MATERIALE PLASTICE
https://revmaterialeplastice.ro
https://doi.org/10.37358/Mat.Plast.1964

Polymeric Geomembranes Used in Municipal Waste Facilities

DORU MIHAI[1], NARCISA ELENA POGURSCHI[2]*, NICOLETA DANIELA SARBU[1], CONSTANTA VALENTINA TUDOR[3], ADINA HORABLAGA[4], ROXANA SALCIANU[1], LUCIAN CRISTIAN MIRCEA[5]

[1]University of Agronomical Sciences and Veterinary Medicine of Bucharest, Faculty of Land Reclamation and Environmental Engineering, 59 Marasti Blvd., 011464, Bucharest, Romania
[2]University of Agronomical Sciences and Veterinary Medicine of Bucharest, Faculty of Animal Productions Engineering and Management, 59 Marasti Blvd., 011464, Bucharest, Romania
[3]University of Agronomical Sciences and Veterinary Medicine of Bucharest, Faculty of Management, Economic Engineering in Agriculturea and Rural Development, 59 Marasti Blvd., 011464, Bucharest, Romania
[4]Banat`s University of Agricultural Sciences and Veterinary Medicine „King Michael I of Romania", Faculty of Agriculture, Timisoara, Romania, 119 Calea Aradului Str., 300645, Timisoara, Romania
[5]University of Bucharest, Faculty of Mathematics and Computer Science, Security and Applied Logic, 14 Academiei Str., 010014, Bucharest, Romania

Abstract. *This research aims to establish the behaviour of geomembranes used for base sealing and for covering municipal waste facilities. The geomembranes used for base sealing are subjected to leachate pressure and to the action of chemical and microbiological pollutants. Geomembranes used for covering waste facilities are subjected to the action of precipitation water and released gases. This paper analyzes the following: the permeability mechanism of geomembranes made of polymers, the process of water vapours diffusion through polymers, diffusion flow, characteristic of permeability and influencing factors. The study also presents data on the permeability of some polymers - the most commonly used in the structure of geomembranes used in household waste facilities - as well as some of the results of ongoing research on the behaviour of high density polyethylene geomembranes in contact with the waste facilities' leachate. Diffusion was determined by measuring the weight of the vessel (water loss) daily for 30 days. The polymer influences the permeability and diffusion through the molecular and inter-molecular chemical structure, the packing density, the degree of crystallinity, the crosslinking density and through the flexibility of the macromolecular chains. The results show that the permeability of polymeric geomembranes is comparable to that of a microporous material (cement stone, bentonite).*

Keywords*: geomembranes, polymers, permeability, diffusion, coefficient of sorbtion*

1.Introduction

Polymer geomembranes show very low water permeability but are still permeable. Moisture transport through geomembranes is a diffusion process; differences in water vapour concentration, pressure or fugacity between the two opposite sides of the geomembrane determine the appearance of a gradient, under the action of which moisture diffuses through the material [1]. Thus, this gradient is the driving force of the diffusion process.

According to a conception agreed by most researchers and scientists, the diffusion in polymers takes place by moving the molecules of the diffuser in jumps, through the existing gaps, which form the free volume. The free iso-volume theory considers that the specific volume of the polymer consists of the sum of two component volumes: the volume occupied by the macromolecular chains and the volume of the gaps between them, called free volume [2]. Below the vitrification temperature (Tv) macromolecules are rigid, their thermal movement being limited to rotations of the structural units around the equilibrium positions. According to this theory, all polymers have the same free volume at the vitrification temperature (Tv), which is so small that segmental motion cannot manifest. However, experimental research shows that the free volume at vitrification temperature (Tv) is not a universal constant, but a

**email:elena.pogurschi@gmail.com*

variable that depends on or is influenced by molecular weight, degree of crosslinking, nature and length of functional groups, type of copolymerization, cooling in vitrification interval. Within the increase of the temperature over the vitrification temperature, the free volume registers an approximately linear increasing variation, described by the relation:

$$f = f_v + \Delta\alpha(T - Tv) \quad (1)$$

where:

f and f_v represent the free volume fractions at temperatures T and Tv, respectively, and $\Delta\alpha$ is equal to the difference (α_1 - α_v) between the coefficients of thermal expansion above and below the vitrification temperature.

