

# Dynamic Mechanical Measurements on Monofilaments

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## Synopsis

Monofilaments were obtained or extruded and drawn to representative degrees. The dynamic mechanical properties of polyether based polyurethane, high density polyethylene, and polycaprolactam monofilaments produced commercially and of laboratory prepared monofilaments of low and high density polyethylene, poly(ethylene terephthalate), and poly(tetramethylene terephthalate) were measured. The data are compared with those from oriented film and amorphous or unoriented film when possible. The effect of orientation on the properties was clearly detectable as was the effect of absorption of water vapor on polycaprolactam.

## INTRODUCTION

Dynamic mechanical properties of polymers are measured usually on isotropic bulk or film samples. In use, many polymers are anisotropic, often in the form of a film or monofilament. In both cases crystallinity may have been induced or changed by drawing. Dynamic response may be changed by plasticizers and fillers, moisture being an important plasticizer for polymers used in textiles. Dynamic testing often includes a survey of the effect of temperature and of test frequency.

A comprehensive survey of this subject is in the book by Murayama.<sup>1</sup> The broader subject of anelastic spectra is discussed by McCrum et al.<sup>2</sup> The interpretation of the spectra of semicrystalline polymers has been developed by Takayanagi and Matsuo.<sup>3</sup> Dynamic mechanical properties are discussed by Nielsen.<sup>4</sup>

Murayama<sup>1</sup> and Nielsen<sup>4</sup> have reviewed the effects of crystallinity and of orientation on properties. Newman and Cox<sup>5</sup> showed that the combined effect of crystallinity and of orientation was greater than the effect of either alone for poly(ethylene terephthalate) and crystalline polystyrene. Ballon and Smith<sup>6</sup> and Thompson and Woods<sup>7</sup> found that orientation had a greater effect on the dynamic properties than did extent of crystallization. Drawing results in orientation regardless of the type of polymer and may enhance crystallization, as well as orienting the crystallites, in semicrystalline polymers.

The effect of draw ratio on the loss factor ( $\tan \delta$ ) is not as clear. Nielsen and Buchdahl<sup>8</sup> found that orientation of amorphous polystyrene increased the maximal  $\tan \delta$  somewhat. Armeniades et al.<sup>9</sup> using a torsional pendulum below 300 K found essentially no change in  $\tan \delta$  upon orienting atactic

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polystyrene, but a slight decrease with increasing crystallinity for isotactic polystyrene. Drawing reduced the  $\gamma$  loss peak of poly(ethylene terephthalate) at 210 K under similar conditions.<sup>10</sup> Frosini and Woodward<sup>11</sup> using a torsional pendulum found that drawing increased the 48 K loss peak and decreased the 149 K loss peak of poly(vinyl propionate) and shifted the 205 K loss peak to 220 K for poly(vinyl acetate).

In this paper, the nomenclature for the loss peaks suggested by Boyer<sup>12</sup> will be replaced by the earlier designations to enable comparison with the literature.

## MATERIALS AND EQUIPMENT

Polymers used were low density polyethylene, high density polyethylene, polyether-based polyurethane, polycaprolactam, poly(ethylene terephthalate), and poly(tetramethylene terephthalate). The dynamic properties of the monofilaments, and the films when used for comparison, were measured on a Rheovibron Model DDV-II.<sup>13</sup> Samples were cooled to liquid nitrogen temperature and heated at a rate of about 2°C/min over the range -180 to 180°C. Frequencies used were 11, 35 and 110 Hz. The chamber was flushed with dry nitrogen during the experiment.

The values of the dynamic modulus  $E'$  and the loss factor,  $\tan \delta$ , were measured at 5°C intervals except near the transition regions when measurements were more frequent. From  $\tan \delta$  and  $E'$  the values of  $E''$  were estimated and  $T_g$ , the glassy transition temperature, and other features were recorded from the computer-plotted graphs.

Slippage of the monofilaments was avoided by knotting the ends in the clamps and of films by roughening the surfaces. Humidity conditioning, when used, was accomplished in constant humidity atmospheres before testing. The dimensions of the samples were measured by micrometers.

The polycaprolactam monofilament was supplied by the Division of Chemistry, National Research Council of Canada as made by Albany International, Perth, Ontario. The high-density polyethylene, low-density polyethylene, poly(ethylene terephthalate), and poly(tetra-methylene terephthalate) monofilaments were extruded and drawn at the University of Waterloo, courtesy of Professor A. Rudin of the Department of Chemistry. DuPont's Mylar film was used as received and after melt pressing and quenching in ice water. Eastman Kodak resin was used to hot press poly(tetramethylene terephthalate) films. Commercial monofilaments were obtained from Rulan Plastics Co., high density polyethylene monofilament, and from Plastics Extrusion Engineering Co. Inc., the polyether-based polyurethane monofilament.

