Prediction of creep of nylon-6,6 at constant stress, temperature and moisture content

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A method is described of accurately superposing creep curves, obtained at different relative humidities, that each covered six decades of time. The superposition required an empirical distortion of the logarithmic-time scale; for which the justification was that it not only gave more accurate superposition, but also that the same distortion could be successfully used for five relative humidities and three stresses and needed the same horizontal shift factor for all stresses except at the highest relative humidity, of 90%. Equations were fitted to the resulting master curves and non-linearity correction factors, enabling the computer to predict creep curves at any constant stress up to 12 MN/m^2 and at any constant humidity up to 90% r.h. No attempt has been made to explain the success of the distortion used, but its usefulness is readily apparent.

INTRODUCTION

The apparatus for accurate measurements of creep under various conditions of stress, temperature and moisture content was described in a previous paper[1], which also presented a basic set of creep data for nylon-6,6 at a range of constant stresses and moisture contents at 23.5°C. In order to design for creep at intermediate values of stress or humidity it is necessary to interpolate; and one aid to interpolation is the time–humidity superposition of a number of measured creep curves to form one master creep curve[2–4]. However, observation of master curves in the literature shows that there is a considerable degree of scatter, in spite of attempts to obtain better superposition of the individual creep curves by such means as shifting the compliance/log time plots parallel to both the compliance and time axes.

This paper describes a method of superposition of the previously described creep curves, using an empirical distortion of the time scale. This distortion was introduced purely for the purpose of obtaining accurate superposition, and no attempt has been made to justify it on theoretical grounds at this stage. With the chosen distortion, relatively accurate superposition was obtained for five relative humidities and three stress levels, and the master curve together with non-linearity correction factors and humidity-shift parameters were incorporated in a computer programme to predict the creep at any specified constant condition.

PREVIOUS WORK

Howard and Williams[2,5] studied time–humidity superposition of oriented nylon-6,6 fibres, using stresses of 0.1, 0.35 and 0.5 g/den (10, 35 and 50 MN/m^2) at temperatures of 25, 35, 60 and 90°C and moisture contents of 0%, 1% and 2%. Using time–temperature superposition they obtained master creep curves for each of the three moisture contents, superposed to a reference temperature of 25°C and using the same temperature-dependent shift factors (a_T)* for all three conditions. Some interesting conclusions are that (i) the temperature-shift factor appears to be independent of moisture, and (ii) the master curves for 1% and 2% moisture are similar to the master curve under anhydrous conditions, but shifted to shorter times by 1.45 decades per 1% moisture. They concluded that the only effect of moisture is to shift the creep curves to shorter times, 1.45 decades for the 1% moisture content and 2.90 decades for the 2% moisture content. They therefore felt justified in treating the effect of humidity as similar to that of temperature and to postulate a temperature-moisture equivalency factor, so that 1.45% moisture is equivalent to 15.1°C. The authors supported this approach by an experiment to check that the effects of changing the moisture content were, in fact, reversible, and that no permanent structural changes occurred. The authors compared their results with those of a number of previous investigators[4,6–11] and found that the above conclusion was consistently supported; even by the results of Williams and Bender[4] which were for undrawn fibres.

Time–humidity superposition was studied in detail for nylon-6 by Onogi *et al.*[3]. They found similar results to those of Howard and Williams provided that the temperatures and humidities were such that the material was near or above the glass transition.

Williams and Bender[4] also studied the superposition of data in unoriented nylon-6,6 filaments up to strains of 2.5 and found that all data could be reduced to a single curve if they plotted strain against an empirical function of time, moisture content, temperature and stress.

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* a_T here is the amount the compliance/log time curve must be shifted parallel to the log time axis to bring it into coincidence with a curve obtained at a selected reference temperature.

