Accurate measurement of creep of nylon-6,6 at constant temperature and humidity

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This paper describes a purpose-built environmental chamber housing three creep machines for accurate measurements of creep in a hygroscopic polymer. The environmental chamber controls the temperature to within ±0.1°C and the relative humidity to within ±1% r.h. or better. The creep machines are sufficiently accurate to limit the error in the measured modulus to ±0.4% at the 0.1% strain level. Also described are new designs of lateral extensometers and of a simplified zero-load control machine based on similar principles to those of the creep machines, but which can also be adapted for accurate creep tests on very small test pieces using loads of as little as 1 N. Creep results are presented of nylon-6,6 at several constant stresses and relative humidities at 23.5°C, each test lasting for six weeks. Evidence is given, in the form of 24 h creep curves, of an aging phenomenon in nylon-6,6: a progressive increase in stiffness with storage time at the test condition following humidification at 90% r.h.

INTRODUCTION

The selection of the dimensions during the design of a polymer moulding that will be stressed in service, is partly determined by the allowable deflection. The deflection under stress over a period of time is a function of the polymer's creep properties. The creep properties are normally measured in the laboratory under constant conditions. These constant conditions, in the case of nylon, normally mean constant stress, temperature and humidity.

In this study the intention was to build accurate creep testing machines, in order to test nylon-6,6 pieces at a constant temperature and at various constant stresses for up to 6 weeks, not only at constant humidities but also, at a later stage, with step changes in the air humidity during the course of tests. These air humidity changes imposed certain constraints on the design of the environmental chamber and, in order to limit the duration of tests, on the thickness of the test pieces. In turn this affected the design of the creep testing equipment.

While this work was proceeding, interest was aroused, as a result of publication by various authors[1-3], in aging of polymers following heating to above T_g, the glass transition temperature; it was found that shortly after cooling the polymer was relatively flexible but it became progressively stiffer with storage time at the low temperature. Since the creep measurements described below were made at relative humidities both above and below a transition, it was felt to be important to determine whether a similar aging phenomenon could be observed after drying a test piece from above the transitional moisture content. Most of the test results given below are from samples that were tested about 2 years after moulding, by which time they had nearly aged to an equilibrium value. However, some additional results are presented to show a 'humidity aging', a progressive decrease in creep compliances following humidification.

PREVIOUS WORK

Details of accurate creep testing apparatus have been described by various authors, especially Darlington and Saunders[4,5] and Mills and Turner[6]. The main distinctive feature of the former apparatus was the use of stable and precise capacitance-type displacement transducers for measuring dimensional changes, whilst the latter used an optical measuring system that was also stable and precise.

Creep data on nylon-6,6 have been published by ICI[7], by Turner[8], by Catsiff *et al.*[9] and by Howard and Williams[10,11].

No results are available of aging effects on nylon-6,6. However, Dunn and Turner[2] studied the effects of aging time after cooling to temperatures below the T_g on the density and modulus of polypropylene. Both were found to increase progressively, and this was attributed to a decrease in free volume. Christie and Darlington[3] also found that the modulus of nylon-6 increased with storage time. The most detailed work on aging of polymers appears to have been done by Struik[1], who found that the rate of aging of PVC, following heating above T_g and quenching, was dependent on temperature, but could be equivalent to a horizontal shift of the creep curves of as much as five decades over an aging time factor of 33 000. He also found that aging occurred in a number of other materials including crystalline ones.

EXPERIMENTAL

Materials

The material used in this study was ICI Grade A 100 nylon-6,6, injection moulded in the form of 1/8 in (3.17 mm) thick ASTM tensile test bars. The density was measured as 1.146 g/cm^3 by flotation on a mixture of toluene and carbon

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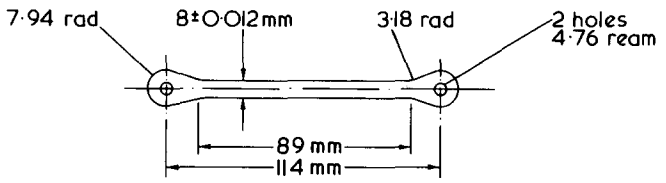

Figure 1 Profile of creep test piece. Dimensions in mm

tetrachloride at 20°C, giving an estimated crystallinity of 36% (from ICI data).

The birefringence of a film cut from the central plane of a similar bar was measured with a Babinet compensator as $3(10^{-3})$ in a plane perpendicular to the thickness direction and $4(10^{-3})$ in a plane perpendicular to the width direction of the test piece.

Because it was planned to make creep tests at a later date with concurrent sorption or desorption of moisture and because moisture in nylon-6,6 has a relatively low diffusion coefficient, it was necessary to use thin test pieces, otherwise they would take too long to reach equilibrium. Therefore a thickness of 1 mm was chosen, giving a half time for sorption of about one week.

