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Stress-Relaxation Hardening of Nylon 66 Filaments

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It was observed that an additional increment in stress was necessary to continue deformation in nylon 66 filaments, which had been relaxed, but not unloaded, before fracture. This stress increment consisted of a small permanent increase in stress, in addition to a larger temporary increase in stress to yield. Both the temporary and permanent increments increased as the strain, strain rate, temperature and humidity increased. Similar effects were observed in other polymers, but not in metals or ceramics.

1. Introduction

Stress-relaxation studies on polymers have been carried out by a number of investigators. An extensive compilation of the available data on polymers has been made by Tobolsky [1]. In particular the stress-relaxation behaviour of nylon 66 has been studied by Hammerle and Montgomery [2]. It has been shown that the relaxation is dependent on previous strain, temperature, humidity, relative viscosity and strain rate.

In general, the previous work on polymer systems has been concerned only with the stress-relaxation behaviour. The present paper describes an unusual hardening behaviour in polymers. It was observed that an additional increment in stress was necessary to continue deformation on reloading filaments which have been stress-relaxed with time under load. The effects of strain, strain rate, time of stress-relaxation, humidity, and temperature on this hardening are described.

2. Experimental Procedure

In this investigation monofilaments of 65 denier as-spun and 15 denier machine drawn nylon 66 of normal commercial molecular weight were used. All stress-strain tests were performed on an Instron tensile testing machine at 25°C, 55% relative humidity and a strain rate of 2.0 in/in/min unless otherwise noted. The machine drawn samples were also tested after exposure to boiling water for one minute in the slack (free to relax during boil-off) and taut (held at constant strain during boil-off) conditions.

3. Experimental Results

3.1. Definition of Terms

Fig. 1 illustrates a typical Instron chart of a sample which has been strained to a stress, σ_1, and a strain, ϵ_1, held at constant strain for a time varying from t_0 to t_1 during which time stress relaxation occurs, and then restrained. In all cases an increment in stress was necessary to continue deformation after the relaxation under load. The dashed line in fig. 1 is the σ-ϵ for a continuous test. We will define σ_R as the amount

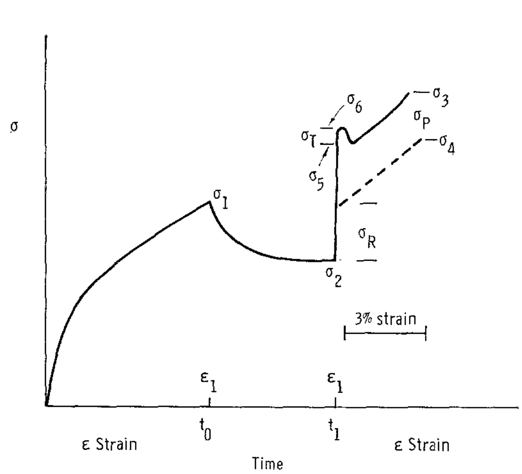

Figure 1 Schematic stress-strain curve in which the specimen is strained to a stress σ_1, relaxed for a time, t_1, and then restrained.

