Effect of Radiation from Low-Level Radioactive Waste Leachate on Antioxidant Depletion in HDPE Geomembrane – 16087

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ABSTRACT

Low-level radioactive waste (LLW) and mixed waste (MW) disposal facilities in the US are required to have a service life in excess of 1000 yr. Understanding the rate of degradation of high-density polyethylene (HDPE) geomembranes (GMs) used in LLW and MW facilities is necessary to assess their service life when conducting a performance assessment for a disposal facility. In LLW and MW disposal facilities, GMs may be exposed to radionuclides that may accelerate antioxidant depletion and degradation. This paper evaluates how radiation dosage affects antioxidant depletion in HDPE GMs and makes inferences regarding the impact of radiation on GM service life. Specimens of 0.04-mm-, 0.1-mm-, and 2-mm-thick HDPE GMs were exposed to a sealed source of Am-241 to simulate alpha radiation from LLW leachate (e.g., uranium). The specimens were exposed to the sealed source for 1–50 h, followed by oxidative induction time (OIT) testing to determine depletion of antioxidants in response to exposure. Penetration of alpha particles in the HDPE GM exposed to the sealed source was evaluated with the program GEometry ANd Tracking (GEANT4). The GEANT4 modeling indicates that physical dose deposition for alpha particles largely occurs on the superficial layers and decreased monotonically with depth to a negligible dose (~ 28 µm). For a 2-mm-thick HDPE GM, there was no change in OIT after exposure, whereas in much thinner GMs (e.g., 0.04 mm), significant antioxidant depletion occurred after exposure, reflecting the shallow penetration of alpha radiation at the surface of HDPE GM.

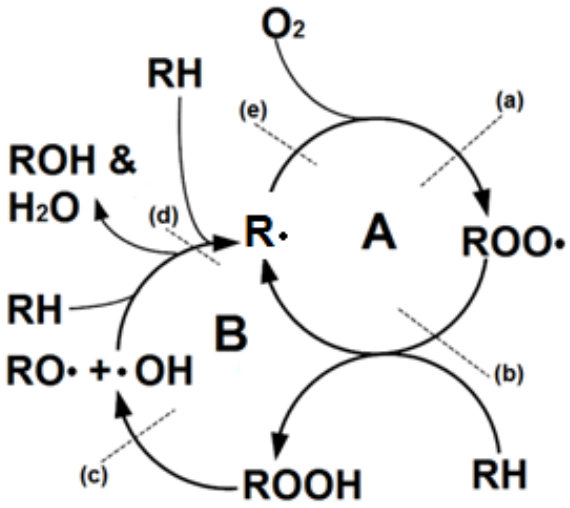
INTRODUCTION

Composite barrier systems are used in low-level radioactive waste (LLW) and mixed waste (MW) disposal facilities to limit contaminant transport to very low rates. Composite barriers consist of a thin polymeric sheet referred to as a geomembrane (GM) overlying a geosynthetic clay liner or a compacted clay liner. High-density polyethylene (HDPE) is the most common polymer used for GMs in LLW and MW facilities, and intact HDPE GMs are considered impermeable to advective flow [1, 2, 3, 4]. LLW and MW disposal facilities in the USA are required to have a service life in excess of 1000 yr. Understanding the rate of degradation of HDPE GMs used in LLW and MW facilities is necessary to assess their service life when conducting a performance assessment for a disposal facility.

GMs undergo non-mechanical degradation in three stages: antioxidant depletion (Stage I), induction time to the onset of polymer degradation (Stage II), and polymer

property degradation (Stage III). Grassie and Scott [5] indicate that the degradation of polyethylene follows the processes shown in Fig. 1. A polymer chain (RH) can break into a free radical polymer chain (R•) and hydrogen (H•) after obtaining the necessary activation energy (e.g., radiation or thermal). R• can react with oxygen (O_2) to form a hydroperoxy free radical (ROO•), which attacks the polymer backbone (RH) to form hydroperoxide (ROOH) and another free radical polymer chain. As oxidation continues, accumulation of ROOH results in decomposition into RO• and OH• and the generation of more free radicals that may attack the original polymer chain. Consequently, this process is auto-accelerating [6, 7].