## RESULTS AND DISCUSSION

### Polyether-Based Polyurethane Monofilament

The composition of this monofilament was not revealed by the supplier. However, the monofilament was tested at frequencies of 11, 35, and 110 Hz over the temperature range -180 to 140°C. The dynamic modulus  $E'$ , loss

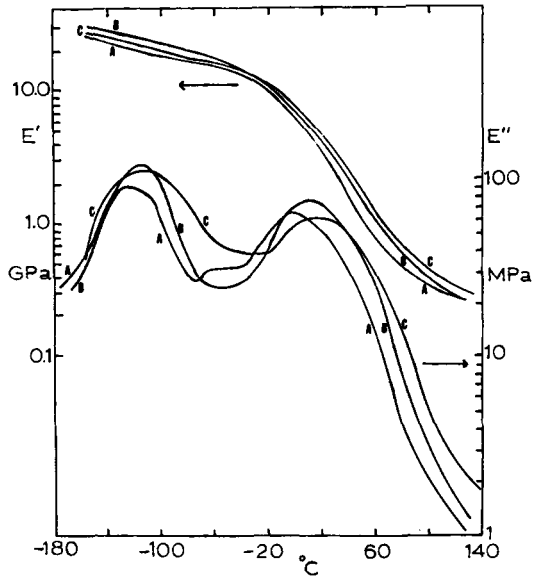


Fig. 1. Effect of test frequency on the  $E'$  and  $E''$  of a polyether-based polyurethane monofilament: (A) 11 Hz; (B) 35 Hz; (C) 110 Hz.

modulus  $E''$ , and loss factor  $\tan \delta$  were recorded and are plotted vs. temperature in Figures 1 and 2. The data are consistent with two relaxation loss peaks one attributable to the  $T_g$  of the soft polyether segment,  $-110^\circ\text{C}$  approximately, and the other attributable to the  $T_g$  of the hard polyurethane segment at  $60^\circ\text{C}$ . The temperatures at which the peaks occur increase with frequency<sup>4,14</sup> as does the magnitude of the peak. Plots of  $\log T$  at the maxima vs.  $\log$  frequency are linear, and an energy of activation for the lower temperature peak at 45 kJ/mol was obtained compared with 142 kJ/mol for the higher temperature peak. Similar differences between the temperature coefficients of low and high temperature peaks have been noted by others.<sup>1,2,4,12</sup> Maung and Williams<sup>15</sup> observed values of 120 and 400 kJ/mol

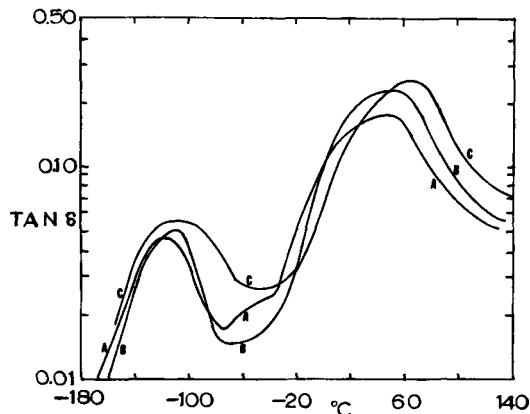


Fig. 2. Effect of test frequency on  $\tan \delta$  of a polyether based polyurethane monofilament: (A) 11 Hz; (B) 35 Hz; (C) 110 Hz.

for the temperature coefficients of the two main loss peaks of block copolymers of polydimethylsiloxane and bisphenol-A polycarbonate.

### Commercial Polyethylene Monofilament

A monofilament, Rulan, yielded the data in Figures 3 and 4. There are two major relaxation peaks, the  $\beta$  at 45 and the  $\gamma$  at  $-100^\circ\text{C}$ , which shift upward in temperature with frequency and become broader. On the log-log plot of the temperature at the peaks vs. frequency, the data are linear and yield energies of activation of 40 kJ/mol for the lower temperature peak and 96 kJ/mol for the higher temperature peak. These data compare with values of 46–63 kJ/mol for the lower temperature peak and 105 kJ/mol for the higher temperature peak obtained by Sandiford and Willbourn<sup>16</sup> and do not differ qualitatively from those obtained for the polyether-based polyurethane.

The data are quite different from those obtained (see later) for low-density and high-density polyethylenes used in the laboratory. No peak attributable to the crystal melting transition, the  $\alpha$  transition at about  $140^\circ\text{C}$ , was noted. The peak at or just below room temperature, attributed to the branched structures, is very pronounced, the  $\beta$  loss peak. The lower temperature peak corresponds to the glass transition temperature, a  $\gamma$  loss peak explained by concerted motion of three or more methylene units in the chain. It is present in the spectra, described later, of high-density and low-density polyethylenes. It would appear that the commercial monofilament could be crosslinked high-density polyethylene blend.

