Stress Relaxation of Some Linear Aliphatic Nylons*

MARY W.-Y. YEUNG† and H. LEVERNE WILLIAMS, *Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A4*

Synopsis

The stress relaxations of unoriented nylons 4, 6, 11, 12, 66, 610, 612, and 666 were measured and compared over a temperature range from 25 to 180°C. Samples were tested after conditioning to 0, 50, and 100% relative humidity. The effect of crystallinity was indicated by the use of annealed samples prepared at 0% relative humidity.

INTRODUCTION

The polyamides form a large family of polymers.[1] The best known members could be oriented and drawn to yield fibers and films. As a consequence, the literature on oriented polymers is extensive. However, the polymers have also become engineering resins that can be extruded and molded into a variety of products. These aspects have been reviewed also.[2,3] Emphasis in this paper is on the linear aliphatic polyamides, which can be considered copolymers of methylene and amide groups with the length of the methylene sequences between the amide groups varying from product to product.

The amide groups are able to hydrogen bond, yielding intermolecular bonds. The formation of these bonds leads to the development of mechanical properties and, when the chains can suitably align, to high-melting crystals. Starkweather et al.[4] showed, especially for nylon 610, that freshly molded samples were low in crystallinity and that crystallinity developed with time. They believed that mechanical properties developed as hydrogen bonding occurred and, by the time the product had achieved about 7% crystallinity, were characteristic.

The second main property is sensitivity to moisture and, of course, to other hydrogen-bonding agents. These disrupt the intermolecular bonding and enable movement of the molecules. As a consequence, the polymeric mass will undergo creep and stress relaxation more readily, the tensile strength and modulus are lower, and molecular motions are easier. This facilitates increased crystallinity, particularly on annealing at temperatures between the glassy and melting transition temperatures.

The similarity of the structures means that effectively the linear aliphatic polyamides behave as a polymer with varying degrees of cross-linking or

---

CCC 0021-8995/86/023695-08$04.00

cure through the hydrogen bonds. Thus the various members of the series are compatible,[5] although signs of incompatibility with dynamic mechanical tests appear for nylons 6 and 12 when blended. The blending tests were done on dry polymers. Testing of blended polymers at various relative humidities remains to be done. Studies of the effects of moisture on the dynamic mechanical properties of the polyamides, particularly nylons 6 and 12, have been extensive.[6] Two recent papers[7,8] also relating to oriented nylon 6 are indicative of the features observed.

Stress relaxation is of importance in predicting the behavior of the polymer over long times under load. Some studies of the stress relaxation of oriented nylon 66 have been reported.[9] A study of the stress relaxation of the unoriented nylons was undertaken in particular to try to relate the resulting performance to hydrogen bonding, at least qualitatively. To that end, samples conditioned to different relative humidities and samples cooled more slowly at 100°C to achieve some annealing and increased crystallinity were included.

EXPERIMENTAL

The nylons used are identified in Table I, and the major properties of interest are listed. Except for nylon,[4] which was synthesized in the laboratory, the samples were standard commercial materials. The glass transition temperatures T_g are quoted from earlier studies on oven-dried samples by Amity Lam using a differential scanning calorimeter. The values agree with published results.[2,3,10] Higher values are obtained using dynamic mechanical estimates of T_g, particularly with thoroughly dried samples.[5,7]

The melting points were obtained by the author using the differential scanning calorimeter and they agree well with literature values for comparable samples.[2,3,10] The melting points are much lower than the equilibrium melting values.[11]

Percentage crystallinities were estimated by calculating the heat of fusion of the 100% crystalline polymer by the group contribution technique outlined by van Krevelen.[12] The values for the heat of fusion so calculated agree well with the literature values available.[10] The intrinsic viscosities are included for comparison purposes and as an indication of the molecular weights.

Films were pressed from a layer of oven-dried pellets using a Carver laboratory press at 10°C above the melting point of the nylon. The platens were covered with aluminum plates coated with aluminum foil, which in turn was sprayed evenly with high-temperature release agent. A minimal time of pressing was used to avoid degradation, usually 3–8 min. Orienting the polymer was avoided. Samples 5 × 25 mm were cut from uniform and fault-free sections of the films. The dimensions were measured exactly using micrometers. To vary the crystallinity, the hot-pressed samples were allowed to cool while between the aluminum plates and under slight pressure either at room temperature or at 100°C, the latter allowing some time for annealing. The crystallinities (Table I) of these unoriented molded samples were low compared with oriented films and fibers, as observed by others.[4] The polymers were not nucleated.

