STUDIES OF DEGRADATION EFFECTS DURING ROTATIONAL MOLDING

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Abstract

This paper describes a program to assess degradation effects on polyethylene, the most common polymer used in rotomoulding. Polyethylene was compounded with a variety of antioxidant (AO) combinations, pulverized to a powder and then rotationally moulded. The impact strength of samples cut from the rotomoulded parts was correlated with assessments of material condition made using Carbonyl Index (CI) and Yellowness Index (YI). Significant differences were observed between different AO formulations.

Introduction

Rotational molding (rotomolding) is a method for manufacturing large hollow plastic objects, which offers a number of advantages compared to other manufacturing processes, such as injection molding and blow molding. Advantages include much lower tooling costs, ease of manufacture of large objects, the achievement of even wall thickness and the absence of weld lines and molded-in stress.

One important feature of rotomolding is its dependence on various types of polyethylene (PE) as its main material of use. It has been estimated that over 97% of all rotomolded parts made today use some form of PE in their manufacture. The reason for the dominance of PE over other potential rotomolding materials is due to the favourable rheology of PE at the zero shear conditions prevalent in rotomolding.

Internal air temperature and especially its peak value (PIAT) have been reported to be a reliable process control parameter for ensuring that the optimum morphology and mechanical properties of a molded PE part have been achieved. A low (PIAT) demonstrates an under-cooked part, where the wall thickness is populated by excessive numbers of microscopic voids, caused by the formation of gas bubbles from air trapped in the intersticies between powder particles during the initial lay-up phase. Given sufficient temperature and time, the gases inside these bubbles will diffuse into the surrounding polymer. On the other hand, excessively high values of (PIAT) would indicate over-cooking and the onset of thermo-oxidative degradation of the polymer, resulting in poor properties [1].

The process of heating takes a long time, compared to other processes, and an industrial rotational molding PE grade must be designed to withstand relatively long heating times (typically in excess of 20 minutes). Commercial rotomolding grades are sufficiently well stabilized to avoid degradation and its subsequent negative effect on the properties of the material and molded part.

In the current study, the effect of progressively increasing rotomolding cook times on the properties of the molded material was evaluated. Four antioxidants (AOs) were used in this study: three different primary phenolic AOs, a secondary phosphite AO and combinations of the two types. The consequences of prolonged cooking times were investigated in terms of properties of the molded parts.

Experimental

Materials: A "barefoot" linear medium density polyethylene (LMDPE), with no stabilizers added, was obtained as a reactor powder, with a typical rotomolding specification.
Three different primary (phenolic) AO's were used, from two different manufacturers. One secondary (phosphite) AO was used.

***Compounding*:** The chosen additives were first dry blended into the reactor powder using a planetary mixer. Subsequently, the resin / additive mix was passed through a single screw extruder; two passes were made to ensure adequate mixing of all the components. The resin that was to be left as a barefoot was also passed twice through the extruder, to ensure that it would undergo the same thermal conditioning as the samples with additives.

***Pulverizing*:** The compounded granules were ground to a suitable rotomolding powder using a single headed 12 inch pulverizer.

***Additive Combinations*:** The primary phenolic antioxidants (AO1, AO2 & AO3) were added at 500 ppm and the secondary phosphite antioxidant (AO4) was added

at 1000 ppm. These addition levels are typical for standard rotomolding grades.

Table 1. Formulations and plot symbols

Sample Marker	♦	▲	■	Ж	◇	Δ	□
Primary AO1	500	0	0	0	500	0	0
Primary AO2	0	500	0	0	0	500	0
Primary AO3	0	0	500	0	0	0	500
Secondary AO4	0	0	0	1000	1000	1000	1000

Rotational Molding: Powder samples were molded at a range of cook times from 9 to 20 minutes on a commercial biaxial rotational molding machine, with an oven temperature of 250°C. Sheet steel test molds were used to produce hexagonal cylinders, from which suitable test plaques (125mm x 125mm) could be cut.

