PLASTICIZER RETENTION IN PVC GEOMEMBRANES

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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. 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.

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. Plasticizerloss 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

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:

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

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 cover, 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).

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

Group	Plasticizer	MW[1]	Volatile loss[2] (%)	Water extraction[3] (%)
Phathalic acid esters	Butyl benzyl phthalate	312	7.7	0.09
	Dimeth oxyethyl phthalate	282	16.7	1.72
	Dibutyl phthatate (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
	Di2- 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	-	-
	Diiooctyl sebacate (DOS)	426	4.2	0.02
	Butyl acetoxystearate	398	5.4	0.55
Miscellaneous plasticizer	Di(ethylene glycol) dibenzonate	314	5.5	0.28
	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

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 deceases the diffusion potential as discussed previously. Also, the plasticizer loss is dependent on the plasticizer level in the PVC (Messadi *et al*. 1981).

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).

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 FIELD OBSERVATIONS OF PLASTICIZER RETENTION

Many researchers (Fayoux *et al.* 1993; Giroud and Tisinger 1993; Hammond *et al.* 1993; Levin and Hammond 1990; Morrison and Comer 1995; Morrison and Starbuck 1984; Young and Kovach 1995) have investigated the mechanism, rate, and factors influencing plasticizer retention in PVC geomembranes.

Giroud and Tisinger (1993) summarize plasticizer retention in PVC geomembranes in the following three cases: canal liners in the Western U.S. (Morrison and Starbuck 1984), a landfill cover in Florida (Hammond *et al.* 1993; Levin and Hammond 1990), and evaporation ponds in the Sahara Desert (Giroud and Tisinger 1993). The case histories are used to develop a relationship between plasticizer loss ratio and exposure time for these three cases. The plasticizer loss ratio is defined by Giroud and Tisinger (1993) as the ratio of removed plasticizer mass to initial plasticizer massand is calculated using:

$$P_L = \frac{C_{P0} - C_P}{C_{P0}\left(1 - C_P\right)} \tag{2}$$

where C_{P0} and C_P are the initial and current plasticizer content by mass, respectively. Giroud and Tisinger (1993) gives the impression that plasticizer loss increases exponentially and will continue until all plasticizer is removed. As noted previously, this phenomenon does not occur in practice because as plasticizer migrates, the tortuosity increases which makes migration more difficult with time. Thus, each case is reviewed below to revise the relationships presented by Giroud and Tisinger (1993) and clarify the chemical behavior of PVC geomembranes.

The performance of 0.25 mm thick PVC geomembranes in canals in the Western U.S. was conducted by The U.S. Bureau of Reclamation (Morrison and Starbuck 1984). All of the PVC geomembranes were covered and protected by a soil layer and had an initial plasticizer content (C_{P0}) between 31% and 40%. Giroud and Tisinger (1993) selected eight different canal locations that correspond to a service period ranging from 2 to 19 years and plotted the average plasticizer loss ratio with exposure time. The U.S. Bureau of Reclamation published laboratory test results and field observations for more than 30 years on the performance of PVC geomembrane canal liners (Morrison and Comer 1995). On the basis of these data, the relationship between the average plasticizer loss ratio and exposure time is reevaluated and the new relationships are shown as trend lines (1) and (2) in Figure 1. The trend line (1) in Figure 1 represents 0.25 mm thick PVC geomembranes above the water level. Although the PVC geomembranes used in these sites are fairly thin, i.e., 0.25 mm thick, the plasticizer loss ratio eventually becomes constant at around 55% after about 20 years of service time, which is in agreement with Giroud and Tisinger (1993). The plasticizer loss ratio is calculated using Equation (2).

The trend line (2) in Figure 1 shows the relationship between plasticizer loss ratio and exposure time for ten sites where 0.25 mm thick PVC geomembranes are placed below the water level. The plasticizer loss ratio eventually becomes constant at around 45% after about 20 years of service time, which does not agree with Giroud and Tisinger (1993) in which the plasticizer loss ratio is still increasing instead of becoming constant after about twenty years.

