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Title: Torsional Properties and Structure-Property Relations in High Performance Fibers

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INTRODUCTION

Progress in the first six months of this new project has been mixed. We have had some difficulty in identifying and hiring a person to fill the post-doctoral position. We have conducted a review of the literature in the area of shear and compressive modulus of high performance fibers, only to find that the available literature is dominated by reports on carbon fibers. We have been very successful in completing the development and the initial application of the first generation of the torsion testing apparatus. This report, then, is a review of the literature for the high performance fibers, and a description of the work to date on the torsion apparatus

LITERATURE REVIEW

High performance fibers have high axial orientation but poor transverse properties. A lot of effort into increasing their compressive strength has been concentrated on the modifications in the fiber microstructure such as incorporating rigid back bone with bulky pendant groups[1] and pseudo-ladder type structures formed by cross linking through intramolecular hydrogen bonds[2]

Much of the published work that we came across during this literature review dealt with carbon fibers. Researchers have tried to analyze the various parameters which contribute to the compressive strength and have then tried to find out ways to improve upon them. All the work can be mainly classified in terms of identification of the parameters, their quantification and finally their improvement.

Identification of Parameters

Primarily, efforts were directed towards developing an understanding of the modes of failure. The types of failure could then be associated with a cause and subsequently related theoretically to some measurable parameter.

There are two main modes of failure for carbon fibers depending upon their properties: failure by microbuckling, i.e., elastic instability, not inferior compressive strength, or failure by yielding due to inherently lower compressive strength. The critical stress for microbuckling is directly a function of Young's modulus and the moment of inertia. The high level of axial orientation leads to the weakness in the lateral strength of the fiber; there could be either intralamellar shear or interlamellar shear.[3,4]

While testing pitch based[5] and PAN based[6] high performance carbon fibers for comparison purposes using recoil testing[7,8] it was determined that bending occurs during the testing which then propagates in a transverse wave form and a shear stress is developed as the wave reaches the constrained end. Thus, there is mixed failure in the low modulus fibers. Also, the texture of the fiber could inhibit the shearing of basal planes giving rise to higher compressive strength. In the high modulus fibers, the possible amplitude for this wave is low and hence only a small shear stress is developed. Thus, mixed mode failure does not occur. Another explanation is the sheet like flat structure which offers low resistance to shear across the basal planes [9].

Quantification of Parameters

After identification of the parameters, it is necessary to identify quantitative relationships between these measurable physical quantities and the desired variable which defines the quality.

Compressive strength can be determined in many ways. The compressive strength of highly anisotropic fibers may be directly related to their shear modulus. Fibers can also be incorporated into a composite and the point of failure of the composite (presuming fiber failure causes the composite failure) can be used to determine the fiber compressive strength. [4] Finally, recoil compression, or recoil from tension, testing is another frequently used method. [5,6,7]

In the recoil from tension test, bending occurs due to the lateral displacement and the stress front travels from the edge that is suddenly released to the constrained end where it is reflected in the opposite direction as a compressive stress. However, 90% of the fractures are due to bending; hence, direct attribution of failure stress to recoil strength would be erroneous. Also, gauge length dependence is observed: different strength distributions are obtained when the gauge length is changed, since the number density of imperfections (or defects) also changes. Various statistical models are used to account for this variation. Jiang, et al., have suggested two models. [6] The first one uses the average of superior limit (lowest stress level) where fiber always suffers recoil fracture, and the highest value (the inferior limit) of stress at which recoil is sustained without any fracture. It is then necessary to find a stress around which 50% of the fibers suffer recoil fracture. This method is quite extensively used for the HPF's.

The second method they suggest is the universal logistic distribution. This incorporates the effect of various gauge lengths and is physically more meaningful. This method, however, is not applicable exactly to fibers whose tensile strength distributions overlap considerably with their compressive strength distributions.

Another method is to apply the Weibull distribution with correctly chosen shape and size parameters (which have often been defined for various fibers). This approach is fairly common in failure testing. So far, encouraging results have been observed here.

Determining fiber compressive strength via composite testing has too many facets for them all to be considered herein. In Waas, et al.,[10] modeling was performed of a failure mechanism that was first detected by Deteresa, et al., [11] and is related to the fiber kinking. This failure occurs if a preferred glide plane is parallel to the direction of compression. The high level of anisotropy in HM fibers also leads to kink bands which are analogous to the 2-D version in Kevlar®. The yield stress for internal collapse of anisotropic fibers is a simple function of torsional modulus G. They demonstrated that a decay buckling mode furnishes values of critical strain which are lower than those predicted by Rosen model (1965).

