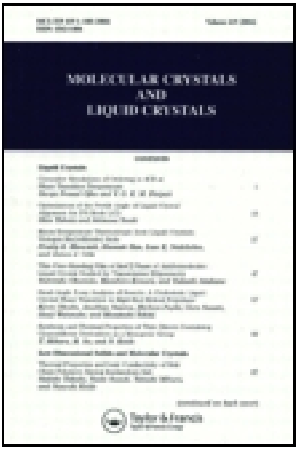

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Macro-structural Deformation of Kevlar® 40 Aramid Fibers

Eric J. Roche [a] , S. R. Allen [a] , C. R. Fincher [a] & C. Paulson [a]
[a] E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware, U.S.A.

Version of record first published: 13 Dec 2006.

Mol. Cryst. Liq. Cryst., 1987, Vol. 153, pp. 547-552
Photocopying permitted by license only

Printed in the United States of America

MACROSTRUCTURAL DEFORMATION OF KEVLAR® 49 ARAMID FIBERS

ERIC J. ROCHE, S. R. ALLEN, C. R. FINCHER AND C. PAULSON
E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware, U.S.A.

Abstract Kevlar® 49 "pleating" has been monitored, via measurement of the corresponding light diffraction intensity while stressing a single filament. The structure responds to stress by opening up, with most of the diffracted intensity disappearing at about 60% of the breaking stress. The pleating is restored upon relaxation.

Polymer fibers of outstanding tensile properties may now be obtained by a variety of processes, all designed to induce very high orientation of the molecular chains along the fiber axis. In the Kevlar® process, this is achieved by taking advantage of the liquid crystalline character of the poly(p-phenylene terephthalamide)/sulfuric acid spinning solution. This unique process results in a variety of original structural characteristics. Ballou[1] first discussed the radical arrangement of the (200) crystallographic planes and the periodic bending of the molecular chains along the fiber direction, later modelized as a "pleated sheet" arrangement by Dobb et. al.[2]. The simplest manifestation of this complex supramolecular organization is the transverse "banding" typical of light micrographs of Kevlar® fibers. Similar optical textures, though with larger characteristic periods, have also been encountered in a variety of lyo- or thermotropic polymeric systems, generally in response to shear-relaxation experiments[3]. The present work was undertaken to understand the relationship between pleating and tensile properties of Kevlar® 49.

Despite its complexity[4], light diffraction appeared the best available technique for quantification of the pleated structure, particularly for dynamic measurements. The experimental set-up is sketched in Fig. 1. A vertically polarized He-Ne laser beam was normally incident upon a horizontal fiber. The diffracted beam (horizontally polarized -4-) was scanned with a photomultiplier and the intensity digitally processed. The filament was mounted on a rig allowing variable stressing and easy immersion in a fluid of matching refractive index (1.62). Conventional tensile testing of the fibers was performed on an Instron machine.

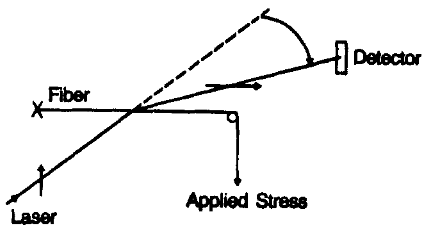

FIGURE 1 Schematic of the experimental set up.

Typical scattering profiles of a Kevlar® 49 filament for increasing stresses are shown in Fig. 2. Each profile has been smoothed to remove the high frequency noise. A progressive reduction of the intensity with increasing stress is noticed until the intensity levels off at high stresses. Because such profiles have been observed to vary widely between filaments and even along a filament, a better measure of the response to stress is given by the integrated intensity. This is presented in Fig. 3 for three different filaments, after normalization to the maximum (no load) intensity. The data indicates an approximately linear response to stress up to a stress of about 1.7 GPa beyond which the scattered intensity remains constant until filament rupture.

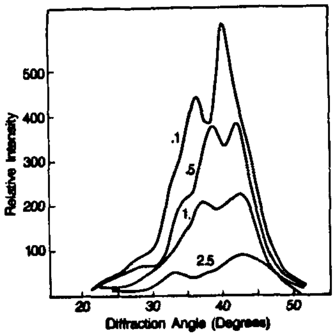

FIGURE 2 Light diffraction profile as a function of applied stress for a Kevlar® 49 fiber. The number on each curve indicates the stress in GPa.

