

Characterising long-term uv stabilization of geomembranes under different environmental conditions

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ABSTRACT: Geomembrane has been used successfully over the past 20 years in many different applications from reservoir liners to fish ponds to landfill liners. Increasing usage in new applications areas leads to higher performance demands on geomembrane. This paper will study the effects of various traditional and new environmental stresses on geomembrane and how to formulate the stabilization package to meet these performance requirements for new applications.

1 INTRODUCTION

The popularity of high density polyethylene geomembrane has increase due to cost effectiveness in containing hazardous and municipal waste and valuable water resources. However there are an increasing number of failures due to many reasons. Studies indicated improper resin selection, installation procedures and improper designs are some causes. While recent studies indicated improper formulation of the UV and antioxidant cause of premature failure. More recently, environmental stress (eg. - chlorine exposure) can lead to premature failure. This paper will discuss methods to stabilize geomembrane from degradation from harmful UV exposure, enhanced stabilization against thermal degradation (via OIT measurements) and designing an improved chlorine resistant geomembrane.

During the past fifty years, various types of light stabilizers have been developed to extend the service life of polymers by inhibition of the degradation processes photo-initiated by ultraviolet light energy from the sun and other sources. Of the various chemical classes developed, the benzophenone and benzotriazole UV absorbers, the hindered amine light stabilizers (HALS), and their combinations continue to satisfy the UV stabilization requirements of most of the large volume outdoor polymer applications. However, many new stabilizer chemistries have been developed for niche market applications. The light stabilizers together with other additives, such as antioxidants, impact modifiers, colorants, fillers, heat stabilizers, plasticizers, etc., have enhanced the properties and extended the service life of poly-

meric materials resulting in the replacement of traditional materials in a multitude of outdoor weatherable applications. Today, most polyolefins can meet rigorous outdoor exposure requirements if formulated with an efficient HALS-based stabilizer system. However, further enhancements in the light stability of polyolefin formulations would allow polyolefins to compete in the most demanding, durable applications that involve UV exposure.

Hindered amine light stabilizer (HALS) technology is currently used in a broad spectrum of polyolefin applications to impart both UV and thermo-oxidative protection. A review of HALS technology is beyond the scope of this paper but many excellent articles on this subject can be found in the literature as Gugumus (1984). HALS has been the stabilizer product of choice for polyolefins because they exhibit multi-functional stabilization activity. HALS are capable of decomposing alkyl hydroperoxides and peracids, can trap free radicals, and can potentially quench excited states, all while regenerating the active species. A number of studies have focused upon the factors influencing the HALS activation step wherein the precursor is converted to the nitroxyl active site. Once activated, the nitroxyl active site undergoes many "turnovers" until it is ultimately deactivated. Thus, the part will begin to degrade at an accelerated rate and will ultimately fail. Although nitroxyl deactivation is a major pathway by which HALS loses effectiveness, there are other causes. Physico-chemical factors that influence HALS loss include volatility, diffusivity, and solubility/compatibility in a particular polymer. In addition, chemical side reactions can occur at various sites within the HALS molecule, and these can directly or indirectly contribute to HALS deactivation and/or

loss. Recent studies have resulted in the development of a new class of light stabilizers with very high efficiency that can extend the life of polyolefin parts, beyond what is afforded by current state-of-the-art HALS technology. Because of their efficiency, these products can also be used at lower loading levels than conventional HALS can to achieve a targeted service life. The light stabilizers together with antioxidants has been demonstrating to be effective in geomembranes stabilization, however they are often subjected to periodic exposure of harsh chemicals as acidic species or chlorine that can deactivate common UV stabilizers and attack the polymer. While thermoplastic geomembranes has good corrosion resistance, it unfortunately is not impervious to attack by chlorine-based disinfectants. The most common disinfectants are chlorine gas, chloramines and sodium hypochlorite/calcium hypochlorite. The exposure of geomembranes to these chemicals needs to be considered when formulating a light stabilization strategy otherwise its service life could be reduced drastically. The geomembranes service life can be assessed and estimated by artificial weathering and/or by OIT testing either treated or untreated with aggressive chemicals.

2 UV STABILIZATION

2.1. Formulations and Processing:

Antioxidant, acid scavenger and UV stabilizers were dry blended with powdered resin and the resulting formulations compounded on a one and one quarter (1 1/4") inch single screw extruder. For injection molded HDPE and PP, the resulting pellets were converted by injection molding on an Arburg Injection Molding Machine into ASTM Type V tensile bars (to determine tensile properties), and 2"x2"x0.060" plaques (to determine color and gloss).

2.2. Test Criteria:

Tensile bars and plaques were exposed in a Ci65 xenon arc Weather-Ometer (Atlas Electric) following the conditions outlined in ASTM Method G-26. The general appearance, including color and gloss, and the tensile properties of samples were determined at equal intervals until physical failure, or until there were no more samples to expose. Tensile strength and percent elongation at break were determined for tensile bars using an Instron tensile tester according to ASTM Method D-638.

2.3. Results and Discussion

The superior performance of the new high efficiency light stabilizers, THT-4611 and THT-6435, is shown in the following studies involving HDPE, and PP.

