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DETERMINING MOISTURE ABSORPTION/DESORPTION PROPERTIES OF COMMERCIAL MEMBRANES BY THERMOGRAVIMETRY (TG)

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A series of different commercial membranes were characterized by their moisture absorption and desorption properties under controlled humidity and temperature conditions. This work was made possible by combining the features of a constant humidity conditioning chamber with those of a thermogravimetric (TG) apparatus. These two modules were interconnected by tubing, rotameters, an atmosphere-recycling microbellows pump and switching valves. Under programmed heating and isothermal conditions reproducible data were obtained in terms of weight-gain or weight-loss *vs.* time and pore size. Evaluation of the resulting TG curves allowed us to report reasonable differences in the materials, some of which had been previously surface-modified by the manufacturer.

Keywords: moisture adsorption/desorption properties of membranes, TG

Introduction

Traditional methods employed in the investigation of environmental moisture absorption by textiles are varied and well documented in the forms of sorption isotherms [1], heats of absorption [2], rates of change of moisture content [3], diffusion in fibre-forming substances [4], moisture and electrical properties [5], simultaneous diffusion of heat and moisture [6], effects of moisture on density and optical properties [7], and finally, effects of moisture on mechanical properties [8].

Our study was based on the need for a simple method to evaluate the potential of membranes as components in clothes. We selected the method suggested by P. G. Tortora [9] who related the amount of moisture on woven fibrous material to increased comfort afforded to the wearer. Moisture regain applies to surface-adsorbed water as well as water absorbed into the fibre. In our procedure, we took a

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membrane sample, dried it thoroughly and cycled a controlled atmosphere into the sample compartment; the temperature was held at 25°C and the relative humidity was maintained at 71.2%.

Customary apparatus for the study of moisture regain are discussed in detail by J. E. Booth [10], most of which are complex in design and expensive. We achieved comparable results simply by assembling thermal equipment already on hand with a variety of inexpensive accessories. This consisted of the combined features of a constant-humidity conditioning system with that of a thermogravimetric (TG) apparatus. These two modules were connected by tubing, rotameters, atmosphere-recycling microbellows pump and switching valves. Under programmed heating and/or isothermal conditions, reproducible data were obtained in terms of weight-gain or weight-loss *vs*. time. Evaluation of the resulting thermograms allowed us to obtain and report reasonable differences in the materials of assorted pore sizes and modified surfaces. Thermograms resulting from this study are similar to those obtained by J. Crank [11].

Experimental

Starting materials

Biodyne^{tm} membrane series were manufactured by Pall Corporation, Glen Cove, NY. These membranes which were obtained in pore sizes 0.04 to 5.0 microns are 6-6 nylon constructed on a nonwoven polyester matrix for high tensile strength. Their surface chemistry, as reported by the manufacturer, had been modified as shown in Table 1.

Table 1 Biodyne^{tm} membranes and properties

Membrane	Properties
Biodyne^{tm} A	50% amino and 50% carboxylate groups;
Biodyne^{tm} B	High-density quaternary ammonium groups;
Biodyne^{tm} C	High density of carboxylate groups

Managraph^{tm} and Magna^{tm} membrane series were manufactured by Micron Separations, Inc., Westboro, MA. These were received in micron sizes 0.22 and 0.45. Information furnished by the manufacturer is given in Table 2.

Dry nitrogen for sample drying was obtained from Matheson Products and was oxygen-purged using a trap containing a potassium hydroxide/pyrogallol solution. Ammonium chloride and potassium nitrate were obtained from Aldrich Chemical Co.

Table 2 Managraph^{tm} and Magna^{tm} membranes and properties

Membrane	Properties
Managraph^{tm}	Naturally hydrophilic and do not require prewetting; possess high thermal and dimensional stability; do not crack, tear or break when handled
Magna^{tm}	Impregnated on inert support web; does not curl or shrink; possesses uniform dimensional strength across its surface

Sample preparation and handling

Uniform samples were punched out using a metal die; size of cut: 1/4" ×1/2". Sample cutting and other handling was done with rubber gloves to prevent skin oil contamination. Extra care was taken with Biodyne^{tm} membranes because creasing or crimping caused the nylon to flake off.

