

Influence of Thermal Treatment Conditions on the Recoil Compressive Strength of Kevlar-29 Fibers

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Abstract: In this paper, thermal treatments of Kevlar-29 fiber resulted in a significant enhancement of compressive strength and corresponding decrease in tensile strength. These changes result from a decreased linearity at the macroscopic level in the fiber. Statistically designed experiments indicate that treatment temperature is the most significant variable in the thermal processing, while treatment soak time also played a role in the shift of properties.

1. INTRODUCTION

Kevlar (poly-p-phenylene terephthalamide or PPTA), shown in Figure 1, possesses a tensile-strength-to-weight ratio significantly superior to that of steel, making it ideal for tensile applications [1–5]. The crystal structure of Kevlar polymer chains can be classified as a monoclinic structure with the following lattice parameters: $\mathbf{a} = 7.87 \text{ \AA}$, $\mathbf{b} = 5.18 \text{ \AA}$, and $\mathbf{c} = 12.9 \text{ \AA}$ with a 90° unit-cell angle. In the Kevlar lattice, molecular chains exhibit two intermolecular interactions: hydrogen bonding (carbonyl oxygen to adjacent chain hydrogen(s)) acting in the \mathbf{b} -direction and Van der Waals dispersion forces acting in the \mathbf{a} -direction [6].

Conformation of the Kevlar fiber into anything other than the “trans”-conformation is sterically unfavorable. Spatially, the Kevlar polymer will always strive for the most linear conformation. Thus, the Kevlar fiber assumes nearly perfect “stiff/rigid-rod” geometry with very little branching or bending. Due to this near-perfect linearity, load can be distributed evenly along the fiber in the \mathbf{c} -direction, owing to its superior tensile strength. This phenomenon, coupled with the weak transaxial forces between the Kevlar polymer strands, makes Kevlar a superior choice for tensile applications. Since linear tolerances

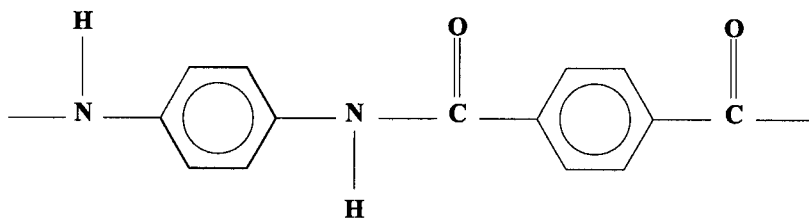


Figure 1. The repeat unit of Kevlar.

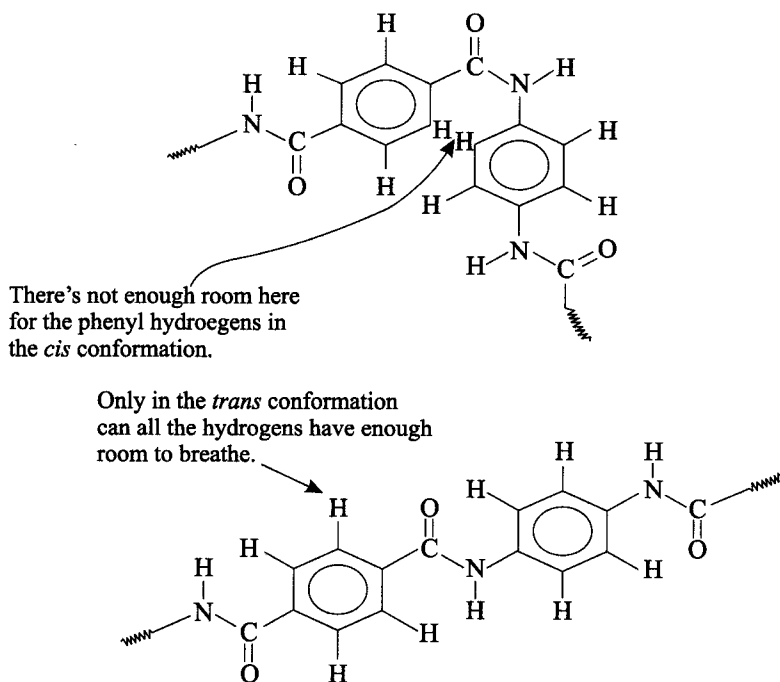


Figure 2. Stereochemical implications of the structure of Kevlar.

