

JUDGING PERFORMANCE OF A POLYETHYLENE PRODUCT

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Summary of Criteria Used in Judging Performance of a Polyethylene Product

The overwhelming consideration in specification and final judgement on any product is performance in actual use. While other considerations such as processing ease and raw material cost are also important, these dim in importance if the part will not perform as required. Ultimately that performance can only be judged by monitoring the part in actual service, under real conditions.

Some applications, such as storage tanks, require that the part perform flawlessly for very long periods, often many years. Therefore, laboratory tests have been developed to give indications of long-term performance. These laboratory tests should be used in combination with actual performance data as it becomes available, and with an understanding of the molecular behavior of polymers so that the nature of failure and survival can be understood and improved. Therefore, the basic nature of polymers, laboratory data, and real performance experience, will all be examined so that these criteria can be combined in judging and predicting the performances of both various polyethylene products.

General Understanding of Polymers

Polyethylene is a polymer – a material composed of many long molecules that are highly entangled about each other. The molecules of polyethylene are made of a backbone or chain of carbon atoms with hydrogen atoms attached to each carbon on the backbone. Occasionally short carbon and hydrogen branches can also be attached to some of the backbone carbons. This material, the first type of polyethylene made, is called branched polyethylene. If only a moderate number of branches are present and the branches are relatively short, the polyethylene molecule is called linear polyethylene – reflecting the general domination of the linear backbone. If the branches are even scarcer, the material is called high-density polyethylene (HDPE) because the molecules form extensive crystalline regions and that increases the density.

The physical and mechanical properties of polyethylene are overwhelmingly dominated by the interactions or intermingling between the polymer chains. Generally, the greater the interactions, the better the properties. This is understood by realizing that as the polymer chains interact, they are separated less easily, thus making it more difficult for cracks to form between them; the force needed to pull them apart is increased, thus increasing strength and stiffness; and their ability to dissipate impact energies is improved, thus increasing toughness. Other properties are increased as well. Therefore, to improve performance, polymer resin manufacturers and molders have consistently worked to increase the amount of interactions between the chains.

One method to increase chain interactions is to increase the length of the chain or, in other words, the molecular weight, which simply increases the amount of entanglement between polymers. Early polymer performance was adversely affected by the inability of polymer manufacturers to achieve high molecular weights. Gradually that problem was solved but then it became apparent that if the molecular weight was increased too high, the polymer could not be processed well. As a result, a compromise was made between property performance and processing capability.

For many products, that compromise was acceptable. However, for applications where long term performance is critical, such as storage tanks, insulation for electrical and telephone wires, tubing and pipes for irrigation, and many others, the compromise invited a serious problem. Long-term exposure to the environment often resulted in massive cracking and total product failure. The problem was simply that the polymer chains did not have the amount of interaction required to give long-term performance. The problem (dilemma) was to increase polymer interactions while maintaining processing capabilities.

Solving the Dilemma of Optimizing Polymer Length for Processing and for Properties

A breakthrough in polymer processing provided the solution to the dilemma. This breakthrough was to crosslink the polymer **after** the part had been formed. Crosslinking of polymers had been known for many years, as a technique to improve properties in thermoset polymers, but was always done during forming, never afterwards. The concept of forming a part and then crosslinking it was brilliant and highly successful.

Crosslinking is simply the formation of bonds between the polymer chains. These bonds, equal in strength and stability to the principal bonds along the polymer backbone, tie the polymers together, thus dramatically increasing molecular weight. In fact, the length of the polymer chains and, therefore, the physical properties, are much better than can ever be achieved without crosslinking.

Several methods were employed to crosslink the plastic after it was formed. One method was to use peroxides and crosslinking agents, much like the technology used in making high performance aerospace parts and fiberglass reinforced plastics. This method was especially well suited to parts made by rotational molding and casting. Another method was to crosslink using electron bombardment – a method especially well suited to parts made by extrusion, injection molding and blow molding. Both crosslinking methods have proven to be highly effective in preventing stress cracking, and have enhanced many other physical properties.

The advantages of **crosslinked** polyethylene are evident in the plastic molding process called **rotational molding** or rotomolding. In this process a weighed amount of non-crosslinked resin powder (which contains the materials required for later crosslinking) is placed into a mold, the mold is closed and then rotated inside an oven. The powder coats the inside surfaces of the mold as the mold gets hot, fuses together, crosslinks, and then solidifies as the mold is cooled. The initial low molecular weight of the non-crosslinked resin is a great advantage during the early stages of processing to help the resin particles uniformly fill the mold, melt, and fuse together. Then, when the part is fully formed, the crosslinking occurs, thus building molecular weight and enhancing the physical and mechanical properties. The additives required for crosslinking and the longer processing time generally add cost to crosslinked parts.

When using **linear** polyethylene, compromises must be made. With linear, it is not possible to have short polymers for processing and then long polymers in the final part because the molecular weight of the polymer does not change during processing. If the initial molecular weight is increased to achieve long-term performance, problems can be encountered in properly filling the mold, in achieving proper part definition, and in fusing the particles together so that no porosity is present. Although linear could, in theory, also be crosslinked, the nature of the resin has resisted effective crosslinking. One further problem with linear has recently been discovered. Linear is susceptible to degradation if held at high temperatures for extended periods, as might be the case if heated too long in rotomolding. Therefore, crosslinked polymers have been found to also be more forgiving in processing than linear. Recent advances using metallocene catalyst systems have resulted in improved properties for both crosslinked and linear resins, although the differences based on molecular weight are still present.

Product Performance Testing

The ranking of polyethylene products in key laboratory tests is just as would be expected from considerations of molecular weight and polymer interactions. Crosslinked parts are better than linear, and linear is better than no crosslinking at all. Crosslinked parts will resist environmental stress cracking more than 15 times longer when compared with linear and with non-crosslinked parts (>1000 hours versus 72 hours versus 47 hours in ASTM D-1693). Izod impact toughness is more than 5 times better in crosslinked parts when compared to linear (17.0 versus 3.3 ft-lb in ASTM D-265). The resistance to crack growth is 10 times better in crosslink than linear (>1000 hours versus <10 hours in ASTM F-1473).

The actual, in use performances of crosslinked parts have been closely monitored for many years and, in general, have confirmed the superiority of the product as indicted in laboratory testing. Therefore, when long-term performance is required, the insistence on using crosslinked resin is strongly recommended.

Additional information on this subject can be obtained from the book *Plastics: Materials and Processing, 2nd Edition*, by A. Brent Strong, Prentice Hall Publishers, (2000).