

# Prediction of Stress-Relaxation Data of Some Nylons from Stress-Strain Data\*

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## Synopsis

Six commercially available nylons were tested for stress-strain and stress-relaxation properties. Use was made of a recently revealed approach to predicting viscoelastic properties beyond the linear region from an analysis of the stress-strain curve. The equations used were three-dimensional employing the Halsey-Eyring viscoelastic model. The necessary constants were calculated and, when applied to the appropriate equations, reconstituted the stress-strain curve and predicted the stress-relaxation curves quite well.

## INTRODUCTION

Experimental and theoretical studies of linear and nonlinear viscosity have been extensive. Of interest is the prediction of nonlinear viscoelastic properties, particularly stress-relaxation, and checking of the predictions against experiment.

Eyring and Halsey described a three-element viscoelastic model.<sup>1-3</sup> Eyring also showed<sup>4</sup> the relationship between viscosity and rate of strain. These concepts were incorporated by Haward and Thackray<sup>5</sup> in a one-dimensional treatment of the Halsey-Eyring model composed of a Hookean spring in series with an Eyring dashpot parallel to a rubber elasticity spring. Titomanlio and Rizzo<sup>6,7</sup> evolved a three-dimensional treatment of an equivalent model, a linear spring parallel to a Maxwell element with a variable viscosity (Eyring) and an allowance for the effect of free volume as expressed by the Doolittle equation.<sup>8</sup>

Ng<sup>9</sup> adapted these systems with some changes. These changes were the choice of a different three-dimensional Maxwell equation,<sup>10</sup> the use of a variable viscosity function, and the imposition of constraints in the evaluation of the model parameters.

Constitutive equations for the three-dimensional models were established and solved by Ng<sup>9</sup> to yield constants which, when fitted into the three-dimensional equations for stress-strain and stress-relaxation, predicted these properties very well not only for the various linear aromatic polyesters which he studied but also for polyethylene.<sup>11</sup>

By curve-fitting the stress-strain curves, Ng<sup>9</sup> obtained a constant from

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which he calculated the  $K$  and the activation volume for the Eyring activation equation. The moduli in the linear range below and above the yield point were then the only other values needed to calculate the stress-strain and stress-relaxation for the one-dimensional model. While the prediction for stress-strain data was good, that for the stress-relaxation was far from realistic. Applying the same technique to the three-dimensional model yielded two constants in addition to the two moduli. The two constants had the dimensions of reciprocal Pascals. While the recreation of the stress-strain curve by this model was not quite as good as for the one-dimensional method, the prediction of the stress-relaxation curve was very good.

The stress-relaxation behavior ought to be predictable for nylons also using this model. Consequently, six nylons (6, 11, 12, 66, 612, and 666) were examined experimentally for stress-relaxation moduli and these experimental results compared to the theoretical predictions based on the stress-strain data to determine the success of the mathematical model.

### EXPERIMENTAL

Six commercially available nylons were studied, namely nylon 6, 11, 12, 66, 612, and 666. Table I shows sources and properties of the various nylons.

Due to the hygroscopic nature of the nylons, it was necessary to oven-dry the pellets in vacuum so as to ensure a low moisture content. The nylons were hot-pressed at approximately 20°C above their melting points in a laboratory press between two aluminum sheets covered with aluminum foil sprayed with hot-mold release agent. The pellets were pressed gently until melting occurred, and, after typically 2 min in the press, the pressure was raised to approximately 7000 psi for one more minute to eliminate bubbles and form a film. After pressing, the samples were allowed to cool at room temperature under load between the plates. They were stored in desiccators until needed.

The stress-strain and stress-relaxation experiments were performed with an Instron Universal Testing Instrument, Floor Model TT, at room temperature (23°C), which is considerably below the glassy transition temperatures of the nylons. In order to perform the tests, the films were cut into standard dumbbell shaped samples with a neck region 1 × 3.5 cm. A thickness gauge and a travelling telescope were used to measure the dimensions exactly.

A 3 cm strip of the neck area of the dumbbell-shaped sample was marked off before straining, and the sample was strained at a constant strain rate

TABLE I  
Nylon Sources and Properties<sup>12,13</sup>

Nylon	Source	$T_m$ (°C)	$T_g$ (°C)	$[\eta]$
6	Algemene Kunstzijde	220	52	1.09
11	BDH Chemicals Can.	186	47	0.3
12	BDH Chemicals Can.	178	36	0.93
66	DuPont Can.	260	46	3.2
612	DuPont Can.	210	50	1.45
666	DuPont Can.	250	55	2.6

of 0.50 cm/min for the required time. Three tests were performed on each nylon. The strain level at which the relaxation was initiated differed for each. Between tests the sample was allowed to relax for periods of up to 20 h, although 10 h was generally sufficient.

