Elastic properties of polycrystalline elemental sulphur

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Oil companies are increasingly interested in the structural properties of elemental sulphur since these control the weight bearing capacity of huge blocks (10,000 m^2 by base, 10 m by height) built as a temporary sulphur deposit, to deal with the by-product of sour natural gas treatment (Claus process). Information on the elastic properties of sulphur is needed to predict block behavior.

To our knowledge, the only experimental data on the elastic properties of sulphur reported in the literature relates to single crystals. In particular we found only three studies [1–3], published in the 1950s, that give the nine elastic constants of single crystal orthorhombic sulphur. Two of the publications [1, 2] report values so widely apart from each other, that their data could not be accepted in the Landolt Börnstein tables [4]. The third is a review [3] that also includes the elastic constants of Rao [2], with a typing error (c_{13} is interchanged with c_{23}). In an older communication [5] Nobel laureate P.W. Bridgman studied the compressibility of pure elements. From his data it is possible to calculate the bulk modulus resulting in $K = 7.93$ GPa at 75 °C and $K = 7.00$ GPa at 30 °C.

In the late seventies [6], Watt calculated the analytical expression of two absolute bounds models for multiphase materials and applied his results to estimate the elastic moduli of polycrystals with orthorhombic symmetry, among them, sulphur. These are the only data on bulk and shear moduli we have been able to find in the literature.

They were compared to our experimental data obtained for polycrystalline sulphur test bars.

Three different groups of samples were characterized, all prepared by using 99.5% pure elemental sulphur produced by the Claus process. In the first group (7 samples) liquid sulphur was poured into horizontal aluminium moulds, $10 \times 10 \times 100$ mm; in the second (28 samples) it was poured into vertical aluminium moulds of the same size. A third group (14 samples) was prepared using thinner horizontal aluminium moulds ($2 \times 10 \times 40$ mm). The samples of the second group were diamond machined in order to obtain test bars with rectangular cross sections ($3 \times 10 \times 50$ mm).

The density of the test specimens was determined by the geometrical method (mass/volume). Sample thickness was measured with a digital micrometer (Mitutoyo IDC 543, full scale 12.5 mm, resolution 1 μm) by measuring each side at least 5 times. The other sides were measured using a digital caliper (Mitutoyo, resolution 10 μm). Both instruments were checked against certified calibrated references, resulting in an accuracy of $\pm 0.25\%$ and a precision to four significant digits. The volumes are the products of the average values of the dimensions. The associated standard deviations are essentially those derived from the lack of planarity and parallelism between the faces of the samples. Since the accuracy and the precision of mass measurements were much higher ($\pm 0.05\%$ and to six significant digits, respectively), the errors reported for the density are those calculated for the volume. As X-ray diffraction confirmed that our samples had orthorhombic symmetry, porosity was calculated referring their density to the single crystal one ($\rho_{teo} = 2.070$ g/cm^3) using the formula: $p = 1 - \rho/\rho_{teo}$.

Young modulus was measured 30 days after solidification by an improved non-contact version of the flexural resonance method, according to the ASTM C 623. The standard set-up consists of a rectangular test bar supported by two sharp knives, that are positioned on the nodal lines corresponding to the fundamental resonance mode. The shear modulus was measured placing the test bar on the central line. In spite of the high sensitivity of our equipment, the fundamental torsional frequency of thicker samples could not be detected. Further equipment details are reported elsewhere [8].

In order to calculate the elastic moduli of an ideal (pore free) polycrystal from the single crystal constants, absolute bounds models are generally used. Accordingly, the expected bulk (K) and shear (G) moduli should fall between the Voigt (V) and Reuss (R) bounds as follows [9]:

$$K_R < K < K_V \qquad G_R < G < G_V$$

Watt [6] applied his results to Hearmon's data [3] and obtained the bounds on elastic moduli reported in Table I for the orthorhombic sulphur polycrystal. From K and G, Young modulus E and Poisson ratio ν are easily calculated.

The interchanged elastic constants in Hearmon's tables [3] caused only minor errors (<0.2%). On the other hand, using the same relationships [6] and Sumer's

