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## **Oxidative degradation of polyolefins in the presence of cupric and ferric stearate additives**

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Ferric stearate- and cupric stearate-containing masterbatches were successfully prepared by reactive extrusion compounding in a twin screw compounder. These prodegradant additives were formed by the reaction of the corresponding hydrated sulfate salts with calcium stearate in the polyethylene melt. High density polyethylene (HDPE) and polypropylene (PP) films containing these metal-based additives showed accelerated ageing in both QUV artificial UV ageing as well as oven ageing at 63 °C.

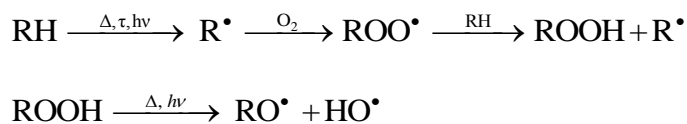
**Keywords:** polyethylene (PE); poly(propylene) (PP); degradation; ageing; compounding

### **INTRODUCTION**

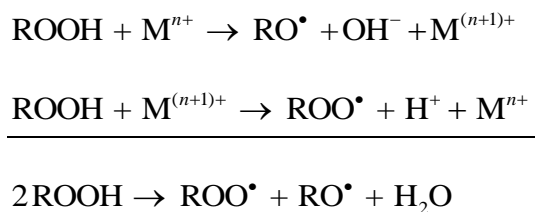
Conventional polymer articles such as plastic shopping bags are resistant to environmental degradation. They have a high surface-to-volume ratio and may also be brightly coloured. Littering of such bags presents a substantial “visual” pollution problem.<sup>[1]</sup> According to Guilet<sup>[2]</sup> the most effective way to deal with this litter problem is to reduce the “life time” of the littered objects. Photodegradation can aid rapid disintegration of polymers into a powdery residue with a much-reduced visual impact.<sup>[3, 4]</sup> Further abiotic degradation of such polyethylene can reduce molecular mass to levels where the material becomes susceptible to biodegradation.<sup>[5-8]</sup> However, this biodegradation process is extremely slow and yields micron-

sized particles (microplastics), that persistent in the environment and which may present a potential source of harm for organisms.<sup>[8]</sup>

The basic process of polymer oxidative degradation is shown in Scheme I. In essence, Scheme I states that a free radical may be generated on the polymer (RH) due to the effect of mechanical stress, heat or UV radiation.<sup>[9]</sup> Oxygen from air then reacts with this free radical to first form a peroxy radical that subsequently abstracts another (labile) hydrogen from the polymer chain to form a hydroperoxide. Under the influence of heat or UV the latter cleaves to form two additional free radicals. This chain reaction causes rapid proliferation of free radicals that ultimately results in polymer chain scission taking place that leads to a loss of mechanical and other desirable plastic properties.<sup>[10, 11]</sup>



**Scheme I.** Simplified reaction scheme for the auto-oxidation of polymers.<sup>[12, 13]</sup>



**Scheme II.** The cycle of redox reactions whereby transition metal ions catalyse the decomposition of hydroperoxides to produce alkoxy and peroxy radicals.<sup>[9, 14]</sup>

Prodegradant additives are used to enhance the oxo-biodegradation of polyolefins.<sup>[4, 11]</sup> Transition metal carboxylates are particularly suitable for this purpose.<sup>[12, 15]</sup> It is believed that they function as catalytic hydroperoxide decomposition agents via the cycle of redox reactions shown in Scheme II.<sup>[14]</sup>

The progression of polymer degradation owing to exposure to UV light can be followed various chemical, physical and mechanical methods.<sup>[14, 16]</sup> However, FTIR is widely used to follow the time evolution of changes in the functional groups present.<sup>[14, 15, 17]</sup> Accelerated testing is

essential for testing new additives as it shortens the product design-development-production cycle. The apparent degree of degradation of polyethylene's can be characterized using a Carbonyl Index (CI) defined in terms of the relative absorbance associated with the carbonyl band near  $1720\text{ cm}^{-1}$  to that of a reference band.<sup>[18]</sup> A suitable choice for the latter is the band at  $720\text{ cm}^{-1}$  due to  $-\text{CH}_2-$  in-phase rocking vibrations of straight chain methylene sequences containing seven or more carbons that are present in polyethylene,.

Synthesis of ferric stearate and copper stearate requires aqueous reaction conditions and generates undesirable effluent. The first objective of this study was to determine whether these compounds can be obtained directly in masterbatch form via reactive extrusion compounding starting with calcium stearate as it is inexpensive and easy to produce. The second objective was to establish whether such masterbatches are effective at accelerating the photodegradation of selected polyolefins.

## **EXPERIMENTAL**

**Materials.** Low density polyethylene (LDPE) powder (grade LT019 with density  $0.919\text{ g/cm}^3$  and Melt Flow Rate  $20\text{ g/10 min @ }190^\circ/2.16\text{ kg}$ ) was obtained from Sasol. It was used for preparing the masterbatches. Stabiliser-free powders of film-grade high-density polyethylene (HDPE) (density  $0.953\text{ g/cm}^3$  and Melt Flow Rate  $0.3\text{ g/10 min @ }190^\circ/5.00\text{ kg}$ ) and extrusion grade polypropylene homopolymer (PP) (density  $0.90\text{ g/cm}^3$  and Melt Flow Rate  $2.0\text{ g/10 min @ }230^\circ/2.16\text{ kg}$ ) were supplied by Safripol. Iron(III) sulfate pentahydrate (97 %) and copper(II) sulfate pentahydrate (98 %) were obtained from SigmaAldrich (now Merck). Technical grade calcium stearate was supplied by Sun Ace.

