From the Noordelyk Technisch Instituut T.N.O. Groningen (Holland)

The Effect of Crystallization and Orientation on the Dynamic Mechanical Properties of Some Polymers

By H. A. Waterman

With 16 figures and 2 tables

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Introduction

Polymers used for the manufacturing of fibres are nearly all partly crystalline. Moreover, to give the fibres the desired properties for their use as a textile material, they are, after spinning, subjected to certain physical treatments. For example, polyamides and terylene just get their desired flexibility after a stretching procedure.

For small deformations the mechanical behavior of polymers can be described by their relaxation spectra. For finite deformations this treatment fails due to the appearance of nonlinear effects. Notwithstanding this it is possible in some cases to deduce from the relaxation spectrum valuable information about the behaviour at finite deformations. It is the aim of this investigation to study the change of the relaxation spectrum of polymers due to stretching.

Measuring Apparatus

To perform the measurements five different devices were used.

Low frequency range 0.2–20 Hz *)

In this frequency range a modified balance and a modified torsion pendulum were used. The modified balance is sketched in fig. 1. The restoring force is delivered partly by gravitation, partly by the stiffness of the samples. The beam of the balance was provided with a mirror which formed the magnified image of a hair along a scale marked on a wall. The balance was set into vibration, and the decaying amplitude was read from the scale. The frequency was measured with the aid of a stopwatch. The modified torsion pendulum is essentially the one described by *Tokita* (1). As a detection system a rotating drum driven by a synchronous motor, and provided with teledeltos paper, was used (2). In calculating tan δ and E from measurements with these devices, corrections were applied for the damping of the devices themselves and their frequencies without inserted samples, resp.

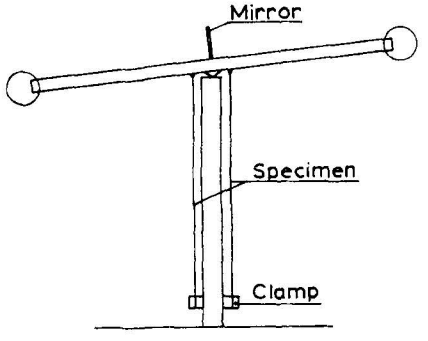


Fig. 1. Modified balance for measurements at low frequencies

Medium frequency range 50–10³ Hz

For this frequency range a resonance method was used. A block-diagram of the apparatus is given in fig. 2. The vibrating system is formed by the sample

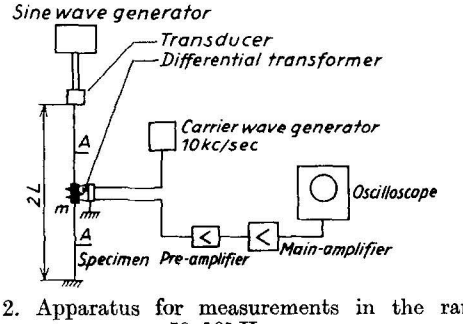


Fig. 2. Apparatus for measurements in the range 50–10³ Hz

*) Hz stands for c/s in accordance with a recommendation made by I.U.P.A.P.

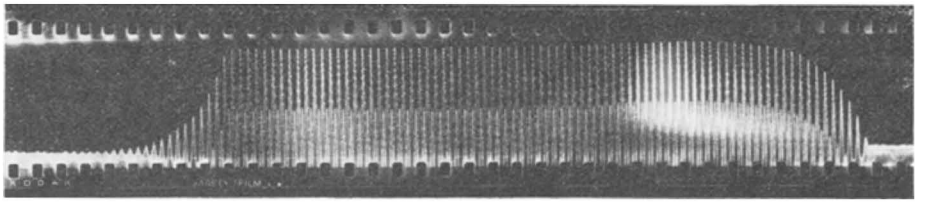


Fig. 3. Oscillogram of a damped oscillation taken with the apparatus of fig. 2

and a mass glued to it in the middle. This mass is made up of two half-cylinders of ferroxcube and forms at the same time the core of a differential transformer. The sample is fixed at one end, and the other end is connected to a transducer of the loudspeaker type. The system is put into resonance by adjusting the frequency of the signal generator driving the transducer. Once resonance is found, the current through the transducer is chopped by a multivibrator which also triggers the oscilloscope. In fig. 3 an oscillogram is reproduced. From the decay of the signal, tan δ can be found. *Young*'s modulus is found from the dimensions of the sample and the weight of the mass. For high frequencies, i. e. small masses, a correction must be applied for the mass of the sample (see Appendix).

High frequency range 10^3–10^5 Hz

In this frequency range the wave propagation method introduced by *Ballou* and *Smith* (3) was used. Until frequencies up to $25 \cdot 10^3$ Hz a phonograph cutterhead was used as an exciter and a commercial piezo-electric crystal as the pick-up. For higher frequencies piezo-electric crystals can be used for the exciter as well. An apparatus was built in which two 100 kHz x-cut quartz crystals served as the exciter and pick-up, respectively. Fig. 4 shows a measurement at 9 kHz for a polyvinyl alcohol multifilament. Here measurements were made point for point. Fig. 5 shows a measurement at 92 kHz for the same material. In this case the pick-up quartz crystal is driven by a synchronous motor and the pick-up signal, after detection, is fed to a recorder. *Young*'s modulus E can be found from the distance between the peaks in figs. 4 and 5, which equals half a wavelength. tan δ can be found by a procedure originating from *Ballou* (3).

