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THE IMPORTANCE OF CHEMICAL STABILIZATION IN RECYCLED MATERIAL FOR CORRUGATED AND CONDUIT POLYOLEFIN PIPES

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Abstract

Much attention has been given to stabilization packages for polyolefin pressure pipes over the past couple decades, however corrugated and conduit pipes have generally been ignored with respect to more robust stabilization packages. Certain groups such as the Florida Department of Transportation have set rules establishing oxidative resistance in HDPE corrugated pipes, but few others have followed this example. A discussion of the simplicity and importance of pipe resin stabilization as well as examples from stabilized pipes will be covered.

Introduction

The worldwide usage of high density polyethylene (HDPE) is estimated at 47,980 thousand metric tons this year, with usage expected to continue to rise over the next several years [1]. While virgin polyethylene has established itself in a wide array of polymer applications, the demand for recycled polyethylene resin in new and existing applications is growing steadily as well.

Degradation of polyethylene is a key concern for end-users in many applications. While polyethylene may not be inherently susceptible to autoxidation on its own, it is highly prone to the phenomena when subjected to any of several common environments [2]. High-shear processing conditions, reactive catalyst residues, high temperatures, impurities, oxygen, time, and other factors contribute to an environment that creates free-radicals within the polyethylene structure. Through radical chain autoxidation, polyethylene structures change from their initial, intended state, into a product with widely varying molecular weights and weight distribution through crosslinking or chain-scission. The resulting, altered polyethylene is often considered low-quality, highly variable in performance, and is often less preferred than virgin resin by many manufacturers due to mechanical, rheological, and optical issues. Along with superior economics, virgin resin's performance quality relegates recycled materials to low-performance, non-critical applications.

The autoxidation of polyethylene has been prevented in the past using a wide array of antioxidant additives. Antioxidant stabilizers are an important class of additives used in polyolefins and other polymers [3]. Phenolic antioxidants, like BASF's Irganox® 1010, are widely used to prevent the chain reaction by reacting with the radical initiator before it can break down the polyethylene structure. Phosphite antioxidants, i.e. "secondary antioxidants" like BASF's Irgafos® 168, protect the polymer from oxidation from peroxides present in the melt during processing. Antacids, like metal soaps, react with and shut down the highly-reactive catalyst residues present in virgin polyethylene resin. Each of these additives protects the polymer structure from changing in the presence of many reactants, from resin production all the way through end use.

These stabilizers are often included as packages in polymer systems, and have a positive influence on the ability to reuse and recycle plastics. When antioxidants are used along with virgin resin, they prevent the polymer from breaking down, and preserve "like-new" properties of the resin, even after several heat histories. Stabilized resins conserve a polymer blend's rheological properties, allowing for higher quality control during processing. Fewer reactions in the polymer structure via autoxidation results in fewer contaminants and better lasting color as well.

These benefits are also passed along to subsequent uses of plastic, via recycling. As the current outlook in the plastics marketplace emphasizes a growing need for environmental awareness and conservancy, formulating with post-consumer resin (PCR) and post-industrial resin (PIR) has become a growing trend, including in non-pressure pipe applications [4]. Today, North American corrugated HDPE pipe manufacturers annually incorporate over 400 million pounds of recycled plastic into HDPE pipe products with sales over one billion dollars [5]. Additionally, recent environmental impact studies have shown that pipe with recycled HDPE is highly energy-efficient and prove to have a favorable lifecycle score [6].

While pressure pipe applications have had high quality standards that disallow recycled material from contributing significantly to the end products, various institutions have updated standards to encourage and monitor the useful implementation of recycled polyethylene in non-pressure pipe applications. Groups like the Florida Department of Transportation are implementing at 25 minute minimum OIT value requirement for Class II HDPE corrugated pipe, indicating that government agencies want to raise the standards for these applications to prevent failure and costly fixes down the road [7].

The American Association of State Highway and Transportation Officials (AASHTO) is a standards-setting body that governs drainage culvert design and specifications. While the AASHTO specification for corrugated polyethylene pipe (AASHTO M 294-18) has typically dealt with prime resin in the past, an update has provided quality specifications for pipes made with PCR and PIR [8]. This was in response to recommendations from studies on new, more-appropriate service life models. This addresses new requirements for oxidative resistance of pipes with PCR and PIR material, which better correlates to the prevention of stress cracking in aging pipes, a primary cause of failure.