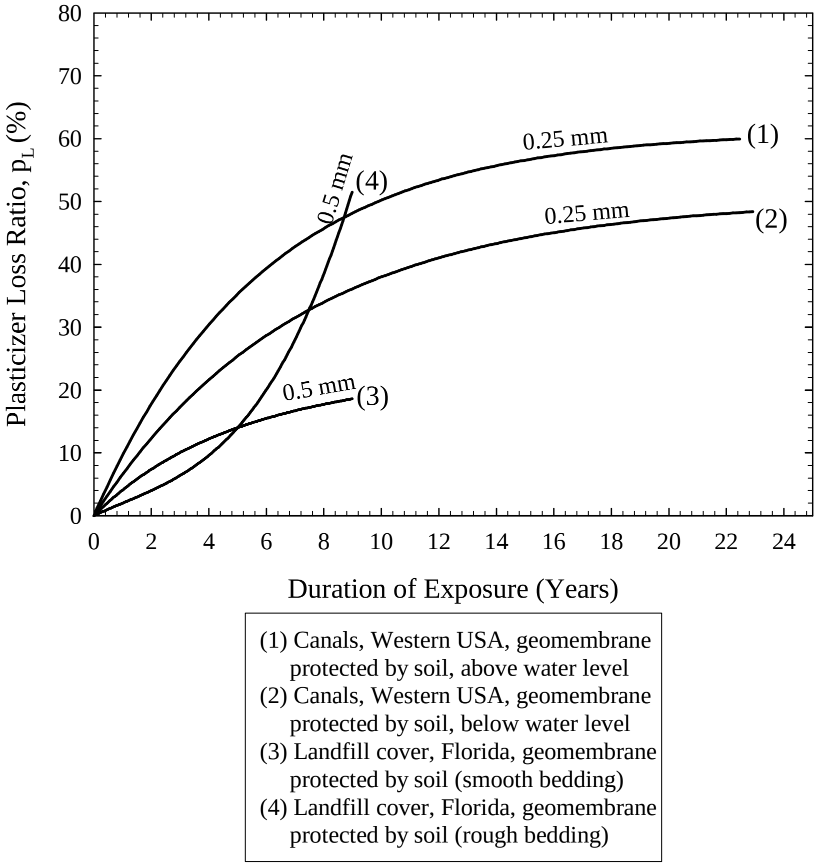

Figure 1. Revised relationship between plasticizer loss ratio versus duration of exposure.

The PVC geomembrane samples obtained from within the water prism generally exhibit less plasticizer migration than those obtained above the water level. The rate of plasticizer loss shown as the trend lines (1) and (2) in Figure 1 is probably an upper bound because the thickness of PVC geomembranes in this case study is relatively thin compared to other PVC geomembrane applications. Morrison and Comer (1995) show the results of laboratory volatility tests that indicate plasticizer loss rates generally decrease with increasing PVC geomembrane thickness because it is more difficult for plasticizer to migrate from the center of the geomembrane to the edge where it can be lost.

Hammond *et al*. (1993) and Levin and Hammond (1990) review the performance of a PVC geomembrane used in a final cover system for the Dyer Boulevard Landfill in West Palm Beach, Florida. The PVC geomembrane was studied after five and nine years of service. A 0.5 mm thick PVC geomembrane was used as the barrier layer in the final cover system. The PVC geomembrane was covered with 0.6 m thick protective soil.

The initial plasticizer content (C_{P0}) was assumed by Giroud and Tisinger (1993) to be 35%. After five years of service, Levin and Hammond (1990) report that the PVC geomembrane lost 13% of the initial plasticizer content. Giroud and Tisinger (1993) report the plasticizer loss ratio for five years as 15%. Nine years after construction of the cover system, portions of the PVC geomembrane that were placed on smooth bedding remained soft and flexible, while portions that were placed on rough bedding became less flexible because of the rough subgrade. The average plasticizer content (C_P) of the soft portions after nine years of service is reported as 26.5% (Hammond *et al.* 1993) and the plasticizer loss ratio is calculated to be 33% using Equation (2). In contrast, the average plasticizer content of the less flexible portions after nine years of service on the rough subgrade is reported as 17.6% by Hammond *et al.* (1993) and the plasticizer loss ratio is calculated to be 60% using Equation (2). The relationships between the plasticizer loss ratio and exposure time for PVC geomembranes placed on smooth bedding and rough bedding are proposed by Giroud and Tisinger (1993). Both trend lines show that the plasticizer loss ratio does not level off but continuously increases with time (Giroud and Tisinger 1993).