### Polycaprolactam Monofilament Plasticized with Water

Polycaprolactam is hydrophylic and absorbs several percent of water into the amorphous region. Samples of the monofilament were conditioned in atmospheres of various relative humidities and compared with a dry sample

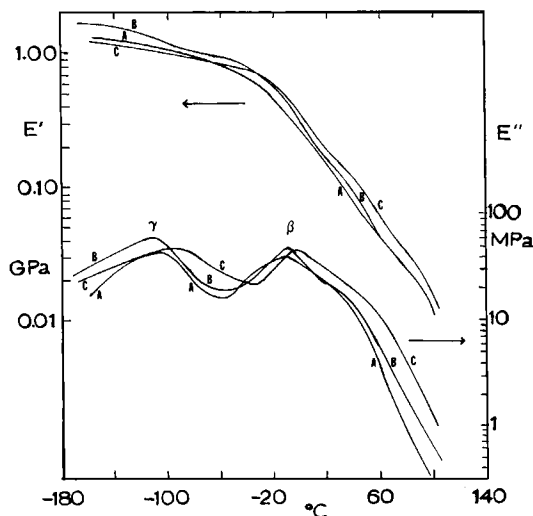


Fig. 3. Effect of test frequency on  $E'$  and  $E''$  of a commercial high-density polyethylene monofilament: (A) 11 Hz; (B) 35 Hz; (C) 110 Hz.

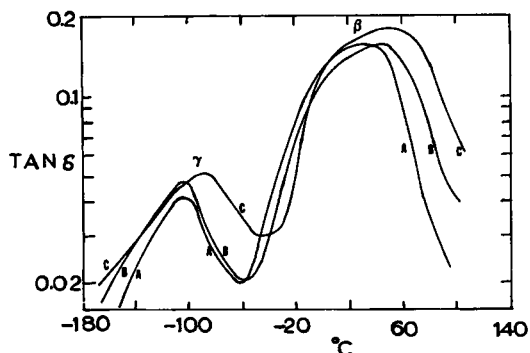


Fig. 4. Effect of test frequency on  $\tan \delta$  of a commercial high-density polyethylene monofilament: (A) 11 Hz; (B) 35 Hz; (C) 110 Hz.

and a sample soaked in water. The dynamic moduli  $E'$ , loss moduli  $E''$ , and loss factors ( $\tan \delta$ ) at 110 Hz are plotted in Figures 5 and 6. The  $\tan \delta$  values and temperatures of the peaks are in Table I.

For the dry polycaprolactam the dynamic modulus decreases rapidly at about  $90^\circ\text{C}$ , the temperature of the uppermost  $\tan \delta$  peak, the  $\alpha$  peak. As the relative humidity is increased, a shoulder appears on the lower temperature side of the upper  $\tan \delta$  peak and grows to be a second  $\alpha$  peak, which shifts to lower temperatures with increasing relative humidity. This shift with moisture was observed earlier for films by Sauter and Grosev in this laboratory. The dynamic modulus below  $-10^\circ\text{C}$  is higher for the samples containing water than for the dry sample, as reported also by Woodward

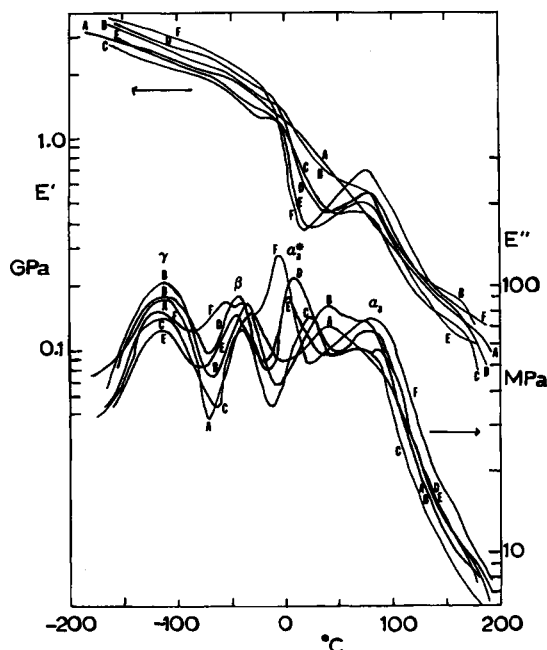


Fig. 5. Effect of relative humidity of conditioning on the  $E'$  and  $E''$  of a commercial polycaprolactam monofilament: (A) dry; (B) 8% RH; (C) 33% RH; (D) 75% RH; (F) water-swollen.