TABLE I
Properties of the Nylons

Nylon	Source	$T_g(°C)$[b]	$[\eta]$[c] (dL/g)	$T_m(°C)$	ΔH_f[e] (kJ/mol)	% Crystallinity Cooled at RT	% Crystallinity Annealed at 100°C
4	Prepared[a]	59	2.25	265	14.2	9	—
6	Algemene Kunstzijde Polysciences	52	1.09	220	21.8	8	11
11	Rilsan BDH Chem. Can. Ltd.	47	0.3[d]	186	40.6	7	10
12	Rilsan BDH Chem Can. Ltd.	36	0.93[d]	178	44.4	9	12
66	Dupont Canada Ltd.	46	3.2	260	43.6	6	9
610	BDH Chem. Can. Ltd. Polysciences	51	0.66	222	58.7	5	8
612	Dupont Canada Ltd. Polysciences	50	1.45[d]	210	66.2	4	9
666	Dupont Canada Ltd.	55	2.60	250	65.4	4	8

[a] Prepared from pyrrolidone by Amity M.-C. Lam.[13]
[b] Amity Lam, using differential scanning calorimeter.
[c] Amity Lam, using an Ubbelhode viscometer.
[d] m-Cresol solvent; otherwise, formic acid.
[e] Calculated heats of fusion.[12]

Samples were conditioned for at least a week before use at three relative humidities in desiccators containing the appropriate strength of sulfuric acid to yield 0, 50, and 100% relative humidity (at room temperature). Samples were stored similarly.

The stress relaxation measurements were made using the stress relaxation attachment for the 943 thermal analyzer with the duPont 990 thermomechanical analyzer. The stress relaxation measurements were made at less than 1% strain over a period of 30 min at the temperatures mentioned. After each test, the load was removed and the samples allowed to recover for 30 min before proceeding to the next higher temperature.

By this technique the strain experienced by the sample is not strictly constant during relaxation but the error is small. A correction was made in calculating the relaxation modulus. The load on the instrument was 100 g, and the load cell constant was 79.4 g/mil.

RESULTS AND DISCUSSION

The stress relaxation curves, plotted as log modulus versus log time, were usually fairly straight lines. A typical series, those for nylon 4, is in Fig. 1. The other nylons yielded similar results, which differed only in detail. To compare the various nylons, the relaxation moduli after 12 and 180 s are listed in Table II. In both Fig. 1 and Table II, the effect of increased moisture (relative humidity) and of increased temperature is to reduce the relaxation modulus.

In general, the relaxation moduli are high, and changes with temperature and humidity are not great over the ranges studied when compared with amorphous polymers. The semicrystalline nature of the nylons and the prev-
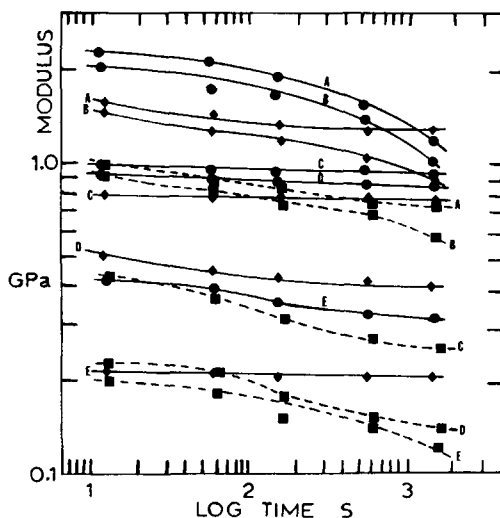

Fig. 1. Log modulus (GPa) versus log time (s) for the stress relaxation of nylon 4: (a) 25°C, (b) 50°C, (c) 100°C, (d) 150°C, and (e) 180°C; 0% relative humidity (●), 50% relative humidity (◆), and 100% relative humidity (■).

