computed using the following expression:

$$\begin{aligned} (\text{meq ends})/(\text{kg polymer}) &\propto \text{time} \\ &\times \text{product quantum yield} \\ &\times \text{quanta absorption rate} \end{aligned}$$

This is the integrated form of a zero-order rate equation. It is consistent with the mechanism discussed above in which oxygen concentration is constant, implying diffusion does not limit the degradation rate.

If the initial number-average molecular weight (M_n) is 20,000,⁵ the initial concentration of polymer ends is 100 meq/kg, and the number-average degree of polymerization (DP_n)[§] at any time during the degradation process is given by

[§] This is done by defining the chain repeat unit to contain one phenyl group with a repeat unit molecular weight of 119. At $M_n = 20,000$, $DP_n = 168$.

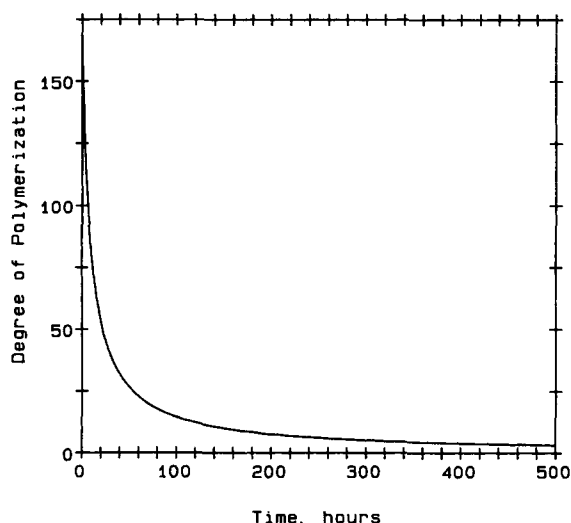


Figure 4 Degree of polymerization vs. exposure time, fibril diameter = $0.3 \mu\text{m}$, product quantum yield = 0.00001, energy absorption rate = 1.3×10^{20} quanta/($\text{cm}^3 \text{s}$).

$$DP_n = (1.68 \times 10^4) / (100 + \text{meq/kg ends produced})$$

The estimated DP_n as a function of exposure time for a $0.3 \mu\text{m}$ diameter fibril is shown in Figure 4. After 500 h exposure, the concentration of end groups in the fibril has increased to the level of a trimer.¹¹ Based on the work cited above (Photolytic Degradation of PPTA section), it is reasonable to assume that further degradation beyond this point takes place very slowly.

Effect of Molecular Weight on Fiber Strength

It is well known that the strength of fibers with high molecular orientation depends strongly on the molecular weight.^{5,10} There are a number of studies, both experimental and theoretical, that have addressed this subject.

Spinning Low Molecular Weight Polymer

A straightforward technique for estimating the fiber strength vs. molecular weight relationship is to spin polymers of various starting molecular weight. Both the upper and lower molecular weights that this method can be used are limited because of changes in the spin solution and fiber formation process that also contribute to changes in strength. Studies of this type have shown that a decrease from

¹¹ $DP_n = 3$.

$DP_n > 168$ to ~ 34 ($M_n > 20,000$ to ~ 4000) results in approximately a 60% decrease in fiber strength.¹⁰⁻¹² These data are shown in Figure 5.

Theoretical Computations

Theoretical computations have been carried out to estimate the ultimate strength of PPTA fibers as a function of molecular weight. These calculations simulate both inter- and intramolecular bond failure and are restricted to ideal fibers composed of perfectly oriented fully extended molecules in which the only defects are the chain ends.¹³ Therefore, the computed strengths are substantially higher (~ 8 GPa) than those experimentally observed. If these computed strengths are reduced by multiplying by a constant fraction, such that the strength at $DP_n > 168$ is comparable to the experimental values (Spinning Low Molecular Weight Polymer section), the agreement is quite reasonable (Fig. 5).

Strength of Hydrolyzed Fibers

Hydrolysis of the fiber in aqueous acidic or basic solution is another approach to estimating the strength vs. molecular weight relationship. Some data are available¹⁴ but show a much lower strength at a given DP_n than do data obtained from direct spinning or computations. This is likely due to preferential hydrolysis in defect bands that are more accessible to the hydrolyzing species.¹⁵ Hydrolysis, therefore, produces clusters rather than randomly

