

MOISTURE CONTENT OF ARAMID AND POLYBENZIMIDAZOLE FIBERS *

STEVEN E. KEINATH and ROGER J. MORGAN

Michigan Molecular Institute, 1910 West St. Andrews Road, Midland, MI 48640-2696 (U.S.A.)

(Received in final form 9 January 1990)

ABSTRACT

The moisture loading characteristics of two Kevlar fibers (49 and 149), two aramid copolymer fibers (X-500 and Technora), and two polybenzimidazole fibers (unmodified and sulfonated forms) were studied as a function of relative humidity (11–97% RH) by TG. The limited literature data on moisture absorption in these high-tech fibers infer a linear dependence of absorbed moisture versus %RH. Our results suggest a nonlinear, sigmoidal dependence on %RH. The temperature of maximum rate moisture loss varied from 75–110 °C, implying that polymer physical packing and chemical structure, including impurities, play a significant role in the amount of moisture absorbed and the degree to which it is bound.

INTRODUCTION

Our interest in absorbed water in fibers used in composites was piqued by reports that microcracks were present in Kevlar/epoxy wing structure laminates on Boeing 757 and 767 aircraft after a period of service [1]. Clearly, if part of the nominally 4–5 wt.% moisture absorbed by Kevlar 49 is present as bulk water, repeated freeze/thaw cycling which a commercial aircraft experiences daily could conceivably lead to mechanical failure through fiber fracture via ice formation.

The textile literature is replete with information on the amount, interaction, and effects of moisture in the traditional natural and synthetic fibers [2]. However, the literature is lacking in this regard for the new high-tech fibers like the Kevlars and PBIs which are used as reinforcements in composite applications. We expect the interest in this area to change quickly driven by the need to more clearly understand the fundamental problems involved in thermal cycle induced nonequilibrium stresses and thermal energy dissipation effects.

* Presented at the 18th Annual NATAS Conference, San Diego, CA, U.S.A., 24–27 September 1989.

MATERIALS AND APPARATUS

Moisture absorption studies were carried out on six high-tech fibers of varying chemistry: (1) Kevlar 49 and (2) Kevlar 149, each obtained from Du Pont, are based on poly(*p*-phenylene terephthalamide). (3) X-500, a non-commercial Monsanto fiber, is an aramid copolymer based on polyamide hydrazide chemistry. (4) Technora, commercialized by Teijin in 1987, is an aramid copolymer polymerized from terephthaloyl chloride and a 50:50 molar ratio of *p*-phenylenediamine and 3,4'-diaminodiphenyl ether. Two polybenzimidazole fibers were obtained from Hoechst Celanese, (5) an unmodified (UPBI) and (6) a sulfonated (SPBI) form.

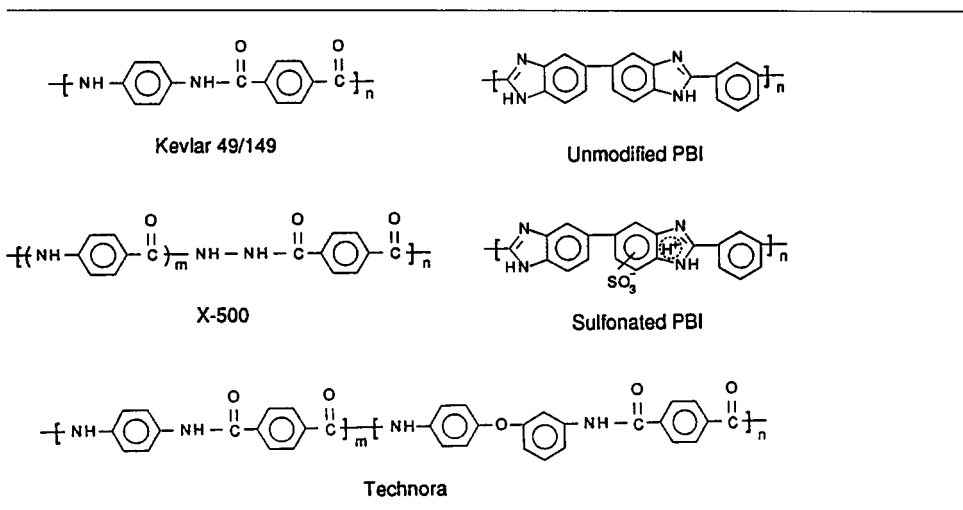
Table 1 depicts the chemical repeat unit for each of the fibers. The fibers were received and studied as multifilament yarns, or tows. The number of filaments per tow varied from a few hundred for X-500 to over 10000 for the PBI fibers [3].

