

Enhancing Sustainability in Rotational Moulding: Evaluating Stabilization Effects on PCR/Virgin Polyethylene Blend Performance

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Abstract

The adoption of recycled plastics in rotational moulding presents unique challenges. While many studies have highlighted the benefits of using post-consumer recycled (PCR) materials in processes like blow moulding and injection moulding, the availability of specially designed PCR grades for rotational moulding is limited. Typically, PCR materials contain materials designed for other processes, leading to issues when selected for rotational moulding. The use of recyclate in polymer processing is a multifaceted challenge with many influential factors for consideration. In this study, the primary focus is to investigate the necessity and impact of various antioxidant and stabilization packages in blends containing 20wt% recyclate. Prior research has suggested that virgin materials may offer sufficient protection for low levels of PCR in blends, but this remains unexplored in the context of rotational moulding. Phenolic primary antioxidants, hydrolytically phosphite processing stabilizers, specially designed PCR restabilization packages, and acid scavengers, are assessed with thermal, rheological and mechanical techniques.

Introduction

Plastic production has been increasing significantly year upon year since commercialization in the 1950s [1][2]. High rates of polymeric material consumption have unfortunately been accompanied by a significant degree of polymer waste.

Only roughly 10% of material produced in the last 60 – 70 years has been recycled leaving 79% arriving in land fill after end of life (EoL) and around 10% being incinerated for ‘energy from waste’, neither contributing to net zero, circularity or sustainable development [1]. An astounding prediction that 25 billion metric tons of plastic waste will be produced by 2050 [2]. Despite such figures, it is extremely difficult to imagine modern society without the use of plastics – hence the increasing global plastic waste crisis.

In light of this, incorporating post-consumer recycled materials (PCR) which would otherwise be waste into rotational moulding (RM) is a solution to add value and upcycling materials. RM is a unique processing method with long cycle times, absence of shear often using powdered polymer materials. As a result it presents new challenges for use of PCR which are not often associated to other polymer processing disciplines. For example, challenges with abundant recyclate viscosities not enabling sintering as they are designed for injection and blow moulding, material not

equipped with the correct stabilizing packages for RM at the start of material life and therefore more so after recycling. This study focuses on the latter. Rotational moulding appears to be an excellent method to consume large amounts of recyclate material, but more importantly increase value of waste materials and therefore ‘upcycling’ (as outlined in Figure 1). Pick et al. [3] discuss scale of the opportunity, outlining that the storage tanks can often be over 5000 L in volume with single shot weights above 300 kg, perhaps up to 1000 kg, evidence that the potential to use a significant quantity of recyclate is clearly outlined, however the author also highlighted a significant lack of baseline data and understanding. This extends to the restabilization of virgin/recyclate blends for rotational moulding.

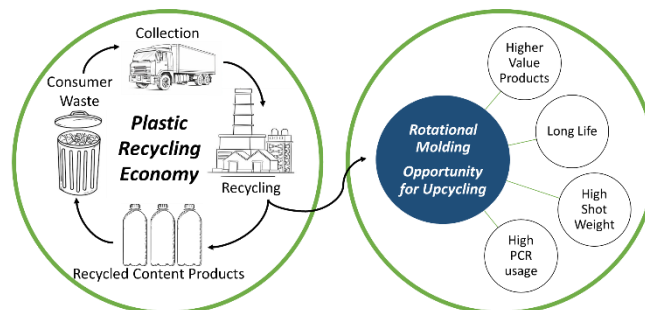


Figure 1. Schematic of PCR usage in rotational moulding

The use of stabilization in virgin materials however has been discussed for rotational moulding applications. Stabilization was demonstrated to be significantly important for virgin material shown in previous studies for RM by *Henwood et al.* [4], but there are differences between virgin and recyclate materials. Impact and carbonyl index assessment of stabilized compounds showed an increase in processing windows while maintaining impact strength when using primary/secondary synergistic systems.

Specifically, recyclate materials contain inhomogeneities due to irreversible changes in the material during product life time, thermo-oxidative damage, photo-oxidation degradation and presence of contaminants which are not factors affecting virgin materials [5]. Stabilizing packages used for virgin material can be used to stabilize recyclate materials, in addition blending virgin resins with PCR can have some stabilizing effects. In some cases studies have shown significant retention in properties for HDPE, LDPE, PP [6]–[11] and reviewed in great detailed by Pfaender [12].