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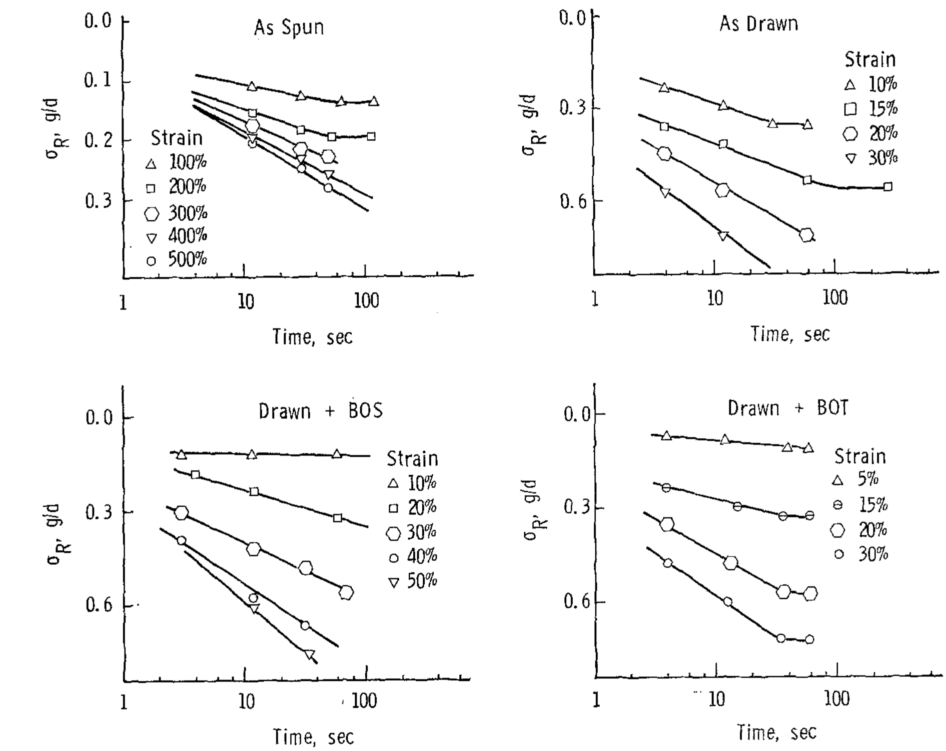

Figure 2 The relaxation stress, σ_R, for samples given the indicated pretreatment as a function of time at a variety of stresses.

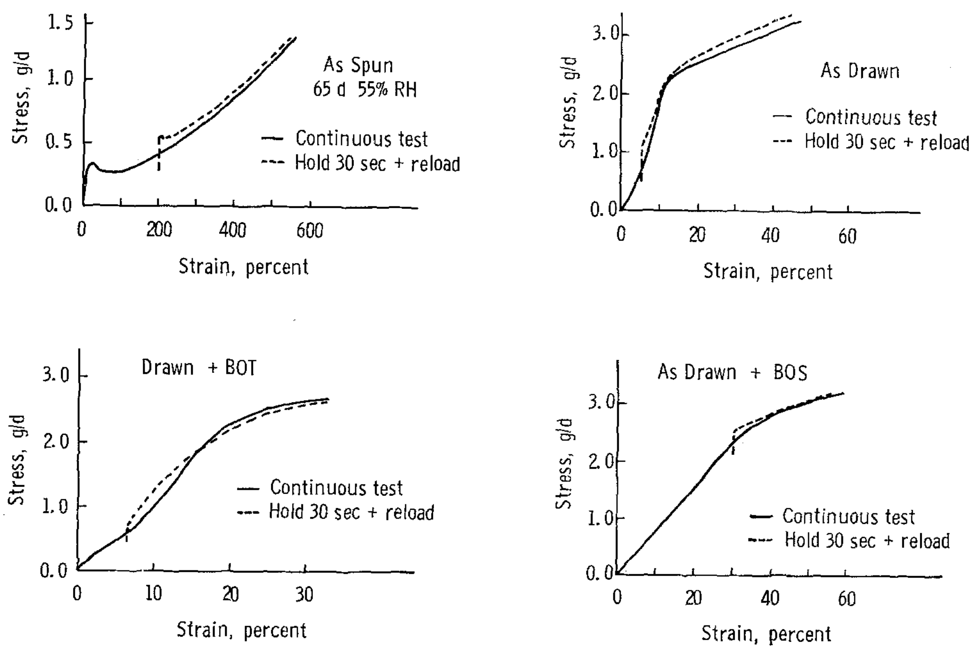

Figure 3 Typical stress-strain curves for samples which have been continuously strained to fracture and for samples which have been strained-relaxed and restrained to fracture.

