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THE THERMOBALANCE USED TO MEASURE CROSSLINK DENSITY BY SOLVENT SWELL*

R. B. PRIME
International Business Machines Corporation, San Jose, California 95193 (U.S.A.)

ABSTRACT

A micro-technique for rapid measurement of solvent swell of crosslinked polymers is described. Crosslink density by solvent swell provides a useful physical parameter (it is equivalent to Young's modulus). But even more important, it is often the only means of monitoring extent of cure or degradation of thermosets and elastomers. An additional benefit of this method is the measurement of the soluble fraction, i.e. that portion of the polymer not bound to the network. The uniqueness of this method eliminates evaporation from the sample so that small, thin samples, which equilibrate rapidly, can be used. Poly(dimethylsiloxane) elastomers, ranging in crosslink density from 7 to 35 × 10^{-5} moles/cc and in sol fraction from 1 to 4%, were studied in hexane and toluene. A Perkin-Elmer TGS-2 thermogravimetric system was used. The critical measurement was the weight of polymer swollen with solvent, which was performed in a solvent-saturated environment. Repeated measurements on several samples demonstrated the method to be precise; comparison with a conventional technique showed it to be highly accurate. A direct correlation was established between swelling data and Young's modulus.

INTRODUCTION

Typically, solvent swell measurements are long (days), tedious, and require some minimum thickness to avoid erroneous results from excessive surface evaporation. This paper describes a unique application of a thermobalance to provide a rapid yet accurate measure of crosslink density by solvent swell, which is not limited by sample thickness. The primary purposes of this paper are to describe the experimental procedures in detail, and to demonstrate that the technique is equivalent to conventional solvent swell measurements and is, in fact, a measure of Young's modulus.

Silica-filled poly(dimethylsiloxane) elastomers, 0.1–0.4 mm in thickness, are the subjects in this study. Bueche[1] studied similar filled systems by solvent swell in toluene ("conventional technique") and found good agreement between crosslink

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densities from swelling and tension measurements. Barrall et al.[2] examined unfilled dimethylsiloxanes by conventional hexane swelling and Hertizian indentation by thermomechanical analysis. They observed that crosslink densities from swelling were 10% lower than those calculated from Young's modulus by indentation. In a conventional measurement of solvent swell, the swollen sample is removed from the solvent, sandwiched between two pieces of similar sized filter paper and placed in a weighing bottle and weighed. Next, the sample is quickly removed from the weighing bottle, which is again weighed. The swollen sample weight is simply the difference between the two weighings. This method was found to be highly precise. Typically, 2–3 days are required to obtain equilibrium. It is not unusual for the swollen sample weight to continue to change over a period of days, weeks, or months, necessitating an extrapolation to obtain the zero-time equilibrium swell ratio[1].

Other micro-techniques for measurement of solvent swell have been published. An optical method for thin samples where the area of the swollen sample is magnified and traced on paper was described by Coran[3]. Specimens of similar thickness (0.2 mm) reached equilibrium swelling in one to five minutes. The use of thin films made possible the determination of the types of chemical bonds responsible for the crosslinks in rubber vulcanizates. A technique where the solvent is extracted from the swollen sample and quantified by gas chromatography was described by Parks and Brown[4]. Swelling of the very thin (0.02 mm) microtomed samples was complete in five minutes. They used this technique to measure the variation in crosslink density through the carcass of an automobile tire.

BACKGROUND THEORY

The crosslink density, v_e/V_o, which is the number of moles of elastically effective crosslinks per unit volume of polymer, may be calculated from measurements of solvent swell or elastic modulus.

Crosslink density from solvent swell

For unfilled elastomers, crosslink density is calculated from equilibrium swelling data by means of the Flory–Rehner[5] equation which relates crosslink density to v_2, the measured volume fraction of polymer in a sample which has reached its equilibrium swollen state.

$$\frac{v_e}{V_0} = \frac{-[\ln(1-v_2) + v_2 + \chi_1 v_2^2]}{V_1(v_0^{2/3}v_2^{1/3} - 2v_2/f)} \tag{1}$$

where χ_1 is the polymer–solvent interaction parameter, V_1 the molar volume of solvent, v_o the volume fraction polymer in the diluent–polymer mixture at the time of crosslinking, and f is the functionality of crosslinks. In this study, v_o is approximately 0.97; the crosslinks are considered to be short and rigid with a functionality of four[1, 6]. For filled elastomers, the calculations are less exact due to assumptions and corrections that must be made[1, 7] and to uncertainties in the polymer–solvent interaction parameter[6, 8, 9]. For these reasons, Young's modulus, which is an unambiguous measure of crosslink density, was chosen as the reference for the solvent swell experiments.

