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The elastic constants of some epoxy resins

A. SMITH, S. J. WILKINSON, W. N. REYNOLDS
Nondestructive Testing Centre, AERE, Harwell, Didcot, Berks, UK

A 1 kbar fluid compressibility apparatus has been used to determine the bulk compressibility moduli of samples of some epoxy resin systems. Combination with recent data on Young's modulus of the same materials has produced some accurate values of Poisson's ratio.

The same quantities have been determined in the MHz range by ultrasonic pulse-velocity methods. They show good agreement with the static measurements. There is a small relaxation in the bulk modulus with an apparent activation energy of about 4½ eV.

1. Introduction

Epoxy resins are widely used as the matrix materials for carbon fibre composites. In order to calculate the elastic constants of such materials with accuracy it is necessary to possess accurate values of the elastic constants of the resins, and measurements of Young's modulus, shear modulus and Poisson's ratio have recently been reported by Goggin [1]. Although the bulk compressibility modulus, K, can be found from these data, the values so obtained are not very precise, so that it has been found useful to measure this constant directly. Values of K obtained for composites have been discussed elsewhere [2]. Also of interest in this connection is the variation of K for resins with temperature, composition and state of cure and results have, therefore, been obtained over a small range for these variables.

The elastic constants of solids can be obtained in the MHz frequency range, at low strain values, by the use of ultrasonic velocity measuring techniques. If the velocity of a pulse of compressional waves and of another pulse of shear waves of the same frequency is determined under the same conditions, a consistent set of elastic constants appropriate to those conditions is obtained. The comparisons of the static and MHz values of the elastic constants of these materials has produced information of both theoretical and practical interest.

2. Experimental techniques

The pressure rig for measurement of compressibility modulus up to 110 MN m^{-2} has been fully described elsewhere [3]. Relative errors in the modulus measured are less than $\frac{1}{2}\%$. The specimens employed are rods about 8 mm in diameter and 128 mm in length and measurement may be made at any temperature between 0 and 100° C. In the present work, complete sets of data were obtained at 25 and 60° C, with the pressure held for about 30 sec.

The first experiments were made on "cold cure" adhesive resins (MY750 + HY951)* cast in a cylindrical mould of the appropriate size. Other specimens were cut and machined from cast bars, with a minimum cure in some cases to ensure a change from liquid to solid.

The ultrasonic measurements were carried out on rectangular specimens with unequal sides of up to 35 mm so that three independent readings were obtained from each specimen. It was verified that the delay times were linear with respect to the distance travelled and the velocity was determined from the slope of the time/distance relationship. This eliminates errors due to end effects.

In order to obtain the shear wave velocities at the same frequency, use was made of a converter device recently produced here [4]. It has been discovered that a suitably shaped section of CFRP can be used to convert compressive

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*The resin systems used were proprietary products of CIBA (ARL) Ltd. The "cold cure" system consists of 100 parts by weight of MY750 diglycidyl ether of bisphenol A plus 10 parts by weight of HY951 triethylene tetramine. The F-MNA-BDMA system is made up from diglycidyl ether of bisphenol A, methylnadic anhydride and benzyl di-methyl amine.

waves to shear waves or vice versa. Thus the same transducers can be used to measure the velocities of both types of wave at the same frequency. This is especially useful in resins because the power available from compressive transducers is often much greater than that from special shear wave transducers, and the attenuation in resins is high. The converter device has the advantage over angled wedges that the shear wave is projected normally to the surface of the material, and there is thus no difficulty over path lengths or internal reflections.

The two velocities, V_C and V_T, and the density, ρ, for each specimen were thus measured to better than 1% relative accuracy and the elastic constants were obtained from the well-known expressions

compressibility, $K = \rho(V_C^2 - \frac{4}{3}V_T^2)$

Young's modulus, $E = \rho V_T^2 \dfrac{(3V_C^2 - 4V_T^2)}{V_C^2 - V_T^2}$

shear modulus, $G = \rho V_T^2$

Poisson's ratio, $\nu = \dfrac{V_C^2 - 2V_T^2}{2(V_C^2 - V_T^2)}$.

