Poly Processing Company

Understanding Environmental Stress Crack Resistance (ESCR) in Rotomolded Polyethylene Tanks

1- **Introduction**:

Environmental stress cracking is a failure of the polymer material due to surface initiated micro cracks or fractures. These are caused by the combined presence of stresses and environmental effects. The polymer's resistance to such failures is called environmental stress crack resistance (ESCR). It seems that the stresses and environmental effects combine synergistically to accelerate the development of these micro cracks. Even though this process is not fully understood, it is suspected that the surface active material present in the environment (a surfactant) interacts with the surface of the polymer to initiate and accelerate the formation of microscopic voids within the polymer chains. Under low stress loads these voids then combine and grow to form larger crazes and cracks, which ultimately lead to the failure of the polymer material.

From the early days of polyethylene's commercial development, environmental stress cracking has played an important role in defining market expansion and end use applications for this resin. Virtually all conventional plastic manufacturing operations, from injection molding and extrusion to blow molding and thermoforming, induce residual stresses within the polymer material. This is due to the orientation of the molecules that occurs during shaping and the sharp cooling rates that the molten polymer undergoes during the molding process. Improvements in these manufacturing processes have reduced the development of these residual stresses but have not eliminated them. In addition, stresses are induced in the polymer material due to normal loading and service use. Even rotational molding, which is considered to be a stress free plastics molding operation, parts will be produced that have some level of residual stress in them. Also, as in the case of rotomolded high end chemical storage tanks, operational stresses are experienced during the filling and discharging of the stored material and the natural thermal expansion and contraction of the tank. It is therefore important for polyethylene resin fabricators, such as roto molders, as well as users of these rotomolded products to get a better understanding of environmental stress cracking and its impact on final product performance. This becomes more critical because it is estimated that 15% of all premature, in-service failures of plastic parts are caused by environmental stress cracking. In fact, some researchers put this figure as high as 40%.

2- **The Morphology of Polyethylene:**

The morphology or microstructure of polyethylene is the driving factor behind this material's resistance to environmental stress cracking. To help us better visualize this relationship, we can imagine that we have a solid polyethylene sample under a very strong microscope. As we start to increase the magnification through several orders of magnitude, we begin to see two distinct regions. The first is a well-ordered and organized region in which the polyethylene molecular chains have a highly oriented, closely packed three-dimensional structure. This is a **crystalline region**. We also see a second region in which the molecular chains are random in nature, spread further apart, and are not organized according to any ordered pattern. This is an **amorphous region**. Materials that contain both types of these solid regions or phases are called semicrystalline, see figure 1. Another way of describing these materials is to say that the amorphous region forms a continuous matrix in which crystalline regions are embedded.

