

DEVELOPMENT OF A POLYOLEFIN STABILIZER BLEND WITH PREDEFINED PROPERTIES AND FOOD CONTACT STATUS

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Abstract

Development of a new additive or additive blend is a complex, time intensive process. Baerlocher has introduced Baeropol Resin Stabilization Technology (RST) as a synergistic stabilizer blend for polyolefins. A discussion of the work necessary to develop a new blend including regulatory, performance, and properties will be discussed.

Introduction

Development of new additives and blends for polymer stabilization is a slow and expensive process. The overall process from inception to commercialization can take many years and cost millions of dollars. The process is further slowed and costs are increased when food contact approvals are necessary. Meeting global food contact regulations in all regions can take more than a decade and cost tens of millions of dollars.

A brief review of currently available stabilizers on the market vs. previous years shows that very few new stabilizers have been developed for food contact approved applications [1]. Most of the new food contact approved stabilizers on the market are based around replacement of molecules such as TNPP which is being phased out or eliminated in specific countries. Making the situation more labor intensive is the amount of energy, time, and risk associated with major polyolefin producers changing formulations, further slowing the process of adding new stabilizers to the market. This is partially why the stabilizer market is dominated with commodity stabilizers that were developed in the 1970's and 1980's.

Developing a new stabilizer takes time and planning. Baerlocher has approached the development of a new stabilizer in a different way. We investigated the synergy that non-antioxidant additives can have with commodity antioxidants. This work was started due to the unintentional discovery of a synergistic additive blend, later called RST. We then investigated how non-antioxidant additives can be put together to form a simple, inexpensive, and food contact approved, multifunctional additive. The development of this product will be discussed.

Materials

Polymer samples were prepared using a Brabender twin screw extruder. Polyethylene and polypropylene

reactor powders were obtained from global polymer producers and used soon after receipt. Non-antioxidant additives were supplied by global suppliers. Additive blends were prepared by homogenization via multiple methods including: powder blends, whirring blenders, extrusion, melt blending, and pellet mills. Polymer/antioxidant blends were prepared by powder homogenization before extrusion.

Specific additives and stabilizers:

- AO-1 – Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate);
- AO-2 – Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate
- PS-1 – Tris(2,4-ditert-butylphenyl) phosphite; aka Irgafos 168
- PS-2 – Tris(nonylphenol) phosphite; aka TNPP
- CaSt – Calcium Stearate (Baerlocher CODE 5900)
- ZnSt – Zinc Stearate (Baerlocher CODE 8600)
- RST – Baeropol RST 92D

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 or 0) 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.

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.

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.

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

Color measurements were determined on pellets using a HunterLab ColorQuest XE colorimeter.

Discussion

Many additives can be used to improve the performance of standard antioxidants. These additives can come from a wide variety of chemistries. These can include boosters, synergists, and functional additives. Synergists such as DSTDP (distearyl thiodipropionate) are commonly used as heat stabilizers for high temperature applications such as under the hood automotive. These stabilizers work at high temperatures and help protect polymer and standard antioxidants from degradation. Other functional additives such as lubricants help reduce shear during extrusion and molding to help protect the antioxidants and polymer from additional degradation.

Screening Additives

Surveying the available non-antioxidant additives that are available on the market, it is possible to find a wide variety of functional additives that can influence antioxidant stability. Additives such as: metal soaps, polymer processing aids, antistats, fatty acids, waxes, antacids, nucleators, flame retardants, slip agents, antiblocks, light absorbers, light stabilizers, and lubricants can all be used to improve the likelihood of a polymer not degrading and thus protecting the available antioxidants. Additives from these classes were screened for improved polymer melt and color stability when combined with standard AO-1, PS-1, CaSt blends. It was found that many functional additives could slightly improve the overall melt and color stability of a polymer.

Subsequent screening of blends of functional additives was used to investigate how they interacted with one another to improve the overall stability of the polyolefin resins. Many specific blends were identified as potential candidates based on individual performance. These blends were put through various forming processes to determine the effect of process and composition. These blends were compared to the original RST that was developed at Baerlocher. Surprisingly, several blends when processed by specific methods, showed dramatic improvements in the overall stability of the polymer. Development showed that several compositions improved the overall effectiveness, often in surprising combinations of additives (Figure 1). These blends were further analyzed and refined to determine

efficacy during multipass extrusion and other standard stability tests (Figure 2).