The volume fraction v_2 is calculated from the measured swell ratio, SR.

$$v_2 = \frac{\text{Volume dry polymer}}{\text{Volume swollen polymer}} = \frac{(w_p/\rho_p)}{(w_p/\rho_p) + (\text{SR}/\rho_s)} \tag{2}$$

where w_p is the weight fraction of polymer in the filled polymer (0.88), ρ_p is the density of the polymer phase (0.98 g/cc), ρ_s is the solvent density (0.660 g/cc hexane, 0.867 g/cc toluene), and SR the weight of solvent sorbed per gram of sample (gel).

Crosslink density from young's modulus

The moles of effective crosslinks per unit volume of polymer may be calculated from the experimentally measured elastic modulus (Young's modulus, E) by

$$\frac{\nu_e}{V_0} = \frac{E}{3v_p RT} \tag{3}$$

where v_p is the volume fraction polymer in the filled elastomer, R the gas constant, and T the absolute temperature.

EXPERIMENTAL

Materials

Poly(dimethylsiloxane) elastomers were the subject of this study. All polymers contained 12% by weight fumed silica and had densities of 1.04 g/cc. Sample thicknesses ranged from 0.15 to 0.39 mm. Crosslink density differences are due to material variability, completeness of cure and type of cure. Solvents for this study were spectral grades of hexane and toluene.

Solvent swell

Measurements were made using the Perkin-Elmer TGS-2 thermogravimetric analysis system. A total of three measurements are required: the initial sample weight, W_i, the swollen sample weight (solvent + gel fraction), W_s, and the final sample weight (gel), W_f. From these measurements, the swell ratio is calculated as

$$\text{Swell ratio} = \frac{W_s}{W_f} - 1 \tag{4}$$

and the sol fraction (≡percent extractables) as

$$\text{Sol fraction} = \frac{W_i - W_f}{W_i} \tag{5}$$

Experimental details are described in the body of this paper.

Elastic modulus

Measurements were made using the Instron Tensile Tester. Sample size was 6 mm × 25 mm; thickness was calculated from the sample weight and density. Measurements were made at 24 °C at a crosshead speed of 0.5 in./min (13 mm/min).

