A Study of Some Linear Aliphatic Nylons by Thermally Stimulated Creep

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Synopsis

The mechanical behavior of nylons 6, 66, 666, 610, 612, 11, and 12 was studied using the method of thermally stimulated creep at 96°C. The resultant creep moduli were calculated. The strain recovery and strain recovery rates were measured and the retardation time spectra calculated as a function of temperature. The effects of humidity on the creep and subsequent recovery behavior were compared using samples conditioned to 0, 33, and 97% relative humidity at room temperature.

INTRODUCTION

The linear aliphatic polyamides (nylons) form one group of a very large family of polymers.[1] One of their important characteristics is that of crystallization on orientation, yielding well-known fibers and films. They have for some time been recognized as engineering resins with outstanding properties.[2,3]

The formation of H bonds between the carbonyl and amino groups is characteristic, leading not only to strength and stability but also to sensitivity to moisture and to other H-bonding compounds. Although most studies of the nylons have been on oriented polymers, it seemed desirable to compare the properties with minimal orientation and with controlled moisture.

Eng and Williams[4] compared the tensile strength and stress–relaxation of the dry nylons and observed that the relaxation rates were very similar. Indeed, the stress–relaxation data for samples under the same initial stresses were virtually identical. Yeung and Williams[5] extended these data using the thermal mechanical attachment on DuPont thermal analysis equipment by including the effect of moisture. Moisture reduced the modulus while crystallinity increased the modulus, as expected, but the relaxation rates were not greatly affected. Master curves could be prepared with appropriate shift factors. Bradley and Williams[6] using the techniques developed by Ng and Williams[7,8] for linear aromatic polyesters were able to predict the stress–relaxation of the nylons from a measurement of the stress–strain properties.

It was of interest to study the stress–relaxation and creep phenomena further using the thermally stimulated creep technique.[9] This has been applied to polyethylene,[9] ethylene and propylene polymers, copolymers, and their blends,[10] polyvinylidene fluoride,[11] and its blends with nylon 12,[12] nylon 66,[13] and

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poly(ether-block-amide).[12] This paper is to extend the technique to other nylons.

EXPERIMENTAL

The sources and properties of the nylons used are in Table I. The T_g are quoted from Yeung and Williams.[5] The melting points were obtained by DSC (temperature at the peak of melting curves for both calibration and tests) and compare well with those determined by Yeung[5] and Eng,[4] and also by Slichter for nylons 66, 610, and 612,[14] and by Garner and Fasulo[15] for nylons 6 and 12. The crystallinities are low and somewhat different from those quoted by Yeung and Williams,[5] who also used the methods of van Krevelen[16] to calculate the heat of fusion and in turn the percent crystallinity from the areas of the crystalline melting peaks of the DSC curves. The calculated crystalline melting points, also following van Krevelen's procedure,[16] tended to be a few degrees higher than the experimental data.[4]

The raw pellets or powders were dried in a vacuum oven for 3 h at 50°C. The polymers were then pressed into films in a laboratory press at 15–20°C above the melting point between aluminum plates covered with aluminum foil sprayed with hot mold release agent. The optimal pressure, applied for 2 min, was determined for each nylon. The samples were cooled at room temperature by removing the aluminum plates from the press and placing under a load. When cool, rectangular strips about 2.5 × 0.5 cm were cut out with a razor blade and the dimensions measured with micrometers. Samples were conditioned to 0, 33, and 97% relative humidity. The first sample was a control and was stored in a desiccator containing calcium chloride. The 33% relative humidity at 25°C was obtained with a saturated solution of magnesium chloride

TABLE I
Properties of the Nylons by DSC

Nylon	Supplier	T_g^a (°C)	T_m (°C)	% Crystallinity at relative humidity		
				0%	33%	97%
6	Algemene Kunstzijde or Polysciences	52	226	9	8	7
11	Rilson or BDH Chem. Can. Ltd.	47	190	5	5	5
12	Rilson or BDH Chem. Can. Ltd.	36	180	11	10	10
66	Dupont Canada Ltd.	46	261	12	10	9
610	BDH Chem. Can. Ltd. or Polysciences	51	224	7	6	6
612	Dupont Canada Ltd. or Polysciences	50	218	7	6	6
666	Dupont Canada Ltd.	55	250	10	8	7

a Quoted from Ref. 5, oven dried at 50°C for 3 h *in vacuo*, stored in desiccator.

hexahydrate and the 97% relative humidity by a saturated solution of potassium sulfate at 25°C.

Thermally stimulated creep was studied using the 943 thermal analyzer attachment to the DuPont 990 thermal mechanical analyzer. The strips of film were clamped into the apparatus and the initial length measured. The displacement of the lower clamp was recorded.

Residual strains in the samples were removed by heating to 96°C, just above the glass transition temperature. Expansion curves before and after this annealing were obtained.

