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Fall 2018

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Recommended Citation

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Abstract
With increased regulation of recycled materials, such as minimum content claims for bags and rigid containers in California, additional research was needed to understand how the recycled content affects the material properties and safety of these polymers. The objective of this research was to investigate how material properties changed as commodity recycled material is incorporated into commercial products, and if these changes can be modeled. Post-consumer recycled (PCR) linear low-density polyethylene (LLDPE) feedstocks were blended with virgin LLDPE to create 0, 20, 40, 60, 80, and 100% wt/wt PCR sample sets. The recycled feedstocks contained either exclusively calcium carbonate or a blend of calcium carbonate and carbon black pigments. The sample blends were extruded on a Wayne single screw extruder into film and sheet. Samples were evaluated using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), ultraviolet-visible (UV-Vis) and fluorescence spectroscopy. Extractions in n-hexane and xylene were performed according to Code of Federal Regulations (CFR) Title 21, B, Part 177.1520 for regulatory compliance with direct food contact applications. Results of this study suggest the potential for modeling of recycled content in pigmented polyethylene, particularly using ultraviolet spectroscopy, and that post-consumer recycled material may be safely incorporated into food contact applications.

Introduction

Recent studies by Lebreton *et al.* estimate between 47 and 129 thousand metric tons of plastic have accumulated within a 1.6 million square kilometer zone of ocean between California and Hawaii, otherwise known as The Great Pacific Garbage Patch [1]. Single use products and packaging, one of the largest market sectors for plastic, are designed for immediate disposal and found in large quantities in the ocean [2]. Waste diversion and management strategies must be implemented to reduce the amount of plastic waste entering the ocean. Successful waste stream diversion strategies incorporate refuse plastic in commercial products. The increased regulation of recycled materials, such as minimum recycled content claims for bags and rigid containers in California, necessitates the need for post-consumer recycled (PCR) standards to verify content claims and the safety of products when using PCR in direct food contact applications [3, 4].

Polymer degradation occurs during synthesis, storage, processing, product use, and reprocessing [5]. Thermo-oxidative degradation of polyethylene involves cleaving main chain covalent bonds and the formation of alkyl radicals. These radicals react with atmospheric oxygen and can form hyperoxides in a chain reaction. Oxygenated products such as alcohols, aldehydes, ketones, acids, and esters are produced by the decomposition of hyperoxides [6]. Vinyl compounds are also produced during degradation. Catalyst type and chain branching can influence degradation product concentrations and whether chain scission reactions will dominate over crosslinking. For example, in linear polymers, chain scission reactions dominate over crosslinking [6]. It has been demonstrated that polymers which had undergone thermo-oxidative degradation had an increased absorption of ultraviolet (UV) light [7]. Determining the carbonyl index using attenuated total

reflection infrared spectroscopy has been used to characterize the degree of oxidation in polyethylene and other polymers [8].

Limited research has been done to evaluate the safety, performance, and commercial application of post-consumer recycled content by concentration for pigmented polyethylene. Previous research by Curtzwiler *et al.*, Boldizar *et al.*, and Vorst *et al.* explored potential methods for evaluating materials containing post-consumer recycled content. However, much of this work has been focused on polyethylene terephthalate (PET) or non-pigmented high-density polyethylene (HDPE) [9, 10, 11, 12, 13]. The PCR resins used in this study were linear low-density polyethylene (LLDPE) sourced from agricultural waste, such as ground cover. Agriculture plastic is usually landfilled or burned, however, advances in recycling have targeted the agriculture industry to reduce its environmental impact [14]. The objective of this research was to understand how material properties change as commodity recycled material, such as pigmented LLDPE, is increasingly used in commercial products. Results of this study suggest there are measurable differences between low and high concentrations of pigmented PCR LLDPE blends that can be evaluated and predicted using linear models. Further research is needed to examine the individual effect of pigment in PCR recycled material and develop non-linear models to predict performance and safety of PCR feedstocks.