In this paper, the initial plasticizer content is reevaluated for this case using the initial PVC geomembrane density and a relationship between geomembrane density and plasticizer content proposed by Giroud and Tisinger (1993). The relationship is expressed as:

$$C_P \approx 2.22\left(1-\frac{\rho_{\mathrm{GM}}}{1450}\right) \tag{3}$$

where ρ_{GM} is the geomembrane density expressed in kg/m^3. Giroud and Tisinger (1993) note that Equation (3) is a rough approximation for C_P because a small change in ρ_{GM} corresponds to a large variation of C_P.

Hammond *et al.* (1993) and Levin and Hammond (1990) report that the initial PVC geomembrane density is 1250 kg/m^3, i.e., specific gravity of 1.25. Therefore, the initial plasticizer content is calculated using Equation (3) to be 30.7% and not 35%. Also, they report the density of exhumed PVC geomembrane after five years of service as 1270 kg/m^3. The plasticizer content after five years of service is calculated using Equation (3) to be 27.6% and the corresponding plasticizer loss ratio is calculated using Equation (2) to be 14.0%. The plasticizer loss ratio of the soft portions after nine years of service is calculated to be 18.6% using Equation (2) and an initial plasticizer content of 30.7%. In contrast, the plasticizer loss ratio of the less flexible portions after nine years of service is calculated to be 51.7% using Equation (2) and an initial plasticizer content of 30.7%. The new relationships between the plasticizer loss ratio and exposure time for PVC geomembranes placed on smooth bedding and rough bedding are plotted as trend lines (3) and (4) in Figure 1, respectively. These trend lines show that plasticizer loss becomes essentially constant for the PVC geomembranes on the smooth bedding, but is still increasing for the rough bedding case after nine years. The reason for the poor performance on the rough bedding is not known but maybe caused by a thinning of the PVC at the rough points which facilitates migration of the plasticizer from the middle of the geomembrane or it may be that the air voids around the rough particles created micro climates where diffusion and evaporation were accelerated resulting in premature aging. Because it is recommended that PVC geomembranes be installed on a smooth subgrade, the rough bedding case is probably not typical of field performance of PVC geomembranes. This highlights the need to have a properly prepared subgrade.

Giroud and Tisinger (1993) summarize the performance of a 1 mm thick PVC geomembrane with an initial plasticizer content of 34% as a liner of evaporation ponds in the Sahara Desert, which is a harsh environment for volatile loss. After 3.5 years of direct exposure to extreme solar radiation, the geomembrane became less flexible and shrank. The geomembrane started developing tension as a result of the shrinkage that accelerated the brittleness of the liner. The plasticizer loss ratio with exposure time was assumed to exponentially increase (Giroud and Tisinger 1993). This case involves an environment of extreme volatile loss of plasticizer because of the exposed evaporation pond application. In addition, the extremely adverse environment including high ultraviolet radiation, high temperature, and no protective soil layer causes photo-degradation and thermal degradation of polymers. Therefore, this case history does not reflect a common application and behavior of plasticizer retention in PVC geomembranes and thus is not included in Figure 1.

4. 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.

4.1 Molecular weight of plasticizer

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 processibility.

Figure 2 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 Daoust 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.

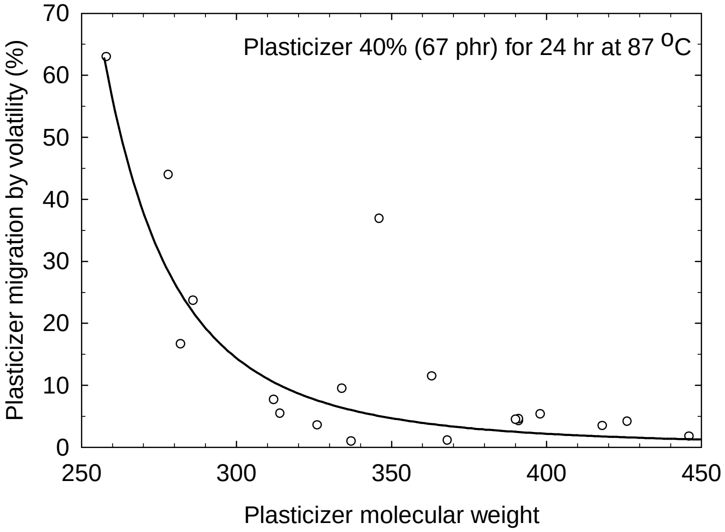

Figure 2. Relationship between plasticizer molecular weight and volatile plasticizer loss.