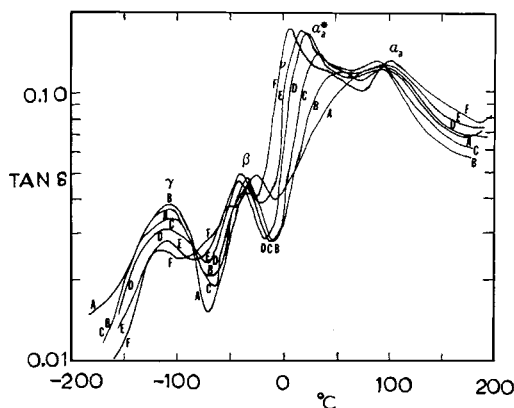


Fig. 6. Effect of relative humidity of conditioning on  $\tan \delta$  of a commercial polycaprolactam monofilament: (A) dry; (B) 8% RH; (C) 33% RH; (D) 75% RH; (E) 97% RH; (F) water-swollen.

et al.<sup>17</sup> It has been suggested that the water forms very stable bonds with the polycaprolactam over this temperature range, resulting in a slightly increased modulus.

Above  $-10^{\circ}\text{C}$  the antiplasticization effect changes to a plasticization effect with a rapid decrease in the storage modulus with relative humidity. The effect increases with relative humidity both as to the rate and the magnitude of the decrease. Perepechenko and Prokazov<sup>18</sup> noted a change from antiplasticizer to plasticizer action of water at  $-48^{\circ}\text{C}$ . The higher temperature in our case may be the result of fiber orientation, the higher test frequency, or other differences in technique.

The dynamic modulus levels off to form a plateau for the samples at lower relative humidity, and then increases for the samples of higher relative humidity to form a peak at about  $75^{\circ}\text{C}$ . It seems likely that loss of water is at least in part responsible, but crystallization may also be a factor. Above  $75^{\circ}\text{C}$  the dynamic modulus decreases with temperature, as one would expect, but the samples which had been at the higher relative humidity tend to have the higher dynamic moduli as if they were somewhat more crystalline.

Papir et al.<sup>19</sup> conducted comparable studies on films. The  $\gamma$  loss peak shifted from 146 K for dry films to 125 K for the films of the highest

TABLE I  
Effect of Relative Humidity on the Location and Heights of Loss Peaks

RH (%)	$\alpha_a$		$\alpha_a^*$		$\beta$		$\gamma$	
	$\tan \delta$	$^{\circ}\text{C}$	$\tan \delta$	$^{\circ}\text{C}$	$\tan \delta$	$^{\circ}\text{C}$	$\tan \delta$	$^{\circ}\text{C}$
0	0.129	93	a	a	0.050	-27	0.037	-107
8	0.133	89	0.124	45	0.049	-34	0.039	-107
33	0.137	90	0.141	32	0.047	-41	0.035	-105
75	0.133	91	0.168	20	0.046	-42	0.032	-106
97	0.137	100	0.171	18	0.050	-41	0.028	-111
b	0.135	99	0.176	6	0.038	-50	0.026	-114

<sup>a</sup> Dry sample no peak.

<sup>b</sup> Swollen with water.

humidity, and the peak height decreased to 0.5. The  $\beta$  loss peak shifted from 230 K to 190 K, the height increasing with water contents below 1.4% and decreasing again slightly as the moisture reached 8%. The  $\alpha$  loss peak shifts considerably more and splits into two. Most of the effect of water is observed with the absorption of about 3% of water with the additional absorbed water having less effect on the loss peak as to position and size.

The peaks in this study were at  $-107$ ,  $-27$ , and  $93^\circ\text{C}$  for the dry monofilament at 110 Hz, somewhat higher temperatures than observed for films. The  $\alpha$  loss peak is related to the amorphous phase and thus is labelled  $\alpha_a$ . This peak splits in the presence of water. One component remains at about  $90^\circ\text{C}$ , the other ( $\alpha_a^*$ ) shifts to lower temperatures irregularly with water content to a low value of  $6^\circ\text{C}$ . Correspondingly, the  $\tan \delta$  value at the peak for the  $\alpha_a^*$  loss increases from 0.124 for 8% relative humidity to 0.176 for the swollen sample. The shift in the  $\alpha_a^*$  loss peak for films has been observed in this laboratory and by others for various polyamide films.<sup>17,20,21</sup> The effect is that typical of a plasticizer. For the  $\alpha_a$  loss peak, which is unaffected by moisture, it must be presumed that the regions responsible are more highly ordered.<sup>22</sup> The same insensitivity to moisture is exhibited by the  $\alpha$  peak of partly aromatic polyamides.<sup>23</sup> The samples may have reached some constant level of moisture content also.

