Copolyester Studies. III. Melt-Spinning, Drawing, and Mechanical Properties of Tetramethylene Terephthalate–Tetramethylene Sebacate Copolymer Fibers

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Synopsis

Fibers have been prepared from tetramethylene terephthalate–tetramethylene sebacate copolymers, containing up to 20 mol % of the latter, using a conventional melt-spinning technique. The mechanical properties of these undrawn fibers and of highly oriented fibers prepared from them have been evaluated. The changes in mechanical properties brought about by the introduction of sebacate groups in poly(tetramethylene terephthalate) have been related to the glass-transition temperatures of the copolymers and to the flexible nature of the sebacate unit. The formation of voids during a continuous drawing process and during mechanical testing is discussed.

INTRODUCTION

In two previous papers we reported the preparation and characterization of tetramethylene terephthalate–tetramethylene sebacate copolyesters containing up to 20 mol % sebacate[1] and the melting and crystallization behavior of these systems.[2] We now report the melt-spinning of these polymers, drawing of the resultant fibers, and the evaluation of their mechanical properties.

EXPERIMENTAL

The polymers were prepared and characterized as previously reported.[1]

The polymers were converted into fibers using a rod-spinning apparatus. Polymer chips (75 g, dried at 100°C/1 mm Hg for 16 hr) were fed into the cylinder of the rod spinner. The upper and lower parts of the cylinder were controlled by separate heaters, so that the polymer was subjected to a minimum residence time at the extrusion temperature (2–6°C above the equilibrium melting temperature of the polymers).[2] A monofilament was obtained from a spinneret having a single central hole 0.5 mm in diameter. The monofilament was allowed to fall freely to the ground (approximately 10 ft) before being wound onto a surface-driven bobbin at the lowest practical speed (200 rpm), so that little orientation was induced in the fiber.

The spun fibers were stored in a constant-temperature/humidity room (20°C/50% r.h.) for at least 7 days before drawing and/or mechanical testing. Drawing was effected using a conventional hot-plate drawing machine[3,4] at temperatures $(T_g + 24)$°C, where the T_g was taken to be E''_{max} derived from dynamic mechanical measurements.[1] The fiber was wound around the drawing frame in such a manner as to prevent slippage, and the drawing tension was

measured by a tensiometer positioned immediately before the hotplate. The drawn fiber was collected on a bobbin as a continuous filament, and immediately after the drawing process, the fiber was cut from the bobbin to provide convenient lengths for mechanical testing. Prior to testing, the fibers were allowed to relax in constant-temperature/humidity conditions for 24 hr. The draw ratio of the conditioned fibers was determined as the ratio of the cross-sectional area of the undrawn fiber to that of the drawn fiber. The radii are determined from electron microscope photographs at known magnification (×500) for 10 samples of each fiber.

The load-extension curves of both drawn and undrawn fibers were obtained from a bench-model Instron tensile testing machine. A standard gauge length (5 cm) and testing speed (5 cm/min) were used throughout. Initially 25 samples were chosen at random and tested. From the results the number of samples (n) required so that the average of the test results would be within 2% of the mean 95% of the time was evaluated.[5] The additional tests required (n-25) were performed, and the mean, standard deviation, and coefficient of variation for n tests were calculated. During tensile testing, slippage of the fiber in the clamps may occur, so that the nominal gauge length is not the effective gauge length.[6] Corrections for slippage were made according to the relevant standard.[7]

The deniers of the undrawn and drawn fibers were determined by accurately weighing 9 m of the monofilament. The drawn fiber was allowed to relax for 24 hr in constant-temperature/humidity conditions before weighing.

The density of the fibers was determined as previously reported.[1]

Samples of fibers for electron microscope studies were prepared by cutting under a small tension. Electron microscope photographs of fiber cross sections were obtained at various magnifications.

RESULTS AND DISCUSSION

The spinning conditions used, and typical properties of the as-spun fibers produced, are shown in Table I.

The drawing conditions and typical properties of the drawn fibers are shown in Table II. The drawing procedure employed was based on the work of Marshall and Thompson,[3,8] who analyzed the process of drawing over a flat heated plate in terms of the temperature dependence of the natural draw ratio. The results in Table II indicate that similar draw ratios were obtained for each polymer when an arbitrary drawing temperature of $T_g + 24°C$ was used. The tension required to produce such draw ratios decreased with increasing sebacate content of the fibers. The large decrease in drawing tension observed for the 20% copolymer

TABLE I
Melt-Spinning Conditions and Fiber Properties

Composition, mole % sebacate	Intrinsic viscosity[a]	Spinning temperature, °C	Fiber density, g/cm³	Fiber denier
0	0.79	242	1.298	185
5	0.78	231	1.283	187
10	0.88	224	1.276	220
15	0.82	217	1.262	190
20	0.74	198	1.250	70

[a] Determined as previously reported (Ref. 1).

