SAFETY-RELATED FAILURE OF POLYETHYLENE PRODUCTS

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Abstract

Safety-related products made of polyethylene, as well as of other plastics, will perform their intended functions only if they remain essentially unchanged as a result of long term exposure to air and light or to liquids in containers. Examples of failure are given for two container applications and for an electrical insulation case. Adequate stabilization against oxidative degradation and attention to damage that can be done by some liquids in contact with polyethylene are particularly important for safe long term service.

Introduction

Polyethylene is a common material used in containers for many laboratory safety-related purposes. An example is small hand-held squeeze bottles containing water to rinse spills in the eye. Another is five gallon containers to hold liquid waste or store liquids. Because such containers may be used for many years, the polymer must remain essentially unchanged in order to perform its function. That requires that the polyethylene be sufficiently well stabilized so that oxidative embrittlement does not contribute to failure. This paper reports on failures which have occurred of these two containers.

Another polyethylene failure was cracking of exposed small diameter electrical hook-up cable at a terminal board close to fluorescent lighting in an electrical utility. This jeopardized a safety system requiring replacement of cracked polyethylene.

Eye Wash Squeeze Bottles

This type of bottle is held in place on the laboratory wall near sinks. If a person experiences a spill in the eye of a potentially hazardous material, the eye can be flushed with water kept in the bottle by holding the eye piece to the eye and squeezing the bottle. Such bottles may be on walls for twenty or more years, and it is taken for granted that when they are needed they will perform as intended. Depending on the level and type of antioxidant system, and the environmental conditions of temperature and exposure to light, embrittlement may occur while on the wall. In one such case, the bottle cracked on being squeezed, rendering it unable to perform it's intended function. Fortunately cracking occurred when the bottle was being tested rather than when it was required to flush out someone's eye.

Yellow color development is often an indicator that the antioxidant is depleted and the polyethylene may be embrittled. The ASTM Oxidative Induction Time Test[a] is useful to monitor antioxidant content as a guide to when to replace bottles. In the OIT test, the polymer is first equilibrated in nitrogen at a temperature such as 200°C, then monitored for the start of an exotherm after changing to oxygen. The most practical test in this case is to actually squeeze the bottle and observe if cracking occurs.

Cracking of Exposed Polyethylene Insulation Near Fluorescent Lighting

When an electrical utility discovered cracking of exposed polyethylene insulation at terminal board junctions, it wanted to know the cause of cracking and whether the unexposed polyethylene, covered with PVC jacket, could be used to replace the cracked exposed polyethylene. Embrittlement was particularly pronounced near fluorescent lighting which was on all the time. Analysis by infrared spectroscopy for carbonyl content, due to bound oxygen, showed that oxidation had occurred. OIT was also zero. Away from fluorescent lighting, embrittlement and oxidation were much less or had not occurred at all. Analysis of nearby polyethylene that had been covered with PVC jacket showed that the covered polyethylene, protected from air and light, had not oxidized or embrittled, and had considerable undegraded antioxidant, as shown by OIT value. To ensure that the safety system that depended on the integrity of the polyethylene insulation was not jeopardized, cracked insulation was cut off and previously unexposed insulation nearby was used to make the terminal connections. Fortunately there was enough slack in the wires to permit this. As a further step to ensure that cracking would not occur in the future, the newly exposed polyethylene insulation was covered with electrical tape.

Explosion of Five Gallon Polyethylene Container

An explosion occurred in a five gallon polyethylene liquid container which was known to contain nitric acid that was being used in experiments with an experimental polymer. Fortunately no one was in the room at the time, so that there

[a]ASTM D3895 (08.03), Test Method For Oxidative Induction Time Of Polyolefins By Thermal Analysis.

were no personal injuries. This type of container is commonly used in the laboratory to store waste liquid. Figure 1 shows the inside surface of a fragment of the bottom of the container that was recovered. Analysis of the recovered part was performed to determine the cause of the explosion. Figure 2 shows infrared spectra of the inside and outside surfaces, which indicate the presence of material at the inside surface which is not at the outside. Thermal desorption gas chromatography/mass spectroscopy[b,c] was performed on samples taken from the inside surface and from the outside surface in order to identify the materials indicated by IR. The chromatogram for the inside surface is in figure 3. In addition to toluene and acetic acid two mononitrotoluenes and two dinitrotoluenes were identified from their mass spectra. While the peak for toluene appears small it was actually in overload and toluene was the major compound detected. There was also indication of a trace of trinitrotoluene, although it could not be conclusively identified in the same way as the other nitrotoluene compounds were from their full mass spectra. It should be noted that the surface analyzed was dry and showed no sign of the compounds identified. This was accomplished only because of the excellent sensitivity of thermal desorption GC/MS and the ability to specifically identify compounds from mass spectroscopy.

