

PLASTICIZER MOLECULAR WEIGHT AND PLASTICIZER RETENTION IN PVC GEOMEMBRANES

Timothy D. Stark, Dept. of Civil & Environmental Engrg., Univ. of Illinois, Urbana, IL, USA
Hangseok Choi, Dept. of Civil & Environmental Engrg., Univ. of Illinois, Urbana, IL, USA
Patrick W. Diebel, Canadian General-Tower Ltd., Cambridge, Ontario, Canada

ABSTRACT

Plasticizers are used to make PVC flexible so it can be used as a geomembrane for containment purposes. Plasticizers can migrate from PVC geomembranes over time because of contact with air, liquid, and an absorbent solid material. Plasticizer migration can reduce the flexibility of PVC geomembranes resulting in brittle behaviour. This paper discusses the three mechanisms of plasticizer migration and the factors influencing these mechanisms, such as plasticizer molecular weight and linearity of plasticizers. The paper recommends that a minimum average plasticizer molecular weight of 400 be used to ensure long-term plasticizer retention in the field. The weighted-average method for calculating the average molecular weight is recommended when two or more plasticizers are incorporated into the PVC geomembrane.

RÉSUMÉ

La géomembrane de CPV (Chlorure de polyvinyle) utilisé pour les systèmes de rétention contient des plastifiants pour la souplesse de la membrane. Cependant avec le temps, les plastifiants peuvent émigrer de la géomembrane de CPV quand ils sont en contact avec l'air, liquides, et matériaux solides absorbants. La migration des plastifiants peut réduire la souplesse et causer la géomembrane de CPV à devenir cassante. Ce document discute les trois mécanismes qui sont la cause et les facteurs d'influence pour la migration des plastifiants, surtout en ce qui concerne le poids moléculaire et le comportement linéaire des plastifiants. Ce document recommande des plastifiants ayant une moyenne minimum moléculaire de 400 pour protéger la rétention des plastifiants pour le long terme. Nous conseillons la méthode de moyenne pondérée pour les calculs des poids moléculaires moyens de deux plastifiants ou plus incorporés dans la géomembrane de CPV.

1. INTRODUCTION

Polyvinyl Chloride (PVC) is one of the oldest and most common plastics in use today because of the low cost, durability, and versatility with respect to fabrication and property modification (Krauskopf 1993). A flexible PVC geomembrane is a common application of this polymeric product. The usage of flexible PVC geomembranes ranges from roofing, landfill liner and cover systems, canal liners, mining applications, to waterproofing for dams. Flexible PVC geomembranes have several advantages over other geomembranes. The advantages include greater flexibility that results in better resistance to differential settlement and puncture, significantly less field seams because it can be factory fabricated into large panels, the field seams can be formed using single or dual-track wedge-welding equipment, use of typical construction quality assurance (CQA) and construction quality control (CQC) procedures, if air channel testing of dual-track wedge-welding is used destructive seam testing can be reduced or eliminated (Stark *et al.* 2004; Thomas *et al.* 2003), smaller geomembrane wrinkles because of high interface strength and a low coefficient of thermal expansion, a larger allowable tensile strain, the lack of a yield point even at low temperatures, and high interface shear resistance (Hillman and Stark 2001) for slope stability.

Most PVC geomembranes contain plasticizers as an additive to increase the flexibility, softness, workability, pliability, and distensibility of the material. Plasticizers are typically a high boiling, organic liquid that reduces the glass temperature of the polymer where the polymer changes from brittle to flexible. Thus, the addition of plasticizer reduces the tensile strength and elastic modulus of PVC but increases the elongation at tensile failure at ambient temperature.

One of the limitations in using plasticized PVC in practice is the possibility of plasticizer migration over time for various service conditions. Plasticizers can be removed from PVC geomembranes by contact with air, liquid, and/or an absorbent solid material. Plasticizer loss reduces the flexibility of PVC geomembranes and in extreme cases results in noticeable shrinkage. In this paper, the mechanisms and factors influencing plasticizer retention are discussed and recommendations for selecting a suitable plasticizer are presented based on the average molecular weight of the plasticizer.

