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Elastic properties of porous thermosetting polymers

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A new equation $E = E_0(1 - bp)^n$ has been derived semi-empirically to describe the porosity dependence of elastic properties of thermosetting polymers. The material constant b is defined as a "pore distribution geometry factor" and the other material constant n is dependent on pore geometry. The equation shows good agreement with the data on porous polyester and epoxy resins.

1. Introduction

Accurate prediction of porosity dependence of elastic properties of thermosetting polymers is of broad scientific and technological importance. Most of the theoretical relations for predicting the porosity dependence of elastic properties are derived from the analytical work on two-phase particulate composites [1–3], considering one of the phases to be pores. One such relation given by Ishai and Cohen [4] is

$$E/E_0 = 1 - p^{2/3} \qquad (1)$$

where E and E_0 are the Young's modulus at volume fraction porosity p and zero, respectively. Their work is based on a two-phase model of cubic inclusion within a cubic matrix given by Paul [5], assuming a uniform normal displacement at the boundary. Paul's own approximate solution for the same model with a normal uniform stress at the boundary is given by

$$E/E_0 = (1 - p^{2/3})/(1 - p^{2/3} + p) \qquad (2)$$

Mackenzie [6] proposed theoretical equations for the shear and bulk moduli of a homogeneous and isotropic solid containing isolated spherical pores. In deriving his equations he used a self-consistent field method using a model of a spherical-hole, surrounded by a shell of pure material, which in turn is surrounded by "equivalent homogeneous material", i.e. material of average properties and porosity. From the expression for the relative shear modulus given by Mackenzie, the relation for the relative Young's modulus can be derived as

$$E/E_0 = [(\mu + 1)/(\mu_0 + 1)][1 - (15[1 - \mu_0]p/ \times [7 - 5\mu_0]) - Cp^2] \qquad (3)$$

where μ and μ_0 is the Poisson's ratio at porosity p and zero, respectively, C is a constant and the other terms are defined as before. The constant C in Equation 3 can be evaluated by the application of a boundary condition. Coble and Kingery [7] assumed that $E = 0$ at $P = 1$ and found the value of C as -0.91 with $\mu_0 = 0.3$. Assuming that μ does not vary with porosity, i.e. $\mu = \mu_0$ for all values of p, then Equation 3 becomes

$$E/E_0 = 1 - 1.91p + 0.91p^2. \qquad (4)$$

Whereas Mackenzie's derivation based on self-consistent field model simplifies the micro-structure of the material by using embedded model of the pores and tends to mask the extent to which neighbouring pores influence their response characteristics particularly at the high porosity end [8], Equations 2 and 3 provide better agreement only at low end of porosity. With a view to finding out a solution of the problem, a new equation has been derived semi-empirically and verified with the data on thermosetting polyester resin. The applicability of the equation to the data reported by Ishai and Cohen [4] on porous epoxy resin has also been evaluated.

2. Mathematical analysis

2.1. Basic derivation

Fig. 1a shows a homogeneous, isotropic porous body of average porosity p having a constant area of cross-section A and length l. When the body is subjected to a load F in the x-direction, the elongation, $\Delta\delta$, of an element $A\mathrm{d}x$ is given by

$$\Delta\delta = (F/Ax)/E_0 \, \mathrm{d}x \qquad (5)$$

where Ax is the solid area of cross-section available in the element $\mathrm{d}x$.

The total elongation, δ, of the body is then given by

$$\delta = \Sigma \, \Delta\delta = (F/E_0 Ax)\,\mathrm{d}x \qquad (6)$$

If E is the apparent Young's modulus then

$$E = (F/A)/(\delta/l) \qquad (7)$$

combining Equation 6 and 7, the relation

$$1/E = 1/E_0 l \int_0^l A/A_x \mathrm{d}x \qquad (8)$$

is obtained. Now, if p_x is the average porosity of the element $A\mathrm{d}x$, then

