A NEW APPROACH FOR EVALUATING THE PROCESSING STABILITY OF POLYOLEFINS USING MICROCOMPOUNDING

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Abstract

The processing stability of polymers is traditionally done by extruding the polymer multiple times, each time retaining a sample to measure physico-mechanical properties sensitive to degradation (such as the melt flow index, yellowness index and, in some instances, mechanical properties). While useful and providing valuable information, multiple extrusion studies have two disadvantages: firstly they require relatively large samples of each of the formulations being studied (typically in the kilogram scale per material studied) and, secondly, each study is time consuming. For studying the efficiency of combinations of stabilizers these disadvantages limit the number of formulations which can realistically be studied in an experimental program and are often carried out without considering reproducibility. A new approach, which uses the re-circulation capability of a X-plore Micro-Compounder, has been developed and evaluated against traditional-scale multiple extrusion methods and is found to provide comparable results with statistical repeatability. This approach can be used in high-throughput screening of complex stabilizer systems by combining multifactor experimental design formulations evaluated measuring the residual stability of samples following extrusion.

Introduction

Extrusion is one of the most widely used processes to transform polyolefins from a basic resin to something useful. Almost all polyolefins experience extrusion at least once – either following polymerization when additives are usually incorporated into the polymer by the resin producer, or during a subsequent compounding process or in the final processing step if the polymer is converted into film, sheet, pipes, profiles, etc. In all cases the polymer chain is submitted to thermal and mechanical stresses which unfortunately promote chemical reactions (such as chain scission and cross-linking) that lead to a loss of mechanical properties. To protect the polymer antioxidants or stabilizers are added to the polymer.

There are many different antioxidants commercially available for use as processing stabilizers in polyolefins. Generally, antioxidants are classified in terms of their stabilization mechanism: radical scavengers (primary antioxidants) and hydroperoxide decomposers (secondary antioxidants). Polyolefins are usually stabilized for processing using synergistic combinations of hindered phenolic antioxidants (which are radical scavengers) and trivalent phosphites (which act as peroxide decomposers)[1,2].

The efficiency of a processing-stabilizer package (consisting of a combination of antioxidants) as well as the influence of processing conditions (temperature, shear and residence time) on degradation is usually carried out using multiple extrusion experiments[3,4,5,6,7]. Multiple extrusion involves repeatedly melting, extruding and pelletizing the polymer (typically five times). Changes in the melt flow index (MFI) and yellowness index (YI) are commonly plotted against the extrusion number[3,6,7] or residence time[8]. The ability of a particular stabilizer system to maintain the initial MFI and color after repeated extrusion is taken as a measure of its efficiency. The simplicity and speed of using MFI to follow degradation makes this the most commonly used physico-mechanical property used in multiple extrusion studies, but changes mechanical properties[6,7], chemical changes (using FTIR)[5] and changes in the molecular distribution (using gel permeation chromatography GPC)[5] are also monitored. The active stabilizer remaining can also be determined either by extraction and chromatography[2,3,4] or using oxidative induction time[2,3] to determine the residual stability of the polymer.

The synergistic (and occasionally antagonistic) performance of combinations of antioxidants mean that it is desirable to investigate the effects of using different antioxidants with different ratios of primary to secondary antioxidants at various addition levels under different processing conditions (polymer, temperature and screw speed). Unfortunately, using traditional-scale multiple extrusion where typically kilograms of each formulation is required to complete a performance evaluation, is not a practical approach for screening large sets of samples: even evaluating only two primary and two secondary antioxidants at three different ratios at a single total antioxidant addition level would require twelve experiments. Multiple extrusion studies using experimental design focus more on the influence of processing conditions[9] or screw design[10] on polymer degradations rather than stabilizer efficiencies.

Most traditional-scale multiple extrusion studies of polyolefins are carried out using 19-25 mm single or twin-screw extruders with an L/D ratio of 30. Micro-extruders with screw diameters less than 15 mm have been developed for processing small samples of polymer.