**Masterbatching.** Prodegradant masterbatches, containing nominally 10 wt-% of either copper- or iron stearate, were prepared as follows. The metal sulfate, calcium stearate and LDPE powders were mixed in a Pyramid high-speed blender. The powder mixes were compounded on a CFAM TX28P twin screw laboratory extruder with a diameter of 28 mm and an L/D ratio of 18. The screw design of this compounder comprised a short feeding section followed by intermeshing kneader blocks with a forward-feeding action. The temperature profile, from

hopper to die, was 140°C/160°C/170°C/180°C. The extruded strands were water-cooled, air-dried, and granulated into pellets on a Chen Shin Machinery Model CT-300 pelletizer.

**Film blowing.** The polyolefin films (thickness ca. 60 µm) were blown using a Collin Model D-85560 film blower. The screw speed of the single screw extruder was 50 rpm. The temperature profiles, from hopper to die, were set at 160/180/180/190/190/190/190/180 °C and 190/210/210/220/220/220/220/195 °C for the HDPE and PP films respectively. The masterbatches were added at mass-based let-down levels of 0, 1, 2 and 5 %. This corresponded to nominal final metal stearate levels in the films of 0, 0.1, 0.2 and 0.5 wt-% respectively. The thickness of blown film samples were measured with Mitutay Digimatic Indicator.

**Accelerated ageing.** Films were mounted on thick cardboard frames. Oven ageing was conducted in a Scientific Series Model 279 convection oven set at 63 °C. Dry cycle artificial weathering was done at the same temperature in a Q-Panel QUV tester fitted with A340 UV lamps set at an irradiance of 0.67 W·m<sup>-2</sup>. The run times between measurements were 50 h or less. The progression of the degradation was tracked by FTIR spectroscopy conducted on a PerkinElmer FTIR Spectrum 100 spectrometer. The resolution was 4 cm<sup>-1</sup> and the recorded spectra represented averages of 16 scans. A Carbonyl Index was used to quantify the extent of photo-oxidative or thermal degradation of the polyolefin films. The 720 cm<sup>-1</sup> band, associated with the in-phase rocking vibrations of straight chain methylene groups (–CH<sub>2</sub>–) with seven or more carbons was selected as reference for HDPE. The symmetric (in-phase or “umbrella”) methyl C-H bending at 1375 was selected as reference band for the PP films. In this study the carbonyl indices (*CI*) for the HDPE and PP films were calculated as the ratio of the areas under the peaks of the carbonyl band to the reference absorbance bands as follows:

$$CI_{HDPE} = \int_{1650}^{1850} A(\sigma) d\sigma / \int_{700}^{750} A(\sigma) d\sigma \quad (1)$$

$$CI_{PP} = \int_{1600}^{1850} A(\sigma) d\sigma / \int_{1340}^{1400} A(\sigma) d\sigma \quad (2)$$

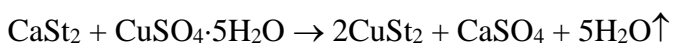
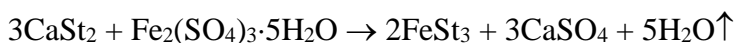
where  $A(\sigma)$  is the absorbance and  $\sigma$  is the wavenumber in cm<sup>-1</sup>. Equation (1) defines the carbonyl index for HDPE whilst Equation (2) defines the carbonyl index used for PP films.

The oxidation induction temperature (OIT) of aged polyolefin film samples was determined with a PerkinElmer Differential Scanning Calorimeter, Model DCS-400. Film samples of ca. 6 mg were placed in open aluminium pans. The temperature was scanned at 10 °C·min<sup>-1</sup> and the air flow was set at 50 mL·min<sup>-1</sup>.

X-ray diffraction was conducted on a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence and receiving slits with Fe filtered Co-K $\alpha$  radiation ( $\lambda=0.17901$  nm) in the 2 $\theta$  range from 2° to 60° at a scan rate of 1.0° min<sup>-1</sup>.