Impact Testing: The sample plaques were conditioned in an industrial freezer at -40°C for a minimum of 24 hours before being subjected to a drop dart impact test. The Association of Rotational Molders (ARM) International standard was adopted for this low temperature impact test. The results of this testing were analysed to produce a weighted average impact energy to break, using the calculation method in the ARM standard.

Yellowness Index (YI) Testing: Two plaques from each molding were reserved for YI testing. Sample plaques were placed air-side (i.e. the molding surface that was opposite that in contact with the mold) forwards into the aperture of a Datacolor™ 400 spectrophotometer, a white tile was placed behind the plaque and a measurement was then made in reflectance mode.

Infrared Spectroscopy: The extent of oxidation of the first few microns of the air-side moulding surface was assessed using a Thermo-Nicolet Continuum FTIR Microscope fitted with a single bounce silicon ATR objective. The absorbance of the carbonyl stretching vibrations centred at 1710 cm^{-1} was measured using two-point baselines. These values were then used to calculate a carbonyl index (CI) for the air-side surface of each sample. The spectra were made up of 64 co-added scans and resolution was set to 2 cm^{-1}. An average value of CI was calculated using at least three replicates.

Results and Discussion

Impact Testing

Figures 1 to 4 show the impact results for the various additive combinations.

Figure 1 illustrates the effect of the three primary AOs on their own (AO1, AO2 & AO3), compared to the effect of no AO and the secondary AO on its own (AO4). In all cases, there is an initial rise in the impact strength from a cook time of 8 minutes. At cook times shorter than 8 minutes, there is incomplete fusion of material and loose powder is still present in the mould at the end of the cycle.

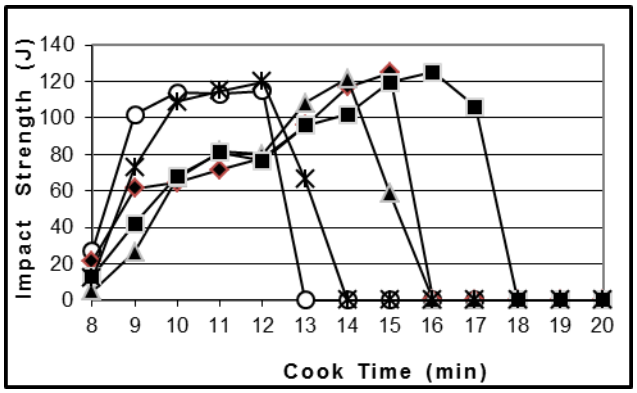

Figure 1: Impact test results for samples containing: ♦Primary AO1 only, ▲Primary AO2 only, ■Primary AO3 only, ЖSecondary AO4 only, and ○No AO.

The samples containing no AO and the samples containing secondary AO (AO4) only both show a faster rise in impact strength than the samples containing secondary AOs. In commonly accepted rotomolding parlance, these materials "cook out" quicker. However, they also lose impact strength quite quickly; overcooking (beyond 12 min in both cases) results in a sudden and catastrophic loss of impact strength. Thus the processing, or molding, window for samples with no AO / AO4 only is confined to approx. 3 min.

The samples containing primary AOs (AO1, AO2 & AO3) exhibit a more gradual rise in impact strength, although by 11 min they have all developed a useful level of impact strength (approx. 80J). They continue to exhibit impact strength as cook time in increased, with catastrophic loss only occurring after 17 min. Thus, in these cases, the molding window has been increased to 6 min, double that of the samples without primary AO.

The reason for the relatively fast rise of impact strength of the samples without primary AO is most likely due to differences in the fusing and sintering behaviour under different additive regimes. An important process

within the fusing and sintering step is the diffusion of gases (mostly nitrogen and oxygen from atmospheric air) trapped in the intersticies between powder particles, as the polymer melts out.

