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Effects of time, temperature and curing on the stiffness of epoxy laminating systems

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Relative creep moduli of a series of epoxy laminating resins were found to be the same in uniaxial tension and in torsion when measured under loads of short duration. However, their tensile creep moduli decreased with time and temperature at different rates, changing their relative stiffness. For one typical resin the short-term tensile and shear moduli decreased with cure temperature reaching minima and then increased slightly. Deflection temperature under load determined by standard tests correlated inversely with the short-term tensile modulus for the typical resin considered and failed to provide a basis for determining the relative stiffness of the different resin systems.

1. Introduction

The possibility of modifying the composition and structure of epoxy systems raises questions about the consequent effects on their mechanical properties. One important aspect of this is stiffness, particularly in connection with the use of epoxy resins in engineering components which are subjected to loads for considerable periods of time and whose allowable deformations are constrained by functional requirements.

In consequence, the authors undertook the study of the stiffness of a related series of epoxy laminating resins, and the effect on it of the type, level and duration of loading and of service temperature. The effects of cure temperature on stiffness of a typical resin were also examined and so were the results obtained from standard tests for the deflection temperature of plastics under load, which are commonly used to select resins for particular applications.

2. Resin systems

The series of resins which were studied by the authors were connected with a requirement for pipes produced by filament winding glass fibres and an epoxy resin for an application where a high degree of dimensional accuracy was essential. This called for a resin which, in addition to being satisfactory in other respects, would creep as little as possible, particularly as the pipes were expected to be stored and transported in long, unevenly supported sections and possibly exposed to high ambient temperatures.

The requirement led to a preliminary selection of five candidate systems on the basis of their handling characteristics, standard short-term property data and general experience. The composition of the five systems, a description of their molecular structure and processing properties, and typical end properties are given below and in Table I.

2.1. System A

100 parts by weight Araldite MY 750 (liquid bisphenol A resin); 27 parts by weight DDM (4,4′-diaminodiphenylmethane; Hardener HT 972).

This composition is well established in glass-reinforced composites, but suffers from processing difficulties because of the high reactivity of the mixture at the temperatures required to dissolve the solid hardener in the resin. Cure may be effected in the temperature range 80 to 160°C, although for maximum thermal properties, post cure at not less than 150°C is essential.

As can be seen from Table I, the system is fairly strong and displays relatively low modulus and high elongation at failure. The deflection temperature is also high.

The molecular structure of system A is shown in Fig. 1. As can be seen, it contains a high

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TABLE I Summary of leading characteristics of the resin systems

System	A	B	C	D	E
Type of hardener	Aromatic diamine (DDM) (Hardener HY 972)	Modified aromatic diamine (Hardener HY 932)	Cycloaliphatic diamine	Aliphatic polyamine (Hardener HY 956)	Cycloaliphatic anhydride (Hardener HY 917)
Additive	None	None	Difunctional epoxy diluent	Monofunctional epoxy diluent	Imidazole accelerator
Ease of mixing	Difficult	Easy	Easy	Easy	Easy
Pot life at 21°C (h) (dependent on bulk)	2-4	4-8	2-4	Under 2	> 8
Initial viscosity at 21°C	1500-3500 cP	1200-2000 cP	60-80 cP	80-120 cP	100-140 cP
Flexural strength* (MN m^{-2})	~125	~150	~140	~140	~140
Flexural modulus* (GN m^{-2})	~3.0	~4.0	~3.5	~4.2	~3.6
Elongation at failure in tension* (ASTM D 638-68) (%)	~7	~5	~2.3	~4.5	~5.5
Ultimate deflection temperature* (ISO R 75, Method A) (°C)	~160	~127	~120	~60	~125

*The figures quoted are typical values based on test data accumulated over a period of years with different (but exhaustive) cure cycles and, in the case of the mechanical properties, a number of different test procedures.