in the polymer enhance tensile strength and transaxial tolerances enhance compressive strength, Kevlar exhibits a compressive-to-tensile-strength ratio of between 0.13 and 0.25 [7]. This obviously puts Kevlar at a disadvantage when it comes to compressive applications. Figure 2 demonstrates the stereochemical implications of Kevlar's molecular structure.

Despite this limitation, Kevlar still has one of the higher compressive strengths among the high-performance polymers [8]. Generally, this has been attributed to its interchain network of hydrogen bonds. Ballauff [9] presented a discussion of this network and its reduction of the degrees of freedom in the material. This reduction dramatically alters the deformation for rigid-rod networks.

Kenner and Witham [10] cross-linked polyparaphenylene benzobisthiazole (PBZT) through ring coupling by the thermal elimination of an activated aryl hydrogen and subsequent combination of the aryl free radicals. However, the crystal structure of Kevlar will not accommodate a high level of cross-linking [11].

McGarry and Moalli [12] analyzed the compressive failure of PPTA. Through scanning electron microscopy, the study finds that the primary mode of compressive failure in PBO and PPTA fibers is the "kink band" phenomenon. This failure mode involves initiation of a fiber kink defect at the fiber surface. From the surface, the kink band defect propagates across the cross-section of the polymer fiber, causing failure. Thus, in order to improve the compressive properties of the Kevlar fiber, interaction between adjacent Kevlar strands has to be improved at the molecular level to reduce the formation and propagation of kinks through the alteration of the hydrogen bonding structure. This paper describes the influence of thermal processing conditions (treatment temperature, heating ramp rate, and dwell time) on the tensile and recoil compressive strengths of Kevlar-29.

2. BACKGROUND

Barton *et al.* [13] examined structure and property development in PPTA during heat treatment. The study did much to quantify the characteristics of the Kevlar fiber under differing heat treatment conditions. They quantified the changes observed using tensile tests, x-ray scattering, and optical microscopy.

No elongation or shrinkage of the PPTA fiber was noted with the heat-treated fiber. Additionally, the heat treatment had no effect on the polymer's tenacity. However, marked improvements were shown in the tensile modulus of the fiber as a strong function of treatment temperature, treatment time (annealing time), and fiber. Improvement in axial distortion of the fiber (degree of crystallite perfection) was also shown to be a strong function of annealing time, fiber tension and treatment temperature. Increases in crystallite size were also seen in the PPTA fiber during the heat treatment studies. The increase in crystallite size was shown to be a strong function of temperature and annealing time but a weak function of tension.

However, this study did not perform the heat treatment process on as-spun commercial fiber batches. Instead, they incorporated the heating treatment into the spinning process. Heat was added while the fibers were under stress, to quicken the evaporation of the solvent used to form the fibers. Additionally, no effort to characterize the compressive properties of the fiber was made.

Sweeny [11] looked into improving compressive properties of high-modulus fibers through cross-linking. Sweeny investigated cross-linking because of the current

unresolved questions surrounding the use of cross-linking as a way of improving compressive strength. The main question he had hoped to address was exactly how much cross-linking is required and how uniform the cross-linking distribution must be to achieve a noticeable difference in compressive strength. Sweeny used active aryl halides on the polymer units themselves. Once the halogen-bearing polymer is exposed to heat treatment, the halogen is eliminated and a free radical is formed in its place. Once this initiation takes place, adjacent molecules of the polymer may react and cross-link. The degree of cross-linking in a given experimental sample may be tracked through the percentage of polymeric halide retained. Figure 10 in that paper demonstrates the retention of iodine with treatment temperature for an iodine-substituted PPDT polymer. Clearly, iodine is released upon heat treatment, indicating that a free-radical initiation is taking place.

