Journal of Macromolecular Science, Part A

Hydrophilic Polymers as Heat and Mass Exchangers

John D. Leeder[a]; Ian C. Watt[b]; Peter J. Banks[c]

[a] Division of Textile Industry, Belmont, Victoria, Australia [b] Division of Textile Physics, New South Wales, Australia [c] Division of Mechanical Engineering, Victoria, Australia

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JOHN D. LEEDER

Division of Textile Industry
CSIRO
Belmont, Victoria 3216, Australia

IAN C. WATT

Division of Textile Physics
CSIRO
Ryde, New South Wales 2112, Australia

PETER J. BANKS

Division of Mechanical Engineering
CSIRO
Highett, Victoria 3190, Australia

ABSTRACT

Recent work on the use of wool in heat- and mass-exchange systems is summarized. Improvements in the transfer of water vapor (e.g., between the inlet and outlet ducts of an air conditioner) have been obtained by application of hydrophilic polymers to the surface of wool fibers. Further improvements in water sorption are obtained by inclusion of deliquescent salts. Drip formation does not occur at high humidities, presumably because of the viscous nature of the polymer/water system. Wool is shown to be a more suitable substrate than polyester.
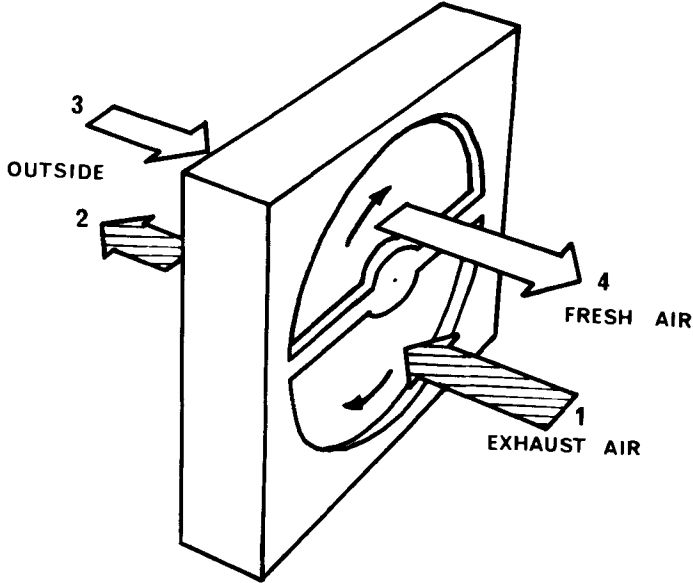
FIG. 1.   Operation of a rotary heat exchanger (schematic).

INTRODUCTION

The use of heat exchangers for recovering sensible heat from
effluent gases and liquids is well established. An enthalpy exchanger
(a type of "heat and mass exchanger") recovers sensible heat plus the
latent heat associated with water vapor in the exhaust air from air-
conditioning systems. Savings in energy and cost are possible by
using the exhaust air to "precondition" the incoming air with respect
to both temperature and humidity. Such a system would find applica-
tion in a building that exhausts air at, e.g., 60% RH, 25°C, into external
conditions of, say, 80% RH, 30°C, but could also be used in cold, dry
climates.

Typically, enthalpy exchangers take the form of a circular porous
matrix that is rotated continuously through adjacent fresh- and
exhaust-air ducts, so that each portion of the matrix alternately
passes through a stream of fresh air and then one of exhaust air (see
Fig. 1). Thus the matrix material repeatedly sorbs and desorbs
water and heat.

Another type of heat and mass exchanger is the regenerative de-
humidifier, which can be similar in form to the enthalpy exchanger
described above but is rotated much more slowly. These dehumidi-
fiers are used together with sensible heat exchangers and evaporative
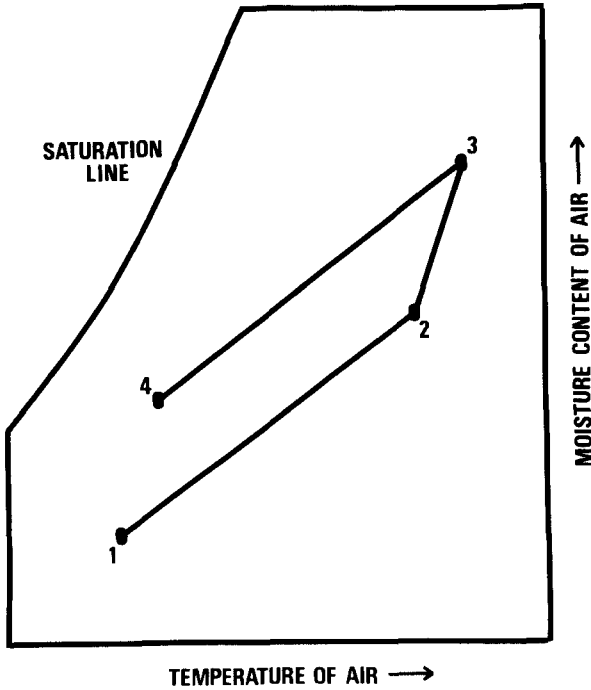coolers to form open cycle cooling systems [2]. These systems can