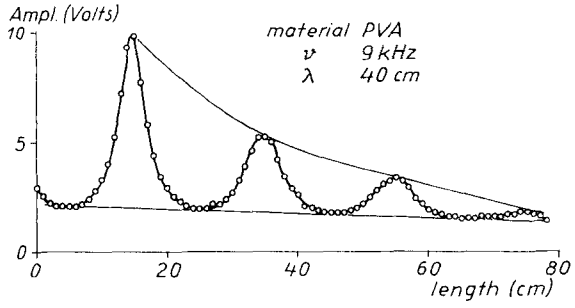


Fig. 4. Measurement by the wave propagation method. Material: polyvinyl alcohol multifilament. Frequency: 9 kHz

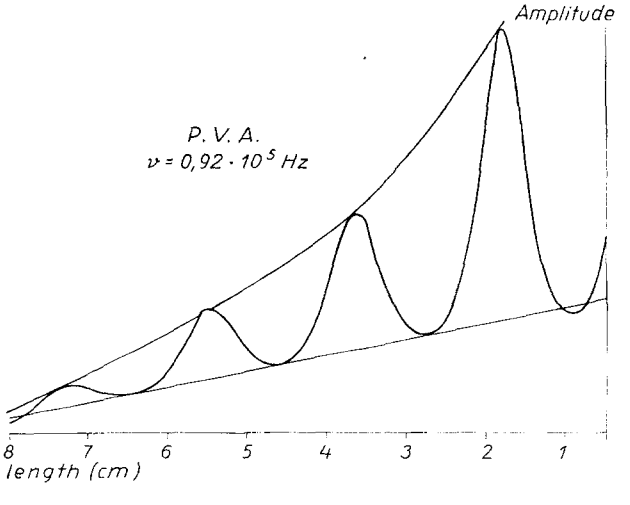


Fig. 5. Measurement by the wave propagation method. Material: polyvinyl alcohol multifilament. Frequency: 92 kHz

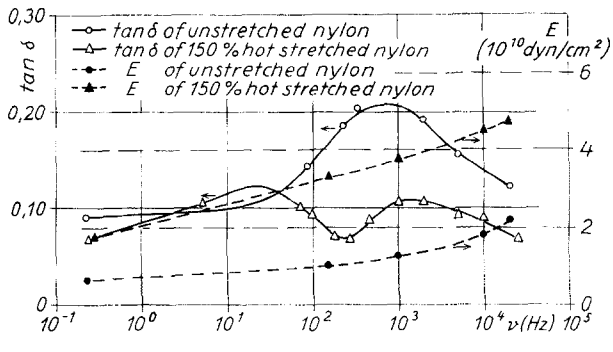
Measuring results

a) Measurements at room temperature and 65% R. H.

Nylon-6

In fig. 6 *Young*'s modulus E and tan δ are given for a nylon-6 multifilament as spun and after stretching at high temperature to 2.5× its original length. It can be seen from this figure that whereas the original material has one relaxation peak in the frequency range measured, the stretched material has two relaxation peaks. This seems a rather surprising result at first sight, but the introduction of an extra relaxation peak in nylon-6 by stretching has already been suggested by *F. H. Müller* (4) on the grounds of dielectric measurements. Measurements of the mechanical loss tangent of nylon-6 stretched by 50% and 100% of its original length has been carried out by *Tokita* (1). He finds a relaxation peak that shifts to lower frequencies as the amount of stretching increases. The relaxation times given by *Tokita* are quoted in table 1, together with the relaxation times deduced from fig. 6.

Fig. 6. *Young*'s modulus E and loss tangent tan δ vs. frequency for unstretched and 150% hot stretched nylon-6 multifilament



The data of table 1 suggest that the relaxation peak with the longest relaxation time, viz. 8×10^{-3} sec, has to be identified with the peak found in the unstretched material. Taking this for granted, the question arises whether the second peak in the stretched sample is a really new peak, which means

Table 1

amount of stretching %	relaxation time (sec) *Tokita*	this investigation
0	0.2×10^{-3}	0.23×10^{-3}
50	2.6×10^{-3}	
100	3.9×10^{-3}	
150		8×10^{-3})
		(0.12×10^{-3})

Table 2

measuring frequency in Hz	frequency location at 20 °C in kHz β	α	Reference
7.1	50–1,000		*Schmieder and Wolf* (6)
5.2		10^{-11}	*Wolf and Schmieder* (6)
10^2	20– 100	$4 \cdot 10^{-12}$	*Becker* and *Oberst* (7)
10^2	30– 200	$3 \cdot 10^{-11}$	*Becker* and *Oberst* (7)
1.66×10^2	200–1,700	$2 \cdot 10^{-13}$	*Kawaguchi* (8)
10^3	30– 100	$5 \cdot 10^{-13}$	*Becker* and *Oberst* (6)
10^5	100		*Yamamoto* and *Wada* (9)
1.46×10^6	350– 500		*Wada* and *Yamamoto* (9)

that we have introduced an entirely new relaxation mechanism by stretching, or that this peak has merely been shifted into the measuring range. To answer this question, we first of all had to identify the peak in the unstretched material. From the work of several investigators on nylon-6 [see e. g. the review article of *Woodward* and *Sauer* (5)], we know that this polymer has four dispersion regions in the temperature range from 80 °K to approximately 500 °K. These regions are frequency dependent, but are located at about 160 °K (γ-dispersion), 230 °K (β-dispersion), 350 °K (α-dispersion) and just below the crystalline melting point (α'-dispersion). Further it has been found that the exact temperature positions of these dispersion regions differ from material to material, depending on the thermal history and/or crystallinity and water content. From the data quoted in the literature, *Woodward* and *Sauer* (5) calculate approximative activation energies of 15–20 kcal/mol and 95 kcal/mol for the β and α mechanisms, respectively. Using these activation energies, the frequency locations of the β and α dispersions at 20 °C were calculated from literature data. These data are collected in table 2. The frequency locations of the peak found by *Tokita*, and in this investigation, are 0.8 kHz and 0.7 kHz, respectively.

