Influence of plasticizer molecular weight on plasticizer retention in PVC geomembranes

T. D. Stark[1], H. Choi[2] and P. W. Diebel[3]

[1]*Professor of Civil and Environmental Engineering, 2217 Newmark Civil Engineering Laboratory, University of Illinois, 205 N. Mathews Ave., Urbana, IL 61801, USA, Telephone: + 1 217 333 7394, Telefax: + 1 217 333 9464, E-mail: tstark@uiuc.edu*

[2]*Assistant Professor of Civil Engineering, University of Akron, 209D ASEC, Akron, OH 44325-3905, USA, Telephone: + 1 330 972 7292, Telefax: + 1 330 972 6020, E-mail: hchoi@uakron.edu*

[3]*Technical Director, Canadian General Tower Ltd, 52 Middleton Street, PO Box 160, Cambridge, Ontario, Canada, N1R 5T6, Telephone: + 1 519 623 1630, Telefax: + 1 519 623 0713, E-mail: PDiebel@cgtower.com*

ABSTRACT: Plasticizers are used to make PVC flexible so it can be used as a geomembrane. Plasticizers can migrate from PVC geomembranes over time because of contact with air, liquid, and/or an absorbent solid material. Plasticizer migration can reduce the flexibility of PVC geomembranes, resulting in brittle behavior. This paper discusses the three mechanisms of plasticizer migration and the factors influencing these mechanisms, such as plasticizer molecular weight and linearity of the plasticizer. Field case histories are used to show how these mechanisms influence plasticizer retention in PVC geomembranes. Finally, it is recommended that a minimum average plasticizer molecular weight of 400 be used to ensure long-term plasticizer retention and adequate field performance of PVC geomembranes. The weighted-average method for calculating the average molecular weight is recommended when two or more plasticizers are used in the PVC geomembrane formulation.

1. INTRODUCTION

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). 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.

Most PVC geomembranes contain plasticizers as an additive to increase the flexibility, softness, workability, pliability, and distensibility of the material. Plasticizers are typically high boiling point organic liquids that reduce the glass transition 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. The 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. FUNDAMENTALS OF PVC GEOMEMBRANE

2.1. PVC geomembrane formulation

A polymer is a large molecule built up by a series of small and simple repeating chemical units. These repeating units are called monomers. In PVC, the repeating unit is the vinyl chloride monomer. The chemical and structural

formula for the vinyl chloride monomer is $CH_2=CHCl$, which possesses a double bond. During polymerization the double bond breaks down, resulting in free valences that can bond to other similar molecules (Brydson 1975).

Polymerization is a process of combining monomer units to produce a long polymer chain. In commercial practice, there are four different polymerization processes: bulk, suspension, emulsion, and solution (Brydson 1975; Giroud and Tisinger 1993). Among the polymerization processes, suspension polymerization is the predominant technique employed to produce PVC geomembranes (Giroud and Tisinger 1993).

The repeating unit of a PVC polymer is $-[CH_2-CHCl]_n-$. Comparing the structure of PVC with polyethylene, i.e. HDPE and LLDPE geomembranes, the repeating unit of $-[CH_2-CH_2]_n-$ is similar except for the presence of the chlorine (Cl) in PVC, which increases the interchain attraction and results in a large value of hardness and stiffness (Brydson 1975).

2.2. Plasticization

The common use of PVC is attributed to the wide variety of stabilizers that can be used to make PVC stable. This has resulted in PVC becoming an extremely versatile and useful thermoplastic compound. Pure PVC resin produces a rigid and brittle compound because of the strong polar attractions between chloride and hydrogen in the chemical structure. However, PVC has a unique characteristic that allows large amounts of plasticizers to be absorbed that can change the physical properties of PVC from a rigid to a flexible solid (Nass and Heiberger 1986). A typical formulation for PVC geomembranes is about 60–65% of PVC resin, 30–35% of plasticizer, and 0–5% of other additives such as fillers and stabilizers (Hammond *et al.* 1993).

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 external plasticization the small monomeric plasticizer molecules absorb into and adsorb onto the porous PVC polymer. Because PVC geomembranes are usually manufactured using external plasticization, only external plasticizers are considered in this paper. Other detailed plasticization processes are described by Mark and Gaylord (1964), Sears and Darby (1982), Nass and Heiberger (1986), and Wilson (1995).

Most commercial plasticizers are mainly organic esters. Plasticizers used in PVC are either monomers or polymers. Monomeric plasticizers are categorized as phthalates, aliphatic diesters, phosphates, and trimellitates. The most typical monomeric plasticizer used in flexible PVC is the phthalate plasticizer. Phthalates are composed of an aromatic ring with two ester linkages forming short hydrocarbon chains (Diebel 2002). Examples of phthalate plasticizers are dioctyl phthalate (DOP), diisodecyl phthalate (DIDP) and diisononyl phthalate (DINP). Polymeric

plasticizers are typically polyesters, nitrile rubbers, or ethylene vinyl acetate derivatives. Compared with monomeric plasticizers, polymeric plasticizers often provide superior physical properties in terms of volatility, migration, and weathering resistance. Polymeric plasticizers are more expensive and take more time and energy to become absorbed into the PVC resin, but are often used in geomembrane applications that require resistance to direct contact with hydrocarbons, such as oils and greases. In most applications direct contact with concentrated hydrocarbons does not occur, and thus monomeric plasticizers are most commonly used in PVC geomembranes.