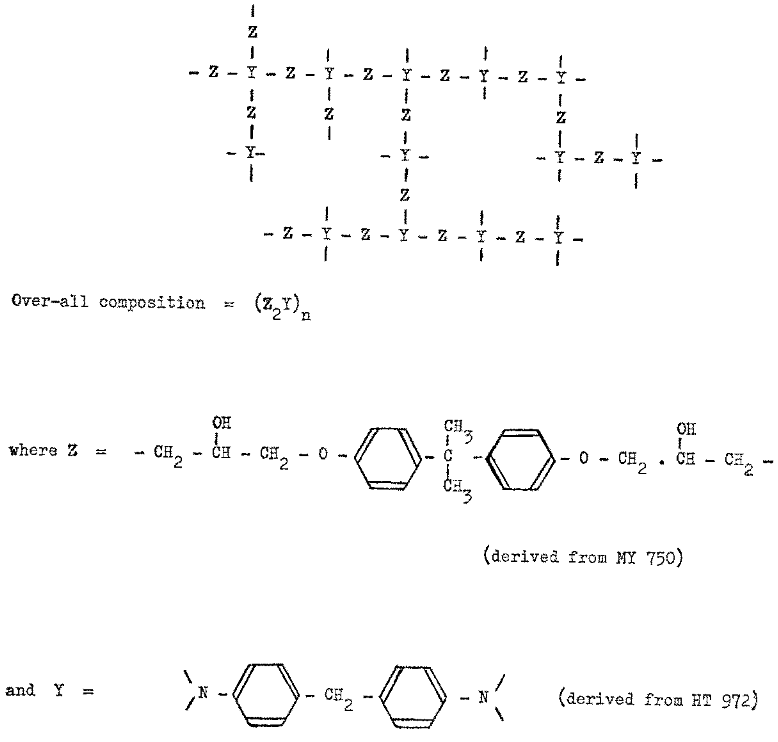

Figure 1 Idealized structure of system A.

proportion of inflexible benzene rings in the polymer network, a feature which contributes to the high deflection temperature but does not confer any high degree of stiffness at room temperature.

2.2. System B

100 parts by weight Araldite MY 750; 32 parts by weight liquid, modified version of DDM (Hardener HY 932).

This is basically similar to system A but the modification of the hardener results in greatly improved processability (easy mixing and longer pot life). Curing may, as before, be effected at 80 to 160°C. The strength and modulus are higher than those of system A, whilst elongation and deflection temperature are lower.

The polymer network is, theoretically, similar to that of system A but with somewhat reduced cross-linking density. However, because of the modification of the DDM, steric and other effects can be expected to operate to produce greater differences in end properties than would be expected solely from considerations of cross-link density.

2.3. System C

85 parts by weight Araldite MY 750; 15 parts by weight butane-1, 4-diglycidyl ether, a flexibilizing difunctional diluent; 36 parts by weight 4,4′-diamino-3,3′-dimethyldicyclohexylmethane.

This composition shown in Fig. 2 differs from the previous ones principally in its content in the polymer chain, of flexible $-O-CH_2-CH_2-CH_2-CH_2-O-$ units from the diluent and of saturated cyclohexane rings from the hardener; the latter replace the relatively rigid aromatic rings of the DDM nucleus.

Processing is simple (liquid components, low viscosity, fairly long pot life), although cure in the range 80 to 140°C is again necessary. The strength is high whilst elongation at break is low. In spite of the low elongation, system C has in practice been found a useful basis for glass fibre plastics composites.

2.4. System D

100 parts by weight Araldite MY 750; 15 parts by weight monofunctional diluent, mixed isomers of octyl glycidyl ether; 27.6 parts by weight hydroxyalkylated polyamine (Hardener HY 956).