Upon inspection of table 2 it follows that these frequencies definitely fall outside the ranges covered by the data in this table.

Now we know from the work of *Becker* and *Oberst* (7) that the water content of the polymer has a pronounced effect upon the α-dispersion. At a frequency of 10^2Hz the peak of the α-dispersion shifts from about 70 °C for the dry polymer to about 0 °C for the polymer saturated with water. The direction of the shift is in accordance with the generally accepted viewpoint that the water in the polymer acts as an internal plasticizer. This means that the internal motion of molecular groups is less restricted in the presence of water, so that in measurements at constant frequency the relaxation peak shifts to lower temperature. Similarly, in measurements at constant temperature (e. g. 20 °C) the presence of water causes a shift of the peak to higher frequencies. In view of this, and the fact that our measurements were carried out at the rather high relative humidity of 65%, it looks reasonable to identify the peak found in the unstretched sample with the α-dispersion. There are two further arguments which support this hypothesis. In the first place, the presence of water effects the β-peak in the same sense as it does the α-peak, i. e. at constant temperature the peak shifts to higher frequencies. As we have seen, however, our peak occurs at a frequency much lower than the frequency we expect from table 2 for the β-peak to occur. A perhaps more convincing argument is found in the height of the peak. Whereas the peak heights in *Tokita*'s and this work are 0.16 and 0.21, respectively, the peak height for the β-dispersion is of the order of 0.02. Therefore, in our opinion, the dispersion found by *Tokita* and reproduced in our measurements is the α-dispersion. Further evidence was gained from measurements at different temperatures, and will be given below. Going to higher frequencies the first peak we expect to meet is the β-peak. Therefore we have to consider the possibility that the dispersion peaking at 1.3 kHz in the 150% stretched material is the shifted β-peak. We saw that the α-peak in the stretched material is shifted by a factor of about 40 with respect to the unstretched material. If for the β-peak we assume a shifting of the same amount, the β-peak in the unstretched material would occur at roughly 10^5 Hz. This is exactly the frequency *Yamamoto* and *Wada* (9) used in their measurements, and they had found the β-peak at 290 °K. Of course many objections can be raised against the foregoing; perhaps the best we can say is

that there is some evidence for the hypothesis that the peaks found for stretched nylon-6 are the shifted α- and β-peaks.

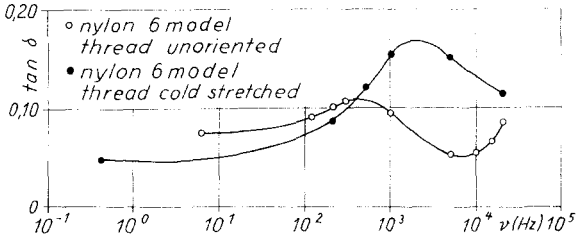


Fig. 7. Loss tangent tan δ vs. frequency for unstretched and cold stretched nylon-6 monofilament

In fig. 7 tan δ vs. frequency is plotted for a nylon-6 model thread of approximately 0.5 mm diameter. In the unorientated material a dispersion is found: the α-peak, as we think, at a somewhat higher frequency (relaxation time 0.8×10^{-4} sec) than the peak in the 0% stretched sample; see fig. 6. This is in accordance with the results of *X*-ray measurements which show that in the 0% stretched sample of fig. 6 there is some orientation, whereas in the 0% stretched material of fig. 7 no orientation could be detected. The thread could be permanently stretched at room temperature, attended with neck-forming. Measurements for this cold-stretched material are reproduced also in fig. 7. Here, too, a shift of the α-peak takes place, while at the high frequency side the β-peak seems to enter the measuring range.

Polyvinyl alcohol

From fig. 8 it follows that essentially the same shifting process takes place in polyvinyl alcohol. For the 100% stretched fibre, two damping peaks fall within the measured frequency range. With increasing orientation the low frequency peak, which is the primary peak in this case, gradually leaves the experimental range. An attempt was made to find out the effect of a change in crystallinity on the relaxation spectrum. To this end, the fibres were heated for 5 minutes at 200 °C while keeping their lengths constant. It turned out, however, that together with an increase in crystallinity the orientation of the crystallites increases. In fig. 8 the modulus vs. frequency curves for these heat treated fibres are reproduced; it can be seen that a further shift takes place.