The 1 mm test pieces were taken from the central core of the 1/8 in (3.17 mm) thick bars by machining equal amounts from both faces. This was done with a fly cutter on a milling machine, using a fast cutting speed, a slow feed rate and a very sharp tool to give a good surface finish. The direction of cutting was set perpendicular to the test piece axis rather than oblique to it, to prevent any twisting of the test piece due to cutting 'drag'.

The 1 mm thick sheet was then cut on the router to the shape shown in *Figure 1*. This was of similar shape to the test piece described by Mills and Turner[6].

All test pieces were preconditioned in sealed boxes containing the appropriate saturated salts. They were stored in a constant temperature room for at least 10 weeks before testing. While they were being mounted in the testing machine the test pieces were exposed to ambient conditions for about 1¼ h, but then they were held at the test conditions for 5 days before loading. This was considered enough time to reduce any conditioning errors to a very low level.

The thin, 50 μm, test pieces were prepared by cutting with a microtome and mounting between 2 thin aluminium end plates with an epoxy adhesive. Since the test pieces were too thin to take the points of the axial extensometer, a 3 mm square piece of PVC self-adhesive tape was placed on each side where the points were located.

Environmental chamber

Three creep machines and a zero-load control machine were housed in a purpose-built environmental chamber. A sectional sketch of the chamber is shown in *Figure 2*. The main design criteria are listed below.

(a) In order to accommodate tests of up to 3 months duration, reliability of control apparatus is very important: a sticky temperature or humidity controller could ruin several months' testing.

(b) Temperature control should ideally be within ±0.2°C at about 23.5°C.

(c) Relative humidity control should ideally be within ±1% r.h. since the moisture content of nylon depends mainly on the relative humidity of the surrounding air.

(d) Fairly rapid changes of relative humidity may be required. Such changes should be 90% complete within 10 minutes, and complete and accurately controlled within 45 min (these times may be compared with approximate half-times for equilibrium sorption of 1 mm thick nylon-6,6 of about 150 h).

(e) Routine inspection and maintenance must be possible with the minimum disturbance of the controlled environment.

To satisfy the reliability requirement (a), trays of wet salts were used to control the atmosphere rather than fully automatic humidification and dehumidification. Although these salts required regular inspection and topping up there was no danger of mechanical failure. The salts used were (at 23.5°C): calcium chloride 29% r.h.; sodium nitrite 61% r.h.; sodium chloride 72% r.h.; sodium carbonate 89% r.h. The calcium chloride was obtained in large pieces, whilst the other salts were spread over porous coke which provided a large surface area for contact with the circulating air.

The reliability requirement (a) and the temperature control requirement (b) required the use of a contact thermometer which of course has no moving parts and in fact gave temperature control of better than ±0.1°C. In order to reduce the possible damage caused by a failure of the associated relay switch, a low power heater was used, together with good thermal insulation of the chamber walls and a room controlled to 20°C. By this means, if the heater failed to switch on, the chamber temperature could slowly fall towards 20°C, whilst if it failed to switch off, it could slowly rise to not more than about 1°C above its nominal operating temperature. In the case of a power failure the wet salts gave a more positive humidity control than, for example, a humidifier alone; and it was found during trials that for slow temperature changes of several °C the salts could maintain the relative humidity accurately.

Although the relative humidity [requirement (c)] was not seriously affected by slow temperature changes, it is known to fluctuate with rapid temperature changes and would be seriously affected by temperature gradients within the chamber itself. For instance, reference to standard

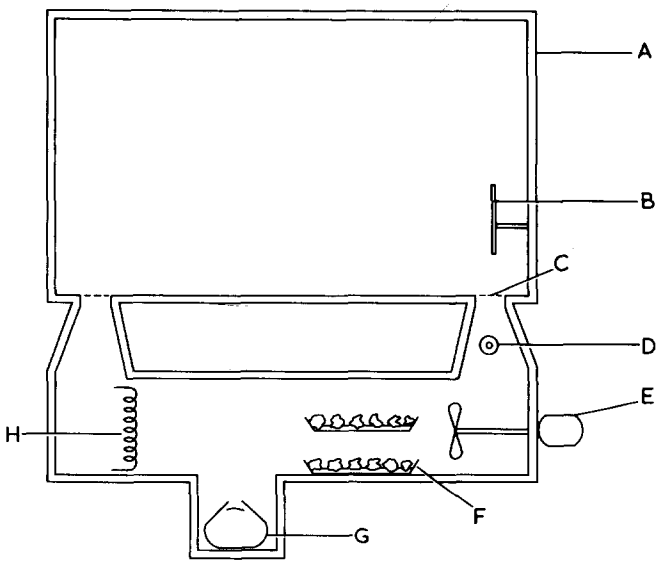

Figure 2 Diagrammatic sectional front elevation of environmental chamber. A, Insulated walls; B, contact thermometer thermostat; C, grill; D, humidistat; E, circulating fan; F, trays of salts; G, humidifier; H, heater