3. Results

Some measurements of the static compressibility modulus K are illustrated in Figs. 1 and 2. From Fig. 1 the effect of increasing cure temperature of the cold curing system is shown for test temperatures of 25 and 60°C. In Fig. 2, the effect of cure time at 120°C on a system F-MNA-BDMA in relative parts by weight 100 to 80 to 1 is shown as measured at 25°C. There is a general tendency for K to decrease by about 10% as the cure proceeds from the initial to the final state.

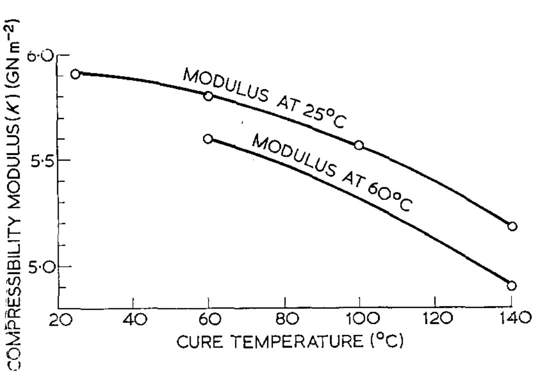

Figure 1 Bulk compressibility modulus, K, for a "cold cure" epoxy resin as a function of cure temperature.

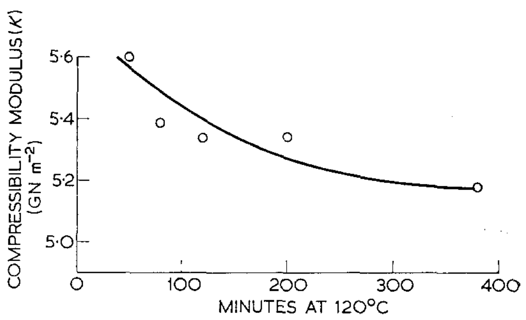

Figure 2 Bulk compressibility modulus, K, at 25° C as a function of cure time at 120°C for a specimen of F-MNA.

A comprehensive list of results at 25 and 60°C is given in Table I, which confirms the general tendency to decrease with cure. There is also a decrease of some 6 to 8% as the measurement temperature is raised from 25 to 60°C.

In Table II the static and dynamic results are compared, and the values of Young's modulus obtained by Goggin [1] at 20°C on the same systems in comparable states of cure have been used to calculate the static Poisson's ratios and shear moduli.

4. Discussion

The results presented in Table II show many features of interest. These are essentially:

(a) the good agreement in all cases between the static and dynamic values of the compressibility modulus, K. This encourages belief in the accuracy of the results obtained;

(b) the combination of static values of K with the values of E reported by Goggin [1] produces values of G in good agreement with his experimental values;

(c) dynamic values of G and E are considerably in excess of static values. This is a general feature of polymeric systems, and is due to shear relaxation;

(d) combination of the static values of K with Goggin's values of E produces accurate values of the Poisson's ratio ν. This point is illustrated in Fig. 3, which shows the variation of ν with the measured ratio on a logarithmic scale for values of ν between 0.25 and 0.5. It is clear that small errors in E/G must result in large errors in ν, whereas a similar error in E/K has little effect on the calculated Poisson's ratio. The sensitivity of ν to the ratio V_S/V_C of shear to compressional wave velocities is intermediate between these extreme cases.