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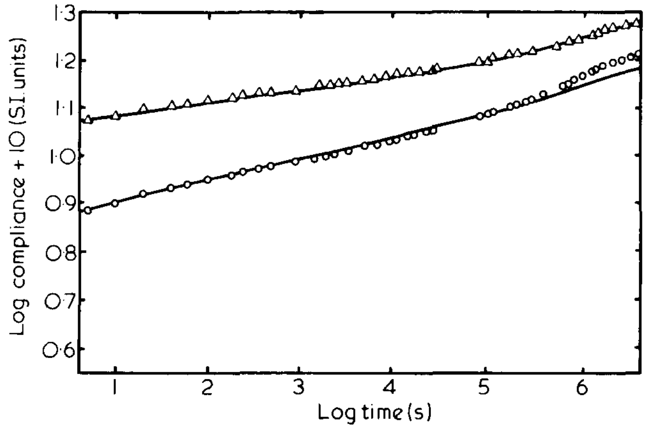

Figure 1 Experimental points and predicted log compliance curves for various humidities. Stress, 4 MN/m^2. 90% r.h., △; 61% r.h., ○; predicted compliance, ——

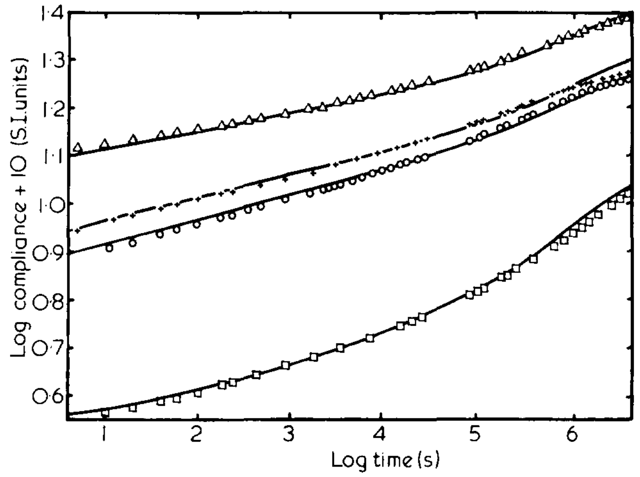

Figure 2 Experimental points and predicted log compliance curves for various humidities. Stress, 8 MN/m^2. 90% r.h., △; 70% r.h., +; 61% r.h., ○; 29% r.h., □; predicted compliance, ——

EXPERIMENTAL

The material used for this study was I.C.I. Maranyl Grade A 100 nylon-6,6 whose characteristics were described in a previous paper[1]. The creep tests were made on machines that had been designed and calibrated to give accurate results, having an error in the modulus of about ±0.4% at the 0.1% strain level. The tests were carried out in an environmental chamber that maintained the temperature constant within ±0.1°C and the relative humidity to within ±1% or better. This apparatus has also been described previously[1].

RESULTS

The experimental results, which are taken from the previous paper[1], are reproduced in *Figures 1*, *2* and *3*.

It is evident from these results that the creep behaviour is non-linear in a viscoelastic sense; since the compliance increases with increasing stress. Therefore it was felt that, in order to simplify the superposition procedure, the necessary first step was to eliminate the non-linearity by extrapolation of the creep data to infinitesimal strains, where the material behaviour could be regarded as approximately linear viscoelastic. This exercise was done by plotting, separately for each relative humidity, log compliance versus stress at log-time intervals of 0.5 for each of the three measured stresses. A smooth curve drawn through each isochronous trio of points was then continued to zero stress to obtain the limiting log compliances as stress (or strain) approaches zero. The infinitesimal-strain compliances so obtained will be referred to as J_0 throughout this paper. On these plots linear viscoelastic behaviour was represented by a horizontal line parallel to the stress axis, and it could be seen that there was almost complete linearity at low compliances; the linear part reducing to lower and lower stresses as the material became more compliant. The accuracy of the resulting J_0 data was checked by plotting the basic creep data on the different axes such as stress versus strain and stress versus compliance, which gave good agreement.

