

The Influence of Electron-Beam Radiation on the Tensile and Recoil Compressive Strengths of Kevlar-29

JAMES A. NEWELL

Department of Chemical Engineering, Rowan University, 201 Mullica Hill Road, Glassboro, NJ 08028, USA

ALLAN A. PUZIANOWSKI

Acsion Incorporated, Ara Morradian Way, Pinawa, Manitoba, Canada R0E 1L0

LUCAS R. SCHMIDT

Department of Chemical Engineering, University of North Dakota, Grand Forks, ND 58202, USA

(Received 14 January 2002)

Abstract: Many research groups have attempted to enhance the compressive strength of high-performance polymers. Unlike more common methods including thermal treatment or the addition of a cross-linking agent during spinning, this paper describes the use of electron-beam radiation to induce cross-linking in Kevlar-29. The data show that the recoil compressive strength of the fiber increases significantly with increasing radiation exposure, reaching 487 MPa at a dose of 1100 kGy. The radiation also reduces the tensile strength of the fiber, but by less than twenty per cent. Observable physical changes that accompany the changes in mechanical properties include a reduction in fiber diameter and a change in color.

1. INTRODUCTION

High-performance polymers such as Kevlar (poly-p-phenyleneterephthalamide or PPTA), shown in Figure 1, possess exceptional tensile strengths that make them ideal materials for use in such diverse products as brake pads, bullet-resistant vests, kayaks, marine ropes, and tennis rackets [1–6]. Kevlar chains can be classified as having a monoclinic crystalline structure with the following lattice parameters: $a = 7.87 \text{ \AA}$, $b = 5.18 \text{ \AA}$, and $c = 12.9 \text{ \AA}$ 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 b -direction and Van der Waals dispersion forces acting in the a -direction [7].

Steric limitations cause Kevlar fiber to strive for the most linear conformation. Thus, the Kevlar fiber assumes nearly perfect “stiff/rigid-rod” geometry. This linearity enables the fiber to distribute a tensile load evenly along the fiber in the c -direction, resulting in

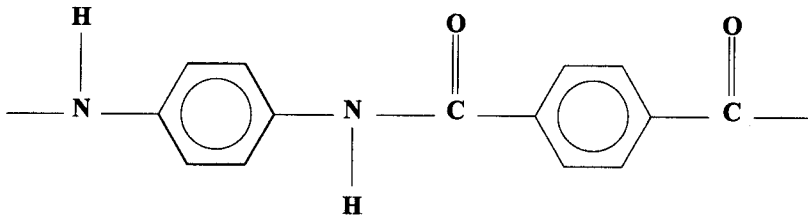


Figure 1. The repeat unit of Kevlar.

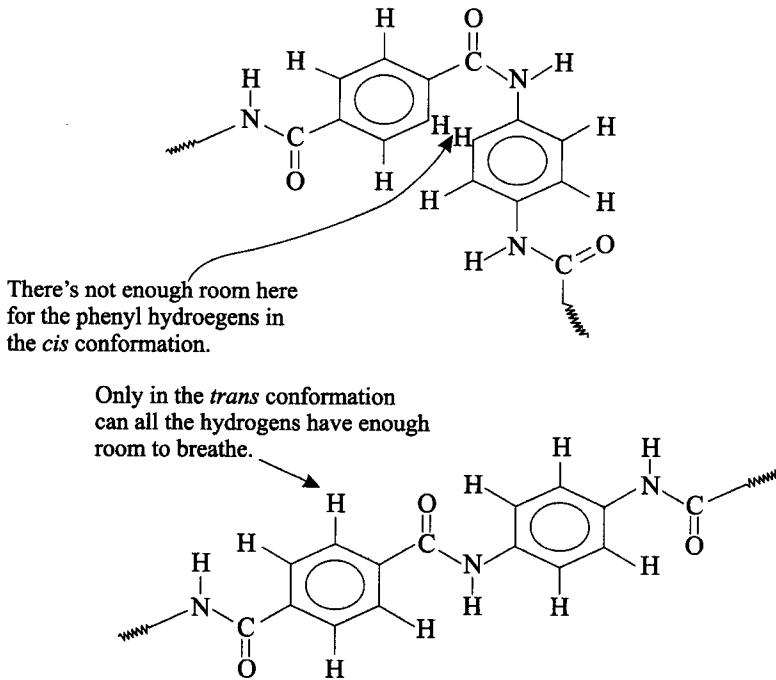


Figure 2. Stereochemical implications of the structure of Kevlar.

superior tensile strength. However, this same linearity, combined with the weak transaxial forces between the polymer strands, limits the ability of the fiber to distribute a load. As a result, Kevlar fibers possess a compressive-to-tensile-strength ratio of between 0.13 and 0.25 [8]. Figure 2 demonstrates the stereochemical implications of Kevlar's molecular structure.