$$A_x/A = 1 - p_x$$

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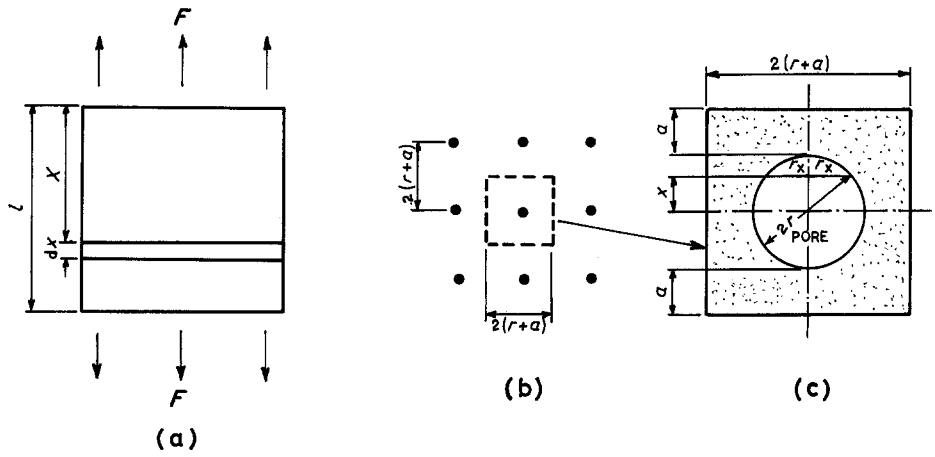

Figure 1 Porous body with pores distributed in simple cubic array.

and Equation 8, therefore, reduces to

$$1/E = 1/E_0 l \int_0^l \mathrm{d}x/(1 - p_x) \qquad (9)$$

The integral on the right-hand side can only be evaluated if p_x is expressed in terms of x. This is possible if certain idealized system is assumed for the pore distribution in the body.

2.2. Idealized system

Fig. 1b shows an amorphous isotropic body in which spherical pores of equal sizes are distributed in a regular cubic array. Because of periodicity, the consideration of the behaviour of a unit cell is equivalent to the consideration of the entire porous body. Such unit cell is shown in Fig. 1c.

At any value of a the average porosity p is given by

$$p = \pi r^3/6(r + a)^3 \qquad (10)$$

where r is the pore radius. For any value of $r > 0$

$$r_x^2 = (r + x)(r - x) = r^2 - x^2$$

$$p_x = \pi(r^2 - x^2)/4(r + a)^2$$

and $p_x = 0$ for $r \leqslant x \leqslant (r + a)$.

Substituting these values in Equation 9 and integrating, E/E_0 is given by

$$E/E_0 = [1/(r + a)[4(r + a)^2/[4\pi(r + a)^2 - \pi^2 r^2]^{1/2} \times \tan^{-1}\{\pi^{1/2} r/[4(r + a)^2 - \pi r^2]^{1/2} + a]\}^{-1} \qquad (11)$$

As can be seen, Equation 9 accounts for the reduction in load-bearing area due to the presence of pores but it does not account for the disturbance of the force-line flux due to the presence of the pore and its neighbour. It is well known that the lines of force can pass through the solid material but not through holes. At zero porosity, there will be no pores to disturb the force-line flux and $E = E_0$. On the other hand, the disturbance will be maximum when the pores touch each other, i.e. $a = 0$. The corresponding value of p is obtained from Equation 10 as 0.5236. Thus we define $p_{\mathrm{cr}} = 0.5236$ as the porosity at which the modulus of the material becomes equal to zero. Because we know that the stress concentration effect gains importance as the porosity increases, a lever rule relation is proposed to account for it and we define E_{eff} as

$$E_{\mathrm{eff}}/E_0 = [(p_{\mathrm{cr}} - p_{\mathrm{i}})/p_{\mathrm{cr}}]E/E_0 \qquad (12)$$

where p_{i} is the instantaneous porosity. This lever rule type of relation is proposed for its simplicity and because it satisfies the boundary conditions $E_{\mathrm{eff}} = E_0$ at $p = 0$ and $E_{\mathrm{eff}} = 0$ at $p = p_{\mathrm{cr}}$.

For different porosity, values of r/a can be evaluated from Equation 10 and then the values of E_{eff} may be obtained by utilizing Equations 11 and 12. These values for different porosities are given in Table I.

