Permeation Mechanism of Deaerated Water into Textile Surface Confirmed by Fiber Density Measurements

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Abstract: Deaerated water is used in many industrial fields because of its high permeable property. We proposed the reason for this, as being the ability to dissolve the gas trapped in tiny narrow voids on textile surfaces. This mechanism was confirmed by density measurement using a density gradient column of aqueous salt solution.

1. Introduction

Deaerated water is used in many industrial fields especially food engineering (1-3). One of the reasons for this is that it has higher permeability than air-containing water. We have examined the apparent higher permeability of deaerated water by various experiments and confirmed its existence [4]. We surmised that this high permeability results from its ability to resolve gaseous molecules trapped in tiny narrow voids on textile fibers [4].

Natural and synthetic fibers spun from concentrated solutions have many voids on their surfaces which arise from the evaporation of water and/or organic molecules. Thus, these fibers can be regarded as containing many kinds of gaseous molecules in their fibers. When these fibers are soaked in water, water molecules cannot always enter the voids because of surface tension which varies with the shape of the void. Thus, the measurement of fiber density in an aqueous medium will yield different values depending on the existence of gas molecules in the tiny voids. Yet it is very important to know the precise density of polymeric materials in order to understand their structure and physical properties, e.g., crystallinity and crystallization. Polymer density can be measured using a density gradient column [5, 6]. However, to measure density accurately, the measuring liquid in the density gradient column must completely fill even the voids.

When gas molecules trapped in tiny voids on textile fibers are resolved into water, the apparent fiber density becomes higher than that of fibers containing gas in their surface voids. We therefore measured the density of porous fiber to confirm the permeability of deaerated water using a density gradient column after soaking the fiber in deaerated water.

2. Experimental

2.1 Materials

Natural and synthetic textile cloths used in this study were unfinished plain cloths purchased from Kansai Iseikatsu Kenkyukai (Osaka, Japan). All cloths were used without further pretreatment but dried in an oven at 110°C for more than 4 h. After being cut into suitable sizes, the samples were stored in a desiccator with silica gel until use.

2.2 Deaerated Water

Deaerated water was prepared using a hollow fiber module (DIC, Japan) described in detail by Anazawa [7]. The degree of deaeration was evaluated from the oxygen concentration in water using an oxygen meter DO-2 (Sibata Sci. Tech., Japan).

2.3 Apparatus

A density gradient column was set up in a water bath whose temperature was controlled at 20°C. Liquids used for density gradients were mixtures of water and calcium nitrate aqueous solution or of ethanol and carbon tetrachloride. Density gradients were measured using glass balls of different densities.

To compare the fiber densities obtained by the density gradient method, fiber densities were also measured by a volume expansion method, using Multi-Volume Pycnometer model 1305 (Micromeritics: U.S.A.) and helium
gas as a measuring gas (8).

3. Results and Discussion

3.1 Production of Deaerated Water

Water contains many gaseous molecules when it presents with various gases at a certain pressure. The amount of saturated gas can be calculated according Henry's law. Consequently, gas molecules in the water can be reduced by decreasing the gas pressure. To do this, a hollow fiber module has been devised and is used in various industries. The water obtained is called deaerated water and the mechanism of removing gas was described in detail in our previous paper (4). The deaerated water for this study was produced using a hollow fiber module (DIC, Japan) at a reduced pressure of about 8 mmHg and under elution speed of about 500 mL/min.

The dissolved gas content was evaluated from the oxygen content in the water using an oxygen meter DO-2 (Sibata Sci. Tech., Japan), under the assumption that other gas molecules would be eliminated in the same way. The oxygen content of the obtained water was about 0.6 ppm. As the saturated oxygen content of water in contact with air under normal conditions at 20 °C is 8.5 ppm, the water of less than 0.8 ppm used in this experiment was considered to be deaerated water. This water was carefully bottled to prevent gas absorption, and the oxygen content was always checked before use.

3.2 Density Gradient Column

The density gradient in a glass cylinder column can be constructed by various methods (9). We selected a method of gradual mixing with a lower density liquid using a glass tube siphon bridge, which is very convenient for both aqueous and non-aqueous liquid systems. The linear density gradient for both liquid systems was confirmed using a long glass cylinder equipped with density-determined glass balls. The density of the materials could be analyzed with an accuracy of within 10⁻⁵ g/cm³.

3.3 Density of Sample Cloths

Small 10 mm² pieces of various dried textile cloths were floated on the surface of an aqueous density gradient solution, and the depth to which they had sunk in the column was recorded over time. All samples sank slowly and gradually reached their stable positions. The recorded densities after 60 min are summarized in Table 1. The data are averages of at least three measured values for each cloth. These densities were measured within ±0.0005 for each sample cloth.