The increase of the free volume favors the movement of the chain segments whose kinetic energy increases with temperature [3].

Starting from the diffusion process, described by Fick's first law, the relation that defines the permeability of geomembranes is established as:

$$P = D.\alpha \quad (2)$$

where:

- P is permeability or permeability coefficient and represents the amount of water vapours that permeate through the surface. It is equal to the unit (acccording to a normal direction along the surface) of the geomembrane of the same unit thickness per unit time, with the pressure difference between the two opposite sides of the geomembrane being equal to the unit;
- P is expressed in: g. s^{-1}. cm^{-1}. atm^{-1}, mol. s^{-1}. cm^{-1}. atm^{-1}, cm^3 (STP). s^{-1}. cm^{-1}. atm^{-1}. cm^3 (STP). s^{-1}. cm^{-1}. cm^{-1} Hg;
- α is called the sorption coefficient, it represents the angular coefficient of the sorption isotherm in the concentration range of the absorbed water vapour;
- D represents the diffusion coefficient.

The sorption coefficient - α - is a measure of the sorption capacity of the polymer; it is a ratio between a measure which represents a concentration and a measure which represents a pressure, α is expressed in g.cm^{-3}polymer. atm.mol.cm^{-3} polymer.atm^{-1}, cm^3 (STP).cm^{-3} polymer . atm^{-1} or in cm^3 (STP) . cm^{-3} polymer cm^{-1} Hg; cm^3 (STP) represents the volume of water vapour corresponding to the standard temperature (T) and pressure (P) (S), ie T = 0, P = 1 atm.

Therefore, according to relation (2), the permeability coefficient P depends on the diffusion coefficient (D) and the sorption coefficient (α). These units are controlled by the characteristics of the polymer, the particularities of the water molecules and the temperature. The polymer influences the permeability through the following: the molecular and intermolecular chemical structure, the packing density, the degree of crystallinity, the crosslinking density and the flexibility of the macromolecular chains.

The sorption capacity depends on the molecular and intermolecular chemical structure of the polymer. Water retention occurs by binding water molecules to the polar functional groups of the polymer by hydrogen bridges; the stronger the bond is the higher the polarity of the group is [4].

In relation to the differences between the electronegativities of the atoms involved in the constitution of the bond and with the symmetry factor, the polarity of the functional groups and of the structural units of the macromolecules varies; the structural unit of the polystyrene macromolecule is nonpolar, while that of polyvinyl chloride, polyvinyl acetate and polyvinyl alcohol shows polarity that increases in the stated order [5].

2.Material and methods

In the practice of measuring the permeability of geomembranes, the most frequently used method is provided by the American standard ASTM E 96 which is based on measuring the diffusion of water

vapours through a geomembrane sample at a constant temperature by using the oven with controlled humidity and temperature (Figure 1).

The experiments were based on the high-density polyethylene samples used by SC ECOREC SA in construction and environmental protection works. High-density polyethylene geomembrane was used for the waterproof of the base and slopes of cell 1, as well as for the sections 1-4 of cell 2 of the Glina landfill.

Low density polyethylene was used to seal the cell 1 in combination with another sealing system while polyvinyl chloride was used for office flooring and materials storage. Table 1 presents the main characteristics of the materials.

Table 1. The main characteristics of the materials

Sample	Density	Traction resistance	Elasticity	Punching resistance
	g/cm³	(N/mm²)	%	N
LLPDE 0.8mm	0.918	-	340	-
HDPE 0.8mm	0.94	50	65	650
PVC -0.76	1.36	50 -75	290	475
HDPE fluorinated 0.8mm	0.95	62	46	740
HDPE 2.5mm	0.96	71	12	820
HDPE extruded	0.96	73	14	820

Figure 1. Oven with controlled humidity and temperature

Figure 2. Experimental assembly

The experimental assembly (Figure 2) made in the laboratory consists of a cylindrical glass vessel with a diameter of 10 cm and a height of 3 cm filled with water, on the edges of which is fixed the geomembrane sample. This vessel was installed on a sensitive scale and everything was placed in the oven where humidity could be controlled. The experiment was performed at a humidity of 20% and a constant temperature of 32°C. Diffusion was determined by measuring the weight of the vessel (water loss) daily for 30 days.