2.3. General solution

For a real system, having pores of different sizes arranged in disordered array, Equation 9 can be written as

$$E = E_0 f(1 - p) \qquad (13)$$

where $f(1 - p)$ is a function of average porosity p. The function $f(1 - p)$ must be of such form that Equation 13 satisfies the boundary condition $E = E_0$ at $p = 0$ and $E = 0$ at $p \leqslant 1$. The simplest mathematical function which satisfies such boundary conditions is a power function of the form $(1 - bp)^n$ where b and n are material constants. Hence Equation 13 can be expressed as

$$E = E_0 (1 - bp)^n \qquad (14)$$

Equation 14 shows $E = 0$ when $p = 1/b$. Thus the

TABLE I Numerical values for theoretical curves

p	E_{eff}/E_0	$E/E_0 = (1 - 1.79p)^{1.673}$	Deviation from exact solution (%)
0.5236	0.0	0.0097	–
0.4800	0.0367	0.0377	+2.60
0.4400	0.0762	0.0749	−1.60
0.4000	0.1240	0.1228	−1.70
0.3600	0.1792	0.1774	−1.02
0.3200	0.2417	0.2411	−0.26
0.2800	0.3118	0.3124	+0.20
0.2400	0.3892	0.3910	+0.46
0.2000	0.4742	0.4765	+0.49
0.1600	0.5664	0.5687	+0.40
0.1200	0.6657	0.6673	+0.24
0.0800	0.7717	0.7722	+0.07
0.0400	0.8837	0.8831	−0.06
0.0	1	1	0.0

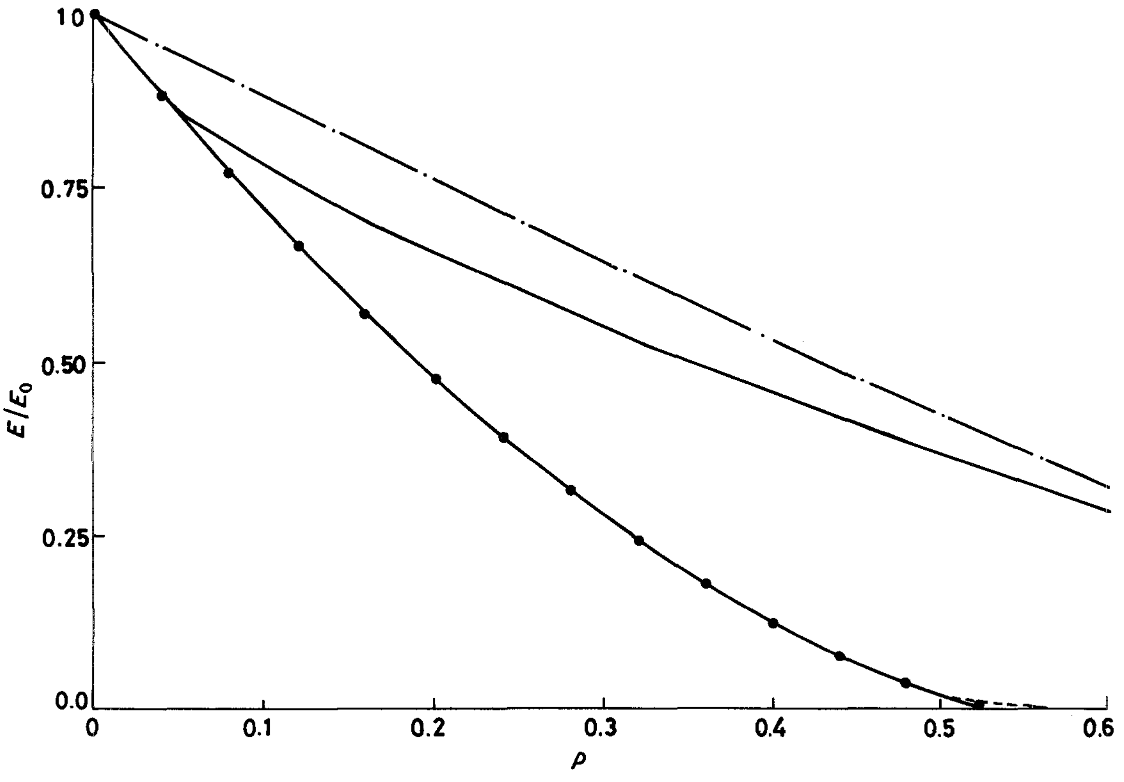

Figure 2 Theoretical relative modulus plotted against volume fraction porosity. (●) Exact solution, (——) Ishai and Cohen, (– – –) proposed equation, (–·–) Paul.