2. MECHANISMS AFFECTING PLASTICIZER RETENTION

The addition of plasticizers in PVC increases flexibility and decreases the glass transition temperature (T_g), which is the temperature the plastic becomes brittle

(Hammond *et al.* 1993). A potential limitation in using plasticized PVC geomembranes is plasticizer retention when the plasticized PVC geomembrane is in contact with a surrounding medium. If an incorrect plasticizer is used or the geomembrane is used in an incorrect application, plasticizer may migrate, resulting in a geomembrane with insufficient flexibility. The mechanisms controlling plasticizer retention in contact with these three media, air, liquid, or a solid, are described below.

2.1 Plasticizer retention in air

Volatile loss or evaporation of external plasticizers from PVC into the surrounding air is a common mechanism of plasticizer migration. Volatile loss from PVC is composed of two major transfer processes, which are: (1) diffusion from inside the geomembrane to the geomembrane surface and (2) evaporation from the geomembrane surface (Sears and Darby 1982; Wilson 1995).

The rate of diffusion is related to the plasticizer molecular structure and the permeability of the PVC geomembrane. The plasticizer molecular structure can be characterized by the molecular weight and linearity of the plasticizer. Shortly after manufacturing, highly plasticized PVC has a higher diffusion rate than lightly plasticized PVC. However, as the plasticizer is volatilized into 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. Papakonstantinou and Papaspyrides (1994) experimentally show a linear relationship between plasticizer loss due to diffusion and the square root of time which is expressed as:

$$\frac{M_t}{M_\infty} = 2\sqrt{\frac{Dt}{\pi l^2}} \quad [1]$$

where M_t is the amount of plasticizer loss at time t ; M_∞ is the amount of plasticizer loss at equilibrium; D is the diffusion coefficient; t is the time; and l is the thickness of PVC. This relationship shows that the diffusion rate will decrease with time because of the increased tortuosity and the plasticizer will not continue to be removed at an increasing rate as suggested by Giroud and Tisinger (1993).

The evaporation rate in the second transfer process is a function of vapor pressure on the surface of the PVC geomembrane. When vapor pressure is a controlling factor for plasticizer loss, volatile plasticizer loss is directly proportional to time and independent of plasticizer concentration if the concentration is over the plasticization threshold (Sears and Darby 1982). In most applications, evaporation is usually the controlling factor for volatile loss, and thus plasticizer vapor pressure provides a good indicator of the rate of plasticizer loss from

the PVC geomembrane under many service conditions (Wilson 1995).

The volatile loss of plasticizer from PVC membranes to the surrounding air plays an important role in outdoor roofing systems and in PVC geomembrane-lined pond systems without a protective soil cover (Bailey *et al.* 1997; Giroud and Tisinger 1993; Holzmann 1988; Orem and Sears 1979; Young and Kovach 1995). Even though a PVC geomembrane is covered with a protective soil layer, the volatile loss cannot be neglected if the protective soil contains little moisture and provides enough free air for evaporation, e.g., poorly compacted and dry gravel, which may provide enough free air for evaporation. To reduce the potential of evaporation, a finer grained soil should be used for the protective soil cover. If a moist fine grained soil is used for the protective cove, diffusion will likely be the main volatile loss mechanism and thus there will not be a significant amount of migration because diffusion decreases rapidly with time.