Dodge and Perry[2] demonstrated that, as cook time was increased in rotomolding, the density of a rotationally molded part increased, due to the decrease in the incidence of bubbles due to trapped gases. The decreased incidence of gas bubbles was correlated with the initial rise in impact strength, as sintering and consolidation of the polymer became complete.

The samples containing primary AOs show a slower initial rise in impact, but the impact strength is sustained at longer cook times. The effectiveness of primary AO in absorbing the radical species (peroxides) responsible for the degradation of the polymer is demonstrated by this effect. Subtle alterations in the molecular structure and polymer crystallisation behaviour under different additive regimes may also account for this effect in some measure.

For the samples containing primary AO, there is an initial increase in impact strength (to approx. 80J), followed by a second rise (to approx. 120J). This phenomenon has been observed and commented on in previous work by Sharifi, Henwood *et al*[3]. Using rheological studies, they demonstrated a link between this second increase of impact strength and the onset of crosslinking of the polymer chains as a result of radical generation in the degrading polyethylene. After extended cook times, catastrophic failure of the polymer is caused by scission of the polyethylene chains, as they finally degrade.

Figures 2, 3 and 4 compare the increase in impact strength for samples containing primary AO only and for samples containing primary AO combined with secondary AO. It can be seen that the samples containing the AO combination show similar, or slightly reduced, impact strength. This lower impact strength should not necessarily be associated with increased degradation but rather with changes in the onset of the previously mentioned crosslinking reactions associated by the generation of radicals prior to the onset of chain scission. These differences in behaviour seem to be more evident in the case of AO1 than with AO2 and AO3.

These trends are in agreement with the work carried out by Li *et al* and Cramez *et al* [4,5]. Li *et al* reported that the impact strength of a piece of rotationally molded truck fender was related to the processing conditions. Increased heating times and temperatures were observed to be beneficial up to a point. Cramez *et al* reported that the optimum properties of a rotational molded product are achieved when the plastic is heated to a point just below which the degradation occurs. They used a kinetic simulation study of the AO consumption to predict the point of the onset of the degradation.

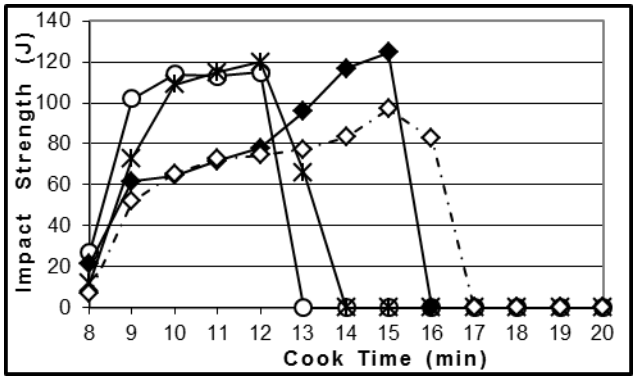

Figure 2: Impact test results for samples containing: ♦primary AO1 only, ◇primary AO1 plus secondary AO4, Ж secondary AO4 only, and ○no AO.

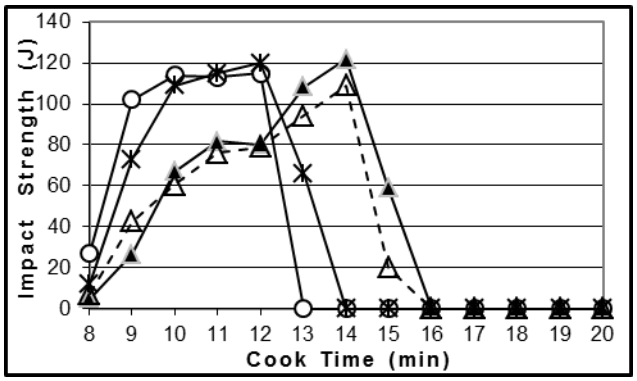

Figure 3: Impact test results for samples containing: ▲primary AO2 only, Δprimary AO2 plus secondary AO4, Ж secondary AO4 only, ○no AO.