For example a combination of phosphites and phenolic antioxidants are often selected in combination [16] and various ratios are investigated to understand yield improved performance. According to studies conducted by *Pospisil et*

al. [13] after reviewing many studies addition of 0.05-0.2wt% of a phosphite/phenol packages, 1:1-1:4 ratios enable optimal processing of rHDPE. In recent years more recyclate restabilization packages have also been available. For example use of Recyclosorb 550 with rHDPE effectively stabilizing recycled material [14], LLDPE films retaining more mechanical properties with Recyclostab 421 and [15]. Addition of 0.4 %wt Recyclosorb 421 prevented reductions of up to 0.5g/10mins in MFI and achieved a tensile strength up to 27% greater than the non-stabilised material [15]. Therefore it could also be a potential solution for recyclate stabilization.

Another stabilizer which can be overlooked when considering restabilization is the addition of acid scavengers. Acid scavengers are weak organic or inorganic acids which can neutralize free radicals and residuals from catalysts, namely calcium stearate, zinc oxide, zinc stearate and hydrocalcite are often used [16]. Practically they influence the retention of viscosity and longer thermostability

The studies presented above, detail that the restabilization does not repair the material but significantly prevent any further molecular changes, damage and restructuring which is observed in thermal processing cycles outlined in Figure 2.

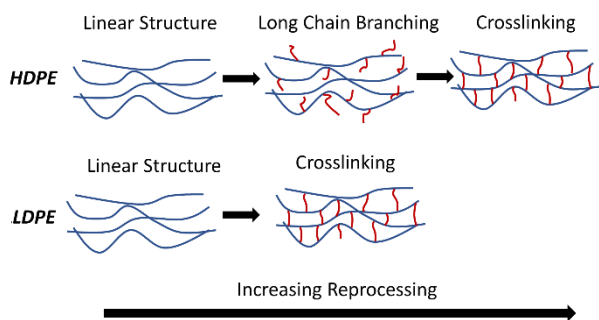


Figure 2. Schematic of degradation mechanisms differencing for types of PE. Adapted from Shi Yin et al [17].

In the context of this study, blending of virgin LLDPE and recycled HDPE is investigated. The main focus is to understand the influence, and the requirements, of additive packages for optimum blend performance in RM.

An investigation into a 20wt% PCR/virgin blend was conducted via twin screw extrusion using additives outlined above. The optimum processing parameters of such blends have also been investigated which is also a novel contribution to RM literature. The study aims to provide baseline data for further RM research and outline key areas for further consideration.

Materials

Post-Consumer (PCR) high density polyethylene (HDPE) recycled from unpigmented post-consumer recycled HDPE food and beverage bottles in domestic waste. Before recycling the material was designed for blow moulding applications with a melt flow rate, 0.35g/10mins (2.16kg/190°C) from ASTM D1238 and

density 0.963g/cm³ from ASTM 1505.

Virgin linear low density (LLDPE) Revolve® N-1010 from Matrix Polymers, is a hexene general purpose grade. The LLDPE has MFI g/10mins (2.16kg/190°C) testing under ISO 1133, and a nominal density of 0.935g/cm³.

Four different stabilization additives were selected for analysis. Named AO1, AO2, RS and AS were phenolic primary antioxidant, hydrolytically phosphite stabilizer, specifically designed recyclate stabilization package and acid scavenger respectively.

Material Preparation

Virgin LLDPE (vLLDPE) and recyclate HDPE (rHDPE) blends were prepared via melt compounding using a co-rotating twin screw extruder (TSE). The TSE had 6 heating sections with a L/D ratio of 25:1. The barrel temperatures were fixed to 160, 160, 170, 180, 185, 190°C from the hopper to the die section. Figure 3 demonstrates the material preparation process.

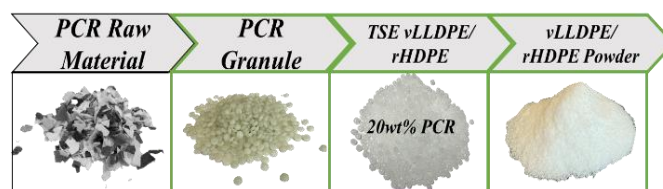


Figure 3. Schematic for the material preparation process of RM vLLDPE/rHDPE blends.

Table 1 outlines the addition of stabilizing chemistries. Materials were then pulverized using the Orenda AF.

Table 1. vLLDPE/rHDPE additive formulations

Additive	AO1	AO2	RS	AS
● (NS)	0	0	0	0
■ (1:1)	1000	1000	0	0
◆ (4:1)	400	1600	0	0
▲ (RS)	0	0	2000	0
◆ (1:1+AS-L)	1000	1000	0	200
▲ (1:1+AS-H)	1000	1000	0	500

Rotational Molding

Powder samples were rotationally molded using the Ferry Carousel RS 1.9 biaxial manufacturing machine. A hexagonal tool was used, with an oven temperature of 260°C and 8.0 rpm major axis and 1.9 rpm on the minor axis. Heating cycles ranging between 9-17 minutes and peak internal air temperature (PIAT) was recorded with a 493K KPaq/Kkord temperature monitoring.