Table 1. Influence of treatment temperature, heating ramp, and hold time on the ratio of compressive to tensile strength for thermally treated Kevlar-29 [10].

Temperature (°C)	σ_c/σ_T
400	0.46
440	0.63
470	0.90
Ramp (°C min ⁻¹)	σ_c/σ_T
2.5	0.67
5	0.62
7.5	0.60
Hold time (min)	σ_c/σ_T
5	0.49
7	0.71
10	0.67

Many groups have tried to enhance the compressive properties of Kevlar through heat treatment [9, 10] or by adding chemical cross-linking agents during spinning [11]. In these studies, 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.

Sweeney *et al.* [10] found that heat treatment resulted in a significant increase in the compressive-to-tensile-strength ratio for Kevlar and that this increase was a strong function of temperature. These results are summarized in Table 1. Sweeney *et al.* postulated that the enhanced recoil compressive strength results from disrupting the interchain networks of hydrogen bonding, as observed by Ballauff [12]. Kenner and Witham [13] used ring coupling from the thermal elimination of an activated aryl hydrogen and subsequent combination of the aryl free radicals to cross-link polyparaphenylene benzobisthiazole (PBZT). However, the crystal structure of Kevlar will not accommodate a high level of cross-linking [11].

Sweeney [11] 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 the through percentage of polymeric halide retained.

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.

Woods and Pikaev [14] have demonstrated that exposing organic substances to high-energy radiation leads to the formation of reactive free-radical species, similar to those formed in the Sweeny study. This radiation polymerization has been described in detail by several researchers [15-17]. One mechanism capable of generating such radiation is through the use of high-powered electron accelerators such as AECL's IMPELAs (Industrial Processing Linear Accelerators) in the energy range above 5 MeV [18, 19]. Primary uses for these accelerators have included curing of composites [20-23], food purification [23], and soil detoxification [24].

Electron-beam (e-beam) radiation offers several potential advantages over thermal processing of polymers. These advantages include ambient temperature processing, improved material compatibilities, and reduced treatment times [25]. Therefore, this paper examines the influence of e-beam radiation on the tensile and recoil compressive strength of Kevlar-29 fiber.

2. EXPERIMENTAL PROCEDURE

As-received Kevlar-29 samples were obtained from the E. I. DuPont de Nemours Corporation. Kevlar-29 samples were irradiated using the AECL I-10/1 electron accelerator at Acsion [26]. This device is shown in Figure 3. Each fiber batch was exposed in air for three seconds to radiation levels of 0 (as a control), 100, 500, 1000, and 1100 kGy. The single-filament testing procedure used in this study followed the procedure described in ASTM Standard D-3379-75 [27]. Fibers were mounted on testing tabs using Hughes Epoxy 220 and placed in a $65\text{ }^{\circ}\text{C}$ drying oven for 24 hours. Fiber diameters were measured using a laser diffraction technique with a 0.95 mW helium-neon red laser. This technique has been found to be accurate to within $0.1\text{ }\mu\text{m}$. For each fiber batch, a minimum of 75 samples were tested in tension and another 75 in recoil compression.

Compressive testing of composites is well established by ASTM [28], but these tests involve many steps and large quantities of fiber. Therefore, it would be advantageous to directly measure the compressive strengths of the fibers themselves. For polymeric fibers, the fiber compressive strengths estimated from composite compression tests agree most accurately with those obtained by the recoil test [8]. Fibers are placed under a static tensile load. Next, the fiber is ruptured using either an electric discharge or surgical scissors. The stored energy travels down both halves of the fiber in the form of a recoil compressive