Materials & Methods

Sample Preparation
Virgin LLDPE resin was blended with two different pigmented PCR LLDPE resin sources from a large domestic agricultural plastic recycler. The first PCR LLDPE resin source was pigmented white, calcium carbonate, and the second resin source was a mixture of white and black resins, pigmented with calcium carbonate and carbon black. The blends were prepared at PCR:virgin ratios of 0, 20, 40, 60, 80, and 100 % weight/weight. Once blended, the samples were dried for 15 hours at 100 °C to remove any moisture. The samples were extruded on a single screw (3/4" diameter screw with a 25:1 L/D ratio) Wayne extruder (Totowa, NJ) with a coat hanger die. Conditions for the heating zones during extrusion were 190 °C in the feed section and 204 °C in the barrel, coupler, and die zones. Extruded blends were characterized for thermal and spectrophotometric properties with solvent extractions to determine Code of Federal Regulations (CFR) compliance for direct food contact applications in accordance with CFR Title 21, B, Part 177.1520 [15].

Thermal Analysis
Differential scanning calorimetry (DSC) was used to observe thermal transitions of the material, such as melt, crystallization, and heat capacity. Approximately 3-7 mg of sample was loaded and hermetically sealed in a T-zero DSC pan in five repeated measures per blend. Samples were ramped at 10 °C per minute from 10 °C to 180 °C, cooled back to 10 °C, and heated a second time to 180 °C using a TA Instruments Q2000 (New Castle, DE) in a nitrogen atmosphere. Glass transition temperatures (T_g) were not observed due to the low T_g of LLDPE (between -130 °C to -10 °C) which is below the temperature bounds of the scan [16].

Thermogravimetric analysis (TGA) was used to evaluate ash content and thermal degradation properties at 5% mass loss, this parameter had been shown to increase as PCR content increased

in previous research conducted by Curtzwiler *et al.* [13]. Approximately 5-10 mg of sample was placed on platinum pans with five repeated measures for each blend. Modulated TGA runs were performed utilizing Blain and Hahn's method with samples heated at a rate of 2 °C per minute with continuous modulation amplitude of ± 5 °C using a TA Instruments Q5000IR thermogravimetric analyzer (New Castle, DE) [17].

Spectrophotometric Analysis
Fluorescence and ultraviolet-visible (UV-Vis) spectroscopy were used to characterize spectrophotometric properties of the blends. Coupons were cut from each extruded blend and thickness measured using a Mitutoyo IP 65 electric digital micrometer (Kawasaki, Japan) in five repeated measures. Sample coupons were loaded into a custom test fixture, measuring 12.7 cm x 8.5 cm x 2.3 cm, to maintain a flat and equal distance from the detector. Both fluorescence and ultraviolet-visible spectroscopy measurements were collected on a Tecan Safire microplate reader (Zurich, Switzerland). The UV-Vis absorbance spectra were collected between 290 nm and 900 nm with a 2 nm step. The absorbance values were divided by the thickness measurements to account for any differences in sample thickness, this was found to be necessary by Curtzwiler *et al.* during UV-Vis spectroscopy analysis of recycled polyethylene terephthalate [9]. Fluorescence intensity was measured in 3D fluorescence mode spanning excitation and emission wavelengths from 300 nm to 600 nm with 5 nm step. Emission spectrum was captured in a fixed z-position at 14,000 µm, utilizing an 80 µs integration time and 10 flashes. The ratio of fluorescence intensity at emission wavelengths 395 nm and 515 nm excited at 300 nm was calculated using methods outlined by Curtzwiler et al [13].

Regulatory compliance for direct food contact: Total Extractables per CFR 21.177.1520
Extractions were carried out following the Code of Federal Regulations Title 21, B, Part 177.1520 to determine compliance for direct food contact applications in both n-hexane and xylene [15]. For this test, only the 0%, 60%, and 100% PCR sample blends were tested to reduce the number of extractions performed. An assumption was made that if the 100% PCR blend passed that the blends with less recycled content would also pass. One liter of n-hexane or xylene was heated to 50 °C in a 2 L round bottom flask fitted with a condenser via a heating mantle. When the solvent reached 50 °C 2.5 g of sample for the hexane extraction, 5 g of sample for the xylene extraction, was added to the extraction apparatus. After refluxing for 2 hours the solvent was filtered through a fritted filter and coarse filter paper. The solvent was distilled until approximately 100 mL remained. The remainder was transferred to a tared crystallizing dish and evaporated to dryness. The crystallizing dishes with residue were placed in a desiccator for 24 hours then weighed to record the weight of the residue. Total extractives cannot exceed 5.5% in n-hexane and 11.3% in xylene to comply with CFR regulatory guidelines for food holding applications. The total extractives cannot exceed 2.6% in n-hexane for direct food contact and holding applications during cooking.

