The influence of molecular weight on plasticizer retention

A key change to specification PGI-1104 improves understanding of long-term PVC geomembrane performance

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Polyvinyl chloride (PVC) is one of the oldest and most common plastics in use today because of its low cost, durability and versatility with respect to fabrication and property modification (Krauskopf 1993). Most PVC geomembranes contain plasticizers as an additive to increase the flexibility, softness, workability, pliability and distensibility of the material. Plasticized PVC geomembranes have advantages over some other geomembranes, such as better resistance to differential settlement and puncture and significantly fewer field seams because PVC membranes can be factory-fabricated into large panels.

Group	Plasticizers	MW	Volatility plasticizer loss	Water extraction
Phathalic acid esters	Butyl benzyl phthalate	312	7.7	0.09
	Dimethoxyethyl phthalate	282	16.7	1.72
	Dibutyl phthalate (DBP)	278	44	0.25
	Butyl octyl phthalate (BOP)	334	9.5	0.04
	Butyl isodecyl phthalate (BDP)	363	11.5	0.08
	Dilsoctyll phthalate (DIOP)	391	4.3	0.03
	Dicapryl phthalate (DCP)	391	4.6	0.08
	Di-2-ethylhexy phthalate (DOP)	390	4.5	0.01
	n-Octyl n-decyl phthlate (ODP)	418	3.5	0.03
	Diisodecyl phthalate (DIDP)	446	1.8	0.02
Phosphoric acid esters	Triphenyl phosphate	326	3.6	0.04
	Cresyl diphenyl phosphate	337	1	0.03
	Tricresyl phosphate (TCP)	368	1.13	0.02
	2-Ethylhexyl diphenyl phosphate	362	–	–
Pholyfunctional fatty acid esters	Diisobutyl adipate (DIBA)	258	63	3.34
	Tri(ethylene glycol) di-2-ethylbutyrate	346	36.9	1.22
	Dibutyl sebacate (DBS)	314	–	–
	Diiooctyl sebacate (DOS)	426	4.2	0.015
	Butyl acetoxystearate	398	5.4	0.55
Miscellaneous plasticizers	Di(ethylene glycol) dibenzonate	314	5.5	0.28
	2, 2, 4-trimethyl-1, 3-pentanediol diisobutyrate	286	23.7	2.83

Table 1. Properties of commonly used plasticizers (from Stepek and Daoust 1983).

Over time, plasticizers can migrate from PVC geomembranes by contact with air, liquid and/or an absorbent solid material. This can result in reduced flexibility and, in extreme cases, noticeable shrinkage. While this is true, sufficient amounts of plasticizer are retained by the PVC material after migration if a minimum molecular weight is used in the plasticizer. For this reason, the PVC Geomembrane Institute (PGI) has developed the PGI-1104 Specification, which requires an average plasticizer molecular weight greater than or equal to 400 to ensure long-term plasticizer retention in the PVC geomembrane.

Comparing the structure of PVC to polyethylene, i.e., HDPE and LLDPE geomembranes, the repeating unit of -[CH2-CH2]n- is similar except for the presence of the chlorine (Cl) in PVC, which increases the inter-chain attraction between chloride and hydrogen in the chemical structure and results in a large value of hardness and stiffness (Brydson 1975). PVC has a unique characteristic that allows plasticizers and stabilizers to be absorbed. It can change the physical properties of PVC from a rigid solid to a soft gel or viscous liquid (Nass and Heiberger 1986). These additives have enabled PVC to be an extremely useful thermoplastic compound for a variety of applications.

Plasticization is classified into two types: internal plasticization and external plasticization (Mark and Gaylord 1964; Nass and Heiberger 1986; Wilson 1995). In internal plasticization, plasticizer molecules are attached to the polymer resin by primary bonds and incorporated as part of the polymer chain. Thus, plasticizer retention is typically not a concern with internal plasticization because of the strong primary bonds. In contrast, plasticizer molecules are not bound chemically to the polymer chain in external plasticization, which can result in the plasticizer being lost by evaporation, migration and extraction under some service conditions. Plasticizers used in PVC are either polymers or monomers. Polymeric plasticizers require a more difficult plasticization process and thus higher cost (Giroud and Tisinger 1993). As a result, monomeric plasticizers are most commonly used in PVC geomembranes.

Although the addition of plasticizers in PVC increases flexibility, softness, workability and distensibility, one of the limitations in using plasticized PVC geomembranes is volatile loss of external plasticizers from PVC into a surrounding medium. Volatile loss from PVC is composed of two major transfer processes:

- diffusion from inside the geomembrane to the geomembrane surface; and
- evaporation from the geomembrane surface (Sears and Darby 1982; Wilson 1995).