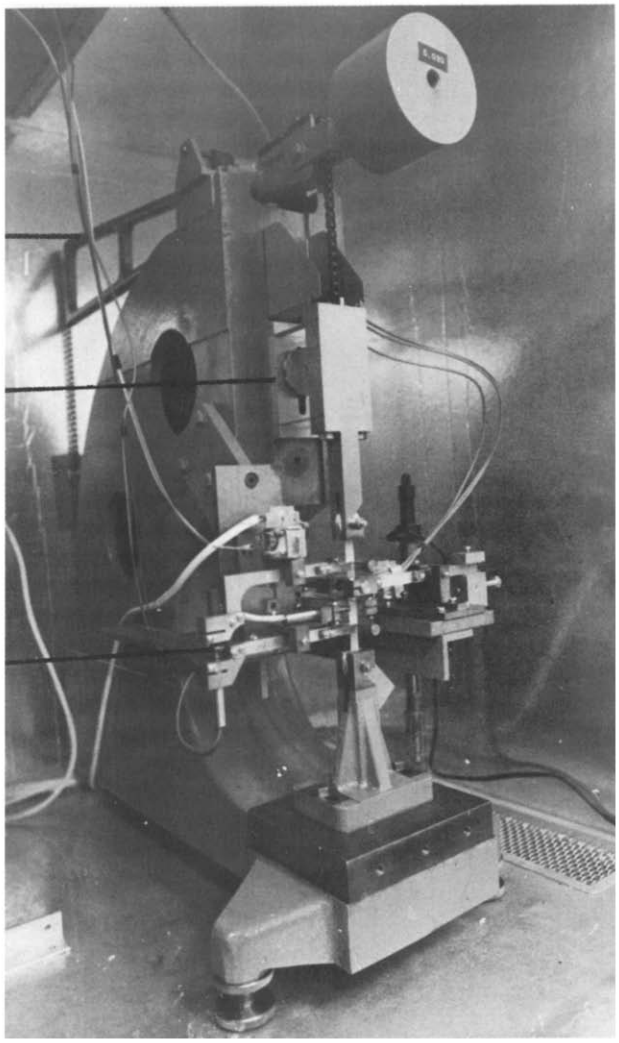

Figure 3 Creep machine with mounted test piece

vapour pressure *versus* temperature and relative humidity charts shows that a 1°C temperature change at the 90% r.h. level would cause a relative humidity change of 6%. Therefore, not only good temperature control with respect to time but also with respect to the space of the chamber was needed. This was provided by good thermal insulation coupled with a low heater output and frequent switching. Checks of air temperature through the chamber showed that all regions appeared to be within the specification, and inspection for condensation at high humidities showed that none occurred within the body of the chamber at temperatures within 0.5°C of dewpoint.

Requirement (d) for rapid changes of relative humidity was approached in two ways.

(i) By the minimum use of hygroscopic materials within the chamber. The walls and ceiling of the chamber itself were lined with aluminium foil, the floor with thicker aluminium sheet, and the trunking was painted with bitumen. All joints were hermetically sealed as well as was practicable.

(ii) Rapid humidification was supplied by an atomizing-type humidifer and rapid dehumidification was supplied by anhydrous calcium chloride, both by manual control. When the relative humidity was near to the required value, control was passed to the wet salts.

The requirement (e), for ease of routine inspection and maintenance, would be best achieved with a 'walk-in' chamber. With the present chamber, glove holes enabled wet-and-dry-bulb thermometer readings to be taken and recorder charts to be changed. Salts were renewed through a trap door that could be opened and closed quickly (in about 2 sec) and the chart recorder showed no observable effect during such openings. Provision was made for refilling the humidifier through a tube leading through the trunking.

Other design features included:

(1) the fan motor was mounted outside the chamber to prevent the heat of the motor affecting the temperature control, and to avoid difficulties of running the motor in high humidities;

(2) spot checks of the relative humidity were made with an Assman wet-and-dry-bulb thermometer. Any running anomalies such as temporary power cuts were observed on a chart recorder incorporating a bimetallic strip thermometer and a hair hygrometer;

(3) while running the chamber at high relative humidities the humidifier was used in support of the salt solutions in cases where the evaporation of water was too slow. For this purpose the humidistat was set at a slightly lower relative humidity than that which the salts provided;

(4) in the centre of the front panel was a small double-glazed inspection window. On either side were larger single-glazed windows which were normally covered with thermally-insulated doors. Two fluorescent lights were incorporated in the ceiling.

Creep measurement apparatus

The lever-type creep machines have been described previously[5], but some small changes were made in order to obtain improved accuracy with the particular creep specimens and creep programme planned. Among these are some changes to the creep machines themselves. Parallel spring guides are used to ensure accurate axial extension of the test piece, and the stiffness of their springs can make a small but significant reduction in the effective load if the deflection is large. Therefore the fixed backing plate of the guide was held by a special bolt with a large knurled head, as shown at A in *Figure 3*, to allow manual adjustment at frequent intervals so as to limit the spring deflection to an acceptably small value, as indicated by a gauge. The initial large deflection on application of the load was estimated and allowed for.