Eight ACS reagent grade inorganic salts were obtained from the Aldrich Chemical Company (Milwaukee, WI) for use in preparing a series of saturated aqueous solutions for controlled humidity conditioning of the fiber samples. These salts, with the corresponding %RH levels given in parentheses [4], included: K_2SO_4 (97), KCl (85), NaCl (75), NaBr (58), $K_2CO_3 \cdot 1.5H_2O$ (43), $MgCl_2 \cdot 6H_2O$ (33), $KC_2H_3O_2$ (23), and LiCl (11).

A Du Pont 951/1090 TG system was used to measure relative weight losses. The normal operating conditions for the TG were a heating rate of $10^\circ C \text{ min}^{-1}$ and nitrogen purge at $100 \text{ cm}^3 \text{ min}^{-1}$. Typical samples weighed about 15–20 mg.

TABLE 1

Chemical repeat unit of fibers



EXPERIMENTAL

Fiber samples were prepared by tying fiber tows into short, tight, single-loop knots and then cutting the tows close to the knots. The knotted samples were convenient to handle and remained tightly bound without appreciable unknotting.

Relative humidity conditioning chambers were assembled in accordance with ASTM standard E104-85 [5] by placing 30 shell vials of capacity 11 ml into 28 oz wide-mouth storage jars of the approximate dimensions: diameter 5 in, height 4 in. Ten of the shell vials contained saturated salt solutions and 20 empty vials were available for holding samples. Each storage jar was capped with a screw-down plastic lid which seated tightly onto a rubber band seal positioned on the shoulder of the jar. All of the shell vials were uncapped, ensuring moisture saturation equilibrium throughout the storage jar.

The eight relative humidity conditioning salts were chosen in order to: (1) cover as wide a humidity range as possible, (2) form saturated aqueous solutions which were relatively insensitive to temperature fluctuations [4], and (3) have minimal toxicity effects. Seven salt solutions were prepared at concentrations of 150% of the quoted solubility levels of the salt [6,7]. The $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ salt required a 200% concentrated solution in order to maintain undissolved salt crystals.

All knotted fiber tow samples were humidity conditioned at room temperature for seven days before TG weight loss measurement. Representative samples of each fiber at each humidity level were also tested after 30 days of humidity conditioning to note any time effects. A minimum of at least two, and often three, TG weight loss measurements were made for each fiber at each %RH level.

Fiber samples were transferred quickly to and from the humidity conditioning jars so as not to disturb the equilibrium moisture conditions within the jars. Prompt transfer of humidified samples from the conditioning jars to the TG unit was found to be critical for obtaining reproducible results because these fibers absorb/desorb moisture very quickly even at room temperature. Thus, a routine procedure of initializing a TG run within 10–15 s after clamping the TG quartz furnace tube to the TG balance assembly was adopted.

RESULTS

All six high-tech fibers portray similar TG behavior, losing moisture over a wide temperature range (25–250 °C), followed by loss of fiber sizing, and then primary thermal decomposition. In nitrogen, Kevlar 49 and 149 both reach a maximum in thermal decomposition rate near 600 °C. The more

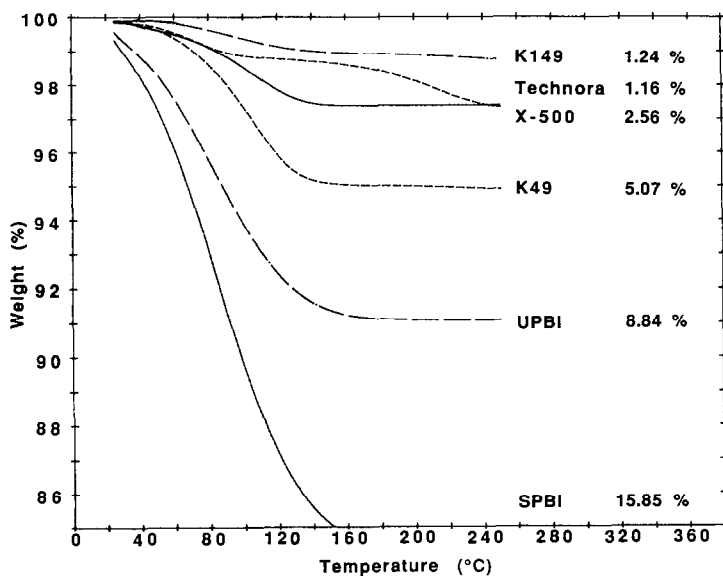


Fig. 1. Nominal rank of high-tech fibers by moisture content.

flexible chain aramid copolymers, X-500 and Technora, thermally decompose some 75–80 °C lower. All four aramids have residual char levels of 36–40 wt.% at 1000 °C. The more thermally stable polybenzimidazole fibers exhibit char levels of about 54 wt.% and 70 wt.% at 1000 °C for the sulfonated and unmodified forms, respectively.