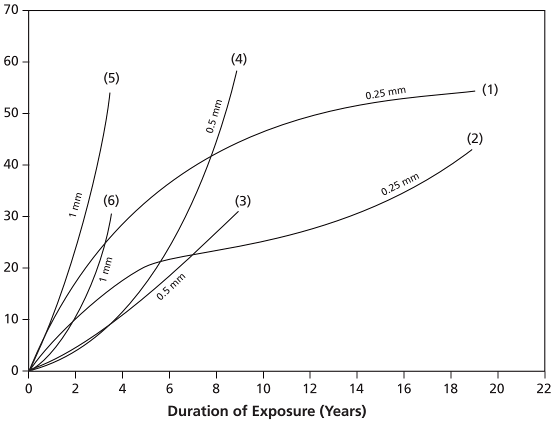
Highly plasticized PVC, which contains a more open structure, has a higher diffusion rate than lightly plasticized PVC. However, as the plasticizer is volatilized into the air, the van der Waals forces among the PVC chains bring the polymer molecules closer together, which increases the tortuosity in the PVC geomembrane. The increased tortuosity results in a progressive reduction in the diffusion rate as the plasticizer content is lowered. Therefore, there's a linear relationship between plasticizer loss due to diffusion and the square root of time. This relationship shows that plasticizer loss is strongly dependent on the initial plasticizer level in the PVC (Sears and Darby 1982; Wilson 1995). More importantly, the diffusion rate decreases with time until it reaches zero because of the increased tortuosity. The plasticizer will not be completely removed, as suggested by Giroud and Tisinger (1993).

Evaporation is usually negligible when there is rapid removal of vapor from the geomembrane surface. It should be noted that because there is no chemical bonding between polymer resin and external plasticizer molecules, evaporation of the plasticizer molecules into the surrounding air can occur continuously even at low temperatures. Once a PVC geomembrane is buried and protected by a soil layer, plasticizer loss due to evaporation is not significant because there is not enough free air to cause the plasticizer to evaporate and the soil temperature is lower and more constant than in air. Conversely, if soil moisture exists in the protective soil, plasticizer migration into the pore-water may occur.

Table 1 provides a list of commonly used plasticizers along with their molecular weight, volatility loss and water extraction. These data show that increasing the molecular weight of the plasticizer increases the resistance to evaporation. The increased retention is caused by the greater difficulty for larger plasticizer molecules to diffuse from inside the sheet to the surface—especially as the tortuosity increases.

Plasticizer migration from plasticized PVC into liquids can be represented by two mechanisms. If the molecular size of the extractant liquid is small enough to penetrate into the PVC polymer structure, extraction of the plasticizer can occur. The major mechanism for this extraction is the extractant diffuses into the plasticized PVC, dissolves the plasticizers, and then diffuses together with the dissolved plasticizers out to the surface of the PVC (Nass and Heiberger 1986). In such a case, the factor controlling the migration process is the compatibility of the plasticizer and extractant and the compatibility of the PVC resin and extractant.

In contrast, if the molecular size of the extractant is too large to penetrate the PVC polymer structure, the extractant cannot dissolve the plasticizer. Thus, migration can occur only by the plasticizer molecules diffusing themselves to the surface of the PVC, then dissolving into the extractant or liquid. In this case, plasticizer loss is controlled by the molecular weight of the plasticizer because increasing the molecular weight decreases the diffusion potential because the molecule size increases with increasing molecular weight.



(1). Canals, Western USA, geomembrane protected by soil, above water level
(2). Canals, Western USA, geomembrane protected by soil, below water level
(3). Landfill cover, Florida, geomembrane protected by soil, smooth bedding
(4). Landfil cover, Florida, geomembrane protected by soil, rough bedding
(5). Evaporation ponds, Sahara Desert, geomembrane exposed just above sulfuric acid level
(6). Evaporation ponds, Sahara Desert, geomembrane immersed in sulfuric acid

Figure 1. Plasticizer loss ratio versus duration of exposure (from Giroud and Tisinger 1993).

