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Effect of hydrogen bonding and moisture cycling on the compressive performance of poly-pyridobisimidazole (M5) fiber

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ABSTRACT

A clear correlation between the degree of intermolecular hydrogen bonding (H-bonding) and axial compressive strength of pyridobisimidazole (M5) as-spun fiber specimens subjected to varying annealing conditions has been established by means of Fourier transform infrared microspectroscopy and single fiber elastica loop testing. As the water initially contained in the as-spun fiber is removed by heat treatment, improvements in polymer chain orientation promote the formation of intermolecular H-bonds, leading to enhanced fiber compressive strength values. M5 fiber specimens with the highest degree of intermolecular H-bonding of 96 ± 1% are found to have a compressive strength of 1.72 ± 0.09 GPa. Moisture cycling experiments of M5 annealed specimens have provided direct evidence of partial H-bond reversibility in this material, as saturation of M5 annealed fiber resulted in the reduction of the degree of intermolecular H-bonding from 93 to 64%. Upon drying the fiber at 120 °C in an inert atmosphere, the degree of H-bonding returned to the original value of 93%. However, repeated fiber moisture cycling resulted in a monotonic reduction in the degree of H-bonding in both the saturated condition (53%) and dry state (62%). The compressive strength of saturated and dried specimens after moisture cycling was found to be statistically equivalent at a reduced level of 1.29 GPa. The original degree of H-bonding and compressive strength could be recovered by re-annealing the fiber under tension.

1. Introduction

High performance organic fibers are produced using a dry-jet wet spinning process, also known as air gap spinning, in which the extruded dope goes through an air gap into the coagulation bath, where the solvent (sulfuric acid for aramid fibers, polyphosphoric acid for pyridobisimidazole (M5) fiber) is removed from the fiber. This is followed by neutralizing and washing operations that result in a fiber that contains a significant amount of water. After a mild drying, the as-spun fiber, which still contains water in its structure, is obtained. Further processing of the as-spun material in the form of fiber heat treatment removes the remaining water as the crystalline structure is perfected. Wide angle X-ray diffraction studies on as-spun wet phenylene terephthalamide (PPTA) fiber performed by Fukuda and Kawai [1] show that, during water desorption, the lateral crystallite size is increased as the excess bulk water filled in the interstitial voids and noncrystalline regions between crystallites is removed. Elimination of the hydrogen-bonded (H-bonded) water at the crystal surface is followed by the formation of intermolecular H-bonds. A similar mechanism of bound water desorption followed by the formation of hydrogen bonds between adjacent polymer chains has been described for the para-aramid Armos fiber [2]. In the case of M5 fiber, the crystal structure of the as-spun material has been described as a two-dimensionally ordered crystal hydrate in which layers of polymer molecules alternate with layers of H-bonded water molecules, preventing the formation of polymer–polymer intermolecular H-bonds [3]. Removal of the water molecules from the M5 structure during heat treatment results in a phase transition into a three-dimensional crystalline ordered structure that improves lateral molecular packing, enabling intermolecular H-bonding [3,4].

Water–polymer interactions involving the amine, carbonyl or hydroxyl groups of high performance organic fibers pose a detriment to intermolecular hydrogen bonding. Jackson et al. [5] have quantified the aqueous accessibility of the amide groups in PPTA as-polymerized polymer, and in fiber form, by performing deuterium exchange of the accessible N–H groups. The fraction of N–H sites converted to N–D was determined by Raman spectroscopy. Jackson et al. found that

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~30–40% of the amide sites in the as-polymerized polymer were exchanged, while ~25% exchange was observed for Kevlar 29 and Kevlar 49, and ~10% exchange was measured for Kevlar 149. The decreased water accessibility in PPTA fiber with respect to the as-polymerized polymer is the result of increased structural perfection during fiber formation [5]. These findings are in agreement with accessibility measurements performed by Chatzi et al. [6] for the N–H groups of Kevlar 49 measured by infrared photoacoustic spectroscopy. Chatzi et al. calculated an accessibility of 30% of the N–H groups in as received Kevlar 49, which was reduced to 17% after the fiber was heat treated at 150 °C for 2 h under a helium atmosphere.