When it became known that toluene and nitrotoluenes were present, it was then learned that toluene had been used to extract a polymer from nitric acid, so that toluene and nitric acid were present together in the polyethylene container. During room temperature storage, nitric acid reacted with toluene to form the mono and dinitrotoluenes. It is very likely that some trinitrotoluene (TNT) was also formed, and the analysis indicated that a trace amount may have been present.

The outside surface contained practically none of the organic compounds. Presumably the presence of water and nitric acids would have impeded the migration of the organic compounds to the outside surface due to their polar nature.

The condition of the inner and outer surfaces were also examined for antioxidant content by the OIT test and for embrittlement by bending the surfaces back. Figure 4 shows that the OIT value for the inside surface is 0, i.e., that all the antioxidant has been depleted. The outer surface with OIT greater that 26 minutes still had a high content of antioxidant to guard against oxidative embrittlement.

The response of the inner surface to being bent back was to create many cracks due to the embrittlement of the inner surface. The outer surface, tested in the same way, was perfectly flexible and did not fracture.

The cause of oxidation of the inner surface may have been the nitric acid. It is also possible that toluene may have extracted antioxidant from the surface. The embrittlement and ease of fracture of the inner surface may have contributed to the fracture of the container when the TNT exploded. Had the inner surface been flexible, the container may have expanded without fracture, thus containing the explosion inside the container. It is also possible that the force of the explosion may have been such as to have fractured a normal polyethylene container not embrittled on the inside. It could also be argued that the embrittlement was the result of the explosion, rather than a possible contributing factor. It would require storage tests with nitric acid to see if the acid causes oxidation of polyethylene.

A contributing factor to the fracture at the bottom of the five gallon container may have been that the polyethylene was thinnest at the bottom, as manufactured. Thickness was about one half that of wall higher up from the bottom.

Conclusions

While polyethylene is an advantageous polymer for safety-related applications, such as liquid containers and as electrical insulation, it cannot be assumed to be capable of long term service unless properly stabilized and not exposed to conditions which deplete the antioxidant. In this paper three such causes have been illustrated: (1) normal long term service itself, of the order of twenty years or more, so that the antioxidant is exhausted; (2) contact with an oxidizing liquid or with solvent that may extract the antioxidant; (3) exposure to ultraviolet light and air. In some cases, such as exposed polyethylene insulation, providing the polyethylene with a cover or jacket to minimize contact with air and light is a practical way of shielding the polymer. In the case of liquid containers, such protection is not readily accomplished and the long term reliability depends primarily on adequate stabilization.

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[b] M. Ezrin and G. Lavigne, "Failure Analysis Using Gas Chromatography/Mass Spectroscopy", Soc. Plast. Eng., ANTEC Conf. Proc., 1991, p 2230-2233.

[c] M. Ezrin and G. Lavigne, "Application of Direct Dynamic Headspace GC/MS to Plastics Compositional And Failure Analysis", Soc.Plast.Eng., ANTEC Conf. Proc, 1992, p 1717-1719.

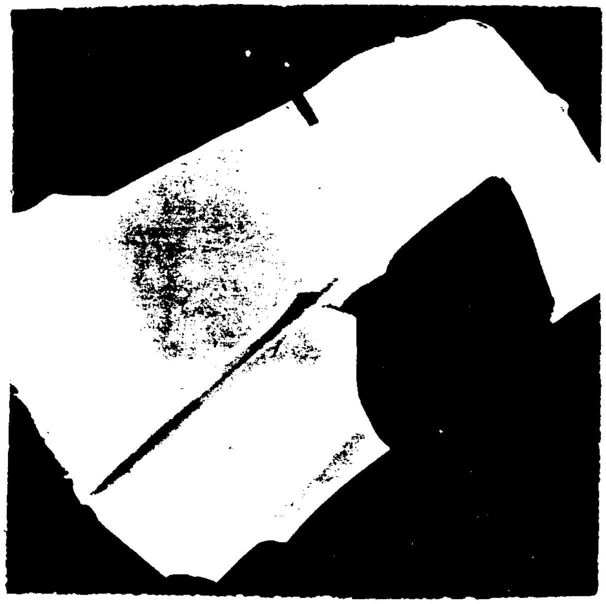

Figure 1. Inside surface of bottom of exploded PE container; 0.36 x mag.