Heat treatment of iodine-substituted PPDT polymer took place under a nitrogen atmosphere at a heating ramp of $2\text{ }^{\circ}\text{C min}^{-1}$. A PPDT control yielded compressive strengths of between 1.2 and 1.5 g d^{-1} . The halide-bearing polymer showed an increase in recoil compressive strength to 2.15 g d^{-1} at $395\text{ }^{\circ}\text{C}$ held for 30 min and 2.9 g d^{-1} at $395\text{ }^{\circ}\text{C}$ held for 60 min. No test group, however, registered a recoil compressive strength above that of the Kevlar control. Additionally, it was observed that fiber toughness dropped with iodine loss. Sweeny hypothesizes that degradation of the polymer into isocyanate accompanies cross-linking and concludes that all aromatic polyamides ortho-halogenated to the carbonyl group would undergo such a mechanism.

3. EXPERIMENTAL PROCEDURE

Three experimental parameters were considered in this study: the maximum treatment temperature, or the maximum temperature to which the Kevlar fiber will be subjected; the soak rate, or the rate of temperature increase of the furnace that is heat treating the Kevlar fiber; and the soak time, or the duration of time for which the Kevlar fiber is subjected to the maximum treatment temperature.

Using a factorial analysis, the experiments can be designed in an efficient way that will encapsulate the effects that each individual experimental factor has on the objective variable(s). For the purposes of this experiment, three levels of each factor are under investigation. Three levels have been chosen in order to factor in any potential non-linearities in the results.

A CCD (central composite design) was used for this three-factor experiment. The central composite design relies upon equation (1) to determine the number of experiments to be run:

$$\# \text{ experiments} = 2^{k-p} + 2k + m \quad (1)$$

where k is the number of factors, p is the fractionalization element of the experiment, and m is the number of center-point experiments. The experimental design in three dimensions is displayed in Figure 3.

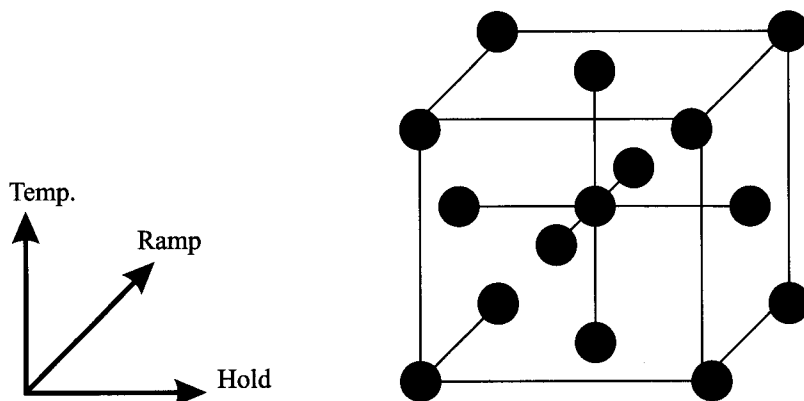


Figure 3. Central composite design with three factors and three levels.

Table 1. Orthogonal experimental ranges.

	Temperature (°C)	Ramp (°C min ⁻¹)	Hold time (min)
High	470	7.5	10
Medium	440	5	7
Low	400	2.5	5

All experimental ranges were originally chosen to accommodate a simple three-level design. Designs exceeding three levels would require impractical numbers of experiments to accomplish. The upper limit for temperature was chosen at the threshold of the pre-carbonization regime for Kevlar fiber [14]. Table 1 shows the actual experimental range utilized in the experiments. The CCD experimental design may be assigned experimental values for each experiment. The first eight experiments involve the "corner points" of the experimental space involving a two-level, three-factor experimental design "backbone". The experiment is framed in three columns, one for each experimental factor. Table 2 represents the first eight experiments in this experimental design.

