

## Dynamic Mechanical Properties of Nylon 66 and the Plasticizing Effect of Water Vapor on Nylon. II

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To extend some work done at 35°C. on the dynamic mechanical properties of nylon 66,<sup>1</sup> the dispersion of tensile modulus and the nature of the corresponding maximum in vibrational energy loss have been observed as functions of relative humidity for nylon 66 at 9 and 60°C. These observations confirm one's expectation that as temperature is increased the maximum in energy loss can appear at lower moisture content for a given frequency, and they agree reasonably well with results reported recently by Woodward et al.<sup>2</sup> on the dynamic mechanical behavior of nylon rods vibrated in their first transverse mode.

### EXPERIMENTAL

The vibrator unit and the experimental technique used to obtain dynamic tensile modulus and energy loss from forced longitudinal vibration of 15 denier nylon monofilament have been described in a previous publication.<sup>1</sup> The work at 9°C. was done in a constant temperature room, and the humidity was controlled by jacketing the test filaments with a Lucite box through which a stream of either dried or humidified air was passed, depending on the relative humidity desired. The temperature of the air stream around the sample was kept at  $9 \pm 0.3^\circ\text{C}$ . The relative humidity of the air stream was measured by an American Instrument Company electric hygrometer and recorded continuously on a Bristol Recorder. For the measurements at 60°C., the test filaments were jacketed by a pair of metal tubes of 3 and 1.5 in. diameter arranged coaxially and insulated on the outside by asbestos cement. Water at 60°C. from a thermostat was pumped through the annular space, and air at 60°C. and of appropriate humidity was circulated over the nylon specimen in the central space. American Instrument Company narrow range, high sensitivity humidity sensing elements were calibrated for 60°C. by extrapolation

(as recommended by the manufacturer) of calibration curves supplied with the elements for temperatures up to 49°C. From the point at which its humidity was adjusted, the air stream was continuously jacketed by water pumped from the 60°C. constant temperature bath. The temperature of the air stream around the sample did not vary by more than  $\pm 0.1^\circ\text{C}$ . from 60°C.

The nylon monofilaments were allowed to creep under a load of 8 g. on 15 denier for some 16 hr. prior to the beginning of a run at the temperature and relative humidity to be used in the experiment. Control of humidity during the conditioning period was, on the average, within  $\pm 5\%$  R.H. from the required humidity. Just preceding and during the run, the humidity was manually controlled to the required humidity  $\pm 1\%$  R.H. In all experiments the vibrational strain amplitude was 0.0015. Multiple runs were made at each of a number of humidities at both 9 and 60°C.

### RESULTS

The variation of dynamic tensile modulus,  $E'$ , with frequency at given relative humidity is shown in Figure 1 for 9°C. and in Figure 2 for 60°C. for several relative humidities investigated at each temperature. With some obvious exceptions, for which only one run was made at a particular humidity, each set of points combines the results of two or three runs made on separate samples at the given humidity. It will be seen that at 60°C. the tensile modulus increases with frequency in the experimental range of  $\omega = 15$  to 200  $\text{sec.}^{-1}$  for all humidities. This behavior corresponds to that observed at 35°C.,<sup>1</sup> but is more clearly defined at the higher temperature. Experimental scatter was greater at 9°C. than at either of the other two temperatures, and variation of modulus with frequency at this temperature is not clearly defined except at humidities above 60%, for which one