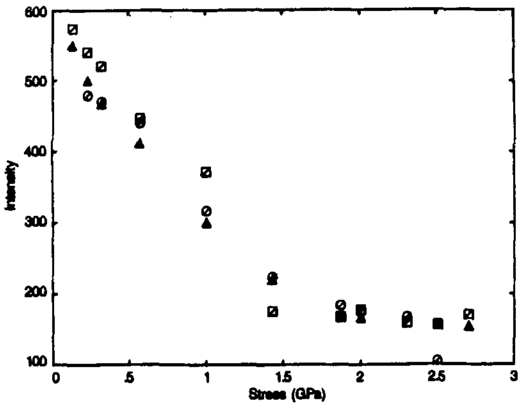

FIGURE 3 Integrated diffracted intensity variation with stress; the different symbols refer to different filaments.

For parallel study of the tensile deformation of similar fibers, modulus vs. stress plots are most instructive. An example is shown in Fig. 4 where the dotted and solid curves represent the first load- and conditioned behavior respectively. The first load- profile is dominated by softening effects due to the expulsion of residual moisture and other irreversible phenomena. On the second loading, however, the modulus is seen to increase quasi-linearly with stress up to a stress of about 2. GPa, a value close to that observed for the diffracted intensity profile. This indicates a correlation between scattered intensity and modulus, at least for the first half of the deformation. The scattering has been shown to result from the variation of the polarization tensor associated to the pleating[4]. In this treatment, the total scattered intensity would naturally decrease for smaller perturbations of the polarization tensor. The modulus increase with stress can, therefore, be accounted for largely, at least for the first part of the deformation, by a progressive opening up of the pleats and corresponding alignment of the molecular crystals. The occurrence of such a phenomenon was suggested on the basis of acoustic pulse velocity measurements[1]. To our knowledge, this constitutes a rare instance where a molecular deformation can be observed through the modification of a "macrostructure". From X-ray data, Northolt also accounted for the stress dependence of modulus by a progressive improvement of the average crystalline orientation, but without consideration of the supramolecular organization[5].

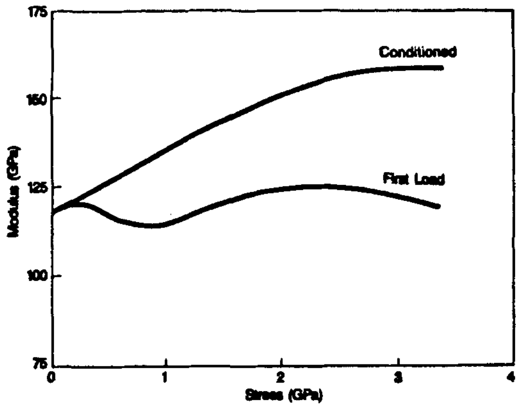

FIGURE 4 Modulus vs. stress curves for a typical Kevlar® 49 fiber.

Most remarkably, the correlation between pleat deformation and modulus is confirmed by cyclic loading experiments: the diffracted intensity variation is reversible. In an additional confirmation of this relationship, one may compare the light diffraction profiles of Kevlar® 29, Kevlar® 49 and the newly developed Kevlar® 149, with corresponding typical moduli of 95., 115, and 150. GPa, respectively. The profiles are shown in Fig. 5. The scattered intensity is indeed lower, the higher the modulus.

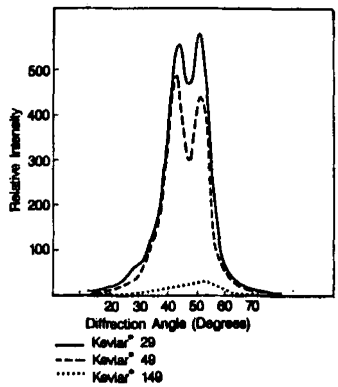

FIGURE 5 Light diffraction profiles for Kevlar® 29, Kevlar® 49 and Kevlar® 149 (from top to bottom). The peaks angular position is shifted when compared to profiles in Fig. 2 because water was used instead of index matching fluid.

The present investigation demonstrates that the optical texture of a liquid crystalline oriented polymer system, which reflects long range structural ordering, may be used in a semi-quantitative way to characterize the system's mechanical behavior. The obvious limitation to a more general application is the yet incomplete understanding of the light scattering phenomenon in Kevlar® fibers.

REFERENCES

1. J. Ballou, Polym. Prep., 17(1), 75 (1976).
2. M. G. Dobb, D. J. Johnson and B. P. Saville, J. Polym. Sci., Polym. Phys. Ed., 15, 2201 (1977).
3. A. M. Donald, C. Viney and A. H. Windle, Polymer, 24, 155 (1983).
4. E. J. Roche, M. S. Wolfe, A. Suna and P. Avakian, J. Macromol. Sci., Phys., B24, 141 (1985).
5. M. G. Northolt, Polymer, 21, 1199 (1980).