

## Studies on Straining of Amorphous Polyethylene Terephthalate above the Glass Temperature

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### INTRODUCTION

When polyethylene terephthalate is melt-spun into fiber form and quickly quenched to room temperature, crystallization does not take place to any significant extent. The undrawn filament has not, at this stage, desirable textile yarn properties. The molecules comprising the filament are in a random state of orientation. Normally a highly oriented and crystallized fibrous structure is produced by a process known as cold or hot drawing. However, it has been known that the amorphous polyethylene terephthalate filament can be stretched at low tension without causing any observable crystallization at the temperature range just above the softening point. This phenomenon has been called as superdrawing or flow drawing.<sup>1,2</sup>

Thompson<sup>2</sup> discussed the superdrawing and strain-induced crystallization of polyethylene terephthalate using a viscoelastic theory based on the Maxwell equation and obtained good agreement between the theoretical results and experimental data.

In this paper an attempt was made to develop a mathematical viscoelastic model which would describe the stress-strain relation of the amorphous polymeric material at temperatures above the softening point and this model compared with the experimental data.

### THEORY

It was shown that if a unit cube of isotropic material, with its edges parallel to the coordinate axes  $x$ ,  $y$ ,  $z$ , is deformed into a cuboid with sides of length  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ , the forces which must be applied perpendicular to the faces of the cuboid in order to support the deformation are given by  $t_1\lambda_2\lambda_3$ ,  $t_2\lambda_3\lambda_1$ , and  $t_3\lambda_1\lambda_2$ , respectively, where  $t_1$ ,  $t_2$ , and  $t_3$  are the forces per unit area acting on the faces perpendicular to three axes, respectively. We now consider a pure homogeneous deformation

in which the extension ratios are changed from  $(\lambda_1, \lambda_2, \lambda_3)$  to  $(\lambda_1 + \delta\lambda_1, \lambda_2 + \delta\lambda_2, \lambda_3 + \delta\lambda_3)$ . The work done by the external forces  $F_{st}$  in this virtual deformation is

$$\delta F_{st} = t_1\lambda_2\lambda_3\delta\lambda_1 + t_2\lambda_3\lambda_1\delta\lambda_2 + t_3\lambda_1\lambda_2\delta\lambda_3 \quad (1)$$

or

$$\delta F_{st} = \frac{\partial F_{st}}{\partial \lambda_1} \delta\lambda_1 + \frac{\partial F_{st}}{\partial \lambda_2} \delta\lambda_2 + \frac{\partial F_{st}}{\partial \lambda_3} \delta\lambda_3 \quad (2)$$

In the case of an incompressible isotropic material, the  $\lambda_i$  are not independent of each other, but related by

$$\lambda_1\lambda_2\lambda_3 = 1 \quad (3)$$

or

$$\frac{\delta\lambda_1}{\lambda_1} + \frac{\delta\lambda_2}{\lambda_2} + \frac{\delta\lambda_3}{\lambda_3} = 0 \quad (4)$$

Equation (2) is now valid for all values of  $\delta\lambda_1$ ,  $\delta\lambda_2$ , and  $\delta\lambda_3$  satisfying this condition. With the use of the method of undetermined multipliers to take account of this restriction, eqs. (1), (2), and (4) yield

$$\begin{aligned} t_1 &= (1/\lambda_2\lambda_3)(\partial F_{st}/\partial \lambda_1) - p \\ t_2 &= (1/\lambda_3\lambda_1)(\partial F_{st}/\partial \lambda_2) - p \\ t_3 &= (1/\lambda_1\lambda_2)(\partial F_{st}/\partial \lambda_3) - p \end{aligned} \quad (5)$$

where  $p$  is an arbitrary constant.

In the case of a simple extension, external force acts only in the direction parallel to the  $x$ -axis, while no forces are applied to the faces of the cube perpendicular to the  $y$ - and  $z$ -axes. In this case

$$t_2 = t_3 = 0 \quad (6)$$

$$\lambda_2 = \lambda_3 = \lambda_1^{-1/2} \quad (7)$$

Introducing these results into the eqs. (5), we obtain

$$t_1 = (1/\lambda_2\lambda_3)(\partial F_{st}/\partial\lambda_1) - (1/\lambda_3\lambda_1)(\partial F_{st}/\partial\lambda_2)$$

$$= \lambda_1(\partial F_{st}/\partial\lambda_1) - (1/\lambda_1^{1/2})(\partial F_{st}/\partial\lambda_2) \quad (8)$$

Now, we consider the deformation of a polymeric network structure. If it is assumed that the chain displacement vector undergoes an affine deformation during extension, the strain energy function can be computed as a sum of the strain energy function of each individual network chains.