material constant b can be defined as $b = 1/p_{cr}$ where p_{cr} is the porosity at which the elastic modulus becomes zero. The values of p_{cr} for uniform-sized spherical holes arranged in cubic, orthorhombic and rhombohedral array, can be deduced as 0.524, 0.603 and 0.74, respectively, from Knudsen's [9] study on contact area as a function of bulk density. Then the corresponding values of b become 1.91, 1.66, and 1.35. The minimum value of b is one corresponding to the maximum value of $p_{cr} = 1$. The value of b therefore lies in the range $1 < b < 1.91$. Thus b may be defined as the "pore distribution geometry factor".

Equation 14 was fitted to values of E_{eff} obtained from Equation 12 following the iterative least-square method given by Lewis [10] yielding values of $b = 1.79$ and $n = 1.673$. Values calculated at different porosities, together with percentage deviation, are given in Table I and plotted in Fig. 2. Also plotted in Fig. 2 are the relations given by Paul (Equation 2) and Ishai *et al.* (Equation 1). As can be seen from Table I and Fig. 2 the proposed Equation 14 closely approximates the theoretical curves over almost the entire range of porosity, the accuracy being well within ±2% up to the range of $p = 0.44$. Fig. 2 also shows that up to a porosity of 0.05 the relation given by Ishai and Cohen agrees with the theoretical solution quite well. On the other hand, Paul's relation overestimates the moduli values over the entire porosity range.

3. Experimental procedure

A cold-setting general purpose polyester resin (HSR 8111-manufactured by Bakelite Hylam Ltd, India) was used to prepare resin rods of diameter 9 ± 0.5 mm by pouring into cylindrical glass moulds (450 mm net length). Methyl ethyl ketone peroxide and cobalt naphthenate were used as catalyst and accelerator, respectively. The specimens of different porosities were obtained by whipping the resin mix with stiff-bristle brush for different times. A small time was allowed before pouring the resin into the mould so that bubbles above a certain size floated to the surface and were eliminated. Tubes were subjected to slow rotation about the horizontal axis until the resin gelled. The rods were cured at room temperature for 24 h, followed by post curing at 80° C for 4 h before being released from the mould. Samples of lengths 150 to 200 mm were cut out from these rods and flexural moduli were determined by using free-free flexural-resonance vibration utilizing a Bruel and Kajaer Complex Modulus Apparatus. The sample was suspended from two nylon-filament loops and two small rectangular strips of magnetic metal were attached at two ends to apply and pick up vibration amplitudes. Flexural modulus was calculated from the fundamental resonance frequency using the relation

$$E = (256\pi f^2 M l^3)/(d^4 \alpha^4)$$

where E is the flexural modulus, f the resonance frequency, M the sample mass, l the length of the sample, and d the diameter of the sample. α is a constant having the value 4.73. The determined modulus was corrected for added mass following the method given by Read and Dean [11]. Random sections were cut from these samples and the pore diameters were measured by an image shearing technique utilizing a Vicker's Image Shearing microscope at a magnification × 40, the accuracy of measurement being 0.1 μm. The specimen densities were determined from dimensions and mass. The void content was calculated from the relation $p = (\varrho_0 - \varrho_s)/\varrho_0$ where ϱ_0 and ϱ_s are the

