Technical note

ASSESSMENT OF POLYETHYLENE GEOMEMBRANE OXIDATION USING ATR-FTIR MICROSCOPE

Summary

Geomembranes are widely used in containment, environmental, hydraulics and geotechnical applications such as ponds, landfill liners, dams, canals, and waste storage centers. They effectively prevent the migration of water, hazardous substances, chemicals, or gases into the environment. Most geomembranes are made from synthetic polymers, often polyethylene (PE), but also other polymers such as PP, PVC, CSPE and others. PE geomembranes are formulated to long-term exposure conditions. The unique combination of additives with the polyethylene matrix allows long-term compatibility with the site conditions. Considering polyethylene, the antioxidant depletion is commonly monitored by testing the oxidative induction time (OIT), before and after aging or field exposure.

Alternative testing to the assessment of antioxidant depletion is of interest for the monitoring of side reactions to the loss of antioxidant, OIT being an indirect method. These side reactions will act synergistically between the additives, the polymers and the chemicals from the exposure media. Several analytical methods are being put forward: ATR-FTIR, Raman spectroscopy, X-Ray small angle diffraction, GC-MS, LC-MS, TOF-SIM and NMR spectroscopy. Besides polyethylene, the common focus is put on attenuated total reflection Fourier transform infrared (ATR-FTIR), for analyzing antioxidants and additives in polymer. When coupling with microscopy, the spectroscopy leads to a high spatial resolution and the mapping of chemicals from the surface of a solid sample. For geomembranes, the analysis of cross sections provides a quick information of the residual antioxidant content as well as the presence of side-reaction products and chemical profile over the thickness.

Discussion

FTIR is utilized to get infrared spectra of compounds or materials as the specific functional groups can be identified. Four sharp peaks dominate the spectrum of PE: The methylene stretches nearly at 2920 and 2850 cm^{-1} and the methylene deformations at 1470 to 1460 and 729 to 719 cm^{-1}. After the period of thermal oxidation, the common carbonyl compounds such as peroxides, ketones, aldehydes, carboxylic acids, esters, etc. in the geomembrane can be formed. These compounds can be identified between 1630cm^{-1} and 1750 cm^{-1} using FTIR.

In addition, the carbonyl index (I) is presumably the most common method to measure the chemical oxidation of polyethylene and to monitor the degradation of geomembranes by finding the ratio of the absorbance of the carbonyl peak (1735cm^{-1}) and the reference peak (2850 cm^{-1}) (I = I absorbance @1735 cm^{-1} / I ref. absorbance @ 2850 cm^{-1}). The reference band (2850 cm^{-1}) which is the absorbance of the symmetric stretching vibration of CH2 at 2850 cm^{-1} was chosen.

In addition, to evaluate the extent of oxidation for all samples on the surface of geomembranes, ATR-FTIR (Attenuated Total Reflectance Fourier-Transform Infrared) spectroscopy technique can be used to study the molecular composition of materials. IR radiation passes through a crystal (often made of diamond) in contact with the sample.

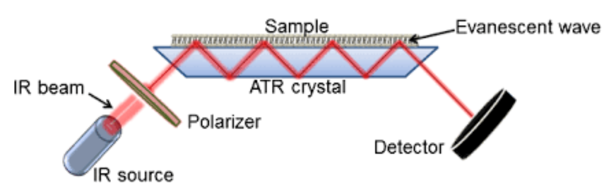

Figure 1 ATR-FTIR Schematic of analysis.

As the infrared light penetrates the crystal, it produces multiple internal reflections at the interface between the crystal and the sample. This creates a near-surface or surface-penetrating wave that interacts with the sample, improving sensitivity to surface interactions.

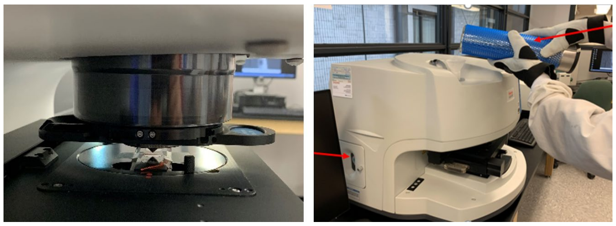

Figure 2 ATR-FTIR Equipment.

ATR-FTIR can be used to quantify and identify oxidation in polymeric materials. The intensity of oxidation peaks can be associated with the level of oxidation of the geomembrane, making it possible to measure its degree of oxidation. For example, the appearance of carbonyl stretching vibrations (C=O) around 1700 cm-1 indicates oxidation.

The diameter of the observed area is about 0.1 mm. Hence, when testing several points across the thickness of the geomembrane, it is possible to observe the profile of oxidation across the geomembrane. For multicomponent geomembranes, it is therefore possible to observe how each layer is affected by oxidation since the level of oxidation varies from the surface and the depth of a geomembrane layer as a function of oxygen diffusion. It is better than testing each layer individually (e.g., thin film test) because the tested sample is 'true', i.e., it takes in consideration possible synergy and interaction between layers, something the thin film test would not consider.

As a preliminary result, Figure 3 shows that there are small differences for the values of the peak intensities of 1732 cm^{-1} (C=O) while the peak values of 2850 cm^{-1} (CH2) for all cross-section surface of the geomembrane are distinctive which could be related to the interactions of phenolic antioxidants, HALS and carbon black.

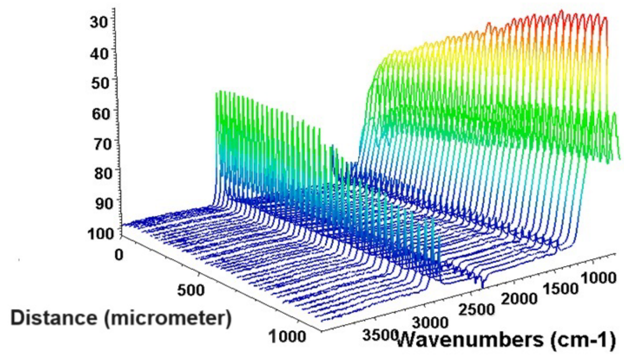

Figure 3 ATR-FTR Spectrum of aged geomembrane.

Conclusion

Understanding that the oxidation resistance of geomembranes is crucial for performance and durability assessment. When using OIT, the antioxidant depletion is correlated to an index of polyethylene resistance to oxidation. Such prediction method is based on the overall behaviour without the consideration of chemical synergistic.

For deep understanding, ATR-FTIR spectroscopy is an effective technique for measuring oxidation-related spectroscopic changes in geomembranes across the thickness of the sample. Unlike OIT, ATR-FTIR provides insights into how oxidation varies across different layers or through the whole thickness of a geomembrane.

ATR-FTIR spectroscopy is a vital tool for analyzing the oxidation and durability of polyethylene geomembranes. This technique provides high spatial resolution, enabling detailed study of localized oxidative reactions and aging processes. By identifying and quantifying oxidation levels, ATR-FTIR complements OIT tests, offering a comprehensive evaluation of the geomembrane's condition. This precise analysis is crucial for industries, ensuring the long-term performance and reliability of geomembranes in various applications.