Krauskopf (1993) states that trimellitate plasticizers are significantly less volatile than phthalate plasticizers because an increase in the carbon number in the alkyl group, i.e., greater molecular weight, imparts significant reduction in plasticizer volatility. Many researchers (Giroud 1984; Mark and Gaylord 1964; Stepek and Daoust 1983; Wilson 1995) suggest that increasing the plasticizer molecular weight and/or decreasing the degree of branching of the plasticizer can reduce volatile loss from PVC. Table 1 provides a list of commonly used plasticizers along with their molecular weight, volatility loss, and water extraction. These data show the plasticizers most resistant to volatilization have higher molecular weights. The increased retention is caused by the greater difficulty for larger plasticizer molecules to diffuse from inside the sheet to the sheet surface especially as the tortuosity increases. The volatility loss is measured for 24 hours at a temperature of 87 °C over activated carbon. The water extraction is performed for 24 hours at a temperature of 50 °C. The detailed mechanism for water extraction is discussed in the following section.

2.2 Plasticizer retention in liquid

Plasticizer migration from plasticized PVC into liquids, such as water, oils, waxes, alcohols, and other agents, 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. At a higher level of initial plasticizer concentration, the extraction can be faster and more extensive if the extractant can diffuse into the PVC (Nass and Heiberger 1986).

Conversely, 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 only occur by the plasticizer molecules diffusing to the surface of the PVC and then dissolving into the extractant or liquid. This phenomenon can occur in heavy oils such as paraffin oil and solvent refined lubricating oils as the extractant of which molecules are too large to penetrate the PVC (Kampouris 1975; Messadi *et al.* 1981). In this case, the diffusion coefficient of the plasticizer is the controlling factor on plasticizer retention, and plasticizer loss is a function of the molecular weight of the plasticizer because increasing the molecular weight decreases the diffusion potential as discussed previously. Also, the plasticizer loss is dependent on the plasticizer level in the PVC (Messadi *et al.* 1981).

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

Group	Plasticizer	MW ¹	Volatile loss ² (%)	Water extraction ³ (%)
Phthalic acid esters	Butyl benzyl phthalate	312	7.7	0.09
	Dimeth-oxyethyl phthalate	282	16.7	1.72
	Dibutyl phthalate (DBP)	278	44.0	0.25
	Butyl octyl phthalate (BOP)	334	9.5	0.04
	Butyl isodecyl phthalate (BDP)	363	11.5	0.08
	Diisooctyl phthalate (DIOP)	391	4.3	0.03
	Dicapryl phthalate (DCP)	391	4.6	0.08
	Di-2-Ethylhexyl phthalate (DOP)	390	4.5	0.01
	n-Octyl n-decyl phthalate (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	0.03
	Tricresyl phosphate (TCP)	368	1.1	0.02
	2-Ethylhexyl diphenyl phosphate	362	-	-
Polyfunctional fatty acid esters	Diisobutyl adipate (DIBA)	258	63.0	3.34
	Tri(ethylene glycol) di-2-ethylbutyrate (DIBA)	346	36.9	1.22
	Dibutyl sebacate (DBS)	314	-	-
	Diioctyl sebacate (DOS)	426	4.2	0.02
	Butyl acetoxystearate	398	5.4	0.55
	Di(ethylene glycol) dibenzonate	314	5.5	0.28
Miscellaneous plasticizer	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	286	23.7	2.83

¹ Plasticizer molecular weight

² Plasticizer 40% (67 phr) for 24 hrs at 87 °C

³ Plasticizer 40% (67 phr) for 24 hrs at 50 °C

Plasticizer migration from plasticized PVC into water is typically observed in a pond liner below the water line. Plasticizer migration can also occur in a landfill liner system if the PVC geomembrane is submerged by leachate. Table 1 shows typical plasticizers used in practice along with each molecular weight and water extraction loss.

2.3 Plasticizer retention adjacent to solid

Plasticizer migration from plasticized PVC into other polymeric materials has not been studied as extensively as plasticizer migration into air (i.e., volatile loss) and liquid. Plasticizers can migrate from plasticized PVC to any adjacent absorbent material if the resistance at the interface between two materials is not too high and if the plasticizer is more compatible with the receiving material (Nass and Heiberger 1986; Papakonstantinou and Papaspyrides 1994; Wilson 1995).