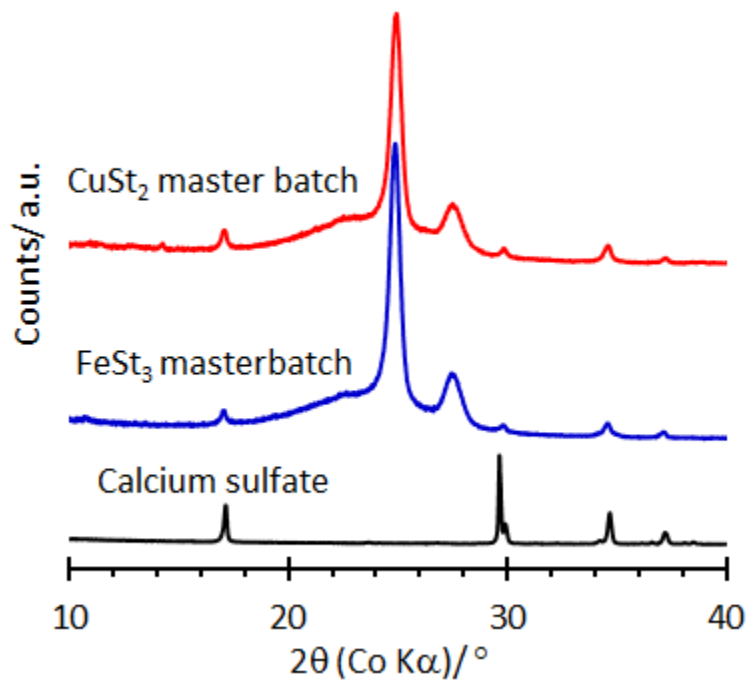
## RESULTS

Figure 1 compares XRD diffractograms obtained for the two masterbatches with that for calcium sulfate. Reflections characteristic of the latter compound are present in the masterbatch compounds. This confirms that the reactions shown in Scheme III occurred and that copper stearate and ferric stearate must have formed in the reactive compounding of the two masterbatches.

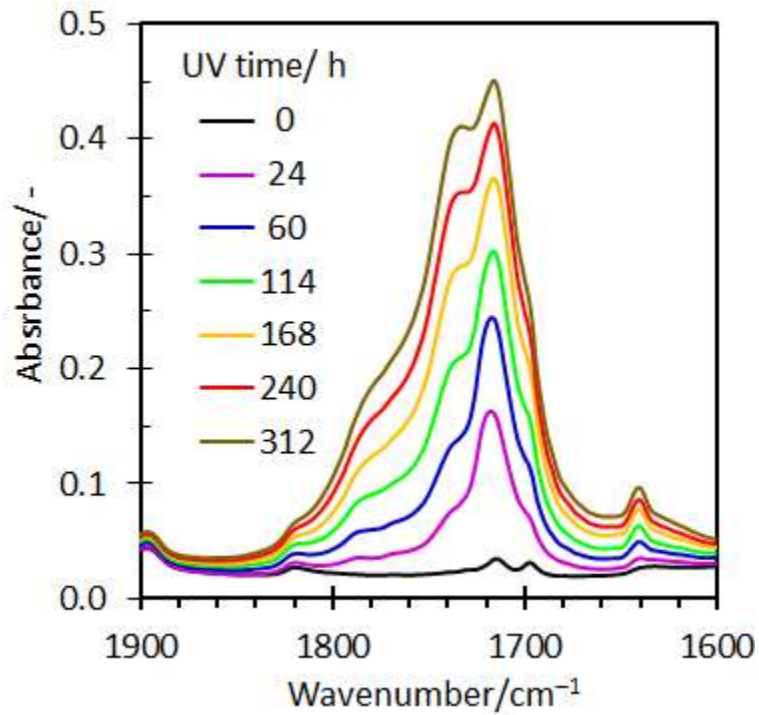


**Scheme III.** Reaction of calcium stearate with hydrated metal sulfates.

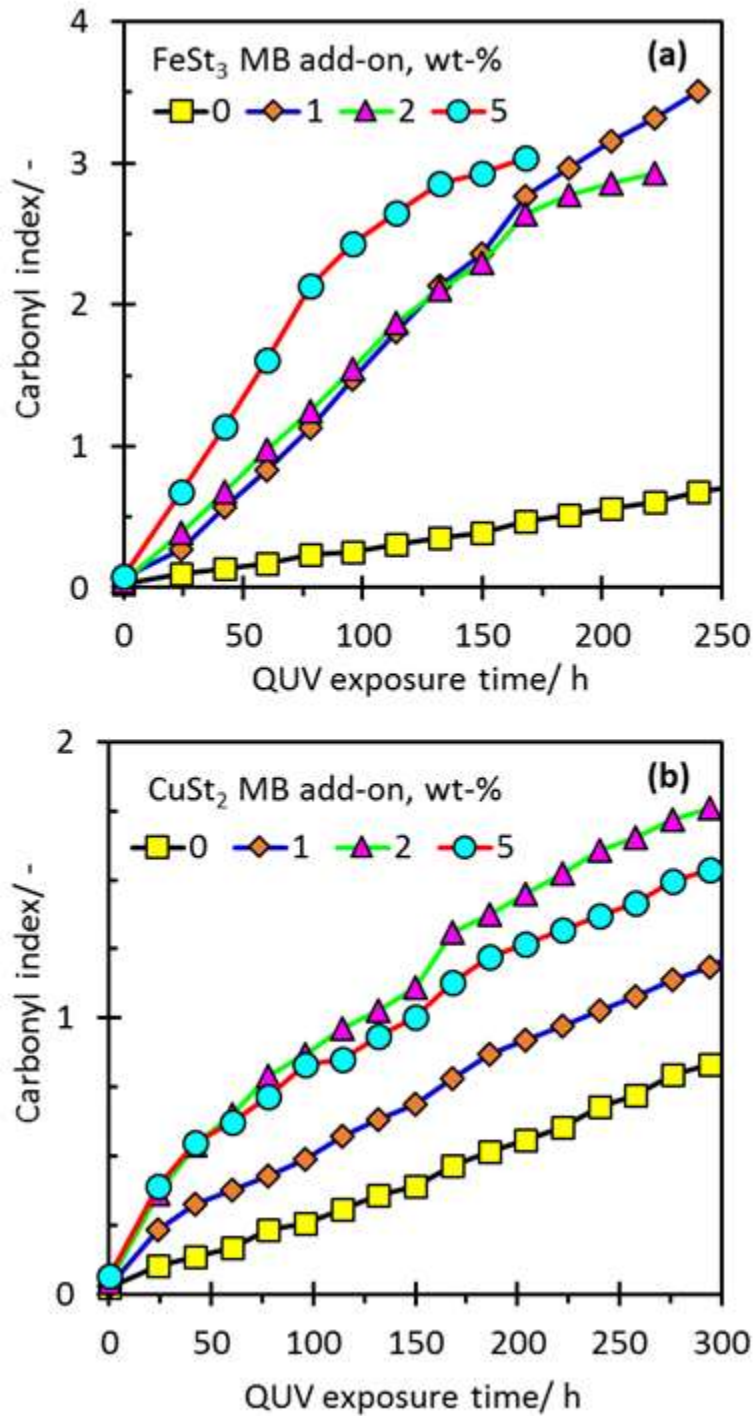
Figure 2 shows representative FTIR spectra for the HDPE film with 5 wt-% ferric stearate masterbatch added. It illustrates the time evolution of the carbonyl absorption band with QUV weathering. In contrast, the absorbance of the reference peak located at 720 cm<sup>-1</sup> remained relatively constant thereby justifying its use as a reference peak to calculate a carbonyl index. Similar observations held for the growth of the carbonyl band in PP films and its corresponding reference band.