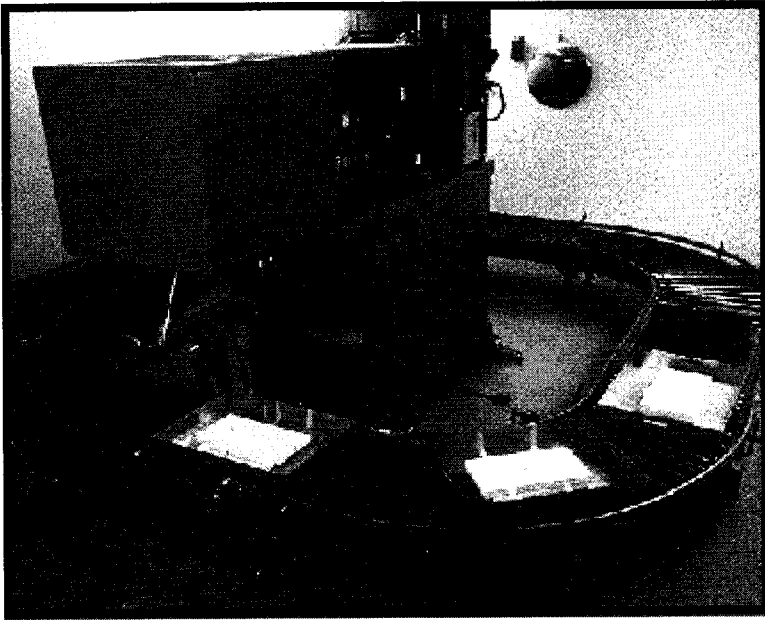


Figure 3. Accion Industries I10/1 electron accelerator.

wave. The two fiber halves either survive this recoil wave or they experience a secondary failure. Mean recoil compressive strengths were estimated using the method of Allen [29].

3. RESULTS AND DISCUSSION

The irradiated fibers showed physical changes as a result of the irradiation process. The color of the fibers changes from a deep yellow to a pale yellow. As Table 2 shows, the diameter of the fibers reduced (by as much as nearly 30% in the case of the 1100 kGy sample) as radiation intensity increased.

Table 3 shows the influence of radiation level on the tensile and recoil compressive strengths of the Kevlar-29 fibers. It is clear from Figure 4 that there is a significant decrease in the tensile strength of Kevlar fibers with increasing radiation. The free-radical reaction induced by the radiation would likely result in partial cross-linking of the fibers, which would disrupt the linear structure. This disruption should decrease the tensile strength while increasing the capacity of the fiber to distribute a compressive load.

Figure 5 demonstrates that there is a substantial increase in the recoil compressive strength of the Kevlar-29 fibers with increasing radiation level, as expected. These data show that exposure to a dose as small as 100 kGy of e-beam radiation induces a significant

Table 2. Fiber diameter as a function of radiation level.

Radiation level (kGy)	Fiber diameter (μm)
0	13.6
100	13.2
200	12.4
500	10.9
1000	10.3
1100	9.8

Table 3. Tensile and recoil compressive strengths of e-beam-treated Kevlar-29 fibers.

Radiation level (kGy)	Mean tensile strength (MPa)	Mean recoil compressive strength (MPa)
0	2160 \pm 63	365 \pm 6
100	2043 \pm 120	368 \pm 8
200	1996 \pm 86	381 \pm 9
500	1891 \pm 71	404 \pm 8
1000	1786 \pm 93	472 \pm 7
1100	1723 \pm 87	487 \pm 7

shift of mechanical properties towards compression can be achieved. This is consistent with the structural changes anticipated as a result of the radiation-induced free-radical reactions.

More intriguingly, these data also indicate that recoil compressive strengths can be increased by more than one-third, while experiencing only an approximately 20% drop in tensile strength. This shift in properties is far superior to the results reported from heat treatment studies [10], in which a loss of more than 50% of the tensile strength was needed to achieve the same improvement in recoil compressive strength. Figure 6 shows a comparative plot of recoil compressive strength versus tensile strength for the fibers tested in this study. It is interesting to note that there appears to be a nearly linear inverse relationship for these fibers. Finally, Figure 7 shows the influence of radiation dose on tensile strength, compressive strength, and fiber diameter expressed as a ratio of change for each property. This graph indicates that an essentially even exchange of tensile for compressive strength occurs during treatment.

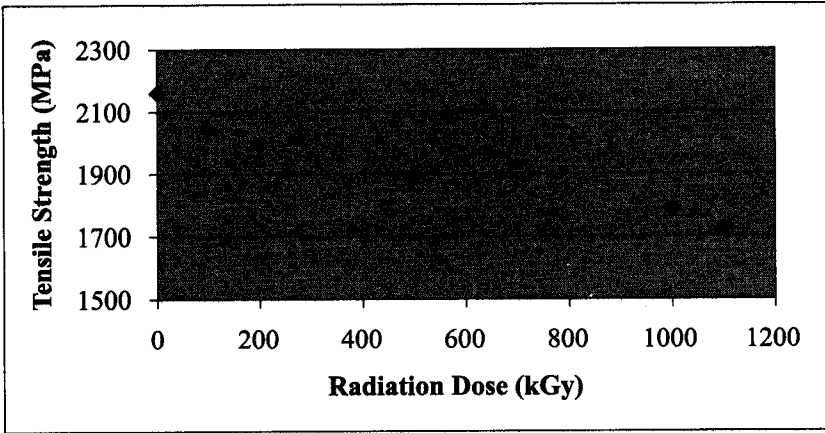


Figure 4. Influence of e-beam radiation on tensile strength.