These are frequently used to study composites[11], blends of polymers or high-performance materials in low output applications (such as certain medical applications)[12].

Generally, the short residence time of the polymer in micro-extruders and the small samples extruded have limited their suitability for processing stabilization studies (especially if the degradation is going to be monitored by MFI). Wroczynski *et al.*[13] has used a micro-extruder to rank the degradation of different processing stabilizers and showed that there was good correlation with the MFI results obtained using traditional-scale multiple extrusions. They also considered alternative methods to MFI determinations: fluorescence spectroscopy and a comparison of the torque values of the screw of the micro-extruder against a control sample. Both approaches resulted in a rank-ordering of different stabilizers that correlated with traditional-scale multiple extrusion[14,15].

In this paper we investigated the use of a micro-compounder to evaluate the relative stabilization performance of various antioxidants in polypropylene. Although the micro-compounder used is of similar design to that used by Wroczynski[13] *et al.*, we use it in a batch re-circulation mode rather than the continuous extrusion mode they used[13,14,15].

Experimental

Unstabilized, deactivated polypropylene homo-polymer (Spheripol PP) was used as received. All stabilizers were from Everspring (Taiwan) and are identified in Table 1. Calcium stearate was from Baerlocher (Germany).

Table 1: *Stabilizers used in this work.*

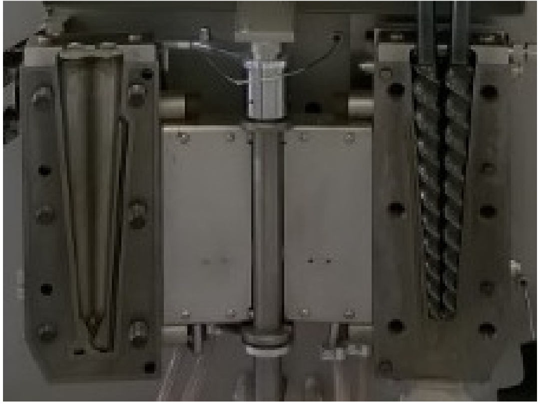
Stabilizer	Chemical Name
Evernox 10	Tetrakis [methylene(3,5- di-*tert*-butyl-4- hydroxyhydro- cinnamate)] methane
Evernox 76	Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate
Evernox 3114	1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione
Evernox 1330	1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl) benzene
Everfos 168	Tris(2,4-ditert-butylphenyl) phosphite
Everfos 626	Bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite
Everfos 9228	Bis(2,4-dicumylphenyl) pentaerythritol diphosphite

The additives (antioxidants and acid scavenger) were pre-mixed with unstabilized (but deactivated) polypropylene powder according to the various formulations under evaluation.

For traditional-scale multiple extrusion polymer samples were melt-blended using a Brabender PL 2000-6 Plasticorder (Brabender Technologie GmbH & Co. KG (Germany) with a single-screw extruder (19 mm, 25D, 3:1 simple screw running at 60 rpm) and a temperature profile of 190°/200°/210°/220°C. The residence time was determined to be ca. 30 sec. The extrudate was cooled in a water bath and pelletized. Pelletized samples were retained for testing and the remaining polymer was re-extruded.

The "compounding–multiple extrusion" was carried out using a Xplore Microcompounder (Xplore Instruments BV, Netherlands). This is a vertical conical co-rotating extruder (see Figure 1) with a barrel volume ca. 15 cm^3 that can be run either as a continuous extruder or in a batch re-circulating mode (the polymer is extruded into a side channel and fed back into the extruder). This paper reports on work carried out using the re-circulating mode.

Figure 1: *X-plore Microcompounder showing the recirculation channel which allows the residence time of the melt in the extruder to be controlled.*



Based on the size of the MicroCompounder batches of ca. 13.5g of each polymer/additive dry blend formulation were injected into the MicroCompounder (running at 100 rpm, 230°C) and circulated for the desired time before being extruded. Samples were retained for testing. Each formulation was run at least five times with samples being taken after 3, 6, 9, 12 and 15 minutes for testing. The force required to maintain a constant screw speed was recorded 60 times per minute for the duration of each run.