To protect a GM from oxidation degradation, an antioxidant package with a combination of two or more types of antioxidants is commonly added to the polymer resin. Antioxidants intercept the links (e.g., a, b, d, and e) by donating or accepting an electron to react with the free radicals (e.g., ROO•, RO•, and OH•) to form a stable product (ROOH, ROH, and H_2O), as indicated by the dashed line in Fig. 1. Secondary antioxidants are designed to covert the ROOH to a stable alcohol (ROH), as shown by the dashed line c [6]. When the antioxidant is completely depleted, the GM becomes vulnerable to oxidation degradation and rapidly progresses through stages II and III of degradation [5, 8]. Thus, antioxidant depletion is an important stage in estimating the service life of HDPE GM.



RH: Polyethylene polymer chain
R•: Reactive free radical
ROO•: Hydroperoxy radical
ROOH: Hydroperoxide

Fig. 1. Oxidation loops for polyethylene [adapted from Grassie and Scott (1985) and Rowe and Sangam (2002)].

Previous studies have investigated antioxidant depletion in HDPE GMs exposed to municipal solid waste (MSW) leachate [8, 9, 10], acidic mine drainage [2], and LLW leachate [3, 4]. Those study indicate that the antioxidant depletion rate is affected by the leachate composition (e.g., surfactants, heavy metals, and extreme pH). Surfactants increase mass transfer between the GM and leachate, resulting in greater diffusive loss of antioxidants to the leachate [11]. Heavy metals accelerate decomposition of ROOH, leading to a higher rate of antioxidant consumption [11, 12]. In comparison to MSW leachate or acidic mine drainage, LLW leachate contains

radionuclides (e.g., Ra-226, uranium, and Tc-99) [3, 13], and radiation from these radionuclides may break down polymer chains and accelerate degradation of a HDPE GM [14].

Whyatt and Farnsworth [14] investigated the longevity of 1.5-mm-thick HDPE GM used in LLW disposal facilities using gamma radiation. They found that HDPE GMs become more rigid after irradiation; i.e., the elongation of HDPE GM decreased and the hardness of HDPE GM increased. However, the predominant radiation from LLW leachate comes from alpha particles emitted from uranium and Ra-226, and beta radiation from Tc-99 [3, 4]. Examination of the effect of alpha and beta radiation from LLW leachate on antioxidant depletion in GMs installed in LLW composite liner systems has not yet been explored.

The objective of this study was to examine the effect of alpha radiation from LLW leachate on antioxidant depletion in HDPE GMs. HDPE GMs with different thickness (e.g., 0.04-mm-, 0.1-mm-, and 2-mm-thick) were exposed to sealed source of Am-241 for up to 50 h to simulate alpha radiation (e.g., uranium) from LLW leachate. After irradiation, oxidative induction time tests were conducted on the HDPE GMs to examine antioxidant depletion. In addition, penetration of alpha particles from a sealed source of Am-241 into the HDPE GM was evaluated using Monte Carlo (MC) simulation with the program GEometry ANd Tracking (GEANT4) [15].

BACKGROUND

Different types of radiation have various effects on polymer degradation [16, 17, 18]. Charged alpha particles may penetrate into a polymer on the order of micrometers, and charged beta particles on the order of millimeters, whereas uncharged particles (e.g., neurons and gamma rays) can penetrate meters into a polymer. Therefore, alpha and beta particles potentially will affect the surface of a GM, whereas gamma rays can affect the entire thickness of a GM.

Previous studies have investigated the effect of radiation on the degradation of polymers [14, 16, 19, 20]. The original polymer chain (RH) can dissociate to a free radical chain (R•) and hydrogen (H•) when exposed to ionizing radiation carrying energy above the energy of the covalent bond energy in the polymer chain. The free radical polymer chain (R•) can form a new chemical bond with an adjacent free radical (e.g., R-R), defined as crosslinking, which makes the polyethylene more rigid and brittle [16, 21]. Additionally, the hydrogen (H•) can attack the RH to form hydrogen gas and R•. The free radicals can react with oxygen to form peroxide and hydroperoxide, accelerating the degradation process, shown schematically in Fig. 1. This process is defined as radiation-induced oxidation [19, 21].

LLW leachate contains uranium, Ra-226, and Tc-99, which emit alpha particles (exceeding 4.2 MeV) and beta particles (294 keV), respectively. The energies of these alpha particles and beta particles are high enough to be categorized as ionizing radiation because the typical bond energy of carbon-carbon typically is in the range of 5–10 eV [16]. Thus, alpha particles and beta particles from LLW leachate can potentially break the bonds in HDPE GMs and lead to an elevated rate of antioxidant depletion. This study evaluated the effect of alpha radiation on antioxidant depletion in HDPE GM. Additional research is ongoing to investigate the effect of beta radiation.

