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Title: 'PPA - the Secret Additive that HDPE & LLDPE Geomembrane Producers Do Not Talk About'

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Abstract

Polymer Processing Aids (PPAs) based on fluorinated rubber are a little discussed additive that are commonly used in the production of HDPE and LLDPE geomembranes to improve processing characteristics and eliminate surface defects. PPAs play a critical role in preventing melt fracture and reducing extrusion pressure, amperage, torque and die build-up during processing. However, the use of PPAs is under threat due to new regulations banning perfluorinated compounds. In this article, we discuss the importance of PPAs in geomembranes and the potential consequences of their absence.

Introduction

HDPE and LLDPE geomembranes play a critical role in modern infrastructure and environmental protection. These materials are used for a wide range of applications, including landfill liners, mining heap leach pads, and containment of hazardous wastes. One of the key factors that determine the performance of geomembranes is the elimination of surface defects during processing. Polymer Processing Aids (PPAs) based on fluorinated rubber are essential additives that aid in this process.

The use of PPAs in geomembranes is becoming increasingly important, as resin suppliers produce geomembrane resins with higher molecular weights and melt viscosity, which are more susceptible to processing defects and surface imperfections.

PPAs improve the processing of these high molecular weight materials by reducing the occurrence of melt fracture, which is a mechanically-induced melt flow instability that occurs during extrusion. Melt fracture can lead to a rough array of sharkskin-like patterns on the film surface, resulting in reduced tensile

properties and reduced gauge uniformity. PPAs also help to reduce defects such as gels, blobs and drool marks that can occur during processing.

PPAs are particularly important for multimodal polyethylenes such as PERT resins. These materials contain low molecular weight polymers that cause die buildup during processing, resulting in inconsistent performance and degraded polymer.

PPAs help to prevent die build-up by establishing a low surface energy between the polymer melt and the metal die surface of the extruder. This means that the geomembrane can be processed at high speeds without melt fracture and avoid die build-up that can lead to defects and pinholes in the geomembrane.

However, the use of PPAs is under threat due to new regulations banning perfluorinated compounds. In February 2023, the European Chemicals Agency published a proposal from five member countries to ban per- and polyfluoroalkyl substances (PFAS) containing at least one fully fluorinated carbon atom.

This ban would include popular fluoropolymers and fluoroelastomers, including PPAs based on fluorinated rubber. Manufacturers are scrambling to reformulate their products before the regulations take effect.

The absence of PPAs in geomembranes could have significant consequences for the industry. Without PPAs, the occurrence of surface defects such as melt fracture and die build-up would increase, resulting in reduced production output and increased costs.

Additionally, the production of geomembranes could become more energy-intensive, as higher extrusion pressures and motor loads would be required to achieve the same results.

2.1.2.6 *Polymer Processing Aid*

A fluorinated elastomer (fluoropolymer) is the most common type of polymer processing aid used in geomembrane resins. Very small levels of a fluoro elastomer such as Dynamar FX 5911X substantially improve the melt processing of high-molecular weight HDPE resins by establishing a low surface energy between the polymer melt and the metal die surface of the extruder. This means that the HDPE can be processed by extrusion at high speeds without melt fracture and avoid die build-up that can otherwise lead to lacings, defects, and pin holes in the geomembrane, such as those shown in Figures 2.12 and 2.13.

Figure 2.12 Lacing hole defect in an HDPE geomembrane caused by die build-up.

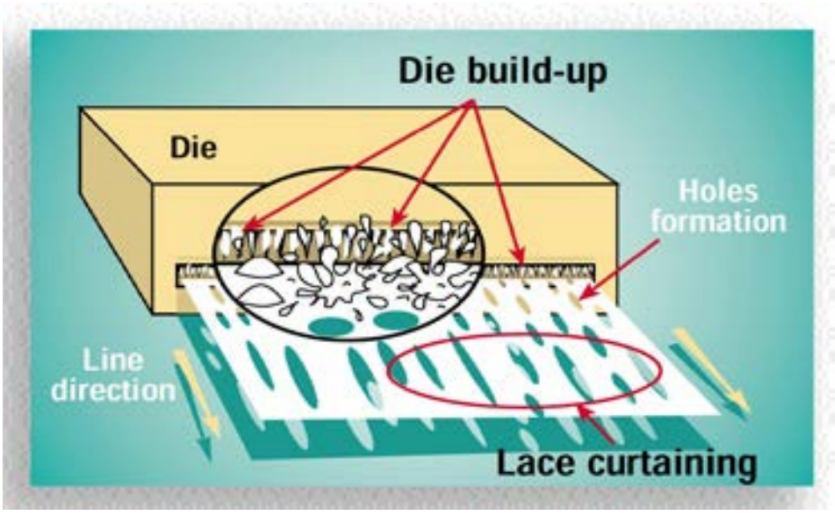

Figure 2.13 Schematic of die build-up causing lacing hole defects in an HDPE geomembrane

Another advantage of a polymer processing aid in HDPE extrusion is that it greatly reduces polymer build-up in dead spots in the extruder, such as on the screw and barrel. Such dead spots create polymer hang-ups that degrade and become carbonized due to their excessive residence time in the extruder. Periodically these degraded particles get swept back in the mainstream flow of the melt and become embedded in the final geomembrane as hard nodular defects such as the carbonized lump defect shown in a microtomed section of HDPE geomembrane in Figure 2.14.