Four polypropylene homopolymer reference samples (each with a different MFI, but all having a similar molecular weight distribution to the polymer used in this study) were run on the micro-compounder (in continuous extrusion mode) and the force measured for each MFI.

For the traditional multiple extruded samples and the four reference samples the MFI was measured according to ISO 1133 at 230°C and 2,16 kg using a Melt Flow Tester Type 6942 (Ceast S.p.A., Italy).

Fourier transform infrared (FTIR) spectroscopy measurements were carried out using a Perkin-Elmer Spectrum Frontier FTIR in attenuated total reflectance (ATR) mode using 4 cm^{-1} resolution with 16 scans between 400-4000 cm^{-1}. The FTIR data is made up of an average of five samples cut from each extruded or micro-compounded sample

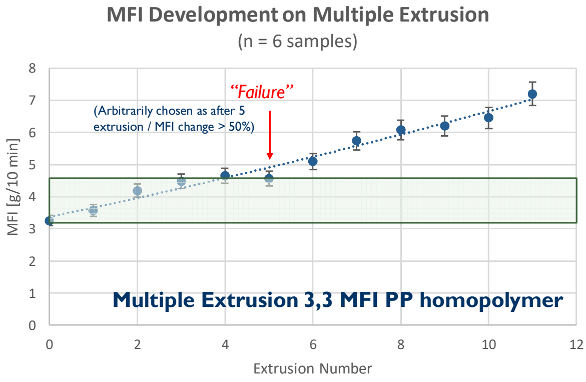
Residual stability was determined using a TA Instruments MDSC 2920. The isothermal oxidative induction time (DSC-OIt) was determined on compression molded samples (± 650 µm) were heated at 200°C min^{-1} under nitrogen to the temperature of interest (usually 180°C) at which time the gas was switched to oxygen and the time until the onset of degradation was measured.

Discussion

The efficacy of different processing stabilizers is usually evaluated using multiple extrusion. Although it is usually impractical to run replicate samples during multiple extrusion (*i.e.*, *n*-samples of the polymer are each multiple extruded *x*-times, and then another sample of the same polymer is multiple extruded fives time), it is important to know how repeatable the degradation is on multiple extruding polymer to be able to determine whether observed differences in stabilization performance is significant. Only if the changes in MFI over several extrusions is larger than any variations observed between duplicate samples with the same extrusion history can we draw any conclusions on performance.

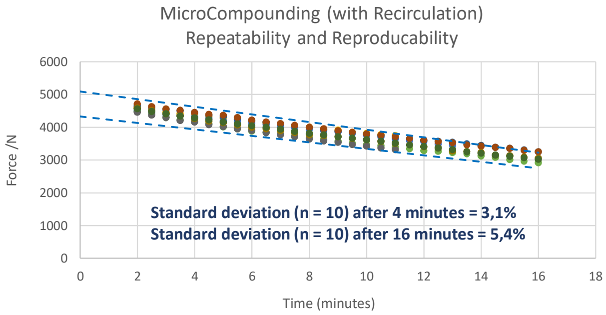
The reproducibility of degradation caused by multiple extruding a sample under identical conditions in a single screw extruder was determined by extruding six samples of a single formulation eleven times (residence time per extrusion ca. 30 sec). Figure 2 shows the average MFI after each extrusion; the average standard deviation was 3%.

Figure 2: *Average MFI for six samples of polypropylene each extruded eleven times on a single screw extruder.*



For comparison ten samples of a single formulation (unstabilized polypropylene powder dry blended with antioxidants and calcium stearate) were micro-compounded for 16 minutes. Figure 3 shows the average force to maintain a constant rpm reported at 30 second intervals. The average standard deviation was found to be 5.4% after 16 minutes.