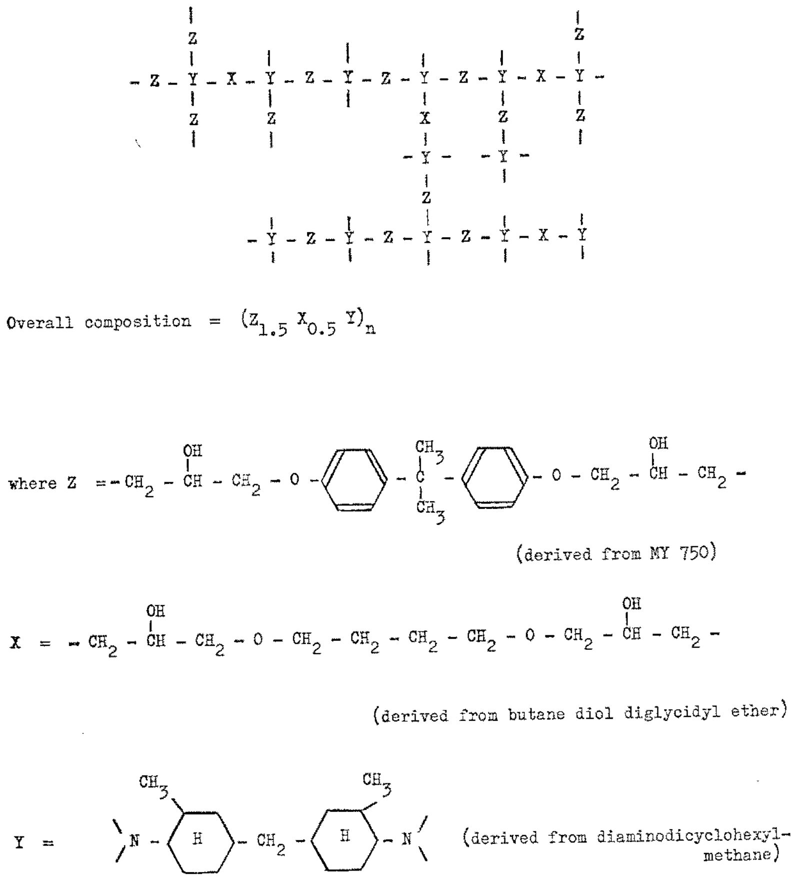

Figure 2 Idealized structure of system C.

This is basically different to systems A to C in both composition and processing characteristics. It utilizes a diluent which reacts into the polymer network to produce pendant long-chain alkyl groups, and the resin is cured with a non-cyclic polyamine hardener. The polymer structure is illustrated in Fig. 3.

The mixture is simple to prepare and can be fully cured at only 60° C, but the pot life is short and the deflection temperature low. Strength, modulus and elongation are all fairly high. System D was included in the series to assess whether a low temperature curing, low deflection temperature composition could be used for such an application without exhibiting too high a creep level at high ambient temperatures.

2.5. System E

100 parts by weight Araldite MY 750; 90 parts by weight methyltetrahydrophthalic anhydride (mixed isomers) (Hardener HY 917); 0.5 parts by weight 1-methylimidazole.

System E is the only composition containing a carboxylic acid anhydride hardener rather than an amine. The polymer produced contains a high proportion of benzene and cyclohexene rings.

The mixture is particularly simple to handle, being prepared from liquid constituents and having a very low viscosity and long usable life; because of these features this and similar compositions find wide use in the production of glass fibre-plastics composites by wet lay-up methods. The mechanical properties and deflection temperature fall within the range covered by the previous systems. Cure is effected at 100 to 140° C.

3. Material preparation

To pursue the study of their deformational behaviour, plaques were cast from all five resin systems. Systems A, B, C and E were cured for

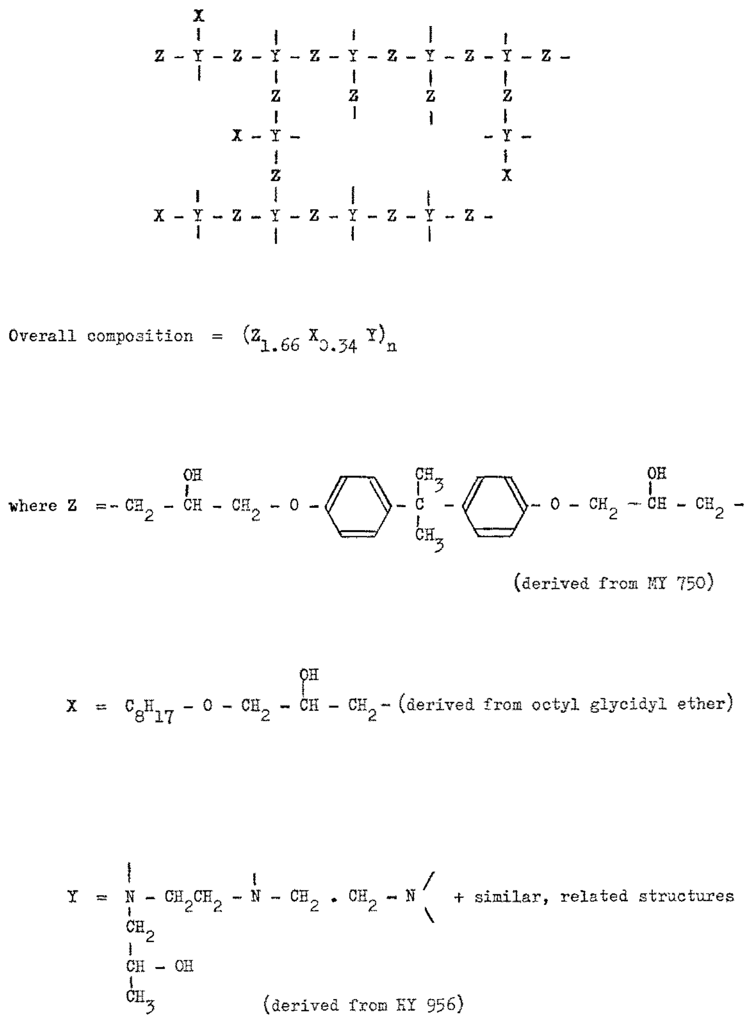

Figure 3 Idealized structure of system D.