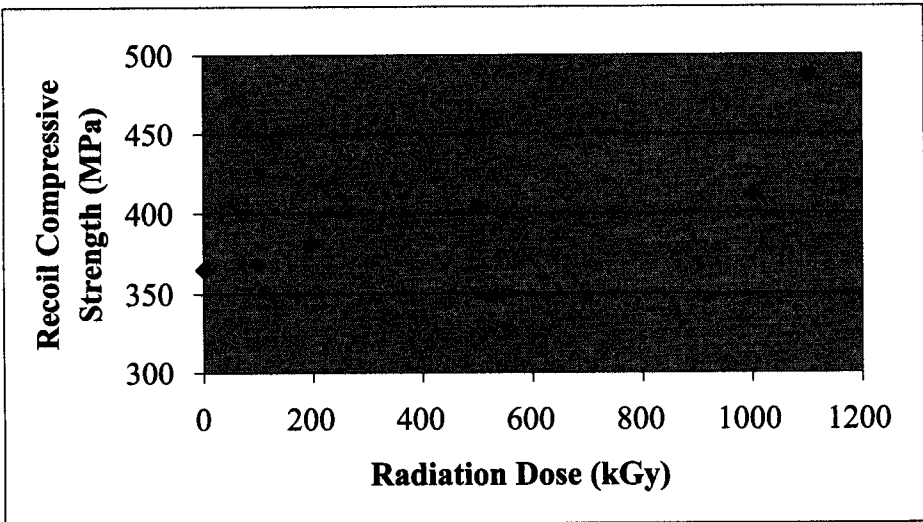


Figure 5. Influence of e-beam radiation on recoil compressive strength.

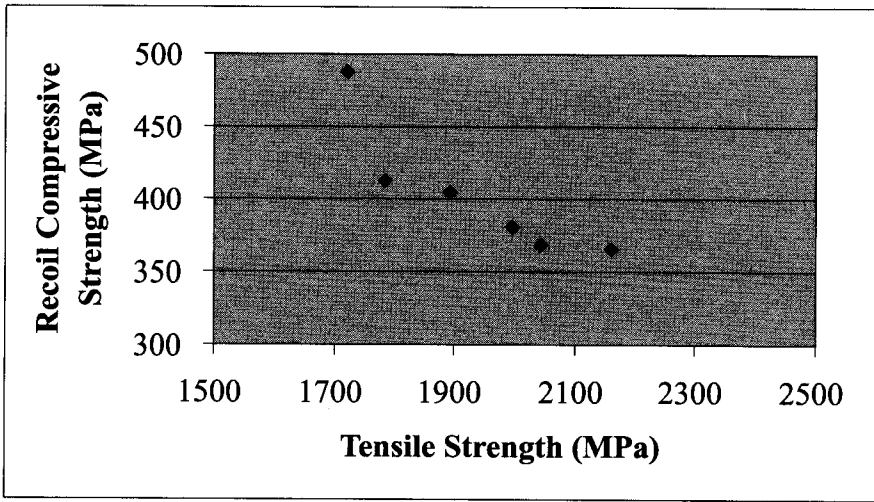


Figure 6. Recoil compressive strength versus tensile strength.