Wilson (1995) summarizes the effect of plasticizer migration into receiving materials that are used as coatings, structural components, and adhesive bonds. Besides the effect of plasticizer migration on the receiving polymer(s), the migration can alter the mechanical properties of the plasticized PVC, which is discussed below.

Papakonstantinou and Papaspyrides (1994) studied plasticizer migration for a system of PVC plasticized with DOP plasticizer and unplasticized PVC that represents a two-sided diffusion condition at a temperature of 64 °C. In this study, the relationship between the migration ratio and the square root of time is linear, and Fick's law can be used to describe the plasticizer migration phenomena from the plasticized PVC for short-time periods.

Wilson (1995) concludes that plasticizer structure plays a major role on plasticizer migration from plasticized PVC to other polymeric materials. Wilson (1995) also shows that increasing the plasticizer molecular weight and decreasing the linearity of plasticizer reduces the migration potential. The significance of molecular weight and linearity of plasticizers will be discussed subsequently.

The phenomenon of plasticizer migration from plasticized PVC into other polymeric materials needs to be considered and tested prior to being specified and used for a landfill liner and cover system. When a flexible PVC geomembrane is used together with drainage geocomposite, comprised of a geonet laminated with geotextiles, it is possible that plasticizer may migrate from the PVC geomembrane to the drainage geocomposite. In addition, when flexible PVC is used in a landfill cover system with a drainage geocomposite to minimize infiltration into the landfill, plasticizer also could migrate into this drainage geocomposite. The current polymers used in these materials are polar (mainly olefins) and thus are not susceptible to plasticizer migration.

3. FACTORS CONTROLLING PLASTICIZER RETENTION

External or environmental factors that influence plasticizer retention include temperature, chemicals, microorganisms, and the characteristic of the contact material, such as air, liquid, and a solid (Giroud and Tisinger 1993; Nass and Heiberger 1986; Wilson 1995). Internal or intrinsic factors controlling plasticizer retention are related to the molecular properties of the plasticizer. There are three relevant molecular properties of a plasticizer that control plasticizer retention (Wilson 1995): (1) molecular weight; (2) linearity; and (3) polarity. Because all of the plasticizers commonly used in PVC geomembranes are polar, only the molecular weight and linearity of plasticizers are discussed in the following section. Prior to commencing experiments to characterize mechanical and chemical properties of plasticized PVC geomembranes, identifying the molecular properties of the plasticizer will facilitate prediction of the long-term behaviour of PVC geomembranes.

3.1 Molecular weight of plasticizer

Plasticizer mobility is one of the main factors in the diffusion of a plasticizer out of the polymer structure. It is common to relate plasticizer mobility with plasticizer molecular weight. The smaller the molecular weight of the plasticizer, the greater volatility and diffusion of the plasticizer. Conversely, the higher the plasticizer molecular weight, the lower the migration. However, a higher plasticizer molecular weight also reduces the compatibility and efficiency of the plasticization process. Increasing the plasticizer molecular weight increases plasticizer retention because as the molecular weight increases the size of the plasticizer increases, which makes it more difficult for the plasticizer to diffuse from the PVC molecular structure to the geomembrane surface. Therefore, a manufacturing dilemma is determining the plasticizer molecular weight that should be used to satisfy the conflicting requirements of increased plasticizer retention and decreased manufacturing compatibility and processability.

Figure 1 presents a relationship between molecular weight of commonly used plasticizers and their volatile loss (i.e., data from Table 1). The volatile loss is measured for 24 hours at a temperature of 87 °C over activated carbon and the initial plasticizer content in each case is 40%, i.e., 67 phr (Stepek and Haoust 1983). Even though there is some scatter in the data, the volatile loss decreases with increasing the plasticizer molecular weight. When the molecular weight is greater than about 400, the volatile loss is less than 2% for this aggressive experimental condition.