Statistical Analysis
All statistical analysis was conducted using JMP Pro 13.0 Statistical Discovery software, SAS (Cary, NC). Data was analyzed for analysis of variance, and comparisons of means using Tukey-Kramer HSD and fitted with general linear regressions.

Results & Discussion

Significant differences were found (P < 0.05) for thermal and spectrophotometric properties between blends containing low levels of PCR content from blends containing higher levels of PCR content and summarized in Tables 1,2.

Table 1. Measured thermal, spectrophotometric, and extractive properties for extruded white pigmented PCR. Means separated by different letters are significantly different.

White PCR wt %	Heat Capacity Ratio	5% Weight Loss °C	Ash Content wt %	Absorbance Area A.U./mil	Fluorescence 395nm/515nm Ex. 300nm	Extractives n-Hexane wt %	Extractives Xylene wt %
0	$0.54^A \pm 0.02$	$333.92^A \pm 0.90$	$0.67^A \pm 0.004$	$3.81^A \pm 0.65$	$3.99^A \pm 0.29$	1.0 ± 0.42	1.62 ± 0.49
20	$0.55^A \pm 0.04$	$329.56^A \pm 7.15$	$0.97^B \pm 0.005$	$13.51^B \pm 0.87$	$2.86^B \pm 0.47$	Not tested	Not tested
40	$0.56^A \pm 0.01$	$331.65^A \pm 3.19$	$1.22^C \pm 0.026$	$24.82^C \pm 1.22$	$2.66^{BC} \pm 0.18$	Not tested	Not tested
60	$0.58^A \pm 0.01$	$332.84^A \pm 2.87$	$1.47^D \pm 0.009$	$32.16^D \pm 0.95$	$2.44^{BC} \pm 0.22$	1.21 ± 0.15	1.82 ± 0.10
80	$0.57^A \pm 0.02$	$325.07^A \pm 2.31$	$1.79^E \pm 0.005$	$41.25^E \pm 0.79$	$2.02^C \pm 0.44$	Not tested	Not tested
100	$0.47^B \pm 0.03$	$326.50^A \pm 3.82$	$2.10^F \pm 0.051$	$48.98^F \pm 0.72$	$1.97^C \pm 0.65$	1.01 ± 0.63	1.82 ± 0.39

Table 2. Measured thermal, spectrophotometric, and extractive properties for extruded mixed pigmented PCR. Means separated by different letters are significantly different.

Mixed PCR wt %	Heat Capacity Ratio	5% Weight Loss °C	Ash Content wt %	Absorbance Area A.U./mil	Fluorescence 395nm/515nm Ex. 300nm	Extractives n-Hexane wt %	Extractives Xylene wt %
0	$0.54^B \pm 0.02$	$333.92^A \pm 0.90$	$0.67^A \pm 0.004$	$3.81^A \pm 0.65$	$3.99^A \pm 0.29$	1.0 ± 0.42	1.62 ± 0.49
20	$0.57^{AB} \pm 0.04$	$323.72^B \pm 4.17$	$1.04^B \pm 0.017$	$34.17^B \pm 11.00$	$2.50^B \pm 0.47$	Not tested	Not tested
40	$0.60^A \pm 0.01$	$321.56^{BC} \pm 3.90$	$1.59^C \pm 0.009$	$66.27^C \pm 6.65$	$3.03^B \pm 0.18$	Not tested	Not tested
60	$0.58^{AB} \pm 0.01$	$312.07^D \pm 3.50$	$2.07^D \pm 0.021$	$98.36^D \pm 16.02$	$2.70^B \pm 0.22$	1.45 ± 0.90	1.15 ± 2.86
80	$0.58^{AB} \pm 0.02$	$318.07^{BCD} \pm 4.31$	$2.46^E \pm 0.019$	$144.14^E \pm 12.56$	$2.96^B \pm 0.44$	Not tested	Not tested
100	$0.61^A \pm 0.03$	$312.07^{CD} \pm 3.05$	$3.17^F \pm 0.059$	$182.45^F \pm 20.84$	$2.81^B \pm 0.65$	1.92 ± 0.66	2.72 ± 0.55