4 h at 60°C and then postcured for 4 h at 120°C, while system D was cured for 60 h at room temperature and postcured for 4 h at 120°C.

In addition, a second batch of system A, which will be designated A_2 to distinguish it from the original A_1 batch, was prepared, for a preliminary exploration of the effects of curing conditions. In consequence, it was cured for 30 min at 120°C and postcured for 3 h at 180°C.

To explore the effect of curing conditions further, six additional batches of system A were finally prepared, all cured for 8 h, at 80, 100, 120, 135, 150 and 180°C, respectively. A cure time of 8 h was adopted for all the cure temperatures since previous experience indicated that physical properties and deflection temperatures of the composition attain essentially constant values within this time.

The cast plaques measured 300 mm × 300 mm in plan view and were 3 mm thick to suit the testing machines. Initially two different moulds were used: in one the resin flow direction during casting was parallel to the free surface while in the other it was perpendicular and castings were used from both moulds. The plaques were stored in a controlled environment at a temperature of 20 ± 0.5°C and a relative humidity of 60 ± 5%. Before specimens were cut from them, the plaques were examined on a photoelastic bench to ensure that specimens were taken from regions where frozen-in stresses and stress gradients were at a minimum.

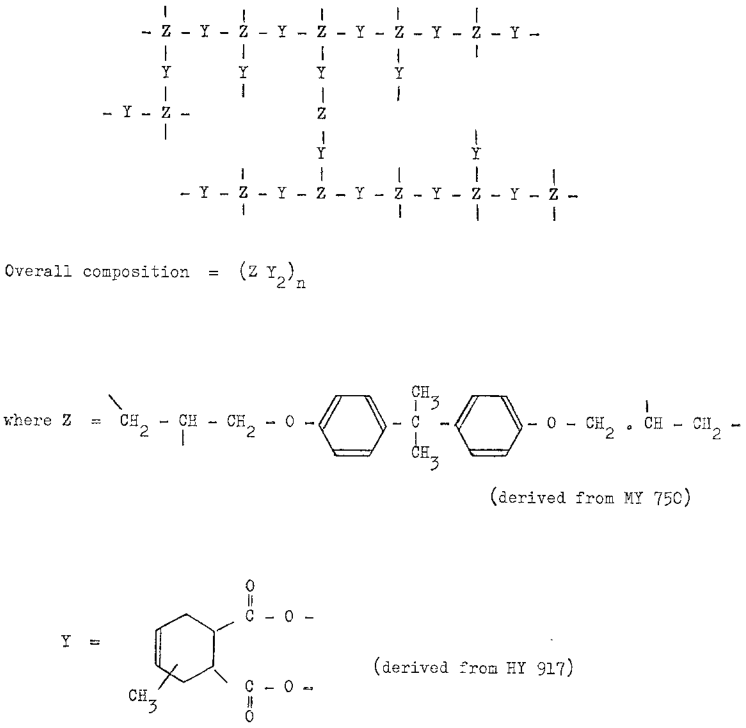

Figure 4 Idealized structure of system E.

4. Experimental approach

4.1. Tensile tests

As the basis of their study of the resin systems the authors adopted constant load uniaxial tension tests, which have become widely used for the evaluation of the deformational characteristics of plastics and which are now embodied in British Standards recommendations for plastics design data [1]. The tests were carried out in GKN-type tensile creep machines [2]. Except for their higher maximum load, these are very similar to the well-documented ICI-type machines developed for the testing of thermoplastics [3], and are used in conjunction with the same type of modified Lamb's optical extensometer with which strains of about 10^{-5} can be resolved. Specimens were machined to suit the creep machines using a high-speed air turbine driven router and, like other specimens of this type, had a parallel section of 100 mm and a cross-section of approximately 5.5×3 mm^2.

The specimens were loaded either using an interrupted step-loading technique to obtain 100 sec isochronous stress-strain curves [4], or using constant loads for period of 5×10^5 sec (about 1 week) to obtain constant load creep curves. Tests based on the interrupted step-loading technique were used (i) for a preliminary characterization of the behaviour of each of the epoxy systems, (ii) as a check on interspecimen variability and on any variation between sheets cast in the two moulds, and (iii) to select suitable stress levels for the creep tests. The latter were chosen so as to give strains of 0.0075 and 0.015 at 100 sec: the lower strain represented the approximate limit of linear viscoelastic behaviour at 100 sec, whilst at the higher strain the behaviour was significantly non-linear.