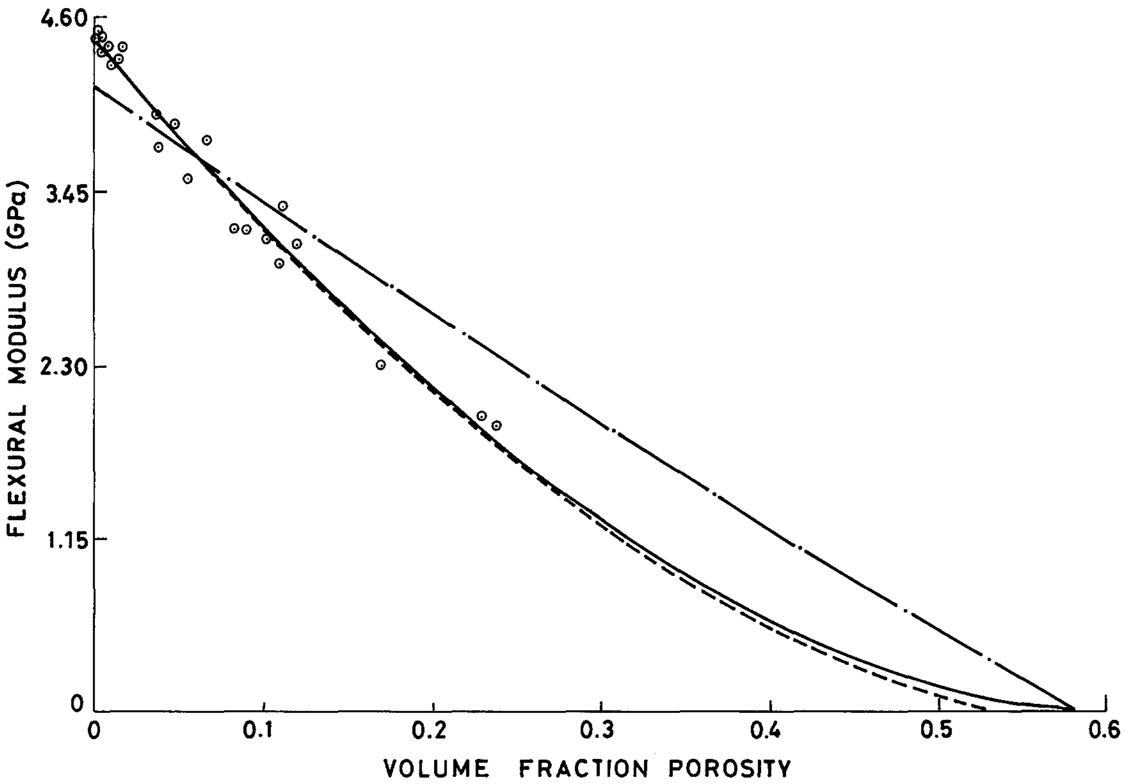

Figure 3 Flexural modulus of porous thermosetting polyester resin plotted against porosity. (-·-) Mackenzie (this study), (——) proposed equation, (- - -) exact solution.

densities of pore free and material of porosity p, respectively. The value of ϱ_0 was determined to be $1.21\,\mathrm{g\,cm^{-3}}$.

4. Discussion

Fig. 3 shows a plot of flexural modulus against porosity. An initial estimate of parameter b was made from Fig. 3 and Equation 14 was fitted to the data by the least square method taking a log–log relationship between the factors involved. Because the change of variables to log-scale will affect the data scatter differently at different points on the curve and also the positive and negative errors differently at the same point on the curve, the equation was fitted following the iterative least square analysis given by Lewis [10] yielding the relation:

$$E = 4.44(1 - 1.72p)^{1.73}\,\mathrm{GPa} \qquad (15)$$

It shows that modulus becomes zero at $p_{\mathrm{cr}} = 1/1.72 = 0.5874$, which is higher than the theoretically calculated value of 0.5236. This is possibly because all the pores were not of equal size and their arrangement was also not as regular as has been assumed in theoretical analysis. Microscopic analysis showed that the mean pore diameter varied from 411.8 to 488.1 μm, and their number being 19 to 25 on any plane for a sample having a porosity of 7%. The zero-porosity modulus value of 4.44 GPa also agrees quite well with the value reported for such polymers in the literature [12].