The strain was measured by measuring the elongation in the neck relative to the initial 3 cm strip. The samples were usually strained beyond the yield point so as to be certain that the tests were in the nonlinear viscoelastic region. The charts from the Instron were used to generate true stress vs. strain and true stress vs. log-time plots. Calculations were based on large scale graphs which were reduced and copied for this publication.

Since the nylons are sensitive to orientation and to moisture, precautions were taken to avoid orientation and exposure to moist air.<sup>13</sup> The samples showed some crystallinity after molding, usually less than 10%.<sup>13</sup>

## RESULTS AND DISCUSSION

Stress-strain curves for the six nylons yielded the data points in Figure 1. The data were analyzed according to Ng's procedure and the parameters shown in Table II were obtained.  $R$  had the value of  $6.67 \text{ GPa}^{-1}$ . These value were then substituted in the appropriate three-dimensional equations to reconstitute stress-strain curves and to predict stress-relaxation.

### Comparison with Theoretical Predictions

It was found that the mathematical model can predict stress-strain and stress-relaxation behavior with reasonable accuracy. Figure 1 shows generally fair agreement between the theoretical lines and the experimental

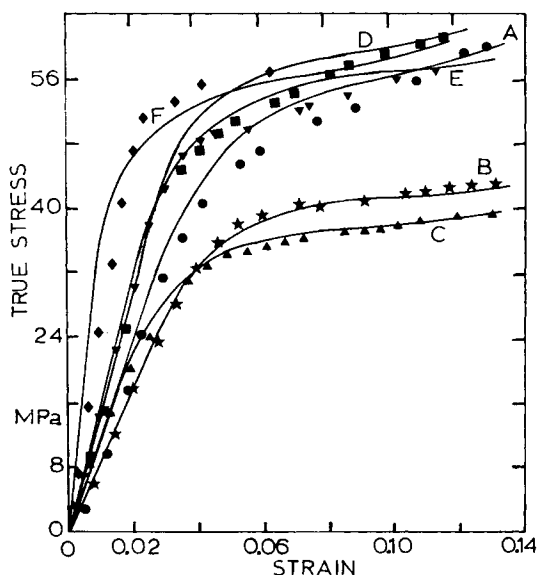


Fig. 1. True stress vs. strain for data for: (●,A) nylon 6; (☆,B) nylon 11; (▲,C) nylon 12; (■,D), nylon 66; (▼,E) nylon 612; (◆,F) nylon 666. solid lines are calculated from parameters according to Ng.<sup>9</sup>

TABLE II  
 Theoretical Model Parameters

Nylon	$G_1$ (MPa)	$G_2$ (MPa)	$3(G_1 + G_2)$ (MPa)	$B$ (MPa <sup>-1</sup> )
6	313	63	1128	0.19
11	266	29	887	0.30
12	310	28	1015	0.36
66	444	55	1498	0.15
612	461	45	1515	0.17
666	792	55	2539	0.19

stress-strain data. There tends to be some disagreement between the theoretical and experimental results near the yield points, nylons 11 and 12 showing better agreement than the others. It is important that there be a good correlation of the data with stress-strain curves since the initial stress for the theoretical prediction of stress-relaxation is chosen from the theoretical stress-strain curve. Any difference between experimental and theoretical stress-strain data will be amplified in the predicted stress-relaxation data. For the most part, the deviation tends to increase slightly beyond the yield point. However, the accuracy in this portion of the non-linear viscoelastic region is still good. These results should be compared with those obtained by Ng for the linear aromatic polyesters. He found that the simpler one-dimensional model reconstituted the stress-strain curves better than did his three-dimensional model used here, and a similar discrepancy may exist for the nylons.

