

# Permeability of Cellulose Polymers: Water Vapour Transmission Rates

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**Abstract**—The water vapour transmission rates (WVTR) through solvent cast polymer films prepared from cellulose acetate, cellulose acetate propionate, and cellulose acetate butyrate have been determined. They were influenced by the relative humidity, the substituent type and the extent of substitution. Increasing the relative humidity from 32 to 90% increased the WVTR 3 to 5 times depending on the polymer used. The WVTR increased in the order of butyrate < propionate < acetate. An increase in the extent of substitution with acetyl and/or butyryl groups resulted in an exponential decline in the WVTR.

Both as packaging materials and in the development of drug delivery systems, the barrier properties of polymers are primary for selecting a particular polymer.

Polymers can be characterized in terms of their mechanical properties (Rowe et al 1984; Sakellariou et al 1985, 1986), dissolution properties (Borodkin & Tucker 1975; Donbrow & Samuelov 1980; Rowe 1986), permeability (Shah & Sheth 1972; Benita et al 1986; Bindschaedler et al 1987; Lee et al 1987; Hadgraft & Ridout 1987; Sun et al 1987; Bhalla & Toddywala 1988), and water vapour transmission (Delporte 1979; Gurny 1976).

The permeability of free polymer films prepared by solvent casting may be influenced by many factors, including polymer hydrophobicity (Lee & Kim 1987; Miyajima et al 1987; Sun et al 1987), solvent composition (Abdel-Aziz & Anderson 1976; Spital & Kinget, 1977a, 1980), and plasticizer content (Crawford & Esmerian 1971; Donbrow & Friedman 1975; Benita et al 1986; Spital & Kinget 1977b). Determining the water vapour transmission rates through free polymer films (Kanig & Goodman 1962; Lachman & Drabulis 1964; Patel et al 1964) is a simple method of assessing the polymer permeability compared to traditional diffusion studies.

Diffusion of a permeant through a polymer may be influenced by several structure-related factors, such as polymer molecular weight, cross-linkage and crystallinity. The permeability of the polymer may be modified by changing the structure of the polymer; for example hydrophilic or hydrophobic substituents could be incorporated into the polymer. In a series of polymers with a similar backbone structure, but with different substituent groups, differences in permeability may be ascribed to the properties of the substituent group.

The purpose of this study was to determine the relative barrier properties of several commercial cellulose based polymers by determining the water vapour transmission rates through various cellulose derivatives at different relative humidities.

The structure of cellulose consists of repeating units of glucose with three free hydroxyl groups per glucose unit and

an acetal linkage (Fig. 1). As a result it is highly hydrogen bonded and is crystalline, which makes dissolution difficult in water or common organic solvents, and processing in general. The free hydroxyl groups account for the hydrophilic character of cellulose even though it is not soluble in aqueous media; to improve the solubility, the free hydroxyl groups can be esterified thereby reducing the hydrogen bonding and interfering with the crystallization. Esterification has most commonly been with acetyl, propionyl, or butyryl groups or combinations thereof. Ether derivatives, such as ethylcellulose, may also be prepared. The derivatives are also more soluble in common organic solvents than cellulose itself. Some commercially available derivatives are listed in Table 1 with the extent of substitution. It seems logical that the type of the substituent (e.g. acetyl vs butyryl) and the extent of substitution will determine the hydrophobicity/hydrophilicity of the cellulose derivative. The type and extent of derivatization should therefore influence the permeability of the polymer to water vapour.

## Materials and Methods

### *Solvent casting*

The polymers were dissolved in an appropriate solvent (see Table 2) to form 3% solutions, 5 mL of which was poured onto glass substrates with raised edges. The thickness of the films was controlled by the volume and concentration of the polymer solution. The rate of solvent evaporation was restricted to minimize the variability between films caused by erratic solvent removal and sufficiently low to produce clear films. The systems were left undisturbed for 48 h to allow complete evaporation at 20°C and atmospheric pressure. Following complete evaporation of the solvent, the films were carefully removed from the glass substrates and stored in a desiccator for at least 24 h before use; defective films were discarded. The thickness of each film was measured in 8 randomly selected places with a digital micrometer with an accuracy of 2.5 µm and are reported as the mean of the four films used in the water vapour study (Tables 3, 4). The effects of the solvents on the microstructure of the films could not be ascertained, since different solvents were needed for the polymers which since they were highly soluble in the solvents