Apparatus

The constant humidity experimental recycling system (CHERS) consisted of the DuPont 951 TGA, connecting Tygon tubing, rotameters, 4-way pyrex switching valves (two each), stainless steel microbellows pump manually adjusted to provide a cycled flow rate of 90 ml/min and humidity bottle (Fig. 1). When assembled, valves were switched to isolate the TG system in order to first heat and dry the specimen at 124°C for 30 min under a stream of dry nitrogen. Afterwards

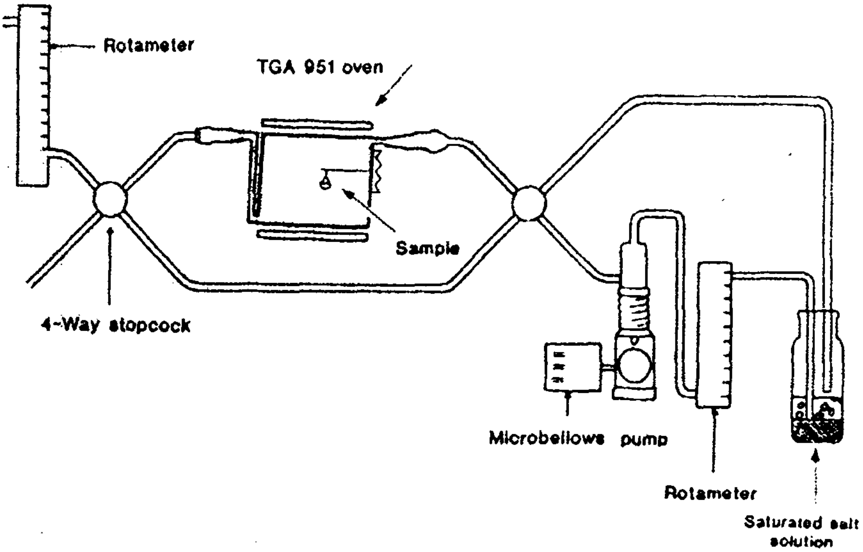

Fig. 1 Constant humidity recycling system (CHRS)

the system was cooled to 20°C for moisture-regain testing. Valves were switched again to isolate the enclosed cycling system, where the internal atmosphere was cycled by a microbellows pump through a rotameter and bubbled through a saturated solution of ammonium chloride/potassium nitrate in equimolar proportions. This solution has been shown to provide a relative humidity of 71.2% at 25°C (72.6% at 20°C) [12]. The conditioned atmosphere continued further to pass over the sample in the TG tube and out to be recycled continuously by the pump at 90 ml/min. Moisture regain was monitored over at least a 200 min period with data points taken at 5 min intervals.

Procedure

With the CHERS assembly in the sample drying mode, specimens were dried using this component under nitrogen at a flow rate of 80 ml/min at a ramp temperature of 10 deg·min^{-1} to 124°C and held isothermally for 40 minutes. After cooling to 25°C and baseline stabilization, valves were switched for the moisture regain mode. The microbellows pump was turned on at the adjusted flow rate of 90 ml/min. The time duration for all runs, except one, was 200 min; one run was extended for 400 min and data points were taken at 5 min intervals. Afterwards, these data were plotted as moisture regain (%) *vs.* time (min).

Results

Biodyne$^{\text{tm}}$ A membranes (50% amino and 50% carboxyl groups)

Moisture uptake for all pore sizes was initially rapid, but the initial regain rates differed slightly among the various pore sizes and did not exhibit a dependence on pore size (Fig. 2). Except for the 5.00 micron specimen, some irregularities are noted in regain rate curves. After the initial moisture uptakes, the 0.04 and 0.45 micron specimens gradually released almost all of the moisture by the end of the 200 min run. On the other hand, the amount of moisture regain for the 0.20, 3.00 and 5.00 micron specimens appears to diminish only slightly during the same time period. The maximum moisture uptake for all Biodyne A specimens was less than 2.5%.

Biodyne$^{\text{tm}}$ B membranes (high density quaternary ammonium groups)

Both specimens had similar moisture regain rate curves showing an initial rapid rate and tended to reduce very slightly during the course of the run (Fig. 3). The maximum moisture regain for both Biodyne B$^{\text{tm}}$ specimens was less than 1.75%.

