The Densities of Polyvinyl Alcohol Film at Moist States

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Introduction

Although there exist a considerable number of papers on the sorption of water vapor by high polymers, only a few works have been carried out about the density of high polymers at moist states, and this phenomenon seems to present an important problem for a course of further studies on the mechanism of water sorption. Such density investigations have already been made with wool (A. T. King[1]), native cellulose fibers (E. Filby and O. Maass,[2] A. J. Stamm and M. Seborg[3]) and regenerated cellulose fibers (P. H. Hermans[4]), whereas there, is, as far as the present authors are aware, none yet with synthetic polymers. The synthetic high polymers, whose crystallinity can be changed more or less easily by heat- or mechanical treatments, have an advantage in such density studies, because the density stands in close relation with the crystallinity, which in turn governs the feature of water sorption. The present study was undertaken as a preliminary investigation of such a problem in connection with our previous works[5,6] on the sorption of water vapor by polyvinyl alcohol (PVA), bearing in mind that there might be some analogy between this substance and cellulose.

Experimental

a) Density Measurements.

i) *Sample*: The sample used was purified by the following procedures. The powdered specimen of PVA (average degree of polymerization: 2100) was dissolved in water at about 80°C. The 1% aqueous solution of sodium hydroxide was added to exclude residual acetyl groups on standing overnight. This solution was then neutralized with hydrochloric acid, and dialysed with distilled water for two weeks in order to eliminate inorganic salts, and then PVA was precipitated by adding methanol-acetone mixture. The films used for experiment were cast from about 2.5% aqueous solution of the purified PVA, on a glass plate placed horizontally in an air thermostat at 50° ±5°C. This took about five hours. The films were about 0.05 mm. thick, and were cut in pieces about 1 mm. × 5 mm.

ii) *Apparatus and procedures*: About 500 mg. sample in a weighing bottle was dried at about 60°C. under a high vacuum (10^{-4} mm. Hg atm. or below), until its weight became constant within ±0.2 mg. This procedure required about 10 days. The dry sample in the weighing bottle was placed in a small desiccator, in which the relative humidity was controlled by an aqueous solution of sulfuric acid of a definite concentration This desiccator was thermostated at 25°±0.05°C. The sorption equilibrium required about three weeks.

The density measurements were made by the flotation method, by using carbon tetrachloride-benzene mixtures as the flotation media. In this case, a minute amount of water contained in the medium will cause a serious uncertainty on the data. So we have taken special precautions to remove the trace of water, by drying benzene with metallic sodium and carbon tetrachloride with potassium hydroxide. One measurement of density took about 15 minutes. When the specimen was suspended stationarily, another one was then immersed in addition after a short time, and it was found that the latter specimen behaved almost in the same way as the former. Thus, it was confirmed that the adsorbed water in the sample was not appreciably transferred to the flotation medium during the measurement. The density of the flotation medium was determined by use of the bicapillary pyknometer.[8]

All of the density measurements were duplicated with different specimens, and the two corresponding readings coincided with each other within ±0.06% except the sample containing 45.5% water.

The density of the sample in water was measured with the ordinary 10 cc. bottle type pyknometer at 25° ±0.05°C. and found to be 1.312 ±0.003 g./cc.

b) Desorption Measurements.—The sample for these measurements was prepared in the same way as that used for the density measurements, in this case the thickness and size being about 0.02 mm. × 17 mm. × 50 mm.

The apparatus was similar to that described in a previous paper[9] with some modifications to

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[1] A. T. King, *J. Text. Inst.*, **17**, T53 (1926); **18**, T274 (1927).

[2] E. Filby and O. Maass, *Canad. J. Res.*, **7**B, 162 (1932).

[3] A. J. Stamm and M. Seborg, *J. Phys. Chem.*, **39**, 133 (1935).

[4] P. H. Hermans, "Contribution to the Physics of Cellulose Fibers," Elsevier Publishing Co., Inc., Amsterdam—New York, 1946, p. 73; "Physics and Chemistry of Cellulose Fibers," same publisher, 1949, p, 206.

[5] I. Nitta, S. Seki and Y. Yano, *Ann, Report Inst. Fiber Res.* (*Osaka Univ.*), **5**, 33 (1950).