TABLE II
Drawing Conditions and Drawn Fiber Properties

| Composition, mol % sebacate	Drawing temperature, °C	Drawing tension, g	Draw ratio	Denier
0	80	36	3.76	35
5	74	31	3.71	35
10	63	33	3.62	37
15	58	26	3.74	34
20	46	12	3.71	13

reflects, in part, the lower denier of the fiber, and also the high concentration of sebacate units.

Orientation of fibers by drawing results in closer molecular packing, and the density of the drawn fiber should increase relative to that of the undrawn fiber. Densities of the undrawn fibers (Table I) were as expected, greater than the experimentally determined amorphous densities of the polymers.[1] Fibers with draw ratios less than 3 exhibited increases in density relative to the undrawn fibers, but fibers with draw ratios of approximately 3.7, as shown in Table II, exhibited densities that were less than the experimentally determined[2] amorphous densities of the polymers. Generally, those fibers that gave anomalously low densities were very lustrous in appearance, whereas fibers of "the expected density" were dull.

Anomalously low densities for drawn fibers have also been reported by Rybnickar[9] for poly-6-caproamide, and Thompson and Woods[10] and Miller and Willis[11] for poly(ethylene terephthalate). Rybnickar, and Thompson and Woods have related these anomalous densities to the presence of voids within the drawn fibers. The presence of voids has also been shown to be responsible for the low densities obtained in the present study, as indicated in the electron microscope photographs shown in Figures 1–3. Thus Figure 1(a) reveals voids in a 4GT fiber with a draw ratio of 3.76, whereas Figures 1(b) and 1(c) show the absence of voids in undrawn 4GT fibers and those with relatively low draw ratios. Voiding was also observed in copolymer fibers of draw ratios of approximately 3.7 containing up to 15 mol % sebacate, as illustrated in Fig. 2. The 20% copolymer fiber of almost identical draw ratio did not, however, show void formation to such a degree (Fig. 3).

Cross sections of voided fiber were selected at random from different batches of drawn fiber, and all showed voids when observed on the scanning electron microscope, suggesting that voiding occurred along the whole length of the fiber. The pattern of voiding was similar for all fibers studied, the voids being in the central region of the fiber, which was surrounded by a clear skin of unvoided material. The latter observation is qualitatively similar to the observations of voiding by Rybnickar[9] and Ludewig[12] for polyester fibers and Hookway[13] for nylon 6/6. Also, Bair et al.[14] have described the fracture surfaces of 4GT rods, drawn to over 100%, as having an inner opaque region that had undergone cavitation surrounded by a clear skin that had drawn without cavitation. Hookway has suggested a mechanism of void formation in polymeric materials based on the theory of plastic flow in metals. The mechanism postulates a stress system consisting of an axial tension uniform across the neck together with a hydrostatic tension that is zero at the periphery and increases to a maximum on the axis.

The theory of Hookway is supported by the work of Ludewig,[12] who has shown
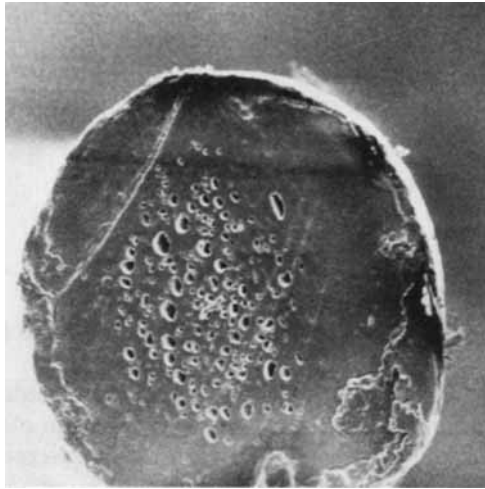
(a)
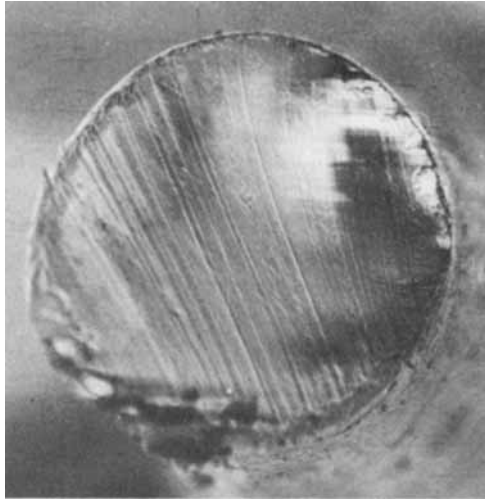
(b)

