Evaluating Plasticizer Loss In PVC Membranes

Plasticizer loss is shown to be minimal in either moist or exposed environments. Membrane usefulness is not affected by the loss that does occur.

By Doug Burwell, PE

Polyvinyl chloride (PVC) and PVC alloys have been used extensively for many years for containment. In fact, a number of sites decades old still have functional PVC liners. Over the past few years, however, concerns have arisen over these liners and the loss of plasticizer under exposed and unexposed or buried conditions.

PVC liner production involves mixing or blending PVC resin, stabilizers, plasticizers and pigments. The plasticizer softens the polymer to make it pliable. When plasticizer is blended with the PVC, a portion of it forms an intimate bond with the PVC, while the remainder is captured in the polymer matrix.

The rate of loss of plasticizer depends on plasticizer type, temperature, sheet thickness and exposure time. The actual mechanism behind this loss is evaporation of plasticizer from the surface of the membrane. Therefore, for highly plasticized PVC, as in this case, the rate of plasticizer loss is dependent on the surface area. Figure (1) shows percent loss is directly proportional to time for a range of thicknesses and this loss varies logarithmically with temperature. Figure (2) shows loss varies inversely with thickness up to approximately 50 percent of plasticizer loss. Loss, therefore, can be expressed by the equation:

$$\mathbf{W = Ae^{bt}} \quad (1)$$

where:

W is the weight loss,

A is a constant depending on time and film thickness,

T is temperature,

B is the slope of the line.

Equation (1) can be expanded to give total weight loss of a vinyl sheet if one set of conditions is known. Equation 2 gives the estimated weight loss if an initial set is known.

$$W_2 = W_1 * \frac{T_2 d_1}{T_1 d_2} K\ T_2 - T_1 \quad (2)$$

where W, T, D, and **T** are weight loss, exposure time, sheet thickness and temperature (°C), respectively.

If the maximum weight loss before detrimental physical effects occur is set arbitrarily at 10 percent, which is 25 percent to 33 percent of total plasticizer loss, and it is recognized most PVC geomembranes specify a maximum volatile loss between 0.9 percent and 0.3 percent according to ASTM 1203A (70°C, 24 hours), a maximum exposure time can be developed.

For example consider the worst case of 0.9 percent loss in 24 hours at 70°C, W1 = 0.009, t1 = 24 hours, T1 = 70°C, and d1= d2. If W2 is set at 0.100 or 10 percent loss, and T2 is set at a maximum temperature of 30°C, substituting these values into Equation 2 yields the following result:

$$0.100 = 0.009 * \frac{T_2}{24} * 1.10^{(30 - 70)} \quad (3)$$

Solving for t2 gives 12069 hours or 502 days. For the minimum of 0.3 percent maximum volatility, 1 0 percent weight loss does not occur until 1508 days. If a temperature of 20°C is used, the time to 10 percent weight loss increases to 3.5 years at 0.9 percent volatility and increases to 10.7 years at 0.3 percent volatility.

This method of calculating the maximum exposure time of a membrane is extremely conservative for two reasons. The first reason is the use of maximum volatility, since much of what is lost is the lubricant used for processing. Also, the more volatile part of the plasticizer will flash off at this time. Secondly, this equation assumes a temperature of 30°C is maintained constantly, where in fact it is maintained only for a short time during mid-day. The conservative values generated from this equation have been confirmed at Florida test sites where samples of PVC exposed to average maximums of more than 33°C in August still retained most of their plasticizer after six years.

Even if these conservative values are accepted as fact, it is highly unlikely a problem would develop in the field due to plasticizer loss before the membrane is installed. It would take more than a year at 30°C temperatures to lose 10 percent of the plasticizer weight.

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Once the membrane is buried, a different set of conditions exists. First, the temperature is much lower and there is not a free amount of air present, which makes loss of plasticizer due to volatility negligible. On the other hand, moisture is present, which will cause some leaching of plasticizer.

Plasticizer is not soluble in water, therefore the mechanism is not simply extraction. The water diffuses into the vinyl matrix and combines with the plasticizer, and a water-plasticizer blend exudes. Plasticizers vary markedly in their sensitivity to water absorption, and ones that are not susceptible to this phenomenon should be selected. In most cases, the water extraction (ASTM D3083A) is around (-0.2) percent, which indicates some water has diffused into the PVC but little exudation has occurred.

Two-year water immersion tests on PVC membranes have been conducted by the National Sanitation Foundation (NSF) at both 23°C and 50°C. Percent weight change in all cases is less than 3 percent.

When tested at 23°C, maximum weight change is less than 2 percent. Modulus at 100 percent elongation at 23°C and 50°C and elongation at break (ASTM D412 die C) show no great loss of physical properties resulting from immersion in water, even at elevated temperatures. See Table 1, If there were a substantial loss of plasticizer, the change in physical properties would be larger than is seen here. Therefore, it can be concluded plasticizer loss due to water leaching is insignificant for PVC membranes.

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TABLE 1
PLASTICIZED PVC IMMERSED IN 100% WATER

Days Immersed	Percent Weight Change	Percent Retention SMOD M	Percent Retention SMOD T	Percent Retention EAB M	Percent Retention EAB T	
WATER 100% 50ºC						
1	0.8	92	95	92	97	
7	1.2	84	87	120	117	
14	1.7	108	108	101	90	

28	1.7	87	94	99	105	
28	2.1	*	*	*	*	
56	1.4	97	98	94	100	
133	2.3	*	*	*	*	
254	2.7	*	*	*	*	
370	2.5	*	*	*	*	
503	2.6	*	*	*	*	
622	2.6	*	*	*	*	
735	2.5	98	*	112	*	
WATER 100% 23ºC						
1	0.1	94	96	105	101	
1	0.3	95	96	107	113	
1	*	93	99	111	104	
7	0.4	85	84	108	114	
7	0.6	84	88	104	111	
7	0.5	85	85	100	115	
14	0.8	94	103	89	100	
14	0.8	90	91	100	106	
14	0.9	89	92	102	107	
28	0.7	93	95	105	110	
28	1.0	*	*	*	*	
28	0.9	93	85	103	116	
28	0.8	93	87	118	121	
56	1.1	109	112	87	91	
56	0.9	100	102	94	93	
56	0.8	96	99	102	92	
132	1.5	*	*	*	*	

247	0.8	*	*	*	*	
370	1.8	*	*	*	*	
503	1.4	*	*	*	*	
622	1.2	*	*	*	*	
737	0.7	100	*	107	*	
From "development of Chemical Compatibility Requirements For Assessing Flexible Membrane Liners"						