Covercoat Retardation of Permeation through Sheet Molding Compound

T. E. GRAEDEL and J. P. FRANEY, *Bell Laboratories, Murray Hill, New Jersey 07974*

Synopsis

Permeation of gases through polymers may be retarded by applying to the polymers a coating of a less permeable material. We have devised techniques to quantitatively measure rates of water vapor permeation at typical atmospheric pressures and compositions through polymer and coating films, and we apply these techniques here to a crosslinked polyester resin with glass fiber reinforcement, coated with a crosslinked thio-ene formulation. The coating is shown to inhibit water vapor permeation by about a factor of thirty over the uncoated value. H_2S permeation constants are also derived; they are some three orders of magnitude smaller than those of H_2O but show similar coated/uncoated permeation effects. The controlling factor in the retardation is suggested by experimental evidence to be a graft copolymer formed at the covercoat–sheet molding compound interface by the ultraviolet curing process.

INTRODUCTION

A variety of applications have been developed for sheet molding compounds (SMC), which are typically formulated of crosslinked polyester resin with glass fiber reinforcement.[1,2] SMC has good processing and strength properties, but its moisture vapor permeability is often excessive.[3] In addition to concern about permeant water vapor, other permeant gases such as corrosive hydrogen sulfide may pose hazards to electronic equipment contained within SMC housings. Because recent permeation studies of H_2S and SO_2 transport through covercoat materials demonstrate that certain covercoats have very low permeation rates,[4] we conceived the idea of reducing permeation through SMC by application of a flexible covercoat. This report describes the experiments and discusses the results that have been derived.

EXPERIMENTAL

Water vapor permeation constants were determined with apparatus developed in this laboratory[5] for performing measurements at atmospheric pressure and in the presence of normal concentrations of the major constituent gases of the atmosphere. This apparatus is capable of detecting water vapor fluxes through the test sample as low as $\sim 5 \times 10^{-7}$ cm^3 H_2O vapor/s. The resulting sensitivity for permeation constant detection is a function of the sample diameter and thickness and of the humidity of the upstream air; for the sheet molding compound tested here the minimum detectable permeation constant was ~ 30 barrers and for the freestanding covercoat it was ~ 3 barrers. [1 barrer $= 1 \times 10^{-10}$ cm^3 gas (STP)·cm thickness/(cm^{2}area·cm pressure·s).] All measurements were performed at room temperature [$(20 \pm 2)°C$].

Hydrogen sulfide permeation constants are also measured at atmospheric pressure, the H_2S being supplied by the "polymer valve" system described by Franey.[6] H_2S detection in the downstream gas flow involves catalytic conversion of H_2S to SO_2 and subsequent detection by pulsed fluorescence using a Thermo Electron Model 43 Detector.   The high sensitivity of the detector and the capability of pressurizing the upstream side of the sample chamber to 760 torr H_2S permit us to derive H_2S permeation constants as low as ~0.1 barrer for the sheet molding compound and ~0.01 barrer for the freestanding covercoat.

The permeant gas concentrations were monitored and recorded continuously by a dedicated desktop computer until stability was reached.   Temperature, flow, and upstream humidity were also recorded.   The permeation constants were then derived by statistical analyses of the experimental data.

RESULTS

Water vapor permeation measurements were initially made for a typical thermosetting sheet molding compound as supplied by the manufacturer (General Industries Product 47942) and for the flexible covercoat (CC) by itself in the form of a freestanding film.   The covercoat used was a thio-ene formulation developed by G. B. Fefferman of Bell Laboratories.   Measurements were also made for the laminate [SMC coated with the flexible covercoat of layer thickness 140 ± 25 μm and cured with ultraviolet radiation (SMC_{uv}/CC)], for a sandwiched combination $(SMC_{uv} + CC)$ of irradiated SMC and a freestanding CC film, and for an irradiated but uncoated SMC sample (SMC_{uv}).   The water vapor permeation results of these determinations are presented in Table I.   The dramatic reduction in the permeation constant achieved by covercoating the SMC (about a factor of 17) is immediately evident, and is consistent with the observations of other workers that extensively crosslinked systems typically demonstrate low values of P.[7,8]   It is also clear that the uncoated SMC is affected by irradiation; the decrease in water vapor permeation presumably implies that additional crosslinking is taking place.   Another feature of the data is the order-of-magnitude decrease in permeation when the covercoat is applied to and cured upon the SMC rather than being processed separately and then physically sandwiched with it.