METHODS

Geomembrane

A commercially available 2-mm-thick smooth HDPE GM representative of GMs used in LLW disposal facilities was used to study the effect of alpha radiation on antioxidant depletion. Thinner GMs were created by mechanically pulverizing the HDPE sheet and then extruding the polymer in a Dayton #6536 Model blower to achieve different GM thicknesses. GM specimens with different thicknesses (e.g., ~0.04-mm, 0.1-mm, and 2-mm) were placed underneath sealed sources of Am-241 (Fig. 2) and irradiated for 1, 5, 10, 20, or 50 h.

Sealed Source

A sealed source of Am-241 (AM1A250U, Eckert & Ziegler, Valencia, California) was used to simulate alpha radiation (e.g., uranium and Ra-226) from LLW leachate due to their comparable energy spectrum for alpha particles. The sealed source of Am-241 has a nominal activity of 1.85 MBq with an active diameter of 9.5 mm and a peak energy of 4.7 MeV.

Oxidative Induction Time (OIT)

Oxidative Induction time (OIT) was measured using differential scanning calorimetry (DSC) to determine antioxidant depletion in HDPE GM in accordance with ASTM D3895 [22]. OIT was measured at the Soft Material Laboratory at the University of Wisconsin-Madison using a TA Instruments Q100 DSC. OIT is proportional to the amount of antioxidant remaining in the HDPE GM; i.e., higher OIT represents more antioxidant in the HDPE GM. OIT tests were conducted on specimens of HDPE GM before and after irradiation.

The initial OIT was 197 min for the 2-mm-thick HDPE GM; however, some antioxidant depletion occurred during preparation of different thicknesses of HDPE film due to the extrusion process that involves heating and cooling in air. As a result, the initial OIT

decreased to 185 min in the 0.04-mm-thick GM samples, and to 191 min in the 0.2-mm-thick GM samples. The extrusion process has more significant effect on antioxidant depletion in thinner GM specimens due to their larger surface area ratio.

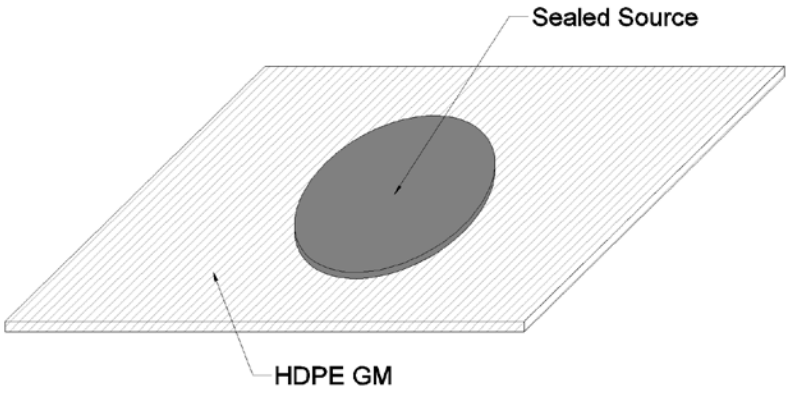


Fig. 2. Theoretical sketch of the geometry for sealed-source experiments and GEANT4 Monte Carlo simulation (Note, the dimension of the sealed source in the simulation was based on information provided by the manufacturer).

Monte Carlo Model to Simulate Sealed Source Experiment

The sealed-source experiments were simulated using GEANT4 to estimate penetration of alpha particles in the HDPE GM. The sealed source was assumed to be placed above a 21 mm × 21 mm HDPE layer in an environment of air (Fig. 2). The GM layer was assumed to consist of CH_2 with a density of 0.942 kg/m^3. In proximately to the source, 2-mm-thick GM was voxelized with a 41 × 41 × 200 voxel grid, with a corresponding voxel size of 0.5 mm × 0.5 mm × 0.01 mm. Based on the manufacturer's information, the sealed source of Am-241 was assumed to have a nominal activity of 1.85 MBq with an active diameter of 9.5 mm and a radiation foil consisting of Am-241 in a gold matrix with aluminum backing. The depth of the active layer in the model was adjusted to match a specified peak alpha energy of 4.7 MeV.