3.Results and discussions

Several researchers agree with the hypothesis that permeability P is independent of the aggregation state - liquid or gaseous - of water; this hypothesis is based on the consideration that the chemical potentials of liquid water and water vapours at the relative pressure (humidity) equal to unity are the same [6-8].

P permeability generally increases with temperature; for example, it has been found that increasing the temperature of polyethylene from 20 to 40°C leads to an increase of more than twice of the permeability, and in the case of polyvinyl chloride by about 20%, to raising the temperature from 25 to 35°C. Table 2 shows the permeabilities of geomembranes made of different polymers.

Table 2. Permeability (P) to water vapours of some polymers [9]

Polymer	P x10^9 $cm^3(STP).s^{-1}.cm^{-1}.cm^{-1}Hg$
Butyl rubber	40 - 200
Butadiene rubber	4900
Butadiene styrene rubber	2400
Nitrile butadiene rubber	1000
Polyethylene	12-110
Polypropylene	70
Polyvinyl chloride	260-630

The influencing factors examined explain the differences between the permeabilities of geo-membranes made of different polymers (Table 1). Among rubbers, butyl rubber has the lowest permeability, much lower than butadiene rubber, butadiene-styrene rubber and butadiene-nitrile rubber.

Polyethylene has a very low permeability, close but lower than butyl rubber and polypropylene, and several times lower than polyvinyl chloride.

The experiments performed for 30 days on medium density polyethylene samples showed a gradual decrease in permeability represented by the reduction of the amount of water loss from 365mg /day to 338 mg/day (Figure 3).

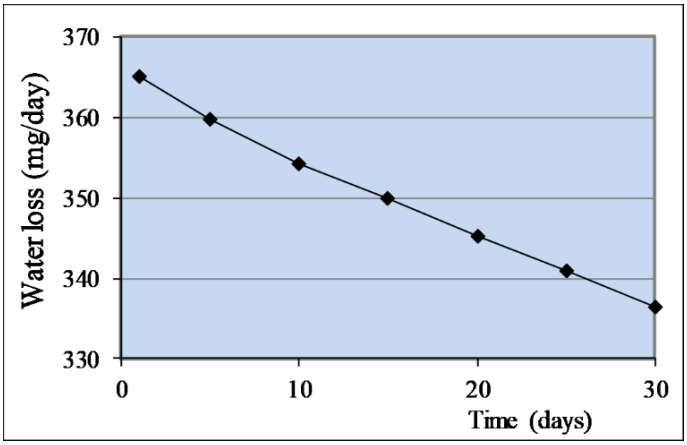

Figure 3 The decrease of lost water amount over time

The gradual decrease in water loss amount can be explained by the gradual filling of the free volume with water molecules. These can be retained in the nanometric pores by adsorption forces that no longer allow water movement through the free volume of the polymer.

The binding of water molecules to the polar functional groups of the polymer by hydrogen bonds leads to the retention of water between groups of macromolecules, the higher the bond the higher the polarity of the group. The polarity of the structural units and functional groups of the polymer varies in relation to the symmetry factor of the macromolecule and to the differences between the electro-negativities of the atoms involved n the formation of the bond.

Increasing the percentage of crystalline phase in the polymer structure decreases the mobility of macromolecules and functional groups, and as a result permeability and diffusion decrease.

The presence of pores and microcracks in polymers can significantly increase the permeability of geomembranes. Some pores characterized by very small but varied sizes (10^{-4}- 40 nm), are structural defects, which can occur during the cooling and formation of the polymer macromolecules. However, pores with significantly larger dimensions are manufacturing defects [10].