TABLE I

Permeation Data

Sample	Thickness (μm)	Permeant gas	P (barrers)
SMC	1590 ± 65	H_2O	2100 ± 300
SMC_{uv}[a]	1590 ± 65	H_2O	1060 ± 225
CC	150 ± 25	H_2O	56 ± 12
$SMC_{uv} + CC$[b]	1730 ± 70	H_2O	570 ± 90
SMC_{uv}/CC[c]	1730 ± 70	H_2O	63 ± 13
SMC	1590 ± 65	H_2S	3.3 ± 0.5
CC	80 ± 15	H_2S	$.020 \pm .006$
SMC_{uv}/CC	1740 ± 70	H_2S	<0.40

[a] SMC_{uv} is used here as a symbol for SMC that has been irradiated with broadband ultraviolet light.   The total energy received by the samples was measured at two wavelengths: 4.2×10^{-4} J cm^{-2} (360 nm), 2.6×10^{-4} J cm^{-2} (250 nm).

[b] SMC_{uv} physically sandwiched with a freestanding covercoat film.

[c] SMC_{uv} together with a covercoat that has been cured upon it.

Results from hydrogen sulfide permeation experiments are also shown in Table I. The pattern is similar to that for H_2O, but the permeation constants are lower by factors of several hundred. This is typical of H_2O/H_2S relative permeation data acquired by manometric methods and summarized by Yasuda.[9] We have demonstrated the scavenging of H_2S by stabilizers employed in formulations of other polymer systems,[10] and suggest that a similar mechanism may be in effect here.

DISCUSSION

The SMC with the applied and cured covercoat may be pictured as a two-part laminate, the mathematical formulation for the permeation of which has been presented by Rogers et al.[11] and by Barrer.[12] The result of import for this work is that the overall permeation constant of the laminate (L) is related to those of its individual components (i) by

$$\frac{l_L}{P_L} = \sum \frac{l_i}{P_i} \tag{1}$$

where the l values are the thicknesses and the P values are the permeation constants. Using the data of Table I, we can insert values into the right side of eq. (1), solve for P_L, and check with the measured value to see whether the two-part laminate description of the system is satisfactory. The result is shown in Figure 1. To the left are the measured permeation constants for the individual laminate components ($\bigcirc, \bullet, \triangle$). In the center are the measured permeation constants for the laminate and for the sandwich ($\square, \blacksquare$). To the near right is the calculated permeation value for the sandwich ($\triangle$, 420 ± 80 barrers), which falls within the error limits of the experimental result when the error limits in the component P_i values are used to estimate the allowable range in the calculated value.

It is clear from these results that the interaction of the covercoat with the SMC cannot be the creation of a simple two-part laminate. To investigate the morphology of the interface that is formed, we performed optical microscopy on samples that were cut from coated SMC, sectioned perpendicular to the surface plane, potted with the interface up, and polished. The result is shown in Figure
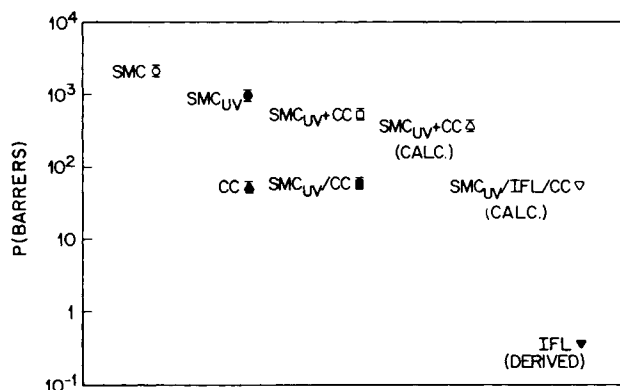

