

Dynamic Mechanical Analysis of Fibers.

I. Effect of Experimental Variables and Material Type

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Synopsis

Depending upon the fiber material, some of the experimental variables can have a profound effect on the dynamic tensile modulus vs. temperature data. With the use of an experimental fiber ($25^{\circ}\text{C} < T_g < 75^{\circ}\text{C}$; $T_m > 220^{\circ}\text{C}$; hot stretched), the effect of several variables, e.g., moisture/volatiles, annealing/relaxation, frequency (strain rate), pretension, and % strain on the modulus retention term $[(E_{100^{\circ}\text{C}}/E_{25^{\circ}\text{C}}) \times 100]$ have been studied. Of these variables, pretension and especially % strain dramatically increase the modulus retention and this effect is attributed to the elastic orientation under force (EOF), i.e., it exists only in the presence of tensile forces and is reversible. Such an effect was insignificant for Kevlar ($T_g \sim 375^{\circ}\text{C}$) and absent for steel wire. Dynamic modulus measurements at 25°C using sonic techniques also support the EOF phenomenon in polyethylene yarns ($T_g \sim -30^{\circ}\text{C}$) but not in Kevlar polyamide yarns ($T_g \sim 375^{\circ}\text{C}$).

INTRODUCTION

Dynamic mechanical properties of fibers have been studied over the last few decades.¹⁻³ Some of the common instruments for such analysis on fibers are Rheovibron viscoelastometer (Toyo Measuring Instruments, Japan), dynamic mechanical thermal analyzer (DMTA) (Polymer Laboratories, U.K.), and Rheometrics dynamic mechanical spectrometer (Rheometrics U.S.). All these instruments analyze fibers in the tension-compression mode of deformation. Recently we have observed that, depending upon the fiber type, experimental factors could significantly affect the dynamic mechanical properties. This would imply that the results might vary from laboratory to laboratory depending upon the selection of instrument and the operating conditions. The present manuscript is intended to illustrate this subject.

EXPERIMENTAL

Materials. Most of the work presented here was done on an experimental multifilament yarn which had been hot-stretched and the T_g and T_m values were $25\text{--}100^{\circ}\text{C}$ and $> 220^{\circ}\text{C}$, respectively. Steel wire and Kevlar yarns used were commercially available. A limited amount of work was carried out on an experimental polyethylene yarn.

Instruments. Most of the work was done on the Polymer Laboratories DMTA unit. For frequency sweep, the Rheometrics RDS-7700 II model was used. Due to the use of multiple instruments and changing experimental

variables, the experimental conditions have been described along with the tabulated data.

RESULTS

For variable temperature applications of fibers, it is important and a common practice to know what the modulus retention is at the use temperature, e.g., 100, 200, or 300°C. In the case of our experimental fiber, we have chosen to study the retention of dynamic tensile modulus (E) at 100°C relative to the value at 25°C; the modulus retention term is being defined as $[(E_{100^\circ\text{C}}/E_{25^\circ\text{C}}) \times 100]$.

Before going into the results, we wish to comment on the nature of the modulus retention term. Figure 1 is an idealized modulus vs. temperature curve for an amorphous polymer which undergoes a 3-order-of-magnitude change in modulus across its T_g . Note that the % modulus retention drops off very fast in the initial stages. Thus, any minor change in modulus in this region (e.g., due to temperature calibration, sample differences, experimental factors, etc.) would dramatically affect the modulus retention term. Assuming that the same material is analyzed in various laboratories and temperature calibration is good, large variations in the data can be expected from laboratory to laboratory due to small differences in experimental conditions employed. Also it should be noted that most of the common synthetic fibers are highly crystalline (e.g., 50–90%) such that the change in absolute modulus prior to melting is relatively small, i.e., corresponding to the initial stages of the curve in Figure 1. Thus, although the experimental variables might cause a small variation in modulus, this effect will appear more pronounced in the modulus retention term, e.g., $[(E_{100^\circ\text{C}}/E_{25^\circ\text{C}}) \times 100]$. Note that the modulus retention term will have a strong dependence on how close the chosen high temperature is to the T_g .