Fig. 1. (a) Electron micrograph of voided 4GT fiber: draw ratio 3.76. ×1020. (b) Electron micrograph of undrawn 4GT fiber. × 540. (c) Electron micrograph of 4GT fiber: draw ratio 2.0. ×1100.

unequivocally that void formation begins in the neck region and that it initially occurs in the center of the fiber and then extends outwards over the cross section. The latter author and Allison and Ward[15] have shown that voiding is dependent on both temperature and drawing speed, increasing with decreasing temperature and increasing strain rates as a consequence of the higher axial and hydrostatic tensions. It is possible that the lower degree of voiding observed in the 20% copolymer fiber is the result of a smaller axial and hydrostatic tension required to produce a similar draw ratio from a fiber of lower denier.

A further facet of void formation during drawing is the "lacunose effect" originally reported by Hookway.[13] The effect is manifest during mechanical
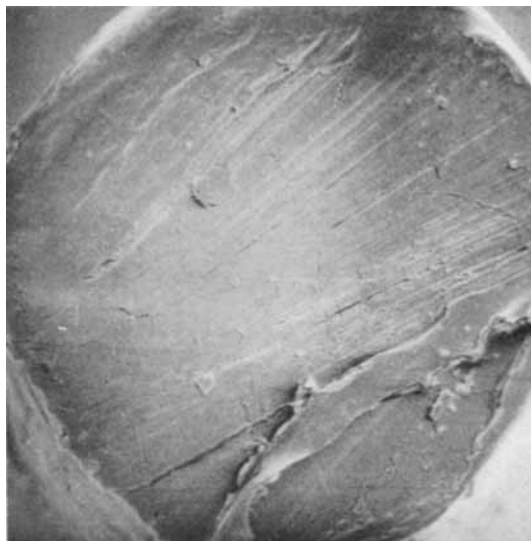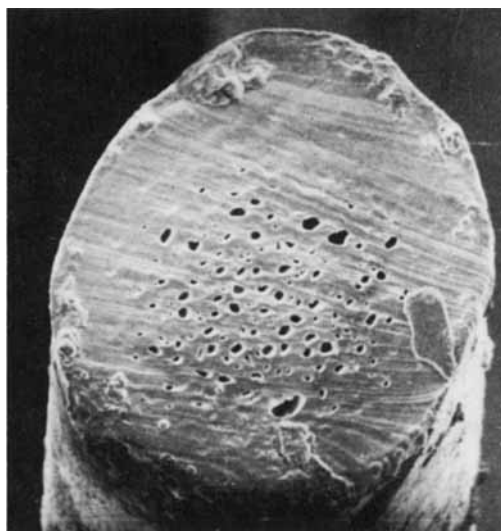
(c)

Fig. 1. (*Continued from previous page.*)

Fig. 2. Electron micrograph of 15 mol % sebacate copolymer fiber: draw ratio 3.74.   ×1120.

testing of undrawn fibers as a sawtooth waveform in the cold-draw region of the
load-extension curve.   In the present study the appearance of the sawtooth
waveform was consistent with alternate lustrous and dark patches in the fiber
under test, the number of lustrous patches being equal to the number of "teeth."
The lustrous patches have been found to contain voids or lacunae, whereas the
dull patches are free of voids.

With all undrawn fibers tested, except those of the 20% copolymer, the lacunose
effect was observed in the cold-draw region at a testing speed of 5 cm/min.
Further experiments on 4GT showed the effect to be dependent on extension
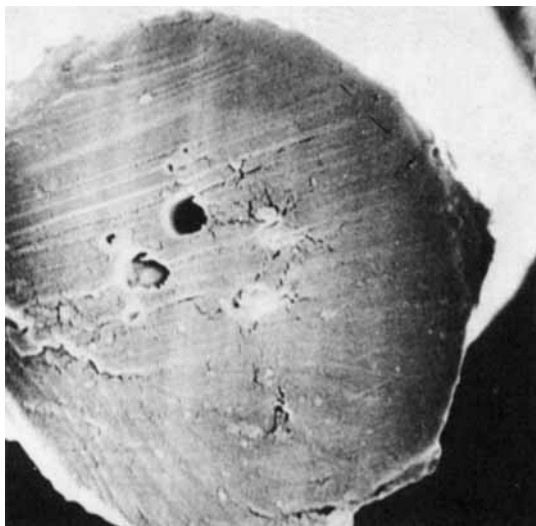rate.   At 10 and 20 cm/min the sawtooth waveform covered the whole of the