The curves of *Figure 4*, $\log_{10}$ compliance versus $\log_{10}$ time for various constant humidities (the limit as stress approaches zero) were constructed from the limiting values J_0 obtained by the above method. Superimposed on this graph is the curve for 0% r.h. taken from the manufacturer's data[12]. The anomalous rise of the 61% r.h. curve at longer times could not be attributed to any known cause.

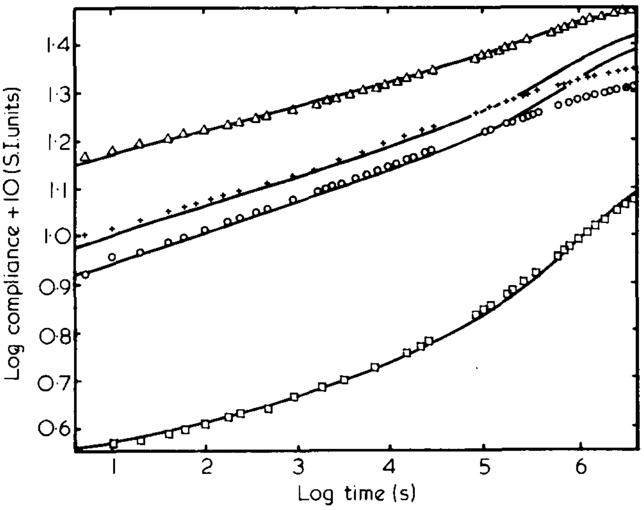

Figure 3 Experimental points and predicted log compliance curves for various humidities. Stress, 12 MN/m^2. 90% r.h., △; 70% r.h., +; 61% r.h., ○; 29% r.h., □; predicted compliance, ——

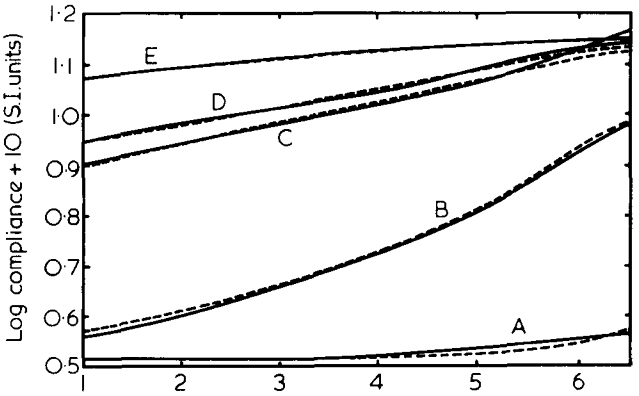

Figure 4 Experimental and predicted log compliance curves for J_0 at various humidities: limit as stress appraoches zero. % r.h. A, 0; B, 29; C, 61; D, 70; E, 90. The 0% r.h. curve was taken from ICI data. Experimental, ——; analytical, – – –

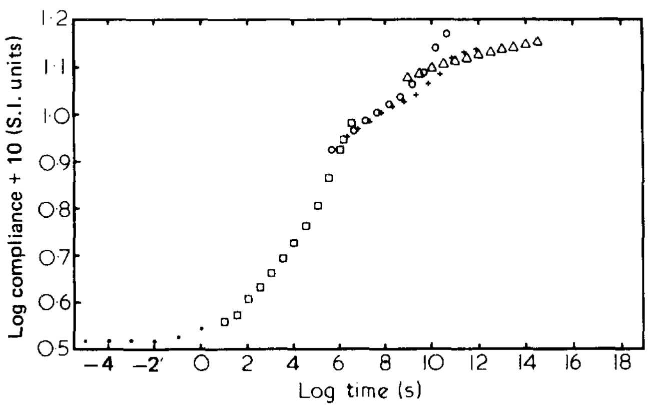

Figure 5 Master compliance curve for J_0 based on a shift of one decade per 7.65% r.h. Reference humidity, 29% r.h. (Note: ICI data shifted one decade per 4.8% r.h.). 0% r.h., ●; 29% r.h., □; 61% r.h., ○; 70% r.h., +; 90% r.h., △