$$F_{st} = \sum_{i=1}^N (f_{st})_i \quad (9)$$

where  $(f_{st})_i$  is the strain energy function of the  $i$ th chain.  $N$  is the number of network chains in a unit volume. If we now let the number of the molecular chains traversing the unit area perpendicular to the  $x$ -axis be  $\nu_x$ , then the sum of the strain energy function of these chains is written

$$(\mathfrak{F}_{st})_x = \sum_{i=1}^{\nu_x} (f_{st})_i \quad (10)$$

with similar expression for  $(\mathfrak{F}_{st})_y$  and  $(\mathfrak{F}_{st})_z$ . When the quantities  $N$ ,  $\nu_x$ ,  $\nu_y$ , and  $\nu_z$  are sufficiently large, we can write

$$N = \nu_x/\langle x \rangle = \nu_y/\langle y \rangle = \nu_z/\langle z \rangle \quad (11)$$

for the isotropical network, where  $\langle x \rangle$ ,  $\langle y \rangle$ , and  $\langle z \rangle$  are the mean values of the projection of the chain displacement vector on the  $x$ -,  $y$ -, and  $z$ -axes and where  $x \geq 0$ ,  $y \geq 0$ , and  $z \geq 0$ . By use of this relation eq. (10) can be rewritten

$$(\mathfrak{F}_{st})_x = \sum_{i=1}^{\nu_x} (f_{st})_i = \langle x \rangle \sum_{i=1}^N (f_{st})_i = \langle x \rangle F_{st} \quad (12)$$

From this relation, it can be seen that  $(\mathfrak{F}_{st})_x$  is the strain energy function for a thin disk,  $\langle x \rangle$  in height, cross-sectioned perpendicularly to the extension direction from the cuboid.

When the body is stretched and its macroscopic deformation is expressed by  $(\lambda_1, \lambda_2, \lambda_3)$ , the components of the chain displacement vector are  $\lambda_1 x_0$ ,  $\lambda_2 y_0$ , and  $\lambda_3 z_0$ , respectively, where  $x_0$ ,  $y_0$ , and  $z_0$  are the components of the chain displacement vector in the absence of the external force. The force acting on the upper and lower faces of the above thin disk is obtained by summation of the tension for these  $\nu_x$  chains

$$\mathfrak{F}_x = \frac{\delta(\mathfrak{F}_{st})_x}{\delta(\lambda_1 \langle x_0 \rangle)} = \langle x \rangle \frac{\partial F_{st}}{\partial(\langle x_0 \rangle \lambda_1)} = \lambda_1 \frac{\partial F_{st}}{\partial \lambda_1} \quad (13)$$

It can be seen from eq. (13) that eq. (8) can be expressed as follows:

$$t_1 = [\text{Sum of the tension of the total molecular chains traversing a unit cross section}]$$

$$- [\text{Sum of the tension of the total molecular chains traversing a unit lateral face}] \quad (14)$$

When the deformation contains plastic flow, a part of the external work is dissipated as the work done against the internal viscous resistance. In this case, eq. (8) cannot be used to calculate the force, while the relation (14) may be used, provided that the stress propagates only through the network chains.

### One-Dimensional Model

Let us now consider the deformation of a plastic body. In the first place, for simplicity, we consider the one-dimensional problem. It is assumed that all chains have the same length  $l_0$  in the equilibrium state. The simplest assumption one can make for the elasticity of the chain is that the tension of the chain is proportional to the extension, i.e.:

$$f = ckT[(l/l_0) - 1] \quad (15)$$

where  $k$  is Boltzmann's constant,  $T$  the absolute temperature, and  $c$  is a constant which depends on the chemical nature of the material.

Now we consider the deformation of the chain (Fig. 1). Two end points of a chain, A and B, move to A' and B' after the deformation, respectively. We denote the distance between A' and B' by  $l_1$ , and the displacement BB' by  $l_2$ . Then the virtual length of the chain is  $l_1$ , while  $l_2$  is the flow distance. In this case we must use  $l_1$  as the chain length in eq. (15). The sum of the tension of chains traversing the cross section is given by

$$\mathfrak{F} = ckT \sum_{i=1}^{\nu} [(l_i/l_0) - 1] \quad (16)$$

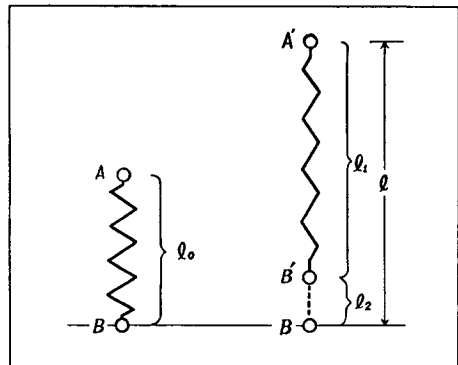


Fig. 1. Displacement of molecular chains.

In general, the velocity of the viscous flow of the chain end is a function of the extension of the chain. For simplicity we assume that the velocity of the viscous flow of the chain end is proportional to the virtual extension of the chain, i.e.:

$$\frac{dl_2}{dt} = \beta(l_1 - l_0) \quad (17)$$

where  $\beta$  is a proportional constant. Since we assumed Hooke's law for the elasticity, eq. (17) means that the flow of the molecular chain is Newtonian flow.

For extension at a constant rate the simplest possible expression for the displacement of the chain is that the position of one end of the chain moves with the same velocity as that of the macroscopic deformation, while the displacement of the opposite end is determined by eq. (17).