[6] I. Nitta, S. Seki, Y. Yano and S. Tajima, ibid., **6**, 13 (1952).

[7] I. Nitta, S. Seki, H. Chihara, K. Kuriyama and S. Nakajima, ibid., **7**, 24 (1953).

[8] M. R, Lipkin, A. D. Davidson, W. T. Harvey and S. S. Kurtz, Jr., *Ind. Eng. Chem, Anal. Ed.*, **16**, 55 (1944).

[9] I. Nitta, S. Seki, M. Momotani and K. Satô, *J. Chem. Soc. Japan.* **71**, 378 (1950).

meet the present requirements. The relative humidity was controlled as mentioned above.

About 200 mg. of the sample was suspended from a quartz spring balance (sensitivity: 0.153 mm./mg.) by a glass string. The accuracy of the travelling microscope was ±0.01 mm., and the temperature of desorption was 25° ±0.05°C. The sample was dried under high vacuum (10^{-4} mm. Hg or below) at 60° ±0.05°C. and then the weight of th bone-dry sample was determined.

Fig. 1 shows that the time required to reach the desorption equilibrium depends to a remarkable degree upon the relative humidity, indicating that the desorption rate under low relative humidity is very low. The rate-determining process should be the diffusion of water molecules in the polymer film.

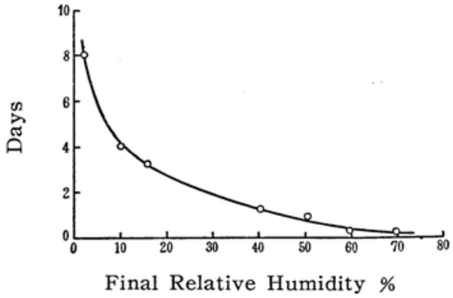
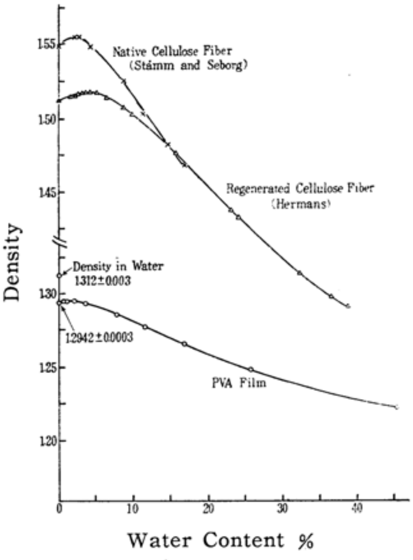


Fig. 1. Relation between time required for desorption equilibrium and final relative humidity.

Results and Discussion

The densities of the PVA film at moist states are shown in Fig. 2*, and those for native cellulose[3)] and regenerated cellulose[4)] are also shown for reference. Each density curve showed a conspicuous maximum at about 1.5, 2.5 and 4.5% water content for PVA, native cellulose and regenerated cellulose, respectivery.



Ffg. 2. Density-water content curves.

The existence of such a maximum has been explained differently by several investigators. Filby and Maass[2)] attempted to explain the maximum for native cellulose by assuming a compression of the bound water in the specimen under about 100,000 atm. pressure, whereas Stamm and Seborg[3)] estimated this pressure as about 3440 atm. However, this compression hypothesis seems to be superficial and to be only a formal interpretation. On the other hand, Hermans' interpretation[4)] is based on the assumption that the apparent volume V_a per 1 g. of polymer in moist state, consists of the following three parts:

$$V_a=(1+a)/d_a=\varphi_w+a+\varepsilon_a,$$

where a is water content in g. per 1 g. bone-dry polymer, d_a, density of the moist polymer whose water content is a g., φ_w, the net volume of the polymer, which should be equal to the specific volume of the polymer measured in water, and ε_a is the volume of the empty space which can be ultimately filled with water molecules but cannot be permeated by the molecules of the flotation medium. As the water content a increases, the empty space ε_a will diminish in proportion and will disappear at last, thereafter the increase in V_a will become equal to the volume of water sorbed and the slope should be 45°. Fig. 3 shows the V_a curves against the water