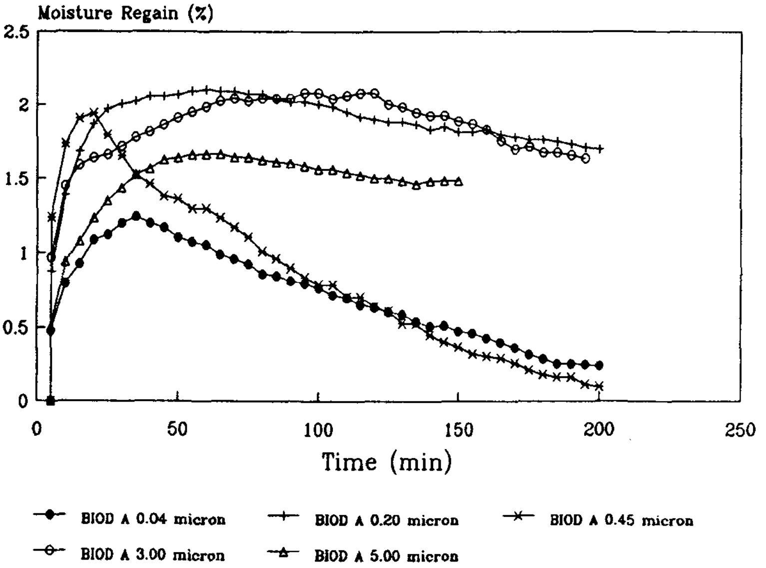

Fig. 2 Biodyne^{tm} A membranes by pore size, moisture regain at 25°C, 71.2% relative humidity

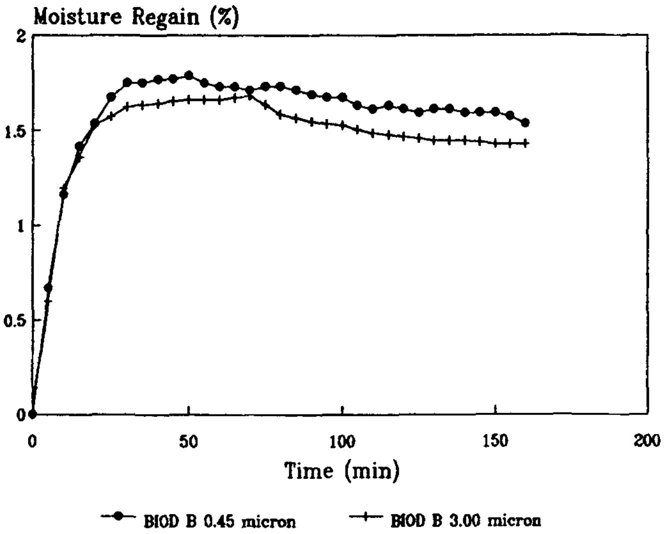

Fig. 3 Biodyne^{tm} B embranes by pore size, moisture regain at 25°C, 71.25% relative humidity

Biodyne^{tm} C membranes (high density in carboxylate groups)

After 15 min exposure, an almost complete reversal of moisture regain is noted for specimens 1.2 and 5.00 microns. The initial moisture regain rates were rapid. However, both membranes gradually expelled almost all moisture by 200 min (Fig. 4). The 0.20 micron specimen had a rapid moisture regain and maintained a near steady state for about half the run time before registering a slight loss. The maximum moisture regain for all Biodyne^{tm} C specimens was less than 2.4%.

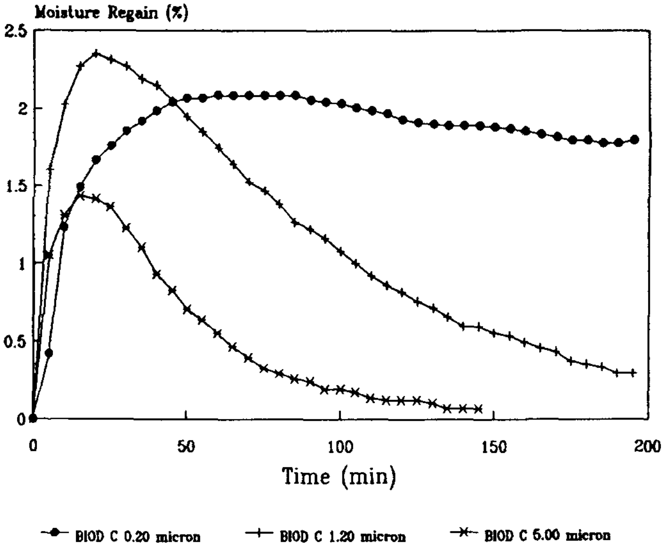

Fig. 4 Biodyne^{tm} C membranes by pore size, moisture regain at 25°C, 71.25% relative humidity