The set of six experiments is described by the star points of the experimental space. In essence, one factor is varied between the high and low levels while the other two factors are held at their mid-point level. Table 3 details these experiments. In addition to the above 14 experiments, a center-point experiment must be incorporated in order to pivot any eventual correlation of data to be derived from the experiments. This center point is merely the experiment run at each factor's mid-level. This center-point experiment was performed at a heating of rate of 5 °C per minute, a maximum temperature of 440 °C and

Table 2. 2^k experimental regime.

Temperature (°C)	Ramp (°C min ⁻¹)	Hold time (min)
400	2.5	5
470	2.5	5
400	7.5	5
470	7.5	5
400	2.5	10
470	2.5	10
400	7.5	10
470	7.5	10

Table 3. 2^k experimental regime.

Temperature (°C)	Ramp (°C min ⁻¹)	Hold time (min)
400	5	7
470	5	7
440	2.5	7
440	7.5	7
440	5	5
440	5	10

with a seven-minute hold time. This experimental design affords a total of 14 degrees of freedom. Using these degrees of freedom, single-factor effects may be analyzed along with factor interactions and non-linearities in factor effects.

Kevlar-29 fibers were heated under positive nitrogen pressure in a Thermolyne series 48000 furnace. Fiber diameters were measured using a laser diffraction technique that has been shown to be accurate to within 0.1 microns [15]. Fibers were tested using a modified Instron Ultimate Testing machine in compliance with ASTM standards [16].

According to the experimental design, each factor was scrutinized separately for its effect on the objective function, tensile strength. The mean and variance were grouped and statistical differences analyzed. The ANOVA method was used for this analysis.

4. RESULTS AND DISCUSSION

Although the tensile strength statistics, summarized in Table 4, can be determined using classical methods, the real thrust of the experiments was to determine not only the depreciation in tensile strength but also the enhancement of the compressive properties of the Kevlar fiber. Table 5 summarizes the recoil compressive data.

Table 4. Data for tensile experiments.

Batch number	T (°C)	Hold time (min)	Ramp (°C min ⁻¹)	Tensile strength (MPa)	Error (MPa)	Standard deviation (MPa)
1	470	5	2.5	570.04	37.74	162.22
2	470	5	7.5	909.61	74.14	318.70
3	470	10	7.5	576.80	67.29	289.29
4	470	10	2.5	437.16	31.45	135.18
5	470	7	5	290.88	24.01	103.20
6	400	5	2.5	790.08	68.86	296.02
7	400	10	2.5	937.14	89.34	384.03
8	440	7	2.5	607.52	46.85	201.41
9	400	10	7.5	706.50	59.82	257.16
10	440	10	5	762.42	49.49	212.73
11	400	5	7.5	862.34	65.22	280.36
12	440	7	7.5	743.32	50.88	218.73
13	400	7	5	1107.92	77.50	333.18
14	440	5	5	1240.82	109.22	469.50
15	440	7	5	764.34	51.90	223.09

Table 5. Summary data for compressive experiments.

Batch number	T (°C)	Hold time (min)	Ramp (°C min ⁻¹)	Compressive strength (MPa)
1	470	5	2.5	600
2	470	5	7.5	630
3	470	10	7.5	600
4	470	10	2.5	N/A
5	470	7	5	N/A
6	400	5	2.5	310
7	400	10	2.5	460
8	440	7	2.5	490
9	400	10	7.5	360
10	440	10	5	510
11	400	5	7.5	450
12	440	7	7.5	500
13	400	7	5	440
14	440	5	5	450
15	440	7	5	500