Following the argument of Manning *et al.* [13], the constant in Mackenzie's Equation 3 was evaluated for the bounary condition $E = 0$ at $p = 0.5814$ with $\mu = 0.3$ yielding the relation

$$E/E_0 = 1 - 1.91p + 0.33p^2$$

Fitting this equation to the data gives a value of $E_0 = 4.16\,\mathrm{GPa}$. The relation is also plotted in Fig. 3. As can be seen from Fig. 3, up to a porosity of 10% the equation agrees fairly well with the data, but at higher porosity data fall below those described by the relation.

Fig. 4 shows plot of relative modulus against porosity for epoxy resin reported by Ishai and Cohen [4]. Equation 14 was again fitted to the data, yielding the relation

$$E/E_0 = (1 - p)^{1.85}$$

This relation is shown in Fig. 4 together with those given by Paul and Ishai *et al.* As can be seen from Fig. 4 the proposed equation describes the data extremely well over the entire porosity range. On the other hand, the relation given by Paul tends to overestimate the modulus over the entire porosity range and the relation of Ishai *et al.* agrees with the data fairly well only up to a porosity of 40%.

The value of $b = 1$ as obtained in this case shows that the modulus becomes equal to zero only at 100% porosity. This possibly indicates that the samples consisted of pores of varying sizes distributed in a random manner. Though no details regarding the pore shape, size, and distribution are available from the method of preparation given by Ishai *et al.*, it can be concluded that spherical pores of varying sizes were distributed throughout the sample.

As can be seen, the values of n obtained in both cases studied here, are nearly equal to 2. An analysis of the data on Young's and shear moduli of glass with spherical holes of varying sizes reported by Hasselman and Fulrath [14] yielded the relation

$$E = 79.7(1 - p)^{2.15} \text{ and}$$

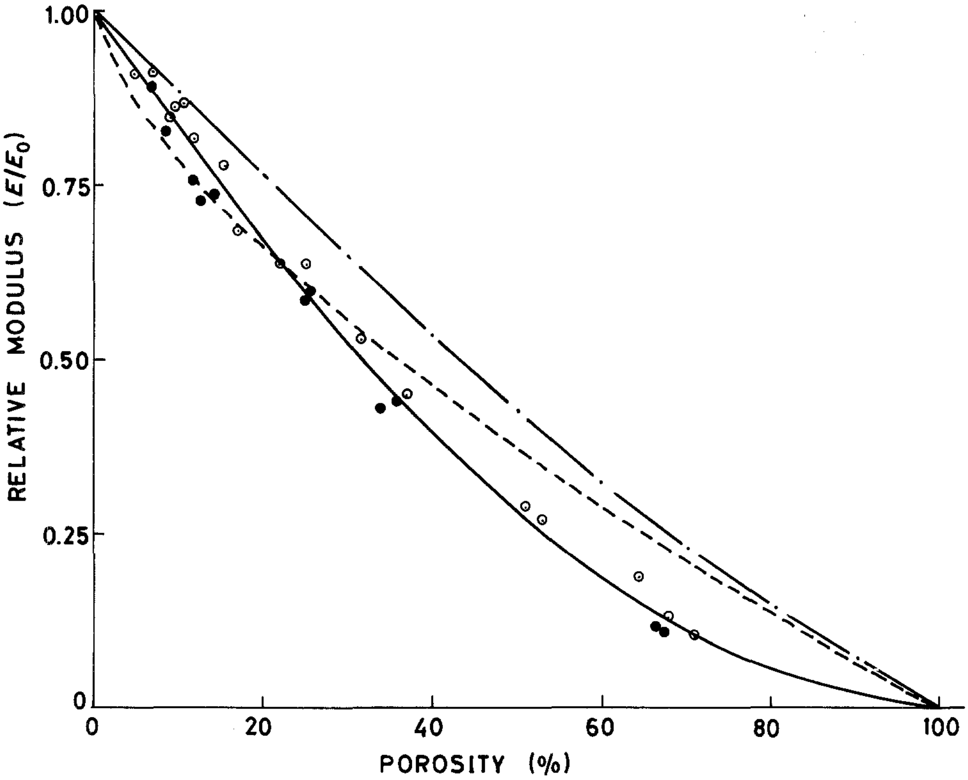

Figure 4 Relative modulus of porous epoxy resin plotted against porosity. (-·-) Paul, (- - -) Ishai, (——) proposed equation. (●) Tension, (⊙) compression.