Polyvinyl alcohol is a very hydrophilic material and, therefore, preeminently suited to demonstrate the role of absorbed water as a plasticizer. To this end, in the medium

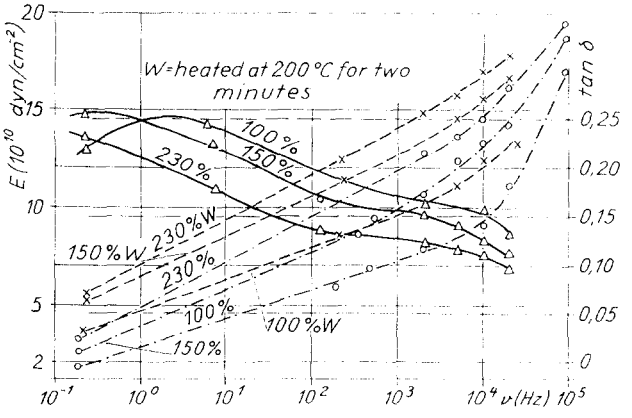


Fig. 8. *Young*'s modulus E and loss tangent tan δ vs. frequency of polyvinyl alcohol multifilament with various stretch ratios and heat treatments

frequency range measurements were performed of *Young*'s modulus and tan δ as a function of the relative humidity of the surrounding air. By mixing different amounts of dry and saturated air, and blowing this mixture into the measuring chamber around the fibres, each value of the relative humidity between 20% and 100% could be realized. The relative humidity was found by measuring the temperature difference between a dry and a wet thermocouple junction. Fig. 9 shows the measuring results for two samples with different amounts of crystalline material. It follows from this figure that the primary peak of the less crystalline (not heat treated) sample occurs at a relative humidity of $\sim$ 82%, when measuring at a few hundred Hz. Further it can be seen that the height of the peak is much greater (tan $\delta_{max} \sim 0.65$) than is found in fig. 8 (tan $\delta_{max} \sim 0.25$). This last feature makes it difficult to find the frequency shift of the primary peak with increasing humidity, when comparing figs 8 and 9. If

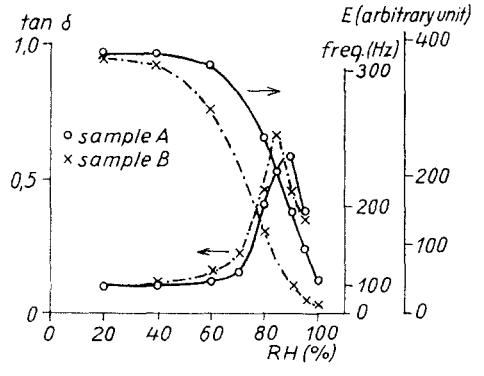


Fig. 9. *Young*'s modulus E and loss tangent tan δ vs. the relative humidity of the surrounding air for two polyvinyl alcohol multifilaments. Sample A is more crystalline than sample B

the peak height remained constant it could be concluded from these figures that in performing measurements at a constant relative humidity of 82%, the relaxation frequency shows a shift of more than three decades with respect to measurements at 65% relative humidity. This is not true when the peak height changes with relative humidity. Assuming that the height of the primary peak is a monotonously rising function of the relative humidity, which seems a plausible assumption, this shift will be even greater. Frequency shifts of many decades were also found by *Onogi* et al. (10) from stress-relaxation measurements. For a particular polyvinyl alcohol film they found a frequency shift of more than five decades in going from 65% to 82% relative humidity.

Further it can be seen from fig. 9 that the curves for the more crystalline sample have shifted to higher relative humidities with respect to those of the less crystalline sample. This is in accordance with the shifts found for the E-curves in fig. 8 for the heat-treated samples.

b) Low frequency measurements in the temperature range −100 °C to +200 °C

In order to obtain additional information about the effect of orientation on the mechanical properties of polymers, the modified torsion pendulum was adapted for measurements in the temperature range from −100 °C to +200 °C. For temperatures < 20 °C air was forced through a copper spiral immersed in liquid nitrogen. This air was mixed with a variable amount of air of room temperature, to reach the desired temperature. For temperatures above room temperature the air was forced through a copper pipe provided with an electrical heating element. As it was thought rather elaborate to control also the relative humidity in the temperature range mentioned, it was decided to eliminate the influence of water in the polymer by using carefully dried air.

Nylon-6

In fig. 10 measuring results are given for nylon-6 filaments with different amounts of stretching. The unstretched polymer is the one used in the measurements represented in fig. 6. The stretching procedure in this case was carried out at room temperature by an apparatus designed by Mr. *J. Seffelaar*[1]). With the aid of this apparatus it was possible to stretch the filaments homogeneously, i. e. without neck-forming, to any given value between 0% and 300%. There are in the temperature range covered two well-developed peaks, which are the β- and α-peak. At the high temperature side the beginning of the α'peak can be seen. This latter peak could not be measured completely, as the filaments started to flow under the small stress needed to keep them tight. The measurements show that after a slight increase for the 50% stretched filament there is a marked decrease of the height of the α-peak at the higher stretch levels, which is accompanied by a broadening of the peak. Also a slight temperature shift seems to occur between 0 and 50% stretching. Contrary to the behaviour of the α-peak, the peak height of the β-peak in-

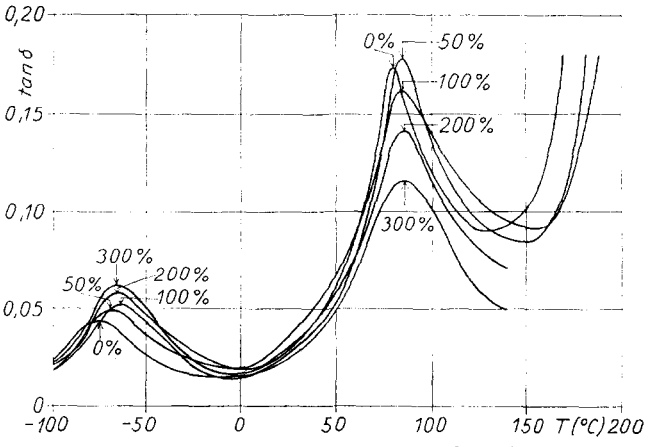


Fig. 10. Loss tangent tan δ vs. temperature for nylon-6 multifilaments with various stretch ratios. Frequency ~ 0.1 Hz