Figure 2 presents a relationship between molecular weight of common plasticizers and plasticizer loss by water extraction (i.e., data from Table 1). The water extraction is measured for 24 hours at a temperature of 50 °C and the initial plasticizer content in each case is 40%, i.e., 67 phr (Stepek and Haoust 1983). The

dependence of plasticizer migration into water is not significant in comparison with the other two mechanisms (i.e., volatile loss and migration into a solid), because as described previously 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.

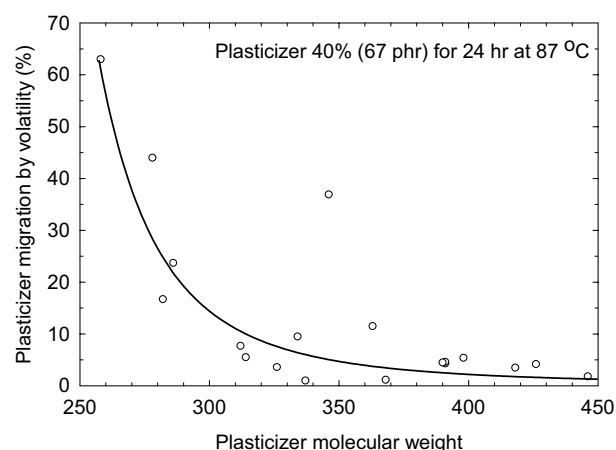


Figure 1. Relationship between plasticizer molecular weight and volatile plasticizer loss

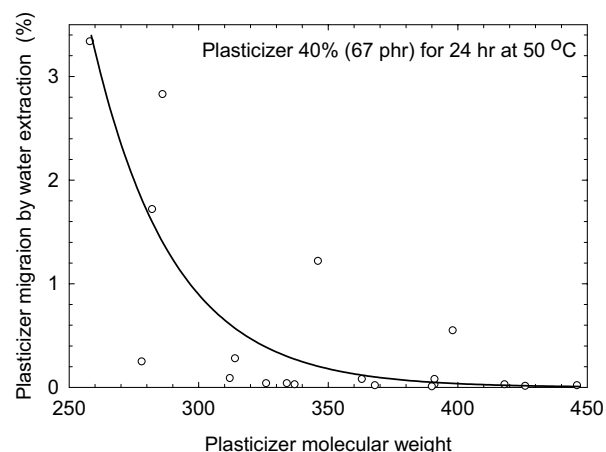


Figure 2. Relationship between plasticizer molecular weight and plasticizer loss by water extraction

Figure 3 presents a relationship between the molecular weight of selected plasticizers and the plasticizer migration rate into flexible polyurethane foam. The migration rate is measured for 24 hours at a temperature of 70 °C and the initial plasticizer content in each case is 50 phr (Wilson 1995). Figure 3 shows that increasing the plasticizer molecular weight decreases the plasticizer migration into the solid. 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 .

In summary, an increase in the molecular weight of plasticizers results in more time and energy required for the absorption of the plasticizer into the PVC resin during manufacturing. However, the advantages of using a higher plasticizer molecular weight include a decrease in the vapor pressure, which lowers the potential for volatile loss into air and migration into liquid and solid. As a result, it is recommended subsequently that a minimum average plasticizer molecular weight of 400 be used for PVC geomembranes to ensure excellent long-term performance. This supports independent testing of PVC with a plasticizer molecular weight greater than 400 submerged in leachate by TRI/Environmental (2003), which showed no significant physical changes after exposure.

