Recyclable Polyolefins: How Plastic Additives Can Enable a Circular Economy

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Abstract

Plastic packaging is essential for the preservation of food and prevention of food waste. Despite the benefits of plastic packaging, there is rising concern for the environment due to its high production volume, often short usage time, and problems related to waste management and littering. Reduction, reuse, and recycling support the aims of the circular economy. These tools also have the potential to decrease the environmental impact of plastic packaging. In this work, we focus on developing plastic additive solutions with the goal of improving the stability and recyclability of polyolefins.

Introduction

The concept of a circular economy has been developed as a tool to prevent and reduce plastic waste and the consequential environmental effects.[1] The circular economy promotes closing loops in industrial systems, minimizing waste, and reducing raw material and energy inputs.[2] The concept has increasingly gained importance in policy making and has been implemented in production, consumption and waste sectors all over the world.[3] "Reduce, reuse and recycle" are three important aspects for the sustainable management of plastic waste. The reduction principle targets the minimization of waste production whereas the reuse principle refers to the repeated use of products or components for their intended purpose. Although reduction and reuse are the most sustainable options, recycling is also perceived as an advantageous solution to the irresponsible disposal of plastic waste.[4]

In 2014, 69.6 million metric tons of packaging waste was collected as part of the municipal solid waste in the US.[5] Approximately 51.5% of the packaging waste was recycled.[5] Food and beverage packaging have an estimated market share of 69% of all consumer packaging and make up the highest concentration of consumer plastic waste.[6] In the context of packaging waste, reuse and recycling have the potential to decrease the environmental impact. Plastic additives play a key role in enabling both solutions by 1) stabilizing the polymer to allow for longer lifetimes and reuse of the material 2) providing sufficient melt processing stability required for recycling and 3) re-stabilizing recycled plastics to yield higher valued materials (**Figure 1**).

In the recycling trade, where demanding economic pressures are perpetually present, it's easy to think of additives as an unnecessary compounding cost. Yet today's recycling markets demand reprocessed resins that meet the same quality standards as their virgin counterparts. Stabilizing additives are one of the best methods for keeping "old" resins acting and looking "new". Some compounders already rely on stabilizers, lubricants, impact modifiers, and other processing additives to raise recycle to a new level of value – sometimes even above that of the original material. At the same time, proper stabilization of virgin materials will enable longer lifetimes of the of the plastic, promote reuse, and overall limit the amount of waste going to the recyclers.

In this paper we will demonstrate how plastic additives can enable a circular economy for polyolefins by concentrating on stabilization of the polymer. Specifically, we will focus on high density polyethylene (HDPE). In Part 1, we will investigate various stabilizer combinations to yield a "*Ready for Recycle"* virgin HDPE. In Part 2, we will demonstrate how plastic additives can re-stabilize recycled HDPE and improve the properties and lifetime of the reprocessed material.

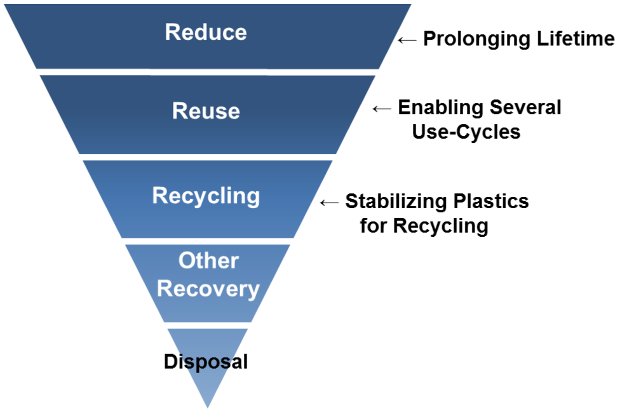


Figure 1: The role of stabilizing additives in the sustainable management of plastic waste.