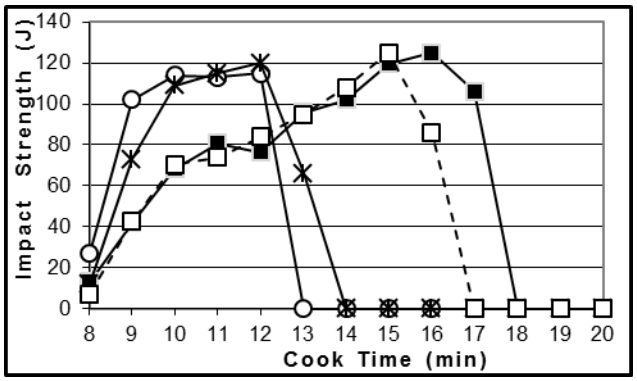

Figure 4: Impact test results for samples containing: ■primary AO3 only, □primary AO3 plus secondary AO4, Жsecondary AO4 only, and ○no AO.

Yellowness Index Testing

Figures 5 to 8 show the YI results for the various additive combinations.

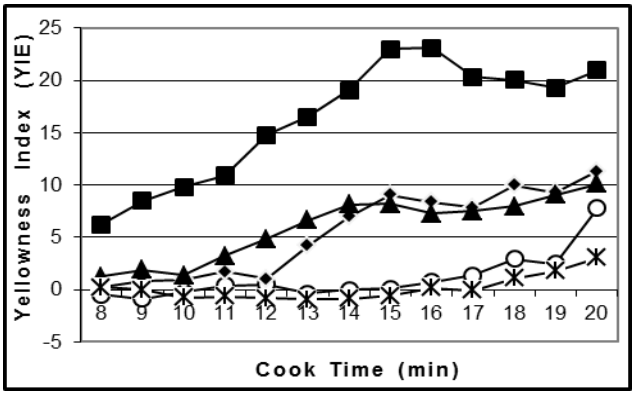

Figure 5: Yellowness Index (YI) versus time data for samples containing: ♦primary AO1 only, ▲primary AO2 only, ■primary AO3 only, Жsecondary AO4 only, and ○no AO.

From Figure 5 it can be seen that there is a gradual rise in YI of the samples as cook time is increased. This is related to the transformation of the phenolic anti-oxidants, to highly chromophoric compounds known as quinones which give rise to the yellowing effect[6,7]. It can also be seen that the YI of the phosphite-containing compound is significantly lower than the samples containing the phenolic AO's and is actually very close to the sample containing no AO. AO3 has the highest YI by a considerable margin in comparison to the AO1 and AO2, which show similar trends but to a lesser extent.

The main group of transformation products responsible for discolouration of the polymer matrix are formed in primary steps of the sacrificial oxidation of phenolic antioxidants: peroxycyclohexadienones (XOO-CHD) and quinone methides (QM). The QM tend to be more stable than the peroxycyclohexadienones, which are formed transiently. Epacher *et al* [8] have reported a color increase as the amount of oxygen during the process was increased. This was more noticeable with the stabilized samples showing strong discoloration.

From Figures 6 to 8, it can be seen the addition of the secondary phosphite AO4 to phenolic AO1, 2 & 3 led to reduced YI. The reduction is most pronounced when the phenolic AO3 is coupled with the phosphite AO4; the effect is also evident when AO4 is combined with AO1 and AO2, but to a lesser extent.

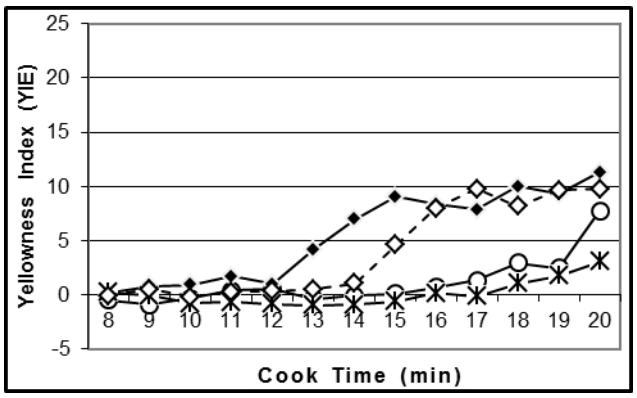

Figure 6: YI versus time data for samples containing: ♦primary AO1 only, ◇primary AO1 plus secondary AO4, Ж secondary AO4 only, ○no AO.