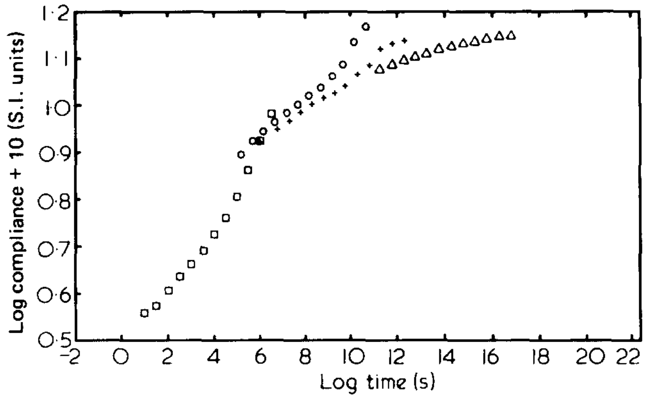

Figure 6 Master compliance curve for J_0 based on a shift of two decades per 1% moisture content. Reference moisture content, 1.46%. 29% r.h., □; 61% r.h., ○; 70% r.h., +; 90% r.h., △

PRODUCTION OF MASTER CREEP–COMPLIANCE CURVES

It can be seen from *Figure 4* that superposition of the curves by a simple horizontal shift would give a poorly-fitting master curve. This is mainly because the individual curves are too steep at longer times; an effect that can also be observed in the data of Onogi *et al.*[3] for nylon-6 even after four decades of time. In the present curves, which were continued for almost six decades, the effect is more marked. Because a horizontal shift would cause the curves to cross each other, the degree of shifting would be somewhat arbitrary. This gave the choice either of aiming for a predetermined shape, or of using a pre-determined shift relationship. It was decided to take the second choice and to follow Onogi *et al.*[3] who found a linear relationship between the logarithm of the shift factor a_H[‡] and the relative humidity for nylon-6. *Figure 5* shows a master curve at a reference relative humidity of 29% r.h., using a linear shift along the log-time scale of one decade per 7.65% r.h.

However, as a check a master curve was also produced assuming a linear relationship between the logarithm of the shift factor a_H and the moisture content, following the findings of a number of previous authors[2,4,6–8]. The resulting master curve is shown in *Figure 6* based on a shift factor a_H of 2 decades per 1% moisture. It should be noted that shift factors from 0.34 to 2.0 decades per 1% moisture have been recorded in the literature for nylon-6,6.

Although *Figures 5* and *6* provide rough master curves, their obvious inaccuracies make them of little use for purposes of prediction. It was felt that continuing the tests for longer times (up to 3 x 10^6 seconds) in the present measurements compared with the creep times of less than 10^5 seconds generally used in the previously-published papers, may have exposed an anomaly in the shapes of the curves at longer times (furthermore great care was taken to ensure that the load was applied steadily in a time of less than one second and that the first strain reading at five seconds was reproducible). It was also noticed that if the log-time scale was expanded at longer times, a simple horizontal shift could give a much better fit than was obtained in *Figures 5* and *6* (note that this is equivalent to arguing that doubling the time from 5 to 10 seconds does not have the same effect on creep at any strain level as doubling it from 5 to 10 weeks). By trial and error a suitable expansion of log time was found. This expansion not only enabled the 29% r.h. and 61% r.h. curves to fit together well, but also the curves for J_0 at the other humidities. Moreover, it also enabled the curves for the other stresses to fit together reasonably well, and using the same shift factors in every case (except at 90% r.h. where there was a small but regular divergence). The new, expanded, log-time scale has been designated θ, which is conveniently defined by the equations:

$$\theta = \log_{10} t + 0.00389\, t^{0.463},$$

for log $t < 6$ and

$$\theta = \log_{10} t + 0.474\, t^{0.2825},$$

for log $t \geqslant 6$ (where t is the time in seconds from the start of the creep test). A visual comparison between log time and θ can be seen in the log compliance versus θ curves for J_0 plotted in *Figure 7*.