These relations are expressed by

$$l = l_0(1 + \alpha t) \quad (18)$$

$$dl_2/dt = d(l - l_1)/dt = \beta(l_1 - l_0) \quad (19)$$

where  $\alpha$  is the extension rate. Thus we have:

$$(dl_1/dt) + \beta l_1 = (dl/dt) + \beta l_0 = l_0(\alpha + \beta) \quad (20)$$

From this equation we have the expression for the virtual elongation of the chain:

$$l_1 = l_0 + (\alpha/\beta) l_0 (1 - e^{-\beta t}) \quad (21)$$

Inserting eq. (21) into eq. (16) we obtain:

$$\mathfrak{F} = ckTv(\alpha/\beta)(1 - e^{-\beta t}) \quad (22)$$

Now we have to calculate the number of chains penetrating the cross section. On stretching, the cross-sectional area become narrower. Though the number of chains traversing the cross section is unaltered in pure elastic deformation, when viscous flow of the molecular chain takes place, it decreases with deformation. In the later case the number of chains may be written

$$\nu = \nu_0(l_1/l) \quad (23)$$

where  $\nu_0$  is the number of chains traversing the cross section in the absence of external force. Inserting eqs. (18) and (21) into eq. (23) we obtain:

$$\nu = [1/(1 + \alpha t)][1 + (\alpha/\beta)(1 - e^{-\beta t})] \quad (24)$$

Using this we obtain an expression for the force necessary to stretch the sample at constant rate:

$$\mathfrak{F} = \frac{E_0}{1 + \alpha t} \{(\tau\alpha)^2[1 - e^{-t/\tau}]^2 + (\tau\alpha)[1 - e^{-t/\tau}]\} \quad (25)$$

$$\tau = 1/\beta \quad (26)$$

$$E_0 = ckTv_0 \quad (27)$$

Replacing  $\alpha t$  by  $\xi$  we rewrite the above relation:

$$\mathfrak{F} = \frac{E_0}{1 + \xi} \{(\tau\alpha)^2[1 - e^{-\xi/\tau\alpha}]^2 + (\tau\alpha)[1 - e^{-\xi/\tau\alpha}]\} \quad (28)$$

The initial elastic modulus is obtained by differentiation with respect to  $\xi$  and putting  $\xi = 0$ .

$$(\partial\mathfrak{F}/\partial\xi)_{\xi=0} = E_0 \quad (29)$$

The tension referred to the deformed cross-sectional area is given by

$$\begin{aligned} F &= \mathfrak{F}(1 + \xi) \\ &= E_0 \{(\tau\alpha)^2[1 - e^{-\xi/\tau\alpha}]^2 + (\tau\alpha)[1 - e^{-\xi/\tau\alpha}]\} \end{aligned} \quad (30)$$

When the deformation is small, the first term in the braces can be neglected as compared with the second term, and eq. (30) can be reduced to:

$$F \simeq E_0(\tau\alpha)(1 - e^{-\xi/\tau\alpha}) \quad (31)$$

This expression is equivalent to that calculated for the Maxwell model. Therefore the quantity

$$\tau E_0 \equiv \eta_0 \quad (32)$$

corresponds to the viscosity constant of the dashpot of the Maxwell Model, where  $E_0$  is the spring constant and  $\tau$  the relaxation time.

### Three-Dimensional Model

To calculate the stress of the three-dimensional model, the assumptions of the kinetic theory in the Gaussian approximation will be adopted. It is known that the strain energy function of a deformed chain is given by

$$f_{st} = (ckT/2)(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) \quad (33)$$

where

$$\lambda_1 = x/x_0$$

$$\lambda_2 = y/y_0$$

$$\lambda_3 = z/z_0$$

and where  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$  are the macroscopic deformations in the  $x$ -,  $y$ -,  $z$ -directions, and  $x$ ,  $y$ ,  $z$

are the components of the chain displacement vector connecting the chain ends in the deformed state.

If we now let the numbers of chains traversing the unit areas perpendicular and parallel to the extension direction be  $\nu_{\perp}$  and  $\nu_{\parallel}$ , respectively, then the sum of the tension of these chains are given by

$$t_{\perp} = ckT \sum_{i=1}^{\nu_{\perp}} (1/x_{0i})(x_i/x_{0i}) \quad (34)$$

$$t_{\parallel} = ckT \sum_{i=1}^{\nu_{\parallel}} (1/y_{0i})(y_i/y_{0i}) \quad (35)$$

Now let us consider the virtual chain length and the number of traversing chains. If we assume Newtonian viscosity for the flow of the molecular chain, then by the analogous treatment as in the preceding one-dimensional model,  $x$  can be expressed by

$$x = x_0[1 + (\alpha/\beta)(1 - e^{-\beta t})] \quad (36)$$

If the material is incompressible,  $x$  and  $y$  are related by

$$\langle x \rangle \langle y \rangle^2 = \langle x_0 \rangle^3 \quad (37)$$

We then have, on the average,

$$y = y_0[1 + (\alpha/\beta)(1 - e^{-\beta t})]^{-1/2} \quad (38)$$

Let the number of molecular chains traversing the unit cross-sectional area in the undeformed state be  $\nu_0$ . The number of chains penetrating the cross section will decrease after the deformation in the way expressed by eq. (23). Considering the decrease of the cross-sectional area we get

$$\begin{aligned} \nu_{\parallel} &= (1 + \alpha t)\nu_0(x/x_0) \\ &= \nu_0[1 + (\alpha/\beta)(1 - e^{-\beta t})] \end{aligned} \quad (39)$$