TABLE II
Relaxation Moduli (GPa) at Two Times for the Nylons at Various Temperatures and
Relative Humidities (RH)

Nylon	T (°C)	0% RH		0% RH annealed		50% RH		100% RH	
		12S	180S	12S	180S	12S	180S	12S	180S
4	25	2.43	2.03	—	—	1.69	1.40	1.05	0.88
	50	2.14	1.72	—	—	1.69	1.41	0.98	0.86
	100	1.02	0.99	—	—	0.87	0.85	0.46	0.33
	150	0.97	0.94	—	—	0.54	0.47	0.25	0.18
	180	0.44	0.38	—	—	0.23	0.21	0.21	0.15
6	25	2.97	2.52	3.16	2.88	2.66	2.42	2.40	2.11
	50	2.35	1.91	2.51	2.19	2.13	1.77	1.47	1.35
	100	1.94	1.18	2.08	1.51	1.40	1.00	1.29	0.98
	150	0.98	0.82	1.31	0.84	0.82	0.68	0.78	0.66
	180	0.73	0.65	0.87	0.78	0.71	0.63	0.66	0.58
11	25	1.98	1.62	2.23	1.86	1.39	1.10	0.89	0.84
	50	0.77	0.59	0.85	0.69	0.68	0.55	0.68	0.53
	100	0.49	0.46	0.63	0.59	0.47	0.42	0.44	0.37
	150	0.45	0.44	0.59	0.57	0.44	0.39	0.41	0.31
	180	0.41	0.31	0.53	0.40	0.32	0.30	0.32	0.28
12	25	2.13	1.65	2.23	1.82	1.68	1.51	1.33	1.30
	50	1.11	0.95	1.22	1.04	1.01	0.86	0.92	0.84
	100	0.62	0.56	0.68	0.62	0.56	0.51	0.51	0.46
	150	0.51	0.47	0.56	0.52	0.46	0.43	0.33	0.30
	180	0.39	0.37	0.43	0.40	0.36	0.33	0.24	0.23
66	25	3.15	2.82	3.33	3.03	1.50	1.50	1.48	1.48
	50	2.37	1.90	2.80	2.05	1.31	1.23	1.04	0.92
	100	1.37	1.18	1.33	1.33	0.92	0.72	0.78	0.54
	150	0.86	0.71	0.96	0.82	0.88	0.52	0.54	0.43
	180	0.80	0.70	0.90	0.76	0.71	0.39	0.32	0.30
610	25	2.55	2.38	2.95	2.66	2.34	1.99	1.81	1.67
	50	1.82	1.53	2.49	2.03	1.69	1.52	1.79	1.47
	100	1.56	1.25	1.76	1.27	1.47	1.24	0.74	0.71
	150	0.94	0.83	1.11	0.83	0.73	0.63	0.64	0.59
	180	0.85	0.64	0.90	0.74	0.61	0.58	0.46	0.31
612	25	2.51	1.88	3.34	2.77	1.78	1.60	1.20	1.17
	50	1.25	1.15	2.00	1.43	1.20	0.90	1.13	0.87
	100	0.87	0.79	1.06	0.91	0.71	0.55	0.55	0.52
	150	0.52	0.48	0.71	0.60	0.52	0.46	0.44	0.35
	180	0.35	0.31	0.46	0.40	0.37	0.24	0.30	0.22
666	25	2.14	1.95	2.59	2.28	1.17	1.09	1.11	0.87
	50	1.91	0.82	2.01	0.83	0.74	0.69	0.73	0.55
	100	0.82	0.70	0.84	0.71	0.59	0.53	0.59	0.50
	150	0.76	0.63	0.77	0.65	0.65	0.56	0.59	0.45
	180	0.60	0.49	0.61	0.50	0.51	0.48	0.48	0.42

alence of H bonding results in the similarities between the nylons and between the nylons and the thermoset polymers. Maximal changes in the moduli occurred during tests near the glass transition temperatures.

At the highest temperature, 180°C, the rapid decline in the relaxation moduli at the longest times may be related to a relaxation toward failure. The samples that had been prepared with higher crystallinities showed

higher values of the moduli above the glass transition temperature, but the effect was negligible below the glass transition temperatures.

The effect of water is first to disrupt the hydrogen bonding in the nylons, leading to reduced strength, and then to form agglomerates in the structure.[6] During an experiment, water may evaporate, reducing the amount exerting a plasticizer effect. There could be less effect on the H bonding so that the relaxation moduli may decrease more slowly with time and may even increase. Loss of water has less effect at 0 and 100% relative humidity than at 50% relative humidity,[14] where the ratio of bound to free water changes rapidly with evaporation. Crystallinity changed little during experiments[14] on nylon 6.