The most common monomeric plasticizers have molecular weights ranging from about 300 to 600, viscosities of 50 to 450 cP, and vapor pressure of less than 3.0 mmHg at 200°C (Krauskopf 1993). Figure 1 shows the molecular structures of several typical monomeric plasticizers. [1]

3. MECHANISMS AFFECTING PLASTICIZER RETENTION

The addition of plasticizers in PVC increases flexibility, softness, workability, and distensibility, and decreases the glass transition temperature (T_g), which is the temperature at which the plastic becomes brittle (Hammond *et al.* 1993). A potential limitation in using plasticized PVC geomembranes is plasticizer migration when the plasticized PVC geomembrane is in contact with a surrounding medium. The surrounding medium may be air, liquid, or a solid. 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 reten-
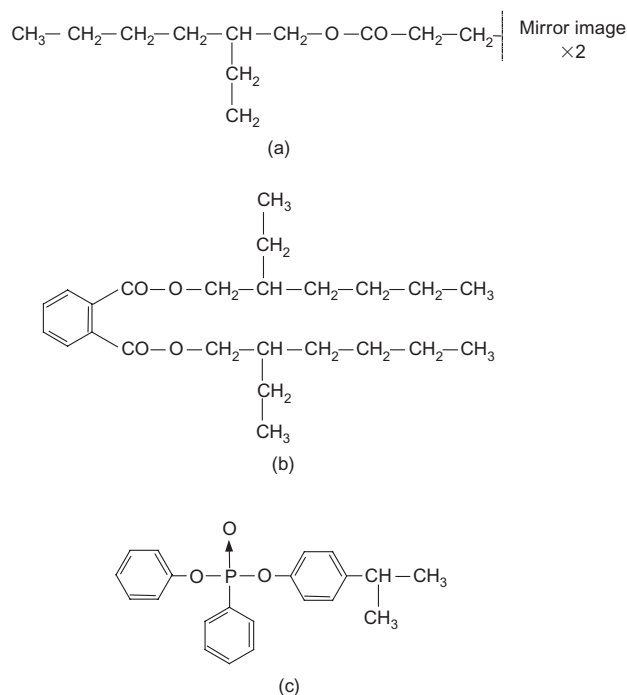

Figure 1. Structures of plasticizers with different degrees of linearity (from Wilson 1995): (a) highly linear plasticizer (e.g. DOA); (b) branched plasticizer (e.g. DOA); (c) highly branched plasticizer (e.g. triaryl phosphates)

tion in contact with these three media – air, liquid, or a solid – are described below.

3.1. Plasticizer migration into air

Volatile loss or evaporation of external plasticizers from PVC into the surrounding air is a common mechanism of plasticizer migration. Because there is no chemical bonding between polymer resin and external plasticizer molecules, evaporation of the plasticizer molecules can occur.

Volatile loss from PVC is composed of two major transfer processes: (1) diffusion from inside the geomembrane to the geomembrane surface, and (2) evaporation from the geomembrane surface (Sears and Darby 1982; Wilson 1995). The diffusion rate and vapor pressure of the plasticizer molecules are important factors in the amount of volatile loss.

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 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.

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 (Orem and Sears 1979; Holzmann 1988; Giroud and Tisinger 1993; Young and Kovach 1995; Bailey *et al.* 1997). 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 provide enough free air for evaporation. To reduce the potential for 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 is likely to be the main volatile loss mechanism.

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 (Mark and Gaylord 1964; Stepek and Daoust 1983; Giroud 1984; 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 that 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 h at a temperature of 87°C over activated carbon. The water extraction is performed for 24 h at a temperature of 50°C. The detailed mechanism for water extraction is discussed in the following section.

3.2. Plasticizer migration into liquid

Plasticizer migration from plasticized PVC into liquids, such as water, oils, waxes, alcohols, and other agents, can be attributed to 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 that 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 factors 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 occur only 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 in plasticizer retention, and plasticizer loss is a function of the molecular weight of the plasticizer

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

Group	Plasticizers	MW	Volatility plasticizer loss (%)	Water extraction (% loss)
Phthalic 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
	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	0.03
	Tricresyl phosphate (TCP)	368	1.13	0.02
	2-Ethylhexyl diphenyl phosphate	362		
Polyfunctional 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) dibenzoate	314	5.5	0.28
	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	286	23.7	2.83

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 covered with leachate. Fayoux *et al.* (1993) indicate that plasticizer migration from PVC samples immersed in leachate for 10 years is less than for samples exposed to air for 10 years. Table 1 shows typical plasticizers used in practice along with each one's molecular weight and water extraction loss.