Fig. 3. Electron micrograph of 20 mol % sebacate copolymer fiber: draw ratio 3.71. ×2080.

cold-draw region; however, at 2.5 and 50 cm/min the lacunose effect was not observed. It is suggested that the dependence of lacunose drawing on extension rate can be explained in terms of Hookway's mechanism of lacunose drawing[13] and that it is related to the dependence of yield stress on extension rate (Fig. 4). Thus, at low extension rates, the yield stress[15,16] and axial and hydrostatic tensions[13] are low, and normal or nonlacunose drawing occurs. As the extension rate is increased, the yield stress and hydrostatic tension may increase sufficiently to cause lacunose drawing.[15] At relatively high extension rates, the heat generated as a result of the deformation process is lost slowly and is conducted into the unyielded part of the fiber. The yield stress and hydrostatic tension decrease and normal drawing results. At very high extension rates there is insufficient time for heat conduction into the unyielded part of the fiber. This will result
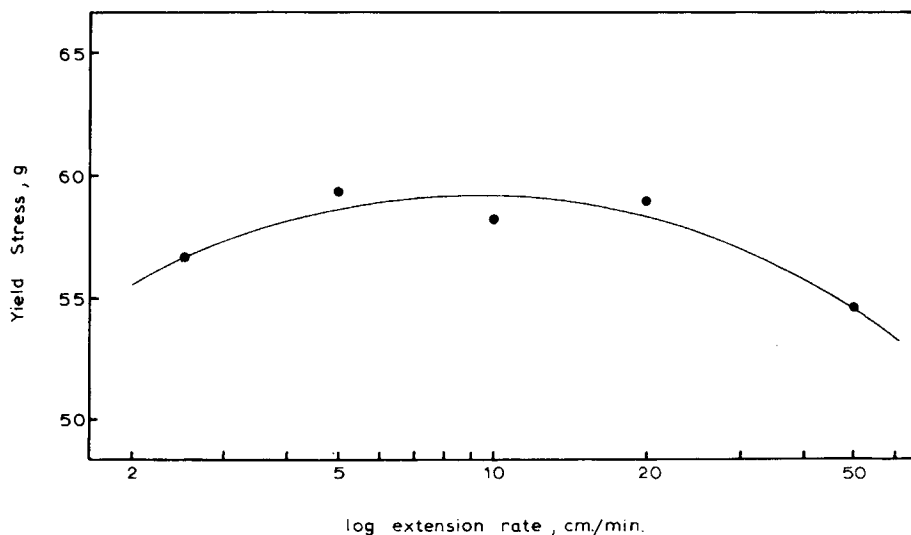

Fig. 4. Variation of yield stress with extension rate for undrawn 4GT fibers.

in a very large yield stress and fracture of the fiber may ultimately occur. Fracture at yield was observed in the present study at an extension rate of 100 cm/min.

Hookway found that the presence of voids in drawn fibers had no significant effect on their mechanical properties relative to unvoided drawn fibers. It has been assumed that this is the case in the present study.

The data presented in Tables III–V show the stress and strain parameters of undrawn fibers and the properties of drawn fibers determined from the load-extension curves. Figures in brackets are the coefficient of variation determined for each parameter.

It has been reported previously[15–17] that increases in crystallinity have a significant effect on the mechanical properties of polymers. However, when low levels of crystallinity, such as are encountered in the undrawn fibers discussed here are considered, the effect is very small: nevertheless, the initial modulus, draw stress, and yield stress all correlate well with the density (Fig. 5) of the fibers. The strain parameters, apart from yield strain, show no correlation with density.

