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S0032-3861(96)00527-7

Polymer Vol. 37 No. 22, pp. 5005–5009, 1996

0032-3861/96/$15.00 + 0.00

Orientation changes in Kevlar® 49 under axial compression

E. P. Socci*, D. A. Thomas and R. K. Eby†
Department and Institute of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA

and D. T. Grubb
Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14852, USA

and W. W. Adams
Materials Directorate, Wright Laboratory, Wright-Patterson Air Force Base, OH 45433-7702, USA
(Received 19 October 1995; revised 29 April 1996)

The orientation of crystals in a single Kevlar® 49 fibre has been measured by X-ray diffraction using a microcompressive device and the Cornell High Energy Synchrotron Source (CHESS). The data show that the orientation with respect to the fibre axis decreases with increasing axial compressive strain. The birefringence has been measured on the same sample with a polarizing optical microscope and a tilting compensator. The results show that the birefringence decreases with increasing axial compressive strain. This also is consistent with a decreasing crystal orientation with increasing strain. Both effects are slightly nonlinear and a graph of the full width at half maximum of the crystal orientation *versus* birefringence is nearly linear. The decreasing crystal orientation in compression is opposite to the increasing orientation with increasing tensile strain. The tensile effect increases the fibre modulus. The compressive effect, on the other hand, should decrease the modulus. The former has a limiting effect, but the latter could have the opposite and might contribute to compressive failure. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(paraphenylene terephthalamide); fibre; compression)

INTRODUCTION

The specific tensile strength of high performance polymer fibres makes them especially suited for use in fibre reinforced composites for which weight saving is critical[1,2]. The family of aramid fibres based on poly(paraphenylene terepthalamide), such as Kevlar®, is an example of materials with high specific tensile properties[3]. However, Kevlar® and many other high modulus fibres as well as their associated composites have been shown to exhibit relatively poor compressive properties[2,4]. The compressive strength is only 10–20% of the tensile strength. This severely limits their use in applications for which compressive loading is required. To further the understanding of the dichotomous relationship between tensile and compressive behaviour, researchers have studied the mechanical properties and the underlying structural changes that take place in fibres and fibre reinforced composites subjected to compressive loading[5–13]. However, practical limitations in applying a purely *axial* compressive load to a single fibre have made this research difficult. Some of the methods used to approximate such a load include the bending beam, elastica loop, tensile recoil and the embedded fibre in matrix methods. Recently, a novel microcompressive device for applying an *axial* compressive load to a single fibre was developed[14]. It uses a piezoelectric crystal to apply small compressive displacements. The fibre is compressed axially, although an absolute determination of the strain is difficult to ascertain due to the compliance of the epoxy 'clamps'[14,15].

In this note, we report the results of wide angle X-ray diffraction and birefringence measurements on a single Kevlar® 49 fibre in axial compression. Effects of compressive loading on crystal orientation and birefringence are examined. The implications of the orientation changes for compressive strength and modulus are discussed.

EXPERIMENTAL

Sample preparation

Kevlar® fibres were supplied by the E. I. duPont de Nemours and Company, Inc. They had diameters which varied a little with an average of approximately 15 μm. A short (~1 cm) sample was placed onto the microcompressive device in a configuration that allows the fibre to be compressed axially across a 50–60 μm gap. The sample was fixed in place by Duro® brand extra strength epoxy globules placed over both ends. To avoid Euler

* Present address: AlliedSignal, Morristown, NJ 07962-1021, USA
† To whom correspondence should be addressed