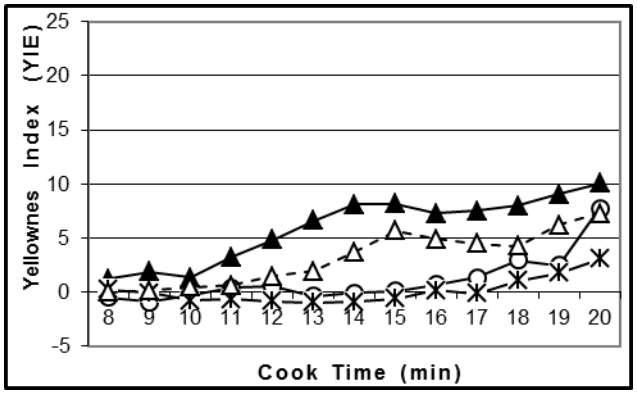

Figure 7: YI versus time data for samples containing: ▲primary AO2 only, Δprimary AO2 plus secondary AO4, Ж secondary AO4 only, and ○no AO.

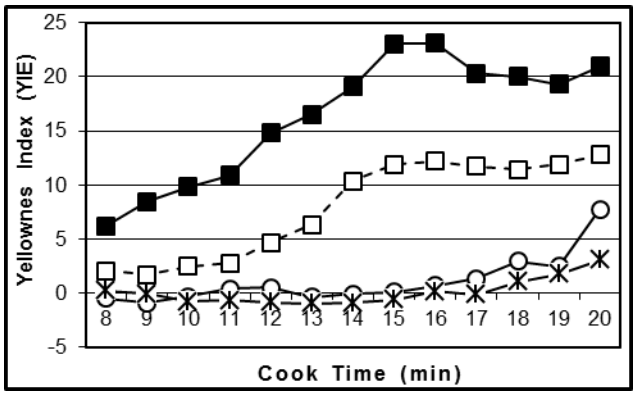

Figure 8: YI versus time data for samples containing:■primary AO3 only, □primary AO3 plus secondary AO4, Ж secondary AO4 only, and ○No AO.

ATR-FTIR Monitoring of Oxidation

The degradation of polyethylene results in the generation of carbonyl species and this is well documented. The measurement of the relative carbonyl emergence and build up, as expressed by the Carbonyl Index (CI) has also been used to measure the degree of the degradation of the polymers [9-11].

In previous work Sharifi, Henwood *et al*[3] showed that, at long cook times, the surface of the polymer facing the mold developed a much lower CI in comparison to the inner surface of the hollow molding which was in contact with the air inside the mold, termed "airside". This may be explained by the presence of the hot, oxygen-rich environment inside the molding which initiates and sustains thermo-oxidative patterns of degradation. It also takes a longer time for the airside material to lose temperature during cooling, in comparison to the mold side material, which cools down faster when in contact with the metal mold. As a consequence, the airside is exposed to higher temperatures for longer times.