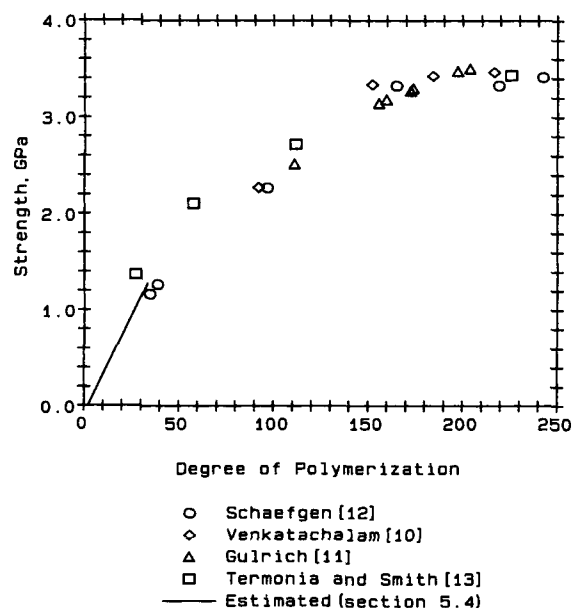


Figure 5 PPTA yarn strength vs. degree of polymerization.

distributed chain ends and, thus, produces lower strength than if the degradation had occurred randomly throughout the fiber.

Because of the necessary role of oxygen in the photolytic degradation, there may be some localization of the degradation and, thus, end group aggregation similar to that of hydrolysis. However, it is likely that the smaller oxygen molecule will be less limited than will hydrated hydroxyl groups or protons, and, therefore, the localization will be smaller. Hydrolysis data have not been used here to avoid the risk of overestimating strength loss and, consequently, underestimating the degraded fibril properties.

Fiber Strength at Very Low Molecular Weights

The solar photolytic degradation of respirable fibrils rapidly (within ~ 60 h) reduces the molecular weight to the lower limit of the available experimental and theoretical values. At this time, the fibrils will still possess significant strength (~ 1.2 GPa). For the purposes of estimating persistence of these fibrils in the environment, it is necessary to develop a reasonable idea of the form of the relationship as the polymer molecules approach a trimer.

Insight as to the form of the strength vs. low degree of polymerization relationship can be gained from an analogy with the strength of uniaxially oriented discontinuous fiber-reinforced composites. The basic concepts in modeling these structures are the same as those used by Termonia on the molecular level modeling discussed above, i.e., fibers (molecules) transfer load via shear. At a length-to-diameter ratio (L/D) greater than some critical value, tensile failure of the fibers (molecules) is a major failure mechanism. At L/D ratios less than the critical value, fiber (molecule) slip is the major failure mechanism. Stress analysis of the low L/D region, where slippage is dominant, predicts that the strength should be linearly dependent on the L/D .¹⁶ A linear extrapolation of the data and values discussed above has been performed from the lowest DP_n data points to a zero strength at a $DP_n = 2$. This extrapolation to zero strength predicts that a fibril in which the polymer has been degraded to a trimer will have a tensile strength of ~ 40 MPa.

The strength value of ~ 40 MPa is not greatly different from estimates of the shear strength of single filaments in the transverse plane,¹⁷ which are 40–70 MPa. This is not surprising because the transverse shear strength is a measure of intermolecular hydrogen bonding and the extrapolation has been performed based on the assumption that mo-

lecular slippage is the failure mechanism at these low molecular weights, also controlled by intermolecular bonding. It is also probably reasonable to use values of the transverse modulus of a single filament as an estimate of the tensile modulus of the highly degraded fibril. The transverse modulus of PPTA filaments has been estimated to vary from 1.2 to 2.2 GPa depending on moisture content and crystallinity.¹⁷ Added support is provided by estimates of the axial shear modulus of single filaments that are in the 1.5–2.0 GPa range.¹⁸ Assuming Hookean stress strain behavior, the break elongation of the degraded fibrils will be 2–3%.

The estimates discussed above can be considered upper limits. They have been made based on molecular scale considerations and have not addressed microcracking of the degraded material and other supramolecular structural deterioration that will very likely occur during the process of such extensive photolytic degradation. Also, clustering of chain ends due to localized degradation (Strength of Hydrolyzed Fibers section) has not been included.

Effect of Photolytic Degradation on Fiber Strength

To develop more confidence that the computed strength loss of a $0.3 \mu\text{m}$ diameter fibril is a good estimate, a comparison was done with data from a single filament strength loss study. In this experiment, the impact of ultraviolet radiation on the mechanical properties of single PPTA filaments with diameters from ~ 8 to $\sim 30 \mu\text{m}$ was investigated.¹⁹

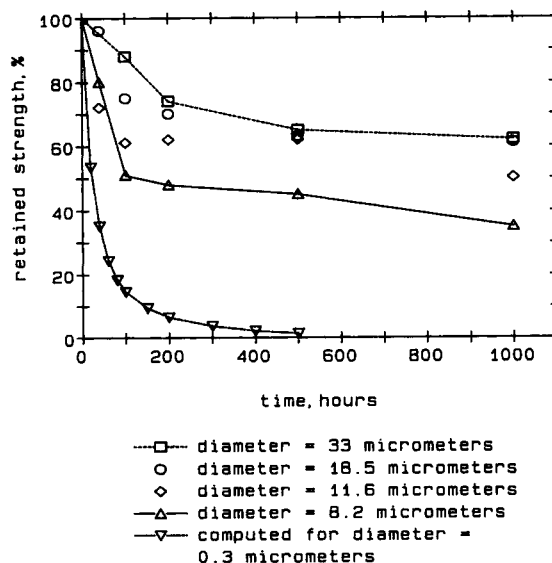


Figure 6 PPTA fiber strength retention vs. simulated solar ultraviolet radiation exposure time.¹⁶