The thermally stimulated creep studies can be conveniently separated into a creep and a recovery stage. The sample was placed under a known stress (2.6 MPa) by adjusting the load on the instrument pan, and allowed to creep at a constant temperature of 96°C until the rate was very slow, and the lengths were recorded. The temperature of the sample was then reduced to −20°C and held constant until the system was stable. At this stage the stress was removed allowing some elastic recovery. Then the sample was heated at a controlled rate of 10°C/min. At some temperature, recovery began and the strain recovery and the rate of strain recovery were recorded as a function of the temperature. The retardation time spectrum was calculated (calculated from the strain and rate of strain vs. temperature curves at various temperatures) as a function of temperature and a value of the glass transition temperature was estimated from the peak of the rate of strain vs. temperature curve.

The degree of crystallinity was found by differential scanning calorimetry. The area under the melting peak of the curves was used to calculate the heat required for melting and this, divided by the calculated heat of fusion, yielded the fractional crystallization.[5] This was done for as-pressed and humidity-conditioned samples.
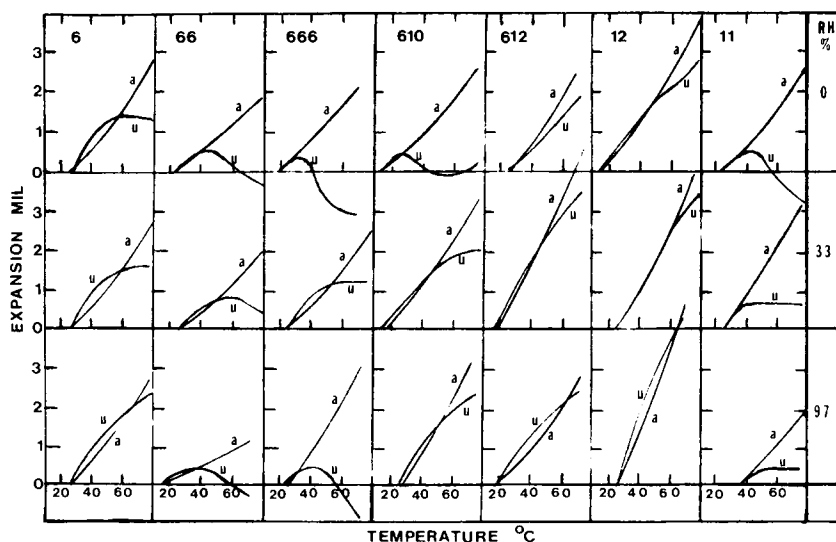

Fig. 1. Linear expansions of various nylons at three relative humidities (0, 33, 97%) for the first (u) unannealed cycle and second or later (a) annealed sample cycle vs. temperature (1000 mil = 25.4 mm).

RESULTS AND DISCUSSION

Thermal Expansion

Conditioning of the samples prior to testing is necessary. As molded, the samples tested in the TMA often showed a negative expansion as crystallization took place and strains were relieved. It was standard practice to put the sample through at least one thermal cycle before testing. The data are in Figure 1.

After annealing, the sample behaved as expected. Also the effect of moisture is to reduce the crystallinity somewhat as indicated by Table I and also by comparison of the curves before and after annealing as a function of water absorption. Since attempts to obtain measures of crystallinity by DSC were clouded by simultaneous crystallization of the unannealed samples, this approach was abandoned.

Although in principle the coefficients of expansion could be calculated, the instrument is not suitable for measurements of that accuracy. In general, all of the data were clustered around 2×10^{-4} cm/cm/°C, approximately double the literature values,[15,17] possibly due to the tension on the samples.

Creep

The creep moduli at 96°C are plotted in Figure 2. The curves are quite similar in shape. The highest moduli were obtained with nylon 66 and 666 with somewhat lower values for nylons 6, 610, and 612 and lowest for nylons 12 and 11, generally decreasing in the same order as the amide to methylene ratio and
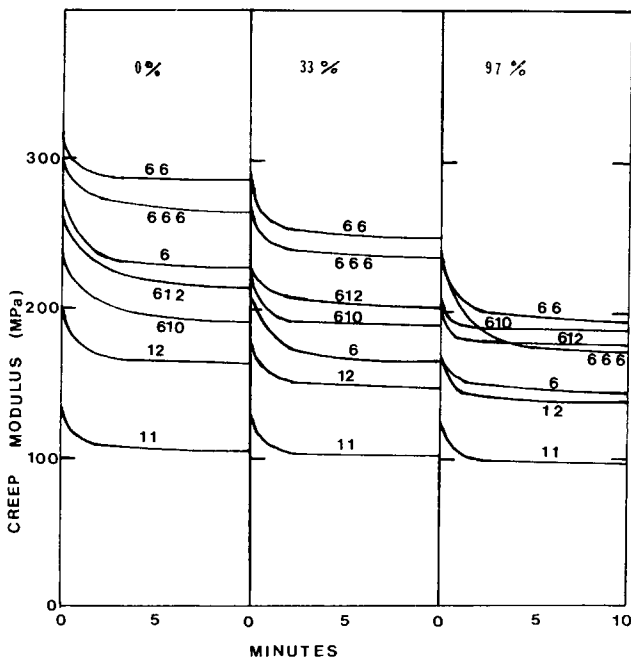