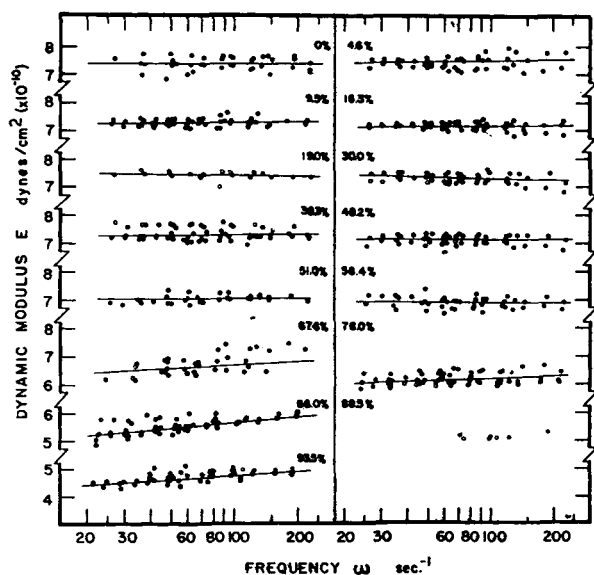


Fig. 1. Dynamic tensile modulus as a function of frequency for various humidities at 9°C.

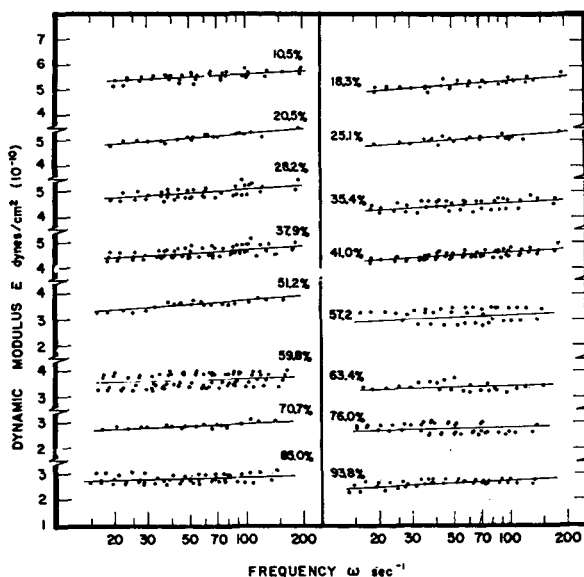


Fig. 2. Dynamic tensile modulus as a function of frequency for various humidities at 60°C.

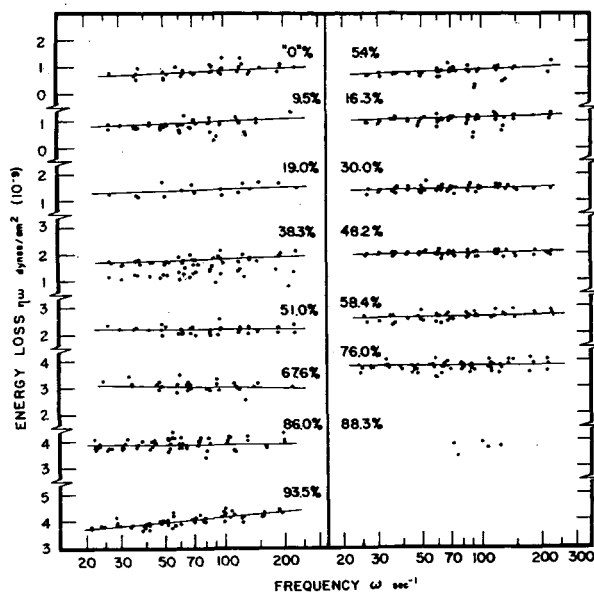


Fig. 3. Dynamic loss modulus (energy loss) as a function of frequency for various humidities at 9°C.

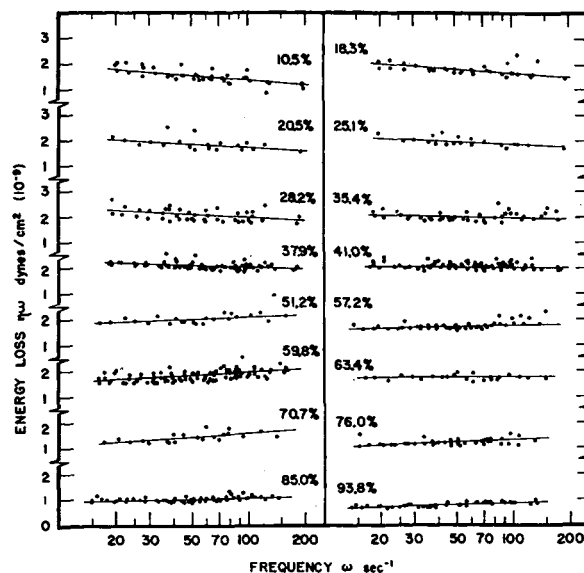


Fig. 4. Dynamic loss modulus (energy loss) as a function of frequency for various humidities at 60°C.