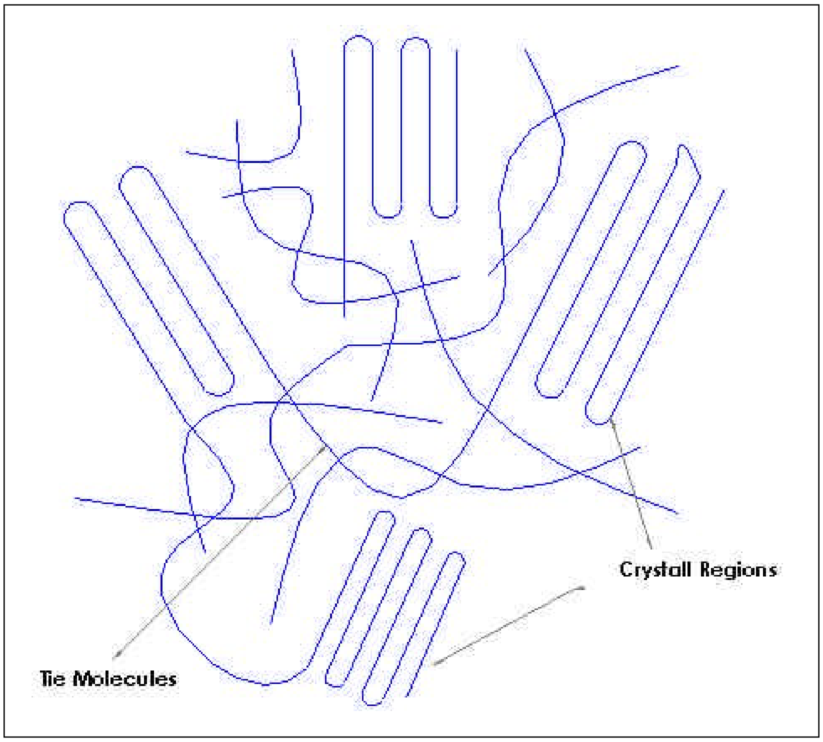

Figure 1 Crystalline and amorphous regions in Polyethylene

There is a third region that is important and critical in the ESCR of a semicrystalline material. This region is the interface between the crystal region and its adjacent amorphous region. If we focus our microscope on this interface or boundary and at even higher magnifications we can see that this region exhibits some level of order with respect to the molecular chains. This interface region connects the crystalline and amorphous phases and without it the polyethylene material would be very weak. This interface or boundary region is the zone through which the loads are carried and transferred between the long molecular chains and the different crystals.

If then, we continue our visualization exercise and increase the magnification further, we begin to notice that the molecular chains along the boundaries of the regions can have several different characteristics or types. They can: (1) extend from a crystal region and terminate in an amorphous region; (2) extend a few molecular lengths into the amorphous region and then loop back into the original crystal; or (3) transverse an entire amorphous region and then become part of another crystal region. It is now believed that these long molecular chains that link or transverse more than one crystal region determine the environmental stress crack resistance of polyethylene. These long molecular chains, sometimes called *tie molecules*, act as binders between the adjacent crystal regions.

3- **Origin of ESCR**:

To understand stress cracking, we should examine both what it is and where it occurs. Intuitively we believe that stress cracking is initiated by the breaking of the molecules, particularly the tie molecules. This break is then propagated to form a micro crack that will ultimately grow to form a crack big enough to be seen and cause product failure. The process of chain breakage or scission is called *degradation*. There is experimental evidence showing that crystallinity is slightly increased when polymer degradation (chain scission) occurs. This is know as Chemicrystallization and it is the process by which the chain end that originated from the crystal springs back and reenters the crystal after chain scission of the tie molecules, or degradation, has occurred. Chemicrystallization due to chain scission is a phenomenon that has been studied and observed in the degradation of polyethylene due to weathering.

This finding suggests that when the molecular chains degrade (break), they somehow add to the crystalline regions at the expense of the amorphous regions. Therefore, we can conclude that the degradation begins either within the existing amorphous regions and then creates new crystalline regions nearby or, alternately, the degradation begins at the amorphous/crystalline boundaries and builds onto existing crystalline regions. It does not begin in the crystalline regions since there would be no mechanism to increase the level of crystallinity.

It is more likely that stress cracking occurs at the interphase or boundary region and does not begin in the middle of the amorphous regions. The rational for this is that the molecular chains in the amorphous regions are highly entangled, even though they do not follow a structured pattern. To create new crystals within an amorphous region would require very high energy levels to untangle these molecules and make them mobile. The crystallization process in polyethylene requires the polymer to be in a molten state where the molecular chains have a very high degree of mobility. Degradation or chain scission can still occur in the middle of the amorphous region, but this scission is not the dominant factor for the observed increase in crystallinity.

Having ruled out the middle of the amorphous and crystal regions as primary locations for the degradation process, it then must be the interphase region where predominate degradation or chain scission occurs. At this interphase region the stresses are the highest in the polymer structure. The crystalline region is a low energy area because of the stability of the crystal structure. The amorphous region, while not as stable as the crystalline regions, is still relatively free of stress because the molecules in that region can move to relieve any stresses that might develop. Thus, at the interface there is a pull effect between these two energy states. One can say that the molecules in the interphase region are “thermodynamically stressed” which makes them more susceptible to environmental stress cracking. That is, it takes less chemical energy/interaction to rupture or chain session these tie molecules in the presence of surface-active agents.

We can also imagine that the molecules in the interphase region are mechanically stressed. These molecules have their ends trapped in regions of quite different natures. Because of the ordered nature of the crystalline regions and low energy level, they tend to be stiffer than the amorphous regions. Thus, when heating or cooling occurs, the crystalline and amorphous areas expand and contract at different rates and to different extents. This will inevitably stress the molecules caught between these different forces. Moreover, because of the lower energy of the crystalline areas, the thermodynamic forces are always trying to enlarge the crystalline areas and thus are mechanically pulling on the interphase molecules, which obviously creates a stress. Because the molecular chains in the interphase region are in tension due to this pull effect, when chain scission occurs, they spring back away from the interphase region and become part of the crystalline region. Therefore, we can now understand why there is an increase in crystallinity with degradation.