Managraph^{tm} membranes (surface pretreatment not given)

The 0.22 micron specimen had a rapid moisture regain followed by a slight loss (Fig. 5). Moisture regain was slower for the 0.45 micron specimen than all other membranes in this study. It reached a maximum uptake between 125 and 160 min, after which a gradual loss was registered. The maximum moisture regain for all Managraph^{tm} specimens was less than 2.4%.

Magna^{tm} membranes (surface pretreatment not given)

Magna^{tm} 0.45 exhibited both a rapid rate of moisture regain and of moisture loss by the end of the 200 min run (Fig. 6). Unlike the Magna^{tm} 0.45 micron sample above, a rapid rate of moisture regain was observed for Magna 0.22 micron but this was followed by a much slower loss. Results suggest that a total loss would have been registered if the run had continued beyond 400 min. The maximum moisture regain for all Magna^{tm} specimens was less than 1.6%.

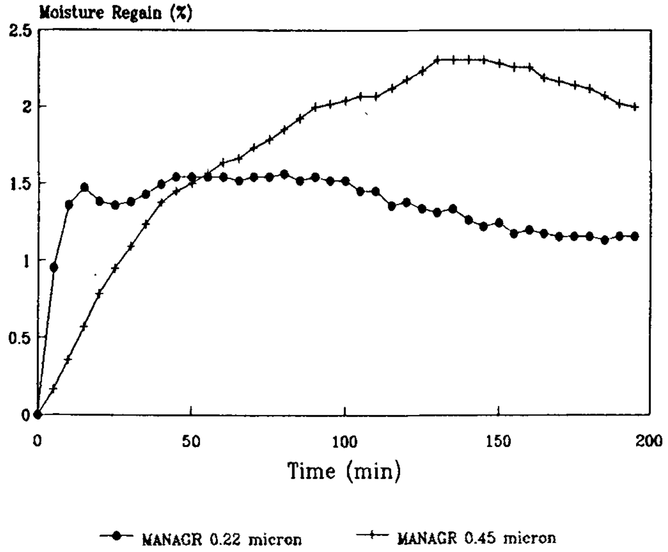

Fig. 5 Managraph^{tm} membranes by pore size, moisture regain at 25°C, 71.25% relative humidity

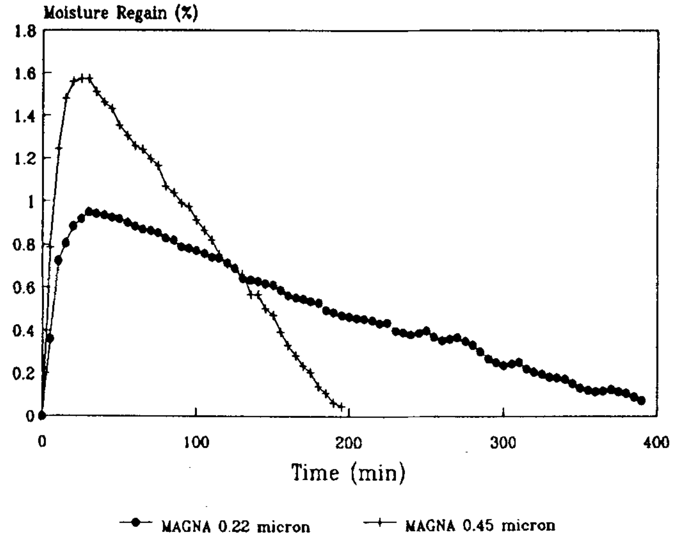

Fig. 6 Magna^{tm} membranes by pore size, moisture regain at 25°C, 71.25% relative humidity

Discussion

Our self-diffusion study of moisture into the polymer structure of the membranes in terms of moisture regain can be interpreted in terms of the presence of hydrophobic or hydrophilic groups, physical polymer arrays (crystallinity), amorphous orientations, temperature and testing atmosphere. These are discussed in detail by Crank [4] and Booth [10]. G. Thau-Alexandrowicz [13] employed tritium (T) and oxygen (O^{18}) tracers to measure the self-diffusion of water across a series of membranes of different pore sizes and chemical constitutions. His conclusion was that self-diffusion rates increase with decreasing pore size. Only tests on the Biodyne^{tm} C (functionalized) nylon membranes have verified this self-diffusion behaviour (Fig. 4); here, an increase in membrane pore size corresponded to an increase in moisture regain as well as loss over the long term.