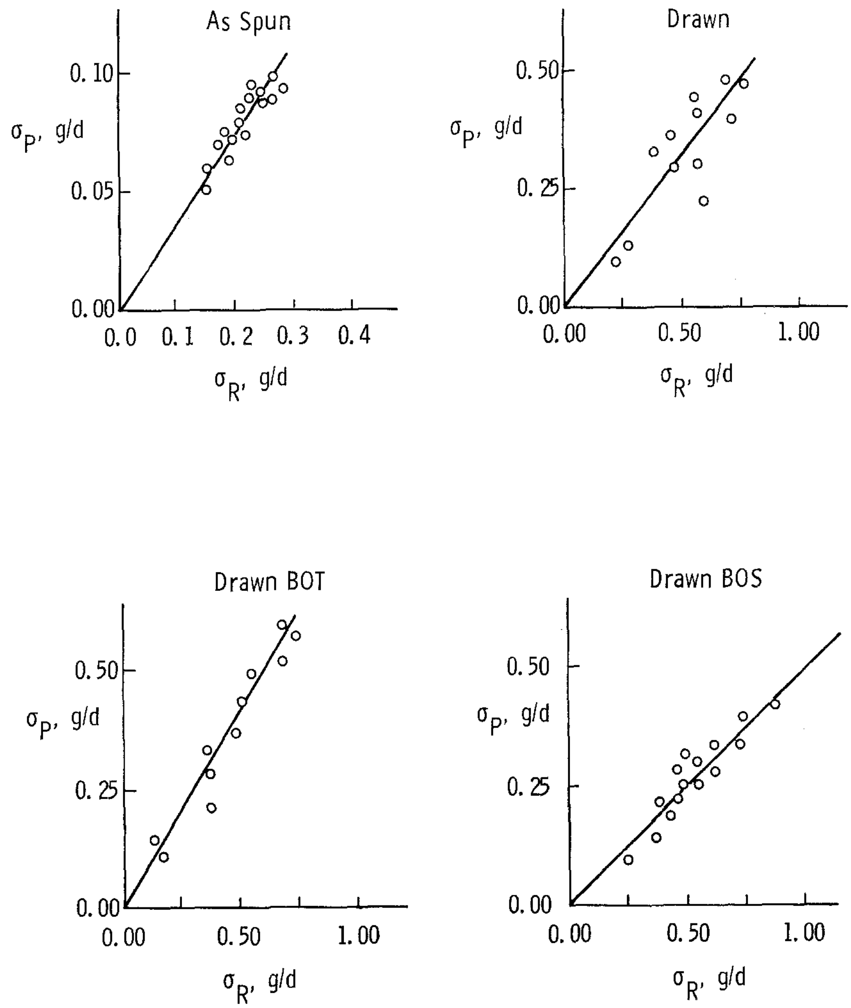

Figure 4 The permanent hardening as a function of the relaxation stress for samples with the pretreatments indicated.

of stress relaxation $\sigma_R = \sigma_1\text{-}\sigma_2$, σ_P as the permanent amount of hardening $\sigma_P = \sigma_3\text{-}\sigma_4$ and σ_T as the transitory increment in stress $\sigma_T = \sigma_6\text{-}\sigma_5$.

3.2. Stress-Relaxation

Fig. 2 summarises σ_R versus log time plots for as-spun nylon 66, machine drawn nylon 66, and machine drawn nylon 66 in the boiled-off slack (BOS) and boiled-off taut (BOT) conditions. In all cases over a limited region a linear relationship is observed. The slope of this linear region increases as the strain increases. It required in the order of minutes to achieve σ_R max.

3.3. Reloading Experiments

Fig. 3 is a plot of typical stress-strain curves of monofilaments in the conditions listed. Also included in the figure are stress-strain curves of samples which have been held at the strains listed for 30 sec and then reloaded. In all cases a permanent and a transitory hardening is required to continue deformation.

The permanent hardening measured after 3% strain ($\sigma_3\text{-}\sigma_4$) is plotted as a function of the relaxation stress in fig. 4. In all cases σ_P is linearly proportional to σ_R. It was also found that σ_T was linearly dependent on σ_R, fig. 5. In this case, however, a stress relaxation of 0.2 and 0.5 g/d was necessary to produce a temporary increment in the as-spun and drawn samples, respectively.