Figure 3: *Force measured every 30 seconds for ten samples of polypropylene each extruded for 16 minutes on a X-plore MicroCompounder.*

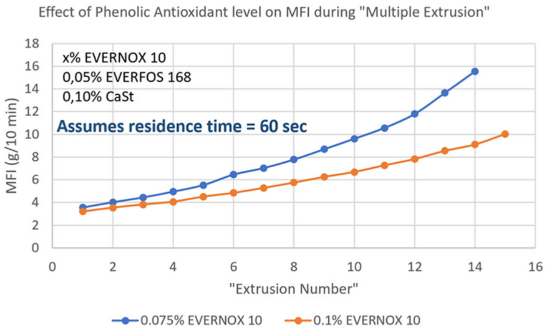


One advantage of evaluating stabilizer performance using traditional-scale multiple extrusion is that changes in the polymer can be described in terms of changes in MFI which is related to the melt viscosity of the polymer. Polyolefin producers use in- and on-line melt rheometers to monitor and control the MFI by measuring the melt viscosity of the polymer. The force required to maintain a constant screw speed in the micro-compounder also depends on the melt viscosity of the polymer and therefore changes as the melt viscosity changes. It is therefore possible to use this force as a proxy for MFI. A correlation between the force to maintain a constant screw speed and MFI was determined by extruding the reference polypropylene on the micro-compounder using the same temperature and screw speed as used for the recirculation studies. This re-stating the force as MFI is done for convenience and assumes that the polymer being studied, and the polymer used for the calibration have similar molecular weight distributions.

The residence time of the polymer in the single screw extruder was determined to be ca. 30 sec at 60 rpm. Scaffaro[11] has determined the residence time for various co- and counter-rotating twin screw and single screw extruders and found them to be in the range 60-100 seconds (depending on the screw speed and melt viscosity of the polymer). More generally the minimum residence time in a simple single screw extruder can be predicted using a simple equation[12] which allows us to link the time sample is re-circulated in the micro-compounder to the residence time of laboratory- or even commercial extruders. For convenience the degradation of the micro-compounded material is discussed here in terms of "number of extrusions" where a residence time of 60 seconds/extrusion pass is assumed.

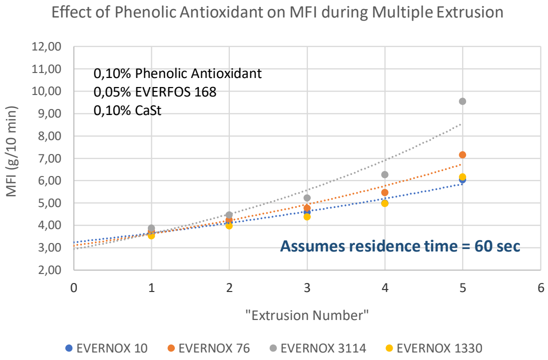
Repeatability is important, but for re-circulating micro-compounding to be useful in studying the efficacy of processing stabilizers it needs to be able to differentiate the performance of different systems. Figure 4 shows the difference in stabilizing performance in two samples containing different levels of the same antioxidant. These samples were each extruded for 16 minutes, but even after six minutes (one compounding extrusion pass and five multiple extrusion passes assuming a residence time of 60 sec) a significant difference in the stabilizing efficiency can be seen based on the level of the phenolic antioxidant added.

Figure 4: *The increase of MFI (approximated from force measurements) for polypropylene stabilized with using different levels of a phenolic antioxidant as determined using a micro-compounder in batch re-circulating mode.*



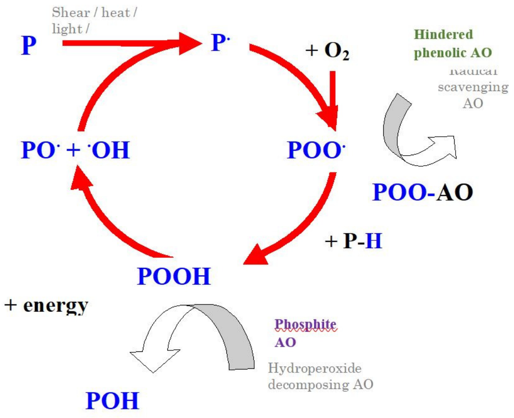
The relative stabilizing performance of four different phenolic antioxidants (all at the same addition level) after five extrusions can be seen in Figure 5.