Our primary interest, here, is on the first weight loss process which is attributed to the loss of absorbed moisture. Figure 1 depicts the relative rank among the fibers in terms of their as-received moisture content. The fibers have not received any specific humidity conditioning treatment, here, simply being stored at nominal laboratory humidity levels. It is quite evident that different fiber chemical and physical structure has a significant effect on the amount of moisture absorbed. All six fibers except Technora show a single weight loss process over the temperature range 25–250 °C. The amount of evolved moisture ranged from about 1.2 wt.% for Kevlar 149 to nearly 16 wt.% for SPBI.

The double weight loss process noted for Technora in Fig. 1 is not due entirely to moisture loss. The first weight loss step that finished at about 125–130 °C was found to be sensitive to the level of relative humidity conditioning imparted to the samples. However, the second, higher temperature weight loss process did not vary with relative humidity conditioning levels, being a constant 1.8 wt.% over the entire humidity range. This second stage behavior is consistent with volatilization of an organic fiber sizing agent. The relatively high amount of fiber sizing for Technora is supported by recent scanning electron microscope work by Anders [8] which indicates a substantially clumped and scaly surface on these fibers.

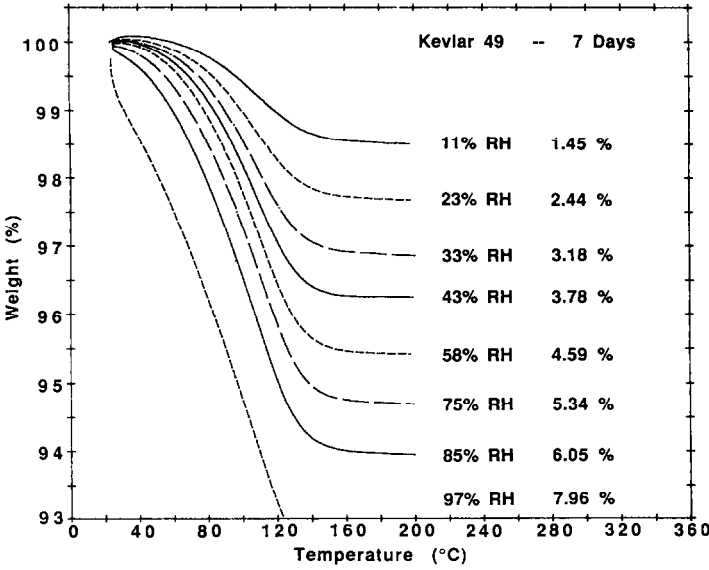


Fig. 2. Family of moisture loss curves for Kevlar 49 after humidity conditioning for seven days at the indicated levels.

Figure 2 shows a typical family of TG weight loss curves, in this case for Kevlar 49, resulting from fiber tow knot samples that have been humidity conditioned for a period of seven days. The amount of absorbed moisture, in terms of wt.%, increases in well-defined increments as the relative humidity level increases. Average amounts of absorbed moisture for Kevlar 49 ranged from 1.5 wt.% for 11% RH conditioned samples to 8.0 wt.% for samples conditioned at 97% RH.

If we plot these data as percent weight loss versus relative humidity we obtain plots of the type shown in Fig. 3. Here, TG weight loss data for both Kevlar 49 and 149 are included as well as some literature data for Kevlar 49

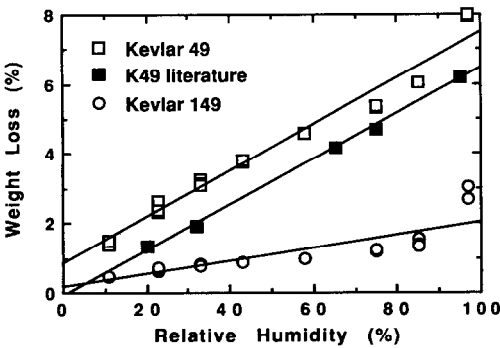


Fig. 3. Moisture loss vs. %RH for Kevlar 49 and 149 and comparison with literature data.