In a single fiber unit thickness composite, the effect of interface shear traction occurring at buckling is to introduce small periodic fluctuations in axial thrust acting on the fiber. It also introduces bending moment on the fiber because of its eccentricity with respect to the center line of the fiber. The stress in the matrix associated with the buckled form of the fiber diminishes exponentially as the distance from the centerline increases. [10] Single fiber compressive strength obtained from the elastica loop and tensile recoil tests are compared with the composite compressive strength on pitch- based carbon fibers by Furuyama, et al. [11a]

Recent reports of torsion testing of fibers, and particularly of high performance fibers, are rare. One such report[12] concerns application of a torsion pendulum to PAN-based carbon fibers. That work found that the torsional modulus was lower for higher initial torsional deformation of the pendulum. This decrease was attributed to the development of permanent shear strain in the fibril microkinks in the deformation bands. Other reports on torsion of single fibers were not focused on high performance fibers.

Improvement of Properties

Based on the available information and quantification methods, various methods have been suggested to improve the compressive strength of high performance fibers. The initial thrust of improvements was towards chemical modification of the fiber which shifted towards modification of fiber structure as more information was accumulated about failure mechanisms.[1,2]

It has been reported that compressive strength decreases with increasing modulus and hence with increasing crystal size.[13] Accordingly, if orientation is increased but the lattice size remained the same, then we could get a high modulus fiber without loss of any compressive strength since essentially we are getting the desired basal plane with smaller crystal size. In that work it was also suggested that controlled development of the sheet structure would enhance the desired fiber properties.

Another possibility, suggested by Northolt, et al., was increasing transverse forces such as covalent bonding which would increase shear moduli and improve compressive properties.[14]

Smith[4] working on high performance carbon fibers has shown that changes could be made either in the number of defects or the morphology or both to improve upon the strength of the fibers. He has also concluded that for a low modulus fiber, improved morphology along with original level of defects performs much better than a standard morphology fiber with less defects. This is because there is hardly any difference in the basic grade fibers. However, for a high modulus fiber, the difference is so large that morphology alone can not override the basic grade. Long distance cracking is very much favored in a high modulus fiber which has longer continuous crystallites. This is very likely to occur at free edges. To improve microbuckling behavior, improvement in the moment of inertia was suggested, since it is directly related to the critical stress for buckling. In order to achieve this, one possibility is to have multilobal fibers; another is to have increased diameter round fibers.

It has been shown that Kevlar fails by buckling of fibrils located just beneath the outer surfaces where lateral constraint is minimal.[11] As the fibrils cascade-buckle through the bulk of the fiber, a kink band is formed. Such kink bands were also observed for poly(p-phenylene benzobisoxazole) (PBO) fiber. The difference, however, lies in the fact that in Kevlar® kink bands form beneath the surface and are less evident, while in PBO fibers they are formed on the outer skin and skin itself buckles first. The authors confirmed that this is the mode of failure for the rigid rod polymers by forming a high modulus ceramic coating on individual filaments and then testing them for compressive strength. The fibers with a well adhered coating on the surface demonstrated a marked increase in the compressive strength. This has been explained on the basis of the stiffening of skin due to coating which provided resistance to buckling.

Conclusions

This report presents a cursory review of a portion of the rather extensive literature on carbon fibers, with a little on the other high performance fibers. A continuing review of the literature will be performed in order to ferret out the few works on single fiber torsion tests on high performance fibers.

TORSION TESTING APPARATUS

The compressive strength of highly anisotropic fibers has long proven to be a serious disadvantage in their use for some composite materials applications. It has been proposed by several workers that the compressive strength of highly anisotropic fibers is directly related to the shear modulus. Fiber anisotropy can be defined as the ratio of tensile modulus to the shear modulus and is inversely proportional to the compressive strength. Although experimental results generally support the assertion of such a relationship between compressive strength and shear modulus, they have not been unequivocal. In order to more clearly establish the relationship between shear modulus and compressive strength, the true relationship between shear modulus and fiber microstructure must be determined. As we worked toward achieving this major objective of this project, to determine the relationship between microstructure and shear modulus in high performance fibers, we developed a fully automated torsion test apparatus for testing fibers in torsion.

Mechanical properties of fibers have typically been investigated through a variety of physical testing techniques in which tensile deformation has been employed. A state of shear in a cylinder is most easily accomplished by twisting (torsion). Knowledge of shear properties may be necessary in analysis of typical textile operations such as yarn formation, twisting and texturing, etc. However, the real significance of these properties may be in their relationship to and indication of fiber microstructure.