On the other hand, it is obvious that the permeability varies with the degree of crystallinity of the polymer, respectively with the reticular density of the crystalline lattice, a statement that can be easily demonstrated in the case of polyethylene geomembranes of different densities or comparing different polymers with different degrees of crystallinity.

Table 3. Permeability and diffusion of organic polymers used in the experiment

SAMPLE	PERMEABILITY		DIFFUSION	
	$m^3/m^2/day$	10^{12}* $m3/m^2/day$	m^2/s	10^{15}* m^2/day
LLPDE 0,8mm	$13.3 *10^{-8}$	13300	$3.5*10^{-13}$	350
HDPE 0.8mm	$1.7*10^{-9}$	1700	$1.8*10^{-13}$	180
PVC -0.76	$8*´10^{-10}$	800	$6.8*10-^{13}$	680
Fluorinated HDPE 0.8mm	$1.5*10^{-10}$	150	$1.5 *10^{-13}$	150
HDPE 2.5mm	$9.4*10^{-11}$	94	$6*10^{-14}$	60
Extruded HDPE	$8.4*10^{-12}$	8.4	$5´10^{-15}$	5

Based on those previously stated, analyzing the experimental results materialized in Table 3 and the graph in Figure 3, the following remarks can be noticed:

- high density polyethylene has permeability ($1.7 * 10^{-9}$ m^3/m^2 /day) 8 times lower than low density polyethylene ($13.3 * 10^{-8}$ m^3/m^2/day);
- the higher density of the HDPE sample, respectively 0.96 g/cm^3, led to the reduction of permeability in comparison to the sample of low density polyethylene (LLPDE) whose density is 0.92 g/cm^3;

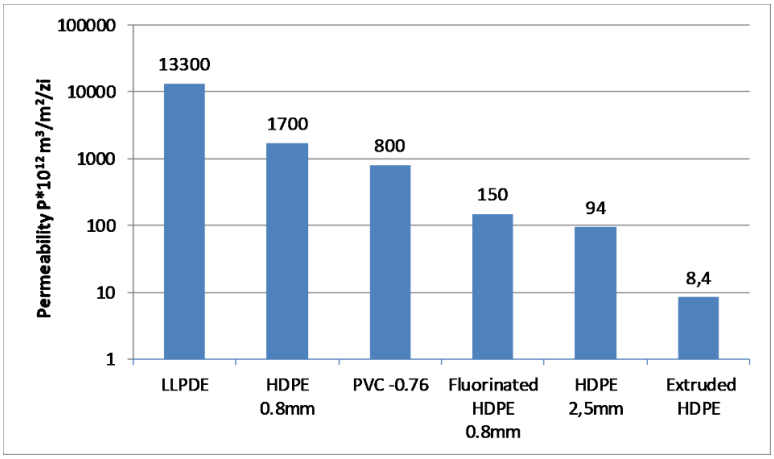

Figure 4. Variation of polymer permeability related to polymer type

- polymer production technology is a very important factor in reducing the permeability of geomembranes from organic polymers. As can be seen in Figure 4, the lowest permeability is shown by high density extruded polyethylene. The extrusion process reduces the free volume of the polymer, restores the functional groups and restructures the material;
- the reduction of the permeability of the fluorinated HDPE samples is explained by the exchange performed by the elemental fluorine applied to the surface of the geomembrane with hydrogen, along the polymer chains;
- in the case of municipal waste landfills, the pressure exerted by the waste layer determines the thickness of the geomembrane used for ditch sealing. The thickness of the geomembrane also determines the size of permeability, i.e. permeability decreases as thickness increases.