TABLE 2

Average moisture weight loss

Fiber	Relative humidity (%)							
	97	85	75	58	43	33	23	11
K49	7.96	6.05	5.34	4.59	3.78	3.18	2.44	1.45
K149	2.86	1.42	1.19	0.98	0.90	0.81	0.67	0.48
X-500	3.79	3.16	2.84	2.55	2.18	1.88	1.75	1.34
Technora	3.04	2.34	2.05	1.53	1.20	0.97	0.79	0.51
UPBI	15.57	12.50	10.50	8.83	8.08	7.78	7.24	6.50
SPBI	18.88	17.59	16.96	15.75	14.84	13.75	13.04	10.81

[9]. The literature data infer a linear fit extrapolating through zero. As we will discuss later, this is perhaps a too simplistic view of the true situation.

Our moisture loss data for Kevlar 49 are about 1 wt.% high across the board in comparison with the literature data, and when fit with a linear least squares treatment extrapolate to a level of nearly 1 wt.% moisture at a humidity conditioning level of 0% RH! The data for Kevlar 149 appear to be more well-behaved except perhaps for the spurious point at 97% RH. The open symbols in Fig. 3 indicate the degree of reproducibility one obtains over two or three weight loss determinations at each %RH level.

Average wt.% moisture loss values of two to three samples at each %RH level are given in Table 2 for the six high-tech fibers studied. Fig. 4 shows these data as a plot of percent weight loss versus relative humidity.

When applying a linear fit to each data set we see that Kevlar 149 and Technora nearly intercept through 0 wt.%, X-500 and Kevlar 49 have an intercept near 1 wt.%, and the two PBI fibers show significant deviations away from intercepting anywhere near 0 wt.%. UPBI intercepts the y -axis near 5 wt.% while SPBI, the most water absorptive fiber of the lot, has an intercept near 11 wt.%. It is obvious, again, from this figure that a simple

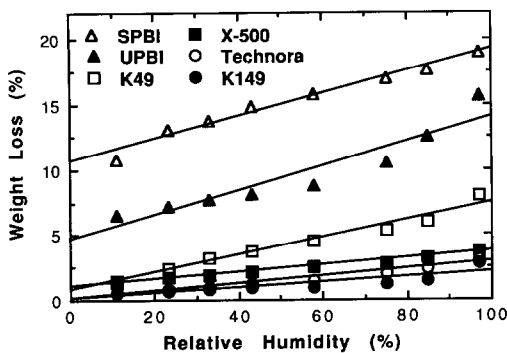


Fig. 4. Moisture loss vs. %RH for all six fibers.

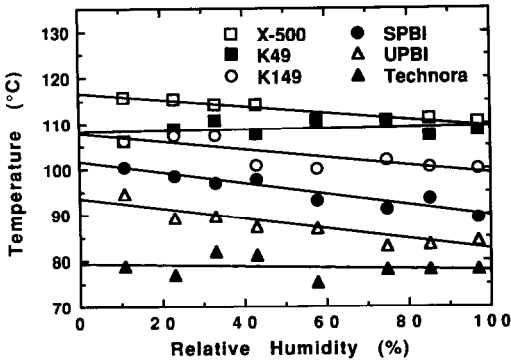


Fig. 5. Maximum rate moisture loss temperature vs. %RH for all six fibers.

linear fit is probably not the best representation of the moisture absorption data for some of the fiber samples, in particular for UPBI.

Average values over two to three runs of derivative TG peak temperatures for each fiber at all eight humidity conditioning levels are plotted in Fig. 5. At a given humidity conditioning level, we note a spread of some 30–35 °C in peak temperature depending on fiber type. Technora loses moisture the earliest, around 75–80 °C, while the X-500 fiber tenaciously holds its moisture until 110–115 °C. Except for Technora, the two PBI fibers exhibit the lowest maximum rate moisture loss temperatures.

Two types of behavior are noted as the relative humidity level varies: (1) no dependence on relative humidity, exhibited by Kevlar 49 and Technora, or (2) a systematic decrease in derivative peak temperature with increasing humidity, the dependence exhibited by the other four fibers. The latter behavior makes more sense, if, as a fiber becomes more highly loaded with water it may be conceivably easier to remove at least a portion of the absorbed moisture at lower temperatures, e.g. in a TG run.