The formation of intermolecular H-bonds in high performance organic fibers leads to a substantial improvement in mechanical properties, particularly in compression, where H-bonds are the main source of lateral molecular interactions. H-bonding in high performance organic fibers typically occurs between hydroxyl or carbonyl functional groups and amine groups of adjacent polymer chains. Fibers like phenylene benzobisthiazole (PBZT) and phenylene benzobisoxazole (PBO), which lack H-bonds between chains, show compressive strengths in the order of 0.30 GPa [7,8]. For aramid fibers such as Kevlar 49, which forms H-bonds through the carbonyl group of a molecule with the secondary amine of adjacent chains, the compressive strength increases to values of 0.40–0.60 GPa [7,8]. M5 fiber, which establishes a well-developed network of intermolecular H-bonds between secondary amine and hydroxyl groups, shows compressive strength values in the order of 1.0–1.7 GPa [8–10].

In this paper, experimentally measured compressive strength values for M5 fibers with known degrees of intermolecular H-bonding are introduced, and the role of intermolecular H-bonds on the compressive performance of M5 fiber is discussed. The extent to which varying ambient conditions induce H-bond reversibility in M5 fiber is analyzed by means of moisture cyclic experiments, and the effect of H-bond reversibility on the compressive properties of M5 fiber is established.

2. Experimental

2.1. Materials

M5 as-spun (M5 AS) fiber, produced by Magellan Systems International LLC, was provided by the U.S. Army Natick Research, Development and Engineering Center. The chemical structure of M5 is shown in Fig. 1 [11]. The fiber tow consists of 250 filaments with a linear density of 1.554 denier/filament.

2.2. Fiber heat treatment experiments

M5 AS fiber tows were annealed in a vacuum oven under a nitrogen atmosphere, at a constant tension of 3 g/denier. Different treatment conditions have been applied to M5 AS tows in order to generate heat-treated specimens with varying degrees of intermolecular H-bonding for mechanical testing. The selected treatments are shown in Table 1.

2.3. Moisture cycling experiments

Saturation and drying experiments have been performed on M5 fiber in order to identify the effect that changes in water content have on the degree of H-bonding in the fiber. The experimental procedure followed to generate the required fiber specimens is depicted in Fig. 2. The initial as-spun fiber was completely saturated at 93% relative humidity (R.H.) before annealing by placing it in a desiccator containing a saturated solution of potassium sulphate. The as-spun, saturated fiber was annealed at 120 °C in a nitrogen atmosphere under a tension of 3 grams per denier (g/d) for a period of 20 h. The annealed fiber was subsequently subjected to 10 saturation (93% R.H., 25 °C) and drying (120 °C, N_2 atmosphere) cycles. The fiber was conditioned at each saturation/drying stage until equilibrium was reached, followed by specimen weight gain/loss measurements. As a final step, the M5 fiber exposed to the 10 moisture cycles was re-annealed.

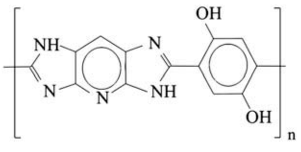

Fig. 1. Chemical structure of M5 fiber [11].

Table 1
Heat treatment conditions used to study the effect of intermolecular hydrogen bonding on M5 fiber compressive strength.

Residence time (h)	Annealing temperature (°C)		
	100	150	200
1	✓	✓	✓
2	✓		✓
5	✓		✓
10	✓		✓

2.4. Single fiber elastica loop test

The elastica loop test provides a technique to measure single fiber compressive strength. The experimental setup for the loop test has been described previously [8]. A loop about 10 mm in diameter is made using a single fiber placed in light oil between glass slides, which are spaced about 150 μm apart. The size of the loop is progressively reduced by pulling the fiber ends, and at each stage, the length of the major and minor axes is measured using an optical microscope. As the fiber enters the plastic region, the ratio of major to minor axis rapidly increases. At this point buckling/kink bands appear on the compression face of the fiber, at the point of minimum radius of curvature, located at the base of the loop. Following the analysis of compressive strength for high performance fibers previously reported [8], the compressive strength (σ_c), (Equation (1)), is calculated as a function of fiber radius (r), the distance (a) from the neutral axis to the point of maximum tensile strain on the looped fiber, axial compressive modulus of the fiber (E_{1c}), and the horizontal diameter (D) of the loop at which the fiber goes into plastic deformation. The parameters used in Equation (1) to calculate σ_c are illustrated in Fig. 3.