RESULTS AND DISCUSSION

Antioxidant Depletion

OIT as a function of exposure time is shown in Fig. 3. OIT of the thinner HDPE GMs (e.g., 0.04-mm, and 0.1-mm) decreased faster as the exposure time to Am-241 increased, and the rate of antioxidant depletion slowed as the exposure time increased. OIT of the 0.04-mm-thick GM decreased from 185 min to 158 min after exposure to the sealed source of Am-241 for 50 h and OIT of the 0.1-mm-thick GM

decreased form 189 min to 179 min over the same time period. In contrast, OIT of the 2-mm-thick GM changed negligible in response to irradiation (Fig. 3).

The decrease in OIT in Fig. 3 reflects depletion of antioxidant due to irradiation with alpha particles. Radiation breaks the C-C or C-H bond, resulting in free radicals [14, 16, 19, 23]. Antioxidants in the HDPE GM react with free radicals to form stable products and protect the HDPE GM from degradation. As the thickness of the HDPE GM increased (e.g., 0.1-mm-thick and 2 mm-thick), less depletion of OIT occurs, possibly indicating that the impact of alpha radiation is limited to the surface of HDPE GM.

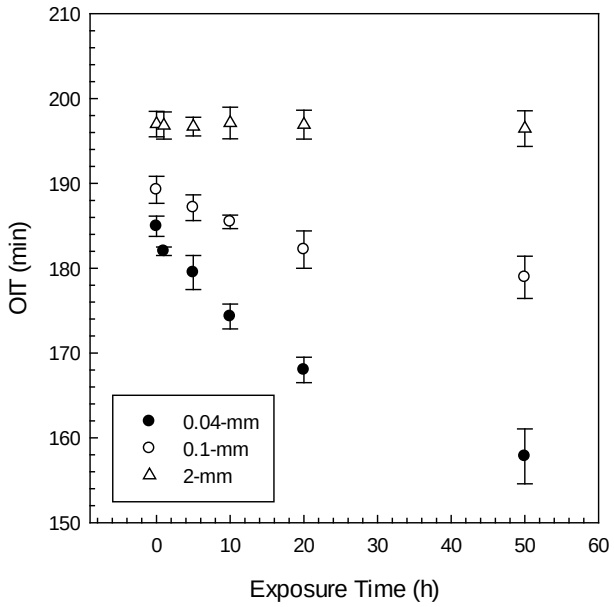


Fig. 3. Oxidative Induction time of 0.04-mm-, 0.1-mm-, and 2-mm-thick HDPE GM specimens exposed to sealed sources of Am-241 for 1−50 h. (Note: the error represents one standard deviation based on three measurements).

Monte Carlo Simulation

To investigate the impact zone of alpha radiation in HDPE GMs, MC simulation was conducted using GEANT4. Results from the GEANT4 MC simulation for a sealed source of Am-241 (alpha particles) are shown in Fig. 4. A peak dose of approximately 0.22 µGy per decay is deposited at the surface of GM, and the dose decreases with depth and becomes negligible at 28 µm. This depth corresponds to the maximum penetration for an alpha particle with approximately 4.7 MeV. HDPE GM material more than 28 µm from the sealed source is not affected by alpha particles.

Based on the MC simulation, alpha radiation can affect approximately 70% of the 0.04-mm-thick HDPE GM specimen, 28% of the 0.1-mm-thick HDPE GM specimen,

and only 1.4% of the 2-mm-thick HDPE GM specimen (Fig. 5). As the thickness of HDPE GM increases, the unimpacted zone becomes thicker, resulting in a higher average antioxidant concentration across the overall thickness of HDPE GM. Consequently, the effect of alpha radiation on antioxidant depletion becomes less significant as the thickness of the HDPE GM increases. Further study is ongoing to estimate the antioxidant depletion in HDPE GM as a function of radiation dose from LLW leachate over a 1000-yr service life.