Background

One of the challenges associated with mechanical recycling is the degradation of polymers during melt processing. Polyolefins degrade by autoxidation. The autoxidation cycle for polyolefins is shown in **Figure 2**. In this cycle, the polymer is subjected to a variety of damaging stresses. This includes high temperatures and shear rates from the multiple melt compounding steps as the product is transformed from reactor powder (melt) to a finished article and ultimately processed again through recycling. In addition to temperature and shear, catalyst residues, entrained oxygen, and other types of impurities might also play a role in promoting further degradation of the polymer.[7]

During these repeated heat histories, free radicals are formed. Once the free radical cycle is initiated, the resultant carbon centered free radicals react with other polymer molecules (either by chain scission or chain linking) and with oxygen entrained in the system, leading to the formation of peroxy radicals. The peroxy radicals react with the polymer generating hydroperoxides and subsequently a new carbon centered free radical is formed and feeds back into Cycle I. The hydroperoxides ultimately breakdown into alkoxy and hydroxy radicals, as depicted in Cycle II. Oxygen centered radicals can react further with the polymer, leading to the formation of more carbon centered free radicals, which feed back into Cycle I. These reactions result in fundamental changes to the polymer architecture via modifications to the molecular weight (MW), MW distribution (MWD), and structure of the polymer backbone. Altering the polymer architecture changes the physical properties, melt processability and the final utility of the polymer during its life cycle.[7]

To prevent the formation of free radicals, a variety of stabilization chemistries can be used. Phenolic antioxidants scavenge oxygen centered free radicals, such as alkoxy, hydroxy and peroxy type species and prevent reaction with the polymer backbone.[7] Phosphites are used to decompose the hydroperoxides into relatively inert products. Additionally, hyperactive stabilization chemistries have been developed that activate early in the degradation process and scavenge the initial carbon centered free radicals before reaction the stabilizing chemistries described here will be explored in this work to demonstrate how very low concentrations (e.g. ≤ 0.1-0.2%) of stabilizing additives can yield more recyclable polyolefins.

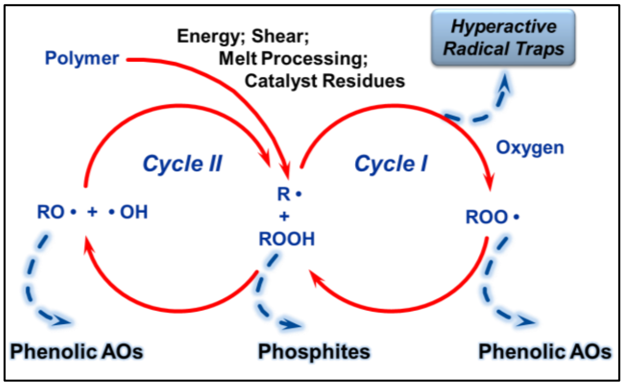


Figure 2: Auto-oxidation cycle for polyolefins; — = path of degradation; --- = path of stabilization.

Experimental

Part 1: "*Ready for Recycle*" Virgin HDPE

The resin used in Part 1 of this work was a blow molding grade HDPE copolymer with a density of 0.954 g/cm3 and melt index of 0.2 g/10min (190°C/2.16 kg). The stabilizer formulations are listed in Table 1 (corresponding structures are in Table 3). The zero-pass melt compounding was done on a twin-screw extruder at 210°C (410°F) under nitrogen. This was followed my multi-pass extrusion (five passes) on a single-screw extruder at 260°C (500°F) under air to simulate several "recycles" of the polymer. The zero, first, third, and fifth pass samples were evaluated for melt flow rate retention and color maintenance. Melt flow rates were measured using an Tinius-Olsen Extrusion Plastometer at 190°C and a 2.16 kg (I_2) and 21.6 (I_{21}) weights. Color development was based on the yellowness index (YI) and was measured using a DCI SF600 Spectrophotometer with a C illuminant and 2° observer. For gas-fade discoloration evaluations, zero-pass samples were compression molded in 10 mil films and placed in a gas chamber for 49 days at 60°C and the YI was measured on a weekly basis. Oxidative induction time (OIT) was measured at 190°C under oxygen using a differential scanning calorimeter (DSC).

Part 2: Re-stabilizing Recycled HDPE

Used HDPE bottle crates (ranging from 2-16 years of age from manufacturing) were ground into chips and washed. The chips were extruded (zero pass) with and without stabilizers (formulations in **Table 2**, corresponding structures in **Table 3**). Multiple pass extrusion (five passes) was done on a single-screw extruder at 250°C under air. All extrusion passes were collected, and the melt flow rate retention was measured. Accelerated weathering tests were carried out following the ISO 4892-1 and ISO 4892-2 procedures.