To confirm the higher permeability of deaerated water, cloth samples were subjected to measurement after soaking in air-saturated or deaerated water for 60 min. The change in position of each textile sample treated with air-saturated water for 60 min was measured every 10 min after floating on a density gradient column. In this measurement, a peculiar sinking behavior was observed for samples having small air bubbles on their surface, and these data were eliminated from the results. The averaged stable position after 60 min, which was closest to the density of each textile sample, is given in Table 1. Compared with the data for un-soaked samples, all densities of samples soaked in air-saturated water for 60 min were much larger.

Density measurements of various textile cloths were also done using non-aqueous solution density gradient columns of ethanol and carbon tetrachloride systems without pre-soaking in the solvents. The averaged density values of various textile sample cloths after 60 min are also summarized in the 5th column of Table 1. Though the densities of various textile cloths differ depending on the solution system used in the density gradient column, the low values found suggest that even in non-aqueous solution, tiny voids on the fiber surface can not be penetrated by liquid molecules in exchange for air molecules in the voids.

The density of these textile fibers was also measured by volume expansion method using helium as a measuring gas with a Multi-Volume Pycnometer model 1305. | Sample cloth | Density gradient column | Volume expansion method |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Un-treated</td>
<td>Dipped 30 min in</td>
</tr>
<tr>
<td>Cotton</td>
<td>1.554</td>
<td>1.566</td>
</tr>
<tr>
<td>Silk</td>
<td>1.339</td>
<td>1.436</td>
</tr>
<tr>
<td>Wool</td>
<td>1.334</td>
<td>1.347</td>
</tr>
<tr>
<td>Rayon</td>
<td>1.545</td>
<td>1.557</td>
</tr>
<tr>
<td>Cellulose Acetate</td>
<td>1.308</td>
<td>1.323</td>
</tr>
<tr>
<td>Acryl</td>
<td>1.185</td>
<td>1.186</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>1.136</td>
<td>1.144</td>
</tr>
<tr>
<td>Polyester</td>
<td>1.305</td>
<td>1.356</td>
</tr>
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</table>
The measurement method is reported in detail elsewhere (8). The measured density values were little bit scattered and within ±0.005. The results, summarized in Table 1, showed different density values from those obtained using the density gradient column of aqueous and non-aqueous mixed solution.

3.4 Effect of Deaerated Water Treatment

Sample textile cloths, before being floated on the density gradient solution, were soaked in deaerated water for 60 min as for the treatment with air-saturated water. They were then subjected to density measurement in the aqueous density gradient column. The averaged sample densities after 60 min are summarized in the 4th column of Table 1. No difference after water soaking for 60 min were found, except in the case of nylon and polyester. However, the sinking velocity for samples soaked in deaerated water at about 10 to 20 min after floating seemed to be faster than for those soaked in air-saturated water.

The sinking behavior of acrylic, nylon, and polyester samples in aqueous density gradient column is shown for untreated samples and those soaked in air-saturated and deaerated water in Fig. 1 to 3. Clearly, the density of cloth samples soaked in deaerated water is greater than...
that of cloth soaked in air-saturated water. This means that deaerated water can permeate more into tiny voids on the fiber surface. However, the density of un-treated cloth was much lower than water-soaked cloths and did not seem to be close that soaked in air-saturated water for nylon and polyester. In the case of such polymers, the effect of salt such as strong acid and weak base must be taken into account.

Surface tension may prevent permeation of the measuring solution into voids on the textile surface. Judging from the densities measured with the non-aqueous density gradient column compared with the reference data, the effect of air in the tiny voids on the fiber surface must be considered for the density measurement. However, this has not been done experimentally.

Calcium nitrate was used to prepare the high density medium of aqueous solution in this experiment. During the density measurement, it is possible that there was a gradual reaction of calcium nitrate with hydroxyl groups of fiber molecule or selective absorption in the fiber solid. The density of cotton, rayon, wool, and silk cloth gradually increased even after floating for 60 min on the column surface. These density values are far greater than those found in reports or textbooks. The sinking behavior of cotton and rayon after floating on the density column, shown in Fig. 4 and 5, respectively, displayed a gradual density increase with time. However, the same tendency is seen of the density of un-treated sample being the lowest and the density of cloth soaked in deaerated water being higher than that soaked in air-saturated water. When a highly concentrated aqueous salt solution is used as the solution system for the density gradient column, careful consideration should be given to the density analysis.

3.5 Effect of Gas Substitution

The apparent permeability of deaerated water is considered to arise from the fact that it can absorb gas molecules from tiny voids on the fiber surface and enter the voids. This can be confirmed by substituting air in the voids with water-soluble gas. For example, water can absorb carbon dioxide gas much more than oxygen and nitrogen gases. Thus, we tried to substitute air in the voids with carbon dioxide gas before placing the sample in the density gradient column.