One may use the Fox relationship<sup>24</sup> to estimate the glass transition temperatures of the components of the plasticized system. There is a linear relationship between the reciprocal of  $T_g$  and the percent water over the range 0.5–4.0% (calculated from Ref. 25) as shown in Table I,  $\alpha_a^*$  column. The  $T_g$  of water is estimated to be  $-144^\circ\text{C}$  in close agreement with Yannas<sup>26</sup> and Rasmussen and Mackenzie,<sup>27</sup> The data extrapolate to the estimated  $T_g$  of dry polycaprolactam.<sup>24</sup>

The  $\beta$  loss peak also shifts to lower temperatures with increasing relative humidity, and diminishes in size, in contrast with the data of Hoashi and Andrews,<sup>22</sup> who noted little change in the  $\beta$  peak intensity with absorbed phenol. Also, the swollen sample yielded two small  $\beta$  loss peaks. The significance of this has not been studied.

The  $\gamma$  loss peak shifts slightly to lower temperatures but, significantly, decreases with increasing relative humidity.

The mechanisms associated with the  $\alpha$ ,  $\beta$ , and  $\gamma$  transitions and relaxations are still the subject of controversy. The  $\alpha$  loss is related to the breaking of strong H-bonds allowing long chain segmental motion in the amorphous phase. Strong H-bonds raise the  $T_g$  similarly to crosslinks. Small amounts of water have an abnormally large plasticizer effect, and larger amounts of water act as a plasticizer with a  $T_g$  of about  $-144^\circ\text{C}$ .<sup>26,27</sup>

Even more controversy is evident in understanding the  $\beta$  loss peak. It is observed when moisture and other low molecular weight materials are present in various polyamides.<sup>17,20,21,23,28</sup> Water may be absorbed in polycaprolactam three ways.<sup>24,29,30</sup> The first third is tightly bound to the polymer, the next third loosely bound, and the remainder undergoes cluster formation. Since "dry" polycaprolactam often shows a  $\beta$  loss peak, extremely small amounts of a tightly bound plasticizer (water or monomer) could be the causative agent, and the  $\beta$  loss peak is that of a water-carbonyl group motion.<sup>20,21</sup>

The  $\gamma$  loss peak is broader than that for polyethylene but very similar and may include the combined motion of amide and methylene groups.<sup>31-34</sup> The polar amide groups appear to be involved since the presence of water reduces the size of the loss peak. The peak may be complex and include various relaxations.<sup>19,22</sup>

### Low Density Polyethylene Monofilament

Polyethylene monofilaments were extruded and drawn to different draw ratios, 1.4, 2.0, 2.7, and 3.5. The properties are plotted in Figures 7 and 8 for the dynamic modulus, loss modulus, and loss factor. The dynamic modulus decreases continuously with major decreases at 110, 10, and  $-91^\circ\text{C}$ . The dynamic modulus increased with increasing draw ratio. The corresponding values of  $\tan \delta$  pass through three peaks, which shift irregularly in temperature with increasing draw ratio. When the log of the values  $E'$ ,  $E''$ , and  $\tan \delta$  corresponding to the  $\gamma$  peak are plotted against draw ratio, the lines are straight.

The  $\beta$  loss peak appears as a shoulder to the  $\alpha$  loss peak and first increases with draw ratio and then decreases with the highest draw ratio. The  $\alpha$  loss peak diminishes slightly with draw ratio. The data suggest that changes in the amorphous phase have been minimal with draw ratios up to 3.5.

The assignment of the mechanisms of the relaxations is still somewhat uncertain, although some agreement has been reached. Four loss peaks have been observed,  $-125$ ,  $-20$ ,  $50$ , and  $120^\circ\text{C}$ .<sup>35</sup> The present study located the peaks for drawn fibers at  $-91$ ,  $13$ , and  $110^\circ\text{C}$ . With some imagination, a peak at  $50$ – $60^\circ\text{C}$  could be noted particularly on the  $E''$  curves. The  $\alpha$  peak is the low temperature side of the melting peak, and the  $\gamma$  loss peak is caused by several methylene groups moving since it is common to polymers with sequences of three or more methylene groups. The intermediate peaks

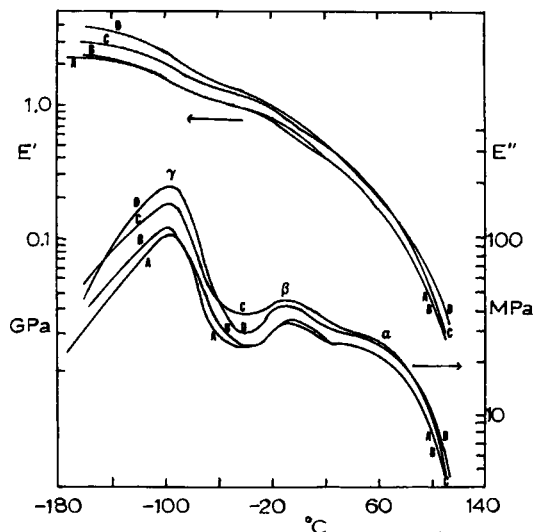


Fig. 7. Effect of draw ratio on  $E'$  and  $E''$  of low-density polyethylene monofilament: (A) 1.4 DR; (B) 2.0 DR; (C) 2.7 DR; (D) 3.5 DR.