where  $x_a$  is the apparent deformation corresponding to  $l$  in the one-dimensional model and  $x$  is the virtual component of the displacement vector in the direction of the external force. Analogously, the number of chains traversing the unit area parallel to the extension direction is given by

$$\nu_{\perp} = \nu_0[1 + (\alpha/\beta)(1 - e^{-\beta t})]^{-1/2} \quad (40)$$

On the basis of these relations the tension is given by

$$\begin{aligned} F &= \mathfrak{F}(1 + \alpha t) = t_{\parallel} - t_{\perp} \\ &= ckTN_0 \left\{ \left[ 1 + \frac{\alpha}{\beta}(1 - e^{-\beta t}) \right]^2 \right. \\ &\quad \left. - \left[ 1 + \frac{\alpha}{\beta}(1 - e^{-\beta t}) \right]^{-1} \right\} \end{aligned} \quad (41)$$

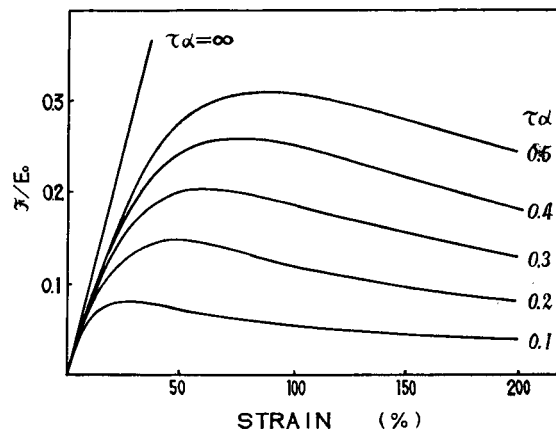


Fig. 2. Calculated stress-strain curves for various values of  $\tau\alpha$ .

The tension per initial unit cross section is

$$\begin{aligned} \mathfrak{F} &= ckTN_0 \frac{1}{1 + \alpha t} \left\{ \left[ 1 + \frac{\alpha}{\beta}(1 - e^{-\beta t}) \right]^2 \right. \\ &\quad \left. - \left[ 1 + \frac{\alpha}{\beta}(1 - e^{-\beta t}) \right]^{-1} \right\} \end{aligned} \quad (42)$$

where  $N_0$  is the number of chains per unit volume and given by eq. (11).

When viscous flow does not occur, the tension is obtained by putting  $\beta = 0$  in eq. (42):

$$\mathfrak{F} = ckTN_0 \left[ (1 + \alpha t) - \frac{1}{(1 + \alpha t)^2} \right] \quad (43)$$

This expression is just the same as that for the rubber elasticity.

In the case of actual polymer, one might expect that eqs. (25) and (42) represent a very drastic oversimplification of the actual mechanism of the deformation. Apart from the adequacy of using the Gaussian approximation, it seems more reasonable to postulate the existence of an array of chains which can be divided into discrete sets of markedly different character. Let us suppose that there are  $N_i$  chains with elastic constant  $c_i$  and relaxation time  $\tau_i$  pr unit cube. Then eq. (42) can be replaced by

$$\begin{aligned} \mathfrak{F} &= \frac{kT}{1 + \alpha} \sum_i c_i N_i \left\{ \left[ 1 + (\tau_i \alpha)(1 - e^{-t/\tau_i}) \right]^2 \right. \\ &\quad \left. - \left[ 1 + (\tau_i \alpha)(1 - e^{-t/\tau_i}) \right]^{-1} \right\} \end{aligned} \quad (44)$$

Figure 2 shows the load-elongation curves calculated by eq. (25) for various  $(\tau\alpha)$ . All curves start with same initial slope and attain to the maximum point. After passing the maximum point

the load declines steadily and asymptotically approaches the abscissa. The load-elongation curves calculated by eq. (42) decline more rapidly.

### EXPERIMENTAL AND RESULTS

We used a polyethylene terephthalate undrawn filament whose intrinsic viscosity  $[\eta]$  in *o*-chlorophenol at 25°C. is 0.60, and whose birefringence is 0.0022 and density is 1.340 at 25°C. An Instron-type tensile testing machine was used for the measurement of the stress-strain curves. For measurement at elevated temperature an electrically heated bath was placed around the sample. Measurements were made over the temperature range from 80 up to 120°C. at various rates of extension. The initial sample length was 10 cm.

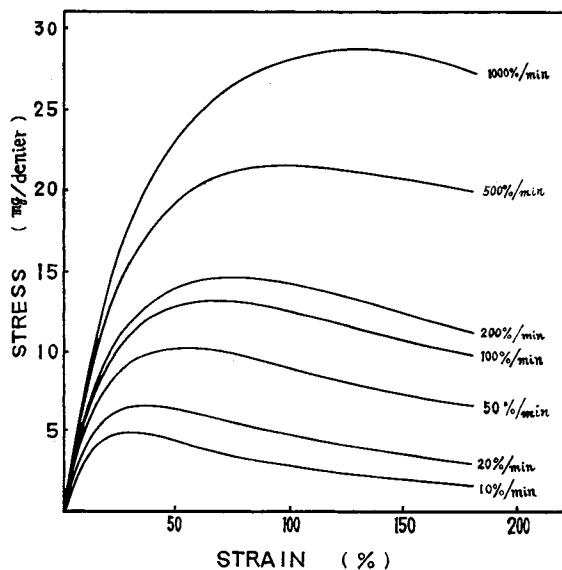


Fig. 3. Stress-strain curves measured at 80°C. in water.