Fig. 1. A graphical representation of the effects on water vapor permeation of sandwiching and laminating a covercoat material with sheet molding compound. The point designations and the relationships between measured and calculated permeation constants are discussed in the text.
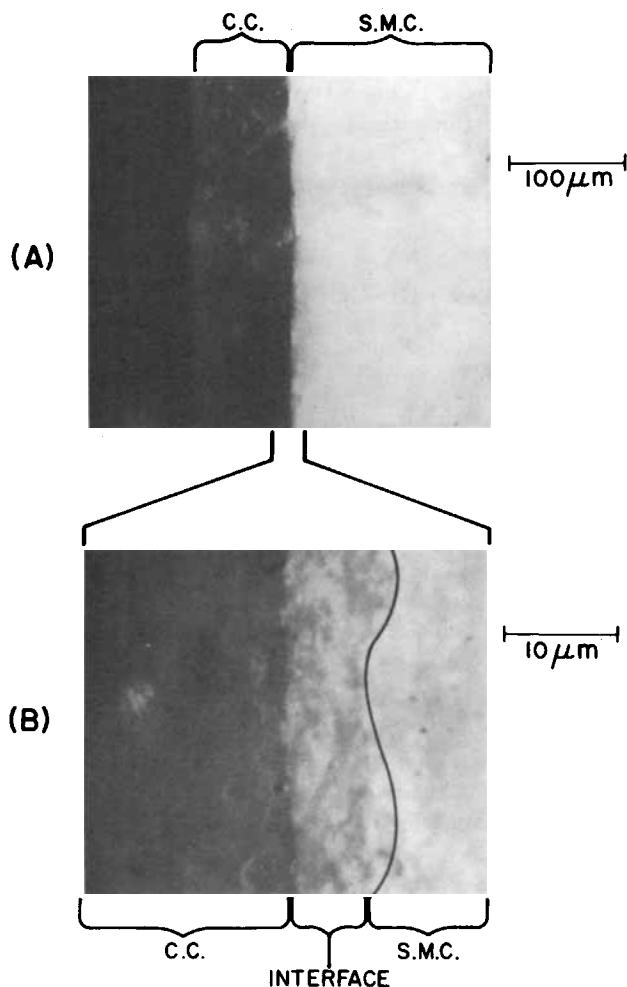
Fig. 2. Micrographs of the interface on a laminated sample between covercoat and sheet molding compound. (A) Low magnification; (B) high magnification.

2. The discoloration in Figure 2(b) at the interface indicates the infusion of the cover coat into the SMC to a depth of 5–10 μm; such a process is reasonable in terms of the surface morphology of the SMC (shown in Fig. 3), in which defects of ~5–10 μm are common. Prior to curing, the covercoat has a viscosity between those of molasses and toothpaste (i.e., $\geq 10^2$ stokes) and thus would be expected to fill the surface defects. Given that the covercoat is infused into the SMC, this circumstance still does not explain the low permeation values achieved by the laminate. If the interface is thought of as a third laminate layer, eq. (1) requires that its permeance (the P/l ratio) be of the order of 1/23. If we choose the thickness of this interface layer (IFL) to be 10 μm (as suggested by Fig. 2), the derived permeation constant is ~0.4 barrers. This is a reasonable number, since it is very near that measured for water vapor permeation through poly(vinylidene chloride)[9] and since the H_2S permeation constants for typical crosslinked films are equal to or lower than those of poly(vinylidene chloride).[4,13] The permeation constants derived for the IFL (▼) and computed for the three-part laminate (▽) are shown at the right of Figure 1.
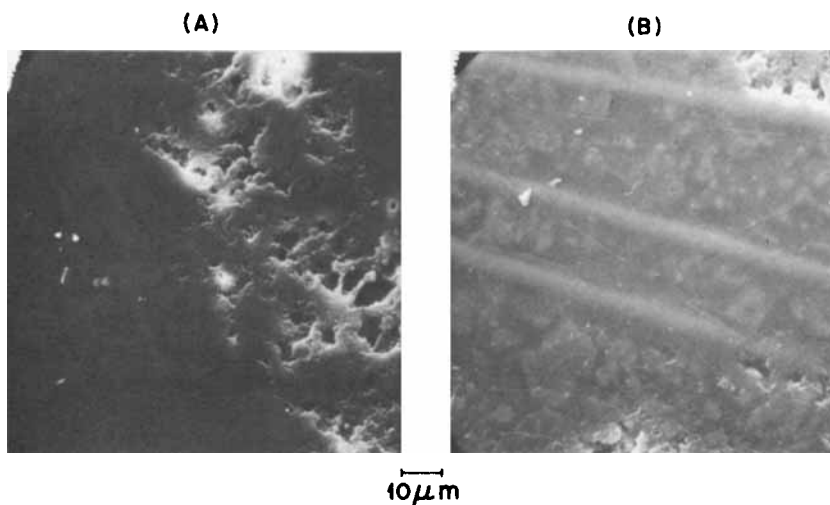
(A) (B)