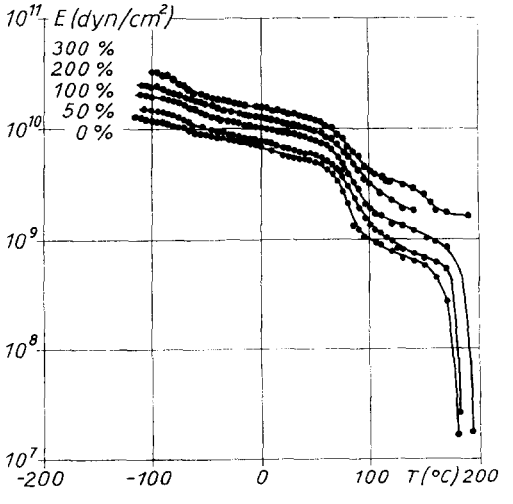


Fig. 11. *Young*'s modulus E vs. temperature for nylon-6 multifilaments with various stretch ratios. Frequency ~ 0.1 Hz

[1]) Central Laboratory T.N.O.

creases with the amount of stretching. Since in our room temperature measurements mentioned earlier, and presented in fig. 6, we found a decrease in peak height in the stretched samples, this supports our idea that the dispersion found in the unstretched samples is the α-dispersion. Also the fact that the peak height of the α-dispersion ($\sim$ 0.18) is nearly equal to the height of this peak (0.21) points into this direction.

Fig. 11 shows the *Young*'s moduli for these fibres. From this figure it can be judged that *Young*'s modulus increases with orientation over the temperature range investigated.

Polyurea

A few measurements were made at polyurea filaments supplied by Dr. *G. M. van der Want*[2]). In the experimental range there are two dispersions regions, as can be seen in fig. 12. For the unorientated, amorphous, material the measuring points in the region where the high temperature dispersion occurs, scatter considerably. This is probably due to the fact that the material starts to crystallize. It can be judged from the figure that this peak would be very high if, by some means, crystallization could be prevented. The low temperature peak, the maximum of which is located at about -40 °C, is very broad. The amorphous filament was stretched 300% at room temperature whereby crystallization was induced. The effect of this stretching on the damping curve is much the same as in the case of nylon-6; the high temperature peak lowers considerably, while the low temperature peak rises somewhat. At the highest temperatures a third peak seems to start. In analogy with the behaviour of polyamides, we expect this last peak to reflect the melting of the crystallites.

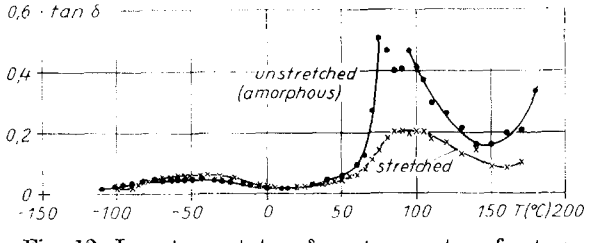


Fig. 12. Loss tangent tan δ vs. temperature for two polyurea monofilaments

Fig. 13 again shows the course of *Young*'s modulus with temperature. Here, too, we see a great difference between both curves in the region where the high temperature peak occurs.

[2]) Institute for Organic Chemistry T.N.O.

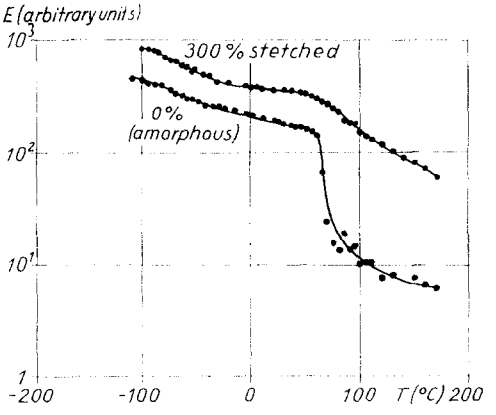


Fig. 13. *Young*'s modulus E vs. temperature for two polyurea monofilaments

Undoubtedly, the drop in *Young*'s modulus would be much greater if no crystallization took place. We think, therefore, that this drop reflects the glass-rubber transition of the amorphous material.

Natural rubber

It has been known for a long time that the stretching of vulcanized rubber results in the appearance of crystallization. From *X*-ray measurements it turned out that the crystallites are orientated in the direction of stretching. Determinations of the amount of crystallization by *X*-ray techniques have been carried out by *Field* (11), *Goppel* (12) and *Goppel* and *Arlman* (13). The latter two authors found for a pure gum compound that crystallization sets in at an elongation of about 200%, has a value of about 4% at 400% elongation and from this point rises linearly with the elongation until a value of about 32% is reached at an elongation of 800%.

