

Method for Structural Characterization of High Polymeric Networks by an Osmotic Pressure Technique

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Synopsis

An apparatus was designed to measure the osmotic pressure of solvent-polymer systems. The method is unique in that semirigid polymers may be incorporated as the solute component without specimen fissures occurring from excessive solvent dilative action. The advantages of this technique are: high polymeric materials both elastomeric and plastic can be structurally characterized by the same technique; the calculated effective molecular weight of the polymer network will reflect a value consistent with the polymer's performance characteristics; and the method is only restricted to lyophilic polymer-solvent systems.

INTRODUCTION

The dilative action of solvents on high polymeric networks may result in specimen swelling to four or more times the unswollen specimen size. Extensive dilation can be accommodated by elastomeric polymer networks, but some semirigid polymer networks will not tolerate a strong solvent dilative action without polymer specimen fissures occurring.¹ Thus the technique used for elucidating the structures of elastomeric polymers by solvent dilation cannot be applied to high polymer networks in general. Regardless of the nature of the network fissures resulting from solvent swelling, a method for measuring solvent action, such as osmotic pressure, involving negligible volume changes in the polymer specimen would possibly be applicable to all high polymer networks. A constant volume method would yield effective molecular weight and crosslink density values considerably higher than those calculated by a solvent swelling technique because most of the weak binding forces will not be eliminated. This condition can be argued favorably, because these weak forces very likely exist during the material's performance and so would be expected to give realistic structure-property relationships. In order to establish a method to measure the osmotic pressure of high polymers, elastomeric and semirigid, two problems had to be resolved. The first problem was to establish a way to measure the increase in pressure in the solute from solvent osmosis. The

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second problem concerned the design of a suitable restraining membrane that precluded polymer specimen swelling but which would freely allow solvent access to the polymer. This investigation describes the resolution of these problems, and the establishment of a suitable procedure for determining the effective molecular weights of three semirigid polyurethane materials.

EXPERIMENTAL

Materials

Three one-shot polyether semirigid urethane materials were compounded to represent a variation in crosslink density or hardness (Table I). The hardness was varied by changing the ratios of the polyether triol (700 MW), and the polyether diol (2000 MW). All materials were crosslinked with

TABLE I
Polyether Urethane Formulation

Formulation number	Parts by weight				Specific gravity	Duro-meter (Shore A)
	CP-700 ^a	P-2000 ^b	TDI ^c	Catalyst ^d		
1	100	—	40.2	0.1	1.149	96
2	55	45	26.2	0.1	1.105	66
3	25	75	16.9	0.1	1.072	55
3a	25	75	16.9	0.1	1.072	50

^a Voranor CP-700, 700 MW triol, Dow Chemical Company.

^b Voranold P-2000, 2000 MW diol, Dow Chemical Company.

^c Nacconate 80, 80% 2,4- and 20% 2,6-toluene diisocyanate, Allied Chemical Company.

^d Dabco triethylenediamine (Houdry Process Corporation) mixed with 80% CP-700.

toluene diisocyanate (TDI) at a 1.05 TDI index. The curative index represents the ratio of TDI equivalent weight to the equivalent weight of the polyols. A catalyst, triethylenediamine, was incorporated as an 80% solution in the polyether triol to allow an accurate addition of small amounts of catalyst.

All materials were degassed for 1 hr. by vacuum before mixing. After mixing, the compounds were again degassed until bubble formation ceased. The compounds were cured in two stages: stage 1, 16 hr. at 23°C.; and stage 2, a program-controlled temperature gradient from 54° to 93°C. over an 8-hr. interval, followed by 16 hr. at 93°C.