The torsion balance provides a wide range of both strain rate and amplitude. It operates on the principle that the sum of the forces in two coupled elements must be equal to zero for an equilibrium condition to occur. A diagram of this apparatus is shown in Figure 1. An element of known shear modulus, typically a wire, is connected to a fiber via a rigid shaft. Twisting of the fiber results in displacement of the wire. A sensor or pointer located on the shaft indicates the amount of rotation, and the torque exerted by the fiber on the wire can be calculated. A modification of this design allows rotation of the wire in the direction opposing the fiber generated torque, in order to bring the sensor element back to its original, or null force position, while monitoring the displacement necessary and thereafter calculating the opposing torque. Knowledge of this torque permits a determination of the shear modulus of the fiber.

While there is at least one torsion balance apparatus commercially available, it is limited to a twisting rate of 1 rpm. Therefore, it was necessary to design and build an apparatus to fulfill the needs of this particular project. The apparatus is controlled by a Macintosh Quadra 950 and interfaced to the computer by a nuLogic Co. nuControl® 3-axis Servo Controller board. A program written in National Instruments Inc. LabVIEW2® is used for simultaneous instrument control and data acquisition. Variables include strain rate and duration of deformation. Data is stored in a spreadsheet format for access by graphing and spreadsheet utilities.

The sample is mounted in specially designed grips. The lower grip is free to move vertically, providing a constant tensile load on the fiber, and allowing the fiber to contract slightly upon twisting. The fiber is coupled to a 0.0055 inch diameter stainless steel (type 304) wire by a shaft and a pin vise. Wires of various diameters may be used alter the resistance to fiber torque. The shaft passes through an air bearing, which provides low friction lateral stability. Attached to the shaft is an encoder wheel, which passes through a gap in the corresponding encoder module. As torque is applied to the fiber through the lower grip by the turning action of a motor, the fiber generates torque against the wire and causes it to turn and to displace the codewheel. The program records codewheel motion data throughout displacement of the fiber and the rotation of the motor.

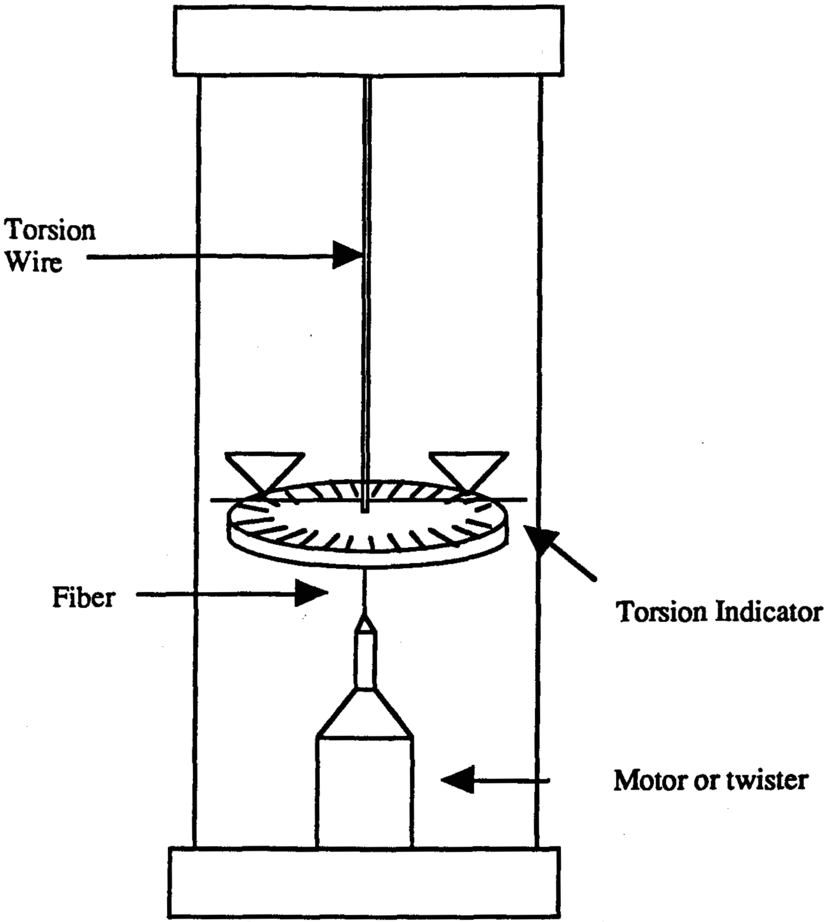

Figure 1. Representation of a Simple Torsion Balance

Results

This apparatus was applied to a series of polypropylene filaments in order to determine the efficacy of this test method. The polypropylene filaments in this study were subjected to different spinning, drawing, and heat treatments; thus, while chemically they are the same material, the filaments as tested have different resultant structures and properties. Only part of those results are reported here.