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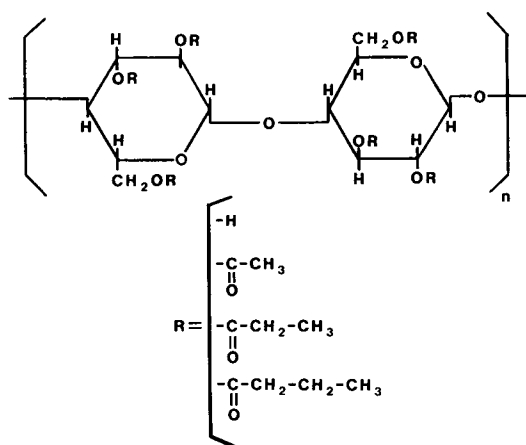


FIG. 1. Structures of cellulose derivatives.

chosen and a low evaporation rate was used, solvent effects, if any, were assumed to be negligible.

#### Cup design

The cups used in the water vapour transmission studies consisted of a plastic body (4.13 cm i.d. × 6.02 cm ht), and a screw cap. Two gaskets (4.47 cm dia.) fitted within each cap. An opening ( $2.22 \pm 0.02$  cm diam.) was cut in each cap and gasket assembly to provide an effective surface area of 3.86 cm<sup>2</sup> for water vapour transmission. The connection between the cup and the screw cap was sealed with parafilm strips. The relative humidity (RH) within the cup was maintained with saturated salt solutions in contact with undissolved salt: CaCl<sub>2</sub> · 2H<sub>2</sub>O (32% RH), NaBr (80% RH), KBr (84% RH), and ZnSO<sub>4</sub> · 7H<sub>2</sub>O (90% RH). These solutions were kept at 20°C and atmospheric pressure.

#### Water vapour transmission studies

A circular section of 4.47 cm diameter was cut from each of four polymer films, each was placed between two gaskets and the assembly was placed in a screw cap. A salt (1 g) was placed in each of the four cups and 10 mL of a saturated solution of the salt was added. The systems were assembled and sealed with parafilm strips. Each assembly was weighed and placed in a standard desiccator (10.23 cm) containing 200 g of 10–20 mesh size Drierite, which was previously dried in an oven at 200°C for at least 12 h. The desiccators were maintained at 20°C. At predetermined times the 4 cup assemblies were removed, reweighed and replaced in the desiccators. The amount (mg) of water vapour diffused was

Table 2. Solvents used in preparing films from various cellulose polymers.

CAB	171-15S	Acetone
CAB	381-2	Acetone
CAB	500-1	Acetone
CA	320-S	Acetone/methanol
CA	398-10	Acetone
CA	436-80S	Methylene chloride
CA	435-75-S	Methylene chloride
CAPr		Acetone

Table 3. The thicknesses of cellulose polymer films used in water vapour transmission studies at 32, 58, 84 and 90% RH (mean ± s.d., n = 16).

Polymer	Thickness (μm)
CAB 500-1	25 ± 3.7
CA 320-S	23 ± 4.0
CA 436-80S	22 ± 4.6
CAPr	27 ± 7.9
W*	5.03

\* Tukey's multiple range criterion calculated from a one-way ANOVA ( $P=0.05$ ).

Table 4. The thicknesses of cellulose polymer films used in water vapour transmission studies at 90% RH (mean ± s.d., n = 4).

Polymer	Thickness (μm)
CAB 171-15S	27 ± 1.4
CAB 381-2	27 ± 6.6
CAB 500-1	26 ± 3.5
CA 320-S	26 ± 3.5
CA 398-10	21 ± 3.1
CA 436-80S	22 ± 5.4
CA 435-75-S	23 ± 3.1
CAPr	22 ± 1.9
W*	9.36

\* Tukey's multiple range criterion calculated from a one-way ANOVA ( $P=0.02$ ).

calculated from the reduction in weight of each cup. The experiments were continued for 48 h.

Two series of experiments were conducted sequentially. In the first, the diffusion of water vapour through five selected polymers (Table 1: CA 320, CA 436, CAB 500 and CAPr) was investigated at (32, 58, 84 and 90% RH). In the second series the RH was kept at 90% and the polymers investigated were increased in number to include CA 435, CA 398, CAB

Table 1. Type and extent of substitution of the various cellulose polymers.