Figure 3 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 Daoust 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 3 that the migration is less than 1% for a plasticizer molecular weight greater than 300.

Figure 4 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 4 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.

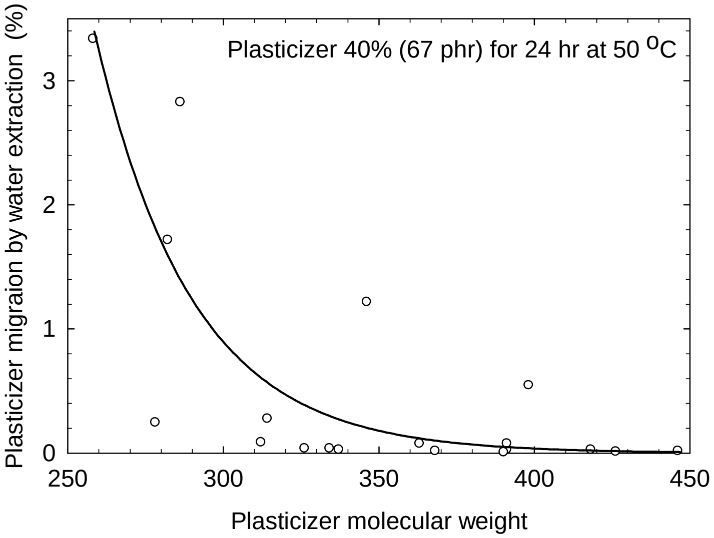

Figure 3. Relationship between plasticizer molecular weight and plasticizer loss by water extraction.

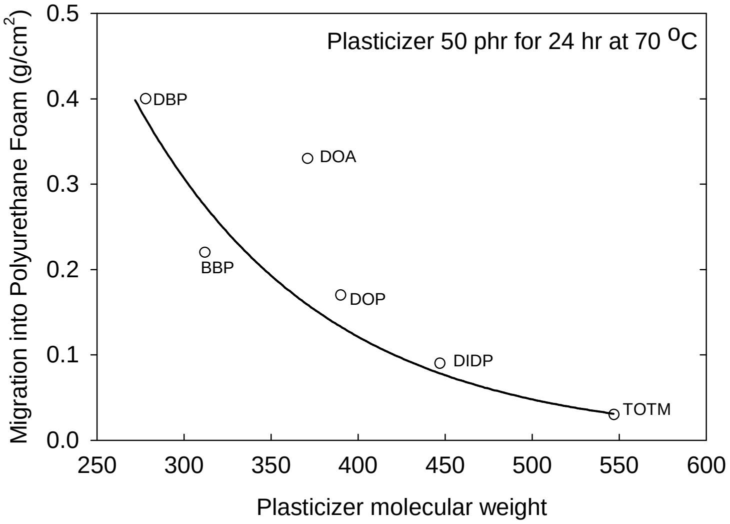

Figure 4. Relationship between plasticizer molecular weight and plasticizer migration into Polyurethane foam.

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 preformance.

4.2 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 4 shows that DOP and DOA (dioctyladipate) 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. 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.

5. 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. 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, 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 to or greater than 400. Figures 2, 3, and 4 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.

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 geomemebrane 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:

$$\begin{aligned}\text{Ave. molecular weight} &= \frac{\left(M_{DOP} \times C_{DOP}\right) + \left(M_{DIDP} \times C_{DIDP}\right)}{C_{TOTAL}} \\ &= \frac{\left(390 \times 30\right) + \left(446 \times 20\right)}{50} = 412\end{aligned} \tag{4}$$

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. 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.

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.

6 CONCLUSIONS

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.

The case studies performed by Giroud and Tisinger (1993) are revised to develop new relationships between plasticizer loss ratio and exposure time. One of the case studies involving a PVC geomembrane in evaporation ponds in the Sahara Desert is removed from the database because this condition does not reflect a typical application. In the revised cases except for a PVC geomembrane placed on rough bedding in a landfill cover in Florida, the plasticizer loss even in thin (0.25 and 0.5 mm thick) PVC geomembranes does not increase continuously with time but eventually becomes constant.

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.

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