Polymer Degradation and Stability 109 (2014) 194–208

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

# Effect of aging on the stress crack resistance of an HDPE geomembrane

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ARTICLE INFO

*Article history:*
Received 28 March 2014
Received in revised form
13 June 2014
Accepted 16 June 2014
Available online 24 June 2014

*Keywords:*
Degradation
Morphological structure
Chain disentanglement
Annealing
Plasticization
Geomembrane

## ABSTRACT

The changes in the stress crack resistance, SCR (measured by the single point notched constant tensile load; ASTM D5397 – appendix) for a 1.0 mm high-density polyethylene (HDPE) geomembrane aged in synthetic leachate at six temperatures (25, 40, 55, 70, 85 and 95 °C) and in air and water at 55 °C were investigated for almost five years. There are observed changes in the SCR before the geomembrane chemically degraded (as manifest by melt index and tensile properties) and even before the antioxidants depletion at temperatures below 70 °C (as manifest by the standard and high pressure oxidative induction times). This change is attributed to morphological changes during aging that affected the inter-lamellar connections due to: (a) annealing that increased the strength of the inter-lamellar connections (over the temperature ranges examined), and (b) the proposed chain disentanglement mechanism. The annealing and chain disentanglement mechanisms have a counteracting effect on the inter-lamellar connections and hence on the SCR. Chain disentanglement dominated over the annealing effect at 25, 40, 55 and 70 °C, resulting, respectively, in a decrease in SCR to an equilibrium $SCR_m$ of 0.83, 0.65, 0.26 and 0.43 of the initial stress crack resistance of the geomembrane ($SCR_o$). The maximum decrease in SCR is observed when the geomembrane is aged in leachate at 55 °C with the SCR decreasing to 0.26 $SCR_o$. The SCR of the geomembrane aged in air and water at 55 °C decreased to about 0.5 $SCR_o$, implying that the surfactant used in leachate may have enhanced the rate and the extent of chain disentanglement (i.e., decreasing the time to reach a lower $SCR_m$) due to plasticization of the amorphous zone.

## 1. Introduction

HDPE geomembranes are prone to stress cracking when subject to tensile stress less than their short-term mechanical yield strength [49,60,75]. This type of failure takes a long-time [42] and varies depending on the geomembrane resin (polyethylene resin and additives [49]). Geomembrane cracking starts with small cracks formed by slow crack growth. These small cracks connect together to form one crack and then, depending on the loading and exposure conditions, the crack can form a rupture (i.e., a fully penetrating crack [2,30,73]). Depending on loading and exposure conditions, the size of the crack/rupture may increase by rapid crack growth and branch many times to produce the appearance of shattering [36,73].

The so called high-density polyethylene (HDPE) geomembranes on the market this century typically comprise 96–97% (by weight) medium density polyethylene resin, 2–3% carbon-black and around 0.5% antioxidants and stabilizers [48,51,87,108]. The carbon-black, antioxidants and stabilizers are used to protect the geomembranes from degradation due to photo-oxidation and thermal oxidation.

For HDPE geomembranes, the single point notched constant tensile load (SP-NCTL [9] – appendix) test is used as an indicator of the stress crack resistance (SCR [49,50]). To decrease the susceptibility of geomembranes to stresses cracking, those used in geoenvironmental engineering applications are usually required to have a minimum SCR measured by SP-NCTL. For example Ref. [15], specifies a minimum SCR of 200 h while Ref. [38] specifies a minimum SCR of 300 h for new HDPE geomembranes. Manufacturers have made great improvements in the SCR and typical HDPE geomembranes have SCR well in excess of 300 h. For example Ref. [29], investigated the aging of three different HDPE geomembranes having SCR ranging from 300 to 900 h and Ref. [81] investigated one having SCR > 5000 h. Although this improvement in SCR has substantially reduced the occurrence of stress cracking of HDPE geomembranes after short service periods, stress cracking is still observed for some geomembranes [74].

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http://dx.doi.org/10.1016/j.polymdegradstab.2014.06.013
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During service, geomembranes used as part of a composite liner at the base of landfills and ash monofills may be at temperatures normally ranging from 0 to 30 °C for landfills in which there are no exothermic biological processes or chemical reactions taking place (with temperature depending on local ambient conditions), 30–40 °C for normal municipal solid waste landfills with organic waste, 40–60 °C in some landfills (e.g., some ash monofills and with aggressive recirculation of leachate in some municipal solid waste landfills), and 60–90 °C in rare cases [78,91]. Thus, there is a need to understand the likely long-term performance of geomembranes over a relatively wide range of temperatures; especially between temperatures of about 25 and 95 °C.