FIG. 2. Psychrometric cycle of enthalpy exchanger. Numbers on graph correspond to inlet and outlet air states shown in Fig. 1.

utilize solar energy or waste heat to regenerate the water-sorbing matrix, and so provide an attractive alternative to conventional, refrigerated air-conditioners in the humid tropics.

Commercial heat- and mass-exchanger matrices are of honeycomb form, constructed from alternate flat and corrugated layers of strip material [1]; a strip material commonly used is asbestos paper impregnated with lithium chloride. This practice results in problems from (1) dripping of salt solution at high relative humidity and (2) the undesirability of using asbestos.

An improved form of matrix construction has been developed by CSIRO for heat exchangers, using polyester film in a continuous wound ribbon construction to make a "parallel plate" matrix [3]. Application of this design to heat and mass exchangers forms part of the present study [4].

The most important requirements for the matrix material of both enthalpy exchangers and regenerative dehumidifiers are: (1) a steep water-vapor sorption isotherm, to provide sufficient potential for water transfer between fresh- and exhaust-air states; (2) a high rate

of sorption and desorption of water; and (3) resistance to the mechanical, chemical, and environmental stresses imposed during use.

Fibrous hydrophilic substrates were considered in terms of these requirements, and the need to make a ribbon suitable for the CSIRO parallel plate matrix. Wool has a steeper water-vapor isotherm than cellulosic materials such as cotton, viscose, and paper; is more resistant to mildew formation; has natural flame resistance; and adequate wet strength. Furthermore, wool, being proteinaceous, will absorb some toxic and/or offensive atmospheric contaminants. Thus the performance of enthalpy exchange matrices made from wool fabrics has been assessed from laboratory and field-trial data, and the potential for energy recovery using these regenerators has been estimated [4].

The purpose of an enthalpy exchanger is to bring the state of the incoming fresh air (4, Fig. 1) as close as possible to that of the exhaust air (1, Fig. 1). Inlet and outlet air states measured on an experimental wool-matrix enthalpy generator are shown schematically in Fig. 2 [4]. The performance of this wool-matrix regenerator is closer to the ideal for sensible heat transfer than for water-vapor transfer [4]. On the other hand, the commercial LiCl/asbestos matrix performs as well as wool for sensible heat transfer, with the advantage that its water-vapor transfer performance equals that for sensible heat transfer [1]. Consequently, attempts have been made to improve the water uptake of the wool matrix, and this work is described in the present paper.

EXPERIMENTAL

A plain-weave, worsted fabric (180 g/m^2) made from 21 μm diameter Merino wool and a continuous filament polyester sailcloth of 80 g/m^2 were used.

The polymers used were:

(a) The potassium salt of poly(methacrylic acid) (Monomer-Polymer Laboratories), made by titrating the free acid polymer with potassium hydroxide.

(b) Calgon Polymer 261 (Calgon Corp.), which is the cationic quaternary ammonium polyelectrolyte, poly(diallyldimethylammonium chloride):

$$\left[\text{CH}_2\text{-CH-CH-CH}_2\right]_n$$

$$\overline{M}_n \sim 50{,}000$$
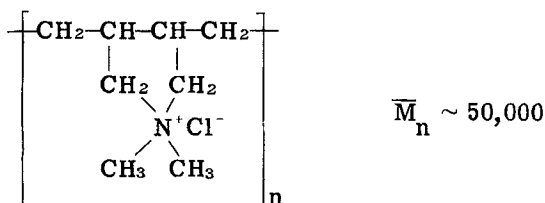
(c) Calgon Polymer 7091, which is similar to Polymer 261 except that a small proportion of cross-linkable comonomer (acrylamide or diacetoneacrylamide [5]) has been included in the structure.