The shift parameters that were used for superposition of log compliance versus θ curves are given in *Figure 8*, where it may be noted that the same parameters were used for all stresses at moisture contents of 0, 1.46, 3.53 and 4.35% (corresponding to 0, 29, 61 and 70% r.h. respectively). At 6.6% (90% r.h.) the same parameter could not be used for

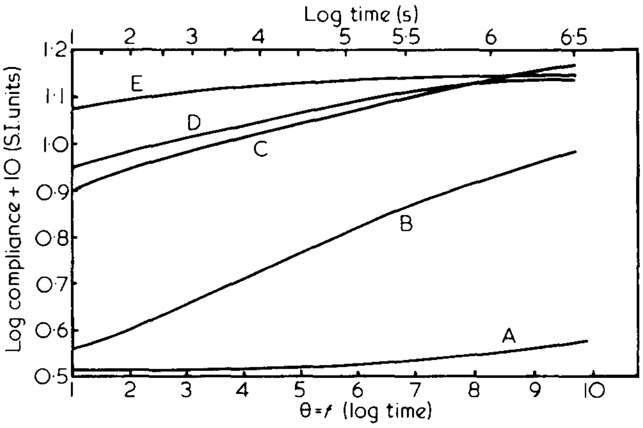

Figure 7 Log compliance versus time function θ for J_0 at various humidities. % r.h. as in *Figure 4*

[‡] a_H here is the amount the compliance/log time curve must be shifted parallel to the log time axis to bring it into coincidence with a curve obtained at a selected reference humidity

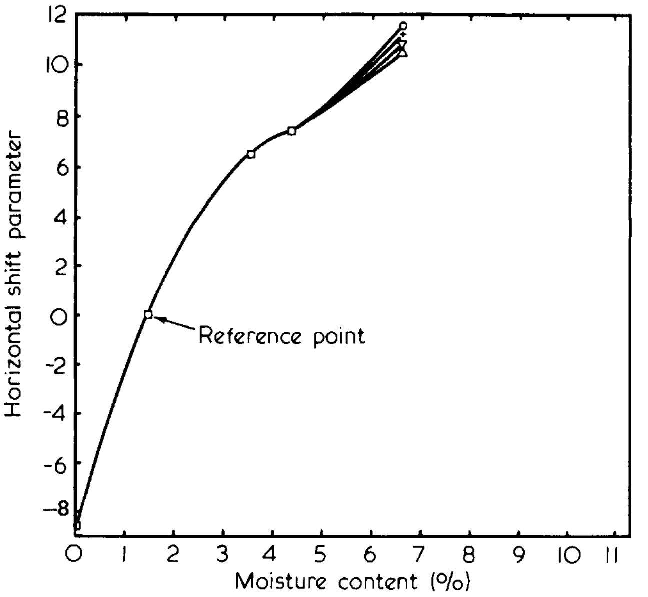

Figure 8 Shift parameter versus moisture content. Points are measured values, lines are analytical values used for master curves. Common to all stresses, □; J_0, ○; 4 MN/m^2, +; 8 MN/m^2, ▽; 12 MN/m^2, △