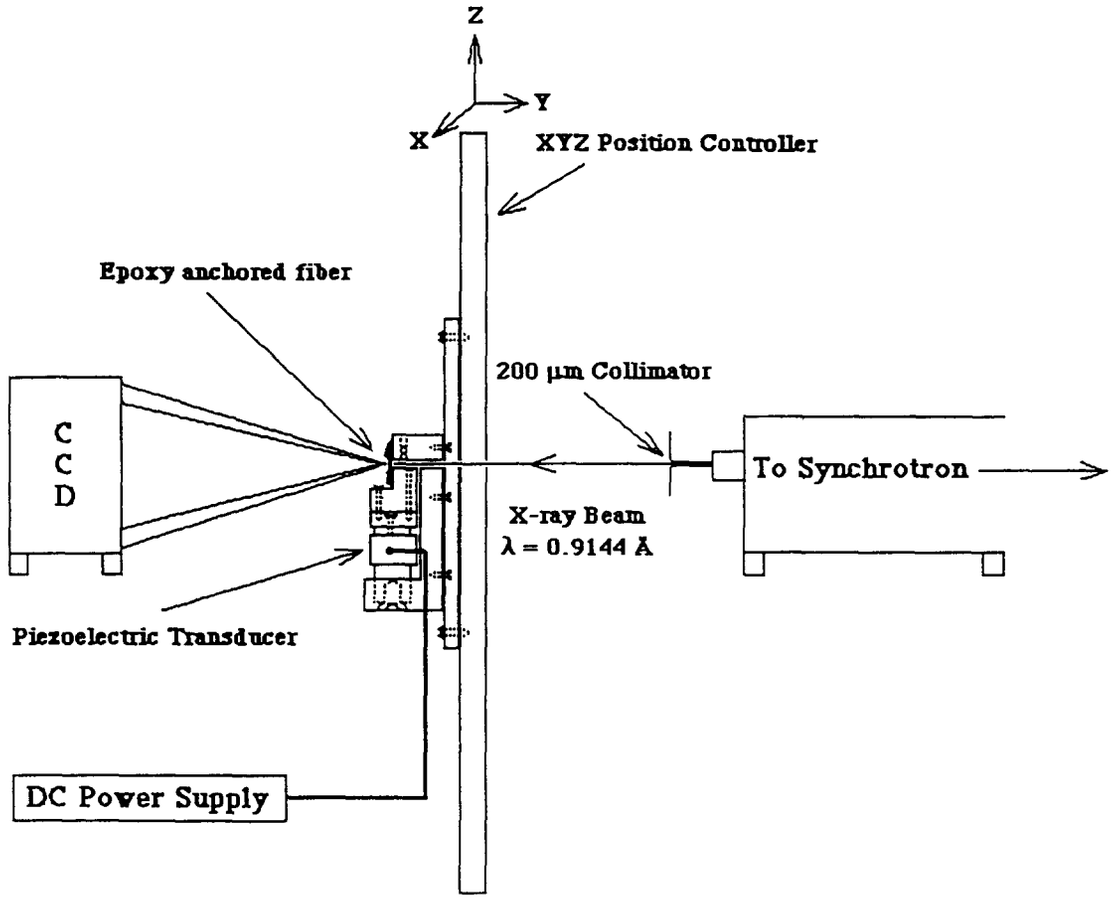

Figure 1 Schematic of X-ray diffraction experimental setup

buckling, the gauge length was kept small (~38 μm). The gauge length was defined as the length of the fibre between the two epoxy covered ends (i.e. the length available to be freely compressed). The piezoelectric crystal was connected to a Keithley Instruments high voltage DC power supply. As the voltage was increased, the crystal expanded placing the fibre in compression.

Wide angle X-ray diffraction

The X-ray diffraction experiments were conducted at CHESS. Data collection was performed on the A1 beam line which uses a 24 pole 1.2 T wiggler magnet to increase the incident X-ray flux and a double-focusing Si (111) monochromator. The total flux into the beam line was approximately 2×10^{13} photons s^{-1}. The energy of the photons was 13.6 keV which corresponds to a wavelength of 0.9144 Å. The sample to detector distance was 90 mm and 200 μm pinhole collimation was used. The microcompressive device was mounted on an XYZ position controller so that it could be adjusted in the X-ray beam. The fibre axis was vertical in the experiments. A schematic of the experimental setup is given in *Figure 1*.

During the X-ray measurements, the input voltage to the piezoelectric crystal was increased from 0 to −960 V in −100 V increments (the last was a −60 V increment). The fibre was exposed to X-rays for 120 s at each voltage. Thereafter, the voltage was raised quickly to the next value. It was maintained at −960 V for 20 min subsequent to the last exposure. The experiment was then reversed. During the reversal, the piezoelectric crystal returned to its original dimensions.