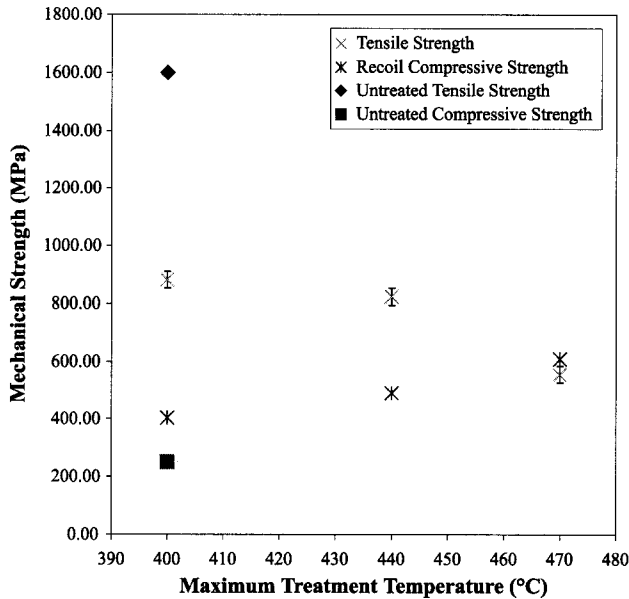


Figure 4. Mechanical properties as a function of treatment temperature.

The compressive data may now be pooled to determine the mean compressive strength demonstrated at the varying levels for each experimental factor. Based on the information presented, comparisons of tensile and compressive properties for each factor may be compared. Figures 4–6 display these comparisons and the ANOVA-derived error ranges for the tensile data.

Based on the experimental limits established by ANOVA, the significant differences become clear. In terms of the temperature effect, there is no significant difference between the tensile strength at the 400 °C treatment temperature and the 440 °C treatment temperature. A significant difference is established by the delineation between the 440 °C temperature level and the 470 °C temperature level. Based on this, we may conclude that the temperature effect has little effect on the tensile strength depreciation until after the middle treatment temperature. This implies that at the higher temperature, there may be the onset of thermal degradation of the Kevlar.

All levels for the ramp effect show significant differences among themselves. There is an optimal tensile strength exhibited at the mid-level for strength. There exists a significant difference between the low and middle levels for the hold time in its bearing on the tensile strength. No significant difference exists between the middle and high levels for this factor. In addition to establishing these factorial differences, it is important to note the homogeneity in the variance in the factor sets themselves. This indicates that a sufficient number of experiments were performed to ensure uniform variance among the groups.

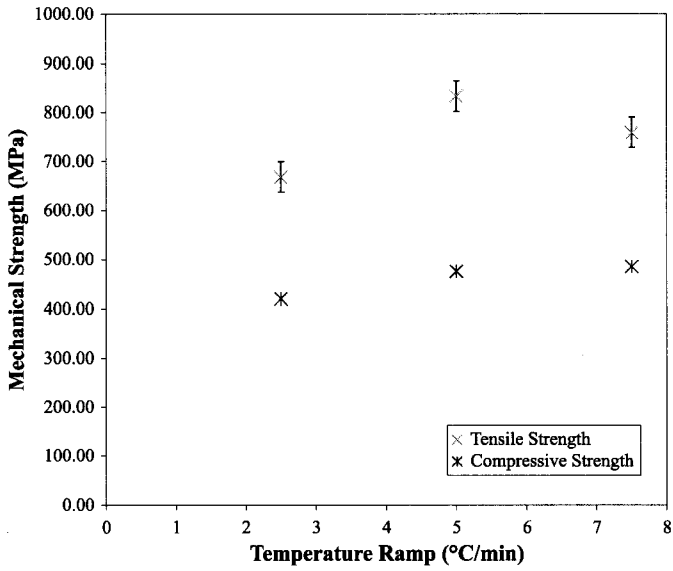


Figure 5. Mechanical properties as a function of ramp rate.