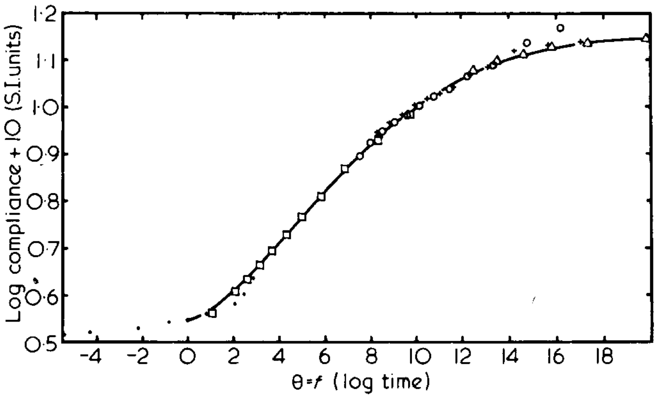

Figure 9 Master compliance versus θ curve for J_0 (stress approaching zero). 90% r.h., △; 70% r.h., +; 61% r.h., ○; 29% r.h., □; 0% r.h. (ICI data), ●; analytical curve (for J_0), ——

all stresses, but the values were found to be uniformly spaced as shown. *Figure 8* also gives least-squares fitted curves that were used as analytical representations of shift versus moisture content. It may be noted that it was not possible to adjust these shift factors to fit a straight line nor even a simple curve, since their values were closely governed by their curve-fitting requirements.

The master curves themselves are given in *Figures 9* to *12* for J_0 and stresses of 4, 8 and 12 MN/m^2 respectively. The points are taken from the experimental curves (estimated curves in the case of J_0) for various relative humidities, generally at intervals of half a decade. Superimposed on these plots are the least-squares fitted quintic curve for J_0 and the analytical curves for the actual stress. The plot of *Figure 9* also includes the manufacturer's data[12] for 0% moisture content. The value of superposing this data is open to argument, since the fit is not very good, as would be expected from the results of Onogi *et al.*[3] who found that the relaxation curves below the transition could not be satisfactorily superposed. However, it was felt that in practice most of the predictions required from these curves would be unlikely to use values of θ below zero; but that nevertheless it could occasionally be useful to have a curve that continues to negative θ values. And since that region is relatively linear viscoelastically, a single master curve is quite easy to describe analytically.

The differences in log compliance between the points on

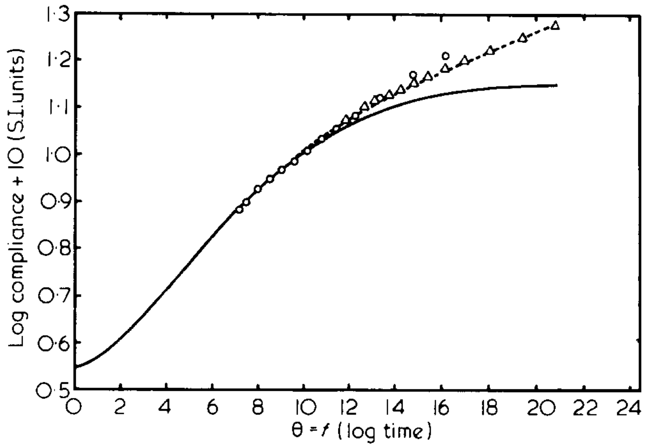

Figure 10 Master compliance versus θ curve for 4 MN/m^2. 90% r.h., △; 61% r.h., ○; analytical curve for J_0, ——; analytical curve for 4 MN/m^2, – – – –