Diffraction patterns were recorded electronically on a two dimensional CCD detector and downloaded to a DEC mini Alpha workstation where they were corrected for detector geometry. They were subsequently analysed on an IBM RS/6000 workstation and a personal computer where an air/epoxy background correction was made. Data analysis was completed with the program GenPlot. The full width at half maximum (FWHM) in chi of the (110) and the (200) equatorial reflections were measured by fitting each peak with a modified Lorentzian function.

Birefringence

Birefringence measurements were made on the same fibre (i.e. it remained attached to the microcompressive device throughout the study) with an Olympus BH-2 polarizing optical microscope and a Leitz tilting compensator. The compensator was used to determine the optical path difference (OPD) of light which had passed through a polarizer, the fibre (oriented at 45°C to the polarizer/analyser) and an analyser. From the OPD, the birefringence, Δn, of the fibre was determined using:

$$\mathrm{OPD} = \Delta n \cdot t$$

Where t is the diameter determined with the microscope. During the experiment, the voltage applied to the transducer was increased in −50 V increments from 0 to −960 V (the last increment was −60 V). The OPD was evaluated five times over a period of 300 s at each voltage. Thereafter, the voltage was raised quickly to the next value.

RESULTS

A plot of the FWHM vs applied voltage is shown in *Figure 2*. The values are an average of the FWHM of the (110) and the (200) equatorial reflections (which agreed within the standard deviation of 0.1 deg). As the fibre was compressed, the FWHM increased indicating a decrease in crystal orientation along the axis with increasing strain. The decrease appears to be reversible. As the voltage applied to the crystal was returned to zero, the FWHM returned approximately to the starting value. Some hysteresis was observed as the orientation initially increased more rapidly during the return.

The birefringence of the fibre is shown as a function of applied voltage in *Figure 3*. The measured value in the uncompressed state (0.651) is comparable to previously determined values of approximately 0.65[16–18] and, when corrected for dispersion[18] (0.41), to other corrected results[18] and results obtained by interference microscopy[19]. The birefringence decreased as the fibre was compressed*[15,17,18]. This is indicative of structural changes that cause the fibre to become less optically anisotropic.

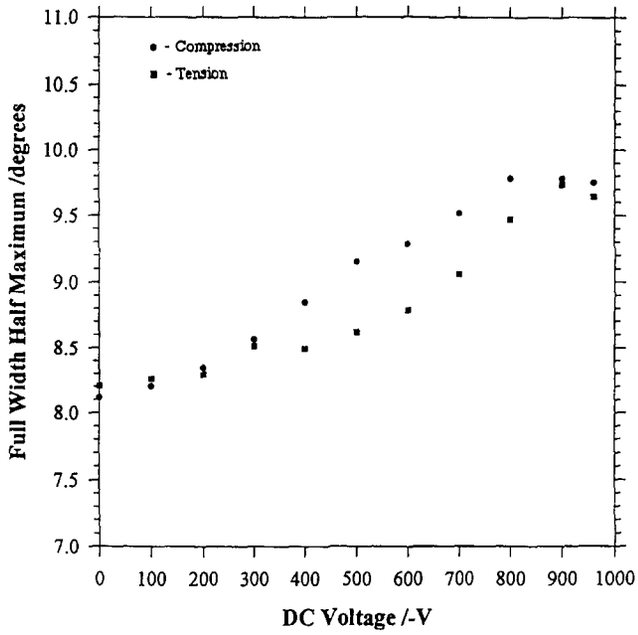

Figure 2 Average full width at half maximum of the (110) and (200) equatorial reflections as a function of applied voltage. The circles represent data for increasing voltage (compression) and the squares represent decreasing voltage. The standard deviation is 0.1 deg