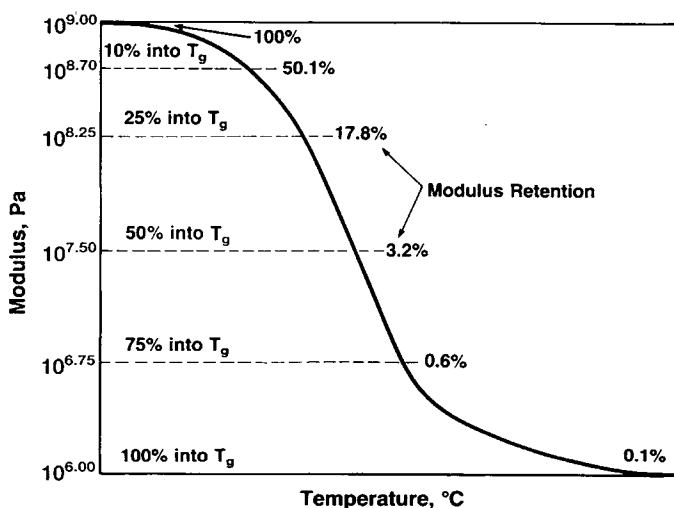


Fig. 1. An idealized modulus vs. temperature curve for an amorphous polymer.

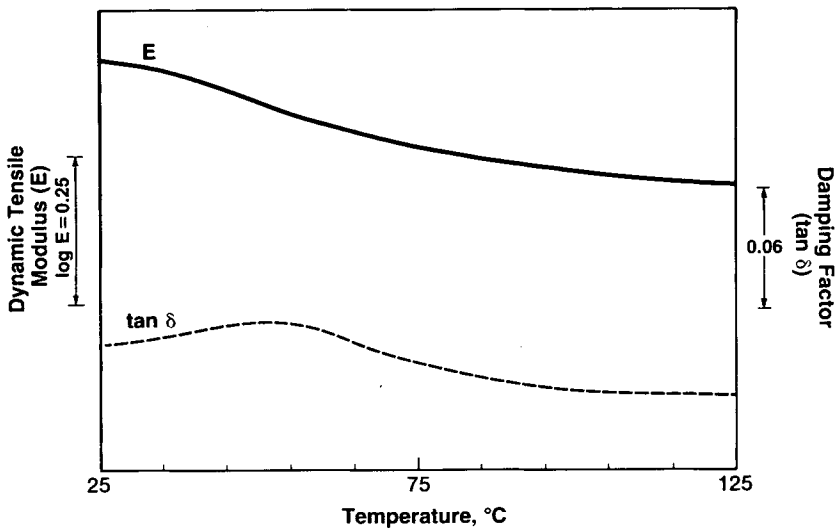


Fig. 2. A typical dynamic tensile modulus E vs. temperature curve of the experimental fiber.

Experimental Fiber vs. Kevlar or Steel

Effect of Moisture / Volatiles. Thermogravimetric analysis suggested that the moisture/volatile content of the experimental fiber was about 1%. Figure 2 shows a typical dynamic tensile modulus (E) vs. temperature curve of the fiber, modulus retention at 100°C being 61%. When the same sample is reheated, i.e., after the loss of 1% moisture/volatiles, the modulus retention increases slightly to 66% (note that during the initial or reheat scans, the monofilament sample was under a pretension of 0.2 N).

Effect of Unconstrained Annealing. During an annealing at 100°C/30 min in the unconstrained mode (i.e., fiber-free to shrink), the experimental fiber had undergone a shrinkage of 0.2% as shown by thermomechanical analysis and subsequent analysis indicated an increase in modulus retention from 61 to 65%. As discussed above, this increase is mostly due to the loss of moisture/volatiles during annealing. However, annealing at 150°C/30 min produced a shrinkage of 0.9% and this annealing accompanied an increase in the modulus retention from 61 to 69%. This increase in modulus retention after 150°C/30 min treatment is partly due to the loss of moisture/volatiles and partly to the formation of microcrystallites or crystalline nuclei.^{4,5}

Effect of Frequency (Strain Rate). The modulus vs. temperature curve is shifted towards higher temperatures as the frequency increases in accordance with the kinetic considerations. Thus, at a constant temperature the higher the frequency the higher the modulus. The idealized curves of modulus M vs. frequency f and/or temperature are shown in Figure 3.