Master curves could be prepared by shifting the curves using 50°C as the reference temperature. The data for the dry samples are shown in Figs. 2 and 3. The lines are quite similar, and all fall within a narrow range of moduli. Master curves can also be made taking 50% relative humidity as the reference humidity, as shown in Fig. 4 for nylon 4. The individual curves for the various temperatures are shown. These, in fact, can also be superimposed to a reference temperature of, say, 50°C. A vertical as well as a horizontal shift[14] may be necessary in preparing master curves. Master curves for oriented nylons 6 and 66 have been prepared by Yoshitomi et al.[14] and by Quistwater and Dunell,[15] respectively.

The ratio of amide to methylene groups in the main variable in the structure. This ratio decreases in the order nylon 4 > 6, 66, 666 > 610 > 612 > 11 > 12. Although the modulus values lie roughly in this order, the deviations indicate that the probability of H bonding is not the only factor affecting the modulus. The H bonding decreased with increasing temperature, but as shown by Garcia and Starkweather,[16] it is still about 60% complete at the highest temperatures reached in this study.
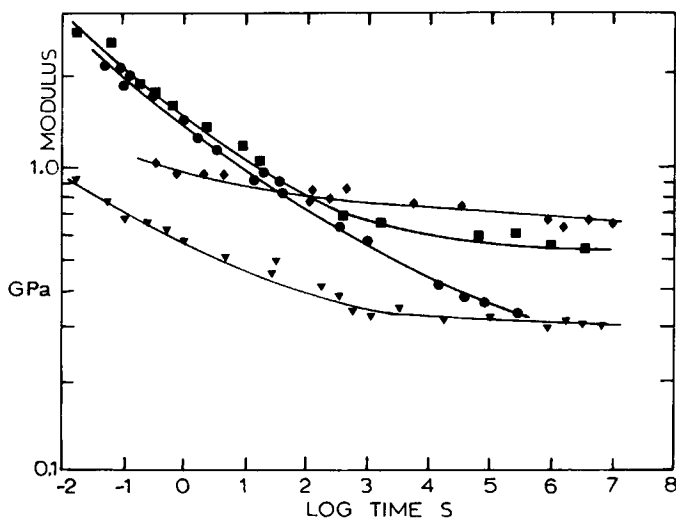

Fig. 2. Master curves referred to 50%C for 0% relative humidity samples: nylon 4 (●), nylon 6 (■), nylon 11 (▼), nylon 12 (◆).
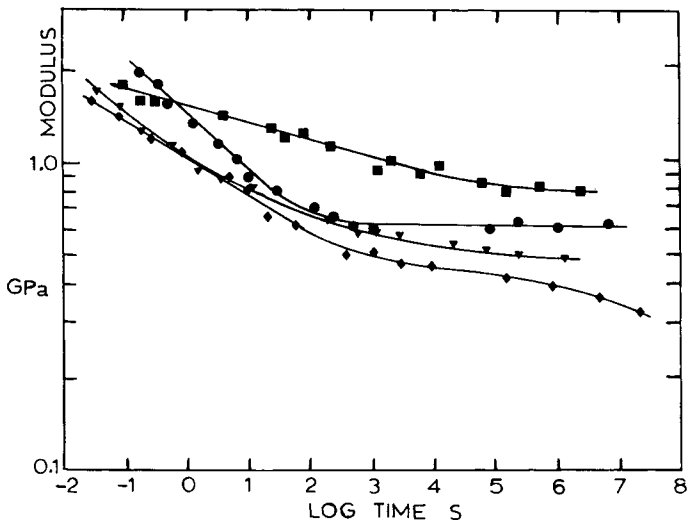
Fig. 3.   Master curves referred to 50°C for 0% relative humidity samples: nylon 66 (●), nylon 610 (■), nylon 612 (♦), nylon 666 (▼).
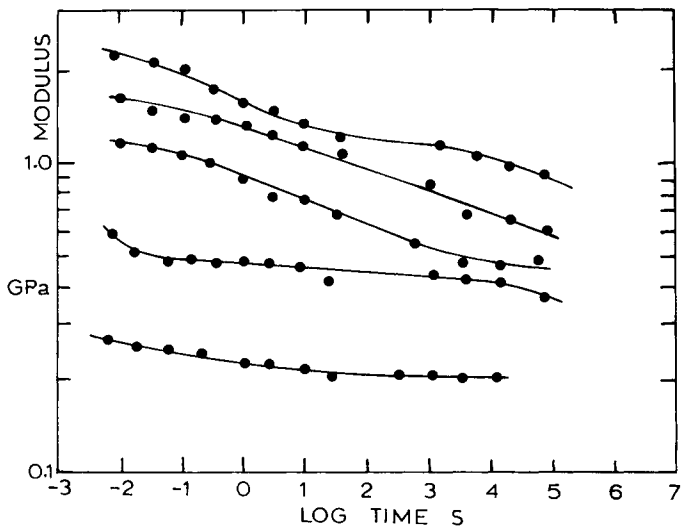