3.3. Plasticizer migration into 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) or 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 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 phenomenon from the plasticized PVC for short time-periods.

The phenomenon of plasticizer migration from plasticized PVC into other polymeric materials needs to be considered and tested prior to its being specified and used for a landfill liner and cover system. When a flexible PVC geomembrane is used together with a drainage geocomposite, consisting of a geonet laminated with geotextiles, it is possible that plasticizer may migrate from the PVC geomembrane to the drainage geocomposite.

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

4. FIELD OBSERVATIONS OF PLASTICIZER RETENTION

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

Giroud and Tisinger (1993) summarize plasticizer retention in PVC geomembranes in the following three cases: canal liners in the Western USA (Morrison and Starbuck 1984), a landfill cover in Florida (Levin and Hammond 1990; Hammond *et al.* 1993), 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. Figure 2 presents trend lines for each site, relating
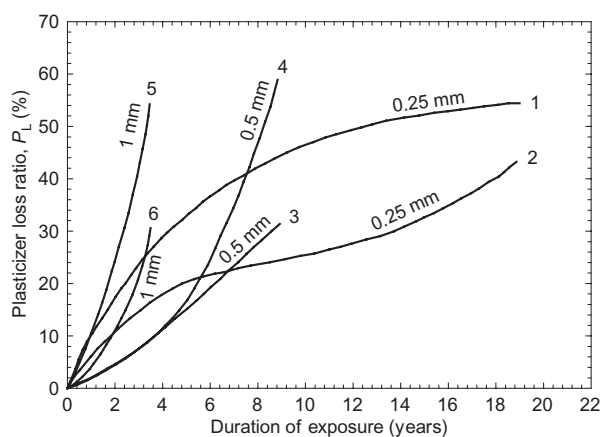
Figure 2. Plasticizer loss ratio against duration of exposure (from Giroud and Tisinger 1993): 1, canals, western USA, geomembrane protected by soil, above water level; 2, canals, western USA, geomembrane protected by soil, below water level; 3, landfill cover, Florida, geomembrane protected by soil, smooth bedding; 4, landfill 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

plasticizer loss ratio (P_L) to exposure time as originally plotted by Giroud and Tisinger (1993). The plasticizer loss ratio is defined by Giroud and Tisinger (1993) as the ratio of removed plasticizer mass to initial plasticizer mass, and is calculated using

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

where C_{P0} and C_P are the initial and current plasticizer content by mass respectively. Figure 2 gives the impression that plasticizer loss increases exponentially and will continue until all plasticizer is removed. This is evident from trend lines 2 to 6 in Figure 2. 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 in Figure 2 and clarify the chemical behavior of PVC geomembranes.

The performance of 0.25 mm thick PVC geomembranes in canals in the western USA was conducted by the US Bureau of Reclamation (Morrison and Starbuck 1984). All 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 corresponded to a service period ranging from 2 to 19 years and plotted the average plasticizer loss ratio with exposure time. Trend lines 1 and 2 in Figure 2 represent the PVC geomembranes above and below water level in this case, respectively. Giroud and Tisinger (1993) noted that, in spite of the plasticizer loss as indicated in trend lines 1 and 2 in Figure 2, strains at break measured in tensile tests were always greater than 100%. However, Giroud and Tisinger (1993) also indicated that the shape of the stress–strain curve probably showed that hardening occurred. Morrison

and Starbuck (1984) reported that the elastic modulus at 100% elongation increased by 30–90% for the service period ranging from 2 to 19 years. However, such information is not sufficient to imply quantitatively how much the original flexibility of the PVC geomembrane had been changed.

The US 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 in Figures 3 and 4. All the seven sets of data in Figure 3 represent 0.25 mm thick PVC geomembranes above the water level except for Fivemile Lateral B, Wyoming, in which a 0.5 mm thick PVC geomembrane is used 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' service, which is in agreement with Giroud and Tisinger (1993). The plasticizer loss ratio is calculated using Equation 2.

Figure 4 shows the relationship between plasticizer loss ratio and exposure time for 10 sites where 0.25 mm thick PVC geomembranes are placed below the water level except for Fivemile Lateral B, Wyoming, in which a 0.5 mm thick PVC geomembrane is used below the water level. Although Figure 4 shows more scatter than the data for above the water level, the plasticizer loss ratio eventually becomes constant at around 45% after about 20 years' service, which does not agree with Giroud and Tisinger (1993). Figure 2 indicates that the plasticizer loss ratio is still increasing (trend line 2), instead of becoming constant after about 20 years.
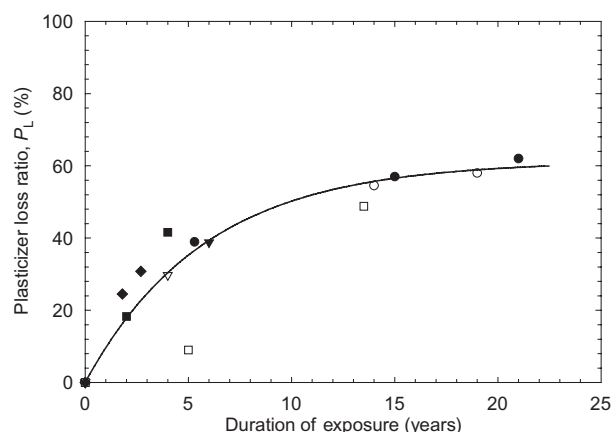
The PVC geomembrane samples obtained from within