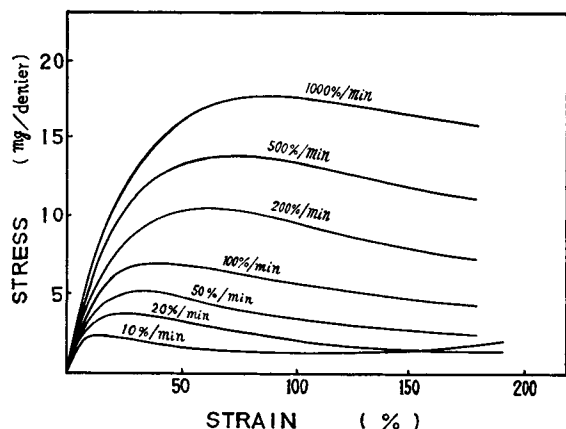


Fig. 4. Stress-strain curves measured at 85°C. in water.

Stress-strain curves measured in the water bath are shown in Figures 3-7. The curves observed in the glycerin bath are shown in Figures 8-14.

As the result of increase of the molecular mobility, the stress induced by strain decreases with rising temperature. The behavior of the material tends towards that of a simple elastoviscous fluid, and in some appropriate condition the filament can be extended to unusually large extensions. At low temperature and high rate of extension, the stress-strain curve is a sigmoid. This sigmoidal shape of stress-strain curve indicates a finite

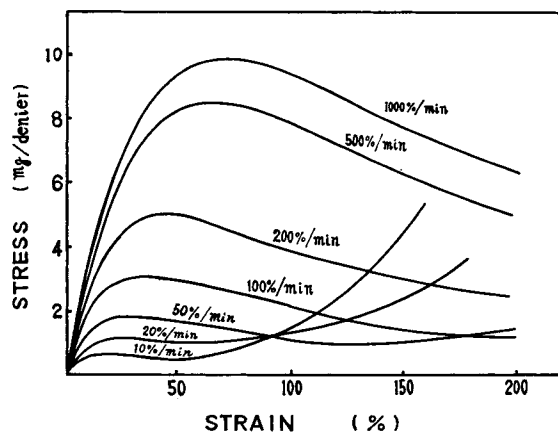


Fig. 5. Stress-strain curves measured at 90°C. in water.

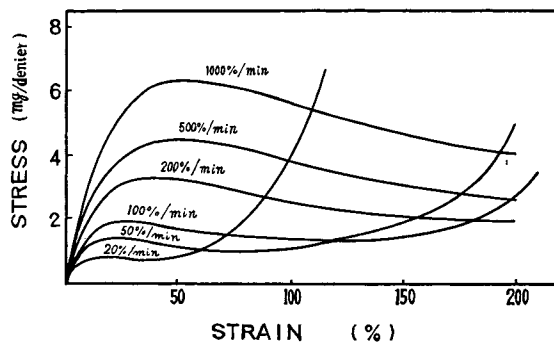


Fig. 6. Stress-strain curves measured at 95°C. in water.

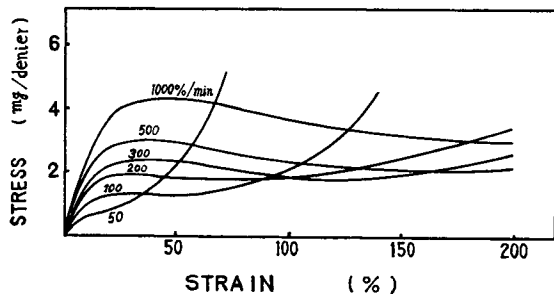


Fig. 7. Stress-strain curves measured at 100°C. in water.

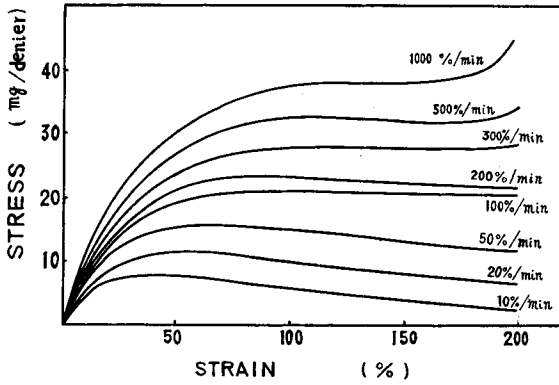


Fig. 8. Stress-strain curves measured at 90°C. in glycerin.

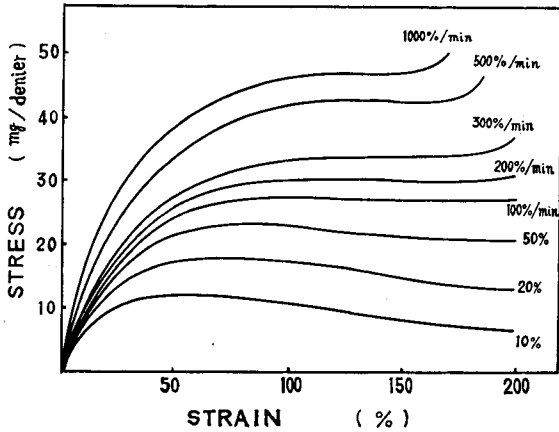


Fig. 9. Stress-strain curves measured at 95°C. in glycerin.