With the understanding that the interphase molecules are in stress and that crystallinity is increased with degradation, we can now accurately link the origin of environmental stress crack resistance to the boundary region. The internal stresses raise the energy level of the interphase region. Therefore, when additional external energy is added to the molecule (as from a bending stress or the presence of a surfactant) the interphase is the place where the molecules are most likely to accumulate sufficient energy to exceed molecular bond strengths and rupture. **Therefore, chain scission from external stress and environmental effects is most likely to occur at the interphase.**

We now need to examine some of the effects of various important molecular parameters so that we can see how to increase ESCR by varying key characteristics of the resin.

a- **Effect of Molecular Weight**:

Molecular weight is simply a measure of the size of the molecules. In most cases, this size can also be related directly to the length of the molecular chains. With all other factors being the same, the longer the molecular chain of the polyethylene polymer, the higher its ESCR.

If we investigate molecular weight further, we find that all polyethylene resins will be comprised of molecular chains that vary in size or length. This can range from a few hundred molecules per chain to over a million. For this reason, both the number average molecular weight and a distribution of the chain lengths are used to characterize a polyethylene resin.

A number of analytical tools and tests are used to calculate the number average molecular weight and the associated distribution of a polyethylene resin. The Melt Index (MI), or Melt Flow Index (MFI), ASTM D1238, of a molten polymer resin is a general predictor or guide for the resin's average molecular weight and distribution. As a definition, the MI is a measure of the rate at which molten resin, at a preset temperature and load is extruded from a capillary die. It is measured in units of grams per ten minutes. The MI provides an indication of the average lengths, molecular weights, of the molecules in the resin and their level of entanglement since all of these affect the way the polymer flows during the test. In general, the lower the MFI value is for a particular polyethylene resin grade, the higher its ESCR, see table 1 on page 6 of this article. This is expected since a lower MFI value means the presence of longer chains, including tie molecules in the resin sample. This index is widely used in the plastics industry, including rotational molding.

We can now ask why increasing molecular weight increases ESCR. Since we empirically know that increasing the molecular weight increases the lengths of the chains and thus increasing the proportion of tie molecules in a distribution, we can assume that the ESCR must be improved as the length of the chain increases. When spring back occurs because of molecular scission, there is a loss of strength in the interphase region (there is one less molecule to hold the amorphous and crystalline regions in place). Therefore, the area becomes more susceptible to expansion due to the degradation defect. This expansion is, of course, the phenomenon that leads to the creation of micro cracks that are the precursors to stress crack failure. However, if tie molecules are abundant, these tie molecules are anchored in two crystalline regions and will, therefore, have a tendency to hold the shape of the interphase region and prevent the growth of the defects. The advantages derived from the tie molecules are greater as there are more of them. There are more tie molecules in higher molecular weight material. Hence, higher molecular weight improves ESCR.

b- **Effect of Short Chain Branching (SCB)**:

In reality the long molecular chains that exist in polymers will have some sections along their chain length that can be more easily incorporated into the crystalline regions and sections that are noncrystallizable. This is due to the presence of side branches or short chain branches along the molecular chain. The amount of short chain branching present in the molecular chain depends on the polymerization conditions during the manufacturing of the polymer. Examples of such conditions include catalyst type, pressure, temperature, reactor type, and the concentration and type of co-monomer, if any.

Increasing the short chain branching will increase the ESCR of polyethylene. The more frequent these branches are, the less the level of Crystallinity in the material. With lower crystallinity or density, comes higher ESCR, as we have already discussed.

This increase in ESCR with density is only true up to a certain level because of the effect of density (crystallinity) on molecular strength. If the strength drops too low, then the resistance of the material to spreading of the defect regions will also decrease. Hence, there is somewhat a complex relationship between molecular strength, density and ESCR.

c- **Effects of Density and Crystallinity**:

As we have already noted, in general, the higher the level of crystallinity or proportion of crystalline to amorphous regions, the higher the density and the lower the ESCR of the material. The explanation arises directly from our analysis of the effects of the interphase region. Even when the density of a polymer is very high, that does not mean that the density is associated with only a few very large crystalline regions. In fact, there continues to be a large number of crystalline regions because, even when the number of short chain branches is small, there are still other factors that limit the size of the crystals. One factor is the presence of some short branch side chains, no matter how high the density is.

Another factor is the high rate of crystal initiation throughout the molecule. That means that as cooling occurs, crystals begin in many different areas throughout the polymer melt. These crystals all grow until they meet another crystalline region. Hence, a highly crystalline material looks like a patchwork quilt with many different crystal regions up against each other.