In undrawn fibers the force required to induce bond rotation for cold-drawing to occur is related to the difference between T_g and the test temperature. In

TABLE III
Strain Parameters of Undrawn Fibers

Composition, mol % sebacate	Yield strain, %	Cold-draw strain, %	Breaking strain, %	Natural draw ratio
0	2.34(5.7)	352(4.0)	602(5.2)	4.5
5	2.40(4.3)	363(3.8)	612(3.0)	4.6
10	2.57(4.4)	371(2.5)	609(4.3)	4.7
15	4.25(10.1)	364(6.2)	693(4.9)	4.6
20	5.45(9.0)	375(4.5)	660(3.6)	4.8

TABLE IV
Stress Parameters of Undrawn Fibers

Composition, mol % sebacate	Initial modulus, g/denier	Yield stress, g/denier	Cold-draw stress, g/denier	Breaking strength, g/denier
0	14.7(4.6)	0.32(6.4)	0.28(5.5)	0.70(7.4)
5	12.8(3.5)	0.28(8.1)	0.24(3.3)	0.53(5.3)
10	10.6(4.4)	0.25(9.8)	0.21(6.0)	0.50(5.8)
15	7.9(4.2)	0.22(4.6)	0.20(4.5)	0.48(4.9)
20	5.0(1.8)	0.19(5.0)	0.16(3.8)	0.36(3.3)

TABLE V
Mechanical Properties of Drawn Fibers

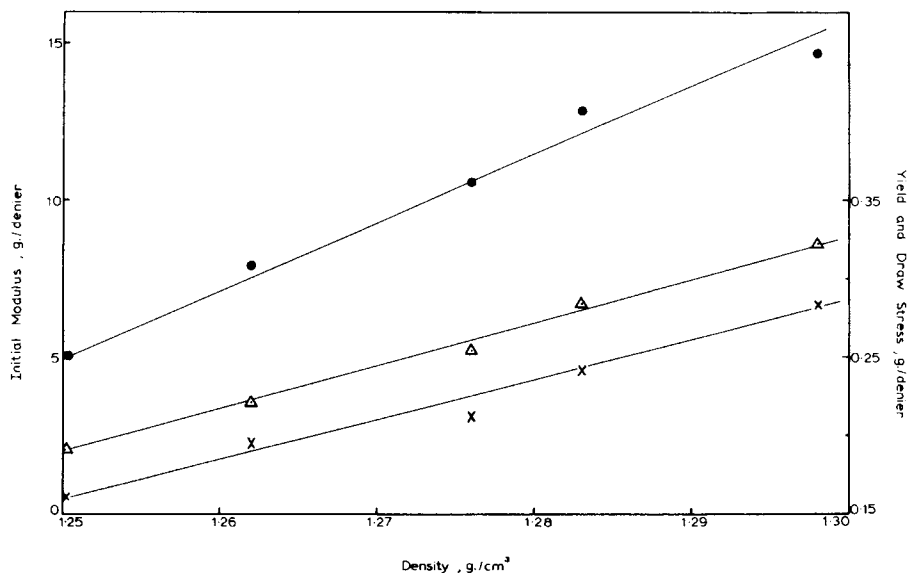| Composition, mol % sebacate	Initial modulus, g/denier	Breaking strain, g/denier	Breaking strength, g/denier
0	41.2(3.6)	32.0(10.5)	3.8(4.0)
5	33.0(3.2)	34.1(9.2)	3.2(3.5)
10	28.8(3.7)	38.4(8.6)	3.5(4.8)
15	25.6(4.0)	41.4(8.8)	2.9(4.1)
20	22.5(4.1)	47.1(11.0)	2.2(6.2)

Fig. 5. Correlation of initial modulus, yield stress, and cold-draw stress with density for the undrawn fibers: ●, initial modulus; △, yield stress; ✕, cold-draw stress.

this context an increase in sebacate content of the fibers is similar to an increase in test temperature. Thus the test temperature (20°C) is 36°C below E''_{max} for 4GT[1]; however, this value decreases with increasing sebacate content until it is only 3°C for the 20% copolymer. If it is considered that the initial modulus and yield and drawing stresses are measures of the force necessary to initiate large-scale molecular motions, then the results in Table IV show that increasing sebacate content, i.e., effectively increasing the test temperature, decreases the force required.

The behavior of parameters such as the initial modulus should also have a quantitative resemblance to the behavior of other properties that are measures of large-scale molecular motion, such as the glass-transition temperature. Figure 6 shows the similarity in the behavior of E''_{max} and initial modulus with increased sebacate content. Such a comparison is valid, since the crystallinity of the undrawn fibers is low and of a similar level to that of the compression-molded films used for determination of E''_{max}.[1]

Marshall and Thompson[3] have shown that an increase in test temperature results in a marked decrease in natural draw ratio. Therefore, if it is considered that an increase in sebacate content represents an effective increase in test temperature, it would be expected that natural draw ratio and cold-draw strain would decrease with increase in sebacate content. The data in Table III show that this was not the case and that a slight increase in natural draw ratio occurred as the sebacate content increased. It is possible that this is due to the flexible sebacate unit being able to assume a more coiled and tangled conformation than the relatively inflexible terephthalate unit, thus allowing greater extension to occur. This general trend is also reflected in the data obtained for yield strain and breaking strain, which both increase with increasing sebacate content.