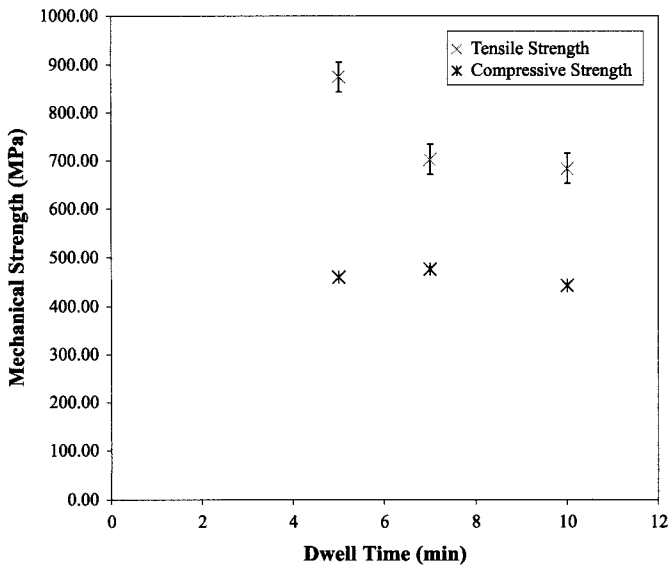


Figure 6. Mechanical properties as a function of dwell time.

Table 6. Mechanical properties expressed as the ratio σ_C/σ_T .

Temperature (°C)	Average ratio	Upper limit	Lower limit
400	0.46	0.50	0.43
440	0.63	0.68	0.59
470	0.90	0.97	0.83
Ramp (°C min ⁻¹)	Average ratio	Upper limit	Lower limit
2.5	0.67	0.73	0.62
5	0.62	0.67	0.57
7.5	0.60	0.64	0.56
Hold time (min)	Average ratio	Upper limit	Lower limit
5	0.49	0.54	0.45
7	0.71	0.76	0.66
10	0.67	0.72	0.62

Clearly, the heat treatment has a marked effect on the compressive strength of the fiber as a function of treatment temperature. As the tensile strength is depreciated, a significant enhancement of the compressive properties of the Kevlar fiber takes place. The raw compressive strength of 250 MPa undergoes substantial improvement while the tensile strength undergoes the associated decrease.

While the tensile strength seems to exhibit an optimum at the middle level for the ramp, there is very little noticeable influence of the ramp on the compressive strength of the Kevlar fiber. Additionally, although the tensile strength decreases in a sharp exponential fashion as a function of hold time, there is very little effect on the compressive strength of the fiber.

Another convenient way of looking at the tensile/compressive mechanical properties as a function of heat treatment parameters is a ratio. This is especially useful in the scenario where a particular experimental group exhibits a compressive strength exceeding that of its tensile strength. Accordingly, for such groups, a compressive-to-tensile ratio of 1 may be conservatively assigned in order to estimate the effect of heat treatment on the mechanical properties of the fiber. Referencing the statistical range established by the ANOVA analysis of variance on the tensile properties of the treated fibers, a range of ratios may be established and significant differences established. For the purposes of this analysis, groups 4 and 5 are set at a ratio value of 1 for the average tensile strength of the groups. Testing for those groups has shown the limitations for the recoil compressive method. Table 6 summarizes these ratios.

The compressive-to-tensile-strength ratio has a definite upward trend as a function of the treatment temperature. All data points are statistically different. On the other hand, no trend in the ratio is seen as a function of the temperature ramp. All data points are statistically similar. A trend resembling a saturated gain curve is seen with the hold time effect on the compressive-to-tensile ratio. The first two experimental levels exhibit ratios that are statistically different while the trend tends toward an asymptote at higher levels of the hold time.

5. CONCLUSIONS

There are clear manifestations of alteration of the Kevlar fiber at the molecular level in the mechanical properties of thermally treated Kevlar-29 polymer. This thermally induced change effects a loss in linearity of the PPTA polymer. The loss in linearity, at the macroscopic level, shows itself in the form of tensile strength degradation and compressive strength enhancement. The experimental series has determined that treatment temperature plays a key and prominent role in both the loss in tensile strength and gain in compressive strength. Furthermore, it was shown that the temperature treatment ramp and treatment soak time have some type of effect over the tensile property degradation of the PPTA polymer.

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