Figure 3. Plasticizer loss ratio against duration of exposure in PVC geomembranes used for canal liners (above water level) in the western USA (data from Morrison and Comer 1995; Morrison and Starbuck 1984): ●, Helena Valley Canal, Montana (installed 1968–69); ○, Bugg Lateral, New Mexico (installed 1961); ▼, Fivemile Lateral A, Wyoming (installed 1978–79); ▽, Fivemile Lateral B, Wyoming (installed 1981–82); ■, Wyoming Canal A, Wyoming (installed 1975); □, Lateral H (Sun River Project), Montana (installed 1966); ◆, Amarillo Canal, New Mexico (installed 1978)
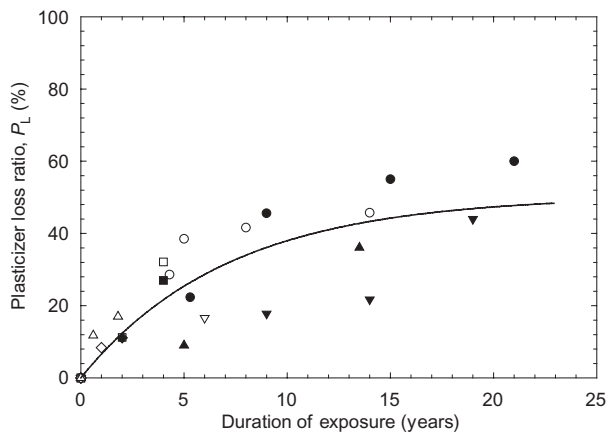
Figure 4. Plasticizer loss ratio against duration of exposure in PVC geomembranes used for canal liners (below water level) in the western USA (data from Morrison and Comer 1995; Morrison and Starbuck 1984): ●, Helena Valley Canal, Montana (installed 1968–69); ○, East Bench Canal, Montana (installed 1969–70); ▼, Bugg Lateral, New Mexico (installed 1961); ▽, Fivemile Lateral A, Wyoming (installed 1978–79); ■, Fivemile Lateral B, Wyoming (installed 1981–82); □, Wyoming Canal A, Wyoming (installed 1975); ◆, Wyoming Canal B, Wyoming (installed 1979–80); ◇, Pilot Canal, Wyoming (installed 1980–81); ▲, Lateral H (Sun River Project), Montana (installed 1966); △, Amarillo Canal, New Mexico (installed 1978)

the water prism generally exhibit less plasticizer migration than those obtained above the water level. The rate of plasticizer loss shown in Figures 3 and 4 is probably an upper bound because the thickness of PVC geomembranes in this case study is relatively thin compared with 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.

Levin and Hammond (1990) and Hammond *et al.* (1993) 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 5 and 9 years' 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%. Levin and Hammond (1990) report that, after 5 years' service, the PVC geomembrane lost 13% of the initial plasticizer content. Giroud and Tisinger (1993) report the plasticizer loss ratio for 5 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, whereas 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 9 years' 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 9 years' 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 represented as trend lines 3 and 4 in Figure 2, respectively, by Giroud and Tisinger (1993). Both trend lines show that the plasticizer loss ratio does not level off, but continuously increases with time.

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

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

where ρ_{GM} is the geomembrane density, expressed in kg/m³. 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.

Levin and Hammond (1990) and Hammond *et al.* (1993) report that the initial PVC geomembrane density is 1250 kg/m³, i.e. a 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 5 years' of service as 1270 kg/m³. The plasticizer content after 5 years' 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 9 years' 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 9 years' 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 5, respectively. Figure 5 shows that plasticizer loss becomes essentially constant for the PVC geomembranes on the smooth bedding, but is still increasing for the rough bedding case after 9 years. The reason for the poor performance on the rough bedding is not known, but it may be 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 create microclimates where diffusion and evaporation are 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
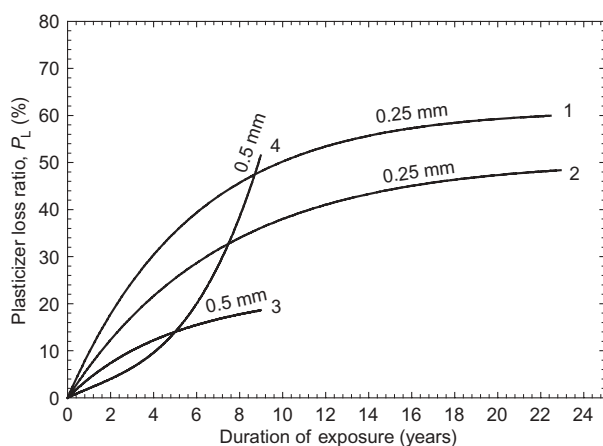
Figure 5. Revised relationship between plasticizer loss ratio and duration of exposure: 1, canals, western USA, geomembrane protected by soil, above water level; 2, canals, western USA, geomembrane protected by soil, below water level; 3, landfill cover, Florida, geomembrane protected by soil (smooth bedding); 4, landfill cover, Florida, geomembrane protected by soil (rough bedding)

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 plotted in Figure 2 (trend lines 5 and 6) was assumed by 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 5, which is a revised version of Figure 2.