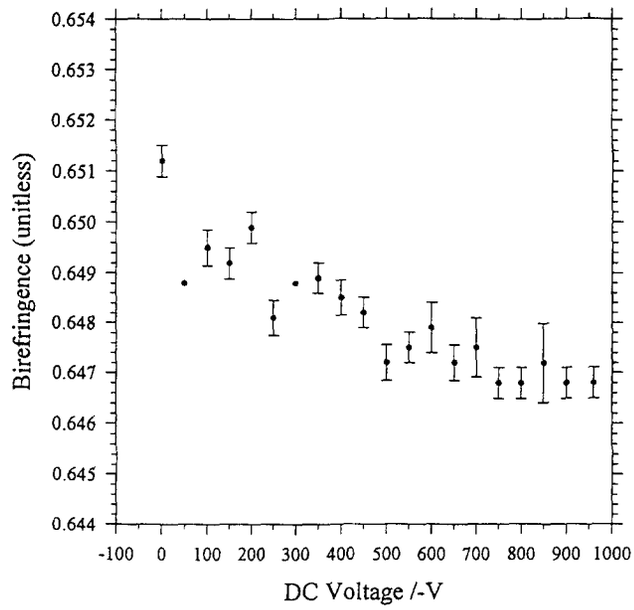

Figure 3 Birefringence as a function of applied voltage. Error bars represent the standard error propagated through the calculations

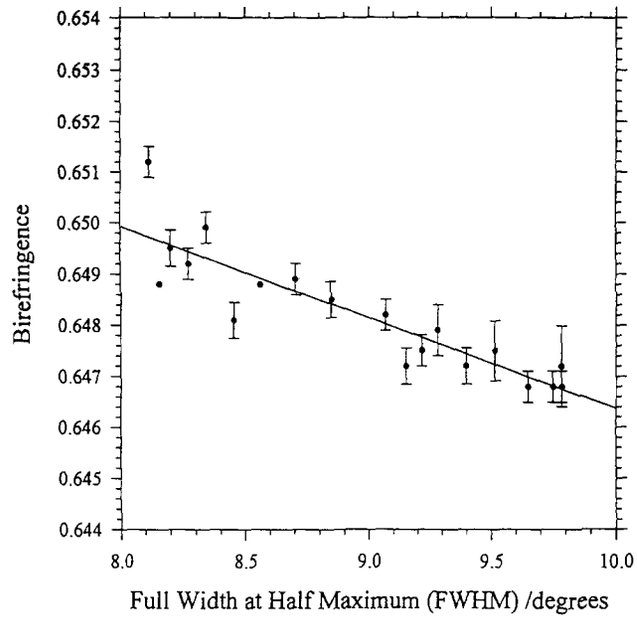

Figure 4 Birefringence as a function of an average of the full width at half maximum of the (110) and (200) equatorial reflections for increasing strain. Error bars for birefringence represent the standard error propagated through the calculations. The standard deviation for the full width at half maximum is 0.1 deg

Figure 4 illustrates the birefringence plotted vs the FWHM for increasing strain. Values for the FWHM were linearly interpolated between the immediately adjacent values at voltages for which birefringence data, but no FWHM data, were available. The slightly nonlinear nature of each separate curve results in a nearly linear relationship between the two quantities (a second order polynomial fit of the data results in an insignificant improvement) (Steiner, R. P., personal communication).

DISCUSSION

The morphology of Kevlar® fibres can be approximated as a series model comprising a linear arrangement of crystallites[20]. They have a narrow orientation distribution about the fibre axis, and are considered to be linked end-to-end. When a tensile load is applied, the orientation relative to the axis increases. As the orientation of the crystallites increases, the modulus of the fibre increases. Complete alignment would lead to a modulus approximating the maximum value (ultimate modulus) for this highly crystalline polymer. Similar effects are observed in fibres of carbon and poly(*p*-phenylene benzobisthiazole)[21–23]. While most of the increase of modulus is associated with the increasing orientation of the crystals[22–25], there is an inherent increase associated with stiffening of the molecules themselves[26].

*A decrease in birefringence with increasing compressive strain has been reported previously[17]

A number of experiments have examined the behaviour of Kevlar® fibres in compression[3,5–8]. The fibres were subjected to compressive loads by an elastica loop test, reciprocating a length of fibre over a pulley, or the matrix shrinkage technique. In each case, the morphology of the deformed fibres was examined by optical microscopy and/or scanning and transmission electron microscopy. The results have been interpreted to indicate that the poor compressional strength is due to the weak lateral interaction between molecules. In this model, the stability of the fibre in compression is controlled primarily by non-bonded interactions such as hydrogen bonding and van der Waals forces.