Rotational moulding processing from 9-17 minutes achieved a range of PIATs from 144±5°C to 230±°C. The thermal exposure and processing for each processing time was investigated with a number of techniques.

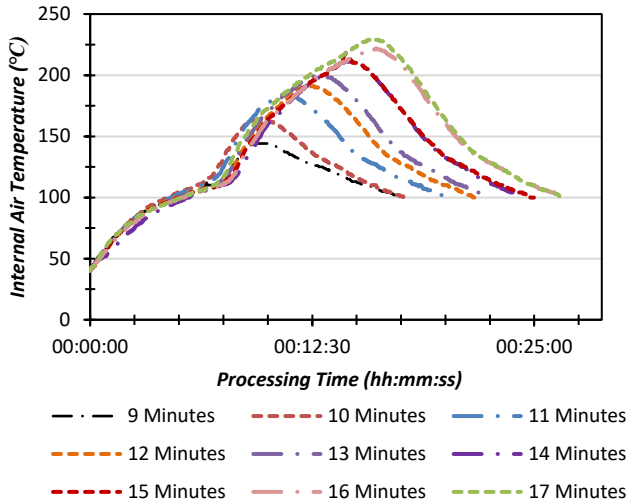


Figure 4. Internal air temperature curves from processing for relative processing times.

Part Density

Density of the molded parts was assessed in accordance with the ISO 1183 standard. Densitometer was used for all parts processed between 9-17 minutes. The porosity was then assessed based on theoretical density of the materials. Evaluated by equations (1) and (2) below.

$$\rho_{th} = (\rho_{vLLDPE} \cdot wt\%_{vLLDPE}) + (\rho_{rHDPE} \cdot wt\%_{rHDPE}) \quad (1)$$

$$Porosity (\%) = 100 - 100 \cdot \left(\frac{\rho_{th} - \rho_{measured}}{\rho_{th}} \right) \quad (2)$$

Where ρ_{th} , wt%, are theoretical density, mass fraction respectively.

Yellowness Index (YI) Testing

YI was undertaken on the base of each moulding on both the internal and external surface. Datacolor™ 400 spectrophotometer was used to measure the index. Each measurement was then made in reflectance mode, with a white tile background under Lab value input of 0, 0, 0.

Mechanical Analysis

Association of Rotational Moulders (ARM) International Impact testing was carried on assays after conditions at -40°C for 24 hours. The results of this testing were analyzed to produce a weighted average impact energy to break, from the AMR standard.

Tensile analysis was conducted was assessed using the Lloyd X LRX instrument and Nexygen software to assess tensile strength, elongation at break and tensile modulus).

Tensile tests were run according to the ISO 527 standard at test speed 50 mm/min after condition at room temperature for 24 hours (23°C).

Thermal Analysis

Oxidation induction time (OIT) was conducted in differential scanning calorimeter (DSC) Mettler Toledo DSC823e to assess the level of thermal stabilization. This was conducted on each formulation in powder and samples cut from the internal surfaces of moldings 11, 13, 15 and 17 minutes. 3-6 mg samples were assessed. Samples were heated under nitrogen atmosphere to 230°C, before exposing to oxygen and measuring OIT.

Rheological Analysis

Rheological behaviour of the blend was assessed for all formulations. The formulations were examined using TA Instruments HR10 Discovery Rheometer. The tests were carried out at 170°C using 25 mm stainless steel parallel plates and 1 mm geometry gap. The frequency sweep was undertaken at 1.0 % strain, between an angular frequency 100-600 rad/s in order to assess the G'/G'' cross-over point. All frequency sweeps were assessed under nitrogen atmosphere to prevent thermal degradation. Furthermore, constant shearing oscillatory conditions of 2%, 10 rad/s were applied in an oxygen environment for 2400s on powder material prior to molding, this was to assess thermal stability enabling comparison of each material blend.

Results and Discussion

Part Density

Material performance, in the interests of this work tensile and impact properties, increase as processing time increases due to the development of density as demonstrated by Dodge and Perry according to Sharifi *et al* [4]. It was therefore necessary to analyze the density across the processing cycle. Figure 5 presents the part density for NS and the AO and RS stabilization. The presence of the AO and RS additions show a reduced rate of increase in part density compared to NS. In previous studies this was attributed to the AOs absorbing some free radicals produced [4].