The expected trend lines in Figures 3 and 4 for the case of canal liners in the western USA and the revised trend lines for the case of landfill covers in Florida are plotted in Figure 5. In each case, except for the PVC geomembrane placed on rough bedding in the case of landfill covers in Florida, the plasticizer loss with time does not increase exponentially but eventually becomes constant as the geomembrane reaches equilibrium with the surrounding environment. The PVC geomembrane exhumed from the rough bedding showed indentation from stones in the subgrade, as described by Hammond *et al.* (1993). As mentioned previously, volatile loss probably plays an important role in the portions placed on rough bedding because large stones in the subgrade may provide enough free air for evaporation. Furthermore, the indentation may cause a decrease in thickness of the PVC geomembrane, and thus the plasticizer can easily migrate from the geomembrane.

Another application of a PVC geomembrane that was investigated for plasticizer retention is a pond liner after 15 years' service (Young and Kovach 1995). The pond is located in Tampa, Florida. The PVC geomembrane was installed without an overlying soil cover, and was maintained under water while in service. The physical property and chemical tests indicate that the liner remained functional for the 15-year service life. Young and Kovach (1995) conclude that it is beneficial to maintain the PVC geomembrane under water to reduce the amount of UV light reaching the geomembrane. Of course, UV degradation is not an issue if the PVC is covered with a protective soil layer.

Fayoux *et al.* (1993) investigate a 1 mm thick PVC geomembrane excavated from a pond liner subjected to domestic landfill leachate in France after 10 years' service. The initial plasticizer content is 33.6%, and the plasticizer retention was assessed for different field conditions. Fayoux *et al.* (1993) show that plasticizer loss from a sample immersed in leachate for 10 years is much less than the samples exposed to air for 10 years. Thus exposure to air causes more volatile loss and UV degradation than the samples immersed in leachate for the same period. The exposure to leachate did not result in a high loss of plasticizer. The plasticizer loss ratio of 37% while exposed to air was much greater than the plasticizer loss ratio of 16% while exposed to the leachate.

Stark *et al.* (2002) investigate a 0.5 mm thick fish-grade PVC geomembrane exhumed from aquaculture ponds. The ponds were constructed in 1971 for the W. K. Kellogg Biological Research Station in Hickory Corner, Michigan. After nearly 30 years' service in an aquatic environment, laboratory tensile testing shows that the tensile behavior is well within current specifications for 0.5 mm thick PVC geomembranes, and this PVC geomembrane retains flexibility and strength, enabling it to perform as a successful water barrier. This indicates that plasticizer retention in an aquatic environment is not a problem, even in a 0.5 mm thick PVC geomembrane.

Once a PVC geomembrane manufactured with compatible plasticizers is buried and protected by a soil layer, plasticizer loss due to volatility 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. For this reason, open gravel is not a suitable cover material. However, there is usually a geotextile between the gravel and the PVC geomembrane.

5. 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, or a solid (Nass and Heiberger 1986; Giroud and Tisinger 1993; Wilson 1995). Internal or intrinsic factors controlling plasticizer retention are related to the molecular properties of the plasticizer. Presuming the mutual compatibility between the plasticizers and PVC resin is satisfied, 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 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 the mechanical and chemical properties of plasticized PVC geomembranes, identifying the molecular properties of the plasticizer facilitates prediction of the long-term behavior of PVC geomembranes.

5.1. 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 to 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 molecules 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 in 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 6 presents a relationship between the molecular weight of commonly used plasticizers and their volatile loss (i.e. data from Table 1). The volatile loss is measured for 24 h 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 increased plasticizer molecular weight. When the molecular weight is greater than about 400, the volatile loss is less than 2% for this aggressive experimental condition.

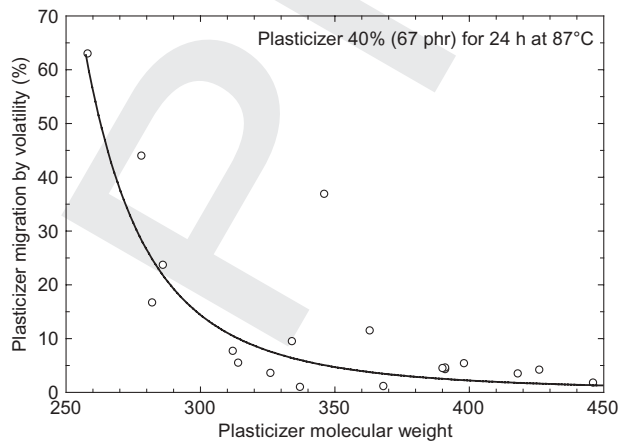Figure 7 presents a relationship between the molecular

weight of common plasticizers and plasticizer loss by water extraction (i.e. data from Table 1). The water extraction is measured for 24 h 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 7 that the migration is less than 1% for a plasticizer molecular weight greater than 300.