Polymer	Designation	% Butyryl	% Acetyl	% Hydroxyl	% Propyl
Cellulose acetate butyrate	CAB 171-15S	17.0	29.5	1.5	—
	CAB 381-2	37.0	13.0	1.5	—
	CAB 500-1	50.0	5.0	0.5	—
Cellulose acetate	CA 320-S	—	32.0	9.0	—
	CA 398-10	—	39.8	3.4	—
	CA 436-80S	—	43.7	0.9	—
Cellulose triacetate	CA 435-75-S	—	43.5	0.9	—
Cellulose acetate propionate	CAPr	—	2.5	5.2	41.5

171 and CAB 381. The control for all these experiments was the unhindered diffusion of water vapour at the same relative humidity through a specified surface area (3.86 cm<sup>2</sup>) using cup assemblies without any polymer films.

The values for the water vapour transmission rates thus obtained were considered as relative rather than absolute values because, during reweighing of the cups, time was required to return the environment within the desiccator to the dehydrated state. Therefore the relative humidity difference across the film was not constant at all times.

#### Statistical analysis

Four replications were done for each vapour transmission experiment. Differences in thickness between films was assessed by a one-way analysis of variance with a Tukey Multiple Range test at an *P* value of 0.05. A similar data analysis was done for the effect of type and extent of substitution on water vapour transmission rates at 90% relative humidity. The influence of polymer type and relative humidity was analysed by a two-way analysis of variance.

### Results and Discussion

#### Water vapour transmission kinetics

Under steady state conditions the diffusion of water vapour molecules through the polymer films may be expressed as

$$\frac{dQ}{dt} = \frac{PA}{h} (RH_{in} - RH_{out}) \quad (1)$$

where *Q* is the cumulative amount of water that permeated through the film at time *t*, *P* is the permeability constant, *A* is the effective surface area, *h* is the film thickness, and *RH<sub>in</sub>* and *RH<sub>out</sub>* are the concentrations of water vapour inside and

outside the cup, respectively, expressed as percent relative humidity.

Since the relative humidity inside the cup (*RH<sub>in</sub>*) was much higher than the relative humidity outside the cup (*RH<sub>out</sub>*), equation 1 may be integrated to yield:

$$Q = \frac{PA RH_{in} t}{h} - \frac{PA RH_{in} t_{lag}}{h} \quad (2)$$

where *t<sub>lag</sub>* refers to the time during which it is assumed that no water vapour transmission occurred. This assumption makes equation 2 an approximation. However, since the lag time is extremely short, the amount of water vapour diffused at the lower rate of transmission during the lag time was assumed to be negligible.

Rearrangement yields:

$$\frac{Q}{A} = \frac{P RH_{in} t}{h} - \frac{P RH_{in} t_{lag}}{h} \quad (3)$$

No significant differences in film thickness between the various polymer films were detected (Tables 3, 4). By maintaining the relative humidity inside the cup (*RH<sub>in</sub>*) constant equation 3 may be simplified to:

$$\frac{Q}{A} = k_0 t - k_0 t_{lag} \quad (4)$$

where *k<sub>0</sub>* is an apparent zero-order rate constant for water vapour transmission, and may be defined as:

$$k_0 = \frac{P RH_{in}}{h} \quad (5)$$

A plot of amount of water vapour permeated per unit surface area versus time yielded a straight line with a slope equal to *k<sub>0</sub>*, which represented the water vapour transmission rate constant (WVTR) at a particular relative humidity. The

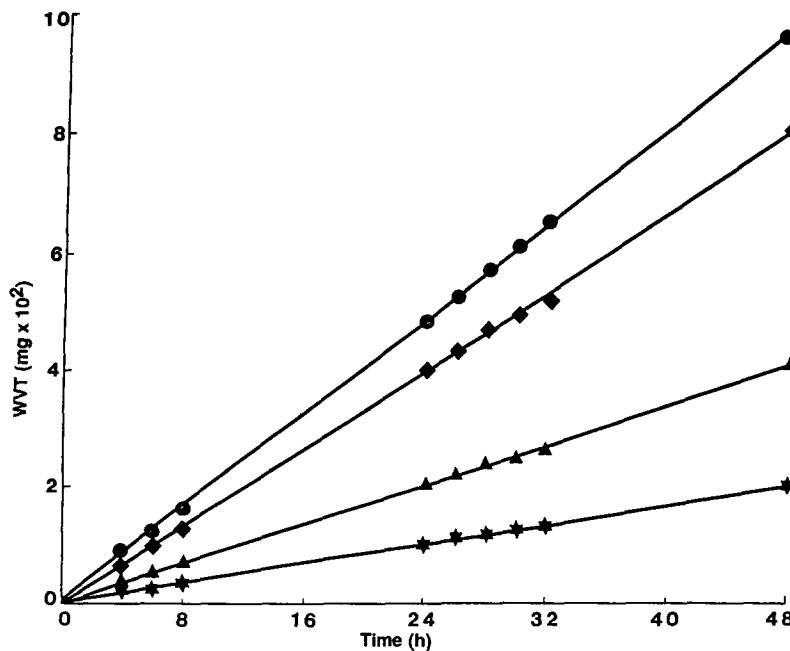


FIG. 2. Water vapour transmission through CA 320 films at different relative humidities. (★) 32%; (▲) 58%; (◆) 84%; (●) 90% RH.