Polymers and salts were applied to the wool or polyester simply by wetting the fabric in the appropriate aqueous solution and passing through a pad mangle to give the required add-on. Weight increases were measured after drying at 10^{-4} torr and 100°C for 1 h.

Measurements of water-vapor sorption were made on 10 mg samples suspended from a helical quartz spring mounted in an evacuable sorption chamber. The vapor pressure was read directly from a differential mercury manometer and the temperature controlled to ± 0.01°C in an air thermostat. Results are given in Figs. 3-7 in the form of sorption isotherms, in which the equilibrium water content (EWC) is plotted against percentage relative humidity.

RESULTS AND DISCUSSION

Sorption Behavior of Unmodified Wool

Figure 3 compares the isotherm for unmodified wool to a partial isotherm [1] for LiCl/asbestos paper. With the latter, the ratio of
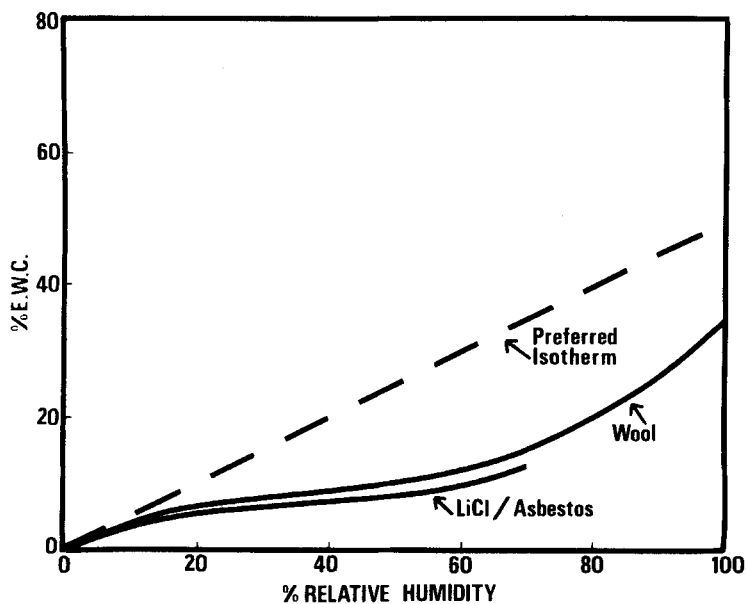

FIG. 3. Water vapor sorption isotherms for wool and a commercial lithium chloride/asbestos matrix.
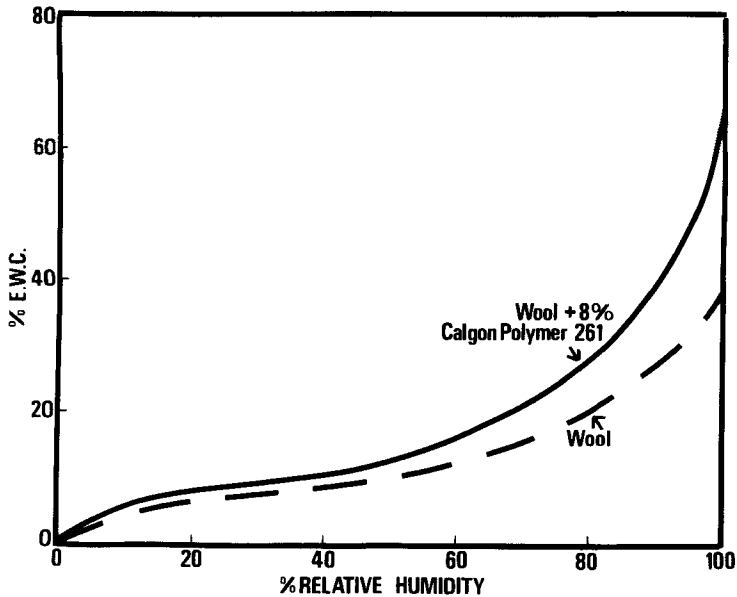
FIG. 4. Effect of Calgon polymer 261 on water vapor sorption by wool.

LiCl to asbestos determines the amount of water taken up by the system. However, because LiCl is deliquescent, large amounts of water are taken up at high humidities. Pockets of salt solution form in the porous structure of the asbestos paper, and when the paper is saturated with solution, an increase in the RH of the adjacent air results in salt solution dripping off the paper. This causes corrosion of the matrix casing and necessitates recharging of the paper with salt to keep the regenerator in operation.