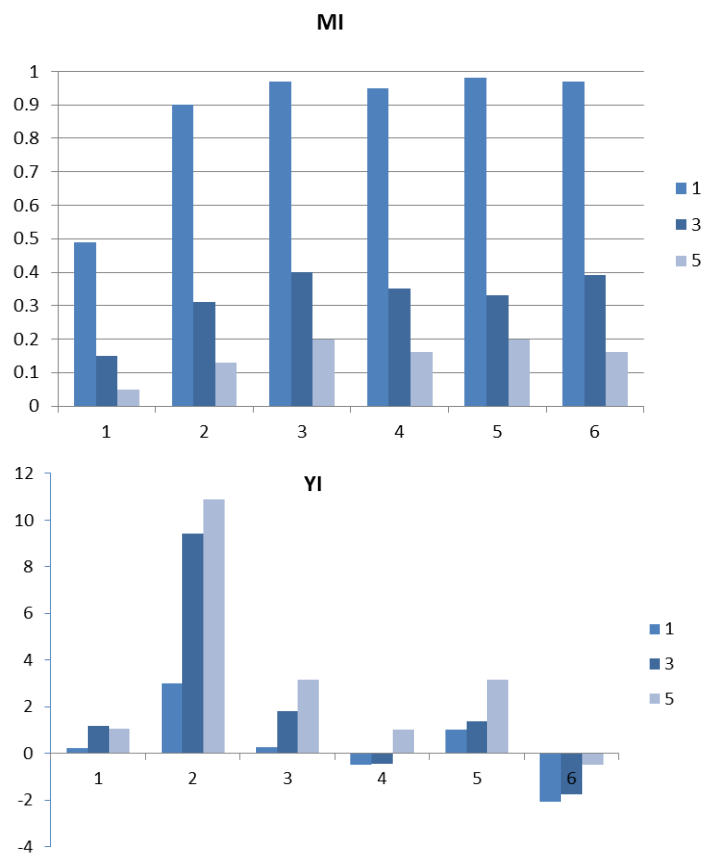


Figure 2. Screening performance via extrusion for MI and Color.

Food Contact

Food contact approval is extremely important for polyolefin producers. This is often due to the fact that a single resin can be sold into multiple applications where some applications may have food contact. Therefore it is important that all resin formulations have a broad variety of food contact approvals. These approvals not only need to be in the country of origin but must also cover all potential countries and regions where the resin and final parts may be exported. A brief list of regulatory agencies that require listing and approvals for use and not necessarily food contact approvals include: TSCA (US), DSL (Canada), EINECS (EU), ENCS (Japan), IECSC (China), KICI (Korea), AICS (Australia), INSQ (Mexico). Additionally other regulatory agencies and initiatives such as REACH, California Proposition 65, MERCOSUR, JHOSPA, European Pharmacopoeia, FDA, and many others all must be met to satisfy the needs of polymer producers. Additionally newer legislation and initiatives such as reduced SMLs in Europe (Specific Migration Limits) and NIAS (Non-Intentionally Added Substances)

can continue to limit usage of an additive in a polymer intended for possible food contact. Lack of approvals in one single area can result in an inability to use or sell a new stabilizer in a region or at all from a global perspective. This also ignores any patent limitations that may prevent use of specific blends in certain applications.

The blends that were identified as potential candidates as stabilizer synergist blends, were all screened versus global regulatory regulations. From this screening, many individual additives were eliminated from contention due to limitations on usage or tight restrictions for dosing.

When complete a much smaller series of blends were available for use as potential RST candidates. These candidates were extensively screened in multiple resins (PE and PP) prepared by various catalyst methods. From this screening only a few candidates remained. These candidates are what make up the basis for Baerolcher's RST technology.