$$G = 33.2(1 - p)^{2.05} \text{ for}$$

Young's and shear modulus, respectively. This is shown in Fig. 5. Because the data reported are only up to 2.5% porosity, these relations can be approximated to linear equations $E = 79.7(1 - 2.15p)$ and $G = 33.2(1 - 2.05p)$ which are identical to those reported by Hasselman and Fulrath [14]. Thus it may be concluded that the value of n will be equal to 2 for materials having spherical pores. It may also be mentioned that this is in total agreement with the approximate relation given by McCullough [15] for Young's modulus of a foam as $E/E_m = V_m^2 = (1 - p)^2$, where E_m and V_m are the Young's modulus and volume fraction of matrix, respectively.

5. Conclusions

A new equation $E = E_0(1 - bp)^n$ has been derived

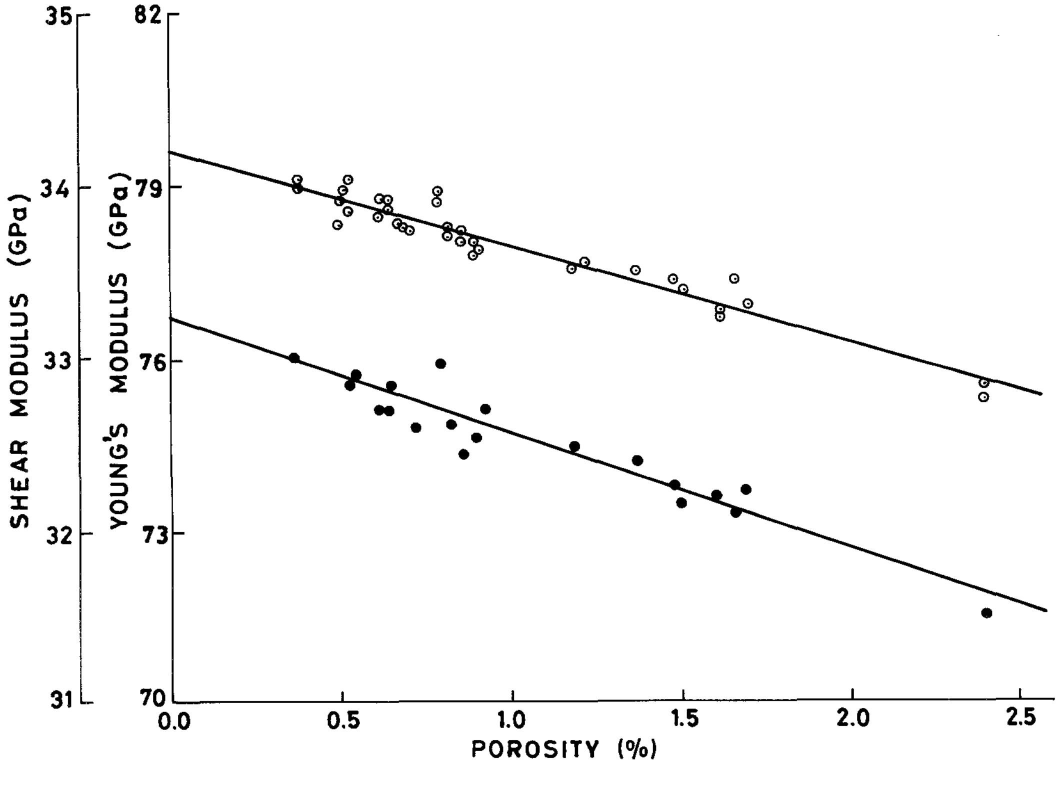

Figure 5 Young's and shear moduli of porous glass plotted against porosity. (⊙) Young's modulus, (●) shear modulus.

semi-empirically to describe the porosity dependence of elastic properties of porous thermosetting polymers. The material constant b in the equation may be defined as the "pore distribution geometry factor", the value of which lies within 1 and 1.91 for spherical pores. The other material constant n is dependent on pore geometry and its value is nearly equal to 2 for pores of spherical shape. The equation showed good agreement with the data on porous polyester and epoxy resins.

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