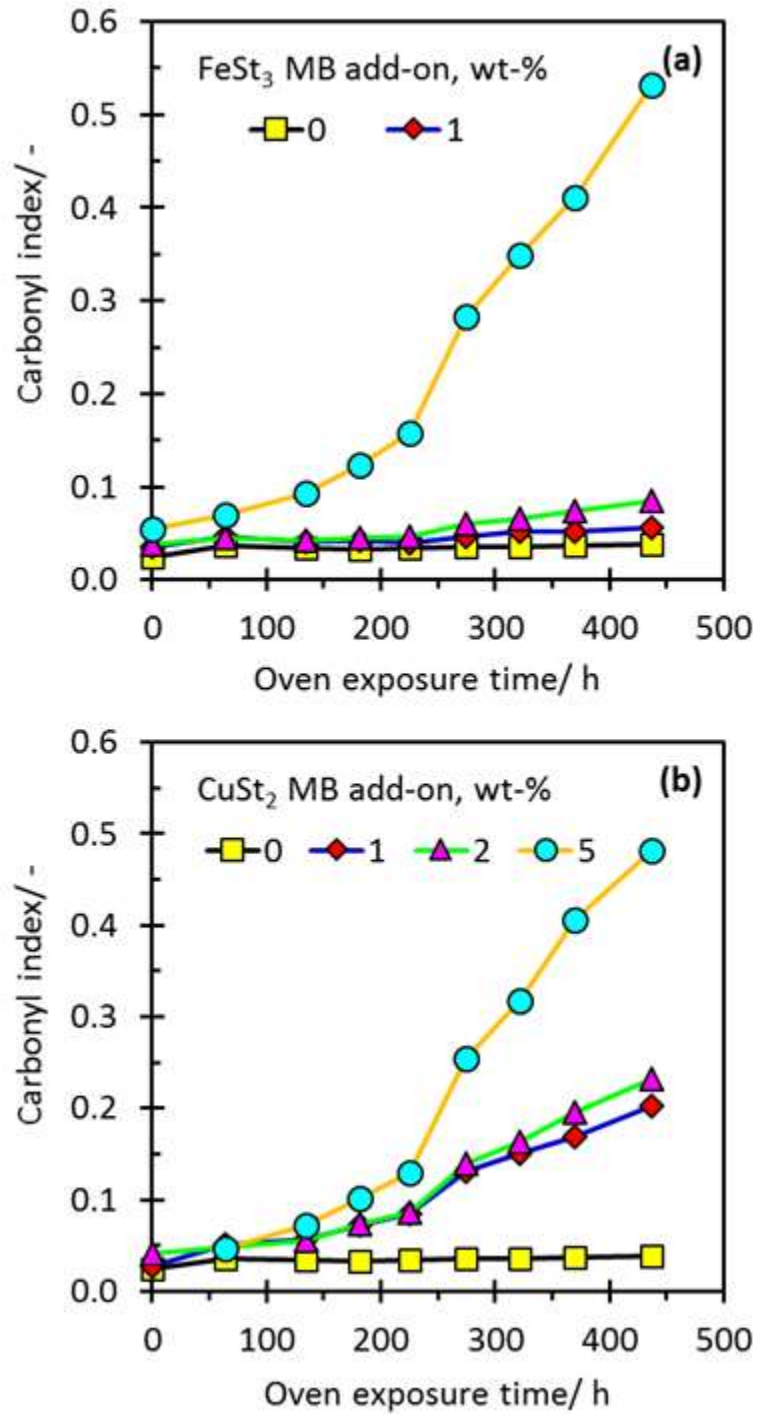
**Figure 1.** XRD diffraction pattern for the two masterbatches compared to that for calcium sulfate



