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Water Vapor Permeability in Layered Polymer Films

The requirement of high water vapor permeability and water repellency on the surface of many polymeric materials such as synthetic leathers has long caused difficulties in specifying the microporous surface structure which can meet these requirements, while at the same time giving adequate mechanical properties such as flex resistance, scuff resistance, resistance to peeling, etc.

The pressure P necessary to prevent water from entering a capillary of radius r is given by

$$P = \frac{2\gamma\cos\theta}{r} \tag{1}$$

where γ is the water surface tension and θ is the contact angle between the water meniscus and the capillary wall.^{1,2} One readily estimates from eq. (1) that high water repellency requires poromeric materials of very small pore sizes, $r \sim 10^{-4}$ mm. Such materials are difficult to manufacture reproducibly. Still, if it were possible, one could combine high water vapor permeability with high water repellency, but at the expense of scuff resistance, luster, and other important surface properties in this application. One way to provide satisfactory surface properties of a synthetic leather is to apply a thin homogeneous polymer film, called finish, to the microporous film of the synthetic leather.

In a series of studies to cope with this problem of composite structures of different poromeric films, we have found that under certain conditions the water vapor permeability can be made almost as high as theoretically possible for a given structure, while at the same time the water repellency is kept high through the proper matching of the film morphology at the interface between the layered films.

Composite film structures were prepared in four ways:

I. Commercially available microporous polyurethane films of 0.4 mm thickness were laid on homogeneous polyurethane finish films of various thicknesses ranging from 5×10^{-3} mm to 5×10^{-2} mm.

II. Chemically blown poly(vinyl chloride) (PVC) films of thickness 0.4 mm, prepared as described in reference 3, were laid on the same polyurethane finish films as in I.

III. A PVC plastisol, prepared as described in reference 3, was cast on the same polyurethane finish films as in I, and expanded and cured as described in reference 3 to give microporous PVC films of thickness 0.4 mm.

IV. The plastisol as in III was cast on homogeneous polyurethane finish films containing 1% silicone oil, F 160 from I.C.I., which was added to the polyurethane solution before the film was cast. The polyurethane films were of the same thickness as in I.

The water vapor permeabilities of all the films and of the combinations I–IV were measured according to DIN 53333. The results are shown in Figure 1. The dashed curve represents the expected water vapor permeability values of the combinations calculated from the respective water vapor permeability values of the individual films according to formula (2), which is valid if the diffusion coefficient of water vapor is independent of the concentration and the solubility is proportional to the pressure in the two films:^{4,5}

$$\frac{1}{WVP_{\text{lam}}} = \frac{1}{WVP_{upf}} + \frac{1}{WVP_{fin}}$$
(2)

where WVP_{lam} , $WVP_{\mu\text{pf}}$, and WVP_{fin} are the water vapor permeabilities of the laminate, the microporous film, and the finish film, respectively. The microporous films in I and II had the same water vapor permeability, 425 g/m² 24 hr. This value was also used to obtain the dashed curve.

The corresponding water repellency values were measured according to SATRA⁶ method STM. 106, the Maeser test, which corresponds to the number of flexes sustained without water penetration

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Fig. 1. Water vapor permeability of combinations of microporous films with homogeneous finish films as a function of water vapor permeability of the homogeneous finish film. Dashed curved is obtained from eq. (2).

to the backside when the finished side is submerged in water. The results are given in Table I. The usual SATRA acceptance test value of water repellency for shoe upper materials is >20 flexes. Combinations III and IV survived at least 500 flexes. The water repellency of combinations I and II could not be measured since the finish film did not adhere to the microporous films.

While thus exhibiting satisfactory water repellency, the water vapor permeability of the film combinations shows significant dependence on the mode of lamination. Experiments I and II exceed the theoretical curve, but nevertheless establish the proper frame of reference for the discussion of water vapor permeability properties of the laminate combinations. Experiment III yields combinations with water vapor permeabilities far below the theoretically possible permeability. The

Film	Water vapor permeability, g/m ² 24 hr	Water repellency, number of flexes
III		
WVP_{fin} = 400 g/m ² 24 hr	90	6000
IV		
$WVP_{fin} = 400 \text{ g/m}^2 24 \text{ hr}$	175	500
IV		
$WVP_{fin} = 350 \text{ g/m}^2 24 \text{ hr}$	150	6000
Microporous PVC film	425	25

TABLE I Water Vapor Permeability and Water Repellency of Lavered Polymer Films

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mere addition of 1% silicone oil to the thin homogeneous polyurethane finish film does not affect the adhesion between the films but raises the water vapor permeability almost to the theoretically possible value.

We surmise that the addition of small amounts of release agents, silicone oils, to the homogeneous polyurethane film suffices to adjust the surface tension in the PVC plastisol to create an open cell structure during the blowing step at the film-film interface to guarantee the optimum water vapor permeability without impeding the mechanical integrity of the laminate.

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