The accuracy was also improved by calibrating the actual lever ratio of the nominally 5:1 loading lever (B in *Figure 3*) to the nearest 0.1%, and by calibrating all masses that were used as loading weights to the nearest 0.001N.

The chief changes to the axial extensometers were:

(A) the 1/8 in (3.17 mm) diameter ball end of the transducer (C in *Figure 3*) was replaced by a ½ inch (12.7 mm) radius end to reduce the contact pressure and the consequent danger of wearing or scratching the opposing face. This opposing face was a microscope slide cover glass backed by an adjustable steel rod whose end had been accurately ground square;

(B) the location of the transducer head was arranged to be as near as practicable to the horizontal line through the transducer-arm pivot. By this means the movement of the transducer during the extension of the test piece was mainly in a vertical direction, with a minimum of lateral movement which would cause the lever ratio to change from its nominal value of one. In turn this meant that there would be a large lateral movement of the mating glass surface, but this should not change the lever ratio of the system;

(C) the screwed locating points that bite into the test piece were prevented from moving in their threaded holes

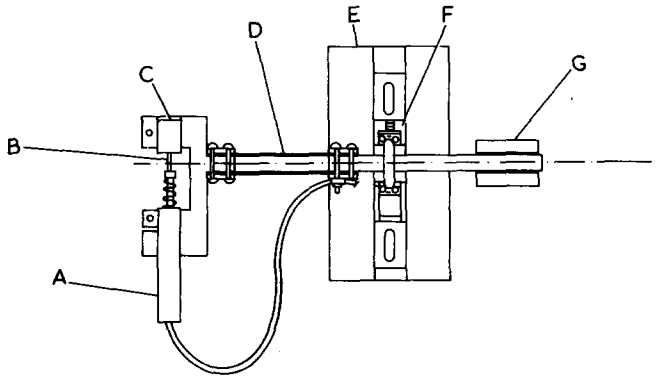

Figure 4 Plan of width extensometer. A, Transducer; B, test piece cross section; C, fixed anvil; D, parallel spring guides; E, base; F, bearing assembly; G, counterweight

by lining them with PTFE tape. However some doubt was felt about whether the two opposing points were accurately aligned. If not, they could apply a small and possibly changing twist or bend to the test piece during tightening. The solution was to grind off one of the points of each pair and polish a small flat surface accurately perpendicular to the axis of the screw. During assembly the remaining point was correctly located and then the flattened screw was screwed in, so pressing the test piece onto the stationary point;

(D) the transducer wires were looped round and attached to the frame of the creep machine in order to standardize the loading on the lower transducer arm.

Finally each extensometer was calibrated, by means of a drum micrometer attached to a split test piece, to give a correction factor relating the transducer readings to the actual movement of the test piece. A gauge-length template was used during assembly of a test piece to ensure that the two extensometer arms were accurately positioned and square.

Width extensometer

A sectional view of the width extensometer is shown in *Figure 4*. The two chief principles incorporated in this design are firstly that as the test piece lengthens and moves the measuring head must move upwards with it, so that the width is always being measured at the same position; and secondly that as the test piece contracts equally from both sides and may also move laterally, both the transducer and the 'fixed' opposing face must be able to move with it.

The upward movement is supplied by the bearing assembly (F) in *Figure 4*, the weight of the transducer and mountings being counterbalanced by the counterweight (G). The horizontal movement is supplied by the parallel spring guides (D), which not only constrain the measuring head to move truly parallel to the transducer axis, but also (when the bearing assembly is offset slightly) provide a small lateral force to ensure good contact between the fixed anvil (C) and the test piece (B). While setting up a test this lateral force was adjusted to approximately half of the 0.1 N force of the transducer spring, to limit the resultant lateral force on the test piece. These small forces were found to be insufficient to cause compression buckling of the thin, 1 mm test pieces.

The transducer leads were retained in a clip, as shown, to prevent them from causing the measuring head to rotate from its square position. Any force caused by trailing extensometer leads beyond the clip could be corrected by a small adjustment of the counterweight.

It may be noticed that the two faces in contact with the test piece are ground flat, to prevent their penetration into the test piece. This does, however, risk error if the two ground surfaces are not parallel to each other and to the edge surface of a correctly aligned test piece. Great care was taken to avoid these errors, both in grinding the surface of the fixed anvil and in adjusting the orientation of the measuring head during assembly.