Figure 5: *The increase of MFI (approximated from force measurements) for polypropylene stabilized with different phenolic antioxidants as determined using a micro-compounder in batch re-circulating mode.*



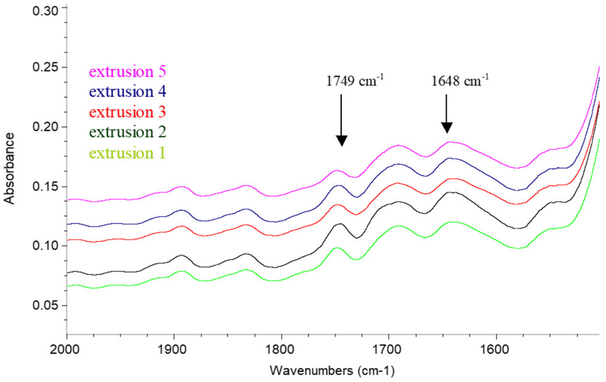
Various authors[3,4,16] have shown that under oxidative conditions (processing under air) the degradation is greater than when the polymer is processed under inert atmosphere. This is attributed to the small amounts of oxygen dissolved in the polymer which react extremely rapidly with the macroalkyl radicals formed by shear forces to form alkylperoxyl radicals ($POO^{\bullet}$) which, in turn, abstract hydrogen chains from the polymer chains to form hydroperoxides (POOH) and alkyl radicals ($P^{\bullet}$). These radicals then initiate further degradation as illustrated in Figure 6. Hydroperoxides, which decompose rapidly at processing temperatures to form alkoxyl radicals ($PO^{\bullet}$) and hydroxyl radicals ($^{\bullet}OH$), are primarily responsible for the branching reactions (i.e., the autocatalytic nature of oxidation).

Figure 6: *The autooxidation cycle of polymers.*



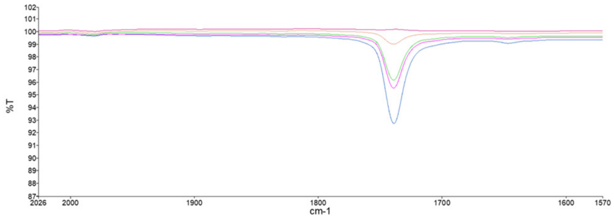
In the traditional multiple extrusion approach the polymer is exposed to air after each extrusion pass. Chemical changes in the polymer caused by oxidation can be followed using FTIR by monitoring the development of carbonyl peaks around 1740 cm^{-1}. Figure 7 shows the development of small peaks with successive extrusions although these peaks are much less prominent than those that develop during oven ageing or UV-weathering. This has also been reported by other authors[5,17,18] studying multiple extruded polypropylene and is a consequence of the lower concentration of oxygen available in the extruder during processing: only oxygen dissolved in the polymer matrix is present in the extruder during processing.

Figure 7: *FTIR absorbance spectra of a series of multiple extruded stabilized polypropylenes.*



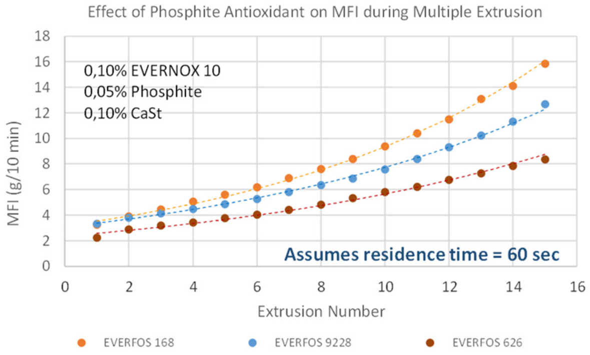
Despite the low concentration of oxygen during traditional multiple extrusion it is possible that even less oxygen is present during re-circulating multiple extrusion resulting in less oxidation. However, Figure 8 shows a similar development of the carbonyl group on re-circulated micro-compounded samples which suggests that the diffusion rate of oxygen into the multiple extruded samples between extrusion passes is too slow to significantly increase the total amount of oxygen dissolved in the polymer compared to the re-circulation approach.