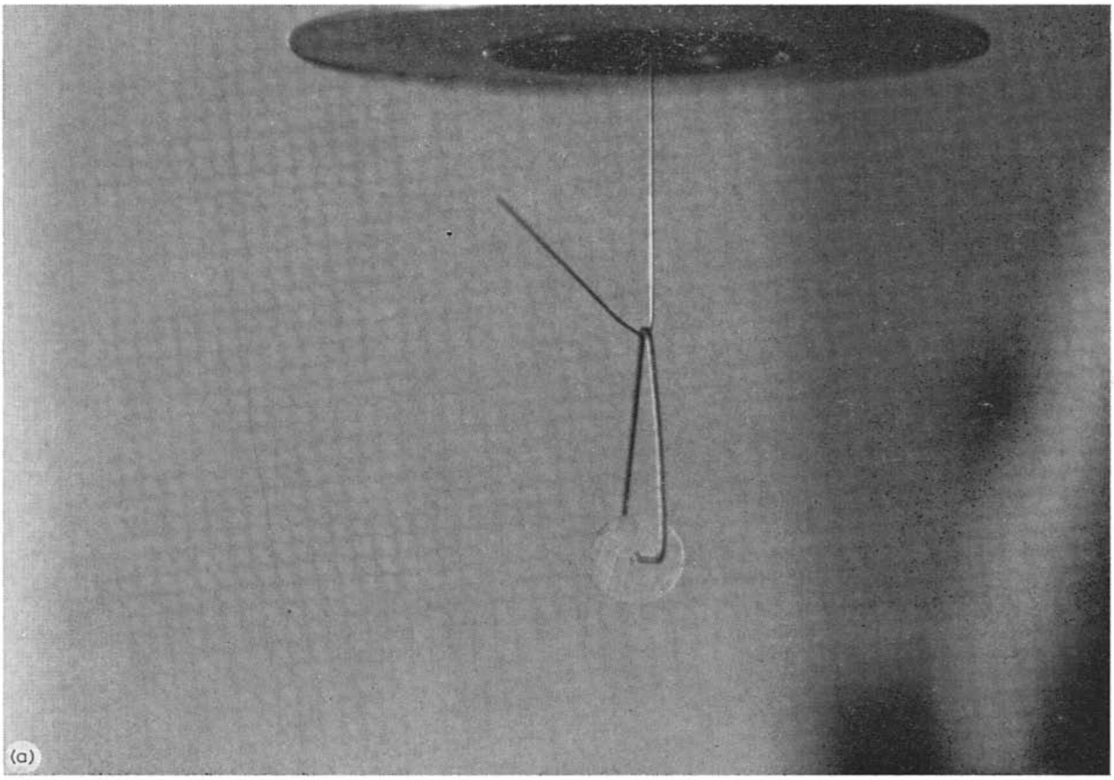
The elastic modulus, E, was taken as the slope of the true stress ($\lambda\sigma_t$) versus true strain (λ-1) for $1.0 < \lambda < 1.75$, where σ_t is the force per original cross-sectional area and λ the ratio of extended length to original length[10].