The test procedure, from the machining of the specimens to the calibration of the machines and extensometers, has been designed to produce results to an overall accuracy of 1% which corresponds to class A of BS 4618 [1]. All the tests were performed in a controlled environment at a relative humidity of 60 ± 5% and a temperature of 20 ± 0.5°C, or at 60 ± 0.5°C. Unloaded control tests were run concurrently with the creep tests at both temperatures so that the effects of any dimensional changes in the material, arising, for example, from relaxation of frozen-in stresses or from further curing, could be taken into account when calculating the creep strains.

4.2. Torsion tests

To assess the relative shear stiffness of the different resin specimens of the same kind as those prepared for the tensile tests were tested in torsion in a machine developed at the ICI Plastics Division for determining the shear modulus of plastics [5] from the basis of earlier apparatus built for the same purpose [6]. The principal improvement incorporated in the machine consisted of the use of air bearings to reduce machine friction to negligible proportions. However, like that of the earlier apparatus, the use of the machine was confined to small shear strains of approximately 0.2 %. This meant that the shear modulus could be calculated from the slope of the straight-line plots of the angle of twist of the specimens versus the applied torque using the standard linear elastic solution to the torsion of prismatic bars [7].

The specimens were strained using an interrupted step-loading technique analogous to that used in the tensile tests and their twist was observed 100 sec after the application of each load. Thus, the torsion tests resulted in 100 sec isochronous torque versus angle of twist curves. Like the tension tests, the torsion tests were carried out in a controlled environment, at 20 ± 0.5°C and 60 ± 5 % relative humidity.

4.3. Deflection temperature tests

In view of the use of the "temperatures of deflection under load" to assess the relative stiffness of plastics, tests were also carried out to determine their values for the different resins. This amounted to recording the temperature at which the central deflection of specimens in three point bending under a constant load reached an arbitrary value, as prescribed in the relevant standard test method of the International Organisation for Standardisation [8].

5. Experimental results

5.1. 100 sec tensile creep moduli

The 100 sec isochronous tensile stress-strain curves obtained at 20°C with the five systems are illustrated in Fig. 5. They show that the systems differ in their stiffness and, since some of the curves cross over, that their relative stiffness varies with strain. The differences are brought out more clearly in terms of the 100 sec tensile creep moduli* at 0.002 and 0.02 strain,

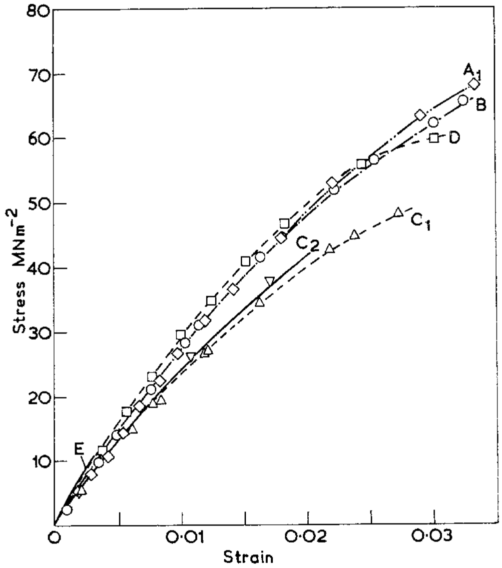

Figure 5 100 sec isochronous stress-strain curves obtained with the different epoxy systems under uniaxial tension.

TABLE II 100 sec creep moduli and deflection temperature

Resin system	Moduli (GN m^{-2}) Tensile at 20°C at 0.002 strain	Tensile at 20°C at 0.02 strain	Shear at 20°C	Tensile at 60°C at 0.002 strain	Tensile at 60°C at 0.02 strain	Deflection temperature (°C)
A_1	2.76	2.45	1.04	2.46	2.15	123
A_2	2.52	1.99	0.98	2.12	1.77	157
B	2.84	2.40	1.05	2.30	1.92	124
C C_1	2.44	2.04	0.92	1.86	1.59	125
C C_2	2.58	2.10	0.95	2.04	1.63	116
D	2.99	2.47	1.11	0.95– 1.49	0.82– 1.08	67
E	3.09	—	1.18	—	—	124

*100 sec tensile creep modulus = (constant nominal stress)/(strain at 100 sec).

which are given in the first two columns of Table II. In both cases, two slightly different results may be noted for system C, labelled C_1 and C_2, these being obtained with specimens from different plaques of the same material cast in the same mould, whilst no significant differences were observed between plaques cast in the two types of moulds from the other resin systems.