Regardless of the frequency, the net change in modulus over a certain temperature range should be essentially constant provided the absence or completion of a transition, if any over this temperature range. For the experimental fiber, the modulus retention varies between 59 and 66% over a frequency range of 0.01–50 Hz but without any trend (Fig. 4). Thus, although

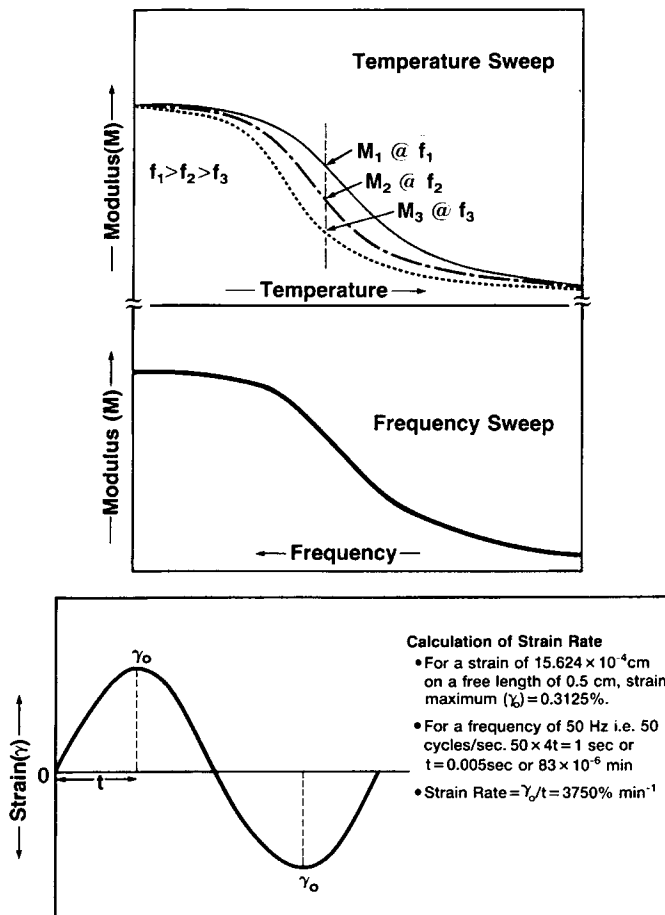


Fig. 3. (a) Idealized modulus M vs. temperature and/or frequency f curves, and (b) calculation of strain rate in a dynamic mechanical experiment.

the modulus increases with increasing frequency at a constant temperature, the modulus retention between 25 and 100°C remains essentially unaffected. Note that by changing the free length and frequency, we have been able to cover a strain rate range of 0.1–3750% min^{-1} ; a sample calculation is shown in Figure 3. (Caution: In transient tests a continuous strain rate of, e.g., 100% min^{-1} is applied whereas, in dynamic experiments, the average strain rate changes from +100, to -100, to +100, and then to -100% min^{-1} during the deformation cycle. Thus, the strain rates in those two tests are not directly comparable.)

Effect of Pretension. Dynamic mechanical analyzers require a certain pretension since small sinusoidal deformations, e.g., < 1%, cannot be applied on slackened samples. Polymer Laboratories Inc. recommends, for their DMTA unit, a certain force, i.e., pretension, needed to produce the strain to be imposed. The recommended force for our experimental fiber was 0.2 N per monofilament and this resulted in a modulus retention of about 61% (Table I). As shown in Figure 5, pretension certainly increases the modulus at 25°C as

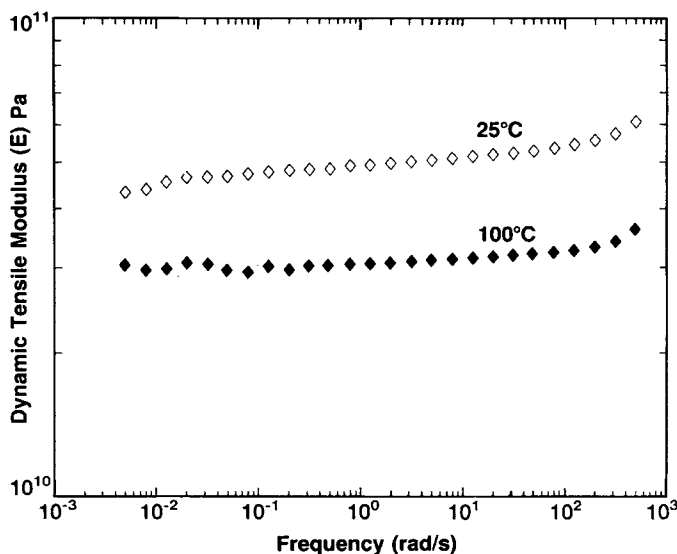


Fig. 4. Dynamic tensile modulus vs. frequency sweep for the experimental fiber at 25 and 100°C.

well as at 100°C. Whereas the measurement of high pretension effect at 100°C could not be made, the modulus retention at 100°C would be expected to be higher (Table I). In fact, the modulus retention at 50°C, i.e., $[(E_{50^\circ\text{C}}/E_{25^\circ\text{C}}) \times 100]$ increased from about 75 to 88% as the pretension increased from 0.002 to 1 N.