can again see an increase in  $E'$  with increasing frequency. The variation of  $E'$  with the amount of water adsorbed at the three temperatures, 9, 35, and 60°C., is shown in Figure 5 for the vibrational frequencies  $\omega = 150 \text{ sec.}^{-1}$  (solid lines) and  $\omega = 20 \text{ sec.}^{-1}$  (broken lines). In all cases, there is a marked decrease in tensile modulus with increasing moisture content of the nylon.

Moisture sorption values for the nylon were calculated for 60 and 9°C. from the data of Bull<sup>6</sup> for stretched nylon at 40 and 25°C. For given weight

of water sorbed at 40 and 25°C., values of the logarithm of the equilibrium vapor pressure were obtained and plotted against  $T^{-1}$ . Straight lines through these two points were extrapolated at each weight of water sorbed to  $T^{-1}$  values for 9 and 60°C. in order to obtain equilibrium vapor pressures.

The variation of energy loss,  $E'' = \eta\omega$ , with frequency at given relative humidity, is shown in Figure 3 for 9°C. and in Figure 4 for 60°C. for the several humidities involved. Again, each set

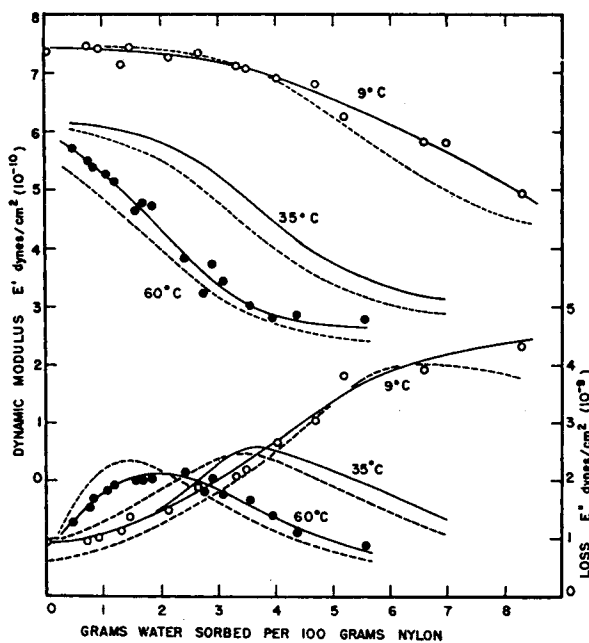


Fig. 5. Dynamic tensile and loss moduli as functions of the extent of water sorption of nylon for 9, 35 (ref. 1), and 60°C. Solid curves for  $\omega = 150 \text{ sec.}^{-1}$ . Broken curves for  $\omega = 20 \text{ sec.}^{-1}$  (points not shown).

of points usually combines the results of two or three runs made on separate samples. At 60°C. the dependence of loss modulus on frequency changes systematically with the change in relative humidity. At low humidity,  $E''$  decreases with increasing frequency; it is effectively independent of frequency near 35 to 40% R.H.; and it increases with increasing frequency at higher humidities. Such behavior is comparable to that at 35°C.<sup>1</sup> At 9°C., however, no systematic change in the dependence of loss modulus on frequency with change in humidity was observed. The change in energy loss with weight of water adsorbed is shown in Figure 5 for the three temperatures 9, 35, and 60°C., and for the vibrational frequencies  $\omega = 150 \text{ sec.}^{-1}$  (solid lines) and  $\omega = 20 \text{ sec.}^{-1}$  (broken lines). The maxima in these curves occur at lower moisture sorption by the fiber (and also lower relative humidity) as the temperature increases. Such behavior is to be expected if both the increase in temperature and in moisture content facilitate the motion of chain segments, and if such increased segmental motion produces increased energy dissipation up to a point at which further increase in ease of motion corresponds to such a decrease in intermolecular forces that the energy loss decreases again. Comparing the curves for loss vs. water sorption at  $\omega = 20 \text{ sec.}^{-1}$

with those at  $\omega = 150 \text{ sec.}^{-1}$  one finds that a higher water sorption is required to achieve maximum energy loss at the higher frequency for a particular temperature.