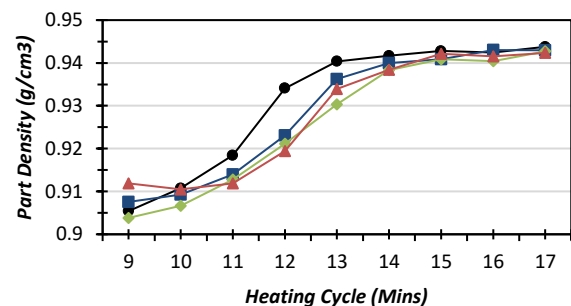


Figure 5. Part density development of the following formulations ●NS, ■ (1:1), ◆ (4:1), ▲ (RS).

Figure 6 illustrates the porosity in the material as the percentage voids in the molded part. This supports the previous observation, as the considered porosity reduction in the presence of any additive package is delayed.

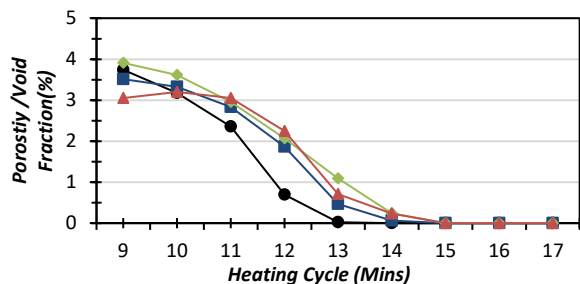


Figure 6. Porosity % of the following formulations ●NS, ■ (1:1), ◆ (4:1), ▲ (RS).

Furthering the restabilization assessment AS was added to the 1:1 formulation and significantly impeded the density development of the blend across the processing window. The greater addition of AS resulting in lower density. This is attributed to great interaction with free radicals as the acid scavenger protects the polymer thus reducing the ability to undergo densification. Further work is required in this area to correlate the additive addition and the density development.

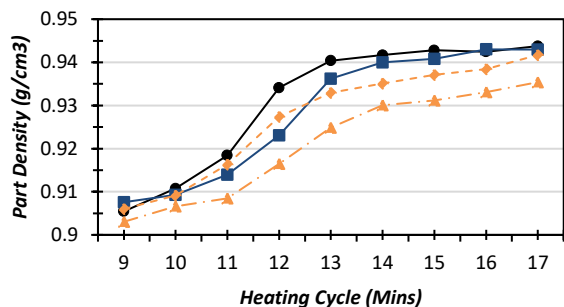


Figure 7. Part Density of the following formulations ●NS, ■ (1:1), □ (1:1+AS-L), ▲ (1:1+AS-H).

Yellowness Index (YI)

From Figure 8 – 11 it can be seen the yellowness index gradually increases with processing time. As reported in a previous study by Sharifi *et al* [4] this is related to the phenolic anti-oxidants transforming to chromophoric compounds [18], [19]. Such compounds, quinones, are the predominant causation of the yellowing which can be observed by eye and by measurement on a spectrophotometer [18], [19]. From figure 8 and 9, the greater quantity of phenolic AO is present in 1:1 formulation at 1000ppm, as a result after 13/14 minutes this presents one of the greatest degree of yellowness on the external and internal surface. RS also appears to have greater yellowing, potentially highlighting high similar quantities of phenolic to 1:1.

Figure 9 presents the YI on the internal surfaces of NS, 1:1, 4:1 and RS. This is significantly more yellow than the external surface due to the extended period of time at elevated temperature caused by the insulative polymer maintaining higher internal air temperatures. Epacher *et al* [20] concluded that the generation of peroxy cyclohexadienes and quinones was greater and therefore greater yellowing was recorded with increased oxygen presence.

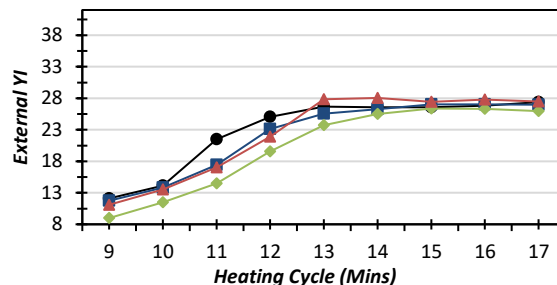


Figure 8. External Surface YI of the following formulations ●NS, ■ (1:1), ◆ (4:1), ▲ (RS).

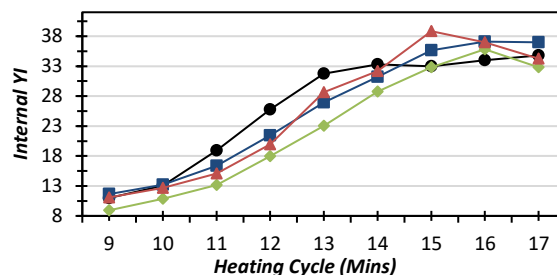


Figure 9. Internal Surface YI of the following formulations ●NS, ■ (1:1), ◆ (4:1), ▲ (RS).