Thickness extensometer

The design of the thickness extensometer was essentially similar to that of the width extensometer except for the measuring head, of which a sketch is shown in *Figure 5*. This contains a spring clamp which prevents the rather flexible 1 mm thick test piece from rotating relative to the transducer. Since the thickness extensometer was located close to the width extensometer, this precaution against twisting of the test piece probably also improved the results from the width extensometer. The measuring surfaces in contact with the test pieces were ground flat, and as for the width extensometers, great care was taken to ensure that these surfaces were parallel to each other and to the faces of a correctly-aligned test piece. However, in contrast with the width extensometers, in this case care was taken that the parallel spring guides did not exert any lateral load on the test piece.

Zero load control machine

The zero load control machine is shown in the sectional view of *Figure 6*. This machine was designed for the purpose, firstly because the ordinary creep machines could not be used with a zero load since a small load is needed to centre the test piece in the hooks, and secondly because it was felt that a less expensive and smaller piece of apparatus than the creep machines would be suitable.

It was decided to make use of the same type of spring guides as are used in the creep machines but to mount them suspended from a horizontal surface so that there would be no counterbalancing problems. The test piece is bolted between two of these spring guides as shown.

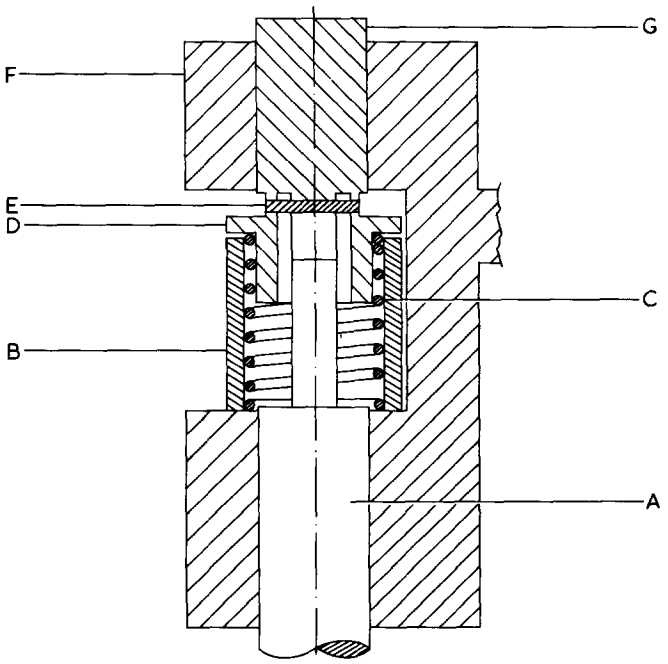

Figure 5 Section through measuring head of thickness extensometer. A, transducer; B, spring housing; C, spring; D, clamping head; E, test piece; F, transducer housing; G, fixed anvil

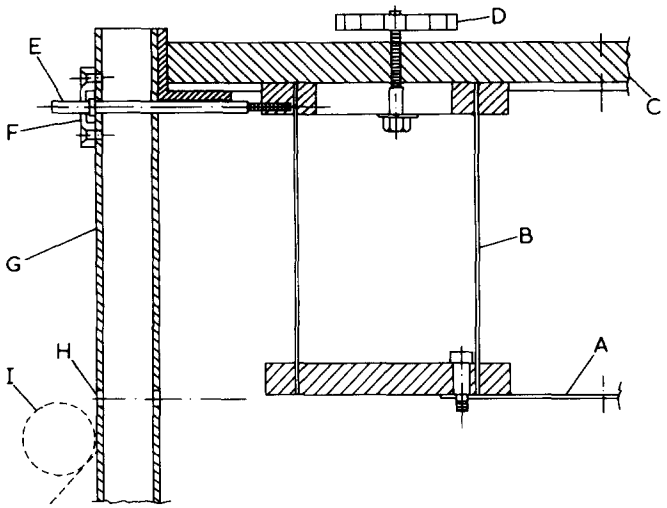

Figure 6 Section through one end of zero load control machine. A, Test piece; B, parallel spring guide; C, mounting beam; D, handwheel and locking screw; E, micrometer screw; F, micrometer-screw housing; G, supporting post; H, loading-filament conduit; I, frictionless loading pulley

The following features may be noted:

(i) The spring diaphragms have been lengthened to approximately 100 mm clear, compared with 50 mm clear for the creep machines. This is to reduce the loading resulting from deflection. Analysis shows that the load on the test piece is 0.15 N per mm of deflection for small deflections.

(ii) The right-hand spring guide (not shown in *Figure 6*) was stiffened by increasing the diaphragm thickness from 0.3 mm to 1.25 mm, so that about 98% of the movement would be confined to the spring guide shown. There were two reasons for this: firstly, the length changes of the test piece would then cause the arms of the extensometer to move in a similar manner to those in the ordinary creep machines (i.e. less movement in the transducer arm); and secondly, the use of very flexible guides at both ends had been found to allow rather large vibrations of the test piece and extensometer system which made readings difficult.