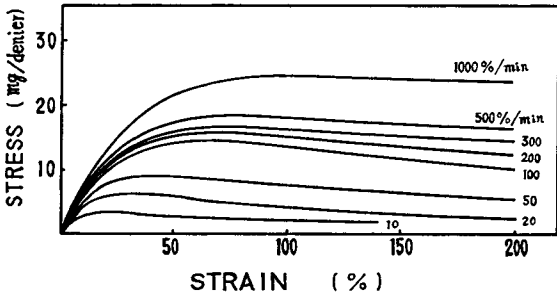


Fig. 10. Stress-strain curves measured at 100°C. in glycerin.

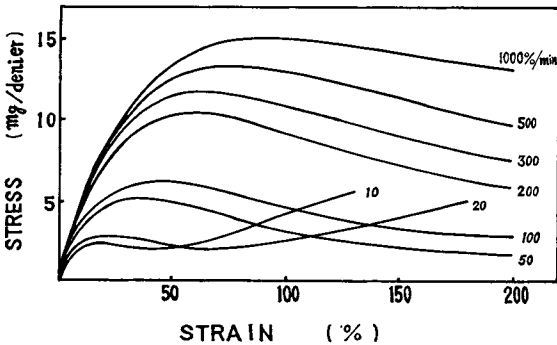


Fig. 11. Stress-strain curves measured at 105°C. in glycerin.

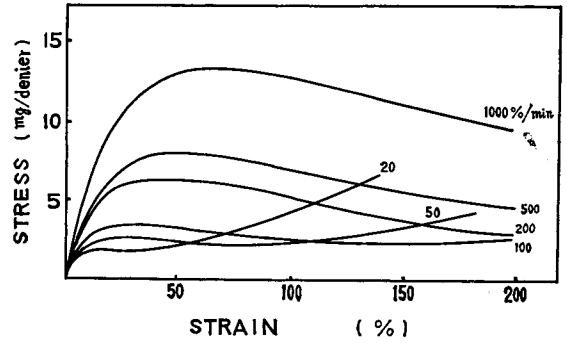


Fig. 12. Stress-strain curves measured at 110°C. in glycerin.

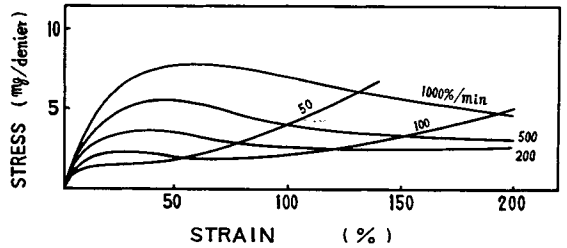


Fig. 13. Stress-strain curves measured at 115°C. in glycerin.

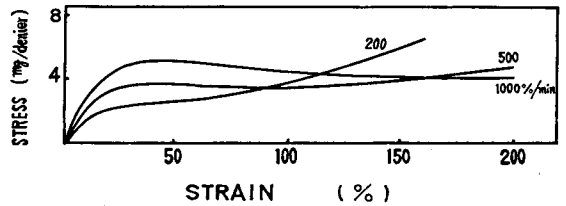


Fig. 14. Stress-strain curves measured at 120°C. in glycerin.

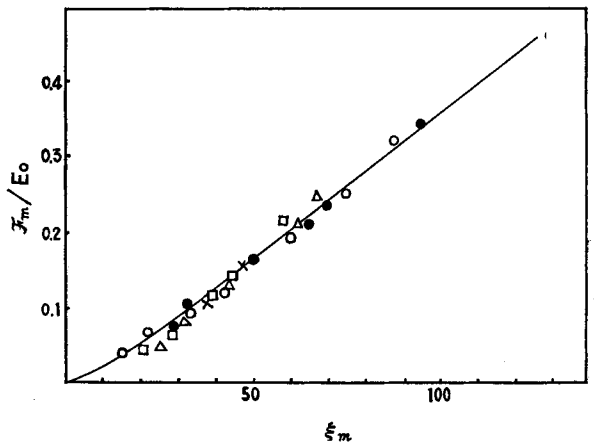


Fig. 15.  $\bar{\sigma}_m/E$  vs.  $\xi_m$ . Data obtained in water at various temperatures and rates of extension: (●) 80°C.; (○) 85°C.; (Δ) 90°C.; (□) 95°C.; (×) 100°C.