Specimen Preparation

The urethane material was cast in a degreased, cylindrical retaining ring of porous brass (Oilite) by use of an aluminum base plate and a glass cover plate (Fig. 1). Air entrapped at the surfaces of the mold when the urethane material was poured caused bubble formation during the curing

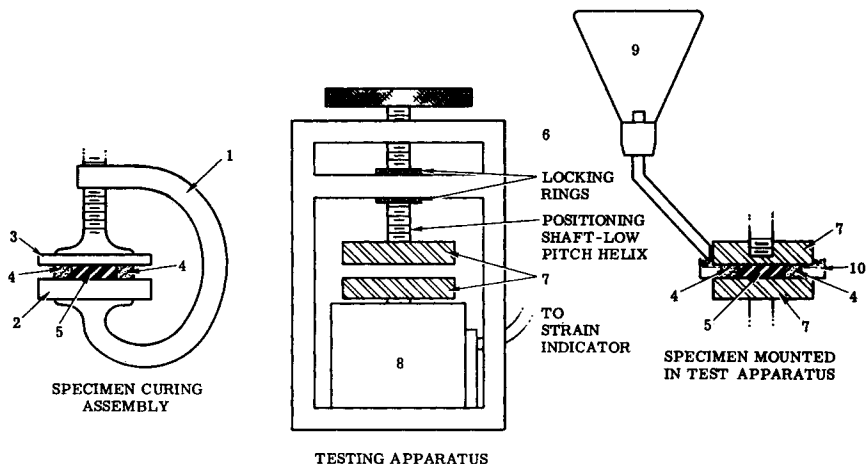


Fig. 1. Test apparatus and specimen curing assembly: (1) C-clamp; (2) Al base plate; (3) glass plate; (4) porous retaining ring; (5) high polymeric material; (6) test apparatus frame; (7) parallel platens; (8) load cell; (9) solvent feed reservoir; (10) specimen mounted in test apparatus with solvent tray (thin Al cup).

operation. However, the following procedure was developed to produce a bubble-free specimen. The base and cover plate were thoroughly cleaned (with solvent), and then coated with the uncured urethane. Next, the coated plates were degassed by vacuum. The retaining ring was then carefully placed on the coated base plate and was filled by slowly pouring the degassed urethane material with a glass rod or spatula. The coated top plate was installed with a slight shearing action to eliminate air entrapment at the top surface of the specimen. The base and top plates were secured in position with slight pressure (C-clamp). The assembly was then subjected to the curing procedure described previously.

Apparatus

The apparatus (Fig. 1) consists of a Baldwin, Model V-1, 1000-pound load cell which is mounted in a steel frame with an overhead adjustable platen parallel to the load cell platen; a tray which rests on the load cell platen and which is used to keep the specimen immersed in solvent during the test; a constant level device for furnishing a supply of solvent to the tray; a Baldwin strain indicator, SR 4, Type L; a permeable specimen retaining ring of porous brass (Oilite) material; and a Conrad constant temperature chamber that maintained a $\pm 1^\circ\text{C}$. temperature control.

Test Procedure

The specimen is placed in the tray and a 4.5-kg. force applied. This amount of force was arbitrarily chosen for the size of specimen used in this work and was considered necessary to insure intimate platen-polymer contact. Next the solvent was admitted into the tray, thus initiating an

experimental run. Readings were taken periodically; the interval between readings varied according to the rate of change in pressure. The test was continued until an equilibrium pressure could be obtained, directly or by graphic extrapolation. It was observed for formulations 1 and 2 that when the specimens were removed from the test apparatus without first removing the solvent, the resulting reduction in pressure and subsequent volume increase caused considerable crumbling of the polymer specimens.

RESULTS AND DISCUSSION

The osmotic pressures were determined directly from equilibrium measurements in one case, and indirectly by extrapolation of dp/dt versus p curves after linearity was noted. The actual times to establish equilibrium pressures were as long as six weeks. However, 5–6 weeks for equilibrium by this method is not unrealistic, considering it takes at least 3 weeks for equilibrium by the swelling technique with similar urethane materials.² At present the only apparent reasonable way to reduce solvent sorption equilibrium times would be to increase the surface area to volume ratio of the polymeric material, i.e., to use film-type specimens.