slopes were calculated by the linear least squares regression method. No lag time ( $t_{lag}$ ) was discernible. Some examples of the linear relationship between water vapour transmission and time are shown in Fig. 2.

#### Effect of relative humidity

According to equation 5, the water vapour transmission rate constant ( $k_o$ ) is directly related to  $RH_{in}$ . An increase in this constant with an increase in relative humidity was observed for every polymer film studied (Fig. 3). However, the relationship was not linear.

At least two factors may be responsible for the lack of linearity: a build up of moisture and a change in the permeability coefficient. At the higher relative humidities the environment within the desiccator outside the cups may not have been completely dehydrated by the Drierite, allowing a build up of moisture. This would have invalidated the assumption of sink conditions necessary for the equation derived. Two considerations reduce the probability of moisture build up being a significant factor in the water vapour transmission. An excess of freshly dried Drierite was used which should have maintained the environment within the desiccator well dehydrated. This would then maintain a constant, large difference between the  $RH_{in}$  and  $RH_{out}$ . As seen in Fig. 3, the water vapour transmission rate constants increased exponentially with RH as a hyperbolic function, which is contrary to what would be expected if there had been a build up of moisture; parabolic function would be expected with a limiting  $k_o$ .

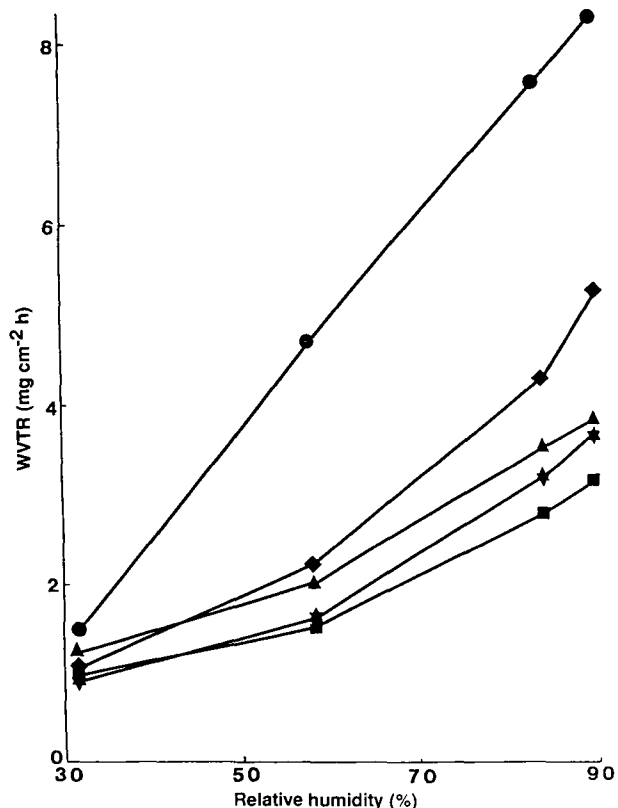


FIG. 3. Effect of relative humidity on water vapour transmission rates,  $k_o$ , through various polymer films. (■) CAB 500; (★) CAPr; (▲) CA 436; (◆) CA 320; (●) control.

Table 5. Effect of type and extent of substitution on the transmission of water vapour through polymer films at 90% RH.

Polymer	Water vapour transmission rate $mg\ cm^{-2}/h^{-1}$
CAB 171-15S	$3.90 \pm 0.23$
CAB 381-2	$3.16 \pm 0.16$
CAB 500-1	$3.12 \pm 0.14$
CA 320-S	$5.28 \pm 0.18$
CA 398-10	$4.36 \pm 0.20$
CA 436-80S	$3.84 \pm 0.45$
CA 435-75S	$4.17 \pm 0.55$
CAPr	$3.74 \pm 0.18$
Control	$8.34 \pm 0.12$
W*	0.68

\*Tukey's multiple range criterion calculated from a one-way ANOVA ( $P < 0.0001$ ).