Because most ultraviolet radiation is absorbed within 1 μm of the exposed surface, even these single filament experiments reflect a situation in which only a fraction of the material at the surface is actually degraded. The large strength loss suggests that the failure of the degraded filaments is a flaw or stress concentration-initiated process, possibly associated with cracking of the highly degraded surface material. Whereas it would be desirable to simply extrapolate strength retention vs. filament radius data to a 0.3 μm diameter, this is risky in view of the fact that such an extrapolation would pass through a transition from nonuniform surface degradation to essentially uniform degradation throughout the fiber.

The results of the above work are shown in Figure 6 as percent filament strength retention as a function of exposure time.[#] Also included is the strength retention vs. time relationship for a 0.3 μm diameter fibril computed from the relationships in Figures 4 and 5. The computed strength loss of the fibril is generally consistent with the experimental data for the much larger fibers.

Degradation and Mechanical Breakdown in the Environment

The hours of exposure to solar ultraviolet radiation indicated in Figures 4 and 6 are not hours in the environment. This time must be increased by a factor to account for night, seasonal variations, weather, and also orientation of the fibril with respect to the sun. A reasonable assumption is that a fibril will, on average, experience ~ 5 h of such radiation per day. Thus, a multiplication factor of $5 \times$ ($\sim 24/5$) is appropriate to convert the time scale of Figure 4 to actual solar exposure.²⁰

Orientation of the fibril must also be considered. In this case, only rotation that changes the angle between the long fibril axis and the incident direction of the radiation needs to be considered. Assuming all orientations are equally likely, this results in a decrease in absorbed energy by a factor of $2/\pi$.^{**}

[#] Exposure was done in an Atlas xenon arc Weather-o-meter. This apparatus has a spectral energy density very much like the sun.³

^{**} This simple averaging for rotation only corrects for reduction in intensity on the fibril surface. It does not include the change in path length within the fibril that also occurs as the fibril rotates. The path-length correction requires that the rotation angle be included in the integral equation of the Degradation Kinetics and Molecular Weight Decrease section.

When done in this manner, the time scale multiplication factor in the limit of very large diameter fibrils ($> 100 \mu\text{m}$) is $\sim \pi/2$ (the path length correction is negligible). For a 0.3 μm diameter

Table I Tensile Mechanical Properties of Undegraded PPTA Continuous Filaments and Expected Properties of Degraded Fibrils

	Initial ^a	Estimated After 160 Days
Strength (MPa)	3500-4500	40
Elongation (%)	> 4	2-3
Modulus (GPa)	80-180	1-2

^a The range represents typical values for PPTA continuous filaments of various orientation and crystallinity. No difference in degraded fibril properties are expected as a result of the type of starting model.

Thus, an additional multiplication factor of 1.57 must be applied to the time scale of Figure 4 to convert in to time in the environment.

Based on the above discussions, it can be estimated that after ~ 160 days (3840 h) in the environment the mechanical tensile properties of a 0.3 μm diameter fibril of PPTA will be reduced to those shown in Table I. A degraded fibril with the properties above is weak and brittle. Its shape and properties not unlike those of a piece of uncooked spaghetti.[‡]

Size reduction of degraded fibrils in the environment will depend on the forces acting on them, the most significant of which will likely be wind and rain. This subject must be addressed further either through actual experimental measurements or modeling.

RECOMMENDATIONS FOR FUTURE WORK

There are a number of aspects that would benefit from further work. A few of the most relevant are listed below:

- Determination of the quantum yield of the ultraviolet photolytic degradation and the extinction coefficient relationship vs. wavelength of PPTA as a function of molecular weight.
- Experimental verification of computed degradation rate curves.

fibril, however, the time-scale multiplication factor is ~ 1.3 (energy absorption rate is higher). The use of the $\pi/2$ (1.57) multiplication factor is conservative in that it introduces an overestimate of the time needed to achieve $DP_n = 3$.

[‡] Testing (3-point bending at 65% RH and 21°C) in our laboratory yielded the following values for a sample of uncooked spaghetti: strength = 53 MPa, elongation = 1.2%, and modulus = 4.6 GPa.

- Extension of strength vs. degree of polymerization computations to very low degrees of polymerization.
- Estimates of size reduction of degraded fibrils in the environment.

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