(iii) The test piece is bolted directly to the lower block of the guides (see *Figure 6*). This was felt to be justified because the faces of the three parts of each block had been ground flat after assembly. In order to avoid bending the test piece in a horizontal plane during mounting, a number of washers were placed between the test piece and the nut, which was done up only 'finger-tight' whilst the bolt remained stationary.

(iv) Later modifications to the apparatus for measuring larger length changes were the handwheel (D) and the micrometer screw (E) and (F) of *Figure 6*. The calibrated micrometer screw adjustment allowed the upper block to be moved along its groove to keep the spring diaphragms flat and so reduce the load on the test piece to zero. The handwheel allowed the clamping screw to be loosened before adjustment and retightened immediately afterwards. This adjustment was done with the gloves from outside the environmental chamber and its magnitude could be determined from the extensometer readings.

(v) A further modification was to adapt this machine for creep tests on very thin test pieces, 50 μm thick, and using low loads of about 1 N. The load was applied by a nylon filament passing through the conduit (H) and attached by a yoke to the test piece clamping bolt. The filament passed over the 'frictionless' loading pulley (I) to a weight hanger. Although this pulley system appears very crude, consisting merely of a light rigid plastics tube resting on a 45° inclined plane, and held in place by the friction of the filament passing over it; no other pulley system could be found to give sufficiently low friction to achieve the required loading precision. The low friction of the system was checked by noting the extensometer readings under increasing and decreasing loads and were found to be almost identical. The pull on the filament due to the weight of the tube was considered to be part of the pre-load.

(vi) A number of modifications had to be made to the extensometers, mainly due to their different mounting orientation. For instance, the axial extensometer arms, being pivoted in a horizontal plane required no counterweights. On the other hand, to prevent the transducer spring from exerting an axial load on the test piece the transducer spring was detached from the barrel of the transducer and held with a retaining clip attached to the fixed anvil arm of the extensometer. By this means a load was exerted between the fixed and moving anvils, without this load being transmitted via the extensometer arms to the test piece.

The width extensometer, being pivoted in a vertical plane, with the arm vertical, required no counterweight and the arm was cut off short just behind the bearing. The thickness extensometer was also pivoted in a horizontal plane and therefore required no counterweight; but its parallel-spring strips needed to be thicker than normal to prevent excessive sagging of the measuring head. Strips of 1.25 mm thickness were used compared with the normal 0.3 mm, giving a lateral load of 65 N/mm of deflection. Great care was taken that this extensometer did not exert a vertical force on the test piece.

Checks on accuracy

In order to check the accuracy of the axial and lateral strain measurements some trial tests were made on several 1/8 in (3.17 mm) thick PVC samples whose 100 sec modulus and Poisson's ratio had been well established at the Materials Department of the Cranfield Institute of Technology. Following preliminary tests a number of minor changes were made, in order finally to achieve an error in the modulus of about ±0.4% at the 0.1% strain level (i.e. a strain error of about 0.0004%). Some examples of the modulus results are given in *Table 1* in which can be seen the expected slight reduction in modulus with increase in strain. A further demonstration of the precision of the machines is seen in the internal consistency of the many tests recorded in *Figures 7, 8* and *9*.

Poisson's ratio data, obtained during the above tests, are also included in *Table 1*. Both lateral extensometers appear-

Table 1 100 Sec modulus and Poisson's ratio measurements on PVC

Sample	Measurement	Strain (%)	Machine		
			Left	Centre	Right
A	Modulus (GN/m^2)	0.1	3.184	3.201	3.196
		0.2	3.163	3.185	3.159
	Poisson's ratio (width)	0.1	0.366	0.350	0.368
		0.2	0.360	0.358	0.369
	Poisson's ratio (thickness)	0.1	0.359	0.355	0.338
		0.2	0.341	0.362	0.351
B	Modulus (GN/m^2)	0.1	3.183	3.187	3.153
		0.2	3.164	3.158	3.145
	Poisson's ratio (width)	0.1	0.355	0.332	0.357
		0.2	0.337	0.350	0.344
	Poisson's ratio (thickness)	0.1	0.370	0.360	0.349
		0.2	0.377	0.358	0.348

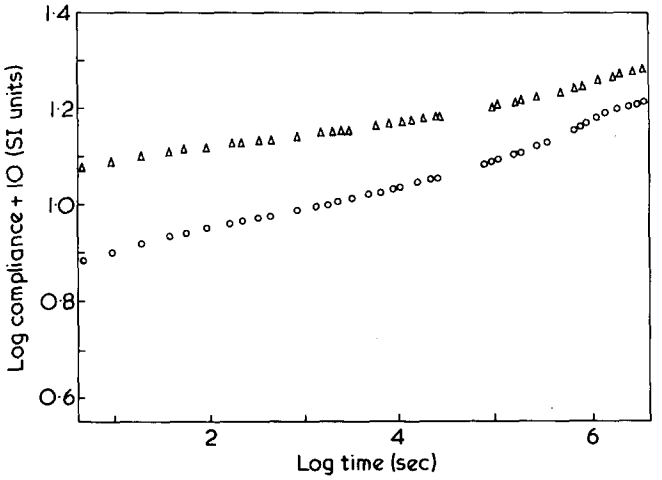

Figure 7 Creep at constant humidity and temperature at 4 MN/m^2. Δ, 90% r.h.; ○, 61% r.h.