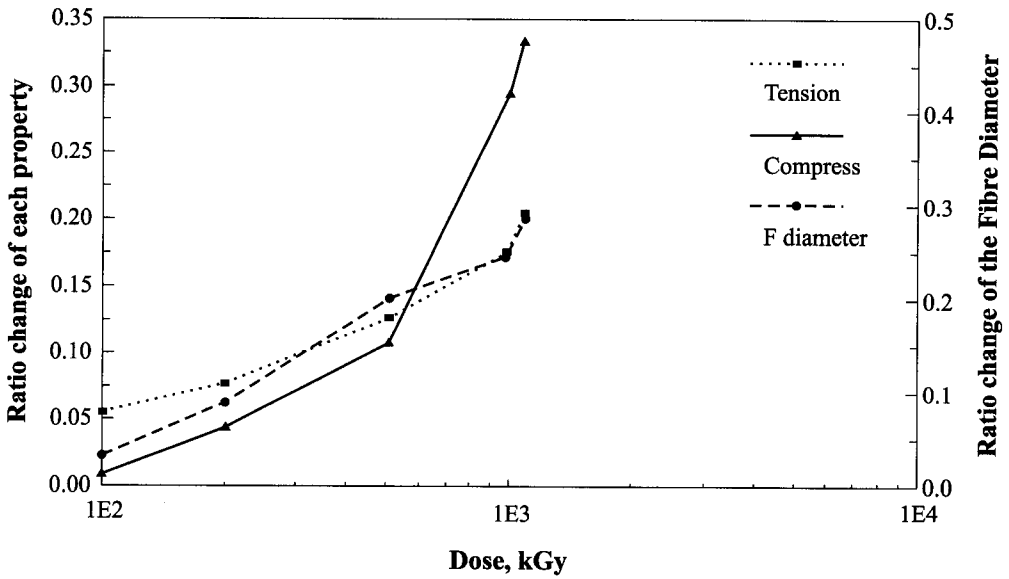


Figure 7. Dose effects on various fiber properties.

4. CONCLUSIONS

Electron-beam radiation has been shown to increase the recoil compressive strength of Kevlar-29 fibers with greater increases in recoil compressive strength corresponding to exposure to higher radiation levels. Increases in excess of 33% were found for the highest treatment level analyzed. Concurrently, e-beam radiation results in a decrease in the tensile strength of the fiber, but only by 20% in even the highest radiation level tested. Finally, this study showed that a nearly linear inverse relationship exists between the gains in recoil compressive strength and the losses in tensile strength.

REFERENCES

- [1] Tanner D, Fitzgerald J A and Phillips B R 1989 *Adv. Mater.* **5** 151
- [2] Hattery G R and Hillman M E D 1986 *High Performance Polymers* (New York: Hanser)
- [3] Krause S J, Haddock T B, Vezie D L, Lenhart P G, Hwang P G, Price W F, Helminiak T E, O'Brien J F and Adams W W 1988 *Polymer* **29** 1354
- [4] Fawaz S A, Palazotto A N and Wang C S 1992 *Polymer* **33** 100
- [5] Newell J A, Edie D D and Fuller E L Jr 1996 *J. Appl. Polym. Sci.* **60** 825
- [6] Newell J A and Edie D D 1996 *Carbon* **34** 551
- [7] Liang Y, Quichen Z and Warner S B 1994 *J. Polym. Sci. A* **32** 2207
- [8] Kumar S and Helminiak T E 1990 *SAMPE J.* **26** 51
- [9] Barton R, Lee K and Schultz J M 1995 *J. Polym. Sci. A* **33** 1
- [10] Sweeney D, Newell J, Picerno S and Kurzeja T 2002 *High Perform. Polym.* **14** 113
- [11] Sweeney W 1992 *J. Polym. Sci. A* **30** 1111
- [12] Ballauff M 1989 *Angew. Chem. Adv. Mater.* **28** 135
- [13] Kenner J and Witham E 1983 *J. Chem. Soc.* **103** 232
- [14] Woods R J and Pikaev A K 1994 *Applied Radiation Chemistry: Radiation Processing* (New York: Wiley)
- [15] Chapiro A 1962 *Radiation Chemistry of Polymeric Systems* (New York: Interscience)
- [16] Charlesby A 1960 *Atomic Radiation and Polymer* (Oxford: Pergamon)
- [17] Wilson J E 1974 *Radiation Chemistry of Monomers, Polymers and Plastics* (New York: Dekker)
- [18] McKeown J, Labrie J P and Funk L W 1985 *Nucl. Instrum. Methods B* **10/11** 846
- [19] McKeown J 1985 *IEEE Trans. Nucl. Sci.* **32** 3292
- [20] Crivello J V, Fan M and Bi D 1992 *Proc. RADTECH 92* p 535
- [21] Silverman J 1981 *J. Chem. Educ.* **58** 168
- [22] Beziers D and Capdepey B 1990 *Proc. 35th Int. SAMPE Symp.* p 1221
- [23] Singh A, Saunders C, Barnard J, Lopata V, Kremers W, McDougall T, Chung M and Tateishi M 1996 *Radiat. Phys. Chem.* **48** 153
- [24] Cleland M R 1995 *IMPELA News* **2**(1) 1
- [25] Singh A, Saunders C, Lopata V, Kremers W and Chung M 1995 *Proc. Int. Conf. on Composite Materials and Energy* p 389
- [26] Barnard J W and Stanley F W 1989 *Nucl. Instrum. Methods Phys. Res. B* **40/41** 1158
- [27] *ASTM Standard D3379-75* (reapproved 1989)
- [28] *ASTM Standards D695 and D3410*
- [29] Allen S R 1987 *J. Mater. Sci.* **22** 853