A new test in this standard is the measurement of Oxidative Induction Time (OIT) using ASTM D3895. In this test, plastic samples are exposed to concentrated oxygen at temperatures above the melting point. As oxidation occurs, a heat transition is observed via differential scanning calorimeter (DSC). The inflection point of that transition is recorded as the OIT value, and is an indicator of the amount of antioxidant present in the sample.

In the past, OIT values for pipe samples were not required to meet a minimum value. Now, with recycled resin being used, an OIT value of at least 20 minutes is required to meet AASHTO standards for all corrugated polyethylene pipe using recycled material, according to an update published earlier this year.

With oxidation prevention now playing a critical role in this market, our team analyzed the effectiveness of various stabilizer packages with resin designed for non-pressure pipe applications.

Materials

Study for this topic was conducted in three parts. The first was an analysis of finished non-pressure pipe samples, determining the levels of antioxidant stabilization over the lifetime of various pipes. The second portion was a rheometric study of resins with added stabilizers. The final portion was a multi-pass extrusion of pipe-grade HDPE resin with varying amounts and types of antioxidant stabilizers.

Finished pipe samples were acquired from a partner company for analysis. The age of these samples varies from new (2017) to the 1970's. Samples were excavated after use and analyzed to determine age.

To study the effects of various stabilizer packages on non-pressure pipe, an analogous HDPE material was used (Chrome-catalyzed HDPE, 0.05 MI, 0.95 density). Unstabilized reactor powder was specially obtained from a polyethylene manufacturer. Two common antioxidants (AO) were used: one primary antioxidant (PAO) and one secondary antioxidant (SAO). Baerlocher's RST synergist additive was used as well, both alone and along with each AO. These three components are now compounded and referred to as "T-Blends." These antioxidants were compounded with the resin:

- "PAO" – Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate); aka Irganox 1010
- "SAO" – Tris(2,4-ditert-butylphenyl) phosphite; aka Irgafos 168
- Baeropol RST 92D
- T-1102: 1:0:2 ratio of PAO : SAO : RST 92D
- T-1214: 2:1:4 ratio of PAO : SAO : RST 92D

Extrusion conditions and sample descriptions can be found in Table 1. Reduced-phosphite and phosphite-free formulations were analyzed to show how RST can reduce the need for phosphites. The stabilized resins were compounded using a conical twin-screw Brabender lab-scale extruder. The polymer melt was cooled in a water bath, dried with an air knife, and strand pelletized. Pellets were sufficiently dry to prevent water carryover between subsequent passes. The first pass (Pass 1) is considered in this set of experiments to be the compounding and/or initial pass. Experiments were carried out such that a total of five passes were obtained and samples were taken and the first, third and fifth pass for comparative analysis.

Oxidation Induction Time (OIT) was carried out using a TA DSC Q20 differential scanning calorimeter. Measurements were made in aluminum pans at 200 °C under oxygen atmosphere after a five minute soak time under nitrogen (ASTM D3895). The experiment was ended when an exotherm of 7.5 mW was obtained and OIT was then calculated by extrapolating to baseline.

Abusive Torque Rheometry was carried out using a Brabender 3 Piece Type 5 mixing bowl. The conditions for the experiment were: 225 °C, 60 RPM, and 40 minutes mixing time. These conditions were sufficient to monitor the crosslinking and eventual chain scission of the polymer. Abusive torque rheometry is used to indicate the extent of crosslinking in a polymer. Crosslinking is caused by free-radical generation and delaying or suppressing the crosslinking mechanism is the goal for improved stability.

Melt Index/Melt Flow Rate (MI/MFR) was determined using a Tinius Olsen Extrusion Plastometer Model MP993 melt indexer using ASTM method D1238.

Discussion

Analysis of the Oxidation Induction Time for the pipe samples gives varied data (Figure 1), but gives us several important factors to consider. Samples A through F are all recently-produced, yet they have wide range of stabilization levels, with OIT levels ranging from 43 to 1. Aging samples consistently show low levels of stabilization, with OIT values for samples from the 1980's and 1970's (samples I through L) falling below 5 minutes. This indicates that any antioxidant additives present have been depleted, and that the pipes are susceptible to oxidation. These values would indicate failure in certain circumstances, based on the governing body.