A variety of formulations were found to be acceptable for the final possible formulations. To enhance the performance of the stabilizer blend, Baerolcher decided that the stabilization package should be multifunctional. Choices, based on successful formulations, allow for the RST blend to be a lubricant, antacid, and partial phosphite replacement. When using this blend it allows for elimination of antacid from the formulation, reduction of phosphite usage, and reduction of lubricants in the final polymer. Usage additionally allows for improved color, melt stability, and heat stability based on the final formulation decisions for RST products. Additional non-commercial products allow for different properties not described here.

Examples

Multipass extrusion samples were prepared as described above. A variety of polyolefin resins were investigated to determine efficacy of RST using approximate commodity stabilization formulations. These results are typical for the variety of polyolefins that have been investigated by Baerolcher.

Ziegler-Natta PP

Multipass extrusion was carried out on 2 MFR PP Homopolymer at 240 °C. To simplify analysis and enhance degradation of the polymer, a set concentration of 500 ppm of each additive listed in Figures 3 through 5 were used.

Melt flow analysis (Figure 3) showed that addition of antioxidant to unstabilized polymer improved retention of MFR. Additionally as expected addition of CaSt (antacid)

to the formulation further improved stabilization due to the antacid protecting the antioxidants from acidic catalyst residues [2]. Addition of RST to the formulation gave slight improvements to the overall stability compared to using CaSt as the stabilizer.

Comparison of color using yellowness index (YI) and whiteness index (WI) further showed the utility of using RST compared to no antacid or standard calcium stearate. Yellowness (Figure 4) showed that addition of RST was able to reduce overall YI by several units over the properly stabilized formulation with CaSt. This was further accentuated in Figure 5, where whiteness was improved by approximately 15 units over the CaSt stabilized sample.

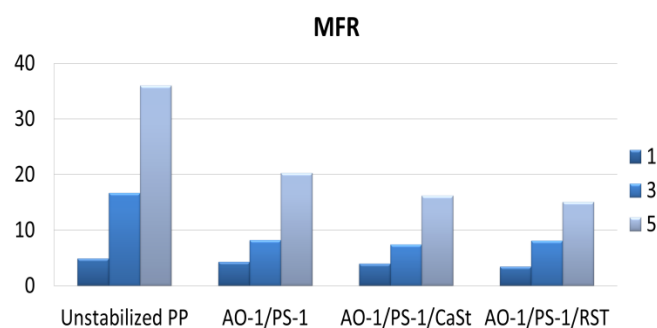


Figure 3. MFR of PP with RST

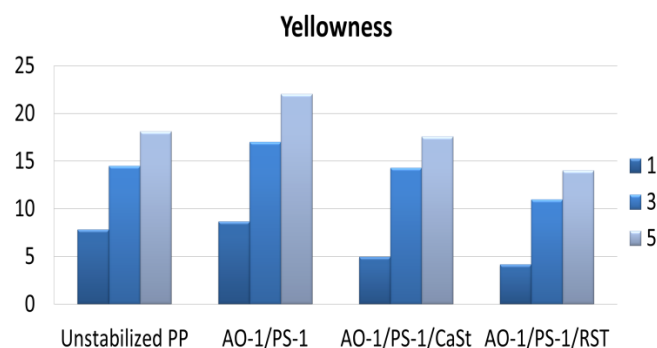


Figure 4. YI of PP with RST

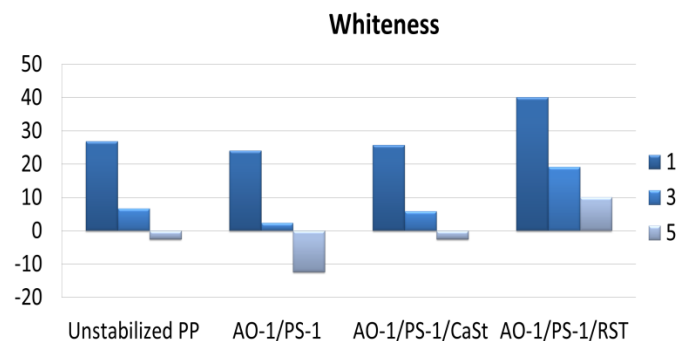


Figure 5. Whiteness of PP with RST.