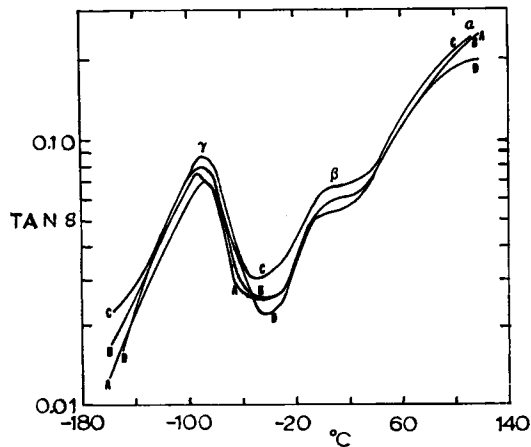


Fig. 8. Effect of draw ratio on  $\tan \delta$  of low-density polyethylene monofilament: (A) 1.4 DR; (B) 2.0 DR; (C) 2.7 DR; (D) 3.5 DR.

below room temperature,  $\beta$ , are believed to be related to branching and the interfacial region<sup>36</sup> and above room temperature to a crystal-crystal transformation on drawing. The  $\gamma$  loss peak is now commonly identified with the glass transition.<sup>37</sup> The transitions have been discussed recently by Boyd.<sup>38</sup>

### High Density Polyethylene Monofilament

High density polyethylene was similarly extruded and drawn into monofilaments at draw ratios of 1.3, 1.9, 2.8, and 3.6. The dynamic moduli, loss moduli, and  $\tan \delta$ , loss factor, are plotted in Figures 9 and 10. The dynamic moduli decrease regularly with major declines at 119 and  $-90^{\circ}\text{C}$ .

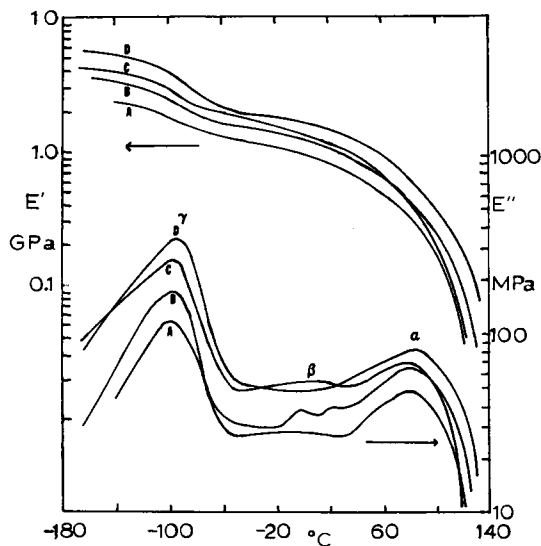


Fig. 9. Effect of draw ratio on  $E'$  and  $E''$  of high-density polyethylene monofilament: (A) 1.3 DR; (B) 1.9 DR; (C) 2.8 DR; (D) 3.6 DR.

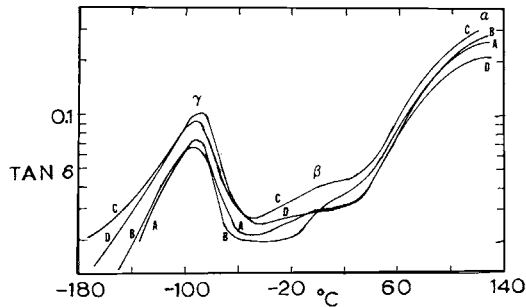


Fig. 10. Effect of draw ratio on  $\tan \delta$  of high-density polyethylene monofilament: (A) 1.3 DR; (B) 1.9 DR; (C) 2.8 DR; (D) 3.6 DR.

There are two major peaks in the  $\tan \delta$  curves. The lower temperature  $\gamma$  peak increases with draw ratio, but the peak does not move from  $-94^{\circ}\text{C}$  except for a slight increase to  $-88^{\circ}\text{C}$  for the highest draw ratio. The larger  $\alpha$  loss peak which is the rising side of the melting peak also increases slightly with draw ratio and decreases for the highest draw ratio. The loss moduli curves are essentially parallel, the lower temperature peak rising from  $-98$  to  $-95^{\circ}\text{C}$  with increasing draw ratio and the upper peak from  $81$  to  $86^{\circ}\text{C}$ . Plots of  $\log E'$ ,  $E''$ , or  $\tan \delta$  vs. draw ratio, unlike those for the low-density polyethylene, are not truly straight lines.