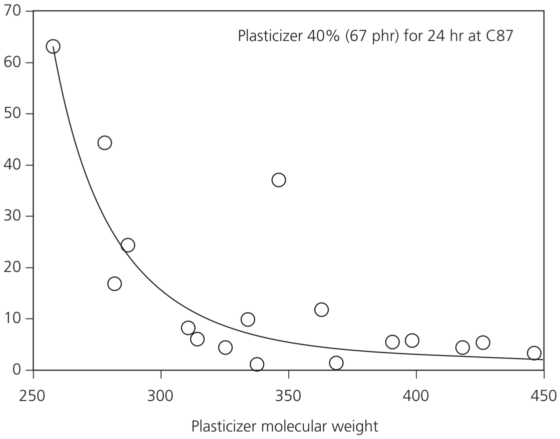


Figure 2. Relationship between plasticizer molecular weight and volatile plasticizer loss.

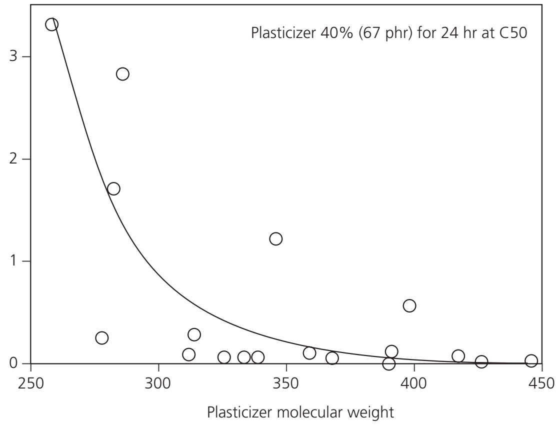


Figure 3. Relationship between plasticizer molecular weight and plasticizer loss by water extraction.

Certified properties[2]	ASTM	PVC 10	PVC 20	PVC 30	PVC 40	PVC 50	PVC 60
Thickness: mil (mm)	D 5199	10 ± 0.5 (0.25 ± 0.013)	20 ± 1 (0.51 ± 0.03)	30 ± 1.5 (0.76 ± 0.04)	40 ± 2 (1.02 ± 0.05)	50 ± 2.5 (1.27 ± 0.06)	60 ± 3 (1.52 ± 0.08)
Tensile properties[3]	D 882[4] (min.)						
Strength at break: lb/in (kN/m)		24 (4.2)	48 (8.4)	73 (12.8)	97 (17.0)	116 (20.3)	137 (24.0)
Elongation		250%	360%	380%	430%	430%	450%
Modulus at 100%: lb/in (kN/m)		10 (1.8)	21 (3.7)	32 (5.6)	40 (7.0)	50 (8.8)	60 (10.5)
Tear strength: lb (N)	D 1004[4] (min.)	2.5 (11)	6 (27)	8 (35)	10 (44)	13 (58)	15 (67)
Dimenstional stability	D 1204[4] (max chg)	4%	4%	3%	3%	3%	3%
Low temp. impact: ˚F (˚C)	D 1790[4] (pass)	-10 (-23)	-15 (-26)	-20 (-29)	-20 (-29)	-20 (-29)	-20 (-29)
Index properties[5]	ASTM	PVC 10	PVC 20	PVC 30	PVC 40	PVC 50	PVC 60
Specific gravity: g/cc	D 792 (typical)	1.2	1.2	1.2	1.2	1.2	1.2
Water extraction loss (max)	D 1239[4] (max loss)	0.15%	0.15%	0.15%	0.20%	0.20%	0.20%
Volatile loss	D 1203[4] (max loss)	1.5%	0.9%	0.7%	0.5%	0.5%	0.5%
Soil burial	G 160[4] (max chg)						
Break strength		5%	5%	5%	5%	5%	5%
Elongation		20%	20%	20%	20%	20%	20%
Modulus at 100%		20%	20%	20%	20%	20%	20%
Hydrostatic resistance: psi (kPa)	D 751[4]	42 (290)	68 (470)	100 (690)	120 (830)	150 (1030)	180 (1240)
Avg. plasticizer molecular weight	D 2138 / D 2124	>400	>400	>400	>400	>40	>400
Index properties	ASTM	PVC 10	PVC 20	PVC 30	PVC 40	PVC 50	PVC 60
Shear strength[3]: lb/in (kN/m)	D 882[4]	20 (3.47)	38.4 (6.7)	58.4 (10)	77.6 (14)	96 (17)	116 (20)
Peel strength[3]: lb/in (kN/m)	D 882[4]	10 (1.8)	12.5 (2.2)	15 (2.6)	15 (2.6)	15 (2.6)	15 (2.6)

1. PGI 1103 replaces PGI 1197 Specification effective 1/1/03 • 2. Certified properties are tested by lot as specified in PGI 1103 Appendix A. • 3. Metric values are converted from US values and are rounded to the available significant digits. • 4. Modifications or further details of test are described in PGI 1103 Appendix B. • 5. Index properties are tested once per formulation as specified in PGI 1103 Appendix A. • 6. Adipates and chlorinated secondary plasticizers shall not be used.