Fig. 4.   Master curves referred to 50% relative humidity for nylon 4 at temperatures (from top to bottom) of 25, 50, 100, 150 and 180°C.

Likewise, the dynamic or storage moduli differ from the relaxation moduli. The dynamic moduli measured from the anelastic spectrum[5] were obtained at a strain of about 0.2%, whereas those measured with the thermomechanical analyzer were obtained at strains up to nearly 1%. In both cases the strains are low, and one could hope that the moduli would match better. However, the change of relaxation moduli with time or temperature may depend more on the rates of formation and disruption of H bonds at equilibrium in a slow test, whereas in the dynamic mechanical tests the vis-

coelastic properties possible under more rapid sinusoidal movements are obtained. The data are in agreement with the concepts of Schroeder and Cooper,[17] but further experiments are needed to attain quantitative relationships.

SUMMARY

Stress relaxation of nylon 4, 6, 11, 12, 66, 610, 612, and 666 were measured and compared. The data are quite similar, taking into account the differing initial moduli. Moisture lowers the modulus but does not significantly change the relaxation rate. Likewise, some increase in crystallinity raises the modulus without a significant effect on the relaxation rate. The curves could be superimposed to a reference temperature or a reference relative humidity and, in principle, to both combined, probably with a vertical as well as a horizontal shift.

References

1. H. K. Livingston, M. S. Sioshansea, and M. D. Glick, *Rev. Macromol. Chem.*, **7**, 29 (1972).
2. W. S. Nelson, *Nylon Plastics Technology*, Newnes-Butterworth, London, England, 1976.
3. M. I. Kohan, *Nylon Plastics*, John Wiley & Sons, New York, 1973.
4. H. W. Starkweather, Jr., G. E. Moore, J. E. Hansen, J. M. Roder, and R. E. Brooks, *J. Polym. Sci.*, **21**, 189 (1956).
5. E. S. Ong, Y. Kim, and H. Leverne Williams, *J. Appl. Polym. Sci.*, **31**, 367 (1986).
6. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effect in Polymeric Solids,* John Wiley & Sons, New York, 1967.
7. S.-D. Rong and H. Leverne Williams, *J. Appl. Polym. Sci.*, **30**, 2575 (1985).
8. M. Yokouchi, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 1635 (1984).
9. T. Murayama, *Dynamic Mechanical Analysis of Polymeric Materials*, Elsevier, New York, 1975.
10. J. Brandrup and E. H. Immergut, *Polymer Handbook*, Wiley-Interscience, New York, 1974.
11. S. Fakirov, N. Avramova, P. Tidic, and H. G. Zachmann, *Polym. Commun.*, **26**, 26 (1985) (and earlier papers).
12. D. W. van Krevelen, *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*, Elsevier, Amsterdam, 1972.
13. R. W. Wynn, S. A. Glickman, and M. E. Chaddix, *Macromol. Syntheses*, **3**, 106 (1969).
14. T. Yoshitomi, K. Magaramatsu, and K. Kosiyama, *J. Polym. Sci.*, **27**, 335 (1958).
15. J. M. R. Quistwater and B. A. Dunell, *J. Appl. Polym. Sci.*, **1**, 267 (1959).
16. D. Garcia and H. W. Starkweather, Jr., *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 537 (1985).
17. L. R. Schroeder and S. L. Cooper, *J. Appl. Phys.*, **47**, 4310 (1976).