Improving the Longevity and Performance of Polyethylene Geomembranes used in Waste Containment Barrier Applications

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Current State of the Art/Practice

Geomembranes, also known as flexible membrane liners (FMLs), are used extensively as barriers for waste containment. These liners typically are 0.5-2.0 mm thick and consist of a thermoplastic polymer (e.g., polyethylene [PE], polypropylene [PP], or polyvinyl chloride [PVC]), although thermostet polymers (e.g., ethylene propylene [EPDM]) and polymer combinations (e.g., PVC-EPDM) also have been used (Sharma and Reddy 2004). Geomembranes have become an industry standard in engineered liner systems (e.g., for landfills, surface impoundments, tailings storage facilities, and heap leach pads) and are commonly employed in final cover systems to minimize water infiltration and prevent uncontrolled release of gases and chemical vapors. According to Koerner (2005), geoenvironmental applications (i.e., liners and covers) may account for as much as 75 percent of the total geomembrane market, which exceeded $1.5 Billion in worldwide sales in 2003. These figures underscore the important role of geomembranes in modern waste containment design.

Among the different geomembrane types available, PE geomembranes are the most commonly employed geomembranes in engineered liner and cover systems, largely due to their superior resistance to chemical attack and impermeability to liquids. Intact PE geomembranes also are excellent barriers to advective transport of miscible contaminants and diffusive transport of inorganic pollutants such as heavy metals (e.g., Pb, Cd, and Zn). However, lingering concerns exist regarding the ability of PE geomembranes to provide effective containment over the potentially contaminating lifespan of a landfill, which is likely to be centuries (Rowe et al. 2004). The most notable of these concerns include (1) the potential for degradation of the geomembrane over time due to oxidation, and (2) inadequate resistance of the geomembrane to diffusive migration of volatile organic compounds (VOCs). Both of these issues were identified as medium- to long-term performance concerns for geomembranes in a recent assessment report on the performance of engineered barriers (National Research Council 2007).

With regard to degradation, antioxidants are added to PE geomembranes to limit oxidation of the PE. However, the antioxidants may become depleted over time, rendering the PE susceptible to deterioration and eventual failure (Hsuan and Koerner 1998, Rowe et al. 2010). This process may result in a substantially reduced service life for PE geomembranes, particularly when exposed to elevated temperatures that may persist in some applications. For example, Rowe (2005) estimated that the service life of high density PE (HDPE) geomembranes (2 mm thick) in a landfill liner application may decreases from 565-900 yr at 20 °C to 130-190 yr at 35 °C and 15-20 yr at 60 °C due to accelerated antioxidant depletion and oxidation of the HDPE.
With regard to VOC diffusion, several studies have indicated that aqueous-phase or vapor-phase VOCs may migrate readily through intact HDPE geomembranes by partitioning into and diffusing through the polymer phase (e.g., Park and Nibras 1993, Sangam and Rowe 2001, Rowe 2007). The lack of resistance of geomembranes to VOC diffusion could result in rapid breakthrough of VOCs through composite liner or cover systems (e.g., see Rowe 2007). As a result, different approaches to improve the resistance of geomembranes to VOC migration are being considered. For example, Sangam and Rowe (2005) showed that adding surface fluorination to an HDPE geomembrane reduced the diffusive flux of aqueous VOCs by 1.5 to 4.5 times relative to an untreated HDPE geomembrane. Also, McWatters and Rowe (2010) recently evaluated the VOC barrier performance of two different types of coextruded geomembranes consisting of an LLDPE outer core and a polyamide (nylon) or ethylene vinyl-alcohol (EVOH) inner core. The coextruded EVOH/LLDPE geomembrane outperformed conventional LLDPE, PVC, and HDPE geomembranes with respect to migration of both aqueous-phase and vapor-phase VOCs (McWatters and Rowe 2010).