## DISCUSSION

Schmieder and Wolf<sup>3</sup> and Woodward, Sauer, Deeley, and Kline<sup>2</sup> have shown that there are four dispersion regions in nylon 66, occurring near 500, 350, 250, and 170°K., which are designated as  $\alpha$ ,  $\alpha'$ ,  $\beta$ , and  $\gamma$ , respectively. Woodward and his colleagues also showed that the  $\alpha'$  dispersion peak shifted to about 280°K. when the nylon specimen was exposed to 100% R.H. for three weeks. It would appear to be well established, then, that the results reported here deal with the  $\alpha'$  dispersion mechanism. The fact that maximum values of  $E'/E''$  observed in this work range from approximately 0.05 to 0.1 also supports the conclusion that one is concerned here with the  $\alpha'$  mechanism rather than the  $\beta$  dispersion because the value of  $Q^{-1}$  ( $= E'/E''$ ) obtained by Woodward et al.<sup>2</sup> for the peak of the  $\beta$  dispersion region was about 0.035. In molecular terms, this energy dissipation mechanism has been interpreted<sup>2,3</sup> as arising from the motion of rather large chain segments that exist within the amorphous regions of the polymer. The decrease in moisture content required to produce a maximum in energy dissipation at higher temperatures agrees with the view<sup>1,2</sup> that restraint of the motion of chain segments by hydrogen bonding is diminished by adsorbed water, and that as increasing temperature decreases the effectiveness of hydrogen bonding, so progressively less water is required to remove remaining restraints.

The systematic change in the variation of both the real and imaginary parts of the complex modulus with frequency as one progresses through the humidity range suggests the possible existence of a "time-humidity superposition principle" by means of which a single plot of the modulus vs. frequency could be made for each of the tensile and loss moduli to include all humidities. Accordingly, a reduced frequency  $\omega_r = a_H \omega$  was defined, following the procedure of Ferry<sup>4</sup> for time-temperature superposition. The empirical parameter  $a_H$  is determined by the extent of displacement along the logarithmic frequency axis required to bring the plot of  $E'$  or  $E''$  against frequency at a particular humidity into coincidence with the corresponding plot at another humidity, so that

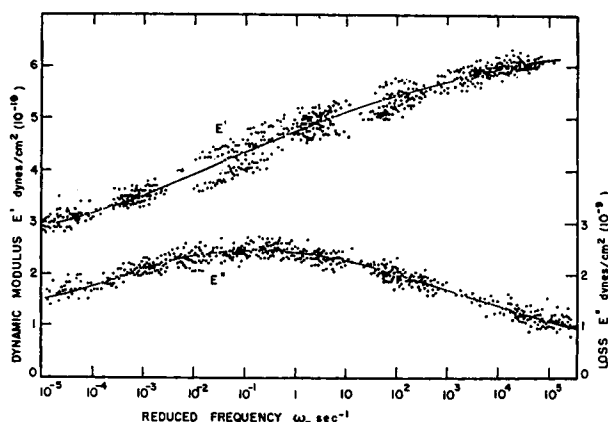


Fig. 6. Dynamic tensile and loss moduli as functions of reduced frequency at 35°C.