Figure 8: *FTIR transmittance spectra of a series of multiple extruded stabilized polypropylenes.*



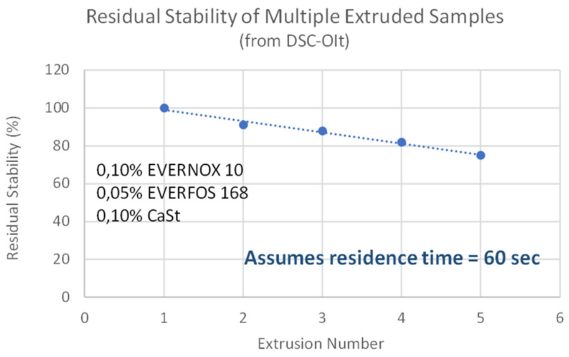
Although oxygen is only present at very low concentrations during processing it is also present in the form of hydroperoxides formed during the oxidation of the polymer exposed to air at ambient temperatures. These hydroperoxides are relatively stable at low temperatures but decompose at elevated temperatures and are responsible for the auto-accelerating polymer degradation. To disrupt the oxidation cycle hydroperoxide decomposers are added as processing stabilizers to reduce the hydroperoxides to alcohols via non-radical reaction paths. Antioxidants based on trivalent phosphites are one of the most widely used hydroperoxide decomposers in polyolefins. Figure 9 shows the stabilizing performance of three different phosphites can be ranked using re-circulating micro-compounding.

Figure 9: *The increase of MFI (approximated from force measurements) for polypropylene stabilized with different phosphite antioxidants as determined using a micro-compounder in batch re-circulating mode*



Besides monitoring changes in the force required to maintain the screw speed (MFI) it would be useful to be able to monitor another property that changes with degradation. In previous work[7,19,20] we found a correlation between the residual stability of traditional-scale multiple extruded polypropylene and common physico-mechanical tests including impact strength. Residual stability is the amount of active stabilizer remaining and it can be determined by extraction followed by chromatography[2] or by measuring the oxidative induction time[7,19,20] (OIt). Figure 10 shows that we can observe the same decrease in residual stability in samples with different residence times in the re-circulating micro-compounder.

Figure 10: *The Residual Stability of multiple extruded polypropylene.*



Conclusions

An alternative approach for evaluating the effectiveness of processing stabilizers has been developed and demonstrated to give comparable results to those obtained using traditional multiple extrusion. This approach is unique in that it uses a micro-compounder with re-circulation; the time the material is extruded is taken as a proxy for extrusion number and the change in force to maintain a constant screw speed as the melt viscosity changes (due to degradation – either chain scission or cross-linking) as an indication of changes in MFI.

Micro-extrusion has the advantage of reducing the size of sample required and the experimental time when compared to traditional methods using multiple extrusion. It is shown that this approach gives results which are reproducible and comparable to results obtained using traditional-scale multiple extrusion with melt flow index measurements monitoring degradation. This approach can rank processing stabilizer effectiveness between different antioxidants and stabilizers added at different loadings. It is also possible to replicate commercial-scale processing conditions in terms of the melt temperature and residence time.

Using force measurements and residual stability measurements this approach is suitable for high-throughput screening of stabilization systems under different processing conditions (screw speeds, melt temperatures and residence times) and allows the power of experimentally designed experiments to be applied to multi-stabilizer formulation studies.

Acknowledgements

Thank you to Dr. Nyambeni Luruli, Hosam Al Qarihi and John Mokwena for their technical assistance.

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