LyondellBasell Technical Tip

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Environmental Stress Crack Resistance

Unstressed polyethylene at room and normal service temperatures up to 60°C (140°F) is highly resistant to a wide variety of rather reactive chemicals such as inorganic acids, alcohols, fatty oils, food chemicals and detergents. However, items made from polyethylene resins can crack when exposed to the same chemical "environment" if they are stretched or bent in several directions at once, a condition known as "polyaxial stress."

Thus, if conditions are unfavorable, various oils or even common household cleaning agents may cause a polyethylene bag, pipe, tank, drum or bottle to crack and split open after only a short period of time. Bottles or other parts designed to contain detergents, solvents or acids must therefore be manufactured from a polyethylene resin that exhibits a high resistance to "environmental stress cracking" (ESC).

- **HOW STRESS CRACKING OCCURS**
  The failure of a container to resist ESC can be the result of stored stresses acquired in the molding or extrusion operation. Stress cracking agents, such as the liquids mentioned above, migrate into minute cracks in the crystalline areas of the polyethylene molecules forming the surface of the container. These microscopic cracks are a result of a breakdown of the polymer chains in the case of acids and solvents, and a "wetting out" of the surface in the case of detergents, largely due to their surfactant components.

  In either case, the surface tension between the crystalline layers is reduced. What once was a microscopic surface imperfection propagates or "zippers open" to a full fledged break in the bottle. ESC failures are accelerated by high temperatures and additional external stresses such as top loaded storage.

- **HOW RESISTANCE IS DETERMINED**
  The resistance of polyethylene to stress cracking increases as density decreases; as average molecular weight increases (melt index decreases); and as molecular weight distribution narrows. Two American Society for Testing and Materials (ASTM) and one Plastic Bottle Institute (PBI) test methods that rate polymers and molded parts on their ability to resist ESG are:

1. **ASTM D 1693: Environmental Stress Cracking of Ethylene Plastics "Bent Strip ESCR"**

   At the Cincinnati Technology Center and other laboratories, Igepal® CO-630, at varying concentrattions, is used as the standard cracking reagent for this test, which is carried out on molded specimens 1/8 in. or ¾ in. thick (depending on the PE type being tested), 1½ in. long and ½ in. wide. The specimens are first heated in boiling water to relax "frozen-in" stresses. A surface cut of a specified length and depth is then made on the sample parallel to the long axis with a mounted razor blade. The specimens are the stressed by bending them 180 degrees. The specimens are then placed in a rack that is put into a test tube containing the stress-cracking agent. To accelerate the effect of the cracking agent, the test tube is placed in a bath at 50°C (122°F).

   Periodically, the specimens are inspected for visual cracks perpendicular to the cuts. At each inspection, the number of failures is recorded. A polyethylene resin is considered to have failed when one half of the specimens in the tube show cracks perpendicular to the cuts.

2. **ASTM D 2561: Environmental Stress Crack Resistance of Polyethylene Blow Molded Containers "Bottle ESCR"**

   The test is usually carried out on 16-oz., 25-g., Boston Round bottles blow molded from polyethylene resin, although a container of any size and shape can be used. Bottle design, processing conditions and the resin used are all variables affecting the results of this test.

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ASTM specifies three environments for this test, so it is important to know which procedure was used in order to compare test results. It is also important to know that while ASTM calls for inspection to stop after 360 hours, many suppliers continue to check the bottles to 500 or 1,000 hours after the test begins. Successful results from these lengthier tests are reported as >500 or >1,000 hours.

Procedure A: A minimum of 15 containers is filled to nominal capacity with the chosen test liquid, usually a proprietary liquid product or an aqueous solution of polyoxyethylated nonylphenol (a surfactant). The containers are heat sealed and placed in an oven at 140°F.

Inspection takes place hourly for the first eight hours and at least once every 24 hours thereafter. Results are reported as the number of hours elapsed before 50 percent of the specimens failed (F_{50}).

Procedure B: A minimum of 15 containers is filled to one-third of their overflow capacity with the same stress cracking solution used in Procedure A. The containers are heat sealed and placed in beakers vertically with the finish up. The beakers are then filled with a sufficient amount of stress cracking agent to cover the chime area of the container and placed in an oven at 140°F Inspection and reporting occurs in the same way as Procedure A.

Procedure C: A minimum of 15 containers is filled to one-fourth of their overflow capacity with the same stress cracking solution used in Procedure A, The containers are then sealed with a special cap assembly and placed in an oven at 140°F. The bottles then are subjected to an internal pressure of five psi, introduced through the cap assembly, for the duration of the test. Inspection and reporting is carried out in the same way as Procedure A.

3. **PBI 11: Recommended Practice for Determining Top Load Stress Crack Resistance of Blow Molded Polyolefin Bottles**

The purpose of this test is to simulate the conditions a container undergoes during shipment or storage. A minimum of 15 bottles is filled to nominal capacity and heat-sealed as in ASTM D 2561. The bottles are then placed in a jig that applies a constant top load for the duration of the test. Bottles and jig are placed in an oven at 1220°F. Inspection and reporting occurs in the same way as ASTM D 2561, Procedure A. Data from this test appears to reproduce reality more closely than ASTM D 2561 or ASTM D 1693.

All of the test procedures described generate valuable data that provides insight into the phenomenon of ESCR. However, these methods are very sensitive to testing error; the data must be used with caution. As an example, some testing errors can occur during the ASTM D 1693 "Bent Strip ESCR" test because of:

- *Surface imperfection on the test specimens*
- *Defective method of fabricating the test specimens*
- *Different rates of cooling of test specimens*
- *Incorrect or inconsistent concentration of the reagent*

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- *Defects in the specimen holder*
- *Temperature variations within the water bath*
- *Inconsistent depth, length or width of the notch cut in the specimen*
- *Inconsistent rates at which the specimens are bent*
- *Defective condition of the die,* if the *specimens are cut from a sheet*
- Inconsistent data reporting

With such a large number of variables, it is not surprising ASTM has found the precision of D 1693, when performed at different laboratories, to be 2.9, which is expressed as two standard deviation limits on the 50-percent failure point. This number means that if one laboratory were to test a material and find that the 50-percent failure point (F_{50}) occurred at 10 hours, other laboratories, testing the same material, could be expected to generate data that varies between 3.4 hours and 29 hours.

ASTM has determined the precision of D 2561 to be 1.8 and PBI reports the precision of PBI 11 is approximately 1.5, which means these two tests are more reproducible than D 1693. However, the ramifications of all these precision numbers are very important. Differences in ESCR performance of various products could actually be attributed to varying degrees to test error. In addition, test method guidelines permitting different surfactants and container styles add to the confusion. Additionally, some resin manufacturers may make minor modifications to the test procedures to suit their own needs.

When considering ESCR, it is important for the resin customer to compare "apples to apples. " Find out test conditions such as temperature, surfactant used, bottle type and weight, among other variables. For best comparison, the polymers in question should be subjected to side-by- side testing, using the same equipment, operator and environment. These conditions minimize much of the test variation and give the fairest comparison.

Equistar technical service representatives are available to assist you in understanding ESCR data. In certain cases, they may even be able to coordinate a test program to evaluate ESCR properties of several different resins of your choice. For further information, please your LyondellBasell sales or technical service representative.

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