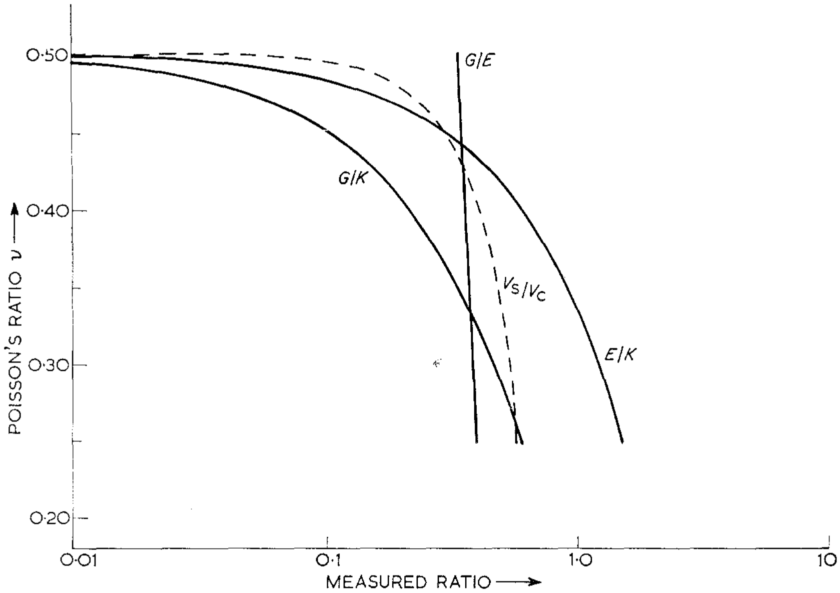

Figure 3 Variation of Poisson's ratio, ν, with measured ratio of elastic constants and ultrasonic wave velocities.

TABLE I Bulk compressibility moduli of resin systems in GN m^{-2}

System*	Cure schedule	K	
		25°C	60°C
MY750-HY951			
100–80	120°C for 3 h	5.4	4.84
100–80	140°C for 24 h	5.01	4.62
F-MNA			
100–80	120°C for 22 h	4.89	4.63
100–80	140°C for 14 h	4.86	4.58
F-MNA			
100–90	120°C for 3 h	5.25	4.8
100–90	120°C for 22 h	4.95	4.66
100–90	140°C for 24 h	4.9	4.65

*N.B. the F-MNA systems also contain 1 part by weight of BDMA.

Our values are some 20% higher than Goggin's but they are confirmed by the good agreement between the static and dynamic results;

(e) in this limited range of data, no systematic variation of dynamic K and ν with state of cure has been detected. The effects are small and may be complex. The variation of K with composition of the F-MNA is however appreciable and consistent with that of the static K.

For the F-MNA system, it is now possible to combine the temperature variation of K from Table I with the frequency variation from Table II to obtain the activation energy, Q, for the compressibility relaxation. The expression involved is

$$Q = \frac{k \ln(\tau_2/\tau_1)}{(1/T_1) - (1/T_2)}$$

where the same change in K is measured between temperatures T_1 and T_2 for a given compression time τ as is found between compression times τ_2 and τ_1 for a given measurement temperature T. Quite apart from the two specimens cured at 140°C for which the dynamic value of K is slightly lower than the static value, the greater sensitivity to small changes of temperature than to the time taken for the measurement suggests a high value for Q of about 100 kcal mol^{-1} ($4\frac{1}{2}$ eV). This value is considerably in excess of that obtained for shear processes in similar resin systems. Arridge and Speake [5] have recently studied variations from about 0.5 to 1 eV for shear relaxation in amine cured epoxies as the state of cure is advanced.

5. Conclusions

Accurate values of bulk compressibility modulus, K, and Poisson's ratio, ν, have been obtained for the resins studied. Variations of K with temperature and measurement time indicate relaxation

TABLE II Static and dynamic elastic constants of resin systems in GN m^{-2}

System	Cure schedule	Static				Dynamic			
		K	E*	ν	G	K	E	γ	G
MY750-HY951									
100–80	120°C for 3 h	5.4				4.88	4.46	0.35	1.66
100–80	140°C for 24 h	5.01				5.0	4.03	0.365	1.47
F-MNA									
100–80	120°C for 3 h		3.85	0.37	1.41	—	—	—	—
100–80	120°C for 22 h	4.89				5.09	3.96	0.37	1.45
100–80	80°C for 6 h+		3.3	0.385	1.19				
	125°C for 16 h			0.385	1.19	—	—	—	—
100–80	140°C for 24 h	4.86				4.67	3.92	0.36	1.44
F-MNA									
100–90	120°C for 3 h	5.25	3.65	0.385	1.32	5.4	4.43	0.36	1.62
100–90	120°C for 22 h	4.95	3.5	0.38	1.26	5.48	3.94	0.38	1.43
100–90	80°C for 6 h+								
	125°C for 16 h			0.38	1.26	—	—	—	—
100–90	140°C for 24 h	4.9				5.35	3.95	0.375	1.43

*From Goggin [4.]

processes with a high activation energy. The techniques involved could produce significant new fundamental data for various polymeric materials.

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