The second possible reason for the non-linearity may be the influence of RH on the permeability coefficient. As seen from equation 5,  $k_o$  would be influenced by changes in the permeability coefficient. This would explain the hyperbolic shape of the graphs in Fig. 3, because the permeability constant would be changing simultaneously with RH.

#### Effect of substituent type

The permeability coefficient is dependent on the physicochemical characteristics of the polymer and is, therefore, influenced by the type of substituent used to make the cellulose polymer. A change in the permeability coefficient would alter the water vapour transmission rate constant ( $k_o$ ). The influence of substituent type on  $k_o$  is most apparent at higher relative humidities (see Fig. 3). When the water vapour transmission rate constants,  $k_o$ , were averaged over the relative humidities the following rank order of substituent types was observed:  $CAB < CAPr < CA$ .

This rank ordering of substituent groups on the cellulose polymer is logical if one considers the chemical structure of the various substituents. These are aliphatic monoacids with carbon chain lengths ranging from  $C_2$  to  $C_4$ . As the hydrophobicities of the substituent groups are directly influenced by group chain length, it therefore, increases in the order acetyl < propionyl < butyryl, which corresponds to the rank ordering of the influence of substituent type on the water vapour transmission rate constant. A similar conclusion was reached by Patel et al (1964).

In at least one instance the effect of substituent type was less influential than the extent of substitution. In general CAB polymers were less permeable than CA polymers, however, the low substituted CAB 171 was more permeable than the highly substituted CA 436 (Table 5). This shows the importance of the combined influence of type and extent of substitution on the overall polymer hydrophobicity, and thereby on the water vapour transmission rate constant.

#### Effect of extent of substitution

In addition to the type of substituent used, the degree of substitution also has a significant impact on the water vapour transmission rate (Figs 4, 5). Cellulose derivatives containing the acetyl and/or the butyryl substituent groups exhibited an

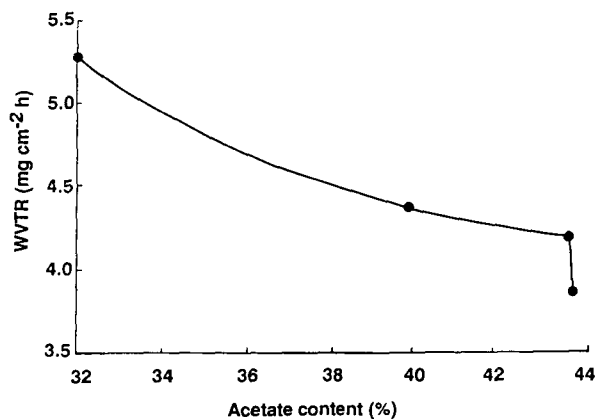


FIG. 4. Effect of acetate content on water vapour transmission rate through CA films at 90% RH.

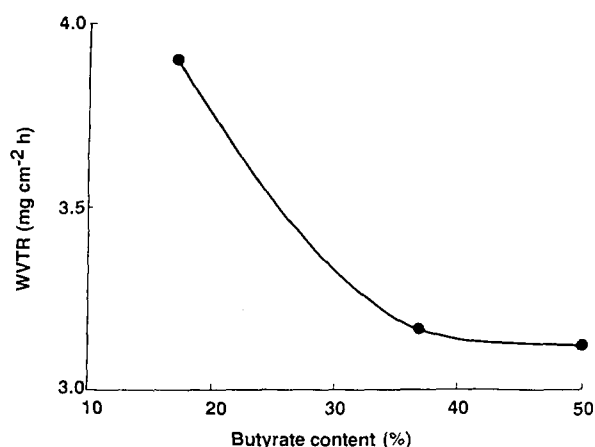


FIG. 5. Effect of butyrate content on water vapour transmission rate through CAB films at 90% RH.

exponential decline in this rate with increase in extent of substitution. By substitution of an increasing percentage of the free hydroxyl groups, the hydrophilic character of the polymer is diminished. The reduction in the affinity of the polymer film for water vapour molecules probably explains the lower transmission rate at higher amounts of substitution.

With the cellulose acetate derivatives a threshold in the extent of substitution seems to exist, beyond which their permeability declines sharply.

#### Conclusion

The water vapour transmission rates through the various cellulose polymer films were affected by the relative humidity used, but not linearly. In general, the rate of water vapour transmission increased in the order of CAB < CAPr < CA, even though exceptions to this trend were observed. The present results show that both the type of substituent and the extent of substitution must be considered together, rather than independently, when a cellulose polymer is being selected.

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