$$\sigma_c = E_{1c}\frac{(2r-a)}{0.4692^*D} \tag{1}$$

From a previous assessment of compressive properties, it is known that the ratio E_{1c}/E_{1t} of compressive to tensile modulus for as-spun and heat treated M5 has values of 0.91 and 0.93, respectively [12]. Since fiber annealing does not produce a significant change in this ratio, the axial compressive modulus values needed to determine fiber compressive strength from Equation (1) are calculated as $E_{1c} = 0.93^*E_{1t}$, where the axial tensile modulus values of the M5 filaments under analysis were determined experimentally via single fiber tensile testing reported elsewhere [12,13].

2.5. Fourier transform infrared spectroscopy of specimens from saturation and drying experiments

Fourier transform infrared (FTIR) spectroscopic analyses have been performed on fiber specimens obtained at each stage of the saturation and drying cycles in order to monitor changes in H-bonding. The methodology followed to quantify the state of

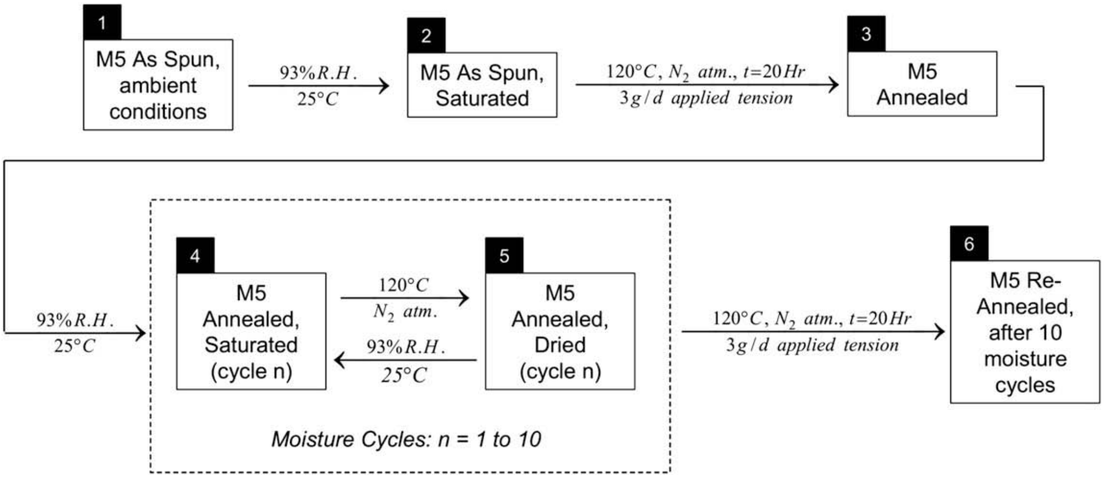

Fig. 2. Treatments performed to generate fiber specimens suitable for studying the effect of moisture saturation and drying on M5 fiber hydrogen bonding and compressive strength.

intermolecular H-bonding in the M5 specimens annealed under varying conditions has been described elsewhere [13]. FTIR microspectroscopy of single filaments in transmission mode was performed using a Nicolet Nic-Plan™ IR microscope with a liquid nitrogen cooled Mercury Cadmium Telluride (MCT-A) detector. The IR Microscope is connected to a Magna-IR 860 spectrometer. Spectra were the result of 512 scans with a resolution of 4 wavenumbers. Variable apertures with an approximate size of 10 μm × 200 μm were used to maximize fiber exposure to the infrared beam while minimizing the spurious energy that reaches the detector.