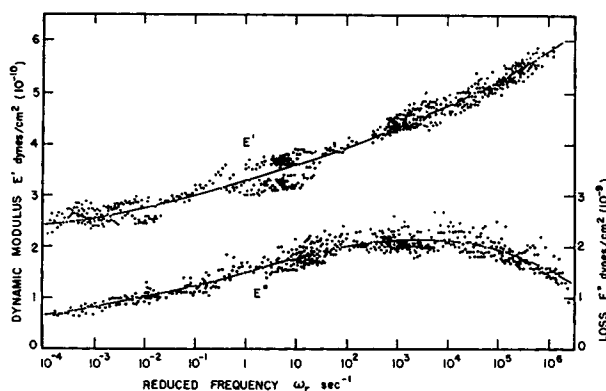


Fig. 7. Dynamic tensile and loss moduli as functions of reduced frequency at 60°C.

points lie on a single smooth curve. The actual values of  $\alpha_H$  are also influenced by the value of the relative humidity chosen as reference, to which all others are reduced in constructing the "master curve." Figures 6 and 7 show plots of  $E'$  and  $E''$  as functions of reduced frequency for 35 and 60°C., respectively. It has already been pointed out that one set of values of the reduction factor  $\alpha_H$  applies approximately as well to the construction of a master curve of one modulus as of the other for either temperature.<sup>5</sup> At 9°C., however, the results are not so straightforward. No composite curve is obtainable for the loss modulus, and although one can be constructed for the tensile modulus between 93 and 58% R.H., it is doubtful whether extension of such a curve to include humidities below 58% is of any significance since the individual plots of  $E'$  vs. frequency at given humidities are effectively independent of frequency and vary only slightly in vertical position on the modulus axis. The values of  $\alpha_H$  that could be

used to construct a fragmentary composite curve of tensile modulus vs. reduced frequency agree moderately well with values for the other temperatures. Failure to obtain satisfactory superposition at 9°C., may perhaps be attributed to a change in the nature of energy dissipation between 35 and 9°C., especially at lower humidities. This view seems consistent with Woodward's results<sup>2</sup> which show the transition from  $\beta$  to  $\alpha'$  loss peak to occur around 25°C. for moderately low humidity. At high humidity, however, he found that the  $\alpha'$  loss peak centered about 7 or 8°C. Thus the question remains as to why no composite curve is obtainable for loss modulus in the higher humidity range at 9°C.

Some attempt has been made to estimate the activation energy involved in this dissipation process. When the shift in the frequency of the energy dissipation maximum with shift in temperature has been available from experimental results, the activation energy has been calculated from the expression  $d \ln \omega_{max}/d(1/T) = \Delta H_a/R$ , where  $\omega_{max}$  is the frequency at the maximum in the curve of  $E''$  vs.  $\omega$ . If this technique of calculation is extended to the variation of  $E''$  with reduced frequency, one obtains  $\Delta H_a = 82$  kcal./mole using  $\log(\omega_r)_{max} = -0.8$  at 35°C. and  $+3.5$  at 60°C. as found from Figures 6 and 7. This value is in reasonable agreement with the value of 73 kcal./mole calculated by Woodward et al.<sup>2</sup> from a combination of their data and those of Schmieider and Wolf.<sup>3</sup>

Another approach to the estimation of an activation energy is an examination of the experimentally accessible derivative  $[\partial \ln E'/\partial(1/T)]_\omega$ . Ferry has pointed out<sup>7</sup> that this quantity does not necessarily lead directly to the activation energy. If we assume that the time-temperature superposition principle applies, and that the activation energy is given by  $\Delta H_a = R[\partial \ln \omega \alpha_T/\partial(1/T)]_\omega$ , the relation may be formulated

$$[\partial \ln E'/\partial(1/T)]_\omega = [H(-\ln \omega)/AE'](\Delta H_a/R)$$

where the relaxation distribution function,  $H(-\ln \omega)$ , is given by approximation relations<sup>8</sup>

$$\begin{aligned} H(-\ln \omega) &\cong AE'(\partial \ln E'/\partial \ln \omega)_T \\ &\cong BE''[1 - (\partial \ln E''/\partial \ln \omega)_T] \end{aligned}$$

$A$  and  $B$  are factors defined in reference 8. The time-temperature superposition principle does not apply in general to polycrystalline polymers because change in temperature produces changes in

the extent of crystallinity and in the constraints acting on the amorphous regions between the crystallites.<sup>9,10</sup> If, in spite of these limitations, one uses the above relations to estimate an order of magnitude for the activation energy, one finds that the value of  $\Delta H_a$  depends on temperature, extent of water sorption, and frequency. The values for 35°C. are the most regular. They range from 44 to 57 kcal./mole. Values for 9 and 60°C. range from 48 to 187, and from 18 to 82 kcal./mole, respectively. The overall average was found to be 60 kcal./mole.