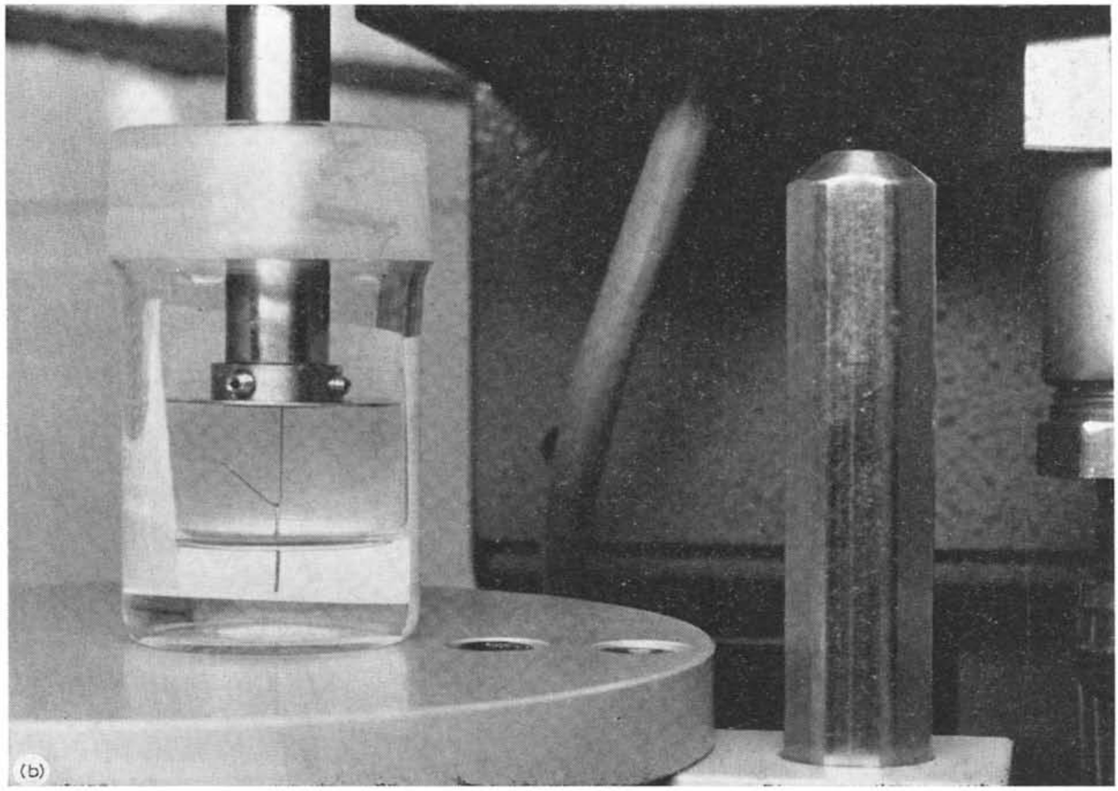
EXPERIMENTAL DETAILS AND RESULTS

As discussed previously, three parameters are measured: W_i, W_s and W_f. Measurement of W_i, the initial polymer weight, and W_f, the final gel weight, is straightforward. The unique part of this technique is the measurement of W_s, the weight of polymer swollen with an equilibrium amount of solvent. The Perkin-Elmer TGS-2 thermogravimetric system was employed, and a slow, 20 cc/min, nitrogen purge was maintained to protect the balance mechanism from solvent vapors. The TGS-2 sample loading platform greatly facilitated these measurements.

Measurement of W_s

Through experimentation, it was found that a 1/8 in. (3.2 mm) diameter sample mounted onto a 10 mil (0.25 mm) Nichrome wire bent into a triangle was the method of choice. The sample was punctured with a sharp instrument, such a very fine

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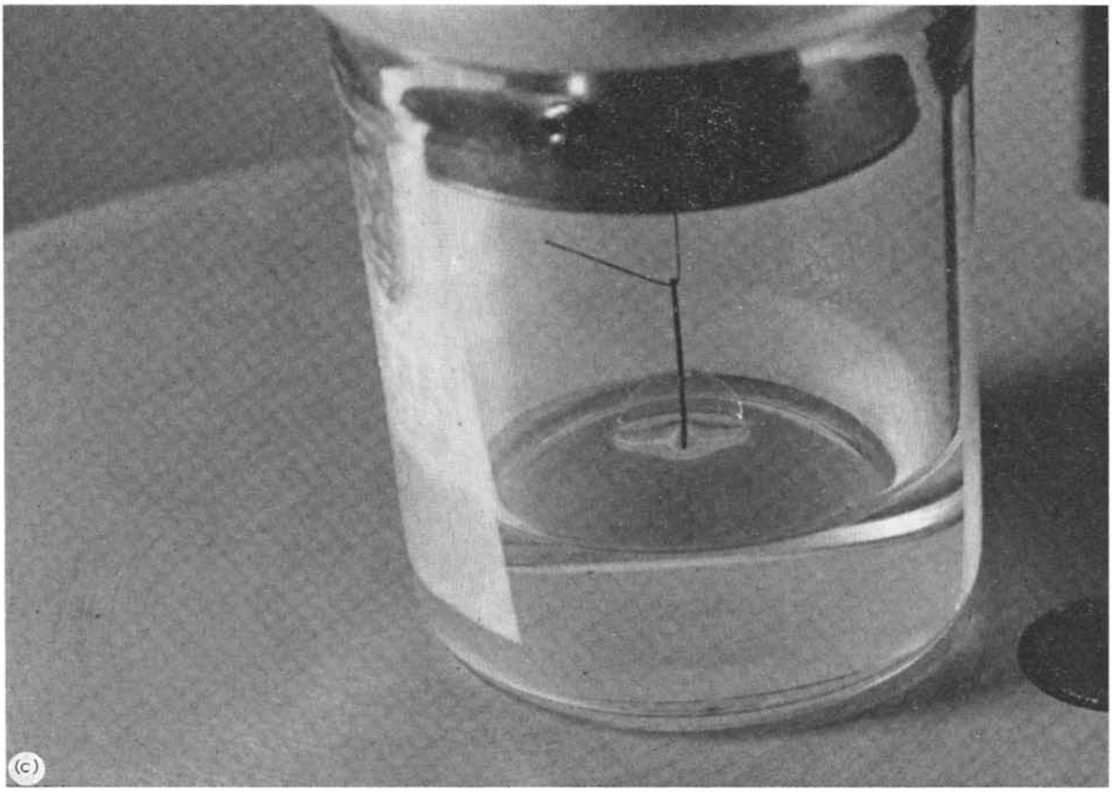
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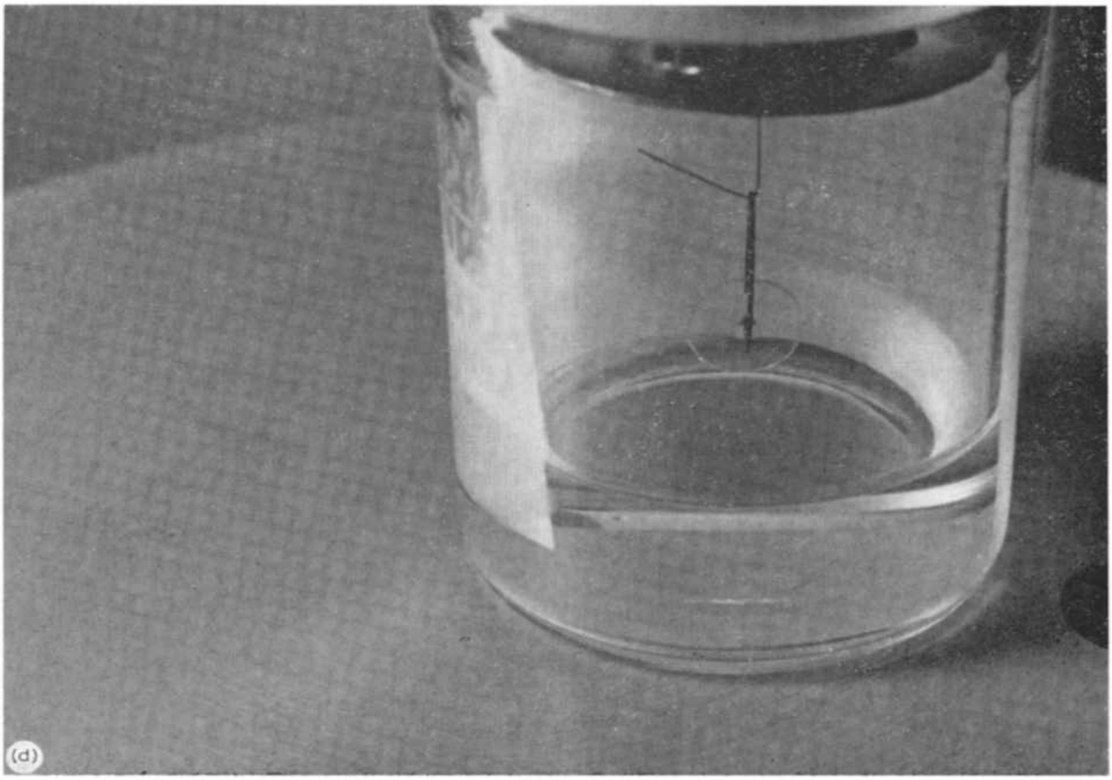