Figure 10 and 11 report the yellowness changes when AS is added at low and high addition rates to 1:1. For both the surfaces across a significant number of processing times the packages with AS present exceed both NS and 1:1 materials. Given addition of AS is increasing the stability of the blend, this is thought to be the variable increasing yellowness. In other cases AS have been found to suppress the yellowing of the material [21], [22]. Given AS remove acid residues from the blend, it would be expected less clinoidal transformation products from phenolics would form due to less free-radical formations [20]. Despite this, the aim of this study was to collect initial baseline data and preliminary observations. This phenomena forms an interesting basis for further study, specifically investigating AS in PCR/virgin RM blends.

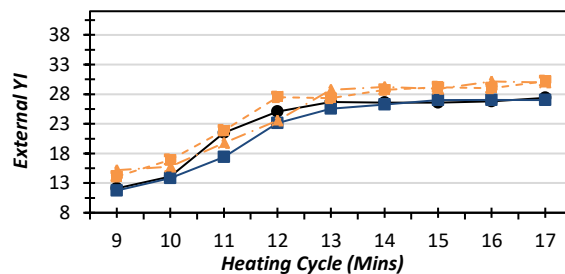


Figure 10. External Surface YI of the following formulations ●NS, ■ (1:1), □ (1:1+AS-L), ▲ (1:1+AS-H).

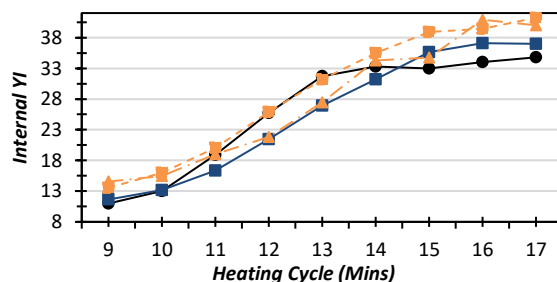


Figure 11. Internal Surface YI of the following formulations ●NS, ■ (1:1), □ (1:1+AS-L), ▲ (1:1+AS-H).

The Lab values were assessed for the external surface of the NS, 1:1 and formulations with the additional acid scavenger at 15 minutes processing (Figure 12). The addition of acid scavenger appears to shift the appearance to a positive value on the abscissa highlighting a fractionally redder surface in both cases. 1:1 appeared to have similar a values, while in all cases of additive addition L and b values were slightly reduced indicating more blue and darker aesthetics from assessment by reflectance. Further studies on the browning index outlined by *Anisko and Barczewski* [23] and greater focus on the additives and Lab is required.

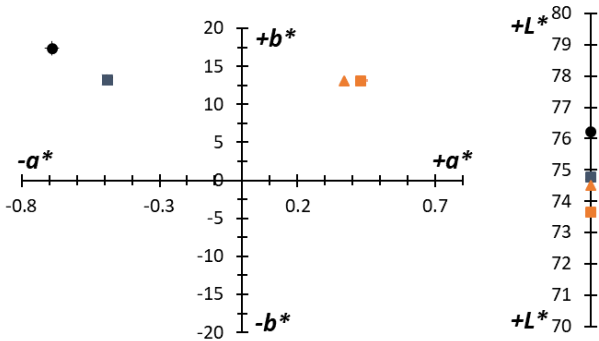


Figure 12. LAB values for ●NS, ■ (1:1), ■ (1:1+AS-L), ▲ (1:1+AS-H).

Impact Performance

Figure 13 demonstrates the comparison of impact performance between non-stabilized and phenolic, phosphite and recycle stabilized materials. In cases before 10 minutes impact performance did not exceed 20J for the 3mm specimens. This is due to partial coalescence and high degree of porosity and voids within the cross-section promoting crack propagation and fracture. This is consistent with observations concluded from part density measurements. The NS blend achieved a greater rate of rise in impact strength, however the material diminishes in impact strength much sooner after 15 minutes, attributed to significant molecular chain damage, chain scission.

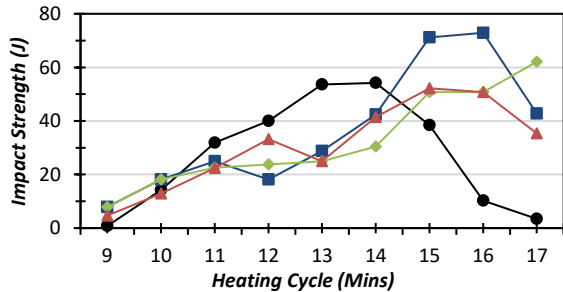


Figure 13. ARM Impact Strength of the following formulations ●NS, ■ (1:1), ◆ (4:1), ▲ (RS).

