

NOTES

Measurement of Elastomer-Based Capacitors in Vapor Fields

Silicone elastomers are highly permeable to vapors^{1,2}; and, because of solvent-polymer interaction, the elastomer swells to a degree governed by the solubility parameter.³ Furthermore, it has been shown that electrical capacitance measurements gauge water absorption in paint films via modification of the paint's dielectric constant.^{4,5,6} This note describes measurement of elastomer-based capacitors exposed to solvent vapors, demonstrating anew the value of such measurements in gas sorption studies in polymer films.⁴

The films used here were made from plasticized Dow Corning Sylgard 182 potting resin (Dow Corning Corp., Midland, Mich.). They were cast by dip-coating Nesa-coated glass (Liberty Mirror Co., Brackenridge, Pa.) from a solution comprising 1 part by weight Sylgard 182, 0.1 part curing agent, 0.55 part 10 ctsk Dow Corning 200 silicone oil for plasticization, and 1.1 part isooctane to obtain a convenient coating viscosity. The conducting Nesa coating served as one plate of the elastomeric capacitor. The dielectric constant ϵ of Sylgard 182 is 2.70, and of plasticizer, 2.65.

After dipping, the elastomer was cured at 110°C for 20 hr. Then, an area-defining Mylar (registered trademark of E. I. du Pont Co.) spacer was attached to the film with RTV Dow Corning Sylgard 184. This spacer had a circular aperture which established an effective sample area of 20 cm². An upper electrode was made by evaporating gold-indium layers onto the elastomer. Capacitance and dissipation of the resulting structure were measured with a General Radio 1615 Capacitance Bridge at frequencies from 1 to 100 kHz with a sampling amplitude less than 1 V RMS.

The sample was exposed to a vapor field by suspending it over an open beaker of the appropriate solvent; both members were enclosed within an outer beaker system to reduce vapor loss. Solvent vapor pressure was that established by an ambient temperature of 22°C. The in situ measurements were made periodically until saturation occurred, generally within 2 hr. After saturation, the sample was removed to determine reversibility. In all cases, capacitance and dissipation reverted essentially to their initial values.

The elastomer thickness in air was 9.5 μm , resulting in a capacitance C of 4911 pF; dissipation at 1 kHz was 0.0053, from which an equivalent parallel leakage resistance R of 6.1×10^6 ohms was computed. Results of the vapor field measurements after equilibrium was established are listed in Table I in terms of percentage change in C and R at a probing frequency of 1 kHz. Similar results were obtained at other frequencies. Listed also are values of the solvent's dielectric constant, vapor pressure at 25°C, and solubility parameter.

It is seen that both C and R change in a vapor field, and the sign of change appears to depend upon the vapor's dielectric constant, among other things. For ϵ of 3.4 and below, ΔC is (-) and ΔR is generally (+); for higher ϵ , ΔC is (+) and ΔR is generally (-).

The framework for understanding these results lies in the dependence of C and R upon geometric and electrical parameters. Assuming sample area does not change in a vapor field, and for small changes,

$$\frac{\Delta C}{C} = \frac{\Delta \epsilon}{\epsilon} - \frac{\Delta l}{l} \quad (1)$$

TABLE I
Capacitance and Resistance Change at 1 kHz in Vapor Fields

	Vapor pressure (25°C), ^a mm Hg	ε ^a	δ, ^b (cal/cc) ^{1/2}	ΔC/C, %	ΔR/R, %
Petroleum ether	154	1.9	7.4	-24	+92
Gasoline	47	1.9	7.3	-18	+50
Isooctane	45	1.9	7.6	-12	+3
Triethylamine	—	2.4	—	-15	≈0 (-)
Trichlorethylene	73	3.4	9.2	-6	-75
2-Propanol	41	18.3	11.5	+1	+13
Methyl ethyl ketone	100	18.5	9.3	+20	-65
Nitrobenzene	0.3	36.1	10	+5	-7
Acetonitrile	87	37.5	11.9	+14	-47
Water	14	78.5	23.9	~0 (+)	-22
Formamide	0.03	109	19.2	~0 (+)	-5

^a Values obtained from *Handbook of Chemistry and Physics*, 54th ed., CRC Press, Cleveland, Ohio, 1973.

^b δ = 7.6 (cal/cc)^{1/2} for poly(dimethylsilicone). Values obtained from H. Burrell and B. Immergut, in *Polymer Handbook*, ed. by J. Brandrup and E. H. Immergut, Interscience, New York, 1966.

and

$$\frac{\Delta R}{R} = \frac{\Delta \rho}{\rho} + \frac{\Delta l}{l} \quad (2)$$

where ρ is resistivity and l is sample thickness. Swelling, assumed to occur to some extent in all cases, but primarily for vapors which match the solubility parameter of the elastomer, causes C to decrease and R to increase. That swelling occurred was verified directly for the case of petroleum ether by means of interferometric thickness measurements. Thickness was found to increase by 8% in the presence of this vapor. Thus, to account for the change in C and R in this case, one needs to postulate a 16% decrease in ϵ and a 76% increase in ρ . The change in ρ can be caused by addition and by rearrangement of ionic impurities by the vapor field, as well as changes in ionization resulting from changes in effective dielectric constant. Swelling may also cause an increase in diffusivity of charge carriers.

Further reduction of data was not attempted because, among other things, the vapor pressure of the solvents differed widely. Quantitative analysis would certainly require an accounting of this fact. This note seeks mainly to reaffirm the potential power of this measurement in sorption studies. The details of coupled dielectric and resistivity changes have obvious scientific merit. Furthermore, the measurement, after sample preparation, is simple and sensitive. For example, vapor pressures as low as 0.03 mm Hg caused an observable effect. Finally, while the effect of the evaporated contact on permeation is presently uncertain, it presumably can be accounted for to permit accumulation of significant results.⁷

References

1. R. M. Barrer, J. A. Barrie, and N. K. Raman, *Polymer*, **3**, 595 (1962).
2. R. M. Barrer and H. T. Chio, *J. Polymer Sci., C*, **10**, 111 (1965).
3. K. B. Yerrick and H. N. Beck, *Rubber Chem. Technol.*, **37**, 261 (1964).
4. D. M. Brasher and A. H. Kingsbury, *J. Appl. Chem.*, **4**, 62 (1954).

5. J. K. Gentles, *J. Oil Colour Chem. Assoc.*, **46**, 850 (1963).
6. K. A. Holtzman, *J. Paint Technol.*, **43**, 47 (1971).
7. C. R. Thomas and R. E. Barker, Jr., *J. App. Polym. Sci.*, **7**, 1933 (1963).

JOSEPH J. WYSOCKI

Xerox Corporation,
Webster Research Center
800 Phillips Road
Webster, New York 14580

Received April 18, 1974