Although transient and permanent hardening were observed after relaxation, the final break tenacity was not significantly different in samples taken directly to fracture, or samples

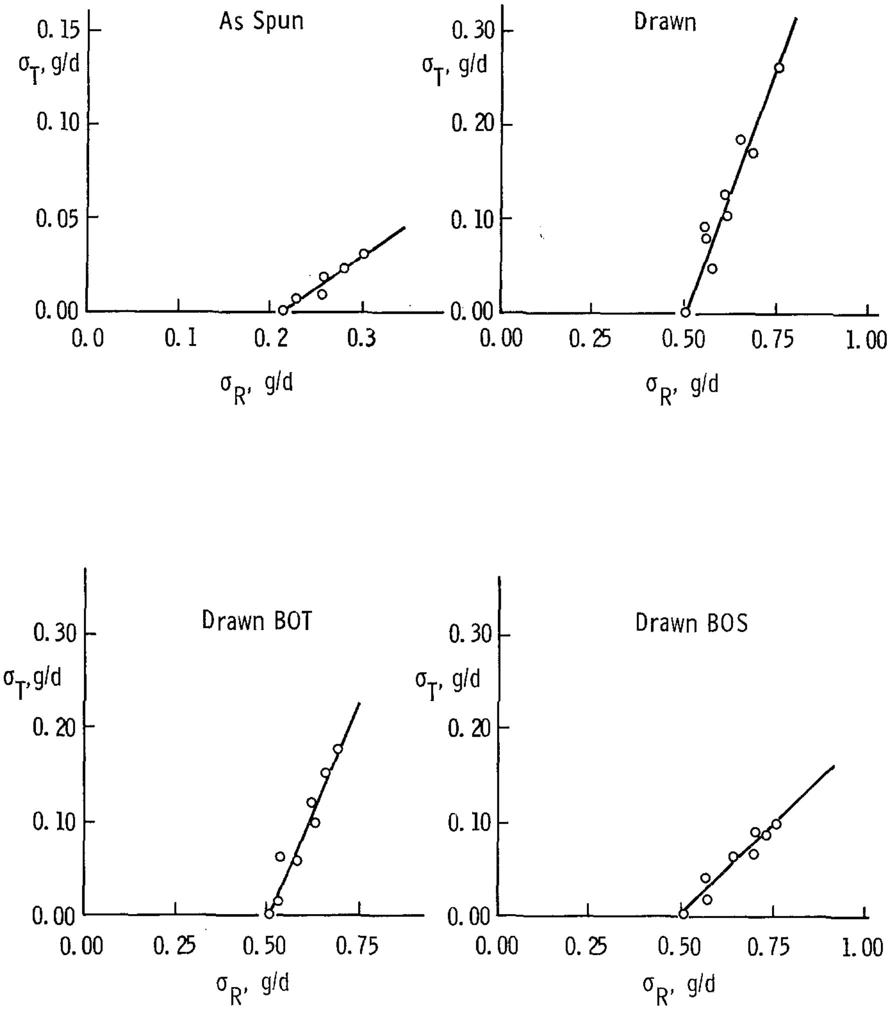

Figure 5 The temporary hardening as a function of the relaxation stress for samples with the pretreatments indicated.

given intermediate relaxations before fracture, fig. 6.

At a constant σ_R both σ_P and σ_T increased linearly, as a function of the log strain rate for as-drawn samples, fig. 7. A similar relationship was observed in the BOS and BOT samples.

3.4. "Coaxing" Test

In the work described above the samples were relaxed once and then reloaded to fracture. A series of tests was carried out in which samples were relaxed several times before fracture. A typical series of "coaxing" tests is summarised in table I for an undrawn fibre. Sample 1 was relaxed for 30 sec at each 100% strain interval; sample 2 was strained 200% and relaxed for 30 sec at each 100% strain interval; sample 3 was, etc. The σ_R, σ_P, and σ_T increased as the number of holds increased. However, σ_R, σ_P, σ_T, the strain to fracture, and the tenacity, were not affected by the number of previous holds for a given strain. These conclusions were also valid for the as-drawn, BOT and BOS nylon.