3. Results and discussion

3.1. Effect of intermolecular hydrogen bonding on M5 fiber compressive strength

The relationship between intermolecular hydrogen bonding and compressive strength in M5 fiber is illustrated in Fig. 4. The plot shows compressive strength and % intermolecular H-bonding values for M5 fiber specimens with different treatment conditions. The selected treatments have residence times of 1, 2, 5 and 10 h at annealing temperatures of 100 and 200 °C, and a residence time of 1 h at 150 °C. The error bars displayed in Fig. 4 represent the standard deviation of 10 specimens tested with the loop test (compressive strength), and 10 specimens subjected to FTIR microspectroscopy (intermolecular H-bonding). Aside from the clear improvement in compressive strength as hydrogen bonding in the fiber increases, it is important to notice that the relationship between hydrogen bonding and compressive strength is independent of the annealing temperature used to promote the formation of intermolecular hydrogen bonds. The development of the property is independent of the annealing path, and multiple combinations of annealing conditions can be used to reach the same degree of hydrogen bonding and compressive strength, as shown by the fibers annealed at 100 and 200 °C. Fig. 4 also shows the measured kink band angles (β) for the different fiber specimens. The angles have been measured between the kink band and the normal to the fiber axis.

The kink band angles (β) shown in Fig. 4 for fibers with intermolecular H-bonding values less than 50% increase from 36° ± 2° to 46° ± 3° with increasing degree of intermolecular hydrogen bonding, and remain constant at 46° ± 3° for fibers with intermolecular H-bonding values greater than 50%. The formation of kink bands is a consequence of the lack of strong lateral support between the highly oriented polymer chains, which leads to failure at low compressive strains as chains slip on each other causing local microbuckling. The propagation of a kink band at an angle with respect to the axis of loading involves both compressive and shearing deformations. The stress transformation equation (Equation (2)) indicates that the maximum resolved shear stress (τ) lies at an angle

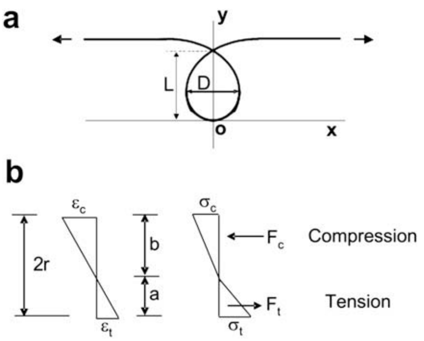

Fig. 3. Diagram of a looped single fiber indicating the location of horizontal loop diameter *D* (a), and strain and stress distribution for a fiber with circular cross-section and radius *r*, with different moduli in tension and compression (b).

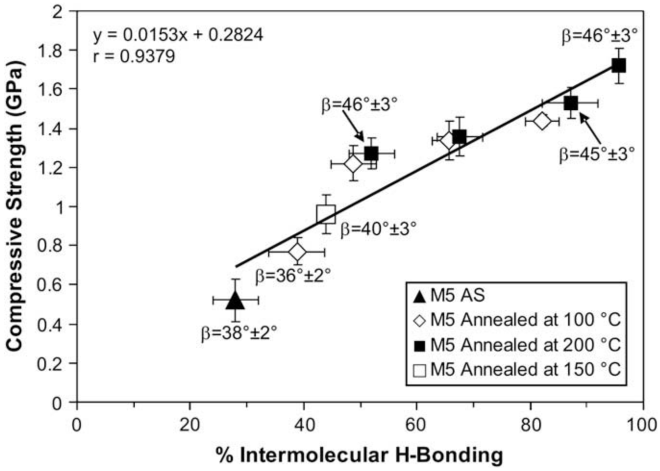

Fig. 4. Relationship between intermolecular hydrogen bonding and compressive strength for M5 fiber.

Table 2
Effect of moisture cycling on weight change in M5 fiber.

Fiber treatment	% Weight change	Fiber treatment	% Weight change
1. As received, saturated	–	12. Drying 5	−18.64
2. Annealing	−20.34	13. Saturation 6	+17.82
3. Saturation 1	+18.85	14. Drying 6	−17.30
4. Drying 1	−18.51	15. Saturation 7	+18.12
5. Saturation 2	+18.28	16. Drying 7	−18.79
6. Drying 2	−18.05	17. Saturation 8	+18.26
7. Saturation 3	+19.05	18. Drying 8	−17.69
8. Drying 3	−19.06	19. Saturation 9	+17.69
9. Saturation 4	+19.00	20. Drying 9	−18.34
10. Drying 4	−19.19	21. Saturation 10	+17.97
11. Saturation 5	+18.84	22. Drying 10	−18.03