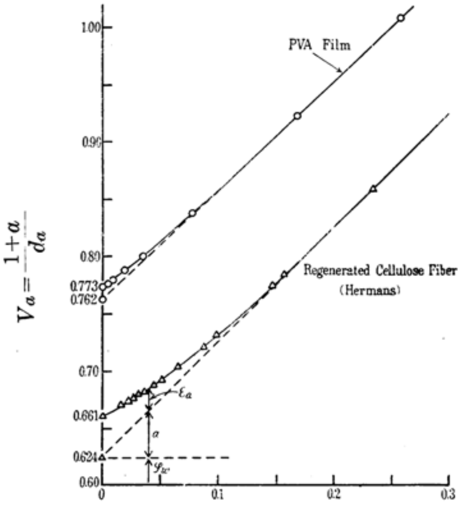


Fig. 3.
Relation between V_a and water content.

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* The density of PVA sensibly depends on the temperature and the duration of drying, heat- and mechanical treatments, degree of polymerization, etc. In connection with these, the experiments of the effect of heat treatment on densities are now in progress in this laboratory.

content *a* for our PVA data together with those for regenerated cellulose by Hermans.[4] In the case of PVA, the slope of the dashed straight line is slightly less than that of regenerated cellulose, whose slope is exactly 45°. This is presumably due to the fact that the interaction of PVA with water is larger than that of cellulose. As to this phenomenon, further study should be made to discover whether the water molecule may infiltrate the crystalline part of PVA or not.

In order to elucidate the nature of the empty space a little more, we calculated the so-called pore size distribution of the PVA film as well as regenerated cellulose fiber from our data of desorption isotherm and of Hermans, by means of Foster's method.[10] The desorption isotherms for PVA and regenerated cellulose[4] are shown in Fig. 4, and the pore size distribution curves are shown in Fig. 5. $V(\phi)$ in Fig. 5 stands for the integrated volume of pores whose diameter is smaller than ϕ. Although the variation of surface tension with the radius of curvature has been recently discussed theoretically by many authors,[11-15] we did not take this effect into our calculation, as these theories seem to be not yet quite decisive. By differentiating $V(\phi)$ with respect to ϕ the size distribution of the pore was obtained.

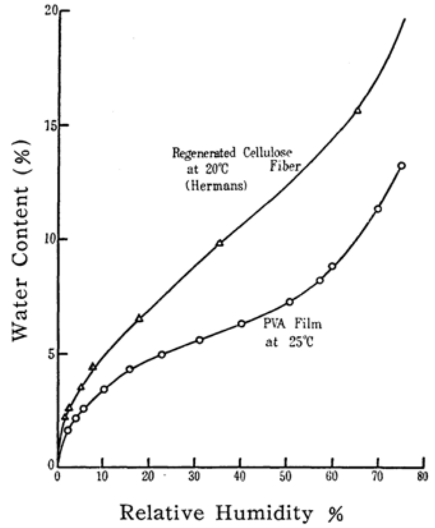

Fig. 4. Desorption isotherms.

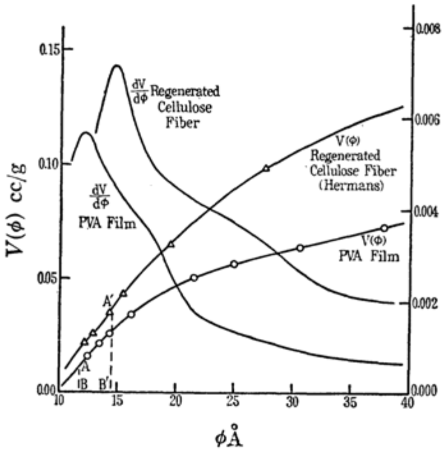

Fig. 5. Pore size distribution curves

The empty volumes $\varepsilon_{a=0}$'s of the present sample and the related substance[3,4] are shown in Table I. In Fig. 5 the pore volumes corresponding to $\varepsilon_{a=0}$'s for PVA and regenerated cellulose are indicated by AB and A'B' respectively. It may be supposed that the pores of the diameter smaller than 11.7 Å. for PVA and 14.5 Å. for regenerated cellulose candot be inhabited by the molecules of the flotation medium, the mixture of carbon tetrachloride and benzene being used as the flotation medium for PVA, and that of carbon

TABLE I

DENSITY DATA AND CRYSTALLINITY

Material	$\varepsilon_{a=0}$ (cc./g.)	Wathr content of max. density (%)	Amorphous part fraction* (%)
PVA film	0.011	1.5	~7** (Nitta Seki, Yano and Tajima[6])
Native cellulose fiber	0.017	2.5	32 (Hailwood and Horrobin[16])
Regenerated cellulose fiber	0.037	4.5	65

* By sorption method.

