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The effect of formulation on the physical properties and durability of flexible PVC geomembranes

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ABSTRACT: This paper summarizes work performed in the laboratory and in actual field conditions. Flexible PVC is composed of a variety of ingredients and there are many ways of formulating to achieve the same initial physical results. The objective was to determine how the choice of the ingredients used in a flexible PVC formulation could determine the functionality and thus, the long-term performance as a flexible geomembrane. The data proves that the ingredient type and in some cases the amount, affect end performance significantly. If the proper physical properties are specified and tested only well formulated flexible PVC geomembranes will pass and thus the type of formulation does not have to be specified.

1 INTRODUCTION

Flexible polyvinyl chloride geomembranes have been used in numerous geosynthetic applications for over 40 years. Flexible PVC geomembranes have been used successfully in many diverse applications such as, landfill liners, landfill caps, canal liners, pond liners, and primary and secondary containment of assorted solutions (Diebel, May 2000).

The vast majority of the applications have performed and functioned well, with no known problems. However, there have been cases where the geomembrane failed prematurely. There are numerous failure modes for geomembrane failure, such as using the wrong product for the application. For instance, while flexible PVC geomembranes have excellent chemical resistance to a wide range of aqueous solutions over a wide pH and temperature range they are not designed for containing certain hydrocarbons such as ketones or ethers. Flexible PVC is also not designed for long term-exposed applications. For example Giroud and Tisinger (1993) presented a case where exposed PVC did not withstand the environmental conditions of the Sahara Desert evaporation ponds at pH of 1.5-2.0. In most non-tropic climates properly flexible formulated PVC geomembranes may be left exposed for 6-12 months without any significant change in properties. If polymeric plasticizers and high pigment loadings are used exposure times of over 10 years can be achieved with a film. If a polyester fabric is incorporated between two layers of film, 25 years of exposed applications are achievable in some cases.

There have been failures over the years where the wrong formulations have likely been used for a geosynthetic application. If the wrong formulation is used the PVC geomembrane will not function as designed.

2 EXPERIMENTS

Sixteen different flexible PVC formulations were prepared in the laboratory. The compound was fused on a lab mill and 20 mil (0.5 mm) films were produced. The lab films were tested to the properties in table 1.

Property	Test Method
Max. Tensile	ASTM D882
100% Modulus	ASTM D882
Max. Elongation	ASTM D882
Max. Tear	ASTM 1004
Low Temp. Impact	ASTM D1790
Dimensional Stability	ASTM 1204
Water Extraction	ASTM D3083
Volatile Loss	ASTM D1203
Hydrostatic Resistance	ASTM D751
Puncture Resistance	ASTM
70 °C Heat Aging	CGT Method
Weatherometer	ASTM G26
Chemical Resistance	Weight Change after 28 days immersed

Table 1. Properties Tested

The chemical resistance involved immersion of lab films in the solutions referred to in table 2. The criteria for rating were change in weight after immersion for 28 days.

Artificial Leachate
37% HCl
20% NaOH
Hexane
Unleaded Gasoline, 89 octane
Neats Foot Oil (animal fat)
Mineral Oil
Corn Oil
Ethanol
Soapy Water
Kerosene
ASTM Fuel C, aromatic hydrocarbon blend

Table 2. Chemicals used in chemical resistance testing

The formulations and the components changed are included in table 3.

2.1 *Table 3. Formulation Components Varied*

Ingredient	Purpose	Variation
PVC Resin	Main Polymer	Molecular Weight
Plasticizer	Flexibility	Type, branching, amount
Stabilizer	Prevent Degradation	Type
Filler	Physical Property Modifier, Reduce Cost	Amount
Pigment	Colour, UV Protection	Amount
UV Aborber	Extend UV Exposure	Type and amount
Biocide	Microbial Growth Inhibitor	Amount
UV Absorber and UV Inhibitor	Inhibit UV degradation	Type and amount

3 RESULTS AND DISCUSSION

3.1 *Affect of individual ingredients on physical properties*

The physical properties will be discussed first. Molecular weight of the resin affects the maximum tensile strength and the modulus at 100% elongation and puncture resistance. For example in this study there was approximately a 10% increase in these properties when the MW of the resin was increased from a 69K resin to an 81 K resin. The tear did not change significantly and the elongation dropped by approximately 10%. This shows that there is a balance between strength and flexibility. For example in actual use the lower MW polymer may move more easily if the substrate settles. The higher MW resin is a larger polymer and this results in greater entanglement, restricting movement.