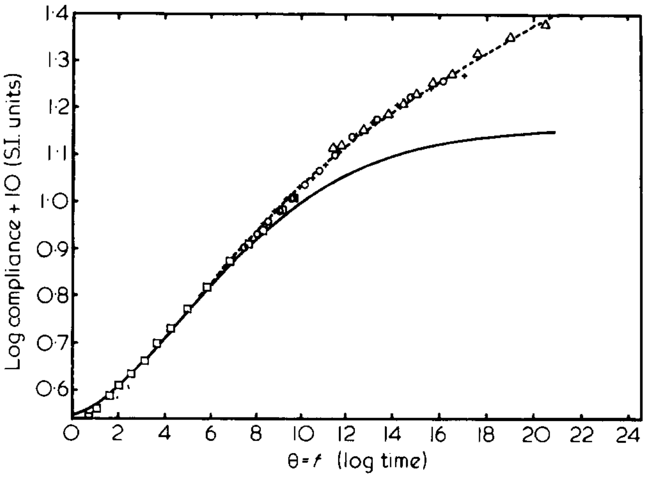

Figure 11 Master compliance versus θ curve for 8 MN/m^2. 90% r.h., △; 70% r.h., +; 61% r.h., ○; 29% r.h., □; analytical curve for J_0, ——; analytical curve for 8 MN/m^2, – – – –

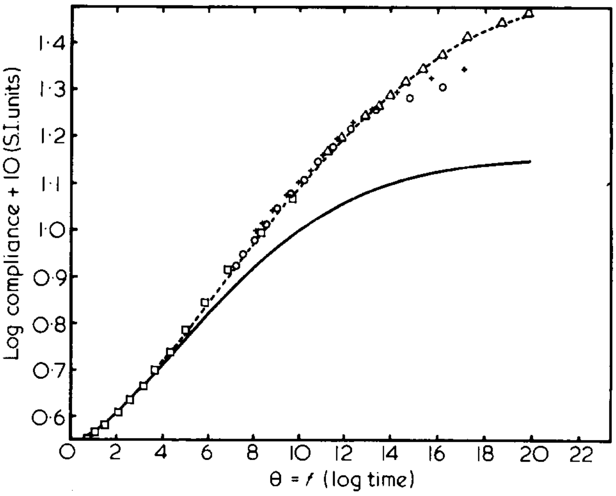

Figure 12 Master compliance versus θ curve for 12 MN/m^2. 90% r.h., △; 70% r.h., +; 61% r.h., ○; 29% r.h., □; analytical curve for J_0, ——; analytical curve for 12 MN/m^2, – – – –

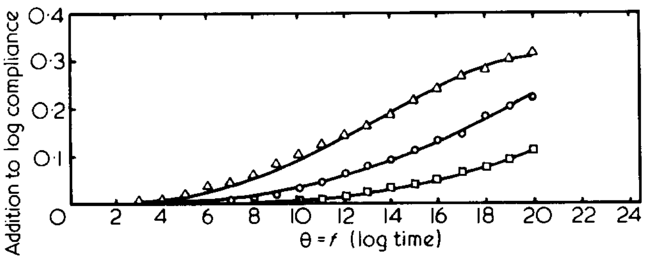

Figure 13 Non-linearity correction factor for various stresses as a function of θ. 12 MN/m^2, △; 8 MN/m^2, ○; 4 MN/m^2, □; analytical curves, ——

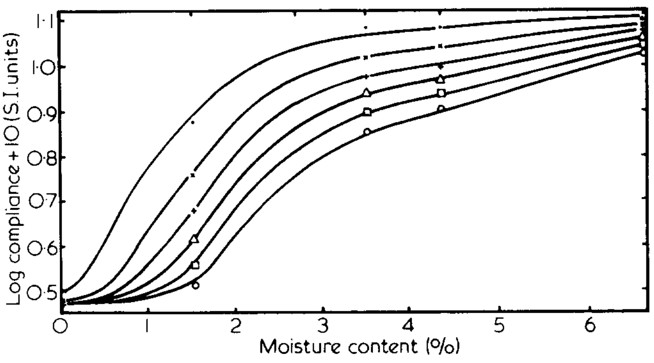

Figure 14 Moisture content transitions for J_0 at various times. 10^6 s, ●; 10^5 s, x; 10^4 s, +; 10^3 s, △; 10^2 s, □; 10^1 s, ○; predicted, ——