Fig. 1. The solvent swell experiment. (a) 3.2 mm Diameter sample on Nichrome holder prior to swelling. Note that the sample plane is vertical. Initial weight taken with sample inside a jar. (b) Sample swelling for minimum of 15 min. (c) Sample being carefully withdrawn from solvent; note how surface tension removes excess solvent from surface. (d) Swollen sample weight taken in solvent saturated environment provided by filter paper.

tweezers, before mounting on the triangle. It was necessary that the sample plane be reasonably vertical to the wire axis (see Fig. 1) to facilitate proper solvent drainage and prevent the swollen sample from touching the sides of the triangle. A bare triangle (~20 mg) served as the reference weight.

In a typical experiment, the tared triangle with sample was suspended from the hangdown wire and the sample weight, W_i, taken to ±1 μg. Using the sample loading platform, a solvent container (16 ml weighing bottle with 25 mm i.d. and 50 mm height) was raised to immerse the sample in solvent [Fig. 1(b)]. After a 15 min soak time, the solvent container was carefully lowered, pulling excess surface solvent from the sample by surface tension forces [Fig. 1(c)]. The weight of solvent-swollen polymer, W_s, was taken in an atmosphere saturated with solvent vapors; the saturation power provided by the filter paper [Fig. 1(d)] is absolutely necessary and a key part of the technique. With this arrangement, W_s could be maintained constant to within ±2 μg for several minutes. W_s was taken as the average of three readings from successive immersion of the sample in and withdrawal from the solvent; a precision of ±10 μg was observed. Finally, the solvent container was removed and the sample allowed