Table 2. PGI-1104, Material Specification for Flexible PVC Geomembranes for Containment.

Plasticizer migration from plasticized PVC into other polymeric materials has not been studied as extensively as plasticizer migration into air or liquid because of the small potential for this phenomenon. The main concern of plasticizer migration into another polymeric material is the change in the engineering properties of the receiving material which can alter the mechanical properties of the plasticized PVC. Wilson (1995) concludes that plasticizer structure plays a major role on plasticizer migration from plasticized PVC to other polymeric materials. Also, Wilson (1995) shows that increasing the plasticizer molecular weight and decreasing the linearity of plasticizer reduces the migration potential.

Three relevant internal molecular properties of a plasticizer that control plasticizer retention are plasticizer (Wilson 1995) molecular weight, linearity and polarity.

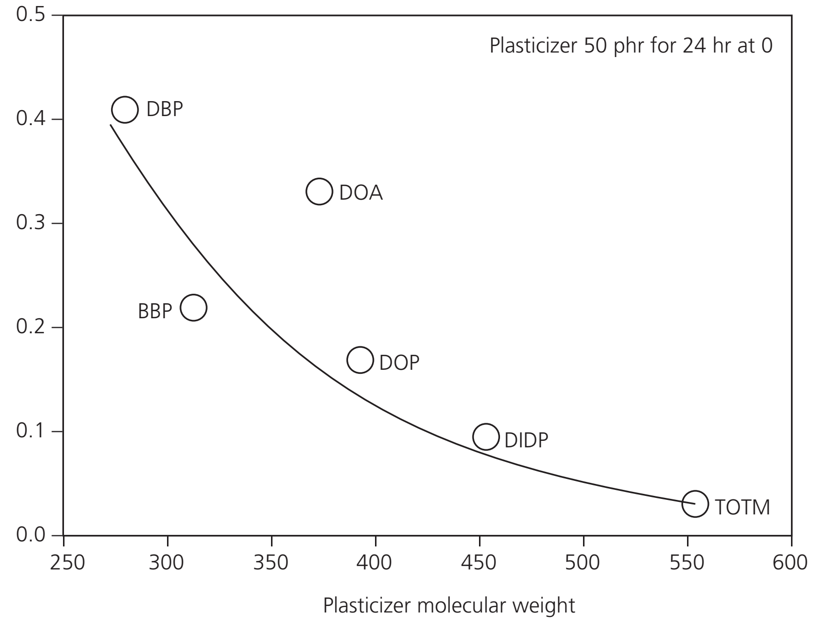


Figure 4. Relationship between plasticizer molecular weight and plasticizer migration into polyurethane foam.

Plasticizer mobility, commonly related to molecular weight, is one of the main factors in the diffusion of a plasticizer out of the polymer structure. The smaller the molecular weight of the plasticizer, the greater volatility and diffusion of the plasticizer. Conversely, increasing the plasticizer molecular weight increases the retention because, as the molecular weight increases, the size and length of the plasticizer increase, which makes it more difficult for the plasticizer to diffuse from the PVC molecular structure to the geomembrane surface. The main manufacturing dilemma is determining the plasticizer molecular weight that should be used to satisfy the conflicting requirements of increased plasticizer retention and maintaining compatibility with the PVC and efficient manufacturing.

Figure 1 presents a relationship between molecular weight of commonly used plasticizers and their volatile loss. Even though there is some scatter in the data, the volatile loss decreases with increasing plasticizer molecular weight. When the molecular weight is greater than about 400, the volatile loss is less than 10% for this aggressive experimental condition.

Figure 2 presents a relationship between molecular weight of common plasticizers and plasticizer loss by water extraction. The dependence of plasticizer migration into water is not significant in comparison with the other two mechanisms because, the nature of the liquid medium strongly affects the water extraction rather than volatility or diffusion. It is evident from Figure 2 that the migration is less than 1% for a plasticizer molecular weight greater than 300.

Figure 3 presents a relationship between the molecular weight of selected plasticizers and the plasticizer migration rate into flexible polyurethane foam. **Figure 3** shows that when the molecular weight is greater than about 400, the migration rate into the polyurethane foam is less than about 0.1 g/cm^2.