The data presented in *Figure 2* indicate a decrease in crystal orientation with increasing compressive strain. This would reduce the fibre modulus in a manner opposite to that by which increasing orientation with increasing tensile strain increases the modulus[22–25]. The latter has a limiting effect, but the former could have the opposite and might contribute to compressive failure. Interestingly, when the compressive load is removed the original crystal orientation is returned, indicating that the compressive deformation was removed. Indeed, scanning electron microscopy observation of another Kevlar® 49 fibre in the microcompressive device indicate that kink bands observed during compressive loading nearly disappeared when the voltage was returned to zero (*Figure 5 a,b*). This recoverable deformation is consistent with other findings that showed kink bands formed in compression can 'heal' after application of a tensile load[7]. The tensile load effectively straightens out the regions that were deformed. (In the present case, tension would be applied to any permanent deformations of the fibre as the piezoelectric crystal elastically contracts with decreasing voltage.) As observed in the SEM during a second compression (*Figure 5c*), kink bands were observed in the same location as on the first compression. This might be the result of either some damage during the first compression or the presence of a flaw at that location triggering the failure. Additional X-ray diffraction experiments are planned in which a fibre will be subjected to a second compressive loading cycle.

The FWHM data in *Figure 2* level off at high applied voltages (high compressive strains). This is probably due to the onset of the formation of kinks. Indeed, optical microscopy of fibres with different gauge lengths in the microcompressive device indicate that the onset of