Opportunities and Challenges: Polymer-Clay Nanocomposite Geomembranes

Another possible approach for improving both the VOC barrier properties and degradation resistance of PE geomembranes is to utilize polymer clay nanocomposite (PCN) technology (see Shackelford 2005). Over the past 20 years, PCNs have emerged as a new class of engineering materials and are receiving considerable attention in both scientific and industrial communities due to the potential for enhanced engineering performance compared to neat polymer or conventional composite materials (LeBaron et al. 1999, Ray and Okamoto 2003, Koo 2006). In general, PCNs are created by dispersing layered silicates (i.e., clay minerals) with a high aspect ratio (typically montmorillonite) within a polymer matrix, such that the dispersed clay layers are on a nanometer length scale (hence "nanocomposites"). Effectively fabricated PCNs can outperform ordinary polymers with respect to various physical properties, including strength, thermal stability, and barrier properties (permeability). These property enhancements may be achieved upon very small clay loading (i.e., typically <5 wt %), leading to minimal weight increase and potentially low fabrication cost. Because of these advantages, PCNs are being considered for a wide variety of real-world applications, particularly in the automotive, aviation, electronics, and packaging industries (Shackelford 2005, Koo 2006).

Property enhancements in PCNs are dependent upon both the level of dispersion of the clay within the polymer matrix and the degree of exfoliation (separation) of the clay particles into individual nanolayers (platelets). In this regard, four states of dispersion/separation are possible, as shown in Fig. 1. The immiscible morphology in which the nanolayers exist as laminated bundles or "tactoids" is characteristic of a conventional composite that generally does not yield substantial property improvements relative to the neat polymer. When the polymer chains penetrate between the clay nanolayers, intercalated morphology with increased interlayer spacing is achieved. Exfoliated PCNs are characterized by single nanolayers separated to the extent that the nanolayers no longer interact. The exfoliated morphologies illustrated in Fig. 1 are most effective for achieving substantial property enhancements (Ray and Okamoto 2003).

Several studies have shown that PCNs can exhibit reduced gas/vapor permeability relative to the neat polymer (e.g., Hotta and Paul 2004, Osman et al. 2005, Frounchi et al. 2006, Swain and Isayev 2007). Moreover, although diffusion rates of organic liquids and vapors through PCNs have been measured in only a limited number of studies, the results indicate that substantially reduced diffusion of organic chemicals is possible. For example, Gorrasi et al. (2003)
Fig. 1. Four idealized states of separation/dispersion in PCNs (black lines = clay nanolayers; gray areas/curves = polymer molecules (redrawn after LeBaron et al. 1999).

demonstrated more than a 10-fold reduction in dichloromethane vapor permeability of a PP-based PCN. The improved barrier performance is attributed to an increase in tortuosity of the diffusion pathway caused by the presence of dispersed clay platelets, as illustrated in Fig. 2. The enhanced tortuosity also can improve the thermal stability of the polymer by resisting mass transport of oxidation products generated during decomposition (Ray and Okamoto 2003).

Based on the above, PCN technology offers the potential for substantial improvement in the performance of geomembranes in waste containment applications. Specifically, development of PCN geomembranes that exhibit greater resistance to gas migration, VOC diffusion, and thermal oxidation represents a potential breakthrough in sustainable waste containment design in terms of performance effectiveness and longevity. However, PCN geomembranes currently do not exist, and a considerable amount of research and testing will be required in order to advance the technology from concept to reality. Also, there are significant technical challenges associated with fabricating polyolefin-based PCNs that exhibit the exfoliated structures shown in Figs. 1 and 2. Most notably, exfoliation is difficult to achieve when hydrophilic clay particles are added to non-polar, hydrophobic polyolefins (e.g., PE and PP), as there is an inherent thermodynamic tendency for the clay platelets to remain as tactoids within the polymer matrix. Researchers have explored various fabrication methods (e.g., melt compounding, in situ polymerization, ultrasonic extrusion, etc.), clay treatments (e.g., modification with organic surfactants), and compatibilizers (e.g., maleated polymers) in an attempt to improve clay exfoliation in polyolefins, (e.g., Liang et al. 2004, Lee et al. 2005, Frounchi et al. 2006, Swain and Isayev 2007), but these approaches generally have produced only intercalated or partially exfoliated PCNs.

Fig. 2. Schematic illustration of different tortuous paths for diffusion through immiscible composites and exfoliated nanocomposites (redrawn after Ray and Okamoto 2003).

Recently, there has been growing interest in a different approach for fabricating polyolefin-based PCNs using a technique known as solid-state shear pulverization (SSSP), which involves compounding the clay and polymer below the melting temperature of the polymer. As shown in Fig. 3, the overall setup and process involved in SSSP are similar to conventional melt extrusion,
Fig. 3. Schematic diagram of the solid-state shear pulverization (SSSP) instrument.

except that the extruder is chilled by circulating a coolant solution along the length of the barrel. The high system viscosity and shearing action aids in physically separating the nanolayers, while the low thermal energy prevents re-agglomeration of the nanolayers.