The advantage of using a higher plasticizer molecular weight is a decrease in the vapor pressure, which lowers the potential for volatile loss into air and migration into a liquid or solid. As a result, it is recommended that an average plasticizer molecular weight of 400 be used for PVC geomembranes.

Giroud and Tisinger (1993) state that linear phthalates generally do not migrate as easily as branched plasticizers. This remark is correct if only volatile loss of plasticizer is considered (Wilson 1995). Orem and Sears (1979) present the volatility of PVC manufactured with four different plasticizers with different levels of linearity. The linear plasticizer is less volatile and thus beneficial over the branched plasticizers when used in PVC for outdoor usage without a protective cover layer (Krauskopf 1993; Orem and Sears 1979).

For plasticizer migration into liquid or a solid, branched plasticizers have less plasticizer loss than linear plasticizers of equivalent molecular weight (Diebel 2002; Wilson 1995). If a plasticizer molecular structure is highly branched, the PVC geomembrane manufactured with this plasticizer will show poorer low temperature performance. Therefore, highly branched plasticizers restrict the range of operating temperature for the geomembrane. However, Diebel (2002) concludes that branched plasticizers perform better than linear plasticizers in extremely acidic and caustic environments. An increase in the branching index of a plasticizer results in an increase in the vapor pressure that increases volatile loss into air. However, the advantage of higher branchness is to retard plasticizer migration into a liquid or a solid and to provide greater resistance to chemical hydrolysis and biodegradation.

The internal factors controlling plasticizer retention should be considered in the manufacture quality control and in selecting the PVC geomembrane appropriate for a specific application. It is necessary to specify a minimum value of plasticizer molecular weight to ensure long-term plasticizer retention in the field. Many flexible PVC geomembranes are manufactured with a mixture of two or more plasticizers. Compounding various plasticizers helps achieve the optimum manufacturing cost/physical performance requirements, such as excellent low temperature performance, less volatility, and higher compatibility with PVC resin (Gonzalez-roa et al. 1991; Tomaselli et al. 1989; Wilson 1995). **Figures 1, 2, and 3** show that a plasticizer molecular weight greater than 400 provides excellent plasticizer retention. Therefore, the specification of average molecular weight of plasticizers equal to or greater than 400 is recommended to ensure excellent plasticizer retention in the field for containment purposes.

Even after publication of the PGI-1103 specification on 1 January 2003, competitors and regulators still expressed concern about whether or not PVC geomembranes will remain flexible. To address this issue head-on, the PVC Geomembrane Institute (PGI) amended the specification to include minimum requirements for the plasticizer used in the formulation of flexible PVC. The amount of the plasticizer does not have to be specified because the plasticizer amount controls the physical properties shortly after manufacturing and the physical properties must meet the required physical properties in the PGI-1103 specification. To ensure a suitable plasticizer is being used for long-term performance, the PGI-1104 specification requires that the plasticizer have an average molecular weight of 400 or greater. The PGI-1104 specification requires that the average molecular weight of the plasticizer be an index property and, thus, the molecular weight of the plasticizer will be measured when preparing and approving a geomembrane formulation. An index test is performed on the final production formulation of the PVC geomembrane. A certified statement of the test results for the formulation is to be made available to the consumer who can verify that the average molecular weight of the plasticizer exceeds 400 to ensure long-term performance of the PVC geomembrane. The molecular weight is tested in accordance with ASTM D 2124 for plasticizer extraction, followed by GC (Gas Chromatograph) or GCMS (Gas Chromatograph, Mass Spectrophotometer) for identification and molecular weight determination. The modified PGI-1104 specification is shown in **Table 2**. The average plasticizer molecular weight of 400, which is required for all geomembrane thicknesses, is listed under index properties. The PGI-1104 specification also precludes the use of adipates and chlorinated secondary plasticizers to ensure long-term plasticizer retention via Note 6 after the material properties (see **Table 2**). All United States-based manufacturers have been complying with this requirement, but the PGI believes modifying PGI-1104 provides a method to ensure the long-term quality of the plasticizer being used in flexible PVC geomembranes before installation. It is recommended that the weighted-average procedure be used to calculate the average molecular weight of the plasticizer when two or more plasticizers are incorporated into manufacturing the PVC geomembrane.

Summary

To ensure long-term desirable properties of flexible PVC, the PVC Geomembrane Institute (PGI) has issued the PGI-1104 material specification to include a requirement that the average molecular weight of the plasticizer exceed 400. It is anticipated that customers, regulators and engineers now can easily verify whether a suitable plasticizer was used in the geomembrane formulation and thus confirm that the resulting PVC geomembrane will exhibit excellent long-term durability. GFR

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