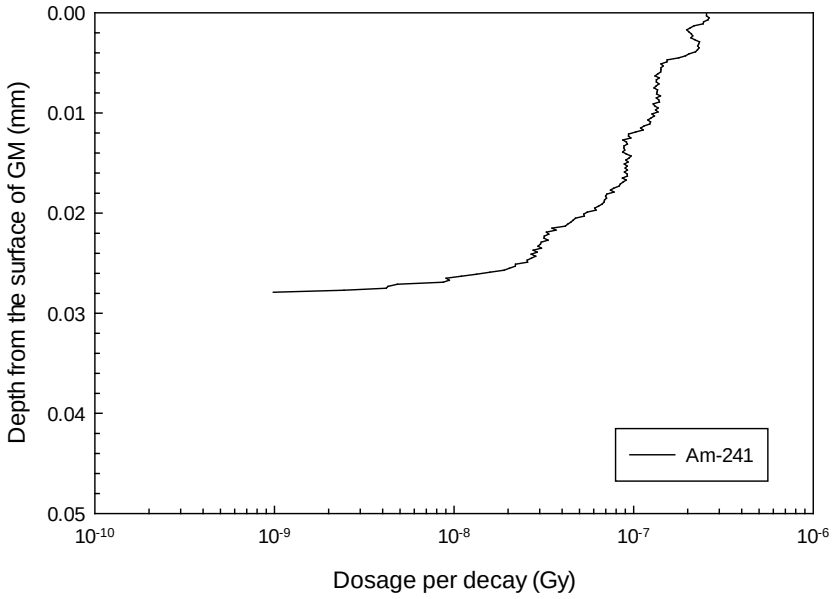


Fig. 4. Monte Carlo simulation for dose deposition in HDPE GM with a sealed source of Am-241 as a function of depth.

SUMMARY AND CONCLUSIONS

This study investigated the effect of alpha radiation from LLW leachate on antioxidant depletion in a HDPE GM. Specimens of HDPE GMs were exposed to sealed sources of Am-241 for 1−50 h to simulate alpha radiation from LLW leachate. OIT tests were conducted on specimens after irradiation to examine antioxidant depletion. The GEANT4 model program was used to investigate penetration of alpha particles from the sealed source of Am-241 into the HDPE GM.

The OIT for thin HDPE GM specimens (e.g., 0.04-mm- and 0.1-mm-thick) decreased with increasing exposure time. However, radiation had negligible impact on the 2-mm-thick HDPE GM, which is representative of GMs used in LLW disposal facilities. The simulation of sealed source experiments indicated that the alpha particles from Am-241 carrying 4.7 MeV can penetrate approximately 28 µm into 2-mm-thick HDPE

GM, and therefore having minimal impact. This agreed with sealed source experiments in which the alpha particles only affected the surface of the HDPE GM.

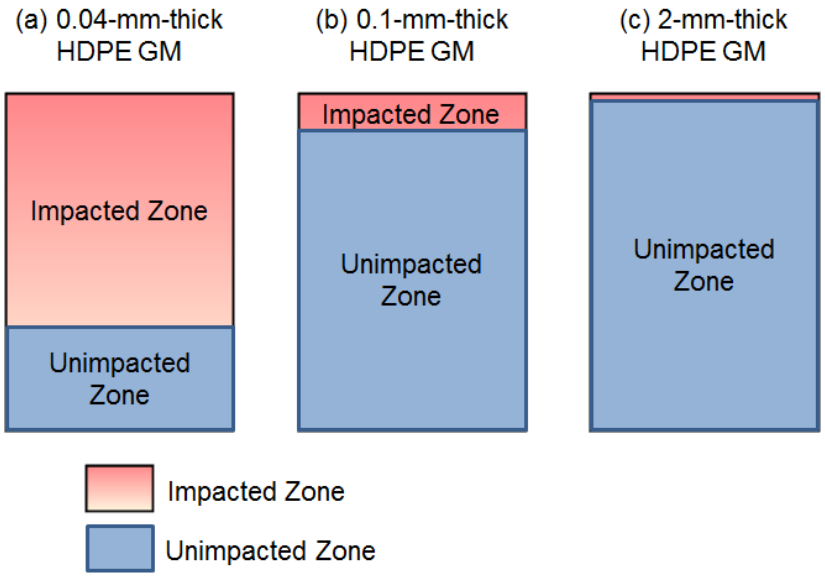


Fig. 5. Theoretical sketch of impacted and unimpacted zones in 0.04-mm-thick, 0.1-mm-thick, and 2-mm-thick HDPE GM specimens exposed to alpha radiation from a sealed source of Am-241.