It can be clearly observed, the addition of AOs delays the increase in impact strength, due to delays in densification, shown in Figure 13. While impact strength is comparable in all cases after 11 minutes NS increases at a greater rate compared to AO blends. Maximum impact strength of the NS blend was around 55J while the addition of 1:1, 4:1 achieved impact strengths 33% and 12% greater at 73J and 62J

respectively. Despite maximum impact improvements, the processing window remained as narrow as NS where the processing time exceeding 40J remained around 3-4 minutes. Analysis of the crystallization for each blend would offer future data and justification for impact observations.

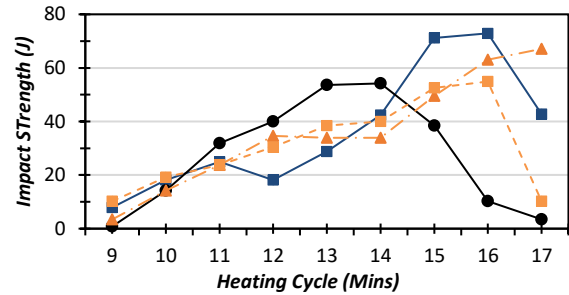


Figure 14. Internal Surface YI of the following formulations ●NS, ■ (1:1), ■ (1:1+AS-L), ▲ (1:1+AS-H).

Acid scavengers were also assessed with the greatest impact strength blend of 1:1. The presence of the acid scavengers increased the initial rate of increase in impact strength when comparing to the 1:1 formulations between 11 – 14 minutes before 1:1 exceed performance with those blends with AS.

The overall increase was more gradual and did not exist as a ‘two-stage’ increase like the previous formulations outlined in Figure 13. In the case of Figure 13 an initial increase to 20-30J was seen before another increase to 50-75J. The two-stage increase was also reported by [4], the second increase attributed by rheological analysis is an effect of crosslinking. The presence of AS experiences a more stable increase, potentially due to controlling the crosslinking process, an observation requiring further research.

The 1:1+AS-L blend experienced very similar performance to the RS stabilization, highlighting potentially similar additive components and quantities. 1:1+AS-H exceed the NS blend performance with improvements over 10J (26%), despite this maximum impact performance did not exceed 1:1. Finally the AS-H formulation did not begin to decrease like other formulations at 17 minutes, thus the material may have not reached optimum impact performance inside the processing range due to a high degree of thermal stability.

Tensile Properties

Assessment of tensile properties at 50mm/min in Figure 15 and Figure present differences in tensile strength recorded and elongation at beak across processing conditions and formulations.

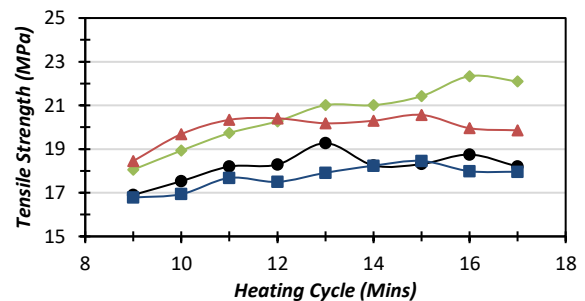


Figure 15. Tensile Strength of the following formulations ●NS, ■ (1:1), ◆ (4:1), ▲ (RS).

Figure 15, shows that 1:1 and NS present a similar development of tensile strength across the processing range, values typically between 17-19MPa. RS and 4:1 experienced higher strength across all cases with 4:1 achieving a maximum of 22.3MPa. The continuous development of density is attributed to the increasing strength and elongation with increasing processing time.

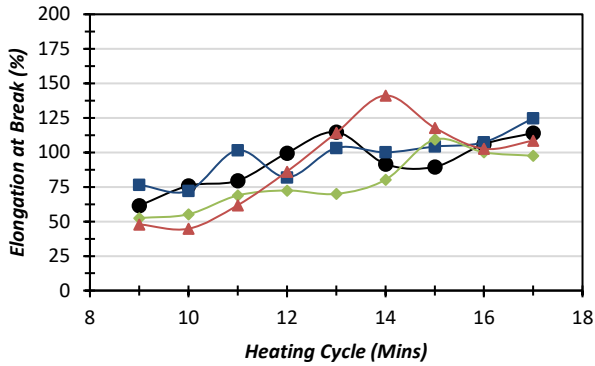


Figure 16. Elongation at Break of the following formulations ●NS, ■ (1:1), ◆ (4:1), ▲ (RS).

Figure 16 shows increasing elongation over processing time, in the range measured the materials were within 25 – 60% of one another. The small difference was attributed to the high-test speed. Increasing elongation with processing time again is attributed to the increase in density development.