of 45° to the axis of loading. Therefore, the closer the kink band orientation is to the plane of maximum shear stress (at about 45° to the direction of applied stress), the higher the degree of shearing between polymer chains in the fiber before failure takes place. The development of intermolecular H-bonds during fiber annealing enhances the compressive and shear properties of the material, resulting in the observed changes in kink band angle as a function of intermolecular H-bonding. When M5 is exposed to short annealing periods (i.e. fiber specimens with intermolecular H-bonding less than 50%), a significant portion of the fiber is still arranged as a hydrate structure, causing the polymer chains to shear during compressive loading either in the direction of existing water–polymer hydrogen bonds or in the direction where the network of intermolecular hydrogen bonds is incipiently developed. This is in agreement with the diffusion analyses of M5 fiber, which show that in specimens with intermolecular H-bonding of less than 50% the amount of diffusing water that has already been removed is less than 70% [13], enabling the presence of fiber domains composed of a hydrate structure. Once the degree of intermolecular hydrogen bonding exceeds 50%, most of the water initially contained by the as-spun fiber has been removed, and compressive strength increases as improvements in polymer chain orientation promote the formation of intermolecular hydrogen bonds. Lammers et al. have indicated that a fully heat-treated M5 fiber has a compressive strength of 1.7 GPa [10]. Fig. 4 shows that M5 fiber annealed at 200 °C with a residence time of 10 h has a degree of intermolecular hydrogen bonding of 96 ± 1%, and a compressive strength of 1.72 ± 0.09 GPa.

$$\tau = \sigma \ \sin(\beta)\cos(\beta) \tag{2}$$

Hageman et al. [4] have studied the role of the hydrogen bonding network on the compressive strength of M5 fiber. From *ab initio* total energy calculations, they conclude that M5 in the heat-treated state has a triclinic crystal unit cell with a sheet-like network of hydrogen bonds, and not a monoclinic unit cell with a bi-directional hydrogen bond network, as initially proposed by Klop and Lammers [3]. Therefore, according to Hageman et al., shearing of the polymer chains in one lateral direction during compressive loading is prevented by the network of hydrogen bonds, while in the perpendicular lateral direction, shearing is prevented by the strength of the intermolecular π–π aromatic ring interactions [4]. The presence of the hydrogen-bonded network is of paramount importance, as observed in the case of PBO, which has a structure similar to M5, capable of developing the π–π interactions, but lacks the network of intermolecular hydrogen bonds, resulting in a compressive strength value almost six times smaller than M5.

3.2. *Effect of moisture cycling on hydrogen bond reversibility and compressive strength in M5 fiber*

Moisture saturation and drying experiments have been performed on M5 fiber in order to evaluate the effect of water gain/loss on fiber weight change, degree of intermolecular H-bonding and compressive strength. Table 2 shows fiber weight change as a function of moisture treatment, while Fig. 5 shows changes in the degree of H-bonding as a function of fiber treatment. The data is revealing in a number of ways. Saturation of the as-spun fiber did not generate a measurable change in the degree of H-bonding (27%). Annealing of the saturated as-spun fiber resulted in a weight loss of more than 20% and an increase of the degree of H-bonding from 27 to 93%. It is interesting to note that saturation of the annealed fiber resulted in a weight gain of 18.85%, along with a reduction in the measured degree of intermolecular H-bonding from 93 to 64%. To the best of our knowledge, this is the first direct evidence of partial reversibility of H-bonding in M5 fiber. However, upon drying the fiber at 120 °C, most of the gained weight was removed once more, and the degree of H-bonding was restored. This behavior, although surprising, is not completely unexpected if we consider that fibers such as Kevlar 49 and polybenzimidazole (PBI) have been reported to absorb water reversibly as well [14,15]. The second cycle of saturation and drying showed a similar trend, although this time the degree of H-bonding was reduced to 53% during moisture saturation. The significance of