Abusive torque rheometry results display the progression of reactions and crosslinking in each blend (Table 2). Unstabilized HDPE powder reacts the quickest, with peak torque values near 500 seconds. The RST 92D synergist provides some stabilization on its own. A traditional combination of PAO and SAO performs better, and the T-Blend of PAO/SAO/RST 92D performs best, peaking at nearly twice the time of unstabilized powder. These results indicate a delay in the breakdown/crosslinking of the polymer backbone in blends that contain antioxidant. Also, that addition of RST 92D to a standard formulation or a phosphite-free formulation is an improvement over the standard phenol/phosphite formulations typically seen in industry, indicating that RST can serve as a substitute for certain phosphite antioxidants, or help promote the replacement of high-performance phosphites with less effective ones in a given formulation.

When blends of PAO, SAO, and RST 92D are combined to stabilize HDPE, the melt flow data shows a positive influence on the recyclability of the stabilized blends (Figure 3). While unstabilized HDPE becomes more viscous with each extrusion pass, the pre-addition of antioxidant stabilizers allows the resin to maintain a constant melt flow, even after several heat histories. This improvement is of considerable interest to processors who are discouraged from using recycled material due to variability in process flow.

The improvement to these resins is readily displayed via OIT (Figure 4), which shows that resin stabilized with T-Blends can maintain levels of stabilization near the initial level of unstabilized resin, even after five extrusion passes. The unstabilized resin depletes its ability to stabilize by the fifth pass.

Conclusions

While the sample size remains small, lab testing of current and used pipe samples show a clear trend toward failure when judged against new standards requiring a higher level of oxidative protection via OIT values. Stabilized pipe samples gave OIT results that would pass AASHTO's requirement for pipe made with recycled material. While the new AASHTO standard does not explicitly require minimum OIT values for pipes made with virgin resin, it should nevertheless be a concern that even brand-new pipes may have such low stabilization.

Pipe made of recycled material will undoubtedly be made up of material that has experienced oxidative abuse in past lives. If the industry is expected to reuse material, it is in the best interest of the industry to maintain the efficacy of the virgin material as best as possible, so that future uses will require less additional stabilizer for each subsequent application.

In this study, traditional antioxidant blends have shown to act favorably with HDPE resin used in pipe applications. These results indicate positive performance and protection from polymer backbone breakdown, an indicator of protection from stress cracking and pipe failure. Blends with RST perform very well as phosphite-replacement, and even better as a T-Blend with primary and secondary antioxidants. This elevated level of oxidative protection would protect virgin resin for new pipe, and performance from these new pipes would carry over into subsequent uses as recycled material.

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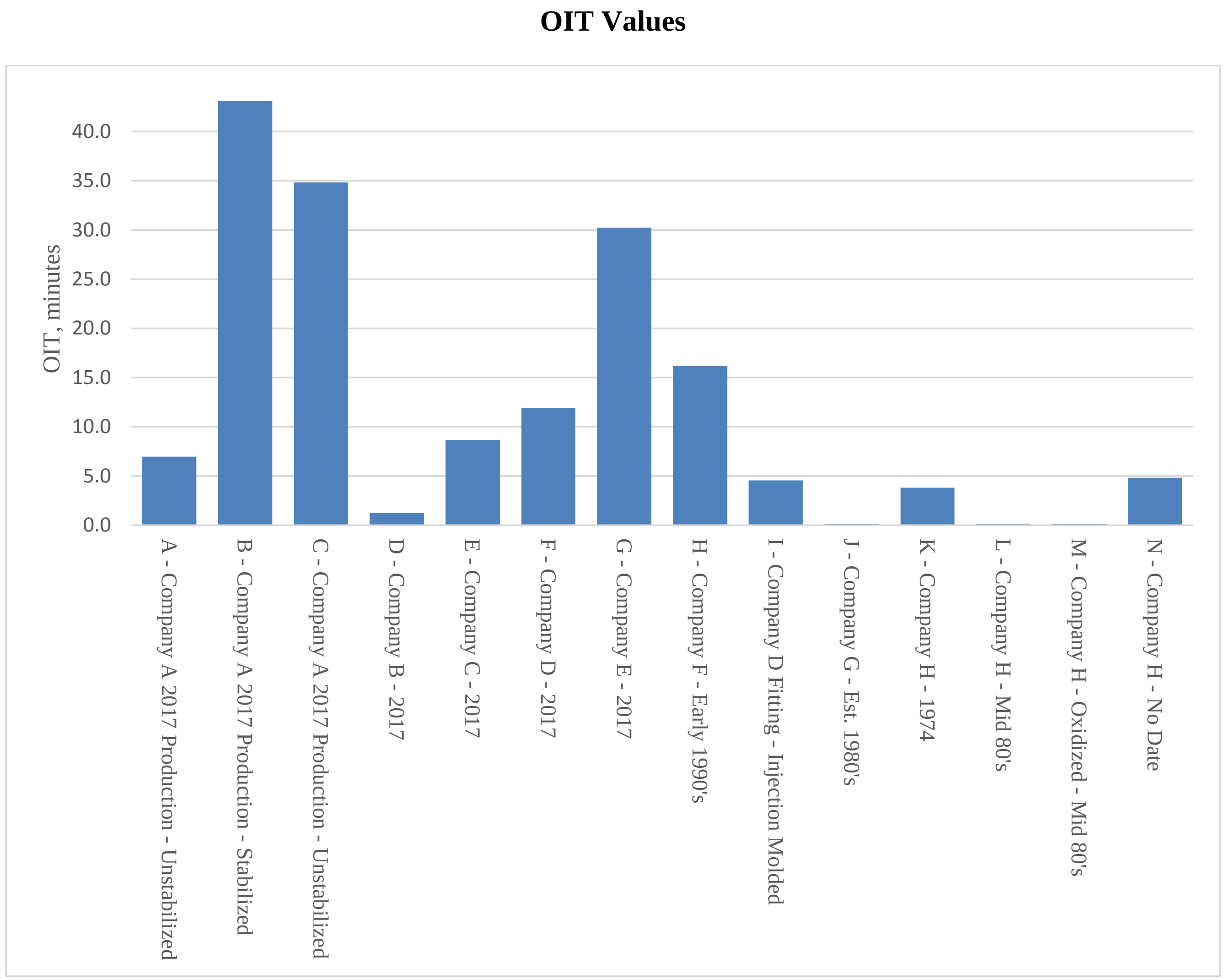