DISCUSSION

When we began our studies of moisture absorption in high-tech fibers in mid 1988, we were struck by the fact that there were few reports in this area. As far as we know, only two reports, both originating from Du Pont [9,10], address the issue of equilibrium moisture uptake as a function of relative humidity in Kevlar 49. A recent report from Japan [11] refers to similar measurements on Technora.

On the basis of the Du Pont data, we anticipated a linear relationship between absorbed moisture and %RH conditioning and have treated our data accordingly even though the data were sometimes poorly fitted by a linear least squares treatment (see Figs. 3 and 4). However, nonlinearity has long been the stance in the traditional textile literature on various natural

and synthetic fibers [2]. Thus, we no longer feel justified in applying linear fits over the entire %RH range, although they may approximate the data reasonably well over a more limited humidity range, say, 20–80% RH. In this regard, we caution the reader to carefully interpret the literature in this area. Overall, the Brunauer–Emmett–Teller equation [12,13], which has been used to explain the nonlinear behaviour of absorbed moisture versus %RH in terms of singly hydrogen bonded, multilayer hydrogen bonded, and bulk forms of water, is probably the best way to treat the data.

Had we plotted our data in terms of moisture “regain” or “% regain” as a textile researcher would have done, we would note somewhat greater “percentages” of moisture at the high end of the relative humidity scale. Although the slopes of linear fits would increase, the y -intercept for the Kevlar 49, X-500, and two PBI fibers still would not pass through zero. One reviewer suggested that these non-zero intercepts may arise from the emission of molecular species other than just absorbed moisture below 250 °C. This is not likely to be true since, for example, Morgan et al. [14] found no evidence for anything but the release of absorbed moisture up to 350 °C when using a TG–MS technique in their studies of Kevlar 49.

The more serious charge we haven’t yet addressed is the fact that we may not be measuring the true moisture absorption capacity of the fibers. Our initial approach was to condition the fibers as-received for seven days at a specified relative humidity level. Preliminary results on humidity conditioned, as-received versus pre-dried, PBI fibers suggest that while it may be possible to saturate them to humidity levels greater than some ambient starting point, it may be more difficult or impossible to pull off water already absorbed in the fibers in an attempt to bring them down to some lower humidity level simply by placing them into relative humidity conditioning chambers. Hydrogen bonding interactions between absorbed water and polar functional groups within the fibers may defeat the driving force to achieve an overall moisture equilibrium. Also, rapid moisture loss from the fiber exterior during pre-drying may result in radial compressive stresses being imposed upon the fiber which may modify subsequent fiber moisture absorption characteristics.

Seven days appears to be ample time for these types of fibers to come to an equilibrium level of moisture saturation at a given %RH level. Routine evaluations of samples humidity conditioned for one month and occasional checks on samples conditioned for longer periods of time exhibit weight loss results identical to those of the seven-day humidified samples. Conditioning times of less than seven days have not been evaluated.

Although we haven’t looked at non-knotted, straight fibers we don’t anticipate spurious moisture effects to be present in our data. Granted, we may be introducing cracks into fibers which are sensitive to compressive stress and form kink-bands; this applies to the aramids in particular. However, the amount of new surface opened up in forming a crack in the

fiber is rather minor in comparison with the equilibrium number of moisture binding sites already present throughout the fiber. Further, even though PBI fibers do not appear to form cracks [8], they exhibit the largest deviations away from extrapolating through zero when applying a linear fit to the data.

There may be several reasons for the wide spread we see in the maximum rate moisture loss temperatures for these six high-tech fibers. First, there are significant differences between the fibers in terms of impurities incorporated during solution-dope spinning. Kevlar 49 is known to have about 1.5 wt.% impurities, with 0.75 wt.% being in the form of Na_2SO_4 clusters deposited periodically in the interfibrillar space, and the remainder being sulfonate substituents attached to the aromatic poly(*p*-phenylene terephthalamide) backbone [15]. We anticipate a similar impurity situation for Kevlar 149. Small amounts of Na_2SO_4 are formed in the Kevlars during the fiber neutralization step following spinning from a H_2SO_4 solvent dope. The copolyaramid [16,17] and PBI [18] fibers, on the other hand, are processed from organic solvents and thus are not expected to have these types of impurities.

