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Porous volume determination of styrene-divinylbenzene copolymers by water uptake measurements

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SUMMARY

A simple method of porous volume determination for styrene-divinylbenzene copolymers has been developed. This method is based on water uptake measurements after surface treatment with methanol in order to reduce the characteristic water repellance of the copolymer beads. The porous volume determined by water uptake is in good agreement with mercury porosimetry measurements.

INTRODUCTION

The characterization of the porosity of styrene-divinylbenzene copolymers is subject of interest since their varied applications are closely related with their porous structures. When the structure is heterogeneous, as in macroporous copolymers, the porosity can be measured by several techniques which only give a partial characterization. A typical analysis is the porous volume determination, which is usually obtained through solvent and nonsolvent uptakes, apparent densities by pycnometry, gas sorption (BET/N_2, He) and mercury porosimetry measurements (1).

The solvent and nonsolvent uptakes are frequently determined by the centrifugation method (2). Although, macroporous copolymers do not swell like gels, they have at least a small swelling capacity (3). Thus, solvent uptake coefficients do not represent specific fixed pore volumes like apparent density by picnometry, gas sorption and mercury porosimetry measurements. Even for nonsolvents like heptane and nitromethane, Millar et al. (4) have found that some solvation of internuclear chains can occur and consequently the accessible pore volume is greater than the fixed one. It has also been suggested that water uptake is a better measure of true pore volume, since water cannot solvate or swell the hydrocarbon network.

It is well known that styrene-divinylbenzene copolymers present a water repellant surface so that water intrusion porosimetry can be performed in these materials without any surface treatment (5). Hence, it is necessary to reduce the hydrophobicity of the copolymers before measuring the water uptake. Millar et al. (4) have done that by immersing the copolymer in methanol for about 16 hours and subsequently washing a column of methanol-treated copolymer with water until methanol was no longer detected.

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Poinescu et al. (6) and Nègre et al. (7) have found that styrene-divinylbenzene copolymers synthesized in the presence of solvating diluents swell in methanol, although this solvent is a well-known poor solvent for polystyrene.

In this work in order to avoid swelling, we have modified Millar's method of water uptake determination by reducing the contact time of the copolymer with methanol. We have taken into account that if there was a fixed pore structure, methanol would have been able to diffuse quickly and wet all the pore surface. The results obtained by water uptake were compared with mercury porosimetry measurements.

EXPERIMENTAL

Styrene-divinylbenzene copolymers have been synthesized by suspension polymerization in the presence of solvent and non-solvent diluents and purified as previously described (8). Water uptakes have been determined by the Pepper's centrifugation method with some modifications (2). About 0.5g of dried copolymer beads were weighed into filter tubes made from a brass tubing to which 200-mesh wire-gauze was soldered at one end. Water was passed through the filter-tubes and after that they were put into polypropylene centrifuge-tubes and closed with rubber caps. The tubes were centrifuged at 500 *g* for 40 min. and reweighed. The weight increase was rather small (less than 8% of water per gram of copolymer), it was considered as water retained among the beads. After that methanol was passed through the filter-tubes until the elution of at least 5 ml of methanol. Then, water was passed through the filter to remove methanol and the tubes were centrifuged as before and finally reweighed. Water uptake values were the difference between water retaining after and before methanol treatment per gram of copolymers. These results were compared with mercury porosimetry measurements. Apparent density was determined by the graduated cylinder method (9).

RESULTS AND DISCUSSION

Water uptakes were determined in triplicate which agreed with an experimental error of less than 3.0%, except for very small pore volumes (Table 1). As expected, the pore volumes (V_p) determined by mercury porosimetry and the water uptakes increased as the apparent density diminished. When the pore volume was greater than 0.1 cm^3/g, the water uptake values were very close to V_p values determined by mercury porosimetry, except for samples DR-21 and DR-25 where the higher V_p values can be due to mechanical stress during mercury pressurization. Our results show that the fixed pore volume of styrene-divinylbenzene copolymers can be well characterized by water uptake measurements with two advantages. First, water cannot solvate or swell the polymer chains and expand the pore structure like organic solvents. In another paper (10), heptane uptake values of a copolymers series were always higher than water uptakes independent of diluent type, dilution degree and DVB content used in the copolymer synthesis. A second advantage is that the pore structure practically

TABLE 1 - Porous characteristics of some styrene-divinylbenzene copolymers

Sample	d_a (g/cm^3)	V_p (cm^3/g)	Water uptake (cm^3/g)
DR-01	0.66	0.027	0.004 ± 25.0%
DR-02	0.66	0.020	0.016 ± 9.0%
DR-03	0.63	0.023	0.047 ± 5.0%
DR-04	0.63	0.022	0.025 ± 8.0%
DR-05	0.63	0.031	0.057 ± 9.0%
DR-06	0.61	0.072	0.100 ± 3.0%
DR-07	0.59	0.221	0.223 ± 1.8%
DR-08	0.58	0.137	0.181 ± 0.6%
DR-09	0.50	0.311	0.329 ± 2.1%
DR-10	0.44	0.501	0.498 ± 1.2%
DR-11	0.43	0.543	0.541 ± 1.9%
DR-12	0.42	0.536	0.556 ± 1.0%
DR-13	0.40	0.572	0.613 ± 2.0%
DR-14	0.39	0.697	0.650 ± 2.8%
DR-15	0.37	0.701	0.708 ± 1.0%
DR-16	0.37	0.755	0.792 ± 2.7%
DR-17	0.32	1.016	1.022 ± 2.3%
DR-18	0.32	0.993	0.997 ± 1.9%
DR-19	0.32	1.010	0.956 ± 1.3%
DR-20	0.29	1.227	1.211 ± 1.7%
DR-21	0.24	1.407	1.000 ± 2.3%
DR-22	0.21	1.631	1.551 ± 3.0%
DR-23	0.20	2.186	2.109 ± 0.9%
DR-24	0.20	2.090	2.059 ± 2.1%
DR-25	0.20	1.796	1.624 ± 2.1%

d_a = apparent density

V_p = fixed pore volume determined by mercury porosimetry does not change during analysis so that the sample can be easily recovered.

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