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### Synopsis

The dynamic tensile modulus and energy loss have been measured for nylon 66 monofilaments at 9 and 60°C. over a wide humidity range in forced longitudinal vibration experiments. The frequency range covered was about 3 to 30 cycles/sec. (radian frequency 20 to 200 sec.<sup>-1</sup>). The results show dispersion of mechanical properties with change in humidity at both temperatures. At 60°C. a well-defined maximum in the energy loss was observed, similar to that obtained previously at 35°C., but occurring at a somewhat lower water content. If a maximum in the energy loss exists at 9°C. (it is not well-defined), it occurs very near 100% R.H.

A time-humidity superposition procedure is discussed by means of which the individual curves of modulus against frequency for the various humidities can be combined into a single "master curve" of modulus against reduced frequency. The order of magnitude of the activation energy for the dissipation mechanism has been estimated at 60–80 kcal./mole.

### Résumé

Le module de tension dynamique et la perte d'énergie ont été mesurés pour le nylon 66 en monofilament à 9° et à 60°C. par des expériences de vibration forcée longitudinale, dans une large gamme d'humidité. L'échelle de fréquence parcourue était de 3 à 30 cycles/sec. (fréquence en radian 20 à 200 sec.<sup>-1</sup>). Quand l'humidité change, les résultats montrent pour les deux températures, une dispersion des propriétés mécaniques. A 60°C. un maximum bien défini dans la perte d'énergie a été observé, analogue à celui obtenu antérieurement à 35°C. mais qui se manifeste à une quantité d'eau moins élevée. Si le maximum de perte d'énergie existe à 9°C. (il n'est pas très précis) il se présente vers 100% R.H. Un procédé de superposition temps-humidité est discuté, à l'aide duquel les courbes individuelles du module en fonction de la fréquence à plusieurs humidités peuvent être combinées dans une seule "courbe principale" de module en fonction de la fréquence réduite. L'ordre de grandeur de l'énergie d'activation pour le mécanisme de dissipation a été évaluée à 60–80 kcal. par mole.

### Zusammenfassung

Der dynamische Spannungsmodul und Energieverlust wurden an Einzelfäden aus Nylon 66 bei 9 und 60°C über einen weiten Feuchtigkeitsbereich durch Versuche mit erzwungener longitudinaler Schwingung gemessen. Der verwendete Frequenzbereich lag etwa zwischen 3 und 30 Hertz (Radiantfrequenz 20 bis 200 sec.<sup>-1</sup>). Die Ergebnisse zeigen bei beiden Temperaturen eine Dispersion der mechanischen Eigenschaften in Abhängigkeit von der Feuchtigkeit. Bei 60° wurde ein wohldefiniertes Maximum für den Energieverlust, ähnlich zu dem früher bei 35°C erhaltenen, beobachtet, das aber bei einem etwas niedrigeren Wassergehalt auftritt. Falls bei 9°C überhaupt ein Maximum im Energieverlust besteht (es ist nicht gut ausgebildet), so tritt es sehr nahe bei 100% RH auf. Es wird ein Verfahren zur Zeit-Feuchtigkeitssuperposition diskutiert, mittels welchen die individuellen Kurven für die Frequenzabhängigkeit des Moduls bei den verschiedenen Feuchtigkeitsgraden zu einer einzigen "Grundkurve" für die Abhängigkeit des Moduls von der reduzierten Frequenz vereinigt werden können. Die Größenordnung der Aktivierungsenergie für den Dissipationsmechanismus wurde zu 60–80 kcal pro Mol geschätzt.

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