Comparison of the data in Tables III and IV with that in Table V shows that orientation produced by drawing significantly affects the mechanical properties of the fibers. Thus the initial modulus dramatically increases with orientation
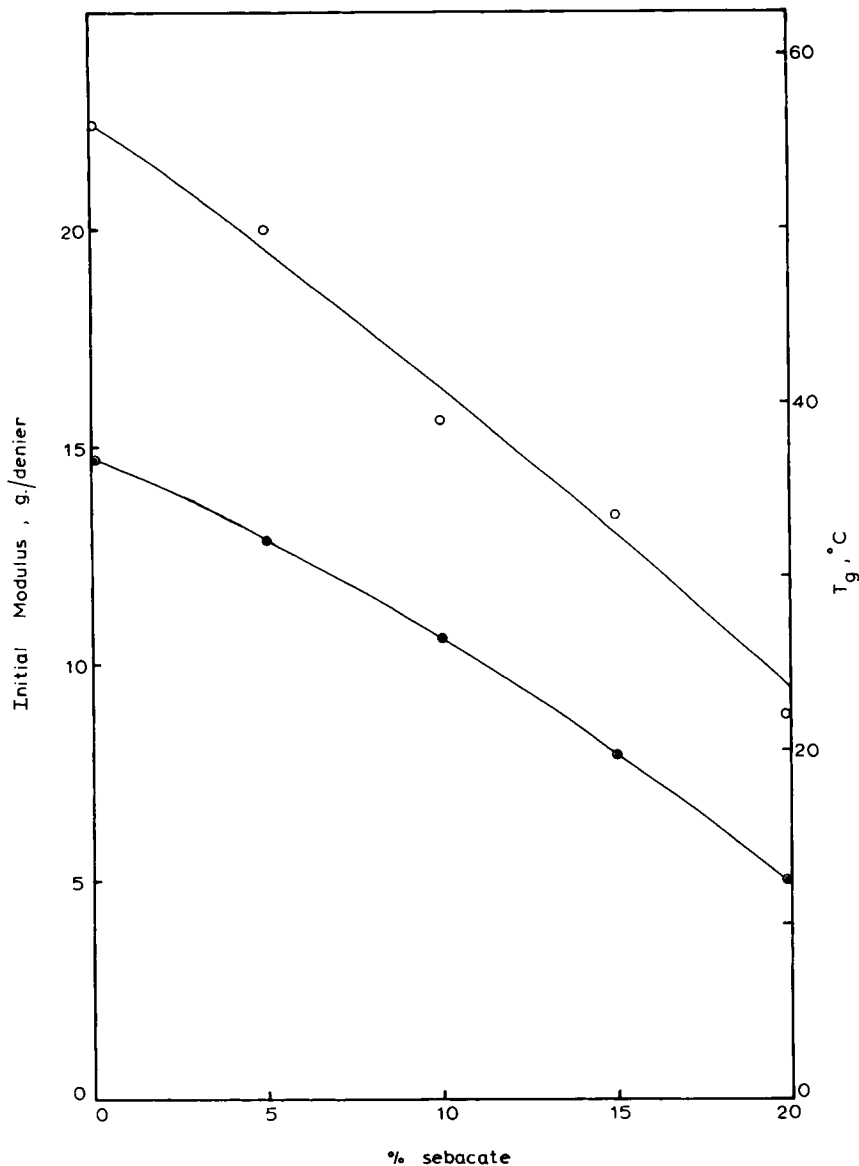
Fig. 6. Relationship of initial modulus and glass-transition temperature E''_{max} with composition: ●, initial modulus; O, E''_{max}.

by a factor of approximately 3, whereas the breaking strengths of the oriented fibers are approximately 6 times greater than those of unoriented fibers. Breaking strain also dramatically decreases with orientation.

The effect of incorporation of sebacate on the properties of the drawn fibers is qualitatively similar to that in undrawn fibers. Thus a marked decrease in initial modulus and breaking strength is observed with increasing sebacate content, whereas the increase in breaking strain is similar to the trend of increase in yield strain, cold-draw strain, and breaking strain in undrawn fibers.

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