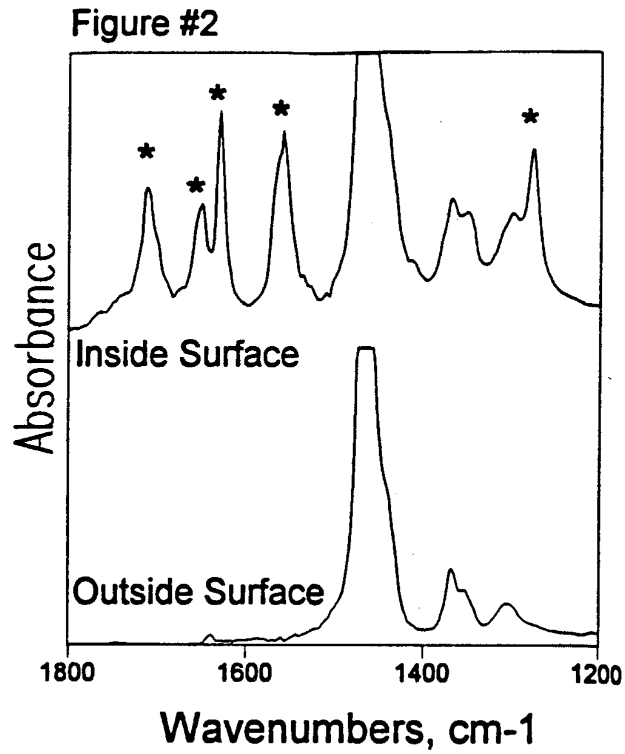

Figure 2. Infrared spectra of surfaces of bottom of exploded PE container; * bands on inside surface and not on outside surface.

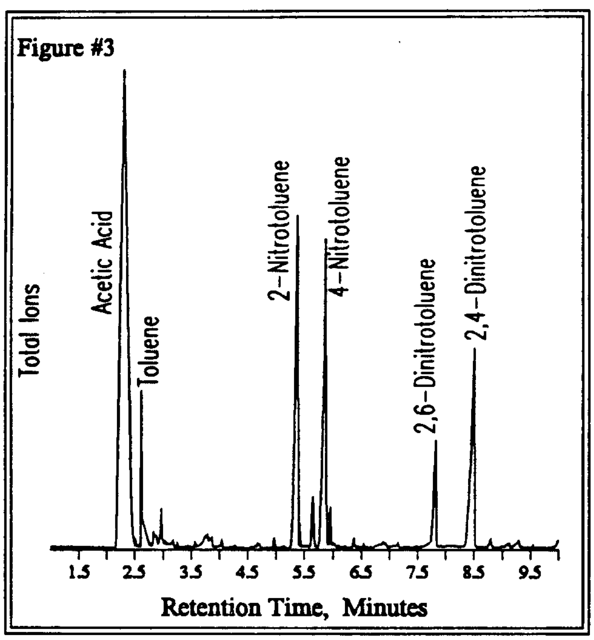

Figure 3. Gas chromatogram of thermally desorbed inside surface of bottom of exploded PE container; desorbed 2'/250°C

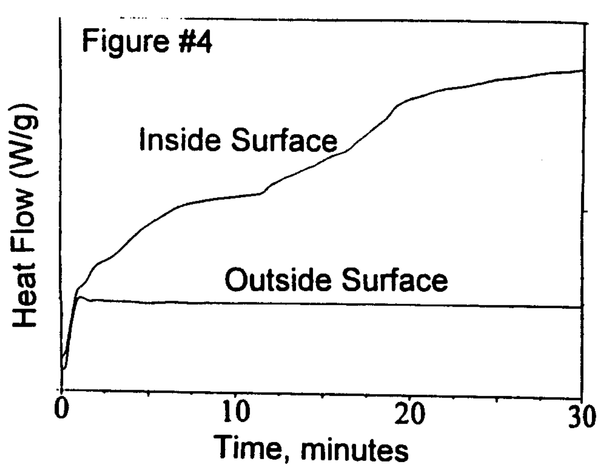

Figure 4. Oxidative induction time DSC test of inside and outside bottom surfaces of exploded PE container; minutes at 200°C in oxygen.

Key Words: polyethylene-failure, safety-related failure