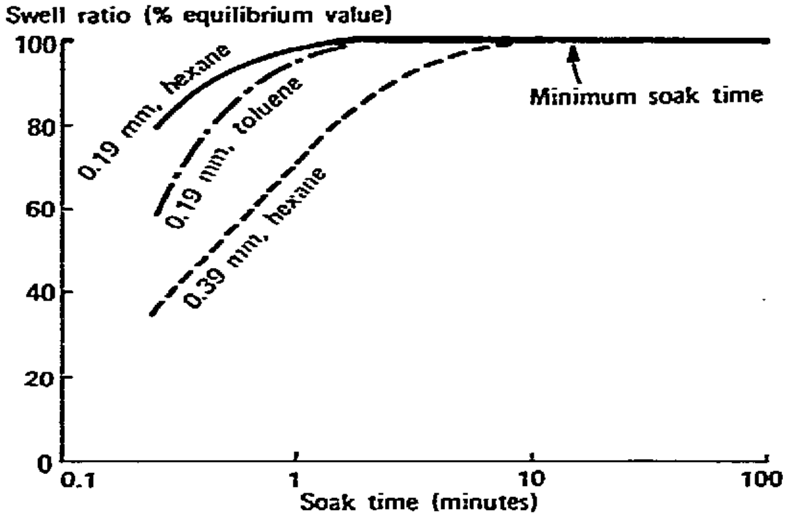

Fig. 2. The time to reach equilibrium swelling is a function of sample thickness and solvent. A minimum soak time of 15 min was adopted for this study.

to dry; W_r, the gel weight, was measured to ±1 μg. Measurements were repeated with fresh sample and solvent to ensure that measured swell ratios agreed to within ±2%. In separate measurements, it was observed that the bare triangle absorbs approximately 1 μg of solvent and that, with time, solvent does condense onto the wire. For this reason, W_s was measured within two minutes from the time of withdrawal.

The soak times required to reach a constant swell ratio were determined for the thickest sample (B) in hexane and a thin sample (C) in hexane and toluene (Fig. 2). In every case, a constant swell ratio was achieved in 10 min; a standard soak time of 15 min was adopted. Bueche[1] observed that the swell ratio for similar polymers continues to rise at a constant rate for several days; because of the 2–3 days to reach the constant slope region, it was necessary for him to extrapolate to a zero time equilibrium swell ratio. To establish whether similar behavior was occurring in this study, the swelling of sample C in hexane was monitored over a 30 day period. A similar continuously increasing swell ratio was observed, but the extrapolation to zero time was identical with the 15 min value adopted by this technique.

It was of interest to establish the equivalency of the TGA method to a conventional method, for example that used by Bueche[1] on similar silica-filled siloxanes and described in the introduction. To this end, two samples of a similar material but with higher filler content were cut from a tensile slab. Each sample was allowed to soak for 48 h in toluene and then the swollen weight measured with each technique. The results, given in Table 1, clearly show that the two methods are identical.

Experimental results for eight samples with widely varying crosslink densities are presented in Table 2. Note that the samples are 5–10 times thinner and 2–3 orders of magnitude lower in weight than conventional tensile slab samples. The data clearly show the precision of the experiment to be ± 2% or better in the swell ratio and approximately 20% for the small sol fractions of these samples. As further illustrated

TABLE 1

SWELL RATIOS BY THERMOBALANCE METHOD ARE IDENTICAL TO CONVENTIONAL TECHNIQUE

Sample: Silica-filled poly(dimethylsiloxane).

(mg) Sample weight	*Toluene swell ratio*	
	Thermobalance	*Conventional*[a]
9.76	1.79	1.81
32.0	1.84	1.83

[a] Ref. 1.

in Fig. 3, there is a direct correlation of the swell ratios with Young's moduli, as there should be [see eqns. (1) and (3)]. This demonstrates that the rapid solvent swell measurements on small samples are indeed an unequivocal monitor of the crosslink density. Thus, physical phenomena which depend on or reflect the status of crosslinking, such as extent of cure or aging and degradation, can be kept track of easily, rapidly and accurately with this technique.