Results and Discussion

Part 1: "*Ready for Recycle*" Virgin HDPE

Retention of Melt Flow Rates

Virgin HDPE resin formulations containing various loadings and combinations of stabilizers were prepared and multiple-pass extrusion was performed to simulate numerous processing steps and recycling of the polymer. The melt flow rate for each formulation (zero, 1st, 3rd, and 5th extrusion pass) was measured and the results are presented in **Figure 3**. The predominant degradation mechanism for this HDPE is MW enlargement and MWD broadening. Improvements in the retention of MW and MWD (i.e. recyclability) is accomplished by either increasing the concentration of stabilizers or changing the components. In Group 1, the phenolic AO1 (see structures in Table 3) alone is compared to combinations with a phosphite (P1) and two different hyperactive stabilizer chemistries (E201 and NOH). An obvious dose response is observed in the melt flow rate when building upon the single component phenolic formulation to a binary phenol/phosphite stabilization system, improving the recyclability of the polymer.

Introducing a hyperactive radical scavenger, E201, provides excellent control of the MW and MWD. Additionally, 680 ppm of the ternary AO1/P1/E201 blend outperforms the melt processing stability of 1020 ppm of the AO1/P1 blend (i.e. 33% decrease in total additive concentration). Somewhat surprisingly, the second hyperactive chemistry studied, NOH, does not have a significant effect on melt flow retention, in this particular HDPE, when compared to 680 ppm of the binary AO1/P1 blend.

Table 1. Formulation Design (Part 1)

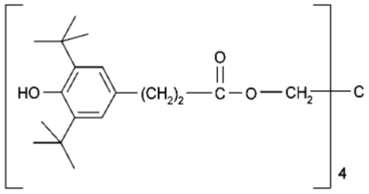
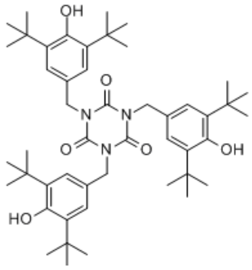
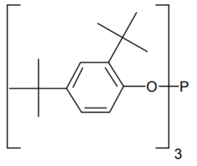
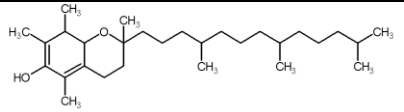
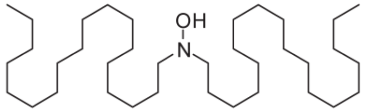
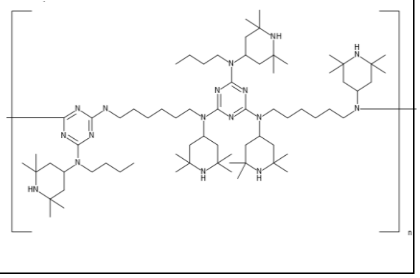
Formulation*	Components
Group 1	
340 ppm AO1	340 ppm AO1
680 ppm AO1/P1	340 ppm AO1 340 ppm P1
1020 ppm AO1/P1	340 ppm AO1 680 ppm P1
680 ppm AO1/P1/E201	340 ppm AO1 255 ppm P1 85 ppm E201
685 ppm AO1/P1/NOH	340 ppm AO1 220 ppm P1 115 ppm E201
Group 2	
340 ppm AO2	340 ppm AO2
680 ppm AO2/P1	340 ppm AO2 340 ppm P1
1020 ppm AO2/P1	340 ppm AO2 680 ppm P1
680 ppm AO2/P1/E201	340 ppm AO2 255 ppm P1 85 ppm E201
685 ppm AO2/P1/NOH	340 ppm AO2 220 ppm P1 115 ppm NOH

**Each formulation contains 180 ppm of acid scavenger.*

Table 2. Formulation Design (Part 2)

Formulation Name	Components
Recycled HDPE	None
Recycled-Low	200 ppm AO1 400 ppm P1 1000 ppm LS
Recycled-High	400 ppm AO1 800 ppm P1 2000 ppm LS

Table 3. Structures of Antioxidants and Light Stabilizers

Name	Structure
AO1 Phenolic Irganox® 1010	
AO2 Phenolic Irganox® 3114	
P1 Phosphite Irgafos® 168	
E201 Vitamin E Irganox® E201	
NOH Hydroxylamine Irgastab® FS-042	
LS Hindered Amine Light Stabilizer Chimassorb® 944	