Cloth samples were set into a glove bag (model S-20-20, Instrument for Research and Industry, U.S.A.) which...
was then changed with carbon dioxide gas. After 20 min, the carbon dioxide was discharged and a fresh sample of the gas was introduced. This procedure was repeated 5 times, then the cloth samples were placed in air-saturated water under an atmosphere of carbon dioxide gas. After being kept in the water for 60 min, the sample density was measured in the aqueous density gradient column. The sinking behavior in the column of polyester cloth treated with deaerated water is shown in Fig. 6. The polyester cloth sank rapidly and showed a slightly higher density than that soaked in deaerated water, as shown in Fig. 6. This was common to all other cloths measured in this study. The densities of carbon dioxide-treated samples at 60 min after floating on density column are summarized in the second column of Table 2. These samples were also placed on deaerated water, but no effect of deaeration on the fiber density was observed, as can be seen in Table 2.

These results of gas substitution led us to conclude that deaerated water has good permeability due to its capacity to absorb gas. This allows water to enter the tiny narrow voids and come into contact with the entire surface of the textile fabric.

Helium-substituted cloth samples were also soaked in gas-saturated water and placed in the aqueous density gradient column. Helium is inert for almost all subst-

Table 2: Fiber Densities Measured by Density Gradient Column after Gas Substitution and by Volume Expansion Method.

<table>
<thead>
<tr>
<th>Sample cloth</th>
<th>Density gradient column After CO₂ subst. dipped in aerated water</th>
<th>Deaerated water</th>
<th>After He subst. dipped in aerated water</th>
<th>Volume expansion method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>1.561</td>
<td>1.565</td>
<td>1.583</td>
<td>1.57</td>
</tr>
<tr>
<td>Silk</td>
<td>1.441</td>
<td>1.449</td>
<td>-</td>
<td>1.37</td>
</tr>
<tr>
<td>Wool</td>
<td>1.339</td>
<td>1.356</td>
<td>-</td>
<td>1.31</td>
</tr>
<tr>
<td>Rayon</td>
<td>1.568</td>
<td>1.565</td>
<td>1.576</td>
<td>1.52</td>
</tr>
<tr>
<td>Cellulose Acetate</td>
<td>1.320</td>
<td>1.320</td>
<td>-</td>
<td>1.33</td>
</tr>
<tr>
<td>Acryl</td>
<td>1.184</td>
<td>1.184</td>
<td>1.183</td>
<td>1.20</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>1.151</td>
<td>1.151</td>
<td>1.152</td>
<td>1.15</td>
</tr>
<tr>
<td>Polyester</td>
<td>1.394</td>
<td>1.395</td>
<td>-</td>
<td>1.43</td>
</tr>
</tbody>
</table>

**Fig. 6** Sinking behavior of polyester cloths in Ca(NO₃)₂ aqueous density gradient column. ●, treated in deaerated water; ▲, CO₂-substituted and treated in deaerated water; △, CO₂-substituted and treated in air-containing water.

**Fig. 7** Sinking behavior of nylon cloths in Ca(NO₃)₂ aqueous density gradient column. ●, treated in deaerated water; ▲, CO₂-substituted and treated in air-containing water; △, CO₂-substituted and treated in air-containing water.
ances and does not resolve easily into water. However, helium-substituted cotton, rayon, and nylon cloth samples sank more rapidly than any other samples and showed the highest density in the aqueous density gradient column as summarized in Table 2. This sinking behavior of nylon cloth is shown in Fig. 7. As helium does not readily dissolve in water, the surface tension between water and helium must be smaller than that between water and other gases. Another possible reason is that helium can migrate even in polymer solid because of its small molecular dimensions.

4. Conclusion

We confirmed the excellent permeability of deaerated water and proposed a permeation mechanism based on gas absorption by water from the tiny narrow voids on textile fabric surface. We tried to confirm using a density gradient column to measure the densities of textile fabrics subjected to treatment with deaerated water. Some differences were confirmed between the densities of cloth samples soaked in deaerated and air-saturated water for 60 min. The difference was not large for natural fibers but was for synthetic fibers such as nylon and polyester.

In order to eliminate gas molecules from voids on the fiber surface, carbon dioxide gas was introduced into the voids. The treated samples showed higher density than those soaked in deaerated water for 60 min. This higher density meant that more water had been introduced than in the treatment with deaerated water. Helium was also used as a substitution gas. Although helium molecules are not considered to be replaced with water molecules on soaking in water, helium molecules can scatter away from the voids to allow water to enter. The density of the helium-substituted cloth sample was the highest among the samples subjected to various treatments.

References