High Density Polyethylene (HDPE):

A HDPE hexene copolymer was formulated with a base antioxidant package (0.15 wt.%, 1:2 AO-2110:AO-2704), zinc stearate, and either UV-783 or THT-4611 as UV stabilizer. The formulations were exposed in an Atlas Ci65 WOM with water spray, and tensile properties were measured as a function of time. After 8000 hours of exposure, the equivalent of over four years of Florida exposure, the sample containing THT-4611 still retained 74% of its initial elongation. In contrast, the sample containing UV-783 failed after 3120 hours. It is interesting to note that the loading of THT-4611 was significantly lower than the loading of UV-783 in this study.

Polypropylene (PP):

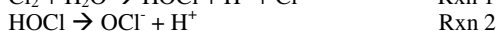
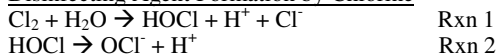
A PP homopolymer was formulated with a base antioxidant package (0.07 wt.%, AO-2777), calcium stearate, and either UV-3346 or THT-6435. The formulations were exposed in an Atlas Ci65 WOM with water spray and tensile properties were measured as a function of time. After 4000 hours of exposure, the equivalent of at least two years in Florida, the formulation containing THT-6435 exhibited significantly higher tensile strength retention than the formulation containing UV-3346. After actual Florida exposure for 4 years, samples containing THT-6435 outperformed samples containing UV-3346, UV-944 and UV-783 by a significant amount.

3. CHLORINE EFFECT ON GEOMEMBRANES SERVICE LIFE.

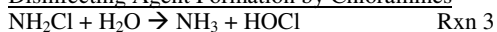
3.1 Degradation Mechanisms

Disinfectants work by generating "free chlorine" (HOCl and OCl⁻), that lead the physical properties of polyethylene geomembrane under severe degradation stress. Below illustrates the formation of the disinfectant free chlorine (HOCl and OCl⁻) from chlorine gas, chloramines and metal hypochlorite.

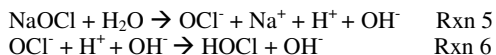
Disinfecting Agent Formation by Chlorine



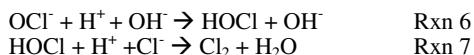
Disinfecting Agent Formation by Chloramines



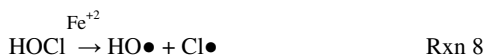
Disinfecting Agent Formation by Metal Hypochlorite (NaOCl/CaOCl)



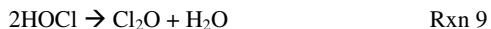
The concentration of HOCl is highly dependent on pH. At a pH of 5.5, HOCl is estimated to be undissociated while at pH of 11 HOCl is completely dissociated. Also at a pH of less than one, Cl₂ gas formation can be expected. The following illustrates the reaction pathway for the dissociation and undissociated HOCl which is dependent on pH.



Chung et al. documented that polyethylene undergo degradation, but little has been written to explain how this polymer can be degraded by hypochlorous acid in an environment that is heterogeneous (solid phase and aqueous phase), free of harmful UV energy and at relatively low temperatures. The degradation mechanism may seem difficult to explain given the relatively mild conditions of commercial use. The concepts below may shed some light on the potential degradation pathway. Candeias et al. have shown that hypochlorous acid can react with iron (II) complex (Fe⁺²) in aqueous solution with the rate constant 220 +/- 15 dm³ mol⁻¹ s⁻¹. In this reaction, free hydroxyl radicals are formed in 27% yield. The hydroxyl radical and chlorine radical can then initiate the degradation of polyethylene geomembrane.



Another study showed that saturated alkanes can be oxidized by hypochlorous acid in darkness, in a two-phase system, and at relatively low temperatures (0-50°C). This study implicated Cl₂O, generated from hypochlorous acid according to Rxn 9, as the radical generating species.



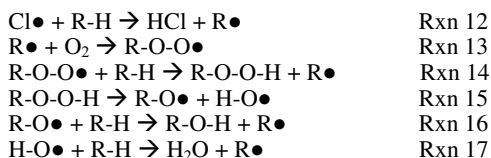
The authors of this study proposed two possible mechanisms for the initiation of free-radical chains. The first involves cleavage of the Cl-O bond in the Cl₂O, which they claim is possible due to the high electronegativity of the Cl and O.



Another potential pathway for the free radical initiation is an electron transfer process between the polyethylene geomembrane and the chlorinating compound (Cl₂O). The scientists drew an analogy between this reaction and the spontaneous free radical fluorination of hydrocarbons by elemental fluorine.



The generation of R• and Cl• in Rxn 10 and Rxn 11 can lead to the accelerated degradation of the polyethylene geomembrane. The polyethylene degradation pathway is described below (Rxn 12 to Rxn 17).