Plasticizers used in PVC are either polymers or monomers. The monomers are different types of esters, while the polymers (often referred to as polymerics) are usually polyesters, nitrile rubbers or ketone ethylene ester polymers.

As known from previous research the plasticizer type and amount is significant. In this study the physical properties of geomembrane manufactured from monomeric adipate type plasticizers were significantly lower than the other types with the exception of the low temperature resistance, where adipates are known to excel due to the mobility gained through their molecular structure. Unfortunately this same structure results in poor permeance and thus in most cases they should be avoided in geomembrane applications.

Monomeric trimelatate plasticizers are often used where high temperature resistance is required. In this study this was evident in the heat at 70 ^{o}C for 4 weeks where the formulation, which incorporated them, lost no weight. For conditions under 50 ^{o}C monomeric phthalates with chain length greater than 7 are adequate. Monomeric phthalates with chains less than 9 and adipates have poor high temperature resistance. The non-heat aged physical properties of the trimelatate formulations did not excel over the others.

The majority of plasticizers used in flexible PVC are monomeric phthalates. Phthalates are composed of an aromatic ring with two ester linkages forming short hydrocarbon chains. The configuration of these chains is what differs in monomeric phthalates and is how they are classified. For instance the number of carbons in these chains used for plasticizing PVC is between 5 and 13 and the chains may be straight or have branching (Wilson, 1995). The number of carbons may be the same (i.e. all 7 or all 11) or it may be a combination (i.e.. A mixture of 7, 9 and 11).

In this study the following types of monomeric phthalates were investigated: short chain linear, long chain linear, linear blends, and mid length branched.

All monomeric phthalates result in very good initial physical properties. The differences are evident when they are required to perform in more demanding applications. For instance, the short chain linear phthalates (C7) had double the weight loss compared to the other phthalates in the volatile loss test and in the heat aging. This is because they are smaller, higher vapour pressure products. Low molecular weight monomeric phthalates should be avoided in geomembrane applications.

Long chain linear phthalates (11 carbons in the carbon chain) made no significant difference in the majority of the initial unaged physical properties although it did result in superior low temperature properties.

It has been inferred in the past that branched phthalates should not be used in geomembranes formulations. Unpublished research conducted by BASF and the results from this study do not support this blanket type of statement. What has been found is that while some branched phthalates are not recommended; certain types actually perform better than linear ones. While branched phthalates result in poorer low temperature properties they have been shown to be more permanent in studies of exposed roofing membranes (Holzmann, 1988). The chemical resistance analysis, which is discussed later, supports that the type of branched phthalate tested were equal to or better than linear phthaltes when tested for chemical resistance. In some cases a blend of branched and linear phthalates would perform best.

Polyester polymeric plasticizers are used when unique properties are required. In this study polyesters did not result in a significant increase in physical properties relative to the monomeric phthalates esters. They did out perform the monomeric adipates.

Mixed metal stabilizers are required in PVC formulations to allow the material to be processed into a film. This study found no significant difference in physical properties between a barium cadmium stabilizer and barium zinc stabilizer. Both metal stabilizers are known to work synergistically with a co-stabilizer, epoxidized soybean oil (ESO). ESO was used in this study and is required for optimum stability. The amount of ESO did not significantly affect the physical properties.

Calcium carbonate is often used as filler in plastics. Depending on the level, calcium carbonate can; increase the modulus, increase the hardness and at very high loadings, decrease the cost of the formulation. This study found that at levels less than 7% by weight the physicals properties were not significantly affected. At levels over 20% the physical properties were compromised and as will be described later, the chemical resistance is severely compromised. Calcium carbonate levels between 7% and 20% require further investigation.