Figures 2-4 illustrate the theoretical and experimental stress-relaxation moduli. Good correlations are found generally. The results were comparable

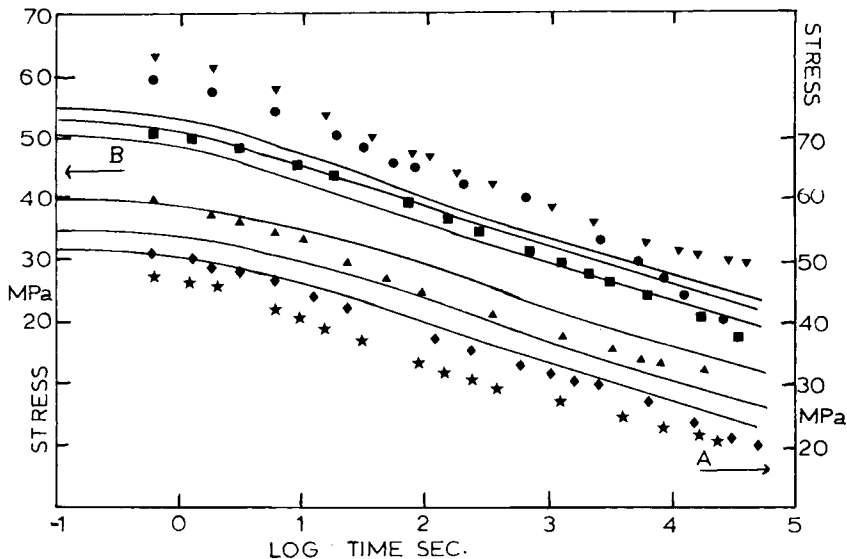


Fig. 2. True stress vs. time data for (A) nylon 6 at initial strains of (▲) 0.133, (◆) 0.086, and ☆ 0.062 and for (B) nylon 666 at initial strains of (▼) 0.0736, (●) 0.0577, and (■) 0.0296. Solid lines are predicted by the method of Ng.<sup>9</sup>

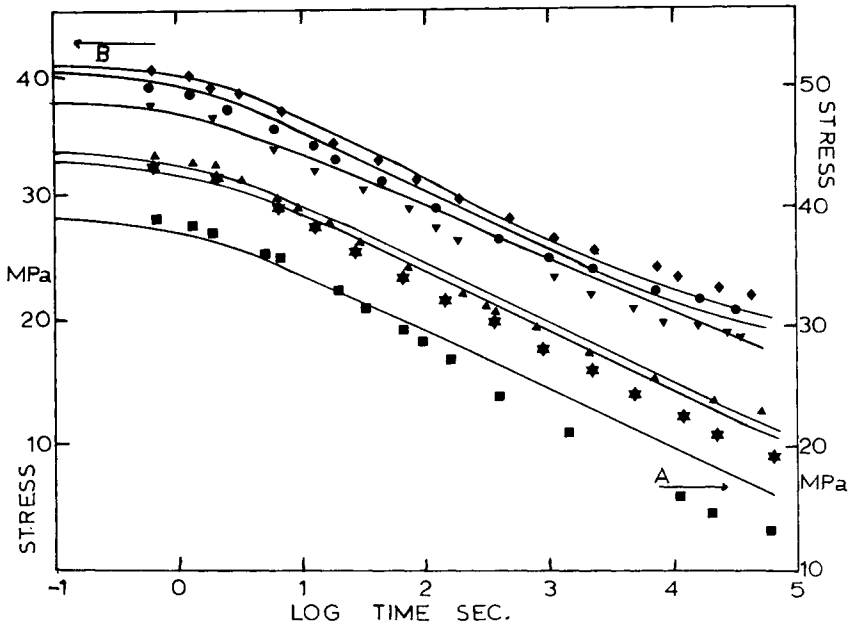


Fig. 3. True stress vs. time data for (A) nylon 11 at initial strains (▲) 0.141, (☆) 0.129, and (■) 0.050 and (B) nylon 12 at initial strains of (◆) 0.145, (●) 0.120, and (▼) 0.095. Solid lines are predicted by the method of Ng.<sup>9</sup>