Regarding the diffusion coefficient from the graphic representation in Figure 5, the following characteristics of the researched polymers can be observed:

- the highest permissiveness for water vapour was recorded by the PVC sample respectively 6.8 * $10^{-13}m^2/s$. The high diffusion is due first of all to the increased polarity of the PVC macromolecules

compared to the non-polar macromolecules of polyethylene and the very low crystallinity of the polyvinyl chloride (which can even be amorphous) secondly;

- among all types of polyethylene, the low density had the highest diffusion, the average value was 3.5 * 10^{-13}m^2/s, being 2 times higher than the diffusion through high density polyethylene of the same thickness;

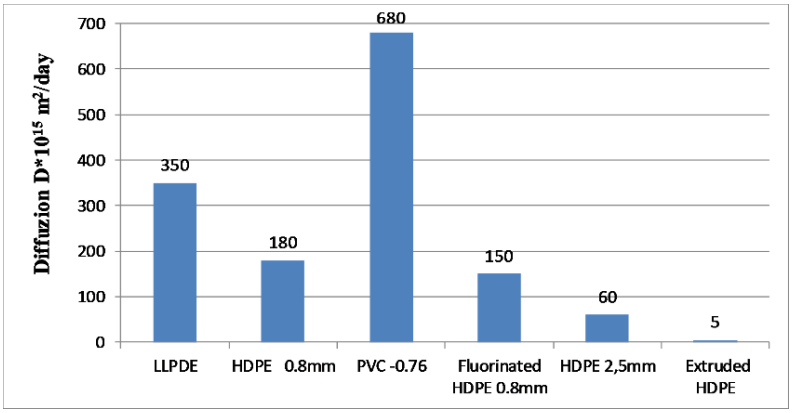

Figure 5. Variation of polymer diffusion related to polymer type

- in the case of diffusion, the fluorination had an effect of reducing the vapour flow much smaller than the thickness of the geomembrane, observing from the determinations made that through the 0.8mm HDPE geomembrane the diffusion values through the fluorinated and the normal sample are close (1.5 * 10^{-13} m^2/s and respectively 1.8 * 10^{-13}m^2/s);
- figure 5 shows that the lowest diffusion is shown by high density extruded polyethylene, because the extrusion process increases the packing density, restructures the material and reduces the free volume of the polymer.

The use of high density polyethylene geomembranes in sealing municipal waste facilities raises a number of issues, namely:

- the behavior of geomembranes in contact with chemical and microbiological pollutants in leachate;
- variation of permeability and diffusion in the aging process of polymeric membranes;
- the composition of polyethylene at thermal variations specific to the environment and specific to the processes of fermentation of organic matter in waste, fermentation that can lead to the development of high temperatures, up to 75^{o}C.

In order to answer some of these questions, laboratory tests were performed on low-density polyethylene samples and high-density polyethylene samples.

The experimental results obtained for the diffusion coefficients in low density polyethylene when the temperature increases from 25 to 75^{o}C are presented in the graph in Figure 6, which shows the increase of approximately 7 times the diffusion at a temperature increase of 50^{o}C.

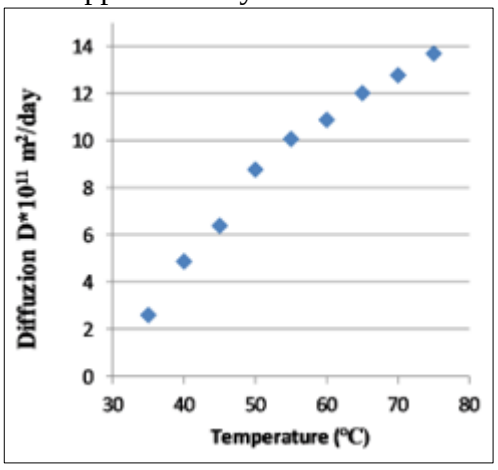

Figure 6 Diffusion variation of low density polyethylene related to temperature

The determination of diffusion on HDPE samples that were exposed to the leachate from the aeration lagoon for 3 years showed an insignificant increase of the diffusion and permeability between 5 and 8%.

4.Conclusions

The polymer influences the permeability and diffusion through the molecular and intermolecular chemical structure, through the packing density, through the degree of crystallinity, the crosslinking density, the flexibility of the macromolecular chains.

Obtained results showed the permeability of polymeric geomembranes is comparable to that of a microporous material (cement stone, bentonite) whose permeability coefficient P is between 10^{-11} and 10^{-13} $cm.s^{-1}$ [9].