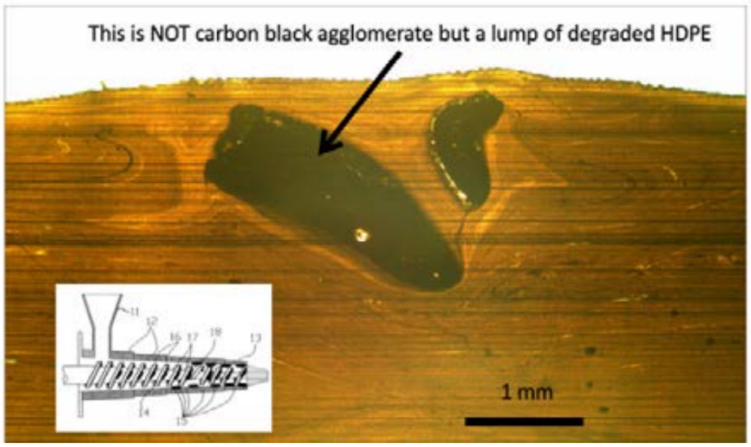

Figure 2.14 Carbonized polymer defects in an HDPE geomembrane.

Market Intel

PPAs are added to the polymer resin to improve the processing characteristics of geomembrane polymers and to eliminate surface related imperfections that occur during processing. The benefits of PPAs include elimination of melt fracture, lower extrusion pressures and motor loads and improved die/extruder clean up. For example, the addition of PPAs to HDPE and LLDPE help prevent sharkskin melt fracture (SSMF or sharkskin), which is a surface imperfection characterized by a pattern of surface ridges perpendicular to the flow direction.

Commonly used PPAs in geomembranes are VITON® FREEFLOW™ Z-200 ("Z-200") produced by Dupont Dow Elastomers of Wilmington, Delaware and DYNAMAR FX5929 produced by Dyneon, a 3M Company. The PPA fluoroelastomer is generally used in amounts of about 1000 ppm to about 2000 ppm. Viton® FreeFlow™ Z110 and Z210 process aids are used to complement the successful Z100 and Z200 products by eliminating melt fracture, and by reducing extrusion pressure, amperage, torque and die build up in moderate mixing situations including solution LLDPE, high carbon black loading masterbatches with over 20 per cent carbon black, blown sheet using 0.3 to 0.8 MFI LLDPE or HDPE, and extrusion under low shear conditions.

Small amounts of PPA, among other things, help eliminate melt fractures in geomembranes made from HDPE and LLDPE resins. This is particularly so for polymer resins exhibiting relatively higher viscosity in extrusion processes such as those with melt index values less than 1.

Melt fracture is a mechanically-induced melt flow instability which occurs, e.g., at the exit of an extrusion die and typically in conditions of high shear rate. Pinhole, linear, and annular die geometries are among those that can induce melt fracture. There are different mechanical regimes that describe PE melt fracture, but all manifest as a very rough irregular polymer surface which persists as the polymer crystallizes.

Commonly in the blown geomembrane industry, a rough array of sharkskin like patterns develop on the film surface, often with a characteristic size from the mm to cm scale, and they depend on both the flow profile and rheology of the polyolefin polymer (e.g., polyethylene). Melt fracture can adversely affect sheet tensile properties and reduce gauge (i.e. thickness) uniformity. Thus, melt fracture-prone polymer geomembrane resin grades often rely on a PPA. Hence small levels of the fluoroelastomer such as Dynamar FX 5911X substantially improve the melt processing of high molecular weight HDPE resins (geomembrane grades with fractional melt indices) by establishing a low surface energy between the polymer melt and the metal die surface of the extruder. This means that the HDPE can be processed by extrusion at high speeds without melt fracture and avoid die build-up that can otherwise lead to lacings, defects, and pin holes in the geomembrane.

PPAs also help to reduce geomembrane sheet defects such as gels, blobs and drool marks. Die buildup means accumulation of polymers, usually low molecular weight polymers, around the extrusion die. Die buildup may result in inconsistent performance of the polyethylene sheet. Die buildup may also cause degradation of the polymer due to the prolonged heating around the die. The degraded polymer buildup can be pulled from the die as the film is extruded, resulting in lumps and inclusions of degraded resin in the sheet that can cause failure in sheet performance by acting as stress concentrations. It is believed that low molecular polymers cause die buildup.

Multimodal polyethylenes such as PERT resins especially rely on PPAs for improved processability. "Multimodal" means that two or more peak molecular weights can be seen by gel permeation chromatography (GPC). For example, a bimodal polyethylene means that two peak molecular weights can be identified. Multimodal polyethylene can be transformed into geomembrane with better high temperature performance. One of the advantages of multimodal polyethylene over mono-modal polyethylene is easier and faster processing with

a reduced energy requirement and increased output. In addition, multimodal polyethylenes show less flow disturbances in thermal processing. However, multimodal polyethylenes often represent a unique die buildup problem. This is partly because multimodal polyethylene inherently contains some low molecular weight polymer that causes die buildup. Therefore processing of PERT resins into geomembranes benefits greatly from the use of PPAs.

In February 2023, the European Chemicals Agency published a proposal from five member countries to ban the so called "*forever chemicals*" based on per- and polyfluoroalkyl substances (PFAS) containing at least one fully fluorinated carbon atom—an estimated 10,000 molecules in all, including popular fluoropolymers and fluoroelastomers. A major manufacturer 3M announced that they would cease making fluoroelastomers pointing to increasingly stringent regulations as well as customer demand for alternatives and said it would walk away from the entire business—which generates annual sales of about $1.3 billion—by 2025.

Conclusions

PPAs based on fluorinated rubber play a critical role in the production of HDPE and LLDPE geomembranes, aiding in the prevention of surface defects and improving processing characteristics. The potential absence of PPAs due to new regulations banning perfluorinated compounds could have significant consequences for the industry, including reduced performance, increased costs, and higher energy requirements. It is critical that the industry continues to develop alternative solutions to ensure the continued success of geomembranes in infrastructure and environmental protection.

References and Further Reading

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