Thermal Analysis

Oxidation induction time (OIT) was assessed using differential scanning calorimetry (DSC). In order to evaluate the thermal oxidation post processing, OIT was conducted on the internal surface at different times.

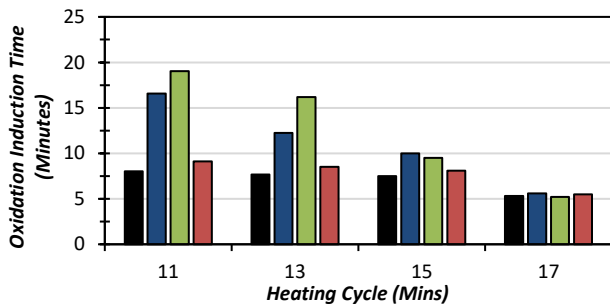


Figure 17. Oxidation induction time for various formulation conducted on internal surface shavings ●NS, ■ (1:1), ◆ (4:1), ▲ (RS)

Despite further analysis required, initial findings showed that NS was unstable throughout the processing range with OIT between 5-8 minutes. In all cases OIT decreases with increasing process temperature. 4:1 appears to be the most stable throughout the processing range with 19 – 5 minutes and 16.5 – 5.5 minutes with 1:1. While the RS additive package provided minimal improvement relative to the NS blend.

Rheological Analysis

Various methods were adopted to assess the rheological properties of the material and thermal stability. Figure 18

illustrates the thermal stability under isothermal conditions. The increase in storage modulus or viscosity during this analysis is a criteria for analysis of thermal stability [23]. The earlier the increase in modulus, the lower the thermal resistance to crosslinking. The addition of such stabilization packages provided significant improvements in stability. In the case of 1:1, 4:1 Similar resistance to LCB/crosslinking was achieved, improving on both the NS and RS blends.

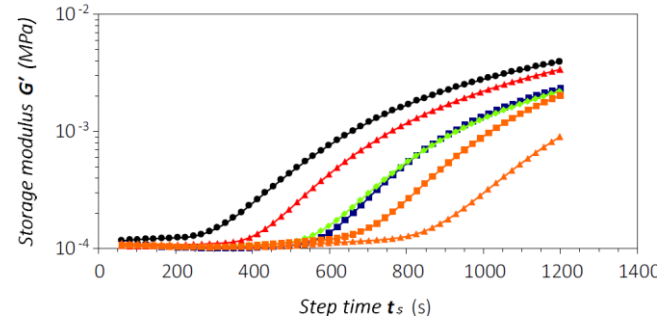


Figure 18. Time sweep to assess thermal stability of additive packages, ●NS, ■ (1:1), ◆ (4:1), ▲ (RS), ■ (1:1+AS-L), ▲ (1:1+AS-H).

The addition of the AS to the 1:1 delayed the onset of degradation by 20-180s, greater resistance to rheological changes was achieved with a higher addition of AS. In the considered case it was attributed to the AS terminating the generation of free radicals during analysis and restricting activity towards the polymer chains.

The G'/G'' cross-over point was also used to determine the extent of the change in the polymer changes for processing. Figure 19 is an example of the cross-over point of G'/G'' . Interpretation of $G'=G''$ relative to molecular architecture is increases is higher modulus values represent a narrowing molecular weight distribution, while increases in angular frequency highlight reduction in overall molecular weight [24], [25]. The orange arrows present the concept of how the coordinates of the cross-over point are attributed out the molecular weight (MW) and the molecular weight distribution (MWD).

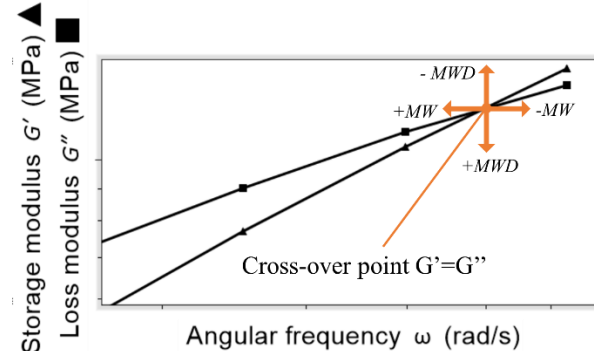


Figure 19. Illustration of $G'=G''$ cross-over point and effect on molecular weight (MW) and molecular weight distribution (MWD)

Figure 20, illustrates the cross-over points, the most stable blend structure was achieved by 1:1+AS-H as the MWD remained constant for all other the processing conditions. In all other cases stabilized and unstabilized the cross-over point significantly reduced in modulus with increasing processing resulting in increasing MWD. Generally, the MW increased

with increased processing, signified by a shift to the left on the abscissa for most blends. Cross-over point was collected for 0, 11, 13, 15 and 17 minutes. Further correlations in this area of research would provide greater insight into changes in molecular structure during RM processing.