Figure 1: OIT Values for Drainage Pipe Specimens Over Time.

Table 1. Chrome-Catalyzed HDPE Formulations Extruded at a Maximum of 260 °C and 50 RPM.

	No AO	**PAO/SAO**	**PAO Only**	**PAO/SAO/RST 92D**	**PAO/RST 92D**	**RST 92D Only**
PAO		1000 ppm	1000 ppm	1000 ppm	1000 ppm	
SAO		1000 ppm		500 ppm	500 ppm	
RST 92D				500 ppm		2000 ppm

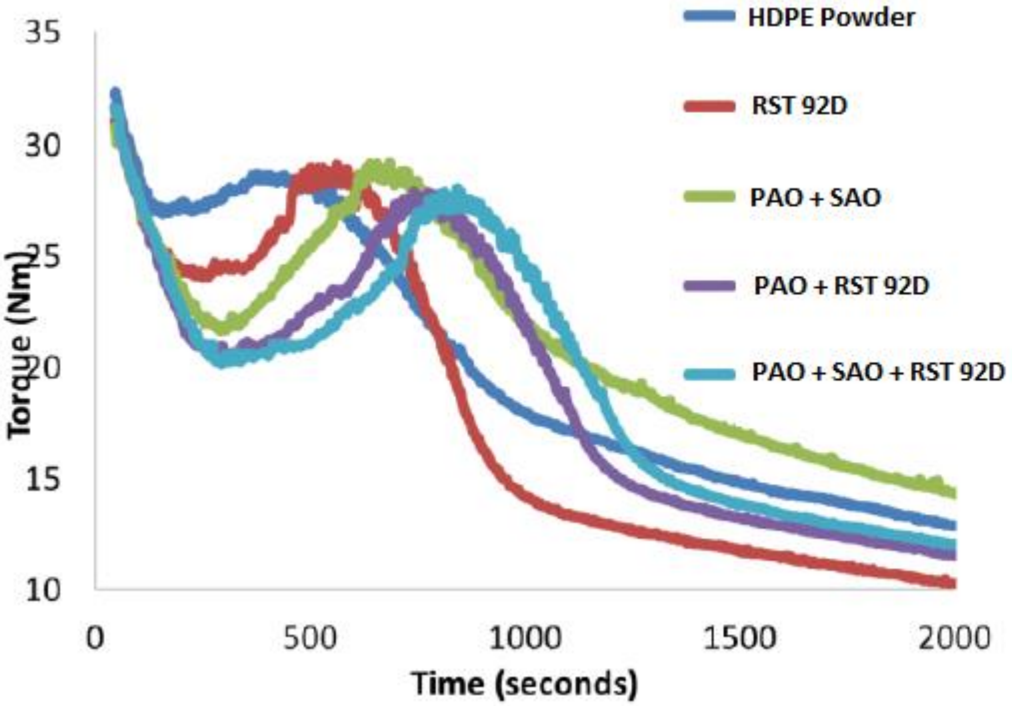

Figure 2: Abusive Torque Rheometry of Chrome High Density Polyethylene with Various Antioxidant Blends