TABLE I
Effect of Pretension on the Modulus Retention of Experimental Fiber^a

Pretension/fil. (N)	Modulus at 25°C ($E_{25^\circ\text{C}}$) (10^{10} Pa)	Modulus at 100°C ($E_{100^\circ\text{C}}$) (10^{10} Pa)	$E_{100^\circ\text{C}}/E_{25^\circ\text{C}} \times 100$
1.0	10.76	(Samples broke)	?
	11.54		
0.5	8.81	(Samples broke)	?
	9.16		
	7.44		
0.2	7.57	4.53	61
	7.30	4.95	65
	8.14	4.18	57
	7.93	5.16	63
0.02	6.79	4.86	61
	6.48	3.42	50
0.002	6.80	3.35	52
	7.87	3.29	48
		4.11	52

^aPolymer Laboratories DMTA unit, argon atmosphere, 3°C/min heating rate, a specified pretension applied to the monofilament used, 0.3% strain, 1 Hz frequency, and a tensile deformation mode.

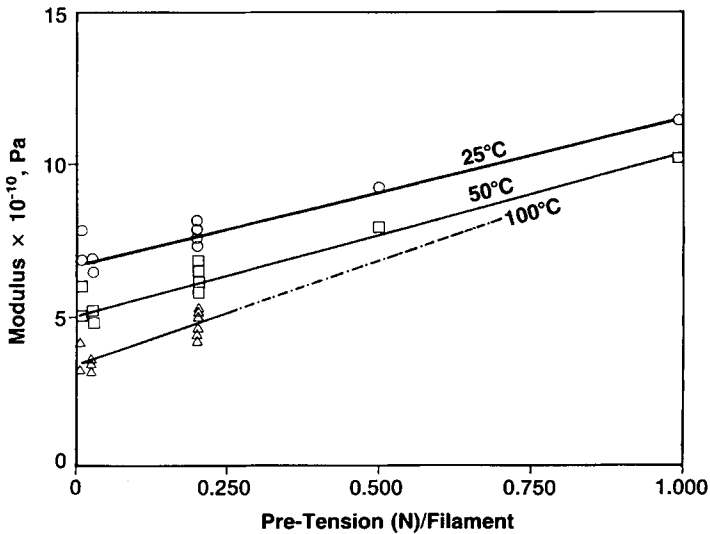


Fig. 5. Effect of pretension on the dynamic tensile modulus of the experimental fiber at 25, 50, and 100°C.

Effect of Strain. Under a constant pretension of 0.2 N per monofilament, an increase in strain from 0.3 to 5% increases the modulus retention at 100°C to the unexpectedly high 90–95% level. It is important to note that the strain related changes in modulus retention are reversible (Table II). Although strains above 0.3% increase the modulus retention, lower strains, i.e., 0.05–0.3%, do not make a difference.

Effect of Pretension and Strain on Kevlar Fiber. Unlike the experimental fiber ($25^{\circ}\text{C} < T_g < 75^{\circ}\text{C}$), Kevlar fiber ($T_g \sim 375^{\circ}\text{C}$) and steel wire are not affected by the pretension and strain applied in dynamic mechanical analysis. At the most, there is a slight increase in the modulus retention of Kevlar fiber with an increase in pretension (Table III).

TABLE II
Effect of Strain on the Modulus Retention of Experimental Fiber and Its Reversibility

Expt. no.	$E_{100^{\circ}\text{C}}/E_{25^{\circ}\text{C}} \times 100$		
	Strain = 0.3125%	Strain = 1.25%	Strain 5.0%
1	59 (Initial heat) 61 (Initial heat at 0.3%)	72 (Initial heat)	90 (Initial heat)
2	63 (Reheat I at 0.3%) → 76 (Reheat II at 1.2%) 61 (Reheat III at 0.3%) ← 65 (Initial heat at 0.3%)		
3	72 (Reheat I at 0.3%) → 95 (Reheat II at 5%) 72 (Reheat III at 0.3%) ←		

^aPolymer Laboratories DMTA unit, argon atmosphere, 3°C/min. heating rate, a tension of 0.2 N for the monofilaments used, 1 Hz frequency, tensile deformation mode, and the strain applied varied as indicated.