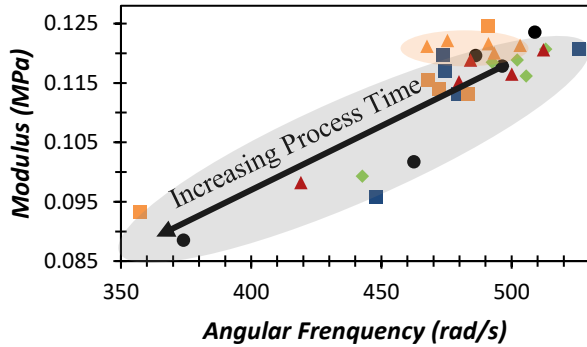


Figure 20. Time sweep to assess thermal stability of additive packages, ●NS, ■ (1:1), ◆ (4:1), ▲ (RS), ■ (1:1+AS-L), ▲ (1:1+AS-H).

Figure 21, correlates the modulus cross-over point with blend stabilization and processing time more directly. This analysis indicated the resistance of the stabilization packages to the increase of MWD. NS due to low stability and lack on antioxidant compounds protecting the material from thermoxidation, free radical attack and long chain branching the MWD increases at the most significantly with increasing processing and to the greatest degree.

Other additive formulations such as 1:1, 4:1, RS and 1:1+AS-L all achieve relatively similar performance, with 1:1+AS-L offering the most inferior resistance. Most significantly 1:1+AS-H maintained the level of modulus for $G' = G''$ attributed to good thermal stability provided by the addition of the additive scavenger.

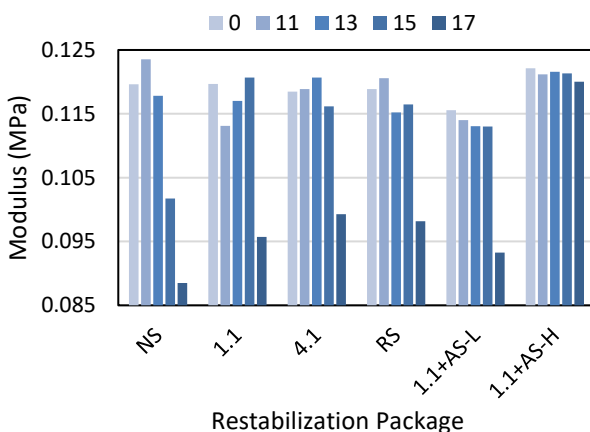


Figure 21. Modulus cross-over point relationship with processing time.

The correlation between MWD, and MW for material performance with this blend would be benefit in order to select and further optimize the material performance.

Conclusions

This work focuses on the addition of antioxidants and other

stabilizing chemistries for RM vLLDPE/rHDPE blends.

Initially, in assessment of part density, it was observed that the addition of any stabilization additives reduced the part density for identical processing conditions. This finding offers further research possibilities to understand relationship between RM additives and porosity.

The yellowing of the blend during processing was most severe with the addition of acid scavengers. Phenolic transformations were also thought to be attributed to some of the yellowing observed.

The addition of additives increased overall impact performance by 33% with the 1:1 AO addition, while others also improved on the unstabilized blends. A significant improvement which is promising for a greater addition of PCR and greater performance. The process window shifted to longer cycle times, this is thought to be due to the delay of crosslinking behaviour. The processing window remained similar for all blends.

OIT and isothermal rheological analysis presented 1:1+AS-H to have the highest thermal stability both unprocessed and processed specimens. Despite this it did not achieve optimum performance due to high degrees of porosity. All additions of additives improved resistance to thermoxidation with different levels of success.

Some initial studies into the molecular configurations after processing were made. In this case MWD broadened and MW increased with increasing processing. However, further analysis is required to corroborate initial findings.

This study has only considered effects of some mechanical and thermal properties in a drive to obtain baseline data. Further work in this area should focus on increasing the recyclate content and assessing the influence of additive packages on material performance. Specifically the relationship between structure, properties and processing. The scope should be extended to other polyethylene systems with the use of recycled LLDPE/LDPE, especially from recycled PCR, postindustrial recyclate (PIR) and end of life RM materials.

An emerging area of the research for stabilization current also focuses on natural antioxidants, it is expected that this will have growing academic interest in the coming years. Given the challenges outlined for the use of recyclate in rotational moulding it is essential to maintain continuous efforts towards greater circularity in rotational molding.

Evidently there are significant benefits to the addition of stabilizers to virgin/recyclate blends in the rotational moulding application shown by this study. Further analysis will proceed in order to contribute to greater material performance, greater upcycling opportunities in RM and greater contribution to sustainable development in the polymer processing industry.

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