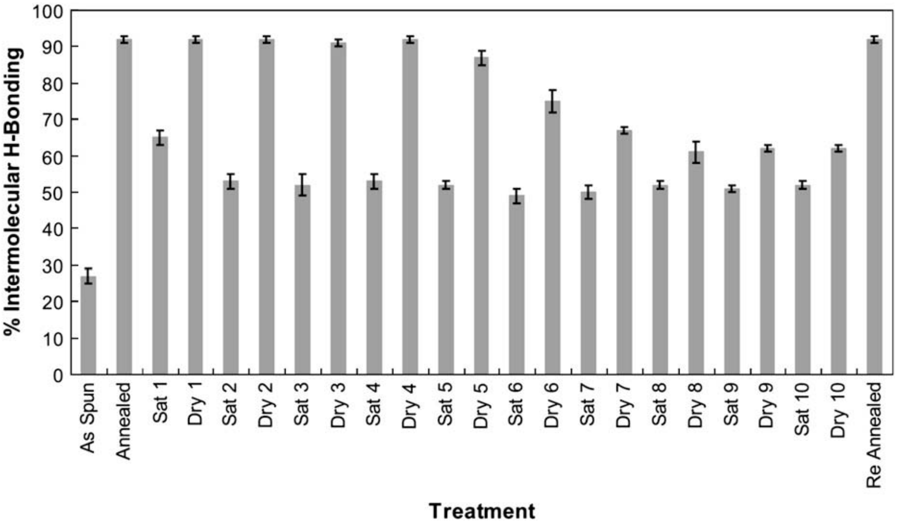

Fig. 5. Effect of moisture cycling on intermolecular hydrogen bonding in M5 fiber. Error bars represent the standard deviation of 10 measured specimens.

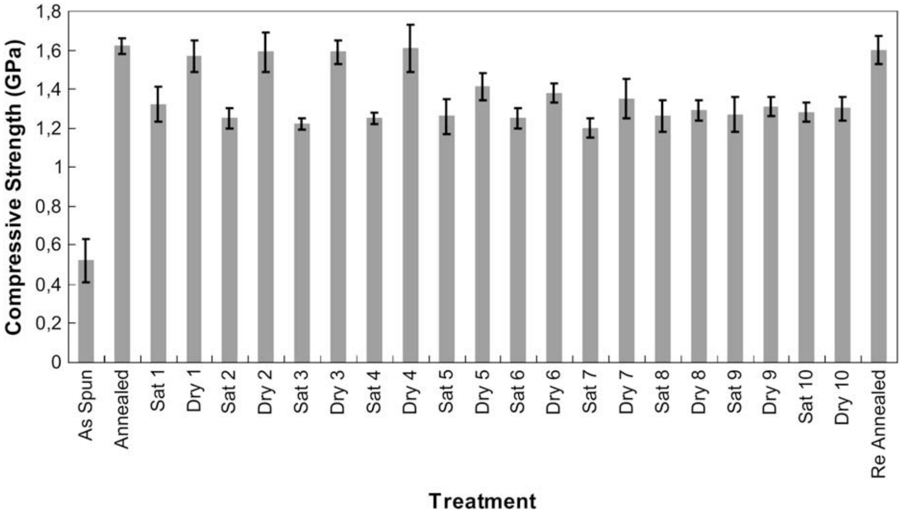

Fig. 6. Effect of moisture cycling on axial compressive strength in M5 fiber. Error bars represent the standard deviation of 10 measured specimens.

these observations lies in the fact that a reduction of intermolecular H-bonding will translate into a reduction in the compressive strength of the fiber.

The data reported in Table 2 indicates that although the ten saturation and drying cycles do not lead to a permanent fiber weight loss, as indicated by the fact that the weight change oscillates around 18% for all moisture cycles, the environmental conditions in which the fiber is stored or maintained will have an impact on its water content.