Thermal analysis of pigmented PCR
Ratios of heat capacity values at 118 °C and 123 °C were compared by blend percentage for both white (Figure 1) and mixed PCR (Figure 2). The behavior shown in the DSC thermogram for the 40% mixed PCR sample (Figure 3) was found to be consistent with all other samples, regardless

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of pigment or recycled content. In Cycle 1, a smaller melting peak was observed at 118 °C before a larger melting peak at 123 °C. In Cycle 2, a wide shoulder was observed before a single melting peak. This shoulder effect has been found in DSC thermograms for recycled polyethene and is attributed to changes in molecular weight, crystal size, chain breakage, and secondary recrystallization [8]. Minimal differences were found in the heat capacity ratios for the blends containing either white or mixed PCR resins. This does not align with previous research conducted by Curtzwiler *et al.* which found an increase in shoulder height as recycled content increased [13]. In non-pigmented polyethylene, mechanical properties such as hardness, density, elastic modulus, and yield stress have all been found to increase due to changes during secondary recrystallization [8,18]. The calcium carbonate used as a pigment and filler in the recycled feedstocks may be acting as a thermal stabilizer at melting temperatures, which has been demonstrated by Abdolmohammadi *et al.* in white pigmented polyethylene [19].
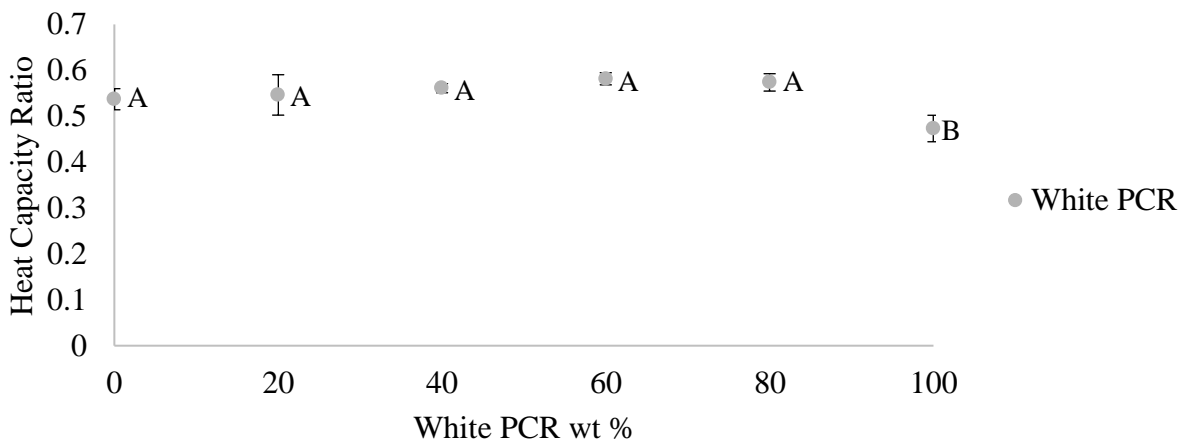
Figure 1. Heat capacity ratios for blends containing white PCR. Means separated by different letters are significantly different.
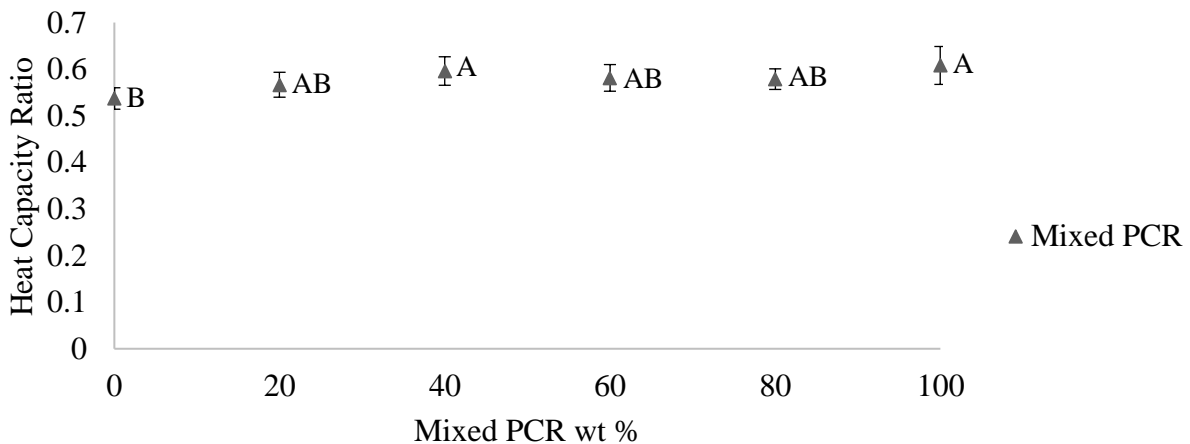