3.5. Effect of Temperature and Humidity

Samples of as-spun and as-drawn nylon were tested at 50 and 90°C at 55% relative humidity. As the test temperature increased, the modulus and the yield strength showed the normal decrease. For a given strain, an increase in temperature increased the quantity $\sigma_{R/\sigma}$ (where σ is the stress at which relaxation began). Although the quantity $\sigma_{P/\sigma}$ was insensitive to temperature, the quantity $\sigma_{T/\sigma}$ increased strongly with tem-

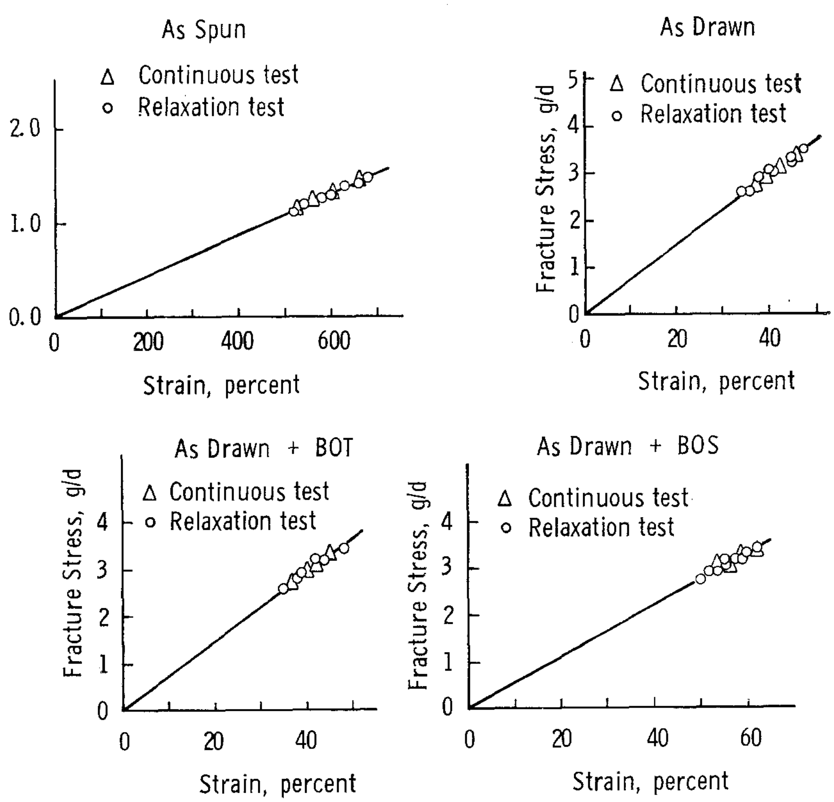

Figure 6 The fracture stress as a function of strain for samples with the pretreatments indicated.

TABLE I As-spun 66 nylon, 65d 55% RH, $\dot{\epsilon} = 2.0$ in/in/min

Sample	Strain %	Relaxation stress grams	Time sec	σ_R gm/d$x10^{-2}$	σ_P gm/d$x10^{-2}$	σ_T gm/d$x10^{-2}$	Strain to fracture %	Tenacity gm
1	100	19	30	8.5	3.0	0	—	—
	200	31	30	11	3.5	0.2	—	—
	300	44	30	14	4.7	0.7	600	89
	400	65	30	15	5.5	1.3	—	—
	500	80	30	16	6.0	2.0	—	—
2	200	29	30	12	3.2	0	—	—
	300	42	30	14.5	4.2	0.7	—	—
	400	59	30	15	5.5	1.2	580	86
	500	78	30	16	6.5	1.8	—	—
3	300	42	30	14	4.5	1.0	—	—
	400	58	30	15	6.0	1.5	670	91
	500	76	30	16	6.4	2.0	—	—
4	400	57	30	15	5.5	1.0	570	85
	500	74	30	16.5	6.0	1.8	—	—
5	500	73	30	16	6.0	2.0	550	85