A second way in which crystallization in natural rubbers can occur is by storage at a suitable, low temperature. The rate of crystallization is greatly temperature dependent. At low temperatures the gain in free energy by crystallization is great but, due to the very small mobility, the necessary diffusion is slow and so the crystallization rate is low. At temperatures just below the melting point of the crystallites the mobility is high but now the gain in free energy is small, resulting likewise in a low crystallization rate. From this it follows that there is an intermediate temperature where the crystallization rate reaches a maximum. Further it was found that on warming up the sample after crystallization, there is a temperature range in which the crystallites melt and besides that

the location of this temperature range depends on the temperature at which the crystallization took place. This complex behaviour makes it difficult to obtain reproducible measurements of the mechanical properties at low temperatures, as the degree of crystallization will depend on the rate of cooling. An example can be found in fig. 14, where tan δ and E are plotted vs. temperature for an unstretched pure gum vulcanizate. In these measurements the sample was cooled down first to the lowest temperature, and measurements were made as the sample warmed up. In fig. 14 the results are given of two series of measurements in which the rates of cooling differed appreciably. In one series, the cooling-rate was the normally adapted one for the measurements quoted below.

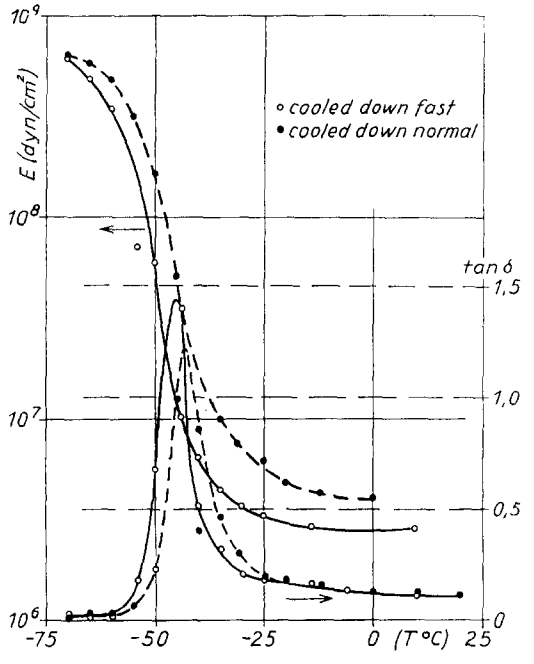


Fig. 14. *Young*'s modulus E and loss tangent tan δ vs. temperature for a pure gum vulcanizate cooled down at different rates

In the other series, the sample was cooled down as fast was possible with the experimental set-up. The effect of crystallization is clearly visible. In the sample cooled quickly, crystallization is restricted; the result is a higher damping peak at a slightly lower temperature. The influence of additional crystallization on the results for the stretched samples is difficult to predict. Probably the influence goes down at the higher elongations. Fig. 15 shows that with increasing elongation the peak height (and also the area under the peak) decreases and the location of

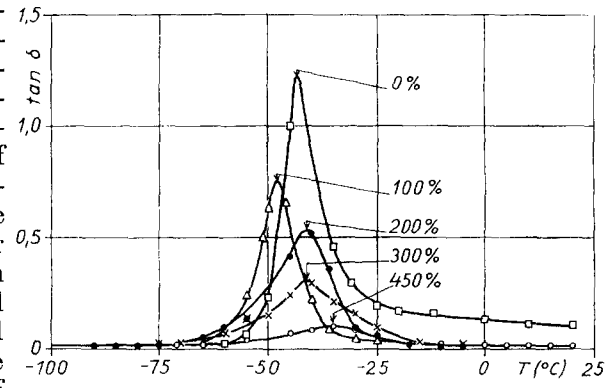


Fig. 15. Loss tangent tan δ vs. temperature for a pure gum vulcanizate extended for various amounts

the peak generally shifts to higher temperatures. At temperatures below -70 °C all damping curves coincide within experimental accuracy. The same is true for temperatures above 0 °C, with the exception of the curve for the unstretched sample.

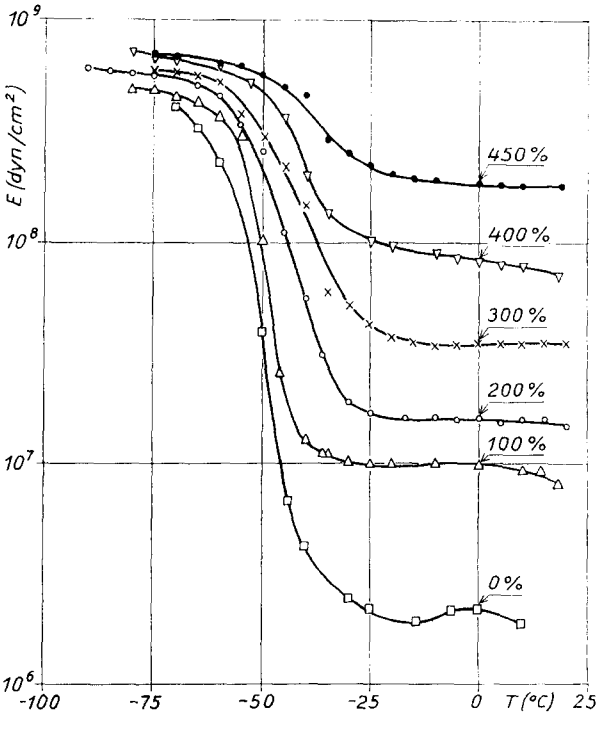


Fig. 16. *Young*'s modulus E vs. temperature for a pure gum vulcanizate extended for various amounts

The effect of the elongation on *Young*'s modulus E is most pronounced at high temperatures, i. e. in the rubbery region of the polymer. Here an elongation of 450% results in an increase of E by a factor of 100, as compared with a factor of about 2 at -70 °C. Measurements of E and tan δ of stretched

natural rubber at a frequency of 1 kHz can be found in a paper by *Mason* (14).