**Figure 2.** Time evolution of the FTIR spectra for the HDPE with 5 wt-% ferric stearate masterbatch addition



**Figure 3.** Effect of QUV exposure time and masterbatch loading level of (a) ferric stearate, and (b) cupric stearate, on the photo-oxidative degradation of HDPE



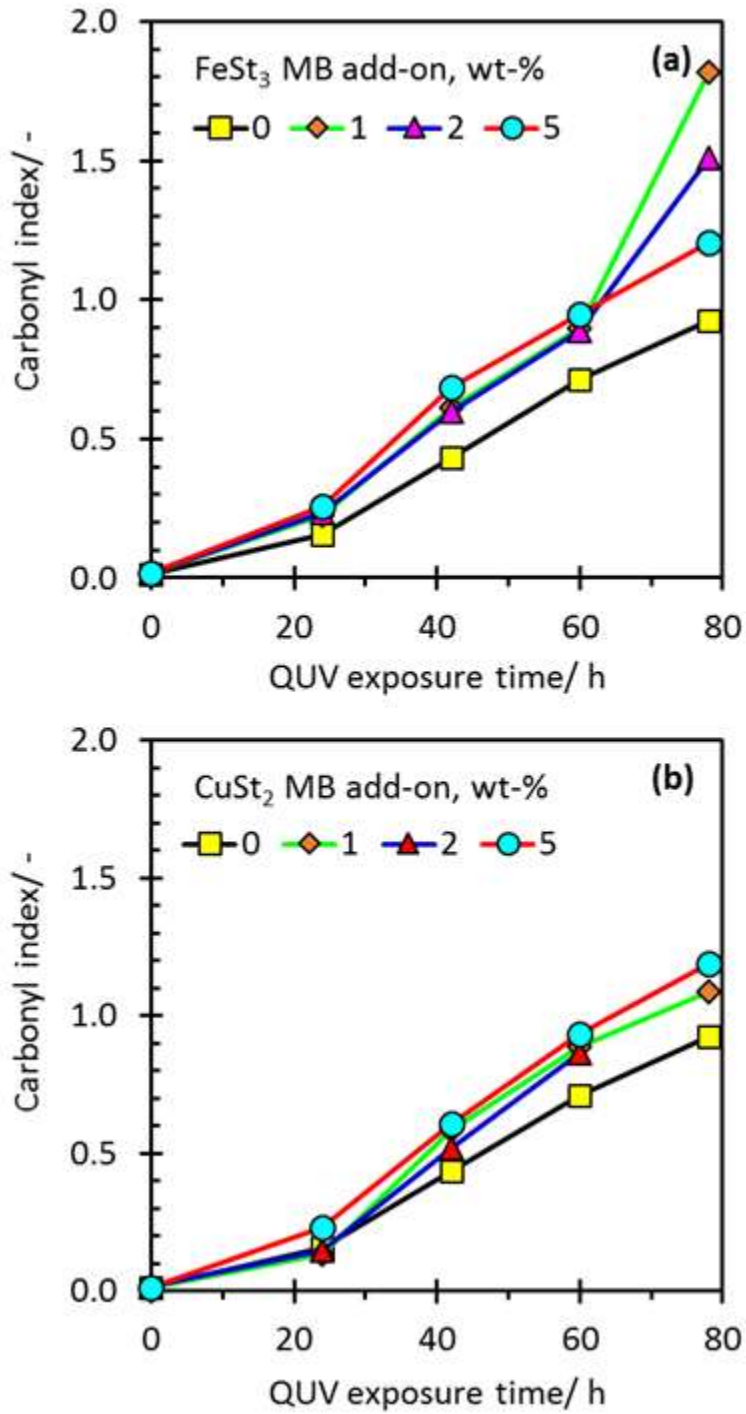
**Figure 4.** Effect of exposure time and masterbatch loading level of (a) ferric stearate, and (b) cupric stearate, on the thermo-oxidative degradation of HDPE films aged at 63 °C in a convection oven