Figure 2. Heat capacity ratios for blends containing mixed PCR. Means separated by different letters are significantly different.
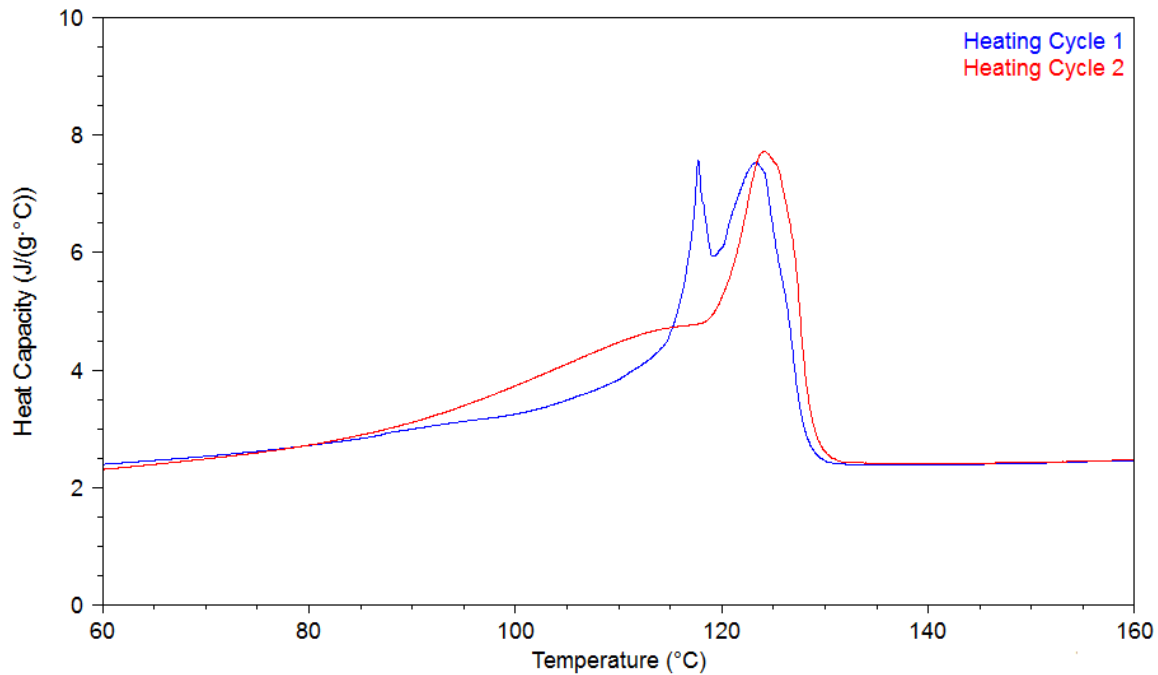
Figure 3. DSC thermogram for 40% mixed PCR sample.