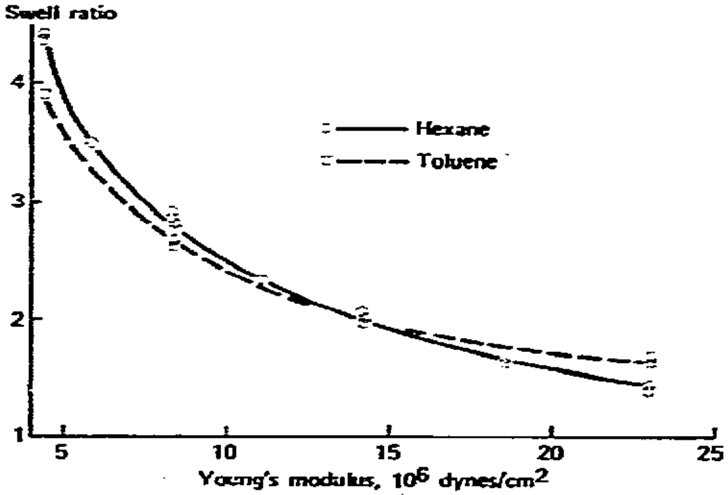

Fig. 3. The direct correlation between equilibrium swell ratio and Young's modulus suggests this rapid, micromethod to be an unambiguous measure of crosslink density.

CONCLUSIONS

Solvent swell measurements utilizing the thermobalance are rapid and precise. They are rapid because samples are thin and reach equilibrium swelling in a short time. For the samples measured, the technique was shown to be precise to ± 2% in the swell ratio and ± 20% in the sol fraction. Accuracy was established by correlation with a conventional technique; both techniques gave identical results. A direct correlation was established between the swell ratios in both solvents and the Young's modulus, demonstrating an unambiguous monitoring of crosslink density.

TABLE 2

EXPERIMENTAL RESULTS ON EIGHT SILICA-FILLED POLY(DIMETHYL-SILOXANE) ELASTOMERS VARYING ONLY IN THICKNESS AND CROSSLINK DENSITY

Sample	*Weight (mg)*	*Thickness (mm)*	*Hexane*			*Toluene*			*Instron*	
			Sol fraction (%)	*Swell ratio*	v_2	*Sol fraction (%)*	*Swell ratio*	v_2	*Young's modulus (10^6 dynes/cm^2) (psi)*	*Crosslink density (10^{-5}moles/cc)*
A	1.3	0.15	2.3	4.38	0.119	2.35	3.92	0.166	4.34 (62.5)	6.6
			2.4	4.30	0.121	2.6	3.92	0.166		
			2.0	4.28	0.122					
B	3.0	0.39	2.0	3.46	0.146				6.20 (90)	9.5
			2.0	3.45	0.146					
C	1.5	0.19	1.7	2.87	0.171	1.4	2.70	0.224	8.54 (124)	13.0
			1.4	2.86	0.172	1.7	2.66	0.226		
D	2.3	0.29	1.4	2.80	0.175				8.68 (126)	13.3
			1.2	2.75	0.177					
E	1.4	0.17	4.1	2.29	0.206				11.20 (162)	17.1
			4.1	2.29	0.206					
F	1.4	0.17	1.2	2.05	0.224	1.9	1.99	0.281	14.50 (210)	22.2
			1.4	2.00	0.229	1.5	1.97	0.283		
			1.05	1.98	0.230					
G	1.5	0.18	4.0	1.70	0.259				18.80 (273)	28.8
			3.6	1.64	0.265					
H	1.4	0.16	1.4	1.48	0.286	1.4	1.66	0.319	23.20 (336)	35.4
			1.25	1.45	0.290	1.15	1.62	0.325		

There is no reason why this technique should not find application to other elastomers and thermosets. Because sample size can be very small, this method can measure crosslink densities not possible by conventional techniques (e.g. small samples, local variability in crosslink density and crosslink density gradients). Due to its rapidity and high precision, applicability should extend from research characterization to quality control (e.g. extent of cure) to aging and degradation of crosslinked polymeric materials.

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