Each of these crystal regions is surrounded by an interphase region. The molecules in these interphases are still highly stressed. Because of the nature of the crystal growth, there are probably more of these interphase regions in a high density material than in one in which large amorphous regions are present. Hence, the areas that are most susceptible to starting stress cracks (the interphases) are even more prevalent in high density materials than in low density materials. This explains why high-density linear polyethylene resin grades have lower ESCR values when compared to low density polyethylene, see table 1 page 6 of this article.

4- **Measuring ESCR**:

There are a number of accelerated tests that are used to determine the polymer's ESCR. The most widely used, and accepted, test, especially in the rotomolding industry, is the Bent Strip method, ASTM D1693. The purpose of this test is to accelerate the conditions that lead to stress cracking so that the effects can be seen in a shorter time frame. Therefore, the rectangular test samples are severely bent, or stressed, and then immersed in a highly active surfactant material (Igepal) often under elevated temperatures. The test can be performed at Igepal concentrations of 100% and 10%. The lesser the concentration, the more active is the surfactant material. Hence the normal condition for testing materials such as polyethylene is under that more stringent condition. To clarify, if we use only soap, which is a surfactant, to wash a greasy hand we will be more effective in washing our hands if we use water with the soap, rather than just pure soap without water.

Table 1: ESCR for Polyethylene resin grades used in the rotomolding industry

Resin Grade	Density (g/cc) ASTM D1505	Melt Index (g/10 min.) ASTM D1238	Flexure modulus (psi) ASTM D790	ESCR (hours) 10% Igepal ASTM D1693
HD-Resin 1	0.942	2.0	93,500	48
HD-Resin 2	0.948	5.0	154,000	9
LL-Resin 1	0.938	3.3	112,000	145
LL-Resin 2	0.936	6.8	102,000	55
Paxon 7004 XLPE[3]	0.945	No flow	100,000	> 1000
CL-200YB XLPE	0.943	No flow	100,000	> 1000

1- High Density (HD) 2- Linear Low (LL) 3- Cross Linked Polyethylene (XLPE)

In addition to the samples being severely bent, they are notched along the centerline to increase the susceptibly of the material to stress cracking. After 50% of the samples have failed the time to failure is taken. This time to failure, measured in hours, is used to determine and compare the polymer’s resistance to cracking. Table 1 lists the ESCR for a number of polyethylene resin grades commonly used in the rotomolding industry.

Table 1 also highlights some of the main discussion points included in this article with regards to ESCR and the material’s morphology. We can see in the linear polyethylene resin grades that reducing the density increases the material’s resistance to stress cracking. This is clearly seen in the difference in hours before failure between high density and linear low density resins. Also included in Table 1 are the very high ESCR values for cross linked polyethylene resin grades. In actuality the cross linked material is so resistant to stress cracking that it does not fail under the Bent Strip test within the 1000 hours of the test duration.

5- **Cross Linking of Polyethylene**:

What is interesting about this cross linked polyethylene material is that it starts out as typical thermoplastic material and at a specific processing temperature, molecular chains are connected to each other (bonded together or bridged) through chemical reactions. This cross linking effect dramatically increases the molecular weight of the polyethylene. The molecular weight grows so high that the melting point actually exceeds the decomposition temperature so that the resin does not flow or melt. Hence, we do not have a listing for melt index for cross linked polyethylene. Recalling the microscope analogy, if we now focus our microscope at the boundary or interphase region of a cross linked polyethylene sample, we will notice that the tie molecules are now infinitely connected. The interphase region is now full of these tie molecules that strengthen the connections between the adjacent crystal regions. Thus even when chain scission occurs along the backbone of the tie molecules, the high or infinite degree of connectivity between the molecular chains is still maintained. This infinite molecular weight is what gives the cross linked polyethylene material its superior ESCR. If we recall in our earlier discussion, the higher the molecular weight, the higher the ESCR for the polyethylene material.

In addition to increasing the ESCR's resistance, the bonds between the molecules may have some additional benefits. They may prevent some of the spring back that decreases the strength of the interphase regions and allow the cracks to grow. Also, the cross links probably serve as crack arrestors to block the growth of cracks should they begin.

6- **Summary**:

It is important to note that these relationships between molecular weight, short chain branching, tie molecules, crystallinity and the ESCR of polyethylene material have been determined through experimental analysis and scientific deduction. The scientific community is still in the discovery stage in terms of fully understanding the mechanics by which each if these factors affect the ESCR of polyethylene. Data from the field suggest that certain polyethylene resin grades perform better than others do. This article is a simple attempt to explain why this is the case. Future work by the scientific community is still needed to fully understand environmental stress cracking of Polyethylene and polymers in general

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