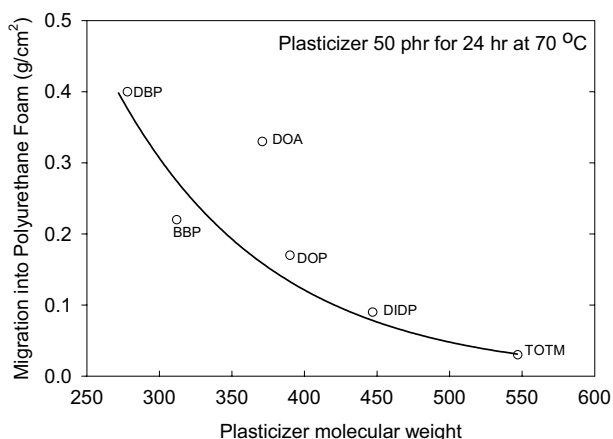


Figure 3. Relationship between plasticizer molecular weight and plasticizer migration into Polyurethane foam

3.2 Linearity of plasticizer

The linearity or branchness of the plasticizer is related to the shape of a plasticizer molecular structure. A plasticizer composed of straight chains is referred to as a linear plasticizer. In contrast, a plasticizer comprised of branched chains in the molecular structure is referred to as a branched plasticizer. To quantify the degree of the plasticizer linearity or branchness, the branching index is usually used. The branching index is the percentage of the total number of carbon atoms contained in side chains (Wilson 1995). The greater the branchness index, the lower the linearity of the plasticizer molecular structure.

Giroud and Tisinger (1993) state that linear phthalates generally do not migrate as easily as branched plasticizers such as DOP. 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 four plasticizers consist of two highly branched plasticizers, i.e., diisodecyl phthalate

(DIDP) and diisononyl phthalate (DINP), one singly branched plasticizer, i.e., DOP, and one linear plasticizer, i.e., heptyl-nonyl-undecyl phthalate. 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 can have less plasticizer loss than linear plasticizers (Diebel 2002; Wilson 1995). Figure 3 shows that DOP and DOA have similar molecular weights, i.e., the molecular weights of DOP and DOA are 390 and 371, respectively. However, the plasticizer migration of DOA is about two times greater than DOP because DOA is a highly linear plasticizer and DOP is a branched plasticizer.

If a plasticizer molecular structure is highly branched, the PVC geomembrane manufactured with this plasticizer will show poorer low temperature performance, i.e., the PVC geomembrane has a higher glass transition temperature, and becomes rigid and brittle sooner as the temperature decreases. Therefore, highly branched plasticizers may have restrictions in the required operating temperature ranges for the geomembrane. Thus, the operating conditions for the geomembrane should be carefully studied to allow the development of an optimal formulation. Diebel (2002) concludes that branched plasticizers perform better than linear plasticizer in extremely acidic and caustic environments. In summary, 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 liquid or a solid.

4. DESIGN SPECIFICATION

Plasticizer retention is controlled by many external and internal factors. The external or environmental factors such as temperature, chemicals, microorganisms, and the characteristic of the contact material such as air, liquid, and a solid, are related to the site-specific condition. These external factors should be considered in design and construction quality control for the liner and cover systems that use PVC geomembranes as a barrier. In contrast to the external factors, the internal factors controlling plasticizer retention include the molecular weight and linearity of the plasticizer. These internal factors should be considered by the manufacturer because the type of plasticizer can influence the processability.

In order to maximize plasticizer retention and to help ensure a functional geomembrane for many years, it is recommended to specify a minimum value of plasticizer molecular weight. The specification recommended subsequently in this paper is that the average molecular weight of the plasticizer in PVC geomembranes should be equal or greater to than 400. 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.

Although some data for plasticizer mixtures have been published and plasticizer suppliers occasionally provide formulating services to develop the lowest cost plasticizer combination, most plasticizer suppliers and literature provide standard physical properties only for an individual plasticizer. Wilson (1995) recommends that a weighted-average method of each plasticizer be used for averaging some physical properties of plasticizer compounds such as the softness number and cold flex temperature if no specific interactions occur between the plasticizers. The weighted-average method can be used to obtain the average molecular weight if more than one plasticizer is used. For example, if the PVC geomembrane uses DOP of 30 phr and DIDP of 20 phr in the plasticization process and the total plasticizer content is 50 phr. The molecular weights of DOP and DIDP are 390 and 446, respectively. The average molecular weight of this plasticizer compound is calculated using the weighted-average method as follows:

$$\begin{aligned} \text{Ave. molecular weight} &= \frac{(M_{\text{DOP}} \times C_{\text{DOP}}) + (M_{\text{DIDP}} \times C_{\text{DIDP}})}{C_{\text{TOTAL}}} \\ &= \frac{(390 \times 30) + (446 \times 20)}{50} = 412 \end{aligned} \quad [2]$$

where M_{DOP} and M_{DIDP} are the molecular weight of DOP and DIDP, respectively. C_{DOP} and C_{DIDP} are the plasticizer content of DOP and DIDP, respectively, and C_{TOTAL} is the total plasticizer content. Although DOP is one of the most common plasticizers used in PVC geomembranes, the molecular weight of DOP (i.e., 390) does not meet the recommended plasticizer molecular weight. However, by compounding DOP with DIDP, which has a higher molecular weight (i.e., 446) than DOP, an average molecular weight greater than 400, i.e., 412, can be obtained to satisfy the recommended value.

Even after publication of the PGI-1103 specification on January 1, 2003, competitors still expressed concern about whether or not PVC geomembranes will remain flexible. To address this issue head-on, the PVC Geomembrane Institute (PGI) decided to amend the PGI-1103 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. However, the type of plasticizer may not be accounted for because the type of plasticizer can affect the long-term behavior of flexible PVC. In other words, the plasticizer may be suitable to satisfy the short-term flexibility and material

requirements imposed by the PGI-1103 specification, but may not satisfy long-term flexibility requirements because of plasticizer migration.

To ensure a suitable plasticizer is being used for long-term performance, the new 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/fabricator 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 measured 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. In the modified PGI-1104 specification, an average plasticizer molecular weight of 400 is required for all PVC geomembrane thicknesses.

The PGI-1104 specification also precludes the use of adipates and chlorinated secondary plasticizers to ensure long-term plasticizer retention. Most, if not all, manufacturers are already 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.

5. CONCLUSIONS

The purpose of this paper is to clarify the mechanisms and factors controlling plasticizer retention in PVC geomembranes and to recommend a means for ensuring that appropriate plasticizers are used in PVC geomembranes to ensure long-term performance. The following conclusions can be discerned from information presented in this paper.

Plasticizer loss can reduce the flexibility of PVC geomembranes. Plasticizer loss is attributed to the following three mechanisms, volatile loss, migration into a liquid, and migration into an absorbent solid. The molecular weight and linearity of the plasticizer play a major role in controlling plasticizer loss caused by these three mechanisms. The advantages of higher plasticizer molecular weight include decreasing the vapor pressure of the plasticizer, which lowers volatile loss into air and slows plasticizer migration into liquids and solids. An increase in the branching index of a plasticizer results in an increase in vapor pressure that enhances volatile loss into air. However, advantages of higher plasticizer branchness include retardation of plasticizer migration into liquids and solids and greater resistance to chemical hydrolysis and biodegradation.

The new PGI-1104 specification requires an average plasticizer molecular weight greater than or equal to 400 to ensure long-term plasticizer retention. 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.