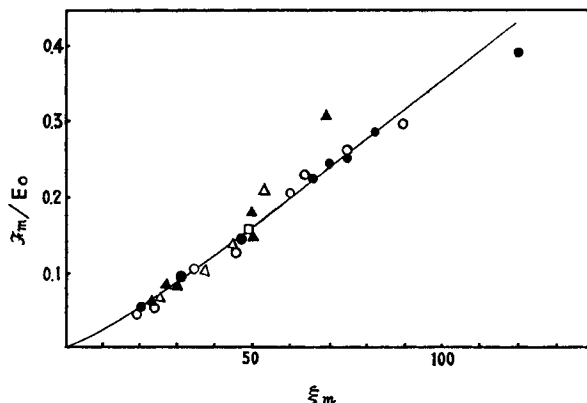


Fig. 16.  $F_m/E$  vs.  $\xi_m$ . Data obtained in glycerin at various temperatures and rates of extension: (●) 100°C.; (○) 105°C.; (▲) 110°C.; (△) 115°C.; (□) 120°C.

extensibility and orientation of a long-chain molecules. This reinforcement may be attributed to the strain-induced crystallization as pointed out by Thompson.<sup>2</sup> On the other hand, at higher temperature and low rate of extension, some reinforcement does occur, presumably due to crystallization induced by an increase of the thermal motion. Therefore, in order to observe the super-drawing phenomenon in polyethylene terephthalate an appropriate range of the straining rate and temperature is required.

It was seen that the stress-strain curves represented by eqs. (28) and (42) have a maximum. The strain at which the tensile stress attains the maximum value is obtained by differentiating the equation with respect to  $\xi$  and equating to zero. Differentiating eq. (28) and equating to zero we get:

$$0 = -\frac{1}{(1+\xi)^2} [(\tau\alpha)^2(1 - e^{-\xi/\tau\alpha})^2 + (\tau\alpha)(1 - e^{-\xi/\tau\alpha})] + \frac{1}{(1+\xi)} [2(\tau\alpha)(1 - e^{-\xi/\tau\alpha}) + 1]e^{-\xi/\tau\alpha} \quad (45)$$

The elongation corresponding to the maximum tensile force,  $\xi_m$ , is given by eq. (45). Inserting  $\xi_m$  into eq. (28) yields the theoretical relation between the maximum value of the tensile force  $F_m$  and the corresponding strain  $\xi_m$ . In Figure 15  $F_m/E_0$  is plotted against  $\xi_m$  for the data observed in the water bath. The corresponding relation for the data obtained in the glycerin bath is shown in Figure 16. The solid curve in the figure is the theoretical curve. In each case all experimental data agree quite well with the theoretical curve.

TABLE I  
Initial Modulus  $E_0$

	Temp., °C.	$E_0 \times 10^{-4}$ , g./cm. <sup>2</sup>
In water	80	7.48
	85	6.46
	90	4.76
	95	3.67
	100	3.26
In glycerin	100	7.65
	105	6.12
	110	5.10
	115	4.47
	120	4.08

The initial elastic modulus data derived from the initial slope of the stress-strain curves are summarized in Table I.

When  $\xi_m$  is known, the relaxation time  $\tau$  is calculated as a function of it by eq. (45). Then the viscosity coefficient can be calculated by eq. (32). The obtained values are shown in Table II and plotted against temperature in Figures 17 and 18. It can be seen that the viscosity coefficient depends not only on the temperature, but on the rate of extension. The variance of  $\log \eta_0$  with  $(1/T)$  at several rates of extension is approximately represented by a set of parallel lines obeying the following relationships:

In water:

$$\eta_0 = \alpha^{-0.506} \exp \{-36.6 + 17200(1/T)\}$$

In glycerin:

$$\eta_0 = \alpha^{-0.512} \exp \{-28.7 + 15100(1/T)\}$$

It is seen to obey an Arrhenius relation and estimated activation energies are 34 kcal./mole in

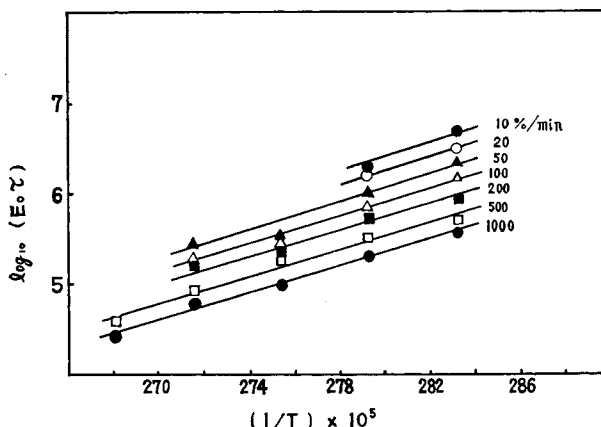


Fig. 17. Temperature dependence of viscosity in water.

TABLE II

	Temp., °C.	log $\eta_0$ , g./cm. <sup>2</sup> /sec., at various extension rates						
		10%/min.	20%/min.	50%/min.	100%/min.	200%/min.	500%/min.	1000%/min.
In water	80	6.65	6.49	6.32	6.16	5.91	5.70	5.56
	85	6.26	6.19	5.99	5.83	5.45	5.49	5.29
	90			5.55	5.51	5.41	5.25	5.01
	95			5.43	5.31	5.25	4.94	4.81
	100						4.60	4.43
In glycerin	100	6.44	6.45	6.28	6.20	5.93	5.62	5.50
	105	6.32	6.17	6.00	5.83	5.75	5.47	5.27
	110			5.67	5.50	5.52	5.18	5.05
	115				5.38	5.27	5.02	4.87
	120							4.75

water and 30 kcal./mole in the glycerin. Marshall and Todd<sup>3</sup> measured the melt viscosity of polyethylene terephthalate. They showed that the activation energy of melt viscosity decreases with the limiting viscosity number to the low molecular weight region. In the low molecular weight region their observed values are scattered, and therefore it is difficult to deduce an accurate value of the activation energy from their results. However,

the activation energy of the melt viscosity of polyethylene terephthalate whose molecular weight is comparable with that of our sample would be presumably between 20 and 40 kcal./mole. Thompson obtained the activation energy of the critical strain rate as about 50 kcal./mole.