Wool, of course, does not go into solution and does not exhibit drip formation, yet its isotherm is as steep, over the "useful" range of 40-90% RH, as that of the LiCl/asbestos system used in commercial enthalpy regenerator matrices. LiCl/asbestos matrices are also used in commercial regenerative dehumidifiers, but with greater salt loading. Preferably, the isotherm should be steep, with a linear increase in equilibrium water content with increasing RH, as shown by the dotted line in Fig. 3. This isotherm is close to that for silica gel, which has been used successfully in regenerative dehumidifiers with matrices of packed particle form (a form inferior to the parallel plate and honeycomb configurations [3]).
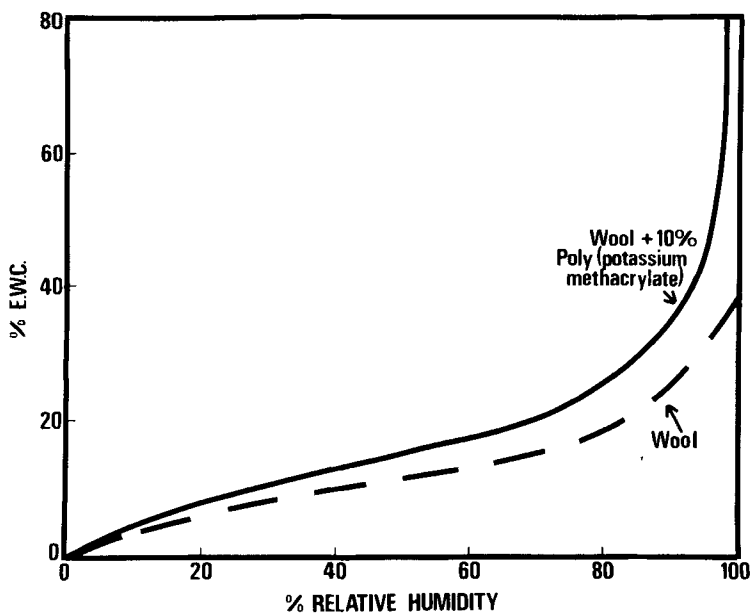
FIG. 5. Effect of poly(potassium methacrylate) on water vapor
sorption by wool.

Attempts to Increase Water Uptake of Wool

Prior sorption studies by the authors have shown that the water-
sorption properties of wool fibers can be improved by chemical treat-
ment, including treatment with bromoacetic acid [6] or alkali [7] and
incorporation of hydrophilic copolymers [8]. If large amounts of
acrylamide are polymerized within the fibers, the isotherm of the
treated wool has the preferred shape over the "useful" range of 40-
90% RH [8]. Also, the copolymer nature of the wool-polyacrylamide
system ensures that drip problems will never occur [9].

However, the rates of sorption and desorption must also be taken
into account, and these will depend on the depth of penetration of the
sorbed water. Thus a better approach would be to locate the hydro-
philic additive, or induce the hydrophilic chemical modification, at or
near the surface of the wool fiber, as occurs, for example, in the
LiCl/asbestos system.

The increases in equilibrium water uptake obtained by the addition
of relatively small amounts of hydrophilic polymers to the wool fiber
surface are shown by the isotherms in Figs. 4 and 5. These polymers
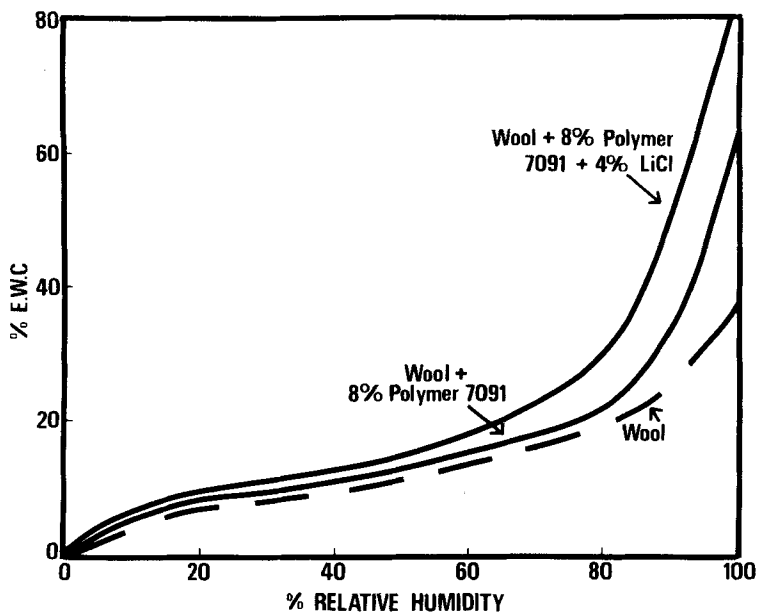sorb large amounts of water in the free state [9], and when applied to