10μm

Fig. 3. Micrographs of surface morphologies of sheet molding compound, examined after molding and before coating. (A) A typical surface area, showing flaws with dimensions of ~5–20 μm. (B) A typical surface area near reinforcing glass fibers. Note the presence of the fibers near the surface and the tendency for surface defects to occur adjacent to them.

The composition and morphology of the interface layer are more difficult to describe than is the layer's existence. It is clear that a true mixed polymer layer of thickness 10 μm cannot be formed, since the free energies and sluggish diffusion of polymer blend components limit such layers to widths of a few nanometers.[14,15] The chemical formulation of the components and our experimental results suggest that the formation of at least a thin interface is likely, however. The SMC is formed from an isophthalic polyester resin with a styrene crosslinking agent. The general tendency of SMCs to yellow under the influence of ultraviolet radiation[2] is due to the general tendency of aromatic ring molecules to form conjugated structures under such conditions.[16] The presence of these active sites in the SMC surface layer may thus provide interface coupling sites for the monomers in the covercoat, particularly in the presence of the free radical generators included in the covercoat formulation.

A schematic impression of the structure we deduce for the covercoated SMC is shown in Figure 4. The interface layer is pictured as a thin boundary between the two principal components. This layer provides the chief impediment to water permeation, a property which implies that it is a highly crosslinked graft copolymer of the resin from the covercoat with the aromatic ester and/or the
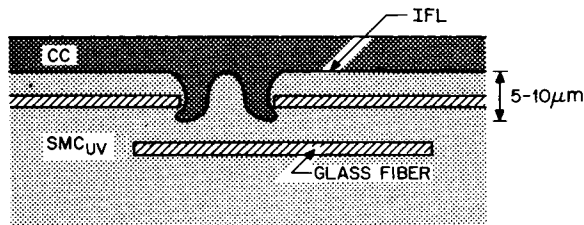

Fig. 4. Schematic conception of the structure of the covercoated sheet molding compound (see text for detailed discussion).

styrene from the SMC. Such a layer, if thin, would have to possess very low permeance, a property consistent both with its implied structure and with the knowledge that folded or crumpled barrier layers retain their barrier properties.[17,18] The layer's most effective function may be to plug the access channels for percolation that are likely to occur in the vicinity of fillers such as the glass fibers.[12]

Although we have not tested other combinations of covercoats and sheet molding compounds, there is reason to believe that the permeation inhibition produced by the covercoating of SMC will be quite general. Phthalic acid resins are the standard SMC resins and thio-ene systems are typical covercoat resins. If the latter is included in a formulation cured by ultraviolet irradiation, formation of a highly crosslinked interface layer should be a result common to arbitrary systems of UV-curable covercoats and sheet molding compounds.

In summary, we have established that the application of a UV-curable covercoat to sheet molding compound results in a substantial decrease in the permeation constants for water vapor and hydrogen sulfide. We attribute this behavior to the formation of a highly crosslinked interface layer between the covercoat and the sheet molding compound.

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