** This is the data of the powder specimen which has the same degree of polymerization as the present sample.

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10) A. G. Foster, *Discussions Faraday Soc.*, No. 3, 41 (1948).

11) R. C. Tolman, *J. Chem. Phys.*, **17**, 333 (1949).

12) J. G. Kirkwood and F. P. Buff, ibid., **17**, 338 (1949).

13) V. K. LaMer and G. M. Pound, ibid., **17**, 1337 (1949).

14) G. C. Benson and S. Shuttleworth, ibid., **19**, 130 (1951).

15) G. M. Pound and V. K. LaMer, ibid., **19**, 506 (1951).

tetrachloride and nitrobenzene for regenerated cellulose.[7] By use of the covalent and van der waals radii, the diameters of the molecules of the flotation media were estimated as follows:

carbon tetrachloride	~6.6 Å.
benzene	~7.3 Å.
nitrobenzene	~8.5 Å.

In spite of the boldness of the assumptions made above, the maximum diameters given above of the pore unaccessible for the molecules of the flotation media may be said to be in the same order of magnitude with the estimated geometrical sizes of these molecules, though the latter come out somewhat smaller. As the sources of such disagreement, the following factors may be pointed out.

(1) The water and nitrogen* sorption areas of polyvinyl acetal (acetal content 9.6%) measured previously by us were 65.9 m.^{2}/g. and 6.0 m.^{2}/g., respectively.[7] From this it may be reasonably assumed that while water molecules can break into the small space between the PVA molecular chains, nitrogen molecules cannot.[17,18] Accordingly, this fact seems to suggest that the geometrical size of the free molecule is not necessarily a decisive factor, but the mode of interaction between sorbent and sorbate must be also taken into account. Moreover, it may be possible that the pore size will vary as the water content increases.

(2) The filling-in of the pores with flotation medium is, quite probably, a matter out of equilibrium during the measurements of the present case.

(3) The Foster method assumes the Kelvin equation. It is now open to question whether this macroscopic equation can be applied to such a small pore of the molecular dimension.[11-15]

Finally, we may consider the relation among the maximum density of Fig. 2, the quantity $\varepsilon_{a=0}$ and the crystallinity determined by the sorption method.[6,16] As shown in Table 1, the water content at which the density shows maximum, and the empty volumes $\varepsilon_{a=0}$'s increase in the following order:

$$\text{PVA} < \text{native cellulose} < \text{regenerated cellulose}$$

and the % amorphous region measured by the sorption method also increases in the same order.[6,16] This fact may be explained by assuming that mainly the amorphous region of these polymers is accessible to water and has nearly the same fraction of the empty volume.

Summary

(i) The densities of PVA film at moist states were measured at 25°C. with flotation method by using carbon tetrachloride-benzene mixtures. The density against water content curve shows a conspicuous maximum at about 1.5% water content.

(ii) The water desorption expriment was carried out using the same specimen. The pore size distributions of PVA film and regenerated cellulose fibers were calculated by the Foster method from our desorption date and Hermans' data, respectively.

(iii) The results are discussed and compared with those of other investigators obtained with native and regenerated cellulose.

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[16] A. J. Hailwood and S. Horrobin, *Trans. Faraday Soc.*, **42**B, 84 (1946).

* These two molecules have nearly the same molecular diameter (N_2: ~4.1 A, H_2O: ~4.0 A.).

[17] K. W. Mooney, A. G. Keenan and L. A. Wood, *J. Am. Chem. Soc.*, **74**, 1367, 1371 (1952).

[18] T. M. Shaw, *J. Chem. Phys.*, **12**, 391 (1944).