The hydrophilic or hydrophobic character of the polymer influences both permeability and the diffusion coefficient.

The progressive reduction in the amount of water lost through the geomembranes can be explained by the gradual filling of the free volume with water molecules that can be retained in their nanometric-sized pores by the adsorption forces that no longer allow water movement through the free volume of the polymer.

Geomembrane thickness is also a factor that determines permeability size, i.e. permeability decreases as thickness increases.

The comparative analysis of the polymer types shows that high-density extruded polyethylene recorded the lowest diffusion as the extrusion process resulted in increased packing density, material restructuring and reduced free volume of the polymer.

In low density polyethylene, when temperature increased from 25 to 75^{o}C, the diffusion coefficients recorded very high increases due to the decrease in material density and free volume expansion.

Water loss through geomembranes occurs due to other physical processes than infiltration through classical materials; therefore, the determination methods are different.

References

1.MCWATERS R.S., ROWE R.K. Diffusive Transport of VOCs through LLDPE and Two Coextruded Geomembranes. *Journal of Geotechnical and Geoenvironmental Engineering* **136**(9), 2010, 1167-1177 https://doi.org/10.1061/(ASCE)GT.1943-5606.0000345

2.AHARI M., TOUZE-FOLTZ N., MAZEAS L. & GUENNE A. Quantification of the adsorption of phenolic compounds on the geotextile and bentonite components of four geosynthetic clay liners. *Geosynthetics International* **18**(5), 2011, 322-331. https://doi.org/10.1680/gein.2011.18.5.322

3.SAHELI P.T., ROWE R.K., RUTTER, A. & BRACHMAN R.W.I. Sorption and diffusive transport of PBDE through an HDPE geomembrane. *Geo-Frontiers, 2011 Advances in Geotechnical Engineering*, Han, J. (ed.), Alzamora, D.A. (ed.), 2011, 1141-1151 https://doi.org/10.1061/41165(397)117

4.CLEARY B.A. & LAKE C.B. Comparing measured hydraulic conductivities of a geotextile polymer coated GCL utilizing three different permeameter types. *Geo-Frontiers, 2011 Advances in Geotechnical Engineering*, 2011,1991-2000 https://doi.org/10.1061/41165(397)203

5.SANGAM H.P. & ROWE R.K., ASCE F. Effect of Surface Fluorination on Diffusion through a High Density Polyethylene Geomembrane. *Journal of Geotechnical and Geoenvironmental Engineering* **131**(6), 2005, 694–704. https://doi.org/10.1061/(ASCE)1090-0241(2005)131:6(694)

6.ROWE R.K., QUIGLEY R.M., BRACHMAN R.W.I. & BOOKER J.R. Barrier systems for waste disposal facilities. *2nd Edition, E&F Spon*, 2004, 587.

7.ISLAM M.Z. & ROWE R.K. Permeation of BTEX through Unaged and Aged HDPE Geomembranes. *Journal of Geotechnical and Geoenvironmental Engineering* **135**(8), 2009, 1130–1140. https://doi.org/10.1061/(ASCE)GT.1943-5606.0000056

8.TOUZE-FOLTZ N., ROSIN-PAUMIER S., MAZÉAS L. & GUENNE A. Diffusion of volatile organic compounds through an HDPE geomembrane. *Geo-Frontiers 2011 Advances in Geotechnical Engineering*, Han, J. (ed.), Alzamora, D.A. (ed.), 2011, 1121 – 1130

https://doi.org/10.1061/41165(397)115
9.GĂZDARU A. & ROȘU G. Why geomembranes are waterproof. *Bulletin of the Romanian Association of Geomembranes and Geosynthetics*, (**1-2**), 1996.
10.PARK M., BENSON C. H. & EDIL T. B. Comparison of batch and double compartment test for measuring volatile organic compound transport parameters in geomembranes. *Geotextiles and Geomembranes* **31**, 2012, 15-30. https://doi.org/10.1016/j.geotexmem.2011.09.001

Manuscript received: 9.07.2020