Figure 8 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 h at a temperature of 70 °C and the initial plasticizer content in each case is 50 phr (Wilson 1995). Figure 8 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
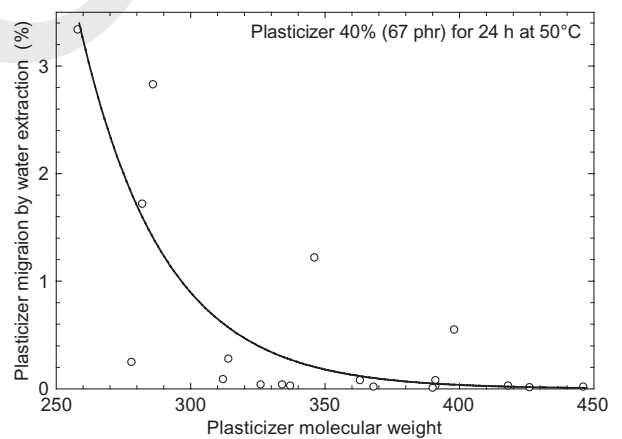
Figure 7. Relationship between plasticizer molecular weight and plasticizer loss by water extraction

Figure 6. Relationship between plasticizer molecular weight and volatile plasticizer loss
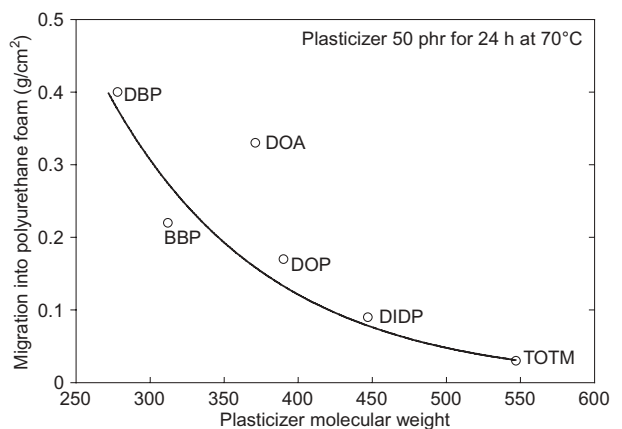
Figure 8. Relationship between plasticizer molecular weight and plasticizer migration into Polyurethane foam.

the absorption of the plasticizer into the PVC resin. 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 by TRI/Environmental (2003) of PVC with a plasticizer molecular weight greater than 400 submerged in leachate, which showed no significant physical changes after exposure.

5.2. 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. This 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. Figure 1 shows the various molecular structures of plasticizers with different linearity.

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 (diisodecyl phthalate (DIDP) and diisononyl phthalate (DINP)), one singly branched plasticizer (DOP), and one linear plasticizer (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 (Orem and Sears 1979; Krauskopf 1993). In addition, the linear plasticizer has better UV durability because of its better photochemical stability.

For plasticizer migration into liquid or a solid, branched plasticizers can have less plasticizer loss than linear plasticizers (Wilson 1995; Diebel 2002). Figure 8 shows that DOP and DOA have similar molecular weights: 390 and 371 respectively. However, the plasticizer migration of DOA is about twice that of 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 plasticizers 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, which increases volatile loss into air. However, the advantage of higher branchness is that it retards plasticizer migration into liquid or a solid.

6. 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, or 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 that a minimum value of plasticizer molecular weight be specified. 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 6–8 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, 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:

Ave. molecular weight

$$= \frac{(M_{DOP} \times C_{DOP}) + (M_{DIDP} \times C_{DIDP})}{C_{TOTAL}}$$

$$= \frac{(390 \times 30) + (446 \times 20)}{50} = 412 \qquad (4)$$

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

If the size (molecular weight) of each plasticizer is substantially different, they are not miscible in all proportions. Accordingly, the weighted-average method for molecular weight is applicable only to the commonly used plasticizers that are mutually compatible, and compatible with PVC resin. For example, a mixture of a plasticizer with extremely high molecular weight (e.g. 700) and a plasticizer with extremely low molecular weight (e.g. 100) should not be considered here. Instead, plasticizers with molecular weights ranging between 300 and 500 that are compatible can be considered in the weighted-average method.

7. NEW SPECIFICATION FOR PVC GEOMEMBRANES

Even after publication of the PGI-1103 specification on 1 January 2003, competitors and regulators still expressed concern about whether or not PVC geomembranes would remain flexible. To address this issue, 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 (ASTM 2004) 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, and the average plasticizer molecular weight is listed under index properties. Table 2 shows that 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 via Note 6 after the material properties (see Table 2). Most manufacturers are already complying with this requirement, but the PGI believes that modifying PGI-1104 provides a method to ensure the long-term quality of the plasticizer being used in flexible PVC geomembranes before installation.