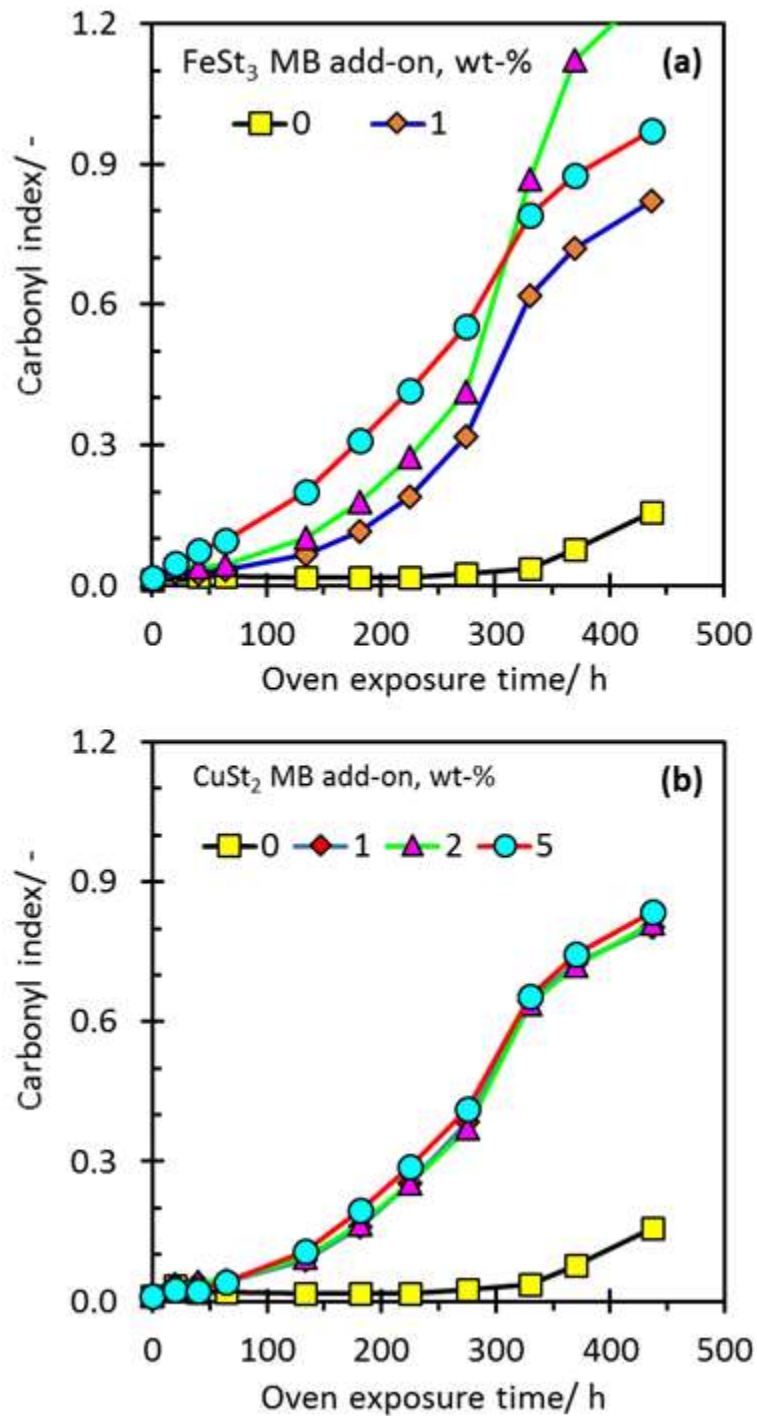
Figures 3 to 6 report the effect that the two metallic stearate additives have on accelerating the QUV artificial weathering and oven ageing of HDPE and PP films. The Carbonyl Index, measured for the neat unstabilised HDPE and PP films, increased approximately linearly with exposure time in QUV weathering. The CI increased more rapidly when the prodegradant masterbatches were added. In HDPE films, ferric stearate facilitated faster degradation than cupric stearate. Increasing the masterbatch loading generally increased the rate at which CI increased. However, Figure 3 shows that 5 wt-% add on of cupric stearate to HDPE caused a slower rate of CI increase than was observed for a 3 wt-% add on. This is attributed to competing UV light absorption of the bluish cupric stearate.

Figure 4 shows the CI growth for HDPE films that were oven aged at the same temperature as was used in the QUV accelerated weathering. This means that the differences between the results presented in Figure 3 and Figure 4 can be attributed to the additional effect of UV light exposure. Figure 4 shows that ferric stearate, at add on levels up to 2 wt-%, had a negligible effect on the CI of HDPE films. However, at the 5 wt-% add on level, a significant increase is observed over the measurement time. However, the CI values found, when the films were exposed to UV light were much higher than found for ageing in the absence thereof. In the case of cupric stearate, even low levels of masterbatch significantly increased the CI at all dosage levels. The results obtained for 5 wt-% cupric stearate masterbatch were similar to those found for ferric stearate at the same dosage level.