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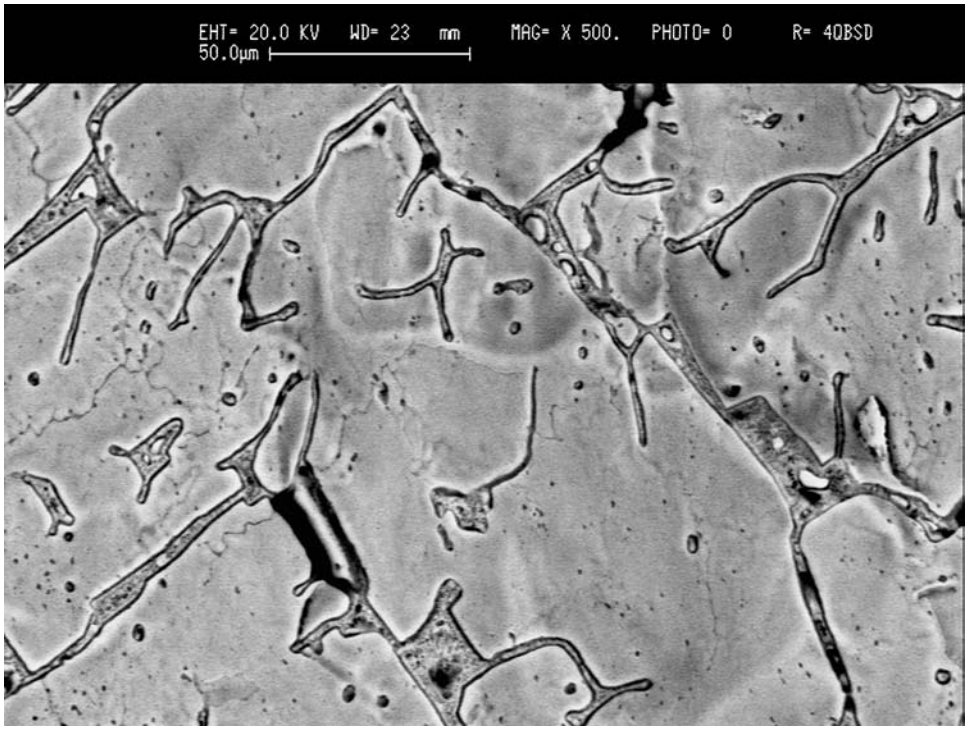

Figure 1 Scanning electron micrograph of sulphur microstructure (bar = 50 μm).

elastic constants [1], we obtained the bounds on moduli reported in the last row of Table I. One immediate observation following these calculations is that the bulk modulus, obtained with Bridgman's compressibility data, agrees quite well with the latter bounds.

At first glance, our experimental values (Table II) look rather scattered: the Young modulus ranges from 9 to 11 GPa and the shear modulus from 3.5 to 4.8 GPa, with the standard deviations shown in the table. They appear somewhat higher than the values calculated using Sumer's data, but far off those calculated with Rao's constants.

Based on density, our samples exhibit a porosity in the range of 4–6 vol%. due to the phase transitions from liquid to solid (monoclinic) and subsequently from monoclinic to orthorhombic. The pore locations are shown in Fig. 1. They can be found in the grain boundary regions (probably corresponding to the first phase transition) and inside the grains (corresponding to the second).

If we consider the porosity, a fairly good agreement with a theoretical model [10] is observed for the elastic properties of porous solids (see Figs 2 and 3). In a previous study [11] we verified that the Ramakrishnan model [10] is sufficiently accurate in the porosity range of our samples.

TABLE I Bounds on elastic moduli calculated by the two sets of elastic constants [1, 2, 3] according to [6]

	K_R (GPa)	K_V (GPa)	G_R (GPa)	G_V (GPa)	E_{inf} (GPa)	E_{sup} (GPa)	ν_{inf}	ν_{sup}
Hearmon	17.6	20.6	6.26	7.22	16.4	19.4	0.340	0.343
Sumer	7.51	7.62	3.27	4.53	8.97	11.35	0.240	0.250

The extrapolated zero-porosity value of that model (Table III) represents the "ideal polycrystal" value of the properties (E_0, G_0), consequently the three groups of samples should exhibit the same value. In fact, the samples prepared in thick moulds have the same Young modulus. On the contrary, the zero porosity value E_0 of thinner samples is higher: 13.0 GPa instead of 12.0 GPa. The difference between the thicker groups and the thinner one has been attributed to the sample size, i.e. cooling speed, which implies the presence of different amounts of the polymeric phase. In fact, we have found 3.0 vol%. of polymer in the thicker and 0.5 vol% of polymer in the thinner sample, as determined by the dissolution of crystalline sulphur in carbon disulphide. Since we expect the values of elastic moduli to be lower for the polymeric phase, its higher percentage

TABLE II Average value of elastic properties of real (porous) sulphur polycrystal

Sample	ρ (g/cm^3)	G (GPa)	E (GPa)
Thick vertical mould	1.956 ± 0.032	4.30 ± 0.26	10.26 ± 0.63
Thin horizontal mould	1.960 ± 0.013	4.63 ± 0.09	11.12 ± 0.33
Thick horizontal mould	1.950 ± 0.015	–	10.32 ± 0.42