6. REFERENCES

- Bailey, D.M., Foltz, S.D., Rossiter, W.J., and Lechner, J.A., 1997, "Performance of Polyvinyl Chloride (PVC) Roofing: Results of A Ten-Year Field Study", Proceedings of 4th International Symposium on Roofing Technology, Gaithersburg, Maryland, pp. 253-264.
- Brydson, J.A., 1975, *Plastics Materials*, 3rd ed., The Whitefriars Press Ltd, p. 731
- Diebel, P.W., 2002, "The Effect of Formulation on the Physical Properties and Durability of Flexible PVC Geomembranes", Proceedings of the 7th International Conference on Geosynthetics, Industrial Fabrics Association International (IFAI), pp. 28 - 34.
- Giroud, J. P., 1984, "Aging of PVC Geomembranes in Uranium Mine Tailing Ponds", Proceedings of International Conference of Geomembranes, Vol. 2, Denver, CO, pp. 311-316.
- Giroud, J. P. and Tisinger, L. G., 1993, "The Influence of Plasticizers on the Performance of PVC Geomembranes", *Proceedings of Geosynthetic Liner Systems: Innovation, Concerns, and Design*, IFAI, St. Paul, MN, pp. 169-196.
- Hammond, M., Hsuan, G., Mackey, R.E., and Levin, S.B., 1993, "The Reexamination of a Nine-Year-Old PVC Geomembrane Used in Top Cap Application", *Proceedings of the 31st Annual SWANA Conference*, San Jose, CA, pp. 365-380.
- Hillman, R.P. and Stark, T.D., 2001, "Shear Strength Characteristics of PVC Geomembrane-Geosynthetic Interfaces", *Geosynthetics International*, IFAI, Vol. 8, No. 2, pp. 135-162.
- Holzmann, 1988, "To Determine the Criteria for Selecting Plasticizers for Roofing Sheet", BASF Internal Technical Report.
- Kampouris, E.M., 1975, "The Migration of Plasticizers into Petroleum Oils", *European Polymer Journal*, Vol. 11, pp. 795-710.
- Krauskopf, L.G., 1993, "Plasticizer Structure/Performance Relationships", *Journal of Vinyl Technology*, Vol. 15, No. 3, pp. 140-147.
- Mark, H.F. and Gaylord, N.G., 1964, *Encyclopedia of Polymer and Technology: Plastics, Resins, Rubbers, Fibers*, Interscience Publisher, New York, U.S.
- Messadi, D., Vergnaud, J., and Hivert, M., 1981, "A New Approach to the Study of Plasticizer Migration from PVC into Methanol", *Journal of Applied Polymer Science*, Vol.
- Nass, L.I. and Heiberger, C.A., 1986, *Encyclopedia of PVC: Vol. 1 Resin Manufacture and Properties*, Marcel Dekker, Inc. p. 702.
- Orem, J.H. and Sears, J.K., 1979, "Flexible Poly (Vinyl Chloride) for Long Outdoor Life", *Journal of Vinyl Technology*, Vol. 1, No. 2, pp. 79-83.
- Papakonstantinou, V. and Papaspyrides, C.D., 1994, "Plasticizer Migration from Plasticized into Unplasticized Poly (Vinyl Chloride)", *Journal of Vinyl Technology*, Vol. 16, No. 4, pp. 192-196.
- PVC Geomembrane Institute (PGI), 2003, "PVC Geomembrane Material Specification 1103", University of Illinois, Urbana, IL, www.pvcgeomembrane.com, January 1, 2003.
- Sears, J.K. and Darby, J.R., 1982, *The Technology of Plasticizers*, John Wiley & Sons, p.1166.
- Stark, T.D., Choi, H., and Thomas, R.W., 2004, "Low Temperature Air Channel Testing of Thermally Bonded PVC Geomembrane Seams", *Geosynthetics International Journal*, accepted and in print.
- Stepek, J. and Daoust, H., 1983, *Additives for Plastics*, Springer-Verlag, p. 243.
- Thomas, R. W., Stark, T. D., and Choi, H., 2003, "Air Channel Testing of Thermally Bonded PVC Geomembrane Seams", *Geosynthetics International Journal*, Vol. 10, No. 2, pp. 56-69.
- TRI/Environmental, 2003, "Laboratory Testing of a 30 mil PVC Geomembrane for Waste Containment: Chemical Resistance Testing", Final Report, TRI/Environmental, Inc.
- Wilson, A. S., 1995, *Plasticizers: Principles and Practice*, The Institute of Materials,
- Young, E.G.J. and Kovach, C.A., 1995, "Study of the Durability of a PVC Geomembrane-Lined Pond Without Soil Cover", *Geosynthetics '95*, pp. 907-919.