Fig. 2. Creep moduli of various nylons at three relative humidities (0, 33, 97%) over the first 10 min at 96°C.

the intrinsic viscosity.[5] The creep modulus was followed for 35–40 min and showed little change after 10 min.

The creep moduli data at relative humidities of 33 and 97% are in Figure 2 also. The nylons with the lowest methylene/amide ratio are more susceptible to moisture as might be expected.

Recovery

The extent of spontaneous recovery and the recovery rates are influenced by the moisture content in the same manner as the creep, explainable by reduced elasticity of the H-bonded network which counteracts the plasticizing effect of water. The recovery curves (corrected for expansion, Fig. 1) are in Figure 3 and the recovery rate curves (from tangents to curves in Fig. 3) are in Figure 4. From the curves of Figure 4 a measure of the glass transition temperature can be made. The values obtained at the peak of the recovery rate curves agree very well with those obtained from the retardation time spectra (see later) but might be expected to be slightly better since the peak is sharper. The values of T_g decrease with moisture level as would be expected from the plasticizing effect of the moisture. The various values are tabulated in Table II.

The retardation time spectra were calculated. They all show a decrease with increasing temperature passing through a minimum or a point of inflection at the glass transition temperature. The data are plotted in Figure 5.

The effect of moisture is to increase the retardation time since the effect of moisture seems to be greater on the elasticity, i.e., retractive force, than on the
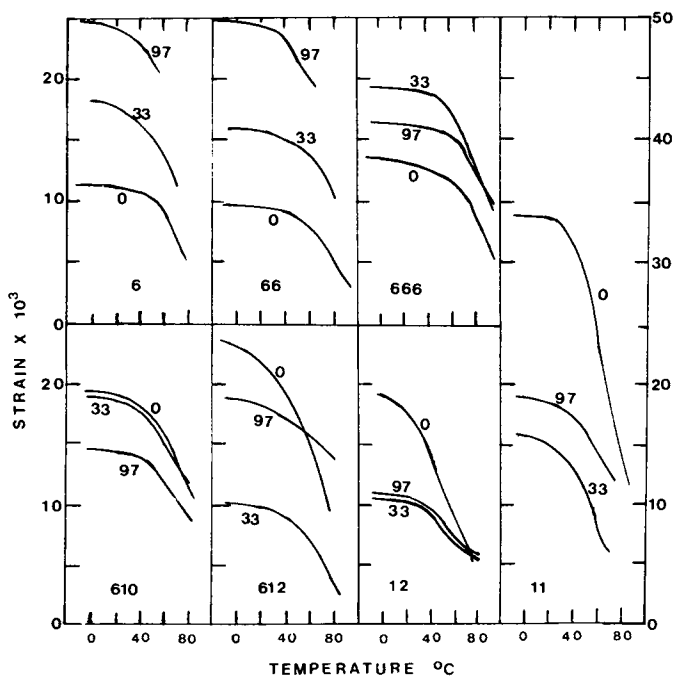

Fig. 3. Strain recovery of various nylons at three relative humidities (0, 33, 97% RH) vs. temperature.
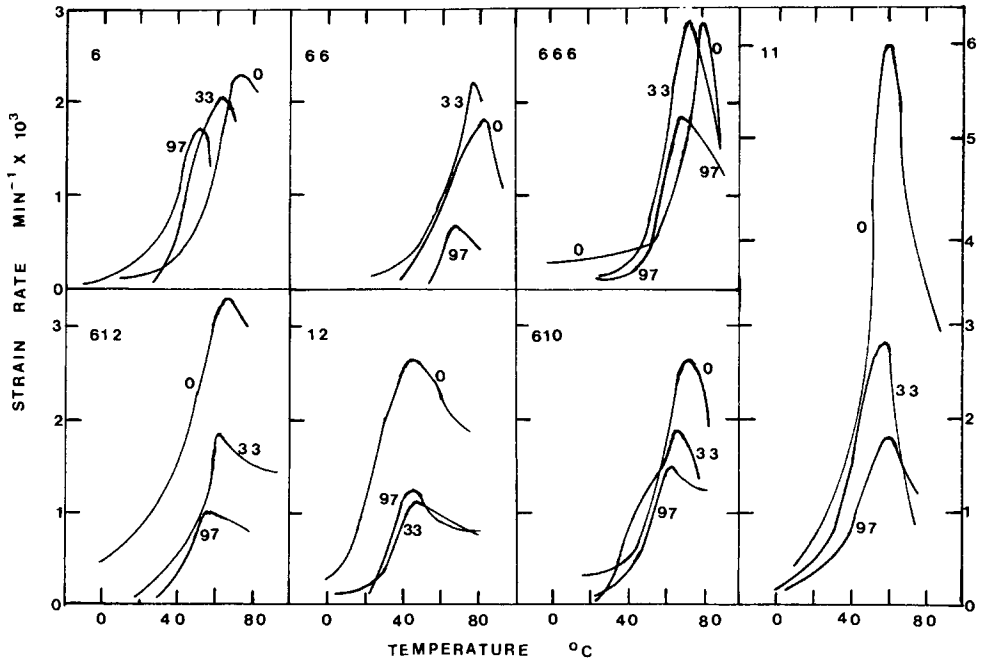
Fig. 4.   Strain recovery rate of various nylons at three relative humidities (0, 33, 97% RH) vs. temperature.