Further analysis of Fig. 5 indicates that the moisture cycles 3 and 4 repeat the pattern observed in cycle 2: reduction of the degree of H-bonding to 53% during saturation, followed by an increase to 93% as a result of fiber drying. This behavior is analogous to the findings of various authors in the case of aramid fibers. As the water sorbed during saturation diffuses through defect and amorphous regions in the fiber, the diffused water molecules are able to interact with the functional groups associated with intermolecular hydrogen bonding as a result of the partial relaxation experienced by the crystallite surfaces that come in contact with the sorbed water, leading to the disruption of intermolecular H-bonds in the polymer fiber [16,17]. Fig. 5 shows that as the fiber treatment moves into cycles 5 through 8, the degree of H-bonding of the dried specimens is progressively reduced from 93 to 62%. Such behavior signals a deterioration of the fiber structure. The lattice defects and decreased molecular orientation induced by water desorption during fiber drying tend to be further extended during water re-sorption, inhibiting the restoration of intermolecular H-bonds [1]. Moisture cycles 9 and 10 shown in Fig. 5 indicate that the degree of H-bonding of the dried specimens stabilizes at the reduced level of 62%. At this point, the partially disordered fiber structure does not show further deterioration as a result of additional moisture cycling. It is interesting to note that, throughout cycles 2 to 10, the degree of H-bonding of the saturated specimens remained relatively constant at values of 49–53%, defining a lower bound to the level of intermolecular H-bonding that is not affected by changes in environmental moisture conditions. The last column in Fig. 5 shows that annealing of the M5 fiber under tension after completing the 10 moisture cycles restores the degree of H-bonding to a value of 93%, the level originally measured on the M5 annealed fiber prior to moisture cycling. Fiber annealing under tension removes defects induced by the moisture cycles and restores fiber molecular orientation to its initial state. Improvements in polymer chain orientation promote the (re-)formation of intermolecular H-bonds.

The effect of moisture cycling on the compressive strength of M5 fiber is illustrated in Fig. 6. Variations in compressive strength as a function of fiber treatment follow a behavior that is similar to what has been described for the degree of intermolecular H-bonding. During the first four moisture cycles, the compressive strength of the annealed fiber alternates between 1.25 and 1.60 GPa as the fiber is saturated and dried, with the dried specimens having the same compressive strength value as the original annealed fiber. Then, at cycles 5 through 7, the compressive strength of the dried specimens shows a reduced value with respect to the original annealed fiber. This behavior is exacerbated at cycles 8–10, where the compressive strength of saturated and dried specimens becomes statistically equal, at a value of 1.29 ± 0.05 GPa. Nonetheless, as in the analysis of intermolecular H-bonding, the annealing of the fiber specimens subjected to 10 moisture cycles restores their compressive strength to a value of 1.60 ± 0.07 GPa, statistically equal to the value of 1.62 ± 0.04 measured on the original annealed fiber. The importance of the presence of a network of intermolecular H-bonds for the compressive strength of M5 fiber discussed in the previous section is further confirmed by these observations. The observed reduction in M5 fiber compressive strength as a result of fiber saturation is in agreement with the reduction of mechanical properties as a function of sorbed water and H-bond reduction reported by various authors for aramid and Armos fibers [1,18,19].

4. Conclusions

M5 fiber specimens heat-treated under different annealing conditions show a clear relationship between the degree of intermolecular H-bonding and axial compressive strength, where compressive strength is improved as intermolecular hydrogen bonding in the fiber is increased. In addition, the relationship between hydrogen bonding and compressive strength is independent of the annealing path (temperature and residence time) followed to improve the property, as multiple combinations of heat treatment conditions can be used to reach the same degree of hydrogen bonding and compressive strength. The presence of a well-developed network of intermolecular hydrogen bonds is therefore of paramount importance for the compressive properties of the fiber, as illustrated when comparing M5 to PBO, a fiber that has a structure similar to M5, but lacks the network of intermolecular hydrogen bonds, resulting in a compressive strength value almost six times smaller than M5.

Moisture cycling experiments of M5 fiber have revealed the first direct evidence of partial hydrogen bond reversibility in this material. During the first four moisture cycles, the original degree of H-bonding is recovered once the fiber is dried. Once the fiber moisture cycling is carried further, the dried specimens are no longer able to return to their original degree of H-bonding, signaling a deterioration of the fiber structure. Throughout the entire moisture cycling experiments, the degree of H-bonding of the saturated specimens remains relatively constant, defining a lower bound to the level of intermolecular H-bonding that is not affected by changes in environmental moisture conditions. Interestingly, annealing of the M5 specimens under tension after completing 10 moisture cycles restores the degree of H-bonding to the value originally shown by the annealed material. Variations in fiber compressive strength as a function of moisture cycling follow a behavior that is analogous to what has been observed for the degree of intermolecular H-bonding.

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