In Group 2, a different phenolic antioxidant (AO2) was studied to determine the effects of varying the phenolic chemistry on the MW control and recyclability. The 1020 ppm binary blend of AO2/P1 almost matches the melt flow rate of the corresponding AO1 blend, with a slight decrease in the fifth pass sample. In contrast to the ternary blends with AO1, the addition of E201 does not to improve the melt flow rates. However, the performance of the 680 ppm blend with E201 matches the performance of the 1020 ppm loading of AO2/P1. This demonstrates the additional benefit of using hyperactive stabilizers in that targeted performance can be achieved at significantly lower concentration of additives. This could indicate that a favorable synergism exists between AO1 and E201 allowing the excellent melt flow rate retention observed in this formulation. Once again, the NOH formulations do not outperform the binary blends of AO2/P1, following the trends observed in the AO1 formulations.

Retention of Color

The color development during multiple pass extrusion (based on YI) is shown in **Figure 4**. In Group 1, slightly better color control is achieved when dosing in P1 with AO1. In the zero-third pass measurements, the YI of the E201 formulations are very similar to the binary blends of AO1/P1. However, by the fifth pass, formulations with E201 yield more discoloration in the resin. A significant improvement in color control is seen when switching the E201 with NOH, especially when looking at the YI's for the zero, first, and third pass samples. Immediately, one can see that changing the phenolic antioxidant from AO1 to AO2 (i.e Group 2) has a significant improvement on color, with AO2 based formulations showing the lowest color development. Similarly, to Group 1, the formulation with E201 yields higher overall color development (within Group 2). These are very common color trends. Typically, formulations that provide the best melt flow control, tend to be slightly more colored.[8-9] Therefore, selection of stabilizers and combinations depend on the critical-to-quality properties for the targeted applications and performance.

Oxidative Induction Time

Another measurement of the oxidative stability of polyolefins is the oxidative induction time (OIT). The OIT measurements for Group 1 and Group 2 formulations are displayed in **Figure 5**. The trends in OIT compare to those observed in the melt flow rate measurements. In Group 1, an obvious dose response in OIT is observed when increasing the phosphite loading with AO1. The addition of E201 results in a dramatic increase in OIT. This explains why the zero and first pass samples of formulation AO1/P1/E201 yielded higher melt flow rates that the binary blends. The hyperactive E201 is an incredibly efficient stabilizer for preserving the MW and MWD of the polymer but has the potential disadvantage of discoloration. Replacing E201 with NOH does not have a significant effect on the OIT and performs similarly to the 680 ppm AO1/P1 binary blend. In Group 2, we see a significant trade-off in OIT performance when switching from AO1 to AO2. All formulations with AO2 yielded lower OIT values than their AO1 counterparts supporting the trends observed in the melt flow rate measurements.

Gas Fade Discoloration Resistance

Stabilizing additives are essential to preserving the polymer architecture of polyolefins during melt processing and can also ensure the polymer structure remains stable during storage. During storage, a polymer can be exposed to a variety of conditions such as elevated temperatures, humidity, and oxides of nitrogen. To simulate long-term storage, compression molded films were held in a gas chamber for 49 days and YI measurements were taken weekly. Gas fade discoloration is a result of the stepwise over-oxidation of a phenolic antioxidant by oxides of nitrogen (i.e. pollution).[8] The results of the gas fade discoloration measurements are shown in **Figure 6**. The results are not surprising. The AO1 and AO2 formulations with E201 yield the highest overall color development. Switching from AO1 to AO2 also has a significant effect, with the AO2/P1 formulations yielding the lowest gas fade discoloration.

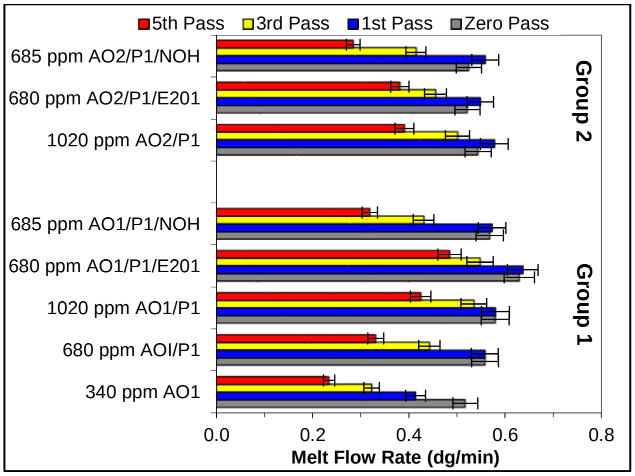


Figure 3: Part 1, melt flow rates for multiple pass extrusion samples of virgin HDPE. Group 1 samples were stabilized with phenolic AO1 and Group 2 with phenolic AO2.