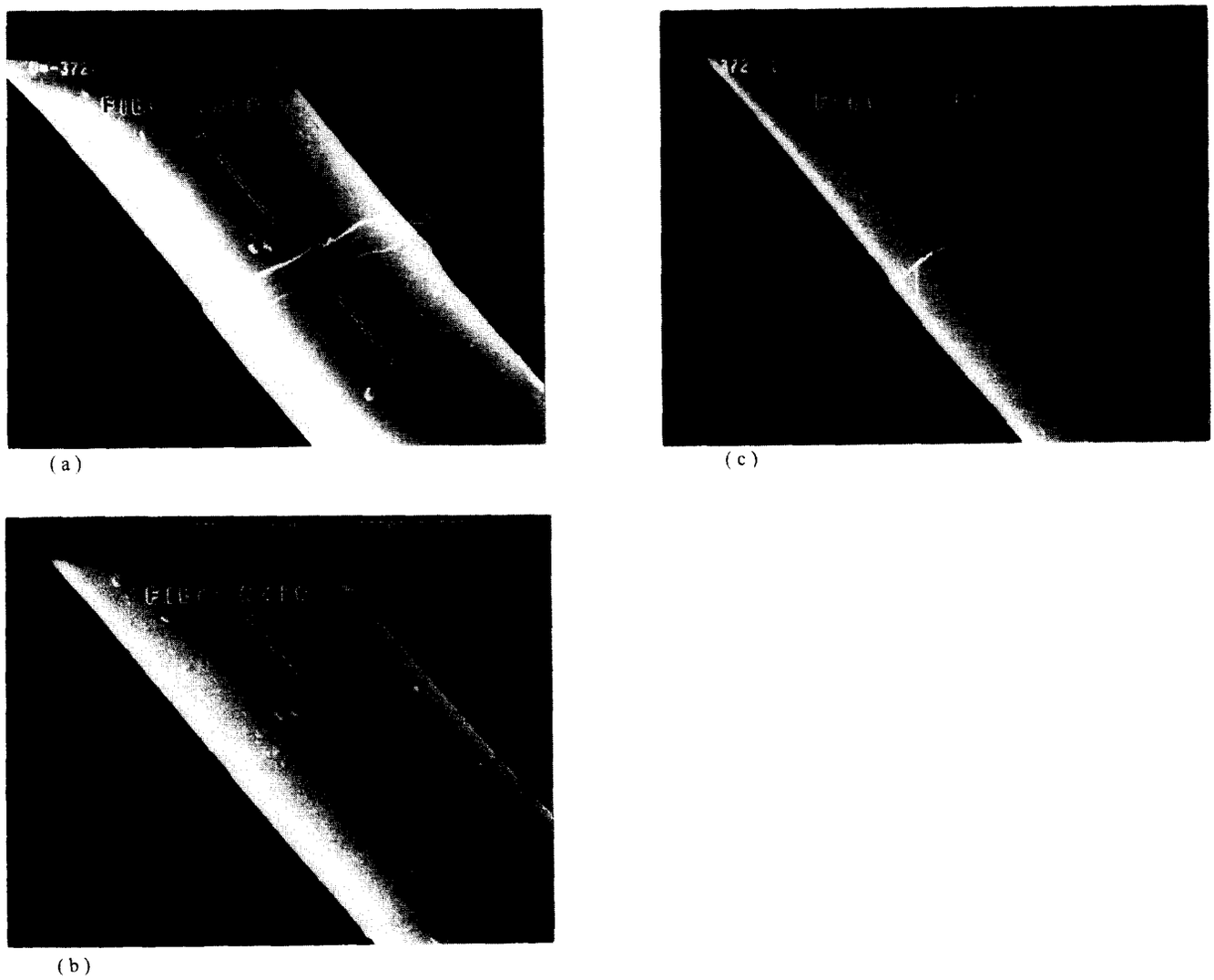

Figure 5 (a) SEM micrograph of Kevlar® 49 fibre under first compressive loading (the arrow indicates kink bands). (b) The same fibre under a tensile load (the arrow indicates the region where kink bands were previously observed). (c) The same fibre under a second compressive loading (the arrow points to a reproducible kink banded region)

kinking occurs at 650 ± 75 V for the present gauge length. (The compressive strain typically quoted for the onset in other types of measurement is 0.5–1%[3,5,6]). This would limit the increase of compressive strain in the area exposed to the incident beam and away from the kinks.

The data in *Figure 3* show a decrease in birefringence with increasing compressive strain indicating that the fibre became less optically anisotropic. The decrease in birefringence appears to level off at large applied voltages. This is consistent with a similar levelling off of the FWHM data at high voltages and, as noted above, with the onset of kink formation. Birefringence is affected by the summation of the contributions from three structural or morphological features in a material. These effects are commonly referred to as: distortion birefringence, orientation birefringence and form birefringence. Distortion birefringence is brought about by conformational changes such as bond stretching, bond angle bending, torsion angle rotation and side group reorientation. (Thus, it is akin to the changing inherent molecular contribution to modulus with changing strain[26].) It can be significant even in extended chain molecules[18,27]. Orientation birefringence is due to changes in the alignment of crystals or other large molecular assemblies under an applied load. Form birefringence arises from the presence of two or more separate phases which exhibit different refractive indices[15]. Due to the high crystallinity of Kevlar® 49, the contribution of form birefringence is expected to be small.

The structural origin of the decrease in birefringence with increasing compressive strain cannot be ascertained solely from the data in *Figure 3*. however, the correlation between the X-ray diffraction data and the birefringence data (*Figure 4*) shows the birefringence to be linearly related to the FWHM. This is consistent with the decrease in crystal orientation leading to a decrease in the overall birefringence of the fibre. However, distortion birefringence also should make a contribution[18,27].

CONCLUSION

The change in crystal orientation with compressive strain was obtained by wide angle X-ray diffraction measurements for a single Kevlar® 49 fibre. The FWHM of the (110) and (200) equatorial reflections increased with compressive strain indicating that the crystal orientation decreases with increasing compressive strain. This is opposite to the behaviour observed in tension, for which the crystal orientation increases with increasing tensile strain. The birefringence of the same fibre decreases with increasing compressive strain indicating that the fibre becomes less optically anisotropic when compressed. A linear relationship exists between the birefringence and the FWHM, indicating that the decrease in crystal orientation (increasing FWHM) contributes to the decrease in birefringence. The increasing orientation increases the modulus in tension and the decreasing orientation in compression would decrease the modulus. The former has a limiting effect but the latter could have the opposite and might contribute to compressive failure.

ACKNOWLEDGEMENTS

This work was supported by the NSF/EPIC Center for Molecular and Microstructure of Composites. Part of the work was done by R. K. Eby while at the Max Planck Institute für Polymerforschung, Mainz, Germany, on an Alexander von Humboldt Senior Prize.

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