3.2 EXPERIMENTAL

In the first phase of this study, commercial polyethylene geomembranes were obtained and immersed in deionized (DI) water while another set was immersed in chlorine water. The concentration of chlorine in the chlorinated DI water was fixed at 5ppm of free chlorine using calcium hypochlorite, at an initial pH of approximately 6.8. This study was carried out at 60°C for both the DI and Cl water. The DI water and Cl water solutions were refreshed once a week. At one week intervals, the oxidative induction times (OIT) were measured following ASTM Designation D3895-98. In the second phase of the study, several developmental compounds were evaluated to measure their effect on increasing the polyethylene geomembrane resistance to degradation caused by exposure to the strongly oxidizing free chlorine. The plaques were also immersed in glass containers containing DI water or 5 ppm chlorinated water (weekly refreshed). Also on a weekly basis the OIT were measured and recorded.

3.3. RESULTS

Phase 1: Commercial Geomembrane Evaluation

The effects of hypochlorous acid on commercial grade polyethylene geomembrane were measured using standard ASTM OIT methods after exposure in a 60°C aqueous solution of 5ppm of free chlorine using calcium hypochlorite (7.3ppms of calcium hypochlorite). In parallel, samples were soaked in 60°C deionized water to create a comparative baseline to measure the extent of polymer degradation. At seven day intervals the calcium hypochlorite solution and water were renewed and the samples re-soaked. Initial OIT of the commercial geomembrane was determined to be 145 minutes. After immersion for 5 weeks in 60°C water, OIT's of 124 minutes were measured and recorded. However in the sample immersed in 5ppms free chlorine, after 5 weeks at 60°C, the OIT significantly decreased to 49 minutes. Below, figure 1 and table 1 show the effects of free chlorine and water on commercial geomem-

branes samples. The OIT results indicated in 60°C water, the polyethylene geomembrane oxygen induction time decreases slightly over time. However, with just 5ppms of free chlorine, oxygen induction time decreases significantly more quickly. After 5 weeks in water, the OIT was measured and recorded at 86% of its original value while in 5ppm free chlorine water; the OIT was measured at only 34% of its original value.

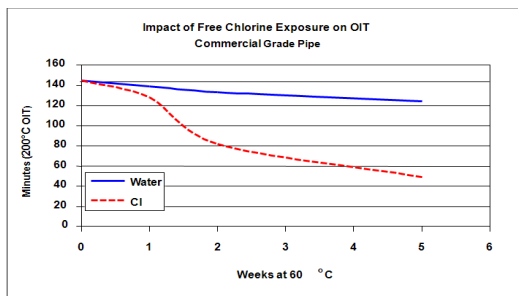


Figure 1. OIT of geomembranes samples immersed in water and 5ppm free chlorine.

Phase 2: Chlorine Resistance of Polyethylene with New Specialty Additives

After defining the deleterious effects of free chlorine water to polyethylene geomembranes, three proprietary specialty additives were evaluated to counter the degradation effects of free chlorine on polyethylene. The first test included the OIT measurements on control and stabilized samples. The proprietary specialty additives are identified as Compound A, B and C in the table 2.

Sample	OIT at 200°C (min.)
Unexposed Control	104

Table 1: Initial OIT of polyethylene samples

3 Weeks at 85°C, 5ppm free chlorine	OIT at 200°C (min.)
Control Sample	42
Additive Compound A	100
Additive Compound B	37
Additive Compound C	15

Table 2: OIT of polyethylene samples immersed in water with 5ppm free chlorine

The OIT of the unexposed sample started with a time of 104 minutes. After 3 weeks in 5ppm free chlorine water at 85°C, the sample OIT dropped to 42 minutes (-60% decrease from original value). However with the incorporation of a specialty additive, Compound A, the OIT was measured and recorded at 100 minutes (less than 4% decrease from

original value). New Compounds B and C did not show a positive effect.

4. CONCLUSIONS

Through such investigations, it was developed a new class of light stabilizers with extraordinary efficiency in polyolefins systems. At equivalent or reduced stabilizer loadings, these systems greatly extend UV stability of polyethylene and polypropylene. This new technology allows for the development of new high performance, durable polyolefin products with extended service lifetimes. In addition, cost reduction of existing products will also be possible with these new stabilizers.

Another study demonstrated the degradation of commercial grade polyethylene geomembrane can accelerate under exposure to free chlorine. Accelerated degradation was observed with a significant decrease in OIT versus samples which did not contain free chlorine. Several additive compounds were evaluated in order to increase the geomembrane's resistance to free chlorine oxidative degradation. Compound A was found to maintain the geomembrane's original OIT even under exposure to 5ppms of free chlorine after 3 weeks at 85°C.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- ASTM Designation D3895-98, *Standard Test Method for Oxidative Induction Time of Polyolefins by Differential Scanning Calorimetry*
- Candeias LP, Stratford MR, Wardman P. Formation of hydroxyl radicals on reaction of hypochlorous acid with ferrocyanide, a model iron (II) complex. *Free Radic Res*,1994 Apr.20(4):241-9.
- Chung, S, Oliphant, K et. al *An Examination of the Relative Impact of Common potable Water Disinfectants on Plastic Piping System Components*, Jana Laboratory.
- Gugumus, F. 1984. Photooxidation of Polymers and its Inhibition. *Oxidation Inhibition of Organic Materials*, Vol. 2.