A comparison of the 100 sec 0.002 strain creep moduli in Table II with the moduli in Table I, shows that they rank the five systems in a different order. For example, system E is seen to have the highest creep modulus whereas standard tests suggest that it would have had a relatively low value.

Differences between the 100 sec creep moduli at 0.002 and 0.02 strain show that the resin systems become non-linear viscoelastic materials at higher strains, since the moduli decrease with strain. The rates at which their stiffness decreases are similar but that of system A_1 decreases less than those of the other.

No modulus values could be determined at strains significantly above 0.002 for system E as specimens of it failed consistently at the loading points at relatively low stress levels. In view of the well-established and successful use of system E and similar compositions in glass-reinforced composites, this apparently high sensitivity of the cast resin was quite unexpected. It is possible that in such anhydride systems, the presence of hydroxyl groups introduced from glass fibre reinforcement modifies the curing process and thereby improves the mechanical properties. The relatively high tensile strength and elongation figures reported in Table I for system E, in cast form, tested by other procedures suggests that the complex stress pattern associated with the particular method of loading adopted in the present work might also have been a contributory factor.

5.2. 100 sec shear moduli and Poisson's ratios

As can be seen from Table II the torsion tests ranked the five resin systems in exactly the same way as their small-strain tensile creep moduli. This suggests, inter alia, that their Poisson's ratios are much the same. In fact, Poisson's ratios range from 0.29 for A_2 to 0.36 for C_2, these being derived from the standard relationship,

$$E = 2G\,(1 + \nu)$$

Where E = tensile modulus; G = shear modulus; ν = Poisson's ratio.

5.3. Effect of temperature on 100 sec tensile moduli

Comparison of the 100 sec tensile moduli at 20 and 60°C, shows that the stiffness of the resin systems decreases with temperature at different rates. Thus, the modulus at 0.002 strain of system D decreases at 60°C to as little as a third of its value at 20°C whereas the modulus of system A_1, which decreases least of all, falls by only 11%. The moduli at 0.02 strain decrease in a similar way.

The low values of the modulus of system D at 60°C are consistent with it being closer to its glass transition temperature than that of the other systems and the scatter in the results may also be ascribed to this. In contrast, very consistent results were obtained with the other systems but no results were obtained at 60°C with system E, which fractured consistently at low strains at 20°C.

5.4. Creep

Typical results of creep tests are illustrated in Figs. 6 and 7, in terms of curves of tensile modulus versus log time and are summarized in Table III. As can be seen, systems A, B and C

TABLE III Tensile creep moduli at 20 and 60°C for two different starting strains

Resin System	At 20°C				At 60°C			
	0.0075 strain		0.015 strain		0.0075 strain		0.015 strain	
	at 10^2 sec	at 10^5 sec	at 10^2 sec	at 10^5 sec	at 10^2 sec	at 10^5 sec	at 10^2 sec	at 10^5 sec
A_1	2.78*	2.49	2.66	2.30	2.41	2.16	2.27	1.89
B	2.81	2.21	2.58	1.88	2.19	1.82	1.94	1.52
C	2.50	2.09	2.17	1.63	1.80	1.47	1.74	1.31
D	2.99	2.14	2.71	1.39	—	—	—	—

*All modulus values in GN m^{-2}.

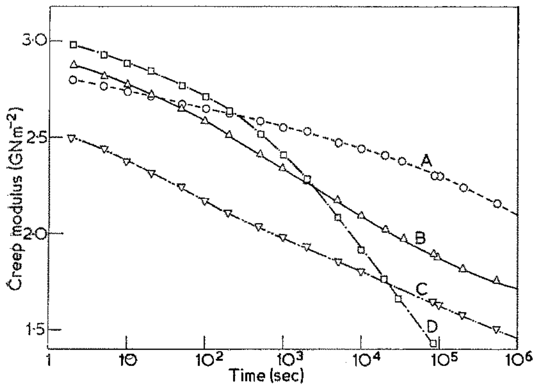

Figure 6 Tensile creep moduli at 0.015 starting strain and 20°C for systems A_1, B, C and D versus log time.

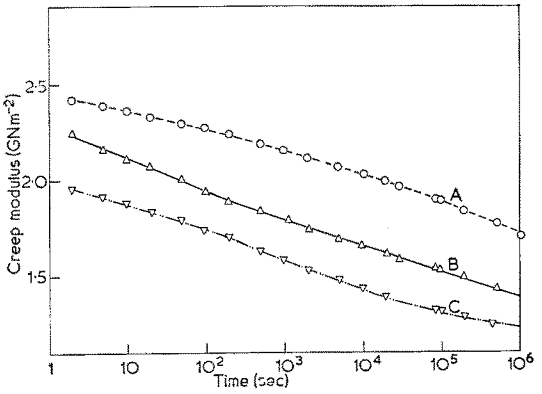

Figure 7 Tensile creep moduli at 0.015 starting strain and 60°C for systems A_1, B and C versus log time.

were tested at both 20 and 60°C but system D was tested at 20°C only, because 60°C was too close to its glass transition temperature for meaningful results to be obtained.