8. 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 the information presented in this paper.

1. 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 commonly used plasticizers 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, which enhances volatile loss into air. However, advantages of higher plasticizer branchness include retardation of plasticizer migration into liquids and solids.

2. 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.

3. 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

Table 2. PGI-1104 material specification for flexible PVC geomembranes for containment

	ASTM	PVC 10	PVC 20	PVC 30	PVC 40	PVC 50	PVC 60
Certified properties[b]							
Thickness	D5199	10 + 0.5 mil	20 + 1 mil	30 + 1.5 mil	40 + 2 mil	50 + 2.5 mil	60 + 3 mil
		0.25 + 0.013mm	0.51 + 0.03 mm	0.76 + 0.04 mm	1.02 + 0.05 mm	1.27 + 0.06 mm	1.52 + 0.08 mm
Tensile properties[3]	D882[d]						
	Min						
Strength at break		/24 lbf/in	48 lbf/in	73 lbf/in	97 lbf/in	116 lbf/in	137 lbf/in
		4.2 kN/m	8.4 kN/m	12.8 kN/m	17.0 kN/m	20.3 kN/m	24.0 kN/m
Elongation		250%	360%	380%	430%	430%	450%
Modulus at 100%		10 lbf/in	21 lbf/in	32 lbf/in	40 lbf/in	50 lbf/in	60 lbf/in
		1.8 kN/m	3.7 kN/m	5.6 kN/m	7.0 kN/m	8.8 kN/m	10.5 kN/m
Tear strength	D1004[d]	2.5 lbf	6 lbf	8 lbf	10 lbf	13 lbf	15 lbf
	Min	11 N	27 N	35 N	44 N	58 N	67 N
Dimensional stability	D1204[d]	4%	4%	3%	3%	3%	3%
	Max Chg						
Low-temperature impact	D1790[d]	−10°F	−15°F	−20°F	−20°F	−20°F	−20°F
	Pass	−23°C	−26°C	−29°C	−29°C	−29°C	−29°C
Index properties[e]							
Specific gravity	D792	1.2	1.2	1.2	1.2	1.2	1.2
	Typical						
Water extraction percent loss (max)	D1239[d] Max loss	0.15%	0.15%	0.15%	0.20%	0.20%	0.20%
Volatile loss	D1203[d]	1.5%	0.9%	0.7%	0.5%	0.5%	0.5%
	Max loss						
Soil burial	G160[d] 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	D751[d]	42 lbf/in^2	68 lbf/in^2	100 lbf/in^2	120 lbf/in^2	150 lbf/in^2	180 lbf/in^2
	Min	290 kPa	470 kPa	690 kPa	830 kPa	1030 kPa	1240 kPa
Average plasticizer molecular weight	D2138 and D2124	> 400	> 400	> 400	> 400	> 400	> 400
Seam strengths							
Shear strength[3]	D882[d]	20 lbf/in	38.4 lbf/in	58.4 lbf/in	77.6 lbf/in	96 lbf/in	116 lbf/in
	Min	3.47 kN/m	6.7 kN/m	10 kN/m	14 kN/m	17 kN/m	20kN/m
Peel strength[3]	D882[d] Min	10 lbf/in	12.5 lbf/in	15 lbf/in	15 lbf/in	15 lbf/in	15 lbf/in
		1.8 kN/m	2.2 kN/m	2.6 kN/m	2.6 kN/m	2.6 kN/m	2.6 kN/m

1. PGI 1103 replaces PGI 1197 specification effective 1 January 2003.
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.

be used to calculate the average molecular weight of the plasticizer when two or more plasticizers are incorporated into manufacturing the PVC geomembrane.

NOTATIONS

Basic SI units are given in parentheses.

C_{DIDP}	plasticizer content of DIDP by mass (dimensionless)	
C_{DOP}	plasticizer content of DOP by mass (dimensionless)	
C_{TOTAL}	total plasticizer content of DOP and DIDP by mass (dimensionless)	
C_{P}	current plasticizer content by mass (dimensionless)	
C_{P0}	initial plasticizer content by mass (dimensionless)	
D	diffusion coefficient (m^2/s)	
l	thickness on PVC (m)	
M_{DIDP}	molecular weight of DIDP (dimensionless)	
M_{DOP}	molecular weight of DOP (dimensionless)	
M_t	mass of plasticizer loss at time t (kg)	
M_∞	mass of plasticizer loss at equilibrium (kg)	
P_{L}	plasticizer loss ratio (dimensionless)	
t	time (s)	
ρ_{GM}	geomembrane density (kg/m^3)	

|4|

ABBREVIATIONS

DOP	dioctyl phthalate
DIDP	diisodecyl phthalate
DINP	diisononyl phthalate
GC	gas chromatograph
GCMS	gas chromatograph mass spectrophotometer
HDPE	high-density polyethylene
LLDPE	linear low-density polyethylene
MW	molecular weight
PGI	PVC Geomembrane Institute
phr	parts per hundred of resin
PVC	polyvinyl chloride
UV	ultra-violet

REFERENCES

|5|

ASTM (2004). Standard Test Method for Analysis of Components in Poly(Vinyl Chloride) Compounds Using an Infrared Spectrophotometric Technique, D2124-99. West Conshohocken, PA: American Society for Testing and Materials.