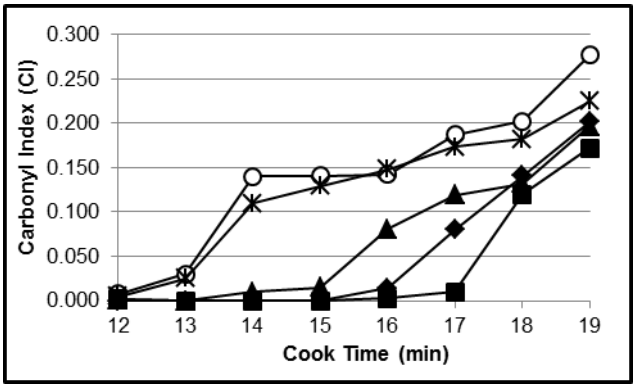

Figure 9: Carbonyl Index (CI) versus time data for samples containing: ♦primary AO1 only, ▲primary AO2 only, ■primary AO3 only, Ж secondary AO4 only, and ○no AO

From Figure 9 it can be seen that the sample containing no AO shows the earliest onset of carbonyl production (ca. 13 minutes). This would be expected due to the absence of any protecting anti-oxidants. Similar behaviour is observed in the sample containing the secondary phosphite AO4 only.

Figures 10, 11 and 12 indicate that samples containing phenolic antioxidants show significantly retarded onset of thermo-oxidative degradation with increasing cook time, therefore indicating higher resistance to thermo-oxidation. Primary phenolic AO3 afforded the most extended retardation of carbonyl growth when used alone. Under the rotomolding conditions used in this study, the addition of secondary phosphite AO4 appears to contribute no synergistic effect. These effects are further illustrated in Figure 13, for three different cook times.

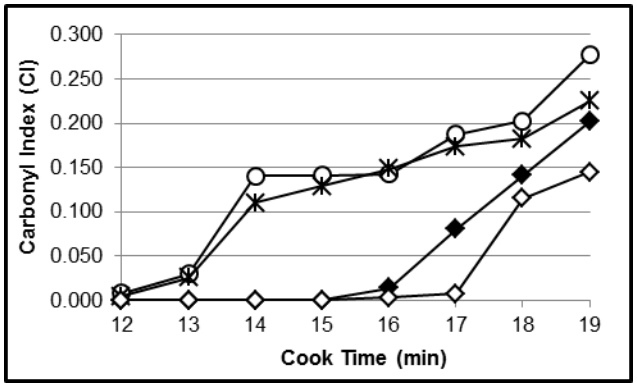

Figure 10: CI versus time data for samples containing: ♦primary AO1 only, ◇primary AO1 plus secondary AO4, Ж secondary AO4, and ○no AO.

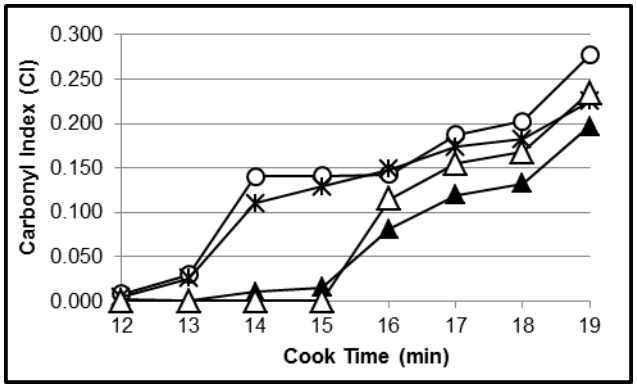

Figure 11: CI versus time data for samples containing: ▲primary AO2 only, Δprimary AO2 plus secondary AO4, Ж secondary AO4 only, and ○no AO.

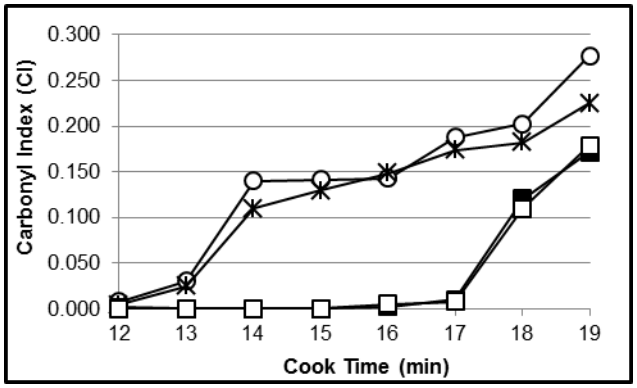

Figure 12: CI versus time data for samples containing: ■primary AO3 only, □primary AO3 plus secondary AO4, Ж secondary AO4 only, and ○no AO.