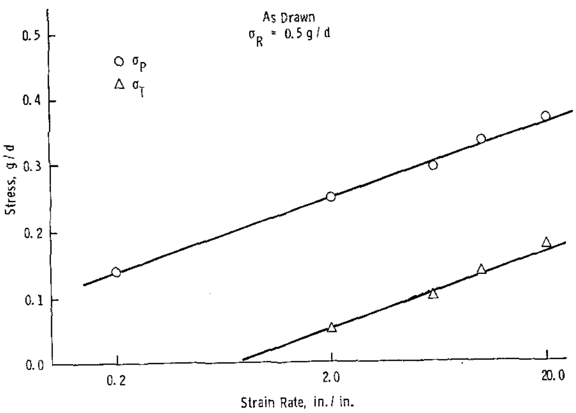

Figure 7 The permanent and temporary hardening as a function of strain rate for as-drawn yarns which have been relaxed 0.5 g/d.

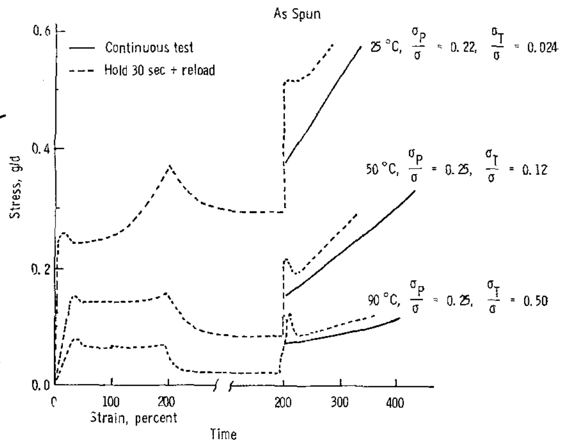

Figure 8 Effect of temperature on the stress-strain-relaxation behaviour of as-spun fibres.

perature. A typical series of curves is shown in fig. 8. In samples tested at 25°C and 72% relative humidity, the stress to achieve a given strain decreased, but σ_R, σ_T and σ_P increased in comparison to the tests at 55% relative humidity.

3.6. Effect of Sample Size

Samples of nylon 66 were cast into 1 in. diameter rods, machined into $\frac{3}{4}$ in. diameter tensile samples and then tested in tension. The same type of behaviour was observed in bulk spherulitic nylon as in fibres, i.e. on holding at strain the stress decreased, on reloading a temporary and permanent increase in stress was necessary to continue deformation. σ_T, however, required a longer strain interval at the same strain to decay out.

3.7. Other Fibres

To determine if the increment in stress after relaxation without unloading was unique to nylon 66, drawn fibres of other polyamides and polyesters were tested. A measurable σ_T and σ_P was observed, but insufficient results were obtained for detailed discussion here.

3.8. Metals and Ceramics

To determine if the temporary and permanent hardening were unique to polymer systems, wire samples of zinc, aluminium, brass, 316 stainless steel, Hastelloy C, alumina, and zirconia were relaxed after straining and then restrained without unloading. In all cases σ_T or σ_P were not observed.

4. Summary

The significant features of foregoing results are.
(i) In room temperature tests on nylon 66 monofilaments which are stress-relaxed and reloaded, both a transitory and a permanent increment in stress was required to continue deformation. This observation was made on as-spun, drawn, and drawn samples after boiling off slack or taut in water. In all cases σ_T and σ_P were linearly dependent on σ_R. A relaxation of 0.2 and 0.5 g/d was necessary to produce σ_T in the as-spun and drawn samples, respectively.
(ii) Relaxation before reloading had no significant effect on the tenacity.
(iii) $\sigma_{T/\sigma}$ and $\sigma_{R/\sigma}$ increased as the humidity and the test temperature increased. The temporary and permanent hardening were not affected by the previous mechanical history, i.e. number of holds.
(iv) σ_T and σ_P are observed in rods and other polymeric fibres, but not in metal or ceramic wires. This phenomenon is apparently limited to polymeric systems.

References

1. A. V. TOBOLSKY, "Properties and Structure of Polymers" (New York, John Wiley & Sons, Inc.) (1960).
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