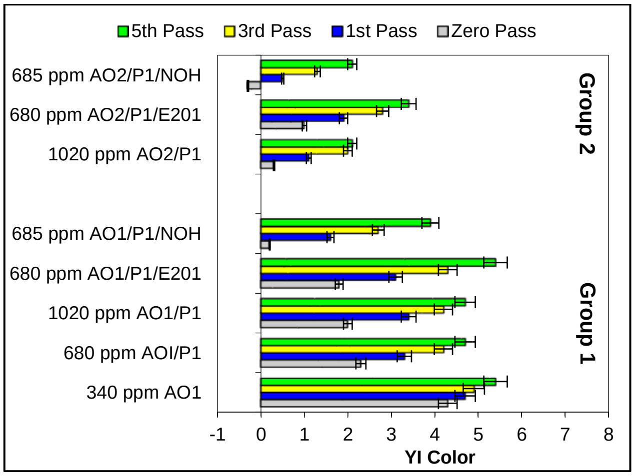


Figure 4: Part 1, YI for multiple pass extrusion samples of virgin HDPE. Group 1 samples were stabilized with phenolic AO1 and Group 2 with phenolic AO2.

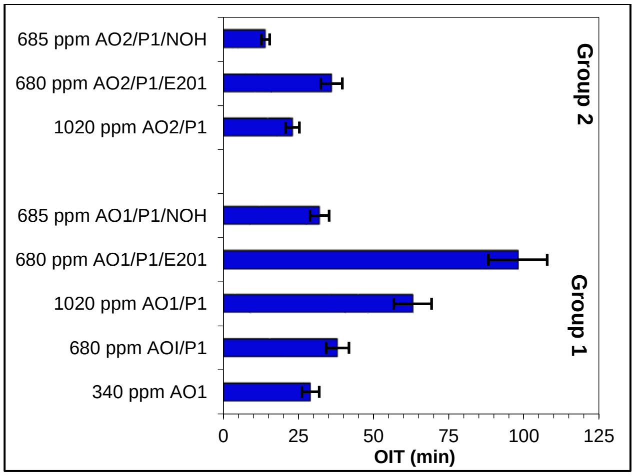


Figure 5: OIT of zero pass, compression molded 10 mil films of virgin HDPE with various stabilizers.

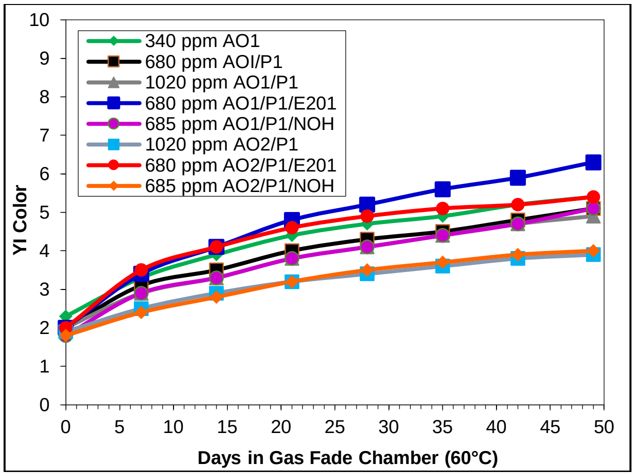


Figure 6: Gas fade discoloration measurements for zero-pass, 10 mil films of virgin HDPE with various stabilizers.

Part 2: Re-Stabilizing Recycled HDPE

In addition to formulating virgin resins to be ready to enter the recycle stream, plastic additive stabilizers can also re-stabilize recycled resins. In this work, used HDPE bottle crates were washed, ground, and recycled (i.e. extruded) into HDPE pellets with and without stabilizers (refer to **Table 2**).[10] Multiple pass extrusion was conducted on the recycled pellets and melt flow rates were measured and presented in **Figure 7** as a function of extrusion pass. It is evident when observing the measured melt flow rates that the unstabilized resin (Recycled-HDPE) undergoes MW enlargement resulting in a significant decrease in the melt flow rate after multiple extrusion passes. Adding 1600 ppm of AO1/P1/LS (Recycled-Low) to the material increases the melt processing stability of the recycled resin by 10% (based on fifth pass melt flow rate). Excellent melt-processing stability is achieved when the resin is re-stabilized with 3200 ppm of AO1/P1/LS (Recycled-High) with a 22% increase in melt flow rate when compared to the unstabilized material. It is evident that a re-stabilization step is necessary to achieve the required melt processing stability of the recycled polymer and avoid "down-cycling" of the material.[10]