It is evident from Figs. 6 and 7 that the four systems creep at different rates. Thus at 20°C, system A_1, which is only the third stiffest at short times, becomes the stiffest material at times greater than 10^4 sec. On the other hand, system D, which has the highest modulus of the four at short time, falls off very rapidly in stiffness with time to become the least stiff material at times of the order of 10^5 to 10^6 sec.

At 60°C, system A_1 has the highest modulus at all times but, except for D, the creep of the systems, i.e. the rate of change of their moduli with time, are broadly comparable at the two temperatures. A comparison of the creep results at 20 and 60°C for systems A_1 and A_2 showed that their creep rates were also comparable.

In the light of this and the other evidence, system A_1 was adjudged to be the most suitable for the application which originally prompted the study.

5.5. Effect of curing temperature on 100 sec creep moduli

The effects on its 100 sec tensile and shear creep moduli of curing system A for 8 h at different temperatures are shown in Fig. 8. In addition, Fig. 8 also includes the results obtained with systems A_1 and A_2, cured as already described, and with system A_3 cured for 8 h at 150°C and postcured for 3 h at 180°C.

It is evident that when the curing time is constant, the values of both moduli decrease with curing temperature until they reach minima and then increase. In cases where the curing temperature is followed by a higher postcuring temperature it appears that it is the latter which governs the stiffness of the material. However, if the curing temperature is already close to that at which the moduli are at their minima, a higher postcuring temperature appears to have no significant effect on the value of the tensile modulus.

The inverse relationship between the 100 sec creep modulus of system A at room temperature and the cure temperature is unlikely to be the result of any dependence of the chemical mechanism of cure on temperature since a fall in modulus occurs if a specimen cured at a relatively low temperature is then postcured at a higher temperature. Also, since cure or postcure

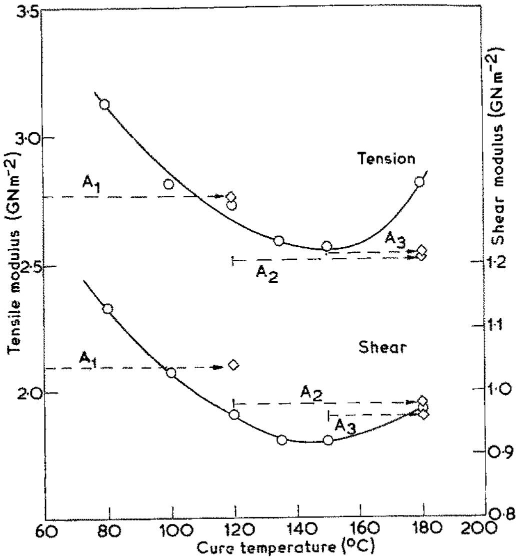

Figure 8 100 sec tensile creep modulus at 0.002 strain and 100 sec shear modulus, both for system A at 20°C, versus cure temperature.

at a higher temperature gives a substantially higher deflection temperature, chemical degradation could not explain the fall in modulus. Possible explanations for the observed facts are either that the morphology or micro-structure of the polymer is affected by the temperature or that, at lower temperatures, some measure of non-covalent interaction (e.g. hydrogen bonding) develops between adjacent polymer chains and that this is irreversibly destroyed at higher temperatures.

5.6. Deflection temperatures

The deflection temperatures recorded for the five systems and listed in Table II, do not correlate either with the 100 sec moduli at 20° C or with the rates of decrease of tensile modulus with temperature, except that the lowest was recorded for system D, whose tensile modulus is lowest at 60° C. The deflection temperatures also fail to correlate with the rates of creep.

However, for system A cured for the same period of time at different temperatures, the deflection temperature is inversly related to the 100 sec tensile creep modulus, at least until a minimum is reached, as shown in Fig. 9. This may seem rather surprising, as one might have expected that the highest deflection temperatures would be recorded with the stiffest material, whereas the opposite is the case but similar results had been obtained earlier from comparisons of deflection temperatures with flexural moduli of system A cured under different conditions.