With long-term aging, HDPE geomembranes are expected to experience a reduction in their mechanical properties [48,69,81] that would lead to eventual geomembrane cracking. This reduction may occur due to chemical degradation of polyethylene and/or a change in the morphological structure of polyethylene with aging. Chemical degradation of polyethylene may involve chain scission and/or chain cross-linking resulting from thermal oxidative degradation [18,39,43,99], photo-oxidation [24], and or thermal degradation in the absence of oxygen [47,62]. In contrast, morphological change in polyethylene (e.g., annealing and physical aging) does not involve chain scission or cross-linking. Although the term physical aging was developed for glassy polymers, it is also said to take place in semi-crystalline polymers in the rigid amorphous zone of restricted mobility [3,61,106]). Chemical degradation is known to have a pronounced effect on the SCR of a geomembrane. Ref. [81]. reported that an HDPE geomembrane having an initial SCR of 5000 h completely lost its SCR after aging for 40–80 months (depending on incubation medium) at 85 °C due to chain cross-linking. Nevertheless, the morphological change in polyethylene would lead to a decrease in the SCR and may eventually lead to stress cracking of HDPE geomembranes before the geomembrane chemically degrades, as inferred from the stress cracking failure cases reported by Ref. [94] for two different HDPE geomembrane liners after two and eight years in service. Ref. [94] attributed the stress cracking to the decrease in the SCR of the geomembranes due to the rearrangement of the crystalline structure of the polymer with aging. The objective of this study is to examine the changes in the SCR of geomembranes aged at elevated temperatures that may arise due to changes in their morphological structure before there is evidence of chemical degradation by either chain scission or cross-linking. Specifically, the study examines the changes in the SCR of a commercial HDPE geomembrane, widely used in landfill liners and mining applications, with aging over a temperature range from 25 °C to 95 °C. This study will show a variation in SCR with aging temperature that has not previously been recognized in the literature. To explain this behavior it is necessary to begin with a discussion of some basic concepts and examine the changes in physical properties that will provide insight into the morphological changes and chemical degradation occurring with aging at the various temperatures between 25 and 95 °C.

## 2. Background

### 2.1. HDPE geomembranes

The classical chemical degradation model for HDPE geomembranes without hindered amine (light) stabilizers (HALS or HAS) conceptually involves three distinct stages [48,96]; Fig. 1a): (a) Stage I: characterized by antioxidant depletion (usually monitored by standard oxidative induction time; Std-OIT [7], (b) Stage II: an induction period, starting after Stage I, in which the geomembrane is attacked by oxygen without a measurable change in engineering properties (e.g., tensile strength; melt index, MI; or SCR), and (c) Stage III: characterized chemical degradation by a measurable change in the engineering properties of the geomembrane (end of Stage II) due to degradation of the polymer that eventually leads to failure.

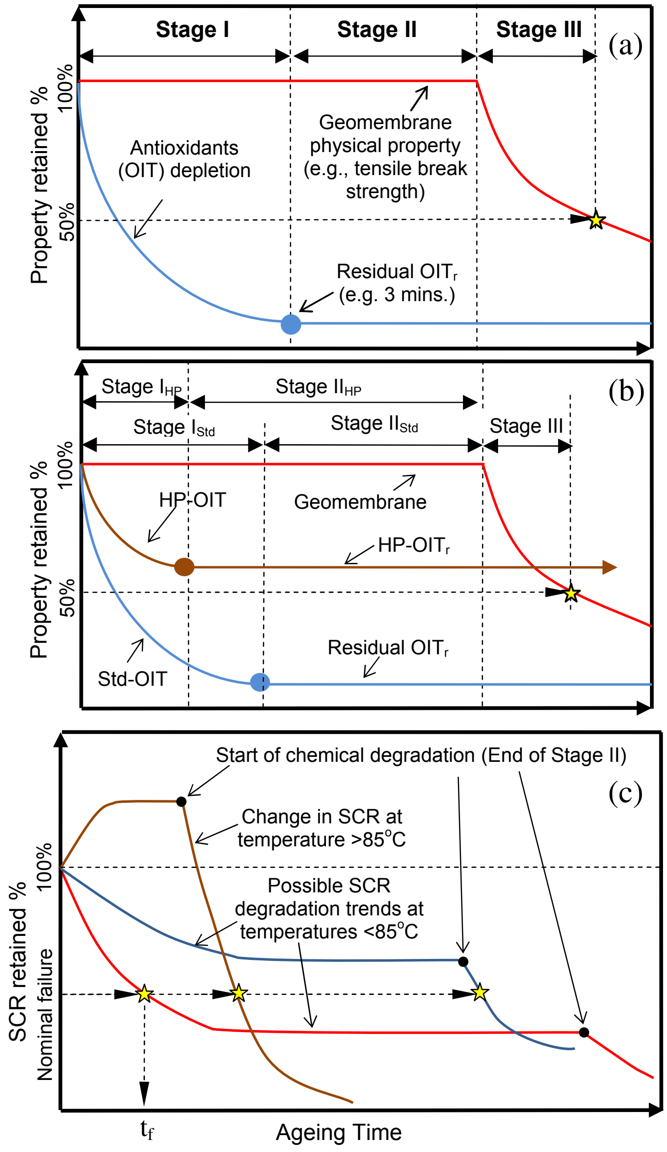

**Fig. 1.** Classical three stages degradation model (a) for geomembranes without HALS [48], (b) for geomembrane with HALS, such that Stage $I_{std}$ may be greater or lesser than Stage $I_{HP}$ depending on the incubation conditions and temperatures [29] and (c) showing the possible changes in the SCR of geomembranes at temperatures above and below 85 °C. Notes: (i) Depending on temperature, for the geomembrane studied in this paper $t_f$ (based on SCR) may be shorter than either Stages I and II (i.e., it can occur before OIT depletion or chemical degradation takes place) (ii) the nominal failure is based on 50% of $SCR_o$ or 50% of required SCR.

HALS are detected by high pressure oxidative induction time (HP-OIT) [10], but not by Std-OIT [95,105]. Thus for a geomembrane with HALS, Std-OIT and HP-OIT do not generally deplete at the same rate. Furthermore, a geomembrane may degrade after the HP-OIT reaches a residual value that can be even greater than the 400 min specified by GRI-GM13 (2011) for a new geomembrane ([29]; Fig. 1b). Thus, one value of Stage I can be inferred from Std-OIT depletion and another value can be inferred from HP-OIT depletion (Fig. 1b).

A geomembrane may be considered to have reached the end of its service-life and have failed when it no longer meets the original design requirements as a hydraulic and diffusive barrier to