Ziegler-Natta LLDPE

Multipass extrusion was carried out on a standard 3.5 MI cast film grade of LLDPE. Extrusion was done out at 220 °C.

In this experimental series, RST was used to switch from PS-2 to PS1 at half the concentration and reduce antacid/RST ratios by half. This was to eliminate the problem with plate out that can be seen when using PS-1 in cast film LLDPE applications.

Table 1. LLDPE formulations

Current	Proposed
AO-2 500 ppm	AO-2 500 ppm
PS-2 1000 ppm	PS-1 500 ppm
ZnSt 1000 ppm	RST 500 ppm

Multipass extrusion of LLDPE resin showed that addition of RST with reduced phosphite loading resulted in better retention of MI than use of metal soap with traditional PS-2 (Figure 6).

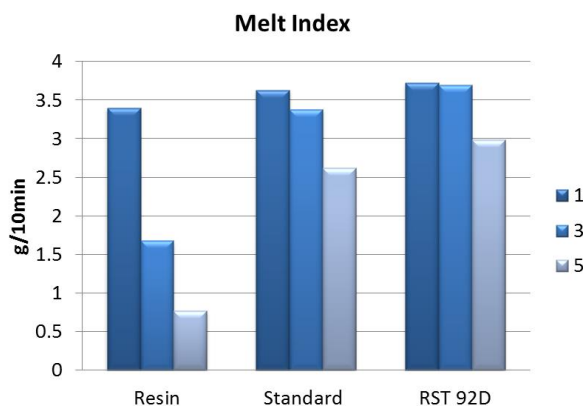


Figure 6. MI of LLDPE with RST.

Oxidation Induction Time was analyzed to determine how effective of a stabilization package the standard vs. RST was. Analysis showed that use of RST improved OIT by approximately 33% (Figure 7). This improvement in OIT was seen despite the overall concentration of the stabilization package has been reduced by 1,000 ppm. This improvement helps to explain why MI was maintained in Figure 6.

Oxidation Induction Time
(minutes)

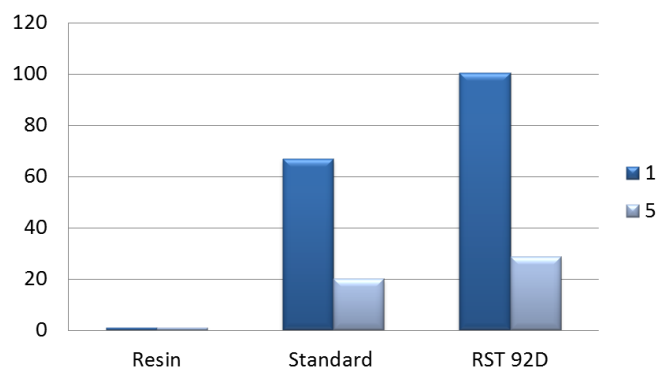


Figure 7. OIT of LLDPE with RST

Color was also analyzed (Figure 8). Results show that color was improved of the resin. This is due to RST protecting the antioxidants and preventing formation of color bodies.

Yellowness Index

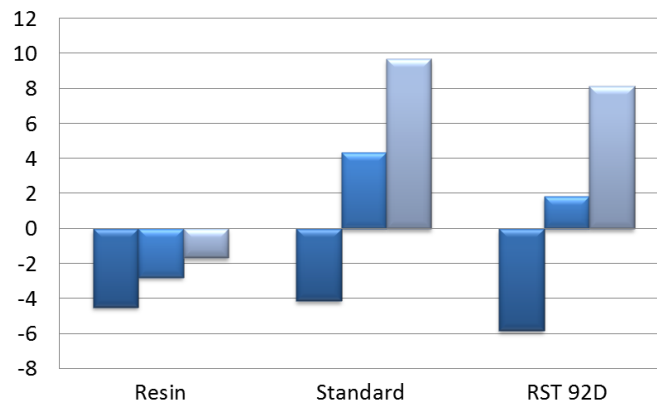


Figure 8. YI of LLDPE with RST.