Discussion

From the measurements described it is hardly possible to differentiate between the influence of crystallization and that of orientation on the mechanical properties. In nearly all cases an increase of crystallization was accompanied by an increase in orientation. The only exception is formed by the experiments on unstretched rubber. Here we have seen that after slow cooling, which prefers crystallization, the subsequently measured E vs. T and $\tan\delta$ vs. T curves are shifted to higher temperatures with respect to the curves measured after fast cooling. Thus, here orientation and crystallization effect the mechanical properties in the same sense. From this fact we must not conclude, however, that this is always the case. Unfortunately, the measurements were not extended to low enough temperatures to see the influence of crystallization in the hard region. A polymer, which is in the hard region at room temperature (at not too low frequencies), is polyethylene terephthalate. Therefore, some additional measurements were performed for this polymer. Using a vibrating reed method, the *Young*'s moduli were measured of two samples; the one completely amorphous, the other with an estimated degree of crystallinity of 40%. It turned out that the *Young*'s moduli of both samples were exactly equal at the measuring frequency of a few hundred Hz. From this we must conclude that the *Young*'s modulus of the amorphous parts of the partly crystalline polymer equals that of the crystallites at the measuring frequency and temperature. This is not too surprising if one realizes that for a polymer in the glassy state all slow movements, i. e. slow with respect to the measuring period, are frozen out. Thus the amorphous parts can respond only by deformation of *Van der Waals* bonds just as the crystallites do. Things are quite different when the amorphous parts are in the rubbery region. In that case large chain parts can move as a whole under the influence of stresses. Restriction of these movements by crystallites causes an increase of *Young*'s modulus. In contrast to crystallization, orientation causes an increase of *Young*'s modulus over the whole temperature range. Examples can be found in figs 11, 13 and 16. The same effect was found in the polyethylene-terephthalate sample. Cold stretching of the amorphous sample resulted in a 9-fold increase of *Young*'s modulus. The explanation for this must probably be sought in the fact that in the orientated polymer the number of *Van der Waals* bonds per unit area perpendicular to the stretching direction is greater than in the non-orientated polymer.

As to the influence of the orientation on the $\tan\delta$ vs. T curves, there is a marked dissimilarity between the results quoted in table 1 and those represented in fig. 10. Whereas in the first case there is a gradual shifting of the α-peak, the temperature location of this peak in the second case does not change with orientation, except for the first 50% deformation. Actually, it looks as if the presence of absorbed water is necessary for the shifting to occur. Now as we have shown for polyvinyl alcohol, the increase of the water content has the effect that in measurements at constant temperature the peak shifts to higher frequencies. The shifting of the peaks in nylon-6 to lower frequencies with increasing orientation can, therefore, simply be explained by the fact that the water content decreases as a result of orientation. In the measurements shown in fig. 10, the water content of the fibres was very small and, therefore, no shifting took place. Another interesting feature seen in fig. 10 is the different behaviour of the α-peak and β-peak with regard to orientation. Whereas the β-peak grows with orientation the α-peak shrinks. The same tendency can be seen in measurements of *Hellwege* and co-workers (15). Most workers agree upon the interpretation of the α-peak. *Woodward* et al. (16), as well as *Kawaguchi* (17) and *Illers* (18) attribute the α-dispersion to the increased mobility in the amorphous regions accompanying the disrupture of hydrogen bonds in those areas. By *Woodward* et al. (16) the β-peak was ascribed first to the onset of motion of chain segments in the amorphous regions involving the co-operation of amide groups not hydrogen-bonded to other amide groups. In a later publication by *Woodward* et al. (19) the possibility is put forward that besides a number of amide groups not bonded with adjacent amide groups, water molecules moving with the amide groups are the cause of this transition. At about the same time *Illers* (18) suggested that the hindered rotation of the water molecules bonded to CO-groups brings about the β-transition. The main foundation of these interpretations in both cases is the experimental fact that in a dry sample the β-transition is very small, or completely absent. In view of these explanations the decrease of the α-peak with

orientation can possibly be attributed to the breaking-up of hydrogen bonds in the stretching process. To explain the simultaneous increase of the β-peak it must then be assumed that the freed CO-groups are able to meet free water molecules. The existence of an equilibrium between free and bonded water molecules is another suggestion made by *Illers* (18), who furthermore assumes that at temperatures below the glass temperature this equilibrium is frozen in due to the very small coefficient of diffusion. It seems reasonable to suppose that during the enormous molecular agitation caused by the stretching process, the diffusion coefficient is temporarily greatly enhanced.

With respect to the increased flexibility after stretching, we think that it is caused by the growth of the β-peak. Our interpretation, therefore, differs from *Müller*'s (4) only in so far that in our opinion the increased flexibility is not obtained by an enhancement of the total damping capacity, but by the increase of the damping in a more effective frequency range (β-peak) at the expense of the damping in a less effective frequency range (α-peak).

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Appendix

Let the length of the thread be $2\,l$ and the mass of the core m. The thread is prestrained, so that for small displacements of the core the thread keeps tight. Neglecting the influence of gravity, it is sufficient to consider half the thread of length l provided with the mass $m/2$.