3.2 *Resistance to uv exposure*

Clear PVC has poor ultra violet light resistance, and is not recommended for extended outdoor applications without additional components that can prolong the outdoor UV exposure. These additives are UV inhibitors and or absorbers. This study shows that once a small amount of pigment is added the UV resistance improves dramatically and that UV inhibitors and or UV absorbers offer no additional benefits. After 3000 hours in a QUV weatherometer both the pigmented and pigmented sample with UV absorbers and inhibitors were still very flexible and there was no significant difference between them. Both passed the original specification. This also indicates that flexible PVC can remain exposed for longer than many thought. Exposures of 12 months or longer in many applications will not significantly change the physical properties of the material provided it is properly formulated. For example PVC liners for swimming pool liners are exposed for 7-12 years and polyester fabric reinforced roofing membranes up to 20-25 years. In both of these applications the pigments served as the sole UV protector. No additional UV inhibitor or absorber is required. Again this reinforces that it is imperative for the formulation designer to understand the end use requirements. If the wrong formulation or the wrong construction is used for the wrong application then it will have a shortened life span. Another example of using a poorly formulated flexible PVC is when years ago certain automotive companies used poorly formulated PVC for automotive interior applications, resulting in degradation of the PVC. Today properly formulated PVC in these applications lasts 10-20 years in the same exposed applications.

Previous work by Orem and Sears (1979) determined that the useful life of outdoor exposed flexible PVC is a function of thickness. There is no reason to believe that this would not be true for buried geomembrane also, although the slope of the curve would be much lower and thus the life expectancy would be much longer. A model for each formulation would be useful. Based on the work Stark and Rohe (2001) completed and independent work the author conducted on various exhumed samples, including the 30 year-old sample from the Kellogg site in Michigan, indicates that a life expectancy well beyond 30 years will occur.

3.3 *Chemical Resistance*

The chemical resistance of geomembranes is extremely important. Synthetic leachate was used as discussed in a paper by Stanford et al (1979). The aerobic version of leachate was used, although most leachates would operate in an anaerobic environment. The results from this research indicate that high filler loadings resulted in excessive weight gain and thus in poor chemical resistance. A PVC formulation incorporating high calcium carbonate loading is by far the most significant negative factor in acidic leachate environments. The formulations with less than 7% calcium carbonate, incorporating a branched or linear phthalate, had less than 5% weight change and more importantly, were still very flexible. These were judged a pass. The leachate is very acidic and the results for 37% HCl, while more aggressive, followed the same trend. Based on actual tests with actual leachate from landfills, the artificial leachate is more aggressive compared to actual leachate.

Most formulations performed well in the concentrated caustic environment (20% sodium hydroxide solution). The formulations containing the trimelatates or the polyester plasticizers had no change. In a caustic environment the adipates performed poorer than the monomeric phthalates. While both the branched and linear phthalates performed adequately the branched phthalates outperformed linear phthalates. The polymerics performed very well in the caustic environment. The filler level did not affect the performance in the caustic environment.

Resistance to Neats foot oil (an animal fat), mineral oil and corn oil all followed the same trend, indicating that adipates plasticizers are to be avoided; branched phthalates performed slightly better than linear phthalates, while polyester polymeric plasticizers are best for oils. Alloys of PVC, which contain nitrile rubbers, or ketone ethylene ester polymers, have also been found to provide superior resistance to oils and grease and many other hydrocarbons. In environments where primary containment of numerous types of hydrocarbons are required, these PVC alloys would likely function well. Individual testing should be done to ensure the product would function as designed.

Hexane, a solvent that is known to aggressively extract monomeric plasticizers, did exactly that. Only the formulation, which incorporated the polyester polymeric plasticizer, performed adequately in this case.

Gasoline, kerosene, ASTM Fuel C and ethanol resistance results were equal to the hexane indicating that PVC plasticized with polyester polymeric plasticizers or other polymeric plasticizers would perform well in these environments.

All of the samples tested had very good resistance to soapy water.

In all cases of chemical resistance the plasticizer loss was higher in the beginning and slowed with time. In no case was all the plasticizer removed. An actual model of this was not created, but would be useful for future study. It is known that while plasticizers do not chemically bond with the PVC polymer the plasticizers adsorb onto and absorb into the PVC. PVC is very soluble in the properly chosen plasticizer. Attractive dipole-dipole interactions, Van der Waal forces, London forces and hydrogen bonding at the molecular level make it very difficult to extract all the plasticizer. Sears & Darby (1982).