Table 3 Membrane details

Membranes	Remarks
Biodyne^{tm} A	The rapid initial moisture uptake of membranes 0.04 and 0.45 microns indicated an internal amorphous (hydrophilic) structure that reversed as moisture was released and the original crystalline array (hydrophobic) was restored. The hydrophilic character of the other three membranes remained, while the amount of moisture regain remained more or less the same.
Biodyne^{tm} B	After a rapid moisture regain rate, a return to the original crystalline state for both specimens was not restored as the moisture amount reduced only slightly and moisture regain levelled off to a new constant value.
Biodyne^{tm} C	The original crystallinity was almost completely restored. Both specimens (1.2 and 5.00 microns) rapidly expelled the regained moisture (Fig. 4).
Managraph^{tm}	The slight dip in the curve of membrane 0.22 micron, after an initial rapid moisture regain rate, was unusual. The gradual downward trend indicated that the original degree of crystallinity might return at a time far beyond that allowed for this experiment. The 0.45 micron specimen had the slowest regain rate of all specimens. The continued rise of the curve probably indicates the add-on of surface moisture.
Magna^{tm}	Both 0.22 and 0.45 microns specimens indicated a trend toward restoration of the original degree of crystallinity, the former requiring about twice the time as the latter. It was noted that the moisture regain of Magna^{tm} 0.45 micron was nearly twice that of Magna^{tm} 0.22 micron.

Since the moisture regain procedure requires oven drying of a sample, a heat capacity change is apparently induced within the material, whereas the degree of crystallinity is somewhat reduced. This corresponds to an increase in amorphous content. Moisture pickup is expected to increase when the structure becomes more amorphous and decrease as crystallinity returns. Many of the membranes studied here may have experienced this effect of polymer morphology, thus complicating simple interpretation of pore size effects. Moisture uptake behaviour is interpreted in terms of morphological effects in Table 3. This mechanism explains our experimental observations.

Conclusions

This investigation has shown that some membrane moisture regain (self-diffusion) properties are influenced by heat pretreatment such as the previously discussed pre-drying step. During heating, molecular chains proceed from regular crystalline arrays to a more amorphous character which accounts for the rapid moisture regain rate. The process reverses over several minutes and moisture is repelled as crystallinity is restored. Other membranes retain moisture to some degree which is function of their natural hydrophilic properties at that temperature and relative humidity. The modified thermal apparatus and procedure related in this study are an excellent means to study and compare moisture regain, polymer crystallinity, pore size and distribution, membrane chemical make-up and temperature. Under the conditions of our experiments, a direct relationship between pore size and moisture regain could only be established for the Biodyne^{tm} nylon membranes.

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Zusammenfassung — Eine Reihe von handelsüblichen Membranen wurde mittels ihrem Feuchtigkeitsabsorptions- und -desorptionsverhaltens unter kontrollierten Feuchtigkeits- und Temperaturbedingungen beschrieben. Dies wurde durch das Vereinen einer Feuchtigkeitskonditionierkammer mit einem TG-Apparat ermöglicht. Die beiden Einheiten werden durch Rohrleitungen, Rotameter, eine Mikrobalgpumpe zur Atmosphärenrückführung und durch Schaltventile miteinander verbunden. Bei programmiertem Aufheizen und isothermen Bedingungen erhält man reproduzierbare Daten in Form von Gewichtszunahme oder -verlust als Funktion der Temperatur und der Porenweite. Die Auswertung der resultierenden TG-Kurven erlaubt die Feststellung akzeptabler Unterschiede zwischen den Materialien, von denen einige zuvor vom Hersteller oberflächenmodifiziert wurden.