Conclusions

Baerlocher has been able to use additives synergistic with commodity antioxidants to produce new additive blends. These blends are based on commodity materials with broad global food contact status. The blend is also made to be cost competitive with existing antioxidants currently available on the market.

Acknowledgments

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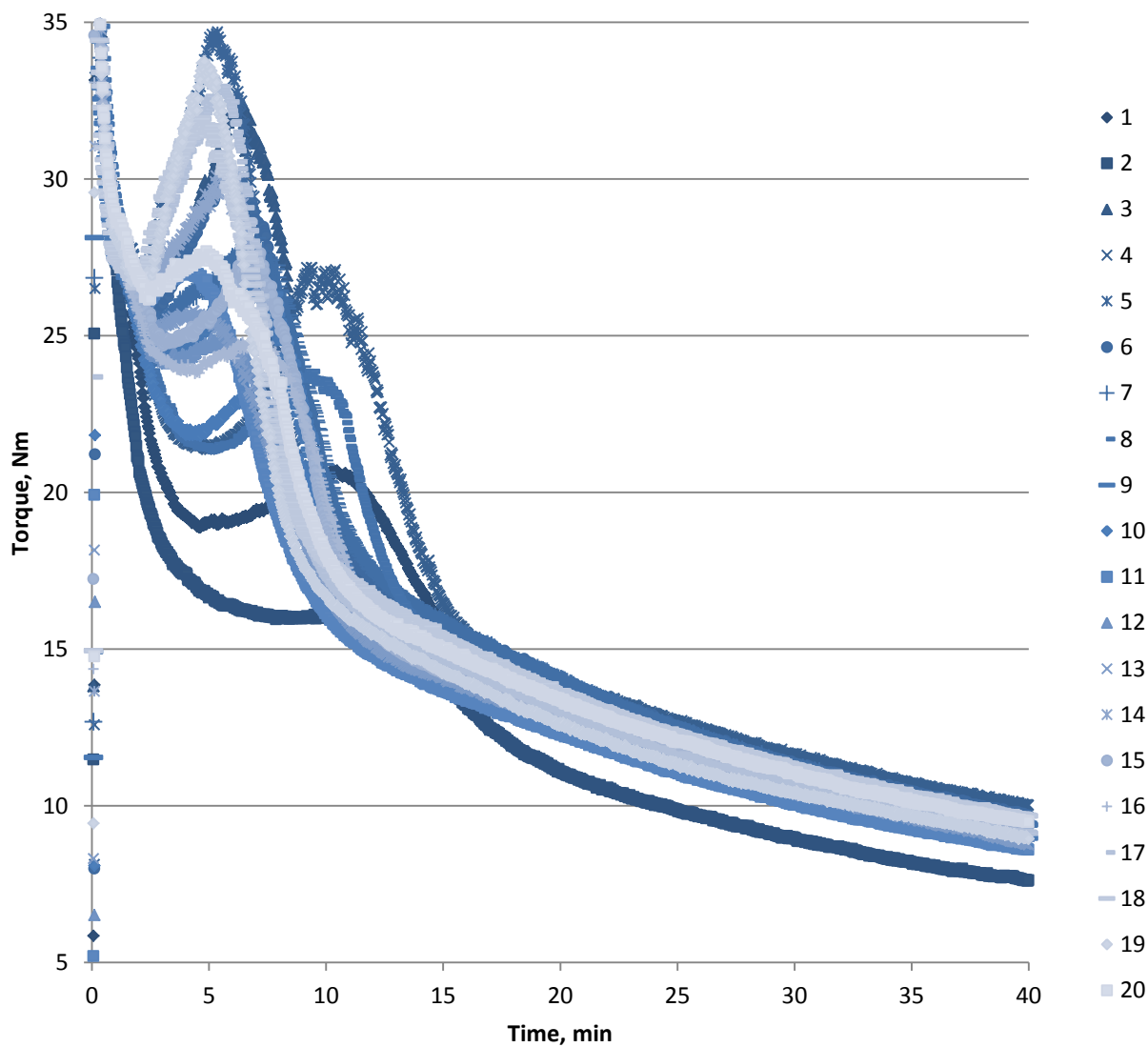


Figure 1. Screening of various blends to determine efficacy.