In contrast, the carbonyl-suppressing effect of primary phenolic AO1 does seem to be enhanced synergistically by using it in combination with secondary

phosphite AO4. Primary phenolic AO2 appears to be significantly less effective in conjunction with secondary phosphite AO4 than when used on its own.

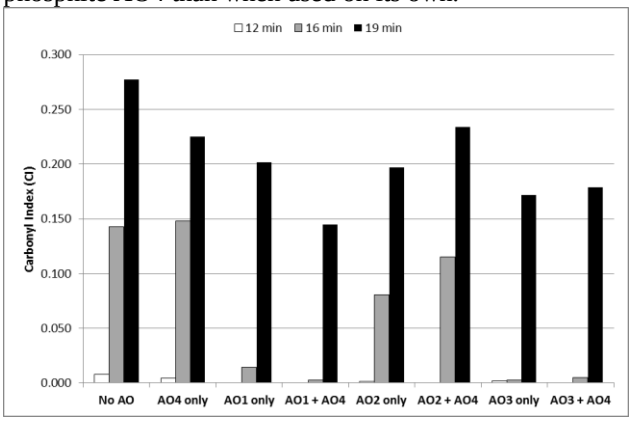

Figure 13: Carbonyl Index (CI) data for different AO combinations, obtained at cook times 12, 16 and 19 min.

Comparison of Yellowness Index (YI) with Carbonyl Index (CI)

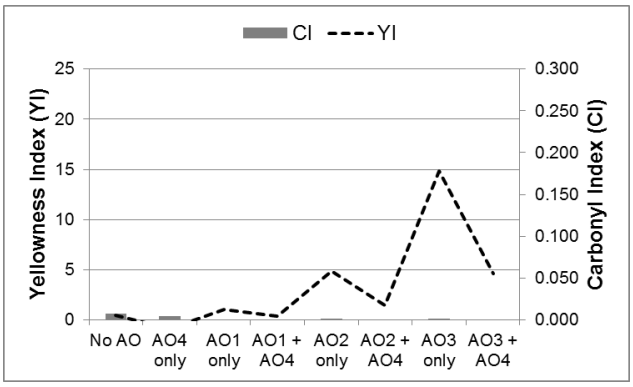

Figure 14: Comparison of CI and YI data for different AO combinations, obtained at 12 min cook time.

Figure 14 compares CI and YI data obtained at 12 minutes cook time, for the various AO combinations. It is apparent that phenolic AOs in isolation give effective suppression of oxidation, however is always accompanied by discoloration; the level of the latter is most severe with AO3 and decreasingly so with AO2 and AO1. In all cases addition of the phosphite (AO4) significantly reduces the level of discoloration, though the ranking of the severity of the discoloration remains the same.

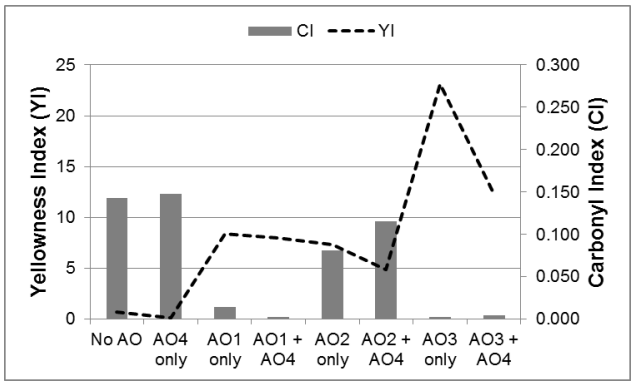

Figure 15: Comparison of CI and YI data for different AO combinations, obtained at 16 min cook time.