In the thread we have:

$$\frac{\partial^2 \xi}{\partial x^2} = \frac{\varrho}{E^*} \frac{\partial^2 \xi}{\partial t^2} \qquad [1]$$

where

x = running co-ordinate along the thread
ξ = displacement in the x-direction
$E^* = E_1 + j\,E_2$ = complex *Young*'s modulus
ϱ = density of the thread

With good approximation, we can consider the core as a point-mass. Then we have the following boundary conditions:

$$\text{for } x = O \quad \xi = O \qquad [2a]$$

$$\text{for } x = l \quad OE^* \left(\frac{\partial \xi}{\partial x}\right)_{x=l} + \frac{m}{2}\left(\frac{\partial^2 \xi}{\partial t^2}\right)_{x=l} = 0 \qquad [2b]$$

where O = cross-section of the thread.

[3]) Now at N. V. Godard, Zeist.
[4]) Central Laboratory T.N.O., Delft.

Separating the variables in [1] and applying [2a] leads to

$$\xi = C \sin \omega^* \frac{\varrho}{E^*} x \cos \omega^* t \qquad [3]$$

where

C = an integration constant
$\omega^* = \omega_1 + j\,\omega_2$ = the complex angle frequency.

[3] represents a damped oscillation. Actually, we can write:

$$\cos(\omega_1 + j\,\omega_2)\,t = \frac{1}{2} e^{j\omega_1 t} e^{-\omega_2 t} + \frac{1}{2} e^{-j\omega_1 t} e^{\omega_2 t}.$$

The second term must be rejected for physical reasons, as it leads to an amplitude continuously growing with time. For the logarithmic decrement we find:

$$\lambda = \frac{2\pi\omega_2}{\omega_1}. \qquad [4]$$

Substitution of [2b] into [3] gives:

$$\frac{lO\varrho}{\frac{m}{2}} = \frac{G}{m} = \frac{\omega^* l \sqrt{\varrho}}{\sqrt{E^*}} \tan \frac{\omega^* l \sqrt{\varrho}}{\sqrt{E^*}}. \qquad [5]$$

where G = mass of the thread.

We write now:

$$\frac{\omega^* l \sqrt{\varrho}}{\sqrt{E^*}} = Z. \qquad [6]$$

where Z is defined as a solution of:

$$Z \tan Z = \frac{G}{m}. \qquad [7]$$

From [6] we find after some manipulation:

$$E_1 = \frac{l^2 \varrho}{Z^2}(\omega_1^2 - \omega_2^2) \qquad [8]$$

$$E_2 = \frac{2 l^2 \varrho}{Z^2} \omega_1 \omega_2 \qquad [9]$$

With the aid of [4], equations [8] and [9] can be reduced to:

$$E_1 = \frac{l^2 \varrho\, \omega_1^2}{Z^2}\left(1 - \frac{\lambda^2}{4\pi^2}\right) \qquad [10]$$

$$\tan\delta = \frac{E_2}{E_1} = \frac{\lambda}{\pi} \cdot \frac{1}{1 - \frac{\lambda^2}{4\pi^2}}. \qquad [11]$$

From [10] and [11] it follows that only for the real part of *Young*'s modulus a correction must be applied for the own mass of the thread.

We may consider the two limiting cases $\frac{G}{m} \to 0$ and $\frac{G}{m} \to \infty$.

For $\frac{G}{m} \to 0$ we find from [7].

$$Z^2 = \frac{G}{m} = \frac{2lO\varrho}{m} \qquad [12]$$

Substitution into [10] yields:

$$E_1 = \frac{lm\,\omega_1^2}{2O}\left(1 - \frac{\lambda^2}{4\pi^2}\right) \qquad [13]$$

which is identical with the relation that is found when the own mass of the thread is neglected at the beginning.

For $\frac{G}{m} \to \infty$ we find from [7]:

$$Z = \pi/2 \qquad [14]$$

Taking into account that $2\,l = \frac{\lambda}{2}$ where λ = the wavelength, we find:

$$E_1 = \varrho\, c^2 \left(1 - \frac{\lambda^2}{4\,\pi^2}\right) \qquad [15]$$

where c = wave velocity in the thread. Equation [15] is the one used in elaborating the high frequency measurements according to the method of *Ballou* and *Smith*. Finally, it should be mentioned that [7] has an infinite number of solutions, so that higher harmonics are theoretically possible. In measurements with very small masses, an indication of the second harmonic was found indeed at the expected frequency, but the resonance was too small to be used.

Summary

Measurements of *Young*'s modulus E and the appropriate loss tangent are reported for nylon-6, polyvinylalcohol, a polyurea and natural rubber in fibreform in the frequency range of 2.10^{-1} to 10^5 Hz at room temperature and at a relative humidity of 65%. The influence of orientation and crystallization on the mechanical properties was studied. At one particular frequency the *Young*'s modulus and the loss tangent were measured as a function of temperature. Here, too, the influence of orientation was studied.

Zusammenfassung

Messungen des *Young*-Moduls E und des zugehörigen Verlustfaktors tan δ wurden für Nylon-6, Polyvinylalkohol, für ein Polyurethan und Naturkautschuk in Borsten (Faser-)-form im Frequenzverlauf von $2 \cdot 10^{-1}$ bis 10^5 Hz bei Zimmertemperatur und bei einer relativen Feuchtigkeit von 65% untersucht. Der Einfluß der Orientierung und Kristallisation auf die mechanischen Eigenschaften wurde studiert. Bei einer bestimmten Frequenz wurden *Young*-Modul und tan δ auch als Funktion der Temperatur gemessen. Auch hierbei wurde der Einfluß der Orientierung studiert.

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Author's address:
Mr. *H. A. Waterman*, Noordelyk Technisch Instituut T.N.O., P.E.B.-Weg 5, Groningen (Holland)