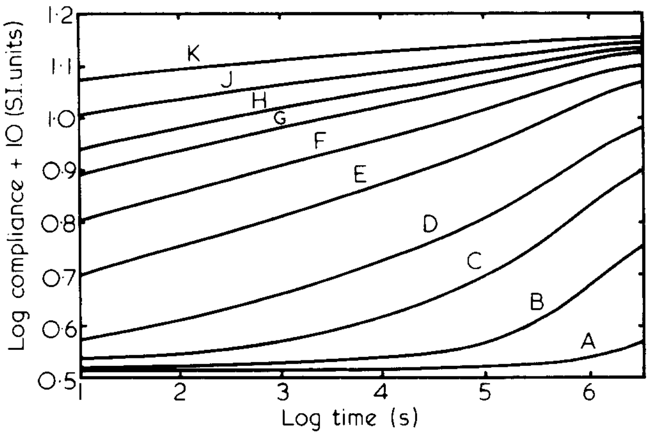

Figure 15 Predicted creep curves for J_0 at various constant humidities. A, 0; B, 10; C, 20; D, 30; E, 40; F, 50; G, 60; H, 70; J, 80; and K, 90% r.h.

the master curve for various stresses and the basic J_0 master curve were plotted against θ in *Figure 13* in order to obtain compliance-correction factors at various stresses as a function of θ. Whilst it is relatively easy to fit analytical curves to the points of *Figure 13* for the measured stresses, several unsuccessful attempts were made to obtain analytical expressions that would interpolate for intermediate stresses. Finally, the only practicable method appeared to be to obtain analytical curves to fit the plotted points as shown, and then to interpolate for intermediate stresses by taking simple proportions. Whilst this seems to be a crude method, it is equivalent to visual interpolation directly from the graph. The correction-factor curves, when superimposed on the analytical J_0 master curve of *Figure 9*, gave the analytical master curves of *Figures 10, 11* and *12* for stresses of 4, 8 and 12 MN/m^2 respectively.

As a check, these analytical master curves were converted back to analytical creep curves by means of the computer and plotted as the solid curves on the log compliance versus log time curves of *Figures 1* to *4*, which include the experimental data obtained previously. The chief discrepancies are at longer times, particularly at the stress of 12 MN/m^2 at the intermediate humidities.

The predicted and experimental results of *Figure 14* show the transition from low to high compliance as a function of moisture content, for J_0. This allows a 'glass-transition moisture content' to be selected in analogy to the more common glass transition temperature. The points are taken directly from *Figure 4*. *Figure 15* shows a set of predicted log compliance versus log time curves for intervals of 10% r.h.

CONCLUSION

It must be emphasized again that the main goal of these creep-prediction methods was to predict the creep compliance of this material under constant stress and humidity conditions; with the possibility of later extending the predictions to creep with varying stress and humidity. Therefore the methods used are mainly empirical, and no attempt was made to justify theoretically the various numerical expressions used.

It is important to resist the temptation to extrapolate to predictions of creep at either much longer times or higher stresses than those actually measured. At longer times the problems of non-linearity become more serious, and without experimental data at much longer times there is no knowledge of the correct shape of the empirical log time versus θ relationship at times beyond about two months. Whilst this study made use of extrapolation of compliance down to infinitesimal strains, this only involved a retreat into the more viscoelastically linear regions of creep behaviour. Extrapolations in the other direction, to stresses above 12 MN/m^2, could give serious errors due to the unknown effects of non-linearity at higher stresses. However, it is interesting to note the hint in *Figure 13* of a return to a kind of quasi-linearity at high values of θ (beyond $\theta = 20$); the 'addition to log compliance' appearing to tend towards a new constant level, possibly around 0.35, after passing through a transition. Such a return to linearity, but at higher temperatures, was observed by Baker and Darlington[13]. If experiment showed this to be the case here, it would considerably improve the prospects of accurate prediction of creep at high stresses and long times.

Although no attempt has been made to justify the use of the time function θ, we believe its utility has been clearly demonstrated and its physical significance is worthy of further study.

ACKNOWLEDGEMENT

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