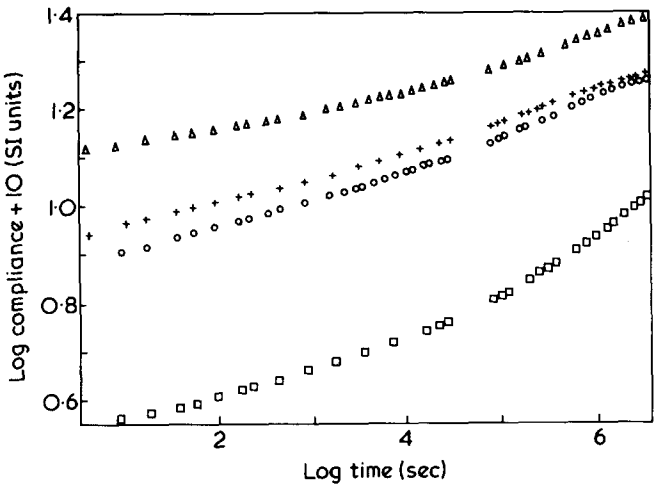

Figure 8 Creep at constant humidity and temperature at 8 MN/m^2. Δ, 90% r.h.; +, 70% r.h.; ○, 61% r.h.; □, 29% r.h.

ed to give reasonably reproducible results. However the mean value of Poisson's ratio of 0.355 in *Table 1* must be compared with a value of 0.39 obtained at Cranfield for both the width and thickness directions.

During the creep programme on the 1 mm thick nylon test pieces, the width extensometers were found to give fairly reproducible results. However, the thickness extensometers showed only qualitatively correct results and are not therefore presented below.

RESULTS AND DISCUSSION

The results of tests at 29, 61, 70 and 90% r.h. at 23.5°C are shown in *Figures 7, 8* and *9* for stresses of 4, 8 and 12 MN/m^2, respectively. These are plotted as $\log_{10}$ (compliance) *versus* $\log_{10}$ time (sec). It may be noted that these curves form a consistent set at all three stress levels and that the compliances are greater at the higher stresses, indicating viscoelastic non-linearity (i.e. stress dependence of isochronous compliance). It may also be seen that at 29% r.h. the material evidently creeps through a transition, whilst at 61% r.h. it appears to be above the transition.

The values of Poisson's ratio obtained from the width extensometers are summarized in *Table 2*. Since no change in Poisson's ratio could be discerned with changes in stress or time, the means and confidence limits given in *Table 2* were obtained from measurements at all stresses and at the arbitrary times of 2 min, 9 h and 1000 h. The wide confidence limits of the results given in *Table 2* do not allow any conclusions other than the apparent increase in Poisson's ratio with relative humidity. However, the trends mirror those obtained on 3 mm test pieces at Cranfield, in which the Poisson's ratio increased through the transition either with temperature or with humidity.

The effect on the creep curve of storage at approximately 22°C and 30% r.h. for 51 months after moulding is shown in *Figure 10*, compared with the curve for testing after 22 months. It can be seen that there is little difference between the two. *Figure 10* also shows the effect of a previous storage at 90% r.h. followed by 26 months at 30% r.h. to give a total aging time of 51 months after moulding. Again there is little apparent effect.

The effect of aging for various shorter periods at 30 and 60% r.h. after 90% r.h. preconditioning is shown in *Figure 11*. The effect of aging is to substantially lower the creep compliance at longer times, with a slight lowering at shorter times. These changes could be easily masked by variations in the level of the relative humidity, particularly at 30% r.h., which is close to the transition. For this reason, great care was taken with the humidity control for these tests, and any in which the relative humidity departed from 29.25% r.h. by more than 0.5% r.h. were discarded or repeated. The results of *Figure 11* were obtained on 50 μm test pieces. Although these measurements were very limited in scope, and therefore

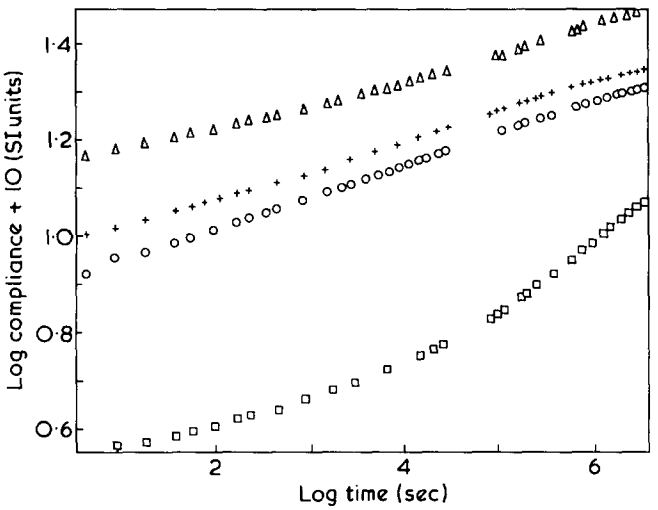

Figure 9 Creep at constant humidity and temperature at 12 MN/m^2. Δ, 90% r.h.; +, 70% r.h.; ○, 61% r.h.; □, 29% r.h.