The SSSP method has been used successfully to fabricate polyolefin PCNs with a highly exfoliated morphology. For example, the results of X-ray diffraction (XRD) spectra for PP-based PCNs fabricated by Kasimatis and Torkelson (2004) using both melt extrusion and SSSP are compared in Fig. 4. The large peak in the XRD spectrum for the melt compounded specimen indicates the prevalence of laminated clay layers (tactoids) within the PP matrix, whereas the major reduction in the peak height for the SSSP specimen indicates that most of the clay has become exfoliated. Based on these results, the SSSP technique shows promise for overcoming the thermodynamic and/or kinetic limitations associated with achieving exfoliation in polyolefin PCNs. Also, unlike batch-type solid-state processing methods (e.g., cryogenic milling), SSSP is a continuous technique that can be employed for large-scale production. However, since the SSSP technique is relatively new, research is needed to elucidate the morphology formation mechanisms and processing-structure-property relationships for PCNs produced via SSSP.

Fig. 4. X-ray diffraction profiles of PP-organoclay PCNs via (a) twin-screw extrusion (melt process) and (b) SSSP (solid-state process). Lower peak height corresponds to greater clay exfoliation. After Kasimatis and Torkelson (2004).

Expertise and Institutional Resources

Dr. Michael A. Malusis has been an Assistant Professor in the Department of Civil and Environmental Engineering at Bucknell University since 2005. His primary expertise pertains to
the waste containment performance and longevity of conventional and enhanced soil and geosynthetic barriers. His recent projects include investigations into (1) the influence of membrane behavior on the containment performance of bentonite-rich barriers, (2) the effect of wet-dry cycling on the hydraulic sustainability of soil-bentonite cutoff walls, (3) use of multiswellable bentonite in soil-bentonite backfills, (4) enhanced adsorption in activated carbon and zeolite amended barriers, and (5) fabrication and characterization of PCN barriers.

Bucknell University is well equipped for a comprehensive research program to investigate the feasibility of high-barrier PCN geomembranes. As a result of a recent NSF award (CMMI #0820993), Bucknell now is one of only two universities to own an SSSP machine. This custom-built machine was received in 2009 and has been installed in a new, on-campus laboratory dedicated to research on polymer nanocomposites. The instrument has twin, co-rotating screws (with modular, interchangeable elements) and can be used for conventional melt extrusion as well as SSSP, which allows for direct comparison of the morphologies and properties of PCNs produced using each method. A wide variety of other instrumentation is available in-house for fabricating, characterizing, and testing polymers/PCNs (e.g., compression mold presses, melt-index analyzer, tensile tester, thermo-gravimetric analyzer, H2O and O2 permeability analyzers, XRD machine, and scanning electron microscope). The Environmental Laboratory houses a full array of chemical analysis equipment for evaluating inorganic and organic pollutant concentrations. In addition, Bucknell maintains a fully-equipped Product Development Laboratory (PDL) staffed by two full-time machinists. The PDL is available for custom fabrication of equipment needed for testing of geomembranes (e.g., diffusion cells).

**Potential US-India Partnerships**

Given the widespread use of geomembranes in modern waste containment systems, approaches for addressing the shortcomings of geomembranes described above should be of interest to researchers in the U.S. and abroad. These shortcomings have received some attention within the geoenvironmental research community, but only recently so. Research on PCN geomembranes, in particular, is still in an infancy stage. Lack of prior consideration of PCNs for waste containment applications likely is due, at least in part, to the fact that materials scientists typically do not have specific expertise in waste containment and are unfamiliar with major performance issues for geomembranes. Similarly, most geoenvironmental engineers have limited expertise in the fundamental materials science behind PCNs. Collaborative, multi-disciplinary partnerships involving materials scientists and geoenvironmental engineers may be useful to advance the technology of PCN geomembranes from concept to reality. In addition, many of the performance issues for conventional geomembranes that have been researched extensively by the geoenvironmental community over the past two decades would need to be re-examined for PCN geomembranes. Thus, numerous collaborative projects among researchers from the U.S. and India are possible on this topic, depending on individual interests, expertise, and resources.

**References**