The recycled material was also exposed to xenon-arc light in the presence of moisture for 8000 hours to simulate weathering effects (ISO 4892-2). The impact strength was measured after varying exposure times and is presented in **Figure 8**. In the unstabilized resin, a dramatic decrease in impact strength is observed after only 1000 hours of exposure. Restabilizing the recycled material with 1600 pm AO1/PS/LS (Recycled-Low) yields a significant improvement in the weatherability of the material with the impact strength remaining stable for up to 5000 hours of exposure. Increasing the concentration of antioxidant and light stabilizer to 3200 ppm (Recycled-High) further improves the weatherability, with no significant changes in the impact strength for up to 8000 hours of exposure. These results demonstrate that re-stabilization with light stabilizers will yield excellent weatherability of the recycled resin.[10]

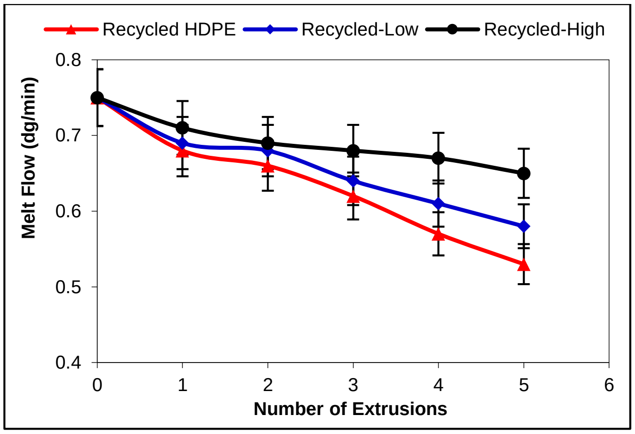


Figure 7: Melt flow rate vs. extrusion pass for unstabilized and re-stabilized recycled HDPE.

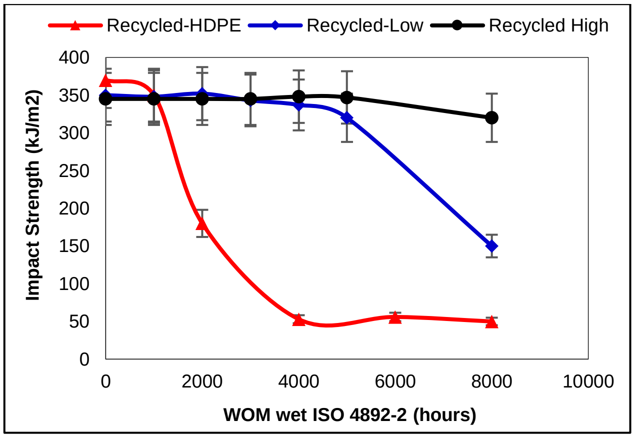


Figure 8: Impact strength as a function of exposure time to xenon-arc light and moisture (ISO 4892-2) for unstabilized and re-stabilized recycled HDPE.

Conclusions

This study provided valuable insight into the variables and issues in developing a suitable stabilization system for virgin and recycled HDPE. Two case studies were presented. In Part 1, various stabilizer combinations were studied in virgin HDPE to identify key formulations to yield a highly recyclable polymer. In Part 2, used HDPE bottle crates were recycled with and without re-stabilization. The results indicate the importance a re-stabilization step in the recycling process to achieve long lasting, durable material. In this work we have demonstrated how BASF plastic stabilizing additives can enable a circular economy for plastics by 1) Yielding longer lifetimes for polyolefins and consequently limiting plastic waste and 2) Providing higher value end applications of recycled plastics through re-stabilization.

Furthermore, with a rising concern over microplastics and the subsequent treat to the environment, the preservation of the MW of polyolefins is more important than ever. Stabilizing additives will play a major role in preserving the MW of plastics that enter the waste stream and preventing the formation of microplastics.

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