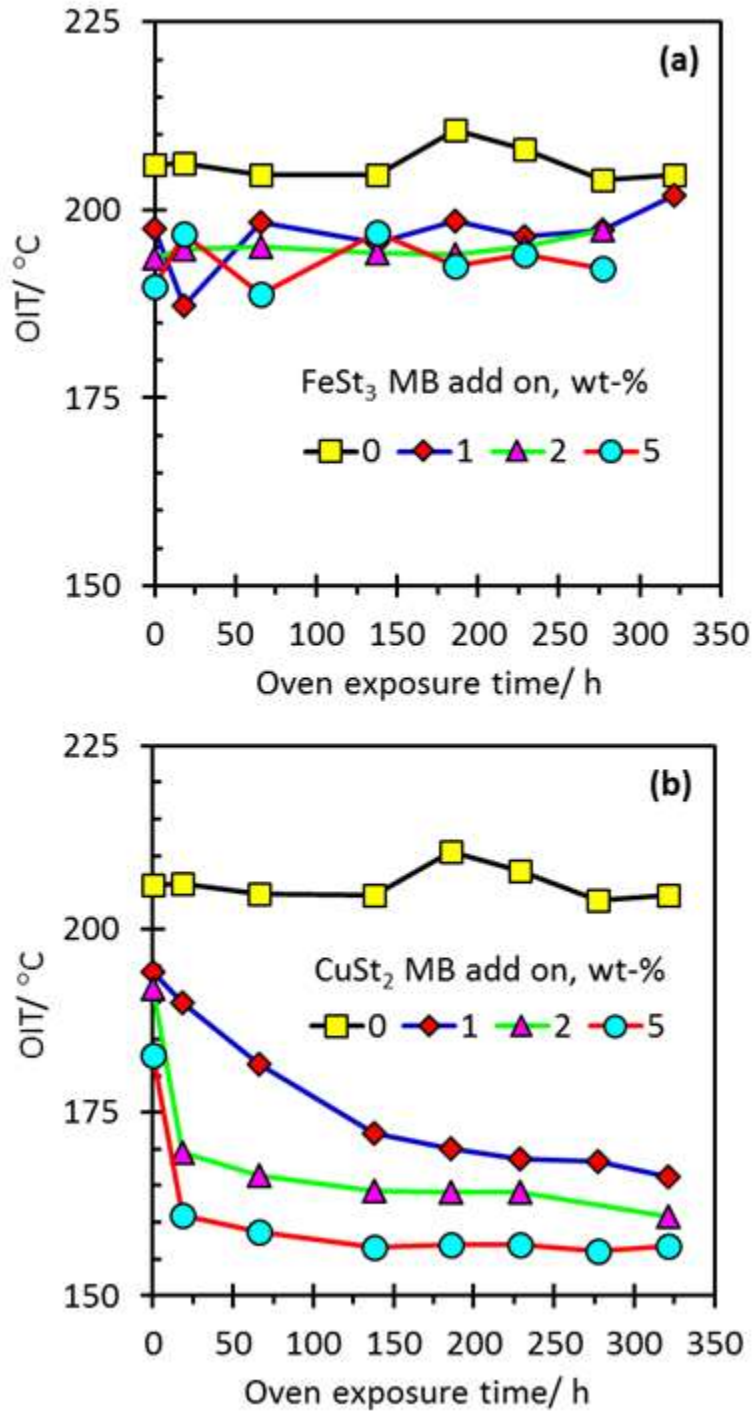
Figure 5 and Figure 6 show that for the PP films, both masterbatches increased the CI indicating that degradation occurred in both QUV weathering and oven ageing tests. In both instances ferric stearate was more effective as prodegradant additive than cupric stearate. Degradation was much faster for PP films compared to HDPE films. In the former case complete film embrittlement was observed after only 100 h of QUV weathering while the HDPE films stayed intact for up to 450 h. Ferric stearate was also more effective as an oxidative prodegradant for PP as the oven aged films showed rapid CI increases. Surprisingly, varying the concentration of the cupric stearate masterbatch did not appear to affect the CI growth as the results shown in Figure 6 for all three levels were very similar.



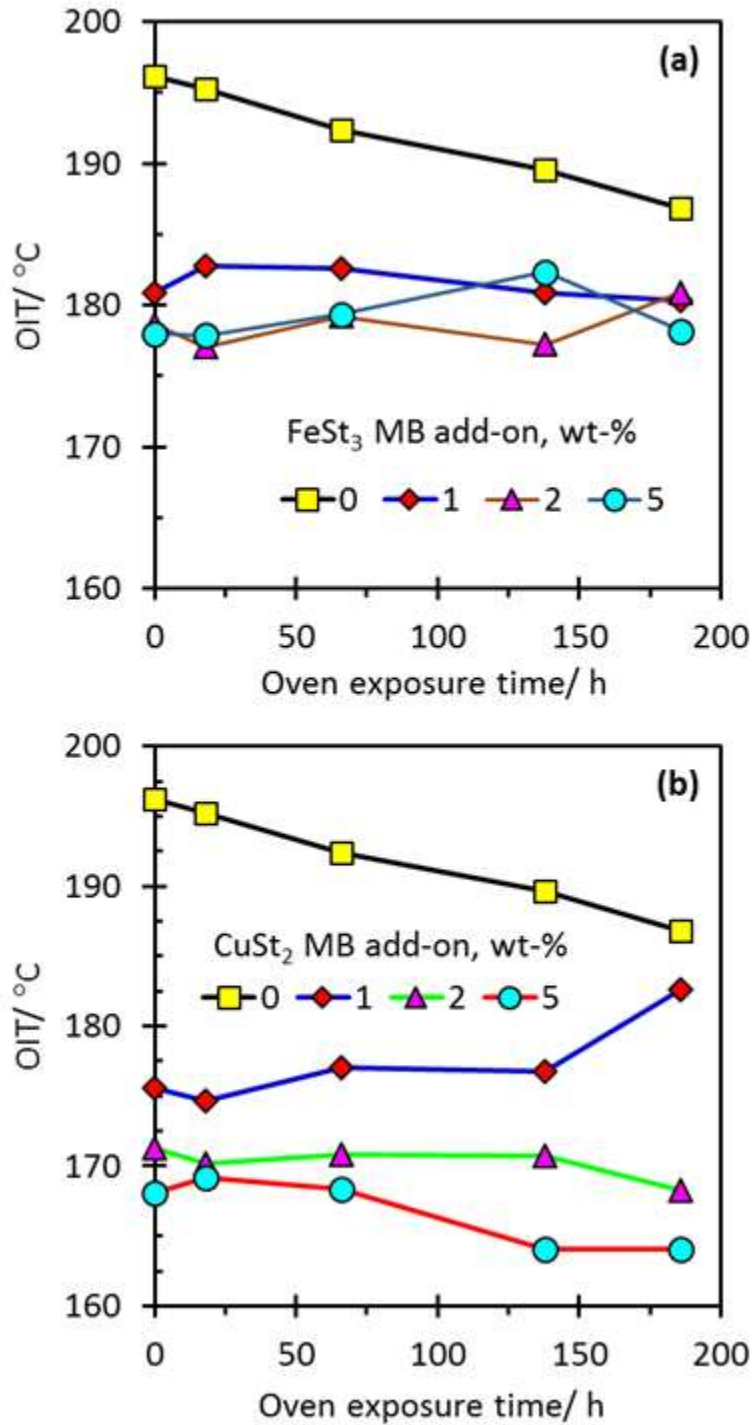
**Figure 5.** Effect of QUV exposure time and masterbatch loading level of (a) ferric stearate, and (b) cupric stearate, on the photo-oxidative degradation of PP