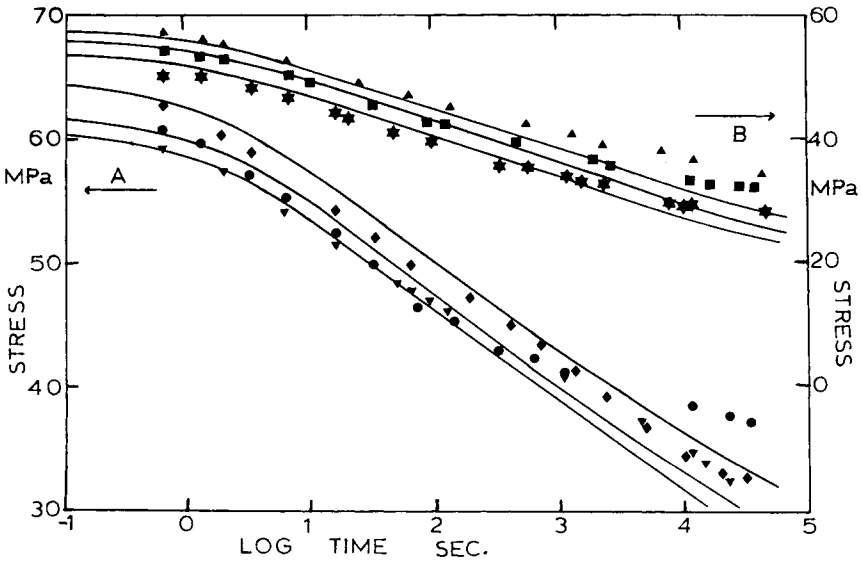


Fig. 4. True stress vs. time data for all (A) nylon 66 at initial strains of (◆) 0.142, (●) 0.114, and (▼) 0.100 and (B) nylon 612 at initial strains (▲) 0.111, (■) 0.089, and (☆) 0.059. Solid lines are predicted by the method of Ng.<sup>9</sup>

for each nylon at each of the three strain levels tested, but typically the lower strain levels agreed marginally better. The model showed no pattern regarding relaxation rates. For some nylons the theoretical relaxation was slower than the actual experimental results, and for others it was faster.

Nylons 6 and 666 (Fig. 2) showed the poorest agreement when compared to the model for stress-relaxation. Not unexpectedly, these two also showed poorer correlations with theory in the stress-strain test. Nylons 11 and 12 both gave excellent results in the stress-strain tests, but nylon 11 (Fig. 3) showed some deviation in the stress-relaxation test. The model tended to relax more slowly. Nylon 12 (Fig. 3) experimentally was in reasonable agreement with the theoretically predicted stress-relaxation curves, the theoretical curve relaxing slightly more rapidly. Nylons 66 and 612 (Fig. 4) tended to give reasonable results in both tests, even though they showed significant deviations near the yield point in the stress-strain tests. For the relaxation tests, the theoretical curve tended to relax more rapidly. An average experimental error for the relaxation tests would be 5-10%, depending on the nylon examined.

The model does not take account of crystallinity when predicting stress-relaxation behavior. The deviations observed could be attributed in part to this. Some of the films showed opacity, indicating crystallinity. Also it was difficult to obtain film samples of nylon 666 large enough to be cut into the required dumbbell shape. As a result, the neck portion sometimes contained small bubbles and blisters which could result in stress concentration.

While efforts were made to keep the humidity at 0%, such as oven-drying of the pellets and storage in a desiccator, some water gain during testing was always a possibility. This would increase the rate of relaxation.<sup>13</sup> The model does not take account of temperature. All samples were tested at 23°C, room temperature, so that slight temperature fluctuations were possible.

### Comparison between Nylons

The relaxation moduli are high and the relaxation rates low compared with amorphous polymers. Crystallites and hydrogen bonding tie the chains together in the polymer matrix, strengthening the polymer. The methylene to amide ratio (M/A) of a nylon is a measure of the hydrogen bonding. Nylons 6, 66, and 666 have low M/A ratios and should show the highest moduli. While Nylon 666 did exhibit the highest modulus, nylons 6 and 66 were intermediate with respect to modulus, similar to nylon 612, which has an intermediate M/A ratio. Nylons 11 and 12, with the largest M/A ratio, showed the lowest moduli. It is believed that all samples, as molded, were low in crystallinity and had reached a useful state of hydrogen bonding.<sup>14</sup>

Since all tests were conducted below the glassy transition temperature, the moduli for the nylons did not vary widely. More importantly, the nylons relaxed at almost the same rates. Operation below  $T_g$  made all six nylons equivalent structurally and rheologically so that the relaxation rates were similar.<sup>13</sup>

## SUMMARY

The three-dimensional equations developed to predict viscoelastic behavior in polymers accurately predict the stress-strain and stress-relaxation behaviors in the nylon polymers. Below  $T_g$ , the relaxation modulus is not much affected by structure since hydrogen bonding and crystallinity are very similar for all of the nylons tested. In general, the lower the methylene/amide ratio, and hence the greater the hydrogen bonding, the greater the tensile and relaxation modulus. The discrepancies between theoretical and experimental relaxation moduli might be explained in part by variations in crystallinity, temperature, and moisture uptake.

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