TABLE III
Effect of Pretension and Strain on the Modulus Retention of Kevlar and Steel

Kevlar monofilament			Steel wire		
Pretension (N)	Strain (%)	$E_{100^\circ\text{C}}/E_{25^\circ\text{C}} \times 100$	Pretension (N)	Strain (%)	$E_{100^\circ\text{C}}/E_{25^\circ\text{C}} \times 100$
0.003		93.4	0.51		97.3
0.031	0.31	94.5	5.11	0.31	100.0
0.15		97.4	10.00		100.4
0.31		98.7			
	0.05	103		0.05	97.5
		104			97.9
0.031	0.31	95	5.11	0.31	100.0
	1.25	100		5.00	99.8
		100			

^a Polymer Laboratories DMTA unit, argon atmosphere, 3°C/min heating rate, 1 Hz frequency, tensile deformation mode, pretension and strain applied as indicated.

Polyethylene vs. Kevlar Fibers

An experimental polyethylene ($T_g \sim -30^\circ\text{C}$) fiber has been studied by sonic modulus technique at room temperature. As shown in Figure 6, with an increase in load from 100 to 1500 g, the dynamic modulus of elasticity E increases from 152 to 177 GPa. (Note: The measurements are made within 1–2 min of applying the load. Also the fiber dimensions do not come into the calculations; $E = \rho C^2$, where ρ is the density and C is the velocity of sonic pulse through the sample.) As the polyethylene fiber is allowed to stay under a load of 1500 g, the modulus increases further to a value of 187 GPa within 24 h and then remains constant. Interestingly enough, as soon as the load

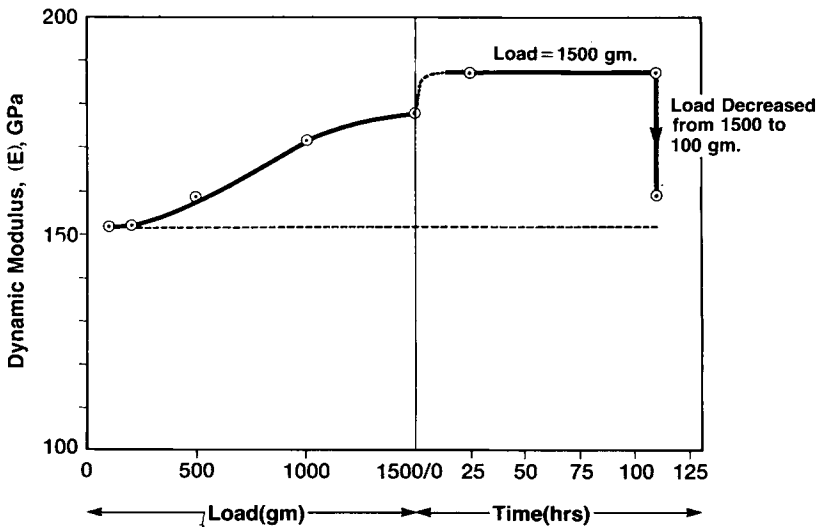


Fig. 6. Dynamic modulus (sonic technique, 5 kHz) of an experimental polyethylene yarn as a function of load history.

is decreased to 100 g, the modulus immediately drops from 187 to 159 GPa (Fig. 6). Thus, whatever changes occur in polyethylene under load are almost temporary, i.e., elastic. No effects of such type were observed for Kevlar fibers, at least to any significant extent.

DISCUSSION

The results described here clearly show that the modulus of fibers at temperatures around or above their T_g increases with an increase in pretension and % strain. More interestingly, the increase in modulus is temporary in nature (i.e., elastic) and is more or less completely recoverable as soon as the pretension and % strain are reduced. We wish to call this phenomenon, elastic orientation under force (EOF) since it is slightly different from the well-known strain-hardening phenomenon.⁶⁻⁸

As per rubber elasticity, elastomers also exhibit the characteristics of the polyethylene and our experimental fibers but the elastomers stiffen only at high extensions (e.g., > 400%) and are crosslinked.⁶ Strain hardening is also quoted for thermoplastics like polyethylene but it occurs in the post-yield regions where the extensions are high (e.g., > 600%) and, of course, there is no question of recovery. Thus, the reversible stiffening effect observed in thermoplastic fibers of polyethylene and our experimental fibers at low strains, e.g., 0.3–5%, is somewhat different and this is why we have termed it as EOF. Actually, the reversibility of stiffness in polyethylene and our experimental fibers can be attributed to pseudocrosslinking due to crystallinity and molecular entanglements. Also the occurrence of this phenomenon at low strains for our fibers can be due to an already high degree of orientation as opposed to elastomers which would require high extensions to achieve an equivalent orientation inherent in the fibers.

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