Bailey, D. M., Foltz, S. D., Rossiter, W. J. & Lechner, J. A. (1997). Performance of polyvinyl chloride (PVC) roofing: results of a ten-year field study. Proceedings of the 4th International Symposium on Roofing Technology, Gaithersburg, MD, pp. 253–264.

|6|

Brydson, J. A. (1975). Plastics Materials, 3rd edn. London: Newnes-Butterworths, 731 pp.

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, Nice, 28–34.

Fayoux, D., Gousse, F. & Rummens, F. (1993) Assessment on a PVC geomembrane in a landfill after ten years. Proceedings of the 4th International Landfill Symposium, Sardinia, **1**, 369–378.

Giroud, J. P. (1984). Aging of PVC geomembranes in uranium mine tailing ponds. Proceedings of the International Conference on Geomembranes, Denver, CO, Vol. 2, pp. 311–316.

Giroud, J. P. & Tisinger, L. G. (1993). The influence of plasticizers on the performance of PVC geomembranes. Proceedings of the Conference on Geosynthetic Liner Systems: Innovation, Concerns, and Design, St Paul, MN, pp. 169–196.

Hammond, M., Hsuan, G., Mackey, R. E. & 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, 365–380.

Hawkins, W. L. (1984). Polymer Degradation and Stabilization. New York: Springer, 119 pp.

|7|

Holzmann, I. (1988). To Determine the Criteria for Selecting Plasticizers for Roofing Sheet. BASF Internal Technical Report.

|8|

Kampouris, E. M. (1975). The migration of plasticizers into petroleum oils. European Polymer Journal, **11**, 795–710.

Krauskopf, L. G. (1993). Plasticizer structure/performance relationships. Journal of Vinyl Technology, **15**, No. 3, 140–147.

Levin, S. B. & Hammond, M. (1990). Examination of PVC in a top cap application. In Geosynthetic Testing for Waste Containment Application, ASTM STP 1081, pp. 369–382. West Conshohocken, PA: American Society for Testing and Materials.

|9|

Mark, H. F. & Gaylord, N. G. (1964). Encyclopedia of Polymer and Technology: Plastics, Resins, Rubbers, Fibers. New York: Interscience Publishers.

Messadi, D., Vergnaud, J. & Hivert, M. (1981). A new approach to the study of plasticizer migration from PVC into methanol. Journal of Applied Polymer Science, **26**, 667–677.

Morrison, W. R. & Comer, A. I. (1995). Use of Geomembranes in Bureau of Reclamation Canals, Reservoirs, and Dam Rehabilitation, Report No. REC-95-01. Denver, CO: US Department of the Interior, Bureau of Reclamation.

Morrison, W. R. & Starbuck, J. G. (1984). Performance of Plastic Canal Linings, Report No. REC-ERC-84-1. Denver, CO: US Department of the Interior, Bureau of Reclamation.

Nass, L. I. & Heiberger, C. A. (1986). Encyclopedia of PVC: Vol. 1 Resin Manufacture and Properties, Marcel Dekker, 702 pp.

|10|

Orem, J. H. & Sears, J. K. (1979). Flexible poly (vinyl chloride) for long outdoor life. Journal of Vinyl Technology, **1**, No. 2, 79–83.

Papakonstantinou, V. & Papaspyrides, C. D. (1994). Plasticizer migration from plasticized into unplasticized poly (vinyl chloride). Journal of Vinyl Technology, **16**, No. 4, 192–196.

PVC Geomembrane Institute (PGI) (2003). PVC Geomembrane Material Specification 1103. University of Illinois, Urbana, IL, www.pvcgeomembrane.com, 1 January 2003.

|11|

Sears, J. K. & Darby, J. R. (1982). The Technology of Plasticizers. New York: John Wiley & Sons, 1166 pp.

Stark, T. D., Newman, E. & Rohe, F. P. (2002). Thirty year old performance of PVC liners in the aquaculture industry. Proceedings of the 7th International Conference on Geosynthetics, Nice, 4–8.

Stepek, J. & Daoust, H. (1983). Additives for Plastics. New York: Springer, 243 pp.

TRI/Environmental (2003). Laboratory Testing of a 30 mil PVC Geomembrane for Waste Containment: Chemical Resistance Testing, Final Report. Austin, TX: TRI/Environmental, Inc.

Wilson, A. S. (1995). Plasticizers: Principles and Practice. Institute of Materials.

|12|

Young, E. G. J. & Kovach, C. A. (1995). Study of the durability of a PVC geomembrane-lined pond without soil cover. Proceedings of Geosynthetics '95, Nashville, TN, 907–919.