Pereña et al.<sup>39</sup> found that the  $\alpha$  loss peak was at a lower temperature after drawing and both  $E'$  and  $E''$  were higher. Our data show that the temperatures at which the peak occurs are not affected but  $E'$  and  $E''$  are definitely increased. The intermediate  $\beta$  loss peaks are poorly defined in the high-density polyethylene. One at about  $80^{\circ}\text{C}$ , vs.  $60^{\circ}\text{C}$  for the low-density polyethylene, shows clearly on the loss modulus curves but is not very pronounced. A very minor peak at about  $10^{\circ}\text{C}$  may be found in the  $\tan \delta$  and the  $E''$  curves. This suggests that the amount of branching is very slight and that the crystal-crystal transformation merges with the melting transition in the  $\tan \delta$  loss factor curves.

### Poly(ethylene Terephthalate) Monofilament

A monofilament of poly(ethylene terephthalate) was extruded and drawn to a ratio of 5.7. The dynamic mechanical properties were measured and compared with those of commercial film and the same film heated to melting in a press and quenched. The last-mentioned sample would be expected to be lower in crystallinity than the original film. The dynamic modulus, loss modulus and loss factor data are in Figures 11 and 12.

The dynamic moduli increase in the order quenched film, normal film, and monofilament. The quenched film shows the decrease in modulus characteristic of the glassy transition at about  $80^{\circ}\text{C}$ , but soon thereafter the increased mobility results in rapid crystallization between  $100$  and  $125^{\circ}\text{C}$ , raising the dynamic modulus. Thompson and Woods<sup>7</sup> have noted a similar phenomenon in amorphous unoriented films.

The peak at the highest temperature of the  $\tan \delta$  loss factor curves is the glassy transition. The peak height is greatest for the quenched sample and the height decreases and perhaps the width decreases with orientation,

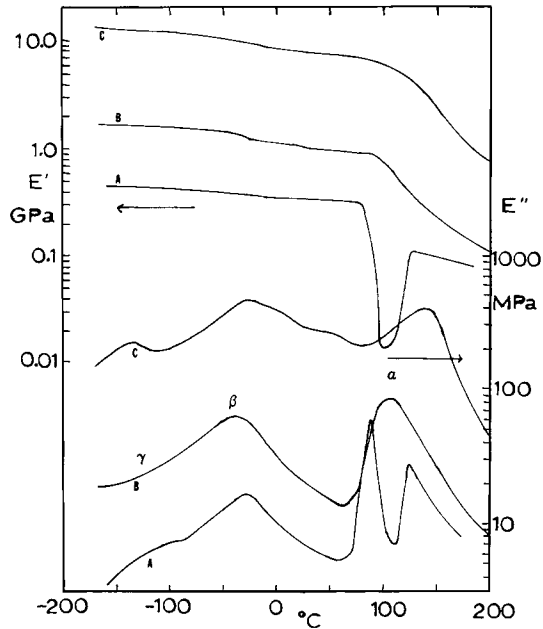


Fig. 11. Effect of drawing on  $E'$  and  $E''$  of a poly(ethylene terephthalate) monofilament: (A) quenched film control; (B) oriented film control; (C) monofilament 5.7 DR.

moving progressively to higher temperatures with orientation (114°C) and drawing (151°C).

The major lower temperature loss peak ( $\beta$ ) is at  $-26^\circ\text{C}$  and is not affected by orientation or drawing.

For the drawn monofilament, ill-developed peaks appear above and below the lower major temperature peak, particularly at  $55^\circ\text{C}$  and perhaps also at 0 and  $-130^\circ\text{C}$ . Illers<sup>40</sup> noted complexity in the drawn fiber monofilament loss factor curve also.

The loss modulus curve shows a deep cut in the peak at the higher temperature corresponding to the crystallization stage in the  $E'$  curve.

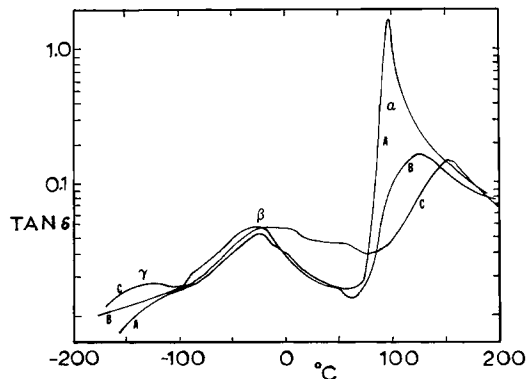


Fig. 12. Effect of drawing on the  $\tan \delta$  of a poly(ethylene terephthalate) monofilament: (A) quenched film control; (B) oriented film control; (C) monofilament 5.7 DR.