It is not unreasonable to anticipate a range of hydrogen bonding behavior and/or water molecule associations to the various potential amide and imide sites. Fiber spinning conditions can lead to different types of physical structure and chain packing, e.g., skin/core morphology and fast diffusion planes arise in fibers spun from liquid crystalline dopes [8,19]. Swelling-induced stresses can lead to changes in physical packing at constant temperature as %RH levels change [19]. Diffusion rates for desorption may vary from one fiber to the next and combinations of two or more effects may be operating. We are not in a position to define which of several effects are more important at this time.

SUMMARY AND CONCLUSIONS

We have begun a series of studies on the amount, interaction, and effects of moisture in several high-tech fibers used in composites. Here, we characterized the relative amounts of moisture associated with two Kevlar, two copolyaramid, and two PBI fibers as a function of humidity conditioning levels. The notion that there is a linear dependence of moisture absorption versus %RH is not upheld, nor does it seem reasonable in view of the textile literature. Our next step will be to characterize the nature of absorbed water in these systems using solid state NMR.

ACKNOWLEDGMENTS

We gratefully acknowledge Dr. George Zahr of Du Pont and Dr. Edward Powers of Hoechst Celanese for providing samples of the two Kevlar and

two PBI fibers, respectively, and for their helpful comments. We also acknowledge Dr. Jack Preston of Monsanto for supplying the sample of X-500 to Dr. David Lewis, now a member of MMI's staff, some years ago, and Dr. Tadahiko Takata of Teijin Ltd. for providing the sample of Technora. We further acknowledge the helpful comments of Dr. Oswald Anders of MMI who is conducting optical and scanning electron microscope studies on these fibers.

REFERENCES

- 1 H.Y. Loken, D.A. Nollen, M.W. Wardle, and G.E. Zahr, *Du Pont Technical Bulletin*, 1987, pp. 1-16.
- 2 W.E. Morton and J.W.S. Hearle, *Physical Properties of Textile Fibers*, The Textile Institute, Heinemann, London, 1975, Chap. 7, pp. 159-177.
- 3 Hoechst Celanese Corporation, Charlotte, NC, *Technical Bulletin SF-7*, 1988.
- 4 L. Greenspan, *J. Res. Natl. Bur. Stand., Sect. A*, 81 (1977) 89.
- 5 *Annual Book of ASTM Standards, Part 41*, American Society for Testing and Materials, Philadelphia, PA, 1985, pp. 637-639.
- 6 R.C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, CRC Press, Cleveland, OH, 58th edn., 1977.
- 7 M. Windholz (Ed.), *The Merck Index*, Merck & Co., Inc., Rahway, NJ, 9th edn., 1976.
- 8 O.U. Anders, Michigan Molecular Institute, Midland, MI, unpublished observations.
- 9 J.J. Pigliacampi, in *Composites, Engineered Materials Handbook*, Vol. 1, ASM International, Metals Park, OH, 1987, pp. 54-57.
- 10 W.S. Smith, in *Kevlar Composites*, T/C Publications, El Segundo, CA, 1980, pp. 94-117.
- 11 M. Fukuda, M. Miyagawa, H. Kawai, N. Yagi, O. Kimura and T. Ohta, *Polym. J.*, 19 (1987) 785.
- 12 W.E. Morton and J.W.S. Hearle, *Physical Properties of Textile Fibers*, The Textile Institute, Heinemann, London, 1975, Chap. 12, pp. 229-264.
- 13 S. Brunauer, P.H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 60 (1938) 309.
- 14 R.J. Morgan, F.-M. Kong and J.K. Lepper, *J. Compos. Mater.*, 22 (1988) 1026.
- 15 R.J. Morgan and C.O. Pruneda, *Polymer*, 28 (1987) 340.
- 16 J. Preston, in A. Ciferri and I.M. Ward (Eds.), *Ultra-High Modulus Polymers*, Applied Science Publishers, London, 1979, Chap. 5, pp. 155-171.
- 17 K. Matsuda, *ACS Polym. Prepr.*, 20(1) (1979) 122.
- 18 E.J. Powers and G.A. Serad, in R.B. Seymour and G.S. Kirshenbaum (Eds.), *High Performance Polymers: Their Origin and Development*, Elsevier, New York, 1986, pp. 355-373.
- 19 R.J. Morgan and R.E. Allred, in S.M. Lee (Ed.), *Encyclopedia of Composites*, Vol. 2, VCH Publishers, New York, 1990, in press.