As the cook time is increased to 16 minutes (Figure 15), the sample with no AO shows considerable signs of degradation (as evidenced by a raised CI), but there is no sign of yellowing. The samples containing secondary phospite AO4 only exhibits similar behaviour. All samples containing primary phenolic AOs start to show increased yellowness, although in some cases (especially AO3) there is no evidence of degradation having taken place. The synergism with regard to suppression of oxidation, between AO1 and the phosphite (AO4) is apparent here, as is the oxidation antagonism between AO2 and AO4. In all cases apart from AO1, addition of AO4 reduces discoloration, though this is most apparent with AO3.

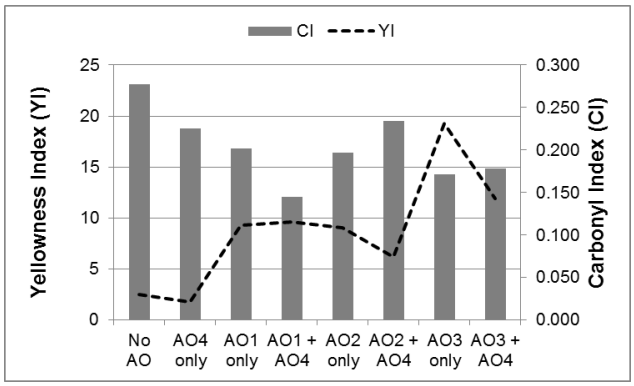

Figure 16: Comparison of CI and YI data for different AO combinations, obtained at 19 min cook time.

As cook time is increased to 19 minutes (Figure 16), all samples now show high levels of oxidation (high CI). However, the most highly degraded samples (no AO and AO4 only) show the lowest yellowing. Even at this level of oxidation, the antioxidant synergism between AO1 and AO4 and antioxidant antagonism between AO2 and AO4 are still apparent. The color suppression activity of AO4 when in combination with AO3 and AO2 is still just about apparent.

This comparison demonstrates that sample discoloration (in this case the yellowing effect measured by YI) is an unreliable indicator of thermo-oxidative degradation of the polymer. The appearance of yellowing is caused mainly by transformation products formed from the phenolic AOs during the course of protecting the polymer.

The results shown in Figure 16 also reinforce the previous observation, that the addition of secondary phosphite AO4 to primary phenolic AO is not universally beneficial. In the case of primary phenolic AO1, phosphite AO4 reduced CI but had a negligible effect on YI. In the case of primary phenolic AO2, phosphite AO4 had an adverse effect on CI but YI was improved. In the case of primary phenolic AO3, phosphite AO4 had a negligible effect on CI but had an improved effect on YI.

Conclusions

The thermo-oxidative degradation of polyethylene has been clearly demonstrated by its effect on impact strength, yellowing and the evolution of carbonyl species.

Thermo-oxidative degradation has the clear effect of ultimately destroying the impact strength of overcooked sample, to the point of sudden and catastrophic loss of mechanical properties. Both the development of impact strength and the extent to which the latter can be maintained, with increasing cook time (the “molding window”), can be significantly affected by the use of primary phenolic and secondary phosphite AOs.

The discoloration of polyethylene during rotomolding has been shown to be primarily associated with the transformation products of the phenolic AOs rather than to thermo-oxidative degradation.

Monitoring the development of carbonyl species, using ATR-FTIR, within the first few microns of the airside surface of the molded part, has been shown to be a reliable indicator of the onset of degradation. The emergence of carbonyl species was effectively retarded when primary phenolic AOs were used, and led to extension of the processing window. The latter effect was most predicable when the phenolic AOs were used alone, though this was at the cost of discoloration.

The synergistic effect between primary phenolic and secondary phosphite AOs has been shown not to be universal in rotomolding. The stabiliser combination must be carefully chosen if any synergism is to be obtained.

This paper represents an initial report of the work carried out. In a future publication, the authors intend to link these observations to measurement of the depletion of AO as cook time is increased.

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Key Words: Additive interactions; Antioxidants; Polyethylene; Stabilization; Discoloration; Long-term Stability and Rotational Molding.