### Poly(tetramethylene Terephthalate) Monofilament

Poly(tetramethylene terephthalate) was extruded and drawn to ratios of 3.9 and 4.2. The dynamic moduli, loss moduli, and loss factors are plotted in Figures 13 and 14. The data are compared with results on slowly cooled (more crystalline) and quenched (amorphous) films. The dynamic moduli increase in the order quenched, slowly cooled, draw ratio 3.9 and draw ratio 4.2. The effect of the draw ratio is very marked.

There are two relaxations noted on the loss modulus and loss factor curves. The lower peak is unchanged in location at about  $-50^{\circ}\text{C}$  after heat treatment or drawing but is increased in magnitude greatly by drawing. This relaxation may be restricted or hindered motion about the ester or methylene links or a cooperative wagging and rocking motion of the rings.<sup>41,42</sup>

The upper peak is the glass transition. The loss peak is diminished by slow cooling and by drawing, and moves to higher temperatures, although the loss modulus is increased. The temperature for the peak changes from  $70$  to  $76^{\circ}\text{C}$  for the loss modulus and from  $75$  to  $85^{\circ}\text{C}$  for the loss factor.

### CONCLUSIONS

Tests on two commercial monofilaments showed that the properties of both were frequency-dependent, the loss peaks moving to higher temperatures with increased frequency similarly to results obtained on films. The monofilament described as high-density polyethylene appeared to lack crystallinity and may have been highly branched.

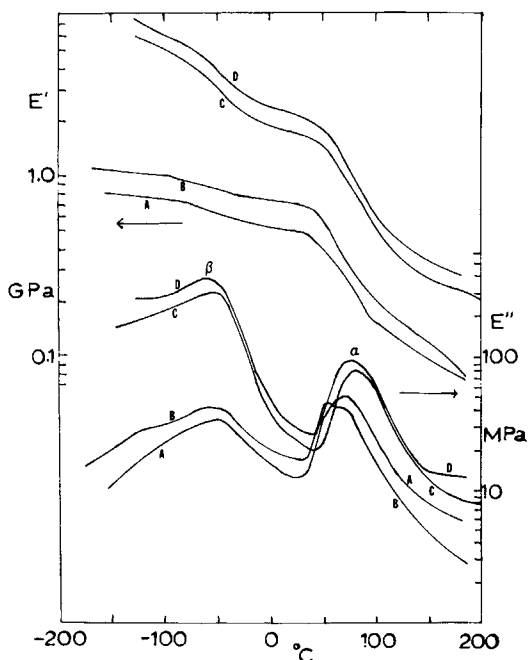


Fig. 13. Effect of draw ratio on  $E'$  and  $E''$  of poly(tetramethylene terephthalate) monofilament: (A) quenched film control; (B) slow cooled film control; (C) 3.9 DR; (D) 4.2 DR.

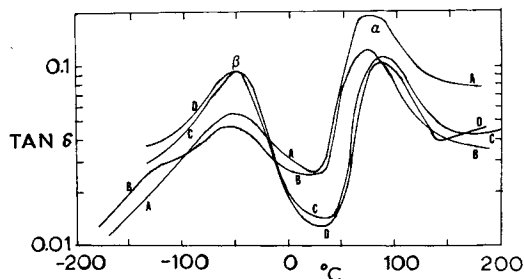


Fig. 14. Effect of draw ratio of  $\tan \delta$  of a poly(tetramethylene terephthalate) monofilament: (A) quenched film control; (B) slowly cooled film control; (C) 3.9 DR; (D) 4.2 DR.

Water acts as a plasticizer and an antiplasticizer above and below  $-10^{\circ}\text{C}$ , respectively, for polycaprolactam. This temperature marks the change from water acting as a strong plasticizer to a strong bonding agent. The glass transition peak of the drawn fiber splits into two, the larger portion moves to lower temperatures with increasing water content whereas the other remains essentially fixed, presumably as the result of order.

The Fox equation can be used to calculate the glass transition temperatures of moist polycaprolactam with an indicated glass transition temperature of  $-144^{\circ}\text{C}$  for water and  $93^{\circ}\text{C}$  for "dry" polycaprolactam. The lower temperature relaxation peak for polycaprolactam does not require the presence of water.

Three peaks in low density polyethylene remain unchanged in position with increasing draw ratio. However, the lowest temperature peak, the glass transition, increases in size with draw ratio. The central peak is attributed to branching. The upper peak is the melting loss peak. Draw ratio has the same effect on high density polyethylene except that the middle peak attributed to branching is very small, if present.

For poly(ethylene terephthalate) and poly(tetramethylene terephthalate) the upper peak, the glass transition, decreases with draw ratio and crystallinity whereas the lower peak remains in the same location but increases in size with draw ratio.

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