Initial elastic modulus and viscosity coefficients measured in the water and glycerin are plotted against temperature in Figures 19 and 20. The values observed in the water at any temperature is nearly equal to that obtained in glycerin at a temperature about 20°C. higher. This means that water attacks polyethylene terephthalate and lowers the softening point about 20°C.

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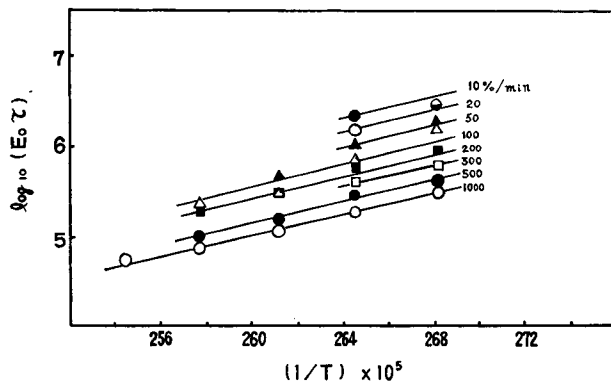


Fig. 18. Temperature dependence of viscosity in glycerin.

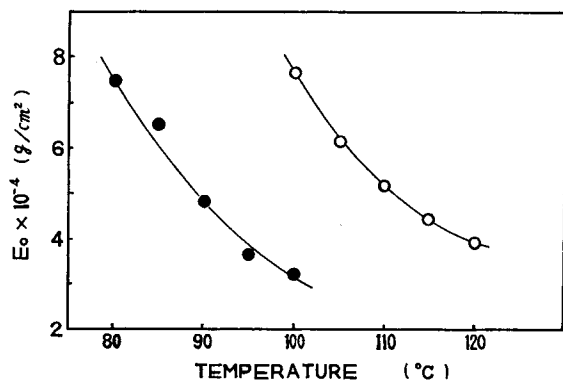


Fig. 19. Temperature dependence of initial elastic modulus: (●) in water; (○) in glycerin.

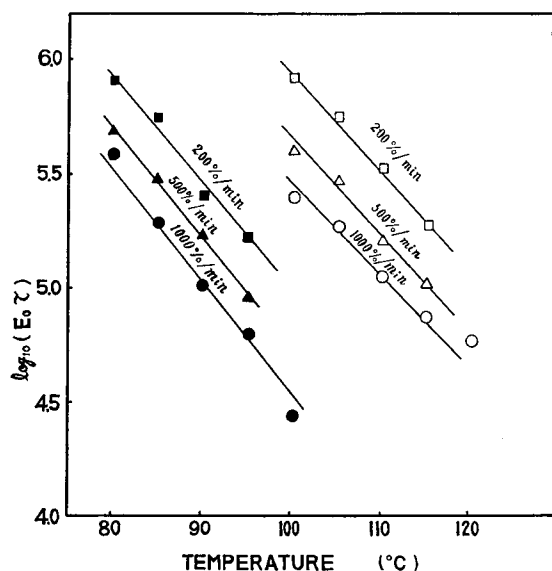


Fig. 20. Temperature dependence of viscosity at various rates of extension: (■, ▲, ●) in water; (□, △, ○) in glycerin.



### References

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### Synopsis

A viscoelastic theory based on a simple model is developed to describe the stress-strain relation of amorphous plastics above the glass temperature. One of the bases of the theory is that the stress is proportional to the number of molecular chains traversing a unit cross section. Experimental results for the stress-strain relation of amorphous polyethylene terephthalate in the range 80–120°C. are presented. These are shown to agree with the theory within the experimental error.

### Résumé

On développe une théorie viscoélastique basée sur un modèle simple, afin de décrire la relation tension-force de plastiques amorphes au dessus de la température de transi-

tion vitreuse. Une des bases de la théorie admet que la tension est proportionnelle au nombre de chaînes moléculaires traversant une section unitaire transversale. On présente des résultats expérimentaux pour la relation tension-force du téréphtalate de polyéthylène amorphe dans le domaine de températures de 80 à 120°C. On voit que ceux-ci concordent avec la théorie, endéans les erreurs expérimentales.

### Zusammenfassung

Zur Beschreibung des Spannungs-Dehnungsverhaltens von amorphen plastischen Stoffen oberhalb der Glastemperatur wurde eine auf einem einfachen Modell beruhende Viskoelastizitätstheorie entwickelt. Eine der Grundannahmen der Theorie ist, dass die Spannung der Zahl der Molekülketten, die den Einheitsquerschnitt durchsetzen, proportional ist. Experimentelle Ergebnisse für das Spannungs-Dehnungsverhalten von amorphem Polyäthylenterephthalat im Bereich von 80–120°C werden angegeben. Diese Ergebnisse stimmen innerhalb des experimentellen Fehlers mit der Theorie überein.

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