viscosity, i.e., plasticizing effect. There is a comparatively small change in H-bonding over the temperature range used here for dry samples,[18] but water would be expected to disrupt these bonds.

The semilogarithmic plots of relaxation times vs. the reciprocal of absolute temperature yielded a series of lines which were usually slightly curved but bunched for each nylon. Energies of activation were not calculated but the slopes decreased in the order nylon 66, 666, 610, 12, 6, 612, and 11. The curves reached a minimum and then increased somewhat. The minimum was interpreted as occurring at the T_g. The data are in Table III. Blanks indicate that no definite minimum was observed.

TABLE II
Glass Transition Temperatures (°C) for the Nylons from Strain Recovery Curves
at Various Relative Humidities

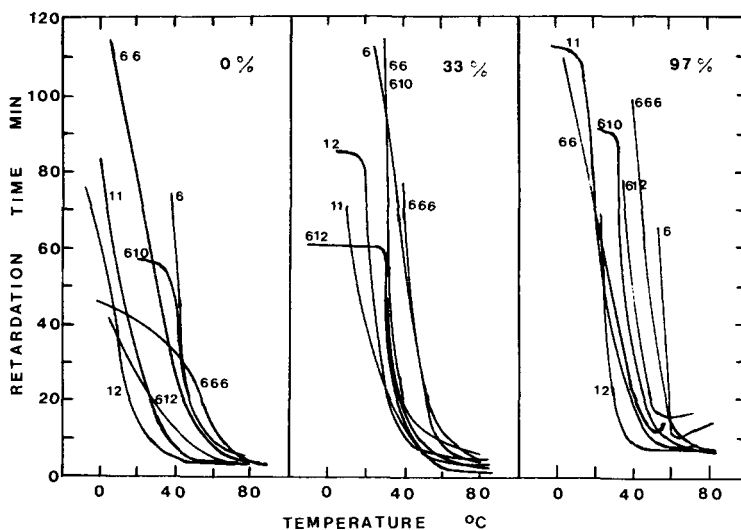|	Relative humidity		
Nylon	0%	33%	97%
6	73	64	51
11	57	55	58
12	46	47	47
66	82	77	65
610	74	67	65
612	66	63	63
666	82	74	70

Fig. 5. Retardation time spectra of the various nylons at three relative humidities (0, 33, 97% RH).

The more refined use of thermally stimulated creep as described by Laca-banne et al.[9] was not attempted in this comparative study.

SUMMARY

The higher moduli resulting from the semicrystalline morphology and the hydrogen bonding nature of the nylons results in the properties varying with the methylene to amide ratio. The higher the ratio, the lower the resistance to creep. The resistance to creep decreased in the order

$$66, 6, 666 > 610, 612 > 12, 11$$

TABLE III
Glass Transition Temperatures (°C) for the Nylons from Plots of the Relaxation Time
vs. Reciprocal of Absolute Temperatures

	Relative humidity		
Nylon	0%	33%	97%
6	> 84	67	51
11	67	63	63
12	—	63	48
66	87	79	67
610	78	74	66
612	—	—	63
666	84	78	75

The retardation time spectra were similar for the various nylons with a broad peak which encompassed the glass transition temperature. As above, the retardation time is decreased with increasing methylene/amide ratio.

Creep resistance and glass transition temperatures are decreased by water absorption but the effect on the retardation time spectra is less certain. The sensitivity to water increases with decreasing methylene/amide ratio. The decrease in elasticity of the H-bonded network seems to override the plasticizing effect of water when water is absorbed.

Thermal history is difficult to control but at least one cycle, carrying the sample from below the glass transition region to just below the melting temperature, is desirable to pass the sample through the temperature of maximal crystallization rate.

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