Table 2 Poisson's ratio measurements on the width of nylon-6,6

Relative humidity (%)	Poisson's ratio	
	Mean	95% Confidence limits
30	0.422	±0.015
60	0.453	±0.009
70	0.449	±0.014
90	0.463	±0.028

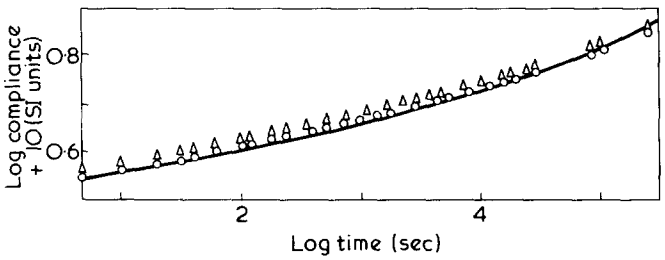

Figure 10 Effects of humidity and aging on creep curves at 29% r.h. and 8 MN/m^2. (———), 22 months at room temperature following moulding; ○, 51 months at room temperature following moulding; Δ, 25 months at room temperature following moulding, then three weeks at 90% r.h. followed by a further 26 months at room temperature and 30% r.h.

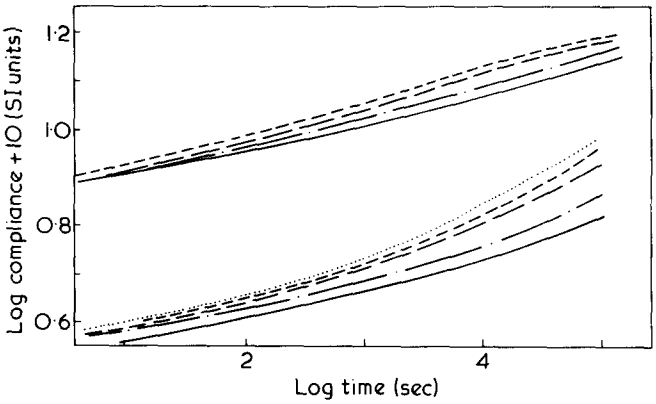

Figure 11 Effect on creep of aging time at test humidity after preconditioning of 50 μm test pieces at 90% r.h. Stress 8 MN/m^2. Upper band of curves at 59.5% r.h.; (- - -), 3 days; (— — —), 21 days; (— · — ·), 65 days; (———), not preconditioned. Lower band of curves at 29.25% r.h.; (.....), 1 day; (— — —), 3 days; (—— ——), 27 days; (— · ——), 110 days; (———), not preconditioned

raise many unanswered questions, they strongly support the idea of an age hardening process following conditioning at 90% r.h. The theoretical explanation is presumably the same as that proposed for aging following heat treatment[2]: the slow return of the free volume to an equilibrium value.

The above creep data obtained under equilibrium conditions, form the baseline for creep data obtained under changing humidity conditions, to be reported in a subsequent publication.

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REFERENCES

1 Struik, L. C. E. *Chim. Ind.* 1976, **58**, 549
2 Dunn, C. M. R. and Turner, S. *Polymer* 1974, **15**, 451
3 Christie, M. A. and Darlington, M. W. *Plast. Polym.* 1975, **43**, 149
4 Darlington, M. W. and Saunders, D. W. *J. Phys. (E)* 1970, **3**, 511
5 Darlington, M. W. and Saunders, D. W. 'Structure and Properties of Oriented Polymers' (Ed. I. M. Ward), Applied Science, London, 1975, Ch 10 pp 334–340
6 Mills, W. H. and Turner, S. *Inst. Mech. Eng. Symposium, Manchester,* 1965
7 ICI Plastics Limited 'Maranyl Data for Design' ICI Technical Service Note N.110
8 Turner, S. *Br. Plast.* 1966, **6**, 306
9 Catsiff, E., Alfrey, T. and O'Shaughnessy, M. T. *Text. Res. J.* 1953, **23**, 808
10 Howard, W. H. and Williams, M. L. *Text. Res. J.* 1963, **33**, 689
11 Howard, W. H. and Williams, M. L. *Text. Res. J.* 1966, **36**, 691