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REFERENCES

1. Foose, G., Benson, C., and Edil, T. “Comparison of solute transport in three composite liners.” *Journal of Geotechnical and Geoenvironmental Engineering*, Vol. 128(5), 1–13, (2002).
2. Gulec, S., Edil, T., and Benson, C. “Effect of acidic mine drainage on the polymer properties of an HDPE geomembrane.” *Geosynthet. Intl.,* Vol. 11(2), 60–72, (2004).
3. Abdelaal, F., and Rowe, K. “Effect of high pH found in low-level radioactive waste leachates on the antioxidant depletion of a HDPE geomembrane.” *Journal of Hazardous. Toxic, and Radioactive Waste*, 10.1061/(ASCE)HZ.2153-5515.0000262, D4015001, (2015).
4. Tian, K., Tinjum, J., Benson, C., and Edil, T. “Antioxidant depletion in HDPE geomembranes exposed to low-level radioactive waste leachate.” *Geo-Congress 2014 Technical Papers*, 1816–1825, (2014).

5. Grassie, N., and Scott, G. *Polymer Degradation and Stabilization*. Cambridge University Press, New York, USA, (1985).
6. Hsuan, Y., and Koerner, R. "Antioxidant depletion lifetime in high density polyethylene geomembranes." *Journal of Geotechnical and Geoenvironmental Engineering*, Vol. 124(6), 532–541, (1998).
7. Rowe. R., and Sangam, H. "Durability of HDPE geomembranes." *Geotextiles and Geomembranes*, Vol. 20, 77–95, (2002).
8. Rowe, R., Rimal, S., and Sangam, H. "Ageing of HDPE geomembrane exposed to air, water and leachate at different temperatures." *Geotextiles and Geomembranes*, Vol. 27, 137–151, (2009).
9. Rowe, R., and Rimal, S. "Depletion of antioxidants from an HDPE geomembrane in a composite liner." *Journal of Geotechnical and Geoenvironmental Engineering*, Vol. 134(1), 68–78, (2008).
10. Sangam, H., and Rowe, R. "Effects of exposure conditions on the depletion of antioxidants from high-density polyethylene (HDPE) geomembrane. *Can. Geotech. J.*, Vol. 39, 1221–1230, (2002).
11. Rowe, R., Islam, M., and Hsuan, Y. "Leachate chemical composition effects on OIT depletion in an HDPE geomembrane." *Geosynthetics International*, Vol. 15(2), 136–151, (2008).
12. Osawa, Z., and Ishizuka, T. "Catalytic action of metal salts in autoxidation and polymerization." *Journal of Applied Polymer Science*, Vol. 17, 2897–2907, (1973).
13. Tian, K. "Durability of high-density polyethylene geomembrane in low-level radioactive waste leachate." *MS Thesis*, Univ. of Wisconsin-Madison, Madison, Wisconsin, (2012).
14. Whyatt, G. and Farnsworth, R. "The high pH chemical and compatibility of various liner materials." *Geosynthetic Testing for Waste Containment Applications, STP 1081*, R. Koerner, editor, American Society for Testing and Materials, Philadelphia, (1990).
15. Agnostinelli et al. "GEANT4-a simulation toolkit." *Nuclear Instruments and Methods in Physics Research A*, Vol. 506, 250–303, (2003).
16. Phillips, D. "Effect of radiation on polymers." *Materials Science and Technology,* Vol. 4, 85–91, (1988).
17. Czvikovszky, T. "Degradation effects in polymers." *Proceeding of International Atomic Energy Agency Meeting,* Notre Dame, Indiana, U.S., (2004).
18. Turner, J. *Atoms, Radiation, and Radiation Protection.* WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, (2007).
19. Costa, L., Carpentieri, I., and Bracco, P. "Post electron-beam irradiation oxidation of orthopaedic UHMWPE." *Polymer Degradation and Stability,* Vol. 93(9), 1695–1703, (2008).
20. Sugimoto, M., Shimada, A., Kudoh, H., Tamura, K., and Seguchi, T. "Product analysis for polyethylene degradation by radiation and thermal ageing." *Radiation Physics and Chemistry*, Vol. 82, 69–73, (2013).
21. Peacock, A. *Handbook of Polyethylene: Structures, Properties and Application.* Marcel Dekker Inc., New York, (2000).
22. ASTM D3895. Standard Test Method for Oxidative-induction Time of Polyolefins by Differential Scanning Calorimetry. ASTM International, West Conshohocken, PA, USA.

23. Mason, L., Doyle, T., and Reynolds, A. “Oxidation induction time correlations with radiation dose and antioxidant concentration in EPR and XLPE Polymers.” *Journal of Applied Polymer Science,* Vol. 50, 1493–1500, (1993).