Since deflection temperature decreases with modulus and the modulus has already been found to decrease with curing temperature one would expect deflection temperature to increase with cure temperature and this is indeed the case as shown in Fig. 10. By itself a relationship of the kind illustrated in Fig. 10 could be misleading as it might suggest that to increase the stiffness of the material one should resort to high curing temperature, which is the opposite of what has been found.

6. Conclusions

The study of the epoxy laminating systems has shown that the relative values of their small-strain 100 sec creep moduli are the same in uniaxial tension and in torsion, which means that under loads of short duration their relative stiffness can be accurately assessed under either type of loading.

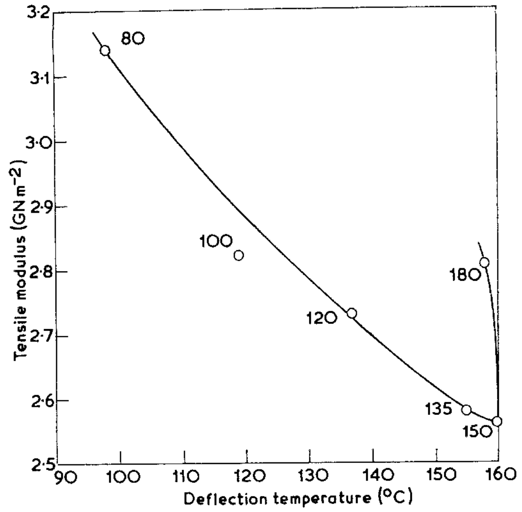

Figure 9 100 sec tensile creep modulus at 0.002 strain and 20° C for system A cured at different temperatures marked on the graph in ° C versus deflection temperature.

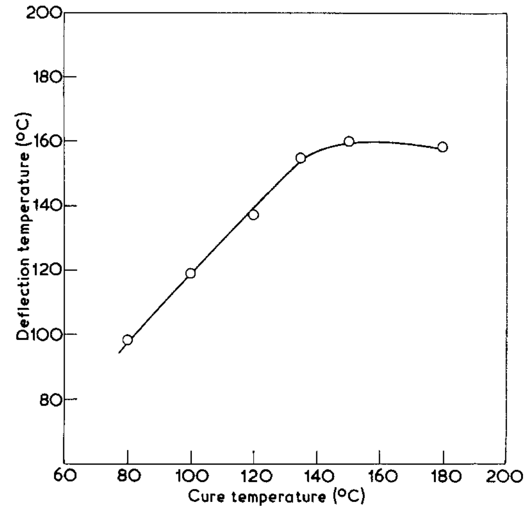

Figure 10 Deflection temperature versus cure temperature of system A.

However, their relative stiffness has been found to change significantly with temperature and with the duration of loading, so that a system, such as D, which might appear attractive for applications requiring dimensional stability because its moduli are high at short times under load, proves to be far less suitable than a system such as A_1, whose creep modulus falls off far less with temperature and with time.

A conclusion to be drawn from this is that tests carried out at normal temperatures and for short periods of time do not provide an adequate basis on which to assess the relative suitability of resin systems for applications involving elevated temperatures and loads applied for significant periods of time. This conclusion applies in particular to standard tests for determining such commonly quoted parameters as flexural modulus and deflection temperature, which in this case failed to accurately rank the stiffness of the epoxy systems even under loads of short duration.

Moreover, contrary to what might have been expected, the deflection temperature for a particular system proved to be inversely related to 100 sec creep modulus, which provides a further warning against undue reliance on standard tests.

As expected, curing temperature proved to have a considerable effect on the stiffness of the systems but in one case at least the tensile and shear creep moduli were found to decrease rather than increase with it.

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References

1. BS 4618: "Recommendations for the Presentation of Plastics Design Data" (British Standards Institution, London, 1970).
2. J. DIMMOCK and C. E. SPEDDING, *Composites*, **1** (1970) 356.
3. W. M. MILLS and S. TURNER, *Proc. I. Mech. E.* **180,** 3A (1965-66) 291.
4. D. A. THOMAS and S. TURNER, In "Testing of Polymer" Vol. 4, edited by W. E. Brown (Wiley, New York, 1969).
5. M. J. WILLIAMS, D. R. MOORE and J. W. ELDRIDGE, to be published.
6. M. J. BONNIN, C. M. R. DUNN and S. TURNER, *Plastics and Polymers* **37** (1969) 517.
7. S. TIMOSHENKO and J. N. GOODIER, "Theory of Elasticity" (McGraw-Hill, New York, 1951).
8. "Plastics—Determination of Temperature of Deflection Under Load", Specification ISO R 75, International Organisation for Standardisation, Geneva, 1958.

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