FIG. 6. Additive effects of Calgon Polymer 7091 and lithium chloride on water vapor sorption by wool.

wool give the desired extra water uptake, but with the additional water located near the fiber surface. Drip formation did not occur, even at very high humidities; presumably, the viscous nature of the hydrophilic polymer prevented the water/polymer system from becoming fluid enough to drip. Results will be presented in detail in a separate communication showing that, when a wool matrix was treated with Calgon Polymer 261, transfer of water vapor between air streams of different state was increased significantly, indicating the potential of this approach.

Lithium chloride is a highly deliquescent salt, and so it would appear possible to increase water sorption further by incorporating LiCl in the polymer solution before application to the wool. This assumption proved to be correct (Fig. 6) and again drip formation did not occur.

Substrates Other than Wool

Whether fibrous substrates other than wool could effectively be used for supporting the polymer/LiCl system and produce satisfactory isotherms, is partially answered by the data presented in Fig. 7,
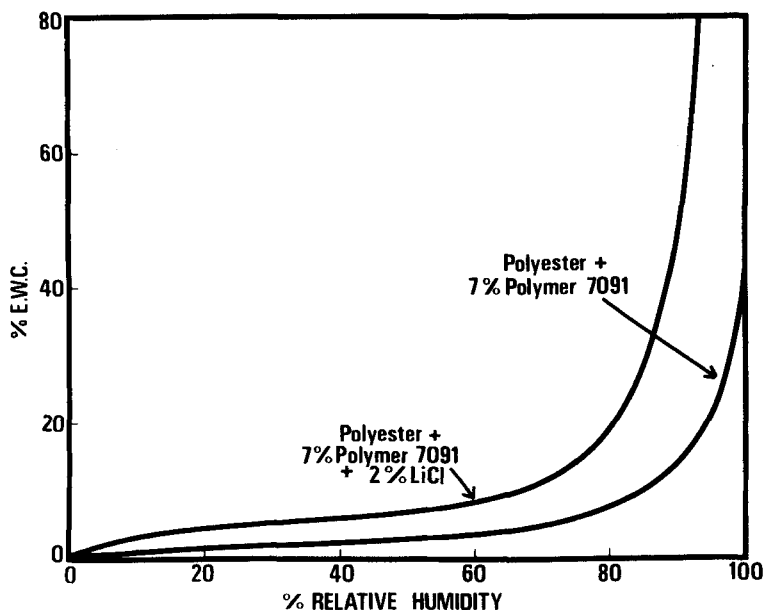
FIG. 7. Water vapor sorption isotherms of polyester + hydrophilic additives.

obtained using a hydrophobic substrate (woven polyester fabric). Clearly the isotherm has a less suitable shape. Furthermore, drip formation occurred at around 95% RH. The extra swelling propensity or different surface texture of the wool fiber is apparently an advantage in a system such as that currently being studied.

Further work is needed on wool and other substrates to optimize the relative amounts of polymer and LiCl required to give maximum water transfer without droplet formation. The feasibility of incorporating further hydrophilic additives in the system (e.g., silica gel powder) is also under consideration, and a more stable support for the additives will be sought by controlled cross-linking of the hydrophilic polymer (this is possible using Calgon Polymer 7091) to make it insoluble in water.

Rates of Water Sorption

The rate at which water is absorbed and desorbed from the surface of the substrate also influences the amount of water that can be

transferred in a single cycle. However, not surprisingly, kinetic measurements made during the present studies have shown that the proportional rate of sorption of the small polar water molecule is not significantly altered, but the steeper slope of the isotherm confers the potential for more water to be transferred in the available time. Furthermore, the uptake of water in a given time increases with a higher surface-to-volume ratio of the hydrophilic additive. For this reason the surface deposition of polymer is more attractive than internal deposition.

CONCLUSIONS

The system wool/hydrophilic polymer/deliquescent salt offers three advantages over the currently used LiCl/asbestos system for heat and mass exchange: (1) asbestos is replaced by wool, (2) the drip problem is eliminated, and (3) higher water uptakes are possible than with the commercial system.

ACKNOWLEDGMENTS

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