Multifilament (612/34) polypropylene yarn bundle samples were supplied by Phillips Fibers Corporation. The least drawn sample, pfc1, was produced on a spin-draw line, while the other yarn, pfc4, was produced by a two-step process, spinning followed by drawing on a draw twist apparatus. The twist level was set at the minimum, and there was no noticeable twist in the filament bundle. Yarn data was supplied by Phillips Fiber Corporation (Table I).

TABLE I
LINEAR DENSITY, DRAWDOWN, AND NOMINAL TENSILE PROPERTIES OF POLYPROPYLENE YARNS (PHILLIPS FIBER COMPANY DATA)

Sample Number	Yarn Denier	Draw Ratio	Max. Draw %	Tenacity g/den	Elongation %
pfc1	608.8	3.25	45	3.48	163
pfc4	623.2	4.72	66	4.67	30

~~Heat treatment of the pfc1 and pfc4 filaments was performed in order to modify their~~ microstructure. Filaments were annealed either with fixed length, designated apfc, or with free ends, designated fpfc, in a 130^{o}C oven for 1 hr.

Birefringence values for five fibers in each group are shown in Table II. There was a statistically significant difference ($p < 0.05$) in birefringence between pfc1 (0.0288) and pfc4 (0.0315). Annealing at constant length resulted in a significant increase in birefringence in both apfc1 (0.0314) and apfc4 (0.0326). Free end annealed fibers fpfc1 (0.0300) and fpfc4 (0.0314) did not have significantly different birefringence than the as-received fibers. Both sets of heat

TABLE II.
DIAMETER, TENSILE PROPERTIES, AND SHEAR MODULUS OF AS-RECEIVED AND ANNEALED POLYPROPYLENE FILAMENTS

Sample ID	Diameter (m)	Birefringence	Tensile Modulus (N/m^2)	Tenacity (N/m^2)	Elongation (%)	Shear Modulus (N/m^2)
pfc1[a]	5.40E-05 (0.27E-05)	2.88E-02 (0.01E-02)	1.06E+09 (0.09E+09)	2.75E+08 (0.15E+08)	227.8 (79.62)	2.58E+08 (4.84E+07)
pfc4[a]	5.58E-05 (0.31E-05)	3.15E-02 (0.07E-02)	1.77E+09 (0.17E+09)	3.75E+08 (0.32E+08)	67.85 (50.29)	2.95E+08 (3.83E+07)
apfc1[b]	5.57E-05 (0.29E-5)	3.14E-02 (0.10E-02)	1.13E+09 (0.11E+09)	2.86E+08 (0.14E+08)	160.1 (95.48)	2.09E+08 (3.79E+07)
apfc4[b]	5.59E-05 (0.30E-05)	3.26E-02 (0.11E-02)	1.94E+09 (0.14E+09)	4.14E+08 (0.25E+08)	42.23 (1.74)	2.86E+08 (5.60E+07)
fpfc1[c]	5.51E-05 (0.29E-05)	3.00E-02 (0.06E-04)	1.13E+09 (0.13E+09)	2.82E+08 (0.23E+08)	161.3 (103)	2.03E+08 (4.22E+07)
fpfc4[c]	5.71E-05 (0.22E-05)	3.14E-02 (0.12E-03)	1.58E+09 (0.11E+09)	3.89E+08 (0.21E+08)	47.17 (1.77)	2.58E+08 (3.83E+07)

[a] See Table I. [b] Annealed at 130°C for 1 hr. at fixed length. [c] Annealed at 130°C for 1 hr. with free ends.

treated fibers did show significant differences in birefringence between the pfc1 and pfc4 filaments.

The tensile mechanical properties are in general agreement with our expectations given the nature of the fibers. (Table II) In addition, the shear modulus values also follow what may be expected from general understanding of structure/property relationships in polypropylene. Many conclusions may be drawn from these results as regards the specific structure/property relationships for polypropylene. For the purposes of this report, it is sufficient to note that the torsion instrument is capable of discerning differences in torsional modulus which arise from relatively small changes in structure in a manner consistent with accepted models. The design changes envisioned for the second year of the project will further increase this sensitivity.

Acknowledgments

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