TABLE III Elastic moduli of an ideal polycrystal of orthorhombic sulphur

	E_0 (GPa)	G_0 (GPa)	K_0 (GPa)	ν_0
Thick vertical mould	12.00 ± 0.15	5.10 ± 0.05	6.25	0.18
Thin horizontal mould	12.98 ± 0.01	5.50 ± 0.06	6.76	0.18
Thick horizontal mould	12.03 ± 0.01	–	–	–
Sumer	10.16	3.90	7.57	0.24

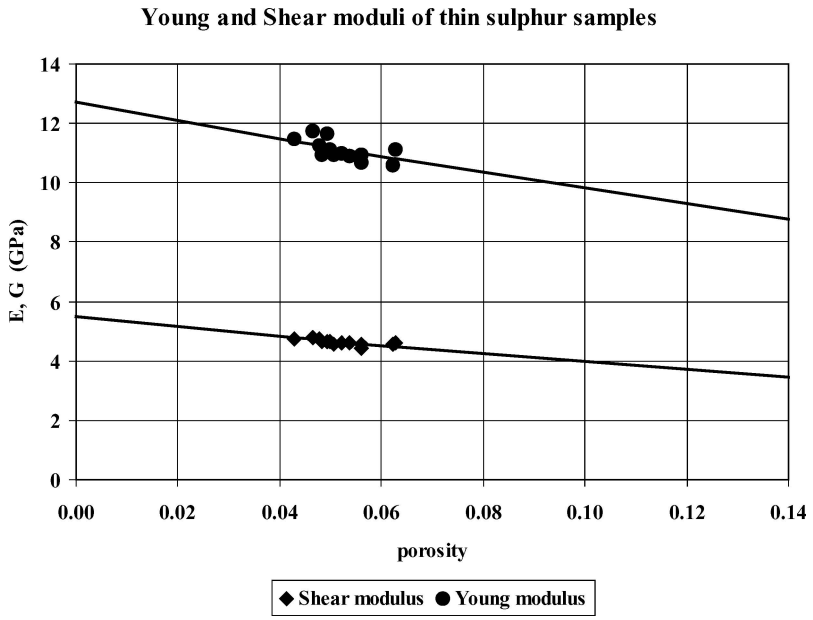

Figure 2 Thin sulphur samples: Young and Shear moduli as a function of porosity.

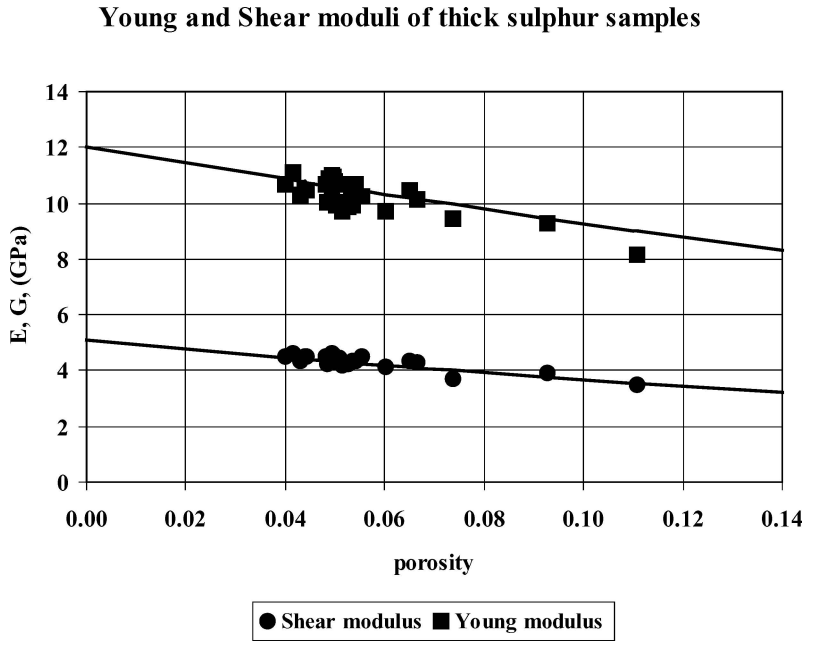

Figure 3 Thick sulphur samples: Young and Shear moduli as a function of porosity.

could explain the observed reduction in elastic moduli. The discrepancy between the Young modulus calculated with Sumer's data (10.16 GPa) and our value, obtained by data extrapolation to zero porosity (12.98 GPa), could be attributed, at least in part, to the propagation of errors due to the very complex relationships between elastic constants and elastic moduli.

In conclusion the real (porous) sulphur polycrystal will exhibit a Young modulus of about 10.5 GPa, depending upon the porosity values, which are in the range of 4–6 vol%.

An analogous point can be made concerning the shear modulus: G_0 values range from 5.1 to 5.5 GPa (the thicker and the thinner samples, respectively).

According to the average porosity of real samples, the expected shear modulus for the real (porous) polycrystal will be about 4.3 GPa.

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