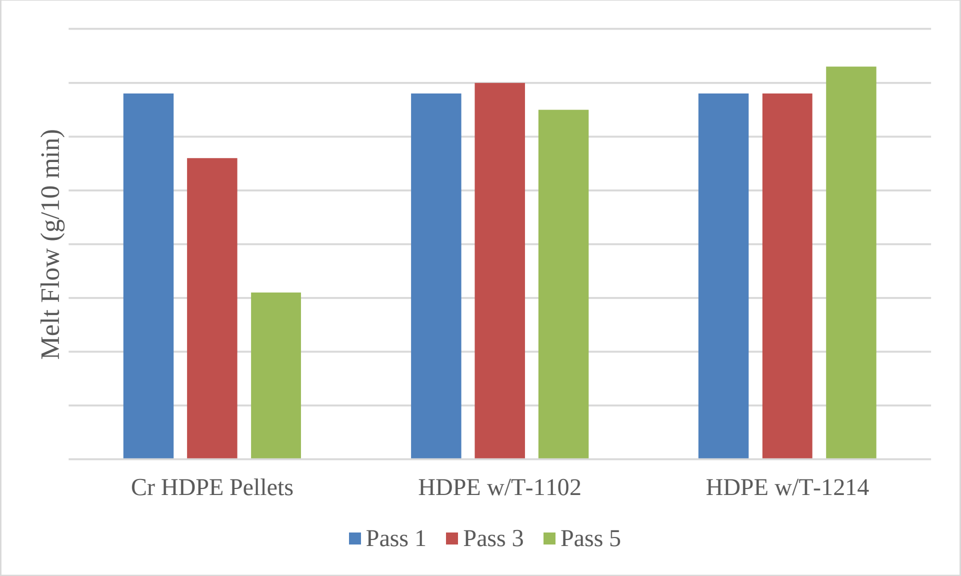

Figure 3. Melt Flow Index for Chrome-catalyzed HDPE with Various T-Blends.

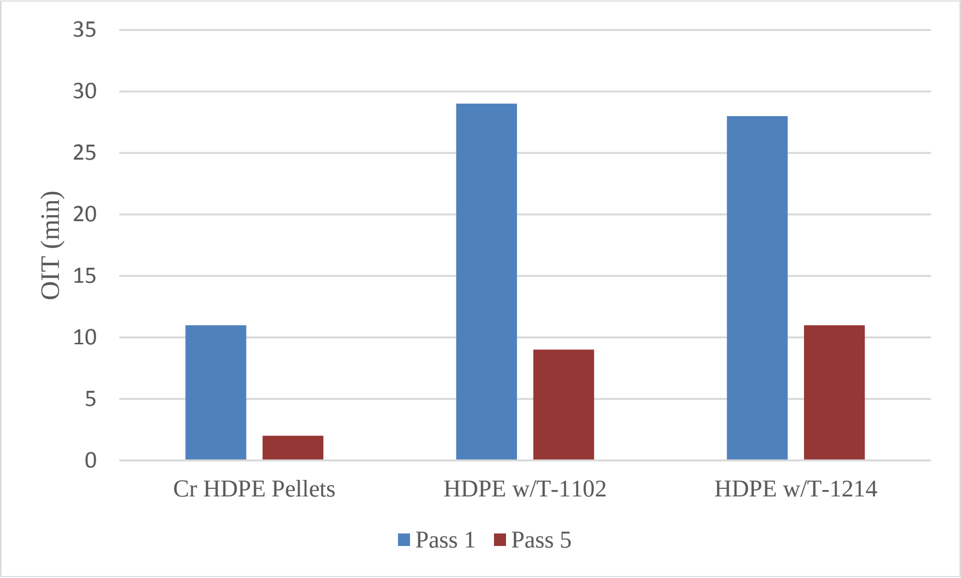

Figure 4: Oxidation Induction Time for HDPE Blends After Multi-Pass Extrusion