Interestingly, the type of stabilizer did have a relationship to chemical resistance in certain cases. This fact must not be ignored when developing or changing a formulation.

Mersiowsky (2002) analyzed various types of PVC in simulated anaerobic landfill environments. In his conclusions he stated, “The reported assays underwent the characteristic stages of landfill development, being subjected to leaching and biodegradation. Because of the extensive observation period, the fate of PVC products and their additives in landfill waste can be assessed. Degradation of the PVC polymer was not observed.” Mersiowsky also found that the type of plasticizer impacts the leachability of the PVC, with the branched monomeric phthalate, DIDP, exhibiting no detectable loss, while the adipate plasticizer had significant loss.

3.4 *Biological Resistance*

The biological resistance of flexible PVC geomembranes has often been questioned and the phthalate plasticizers have been thought to a food source for microorganisms. This was not found to be the case.

All the different ingredients in a flexible geomembrane formulation were subjected to ASTM G21, which involves inoculating the individual raw materials with an assortment of naturally occurring fungi and then incubating the samples for 4 weeks in an environment where the fungi are known to thrive. None of the raw materials were found to be easily metabolized by the fungi. The monomeric phthalate had no evidence of attack by the fungi. Previous research has shown that adipates and sebacates are susceptible to biological growth and thus should be avoided (Klausmeir & Anderson, 1981).

Another unpublished study by Diebel in 1999 involved submersing flexible PVC in liquid pig, chicken and cow manure for 6 months. These samples were exposed to numerous microorganisms and a very aggressive aqueous environment. The physicals of the 6-month-old samples were not significantly different from the control indicating that PVC plasticized with monomeric phthalates functions very well in containing manure waste.

Flexible PVC normally incorporates a biocide as an extra precaution. In many cases the biocide is not required since the individual raw materials were shown to be resistant to microorganism metabolism.

The author analyzed a 30-year old flexible PVC with no biocide in the original blend that was exhumed from the Kellogg site in

Michigan and there was no evidence of any microbiological degradation. Stark & Rohe (2001) also reported on this.

Formulations with and without biocide were subjected to a soil burial test, which involves burying the sample in a soil that has active microorganisms present. Post burial physical results of both formulations passed the PGI 11-97 specification.

It should be mentioned that not all of the types of plasticizers were tested for resistance to microorganisms in this study and that certain types are likely more susceptible.

4 CONCLUSIONS

While a minimum molecular weight of 69K PVC resin is required there is no advantage to go beyond that in most cases. All types of plasticizers tested had very good initial physical properties. Polyesters polymeric plasticizers result in superior resistance to hydrocarbons. Monomeric adipate plasticizers should be avoided in flexible PVC geomembranes since they have poor long-term aging and chemical resistance properties. Monomeric trimelatate plasticizers performed very well and are a good choice for buried flexible PVC geomembranes, especially if the conditions will be a sustained high temperature (greater than 50 °C). Branched, linear or a blend of monomeric phthalates with carbon chain average greater than seven will perform well in most flexible PVC geomembrane applications and are a good choice for most applications of flexible PVC geomembranes. Branched phthalates performed better than linear phthalates in extremely acidic and caustic environments. There was no measured difference in physical properties between a BaCd and a BaZn stabilizer system although it was determined that the type of stabilizer can impact the chemical resistance by a small, but significant amount. Calcium carbonate filler loadings of greater than 7% should be avoided in low pH (acidic) environments. Although un-reinforced PVC is not recommended for long term outdoor exposure, properly formulated flexible PVC can be left exposed for 12 months in most environments without significant change due to weathering. If polymeric plasticizers are used or if a reinforcing scrim is incorporated into geomembrane outdoor exposure is greatly increased to 20+ years. Proper pigment type and loading level is required for exposed applications and if proper pigment selection is used then additional UV absorbers and or inhibitors are not required. Properly formulated flexible PVC is not prone to microbiological attack. If the proper specification is used it will force the use of a functional formulation. In the past the wrong formulations have been used for applications where they should not have been and premature failures resulted. Chemical resistance testing should be done on all new formulations. A chemical resistance test should be considered to any new or existing specifications for flexible PVC geomembranes. The formulator of the flexible PVC geomembrane must be aware of the interactions between the ingredients and design the formulation to be as robust as possible.

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