TABLE II
Osmotic Pressures of Polymethane-Toluene Systems

Formulation number	Temperature, °C.	Π , kg./cm. ²	\bar{M}_e
1	23	84.9	340
2	23	92.7	300
3	23	72.7	370
3a	23	54.8	490
	14	53.8	485
	5.5	50.0	505
	-2.5	47.8	515
	-9.5	46.0	520
	-18.5	43.8	530

The data in Table II show that the measured osmotic pressures tend to decrease with decreasing polymer network densities and equilibrium temperatures. The low osmotic pressure noted for formulation 1 is likely to be a false value due to a low permeable structure of the restraining ring from faulty manufacture or possibly due to damage of the porous structure of the ring resulting from the 4.5-kg. preloading on the specimen.

The effective molecular weights of the crosslinked urethanes have been calculated and are shown in Table II. These values were derived on the basis of two assumptions: (1) the polymer concentration at equilibrium is very nearly its density before solvent sorption; and (2) ideal osmotic pressure laws apply. The first assumption should not involve appreciable

errors in equilibrium pressures except at high pressures where load cell deflection may be an affecting factor on concentration. The second assumption utilizing the $\Pi = CRT/\bar{M}_e$ relationship is a first approximation. Previous related work would indicate that an expression advanced by Ostwald,³ $P = CRT/M + kC^n$, would likely be more appropriate for the data here, where P represents the swelling pressure, the first right-hand term represents the osmotic effect, the second right-hand term is related to the isothermal sorption phenomena, and M is identical to the effective molecular weight, \bar{M}_e .

The calculated \bar{M}_e values show a close similarity in the three formulations with the expected increasing trend for the less rigid formulations. At low swelling, highly crosslinked polymer networks include a considerable quantity of secondary binding forces which would contribute to low molecular weights. The small differences in network structures between varying crosslinked silicone formulations at low swelling have been reported earlier by Seeley.⁴ The increase in \bar{M}_e values with decreasing temperature for formulation 3 is expected, as well as the fact that the effective molecular weights show a constancy at temperatures below 0°C. where solvent activity would be less.

CONCLUSIONS

An apparatus has been designed to measure the osmotic pressures of semirigid polymer-solvent systems. These measurements will allow one to calculate the effective molecular weights or effective crosslink densities of the polymers. An experimental procedure was described for urethane-toluene systems. The osmotic pressure measurements were incorporated in a simple equation of state to determine effective molecular weights of three polyurethane polymers to check the performance characteristics of the apparatus. The resulting data reflect variations in agreement with known solvent-solute behavior.

This apparatus should be useful for characterizing other high polymers, such as the more elastomeric polymers. Further investigations are warranted on utilizing smaller polymer specimens to reduce the long equilibrium swelling times encountered in this work.

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References

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Résumé

Un appareil a été construit en vue de mesurer la pression osmotique de systèmes solvant-polymère. La méthode est unique en ce sens que des polymères semi-rigides peuvent être incorporés comme composants solutés sans qu'il y ait des fissures au sein de l'échantillon par suite de l'action dilatante d'un excès de solvant. Les avantages de cette technique sont: des matériaux polymériques à la fois élastomères ou plastiques peuvent être caractérisés structurellement par la même technique; le poids moléculaire effectif calculé du réseau polymérique fournira une valeur en accord avec les caractéristiques de performances des polymères; la méthode est uniquement limitée à des systèmes lyophiles polymères-solvants.

Zusammenfassung

Ein Apparat zur Messung des osmotischen Druckes von Lösungsmittel-Polymer-systemen wurde konstruiert. Die Methode ist insofern neuartig, als halbstarre Polymere als gelöste Komponente verwendet werden können, ohne dass durch die dilatierende Wirkung des überschüssigen Lösungsmittels Risse auftreten. Die Vorteile dieses Verfahrens sind: hochpolymere Stoffe sowohl elastische als auch plastische, können mit dem gleichen Verfahren strukturell charakterisiert werden; das berechnete effektive Molekulargewicht des Polymernetzwerks gibt einen mit der Gebrauchscharakteristik des Polymeren konsistenten Wert wieder; die Methode ist nur auf lyophile Polymer-Lösungsmittelsysteme beschränkt.

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