**Figure 6.** Effect of exposure time and masterbatch loading level of (a) ferric stearate, and (b) cupric stearate, on the thermo-oxidative degradation of PP aged at 63 °C in a convection oven



**Figure 7.** Effect of exposure time on the OIT of HDPE films containing ferric stearate or cupric stearate as prodegradant additives aged at 63 °C in a convection oven



**Figure 8.** Effect of exposure time on the OIT of PP films containing (a) ferric stearate or (b) cupric stearate as prodegradant additives aged at 63 °C in a convection oven

The oxidative stability of oven aged films was also characterised by OIT measurements. A decrease in OIT is an indication of an increase in the extent of thermal degradation of a polyolefin film.<sup>[19]</sup> The results are shown in Figure 7 for HDPE and in Figure 8 for PP. The OIT for HDPE was, for all practical purposes, not affected by the oven ageing. Considering all the measurements conducted over a total time of 325 h yields an average value of  $205.1 \pm 1.7$  °C. Adding the ferric stearate masterbatch to the HDPE reduced OIT to  $197 \pm 4$  °C  $294.9 \pm 1.2$  °C  $193 \pm 3$  °C for add on levels of 1, 2 and 5 wt-% respectively. Adding cupric stearate also dropped the OIT to lower levels. However, unlike the case for ferric stearate, the OIT values initially showed decreasing trends with oven ageing time before settling on plateau values of  $168.3 \pm 1.6$  °C  $163.4 \pm 1.7$  °C  $156.6 \pm 0.4$  °C for add on levels of 1, 2 and 5 wt-% respectively.

The OIT of the neat PP film was ca. 196 °C. It showed a linear decrease with oven ageing time reaching a value about 10 °C lower after 186 h. Values measured with ferric stearate masterbatch added showed scatter such that no trend with oven ageing nor additive level could be discerned. Taking all the values together yielded an OIT of  $180 \pm 2$  °C. Values obtained for cupric stearate addition generally showed OIT values that decreased with masterbatch addition level as well as exposure time.

The results obtained for accelerated QUV weathering and oven ageing tests confirms conclusions made by previous studies that ferric stearate can be used as a pro-degradant for PP films.<sup>[20]</sup> In addition, it should be mentioned that the degradation of plastic films in real-life applications will be more complicated. In particular they will experience cyclic deformations (fatigue) and this will involve competition (dependent on deformation frequency, amplitude, and the number of cycles) between the formation of fatigue damages (microcracks, etc.) which promote degradation and orientation of structure which reduces the degradation process.<sup>[21]</sup>

## CONCLUSIONS

UV prodegradant masterbatches containing either cupric or ferric stearate can be prepared by reactive extrusion compounding in a twin screw compounder. The active compounds form inside the polyethylene carrier polymer by the reaction of the corresponding hydrated sulfate

salts with calcium stearate. X-ray diffraction confirmed the formation of crystalline calcium sulfate as a filler component.

Blown high density polyethylene (HDPE) and polypropylene (PP) films containing these metal-based additives degraded rapidly when subjected to artificial weathering in a QUV machine fitted with A340 lamps at a test temperature was 63 °C and an irradiance was set at 0.67 W·m<sup>-2</sup>. The degree of oxidative degradation, estimated from FTIR spectra recorded after selected irradiation times, was quantified using a Carbonyl Index defined by the ratio of the areas below the carbonyl band located at 1720 cm<sup>-1</sup> to the reference bands located at 720 cm<sup>-1</sup> and 1320 cm<sup>-1</sup> for HDPE and PP films respectively. In addition, oxidative stability was determined via oven ageing tests conducted at 63°C. The thermal degradation in the oven ageing tests was also followed with FTIR spectroscopy. The oxidation onset temperatures were determined by differential scanning calorimetry (DSC) in an air atmosphere at a temperature scan rate of 10 °C·min<sup>-1</sup>.

Low level additions (5 wt-% or less) of either cupric stearate or ferric stearate significantly reduced the UV stability of both the polyethylene and the polypropylene film samples. However, at the 5 wt-% addition level copper stearate provided a stabilising effect on the HDPE films. This could be due to the increased absorption of the incident UV radiation. Both additives also accelerated the oxidative degradation of the PP in oven ageing tests but the ferric stearate showed little effect on HDPE at let-down levels of up to 2 wt-%.

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