Analysis using TGA did not find significant differences ($P > 0.05$) or linear relationships of PCR content and 5% weight loss temperature for the white PCR blends (Figure 4). However, for the mixed PCR blends, a significant ($P < 0.05$) linear decrease in the 5% weight loss temperature as PCR content increased was realized (Figure 5). Previous research conducted by Curtzwiler et al. demonstrated an increase in the 5% weight loss temperature from 0% through 60% PCR in non-pigmented polyethylene [13]. Wen *et al.* investigated thermal degradation as a function of carbon black concentration in polypropylene and found an increase in 5% and 10% mass loss temperatures as pigment load increased [19]. In both studies thermal degradation was delayed due to recycled content and pigment concentration. The results of this study suggest thermal degradation occurred earlier as recycled content increased, which is not supported by previous findings. Degradation onset may be influenced by contamination, such as cellulose, that can be found in recycled agriculture plastic. This suggests further investigation of thermal degradation of recycled and pigmented polyethylene is needed. Initially it was hypothesized that stratification may have occurred in the hopper due to differences in size and shape of the virgin and recycled material, however this hypothesis was rejected after analyzing the residual ash content using TGA. Ash content was determined to be unique ($P < 0.01$) for each blend of the white PCR (Figure 6) and mixed PCR (Figure 7), indicating there was little stratification during extrusion.
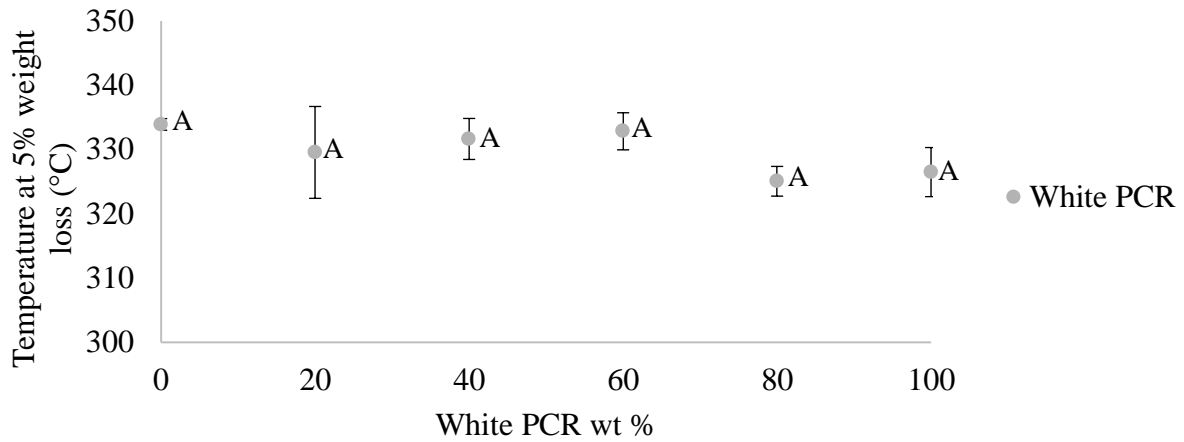
Figure 4. 5 % weight loss temperatures by white PCR %. Means separated by different letters are significantly different.
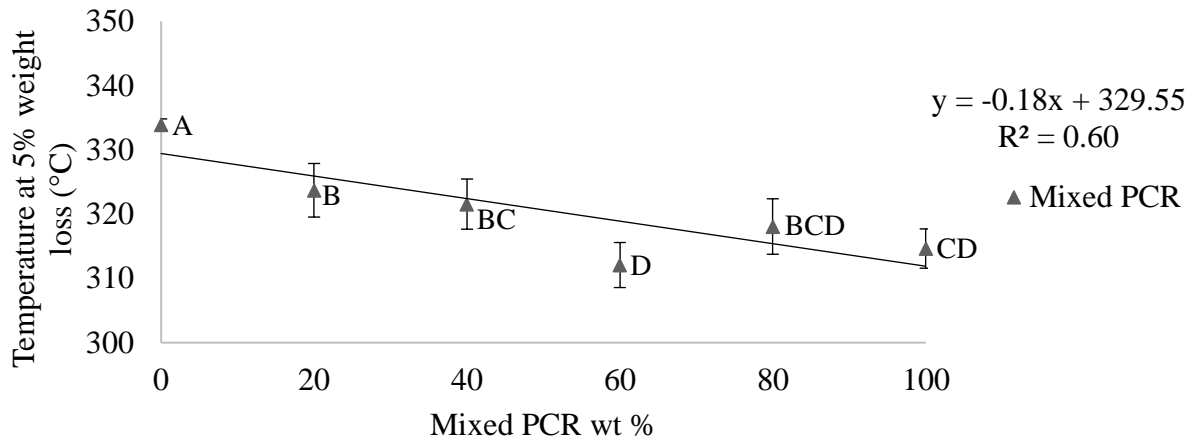

Figure 5. 5 % weight loss temperatures by mixed PCR %. Means separated by different letters are significantly different.
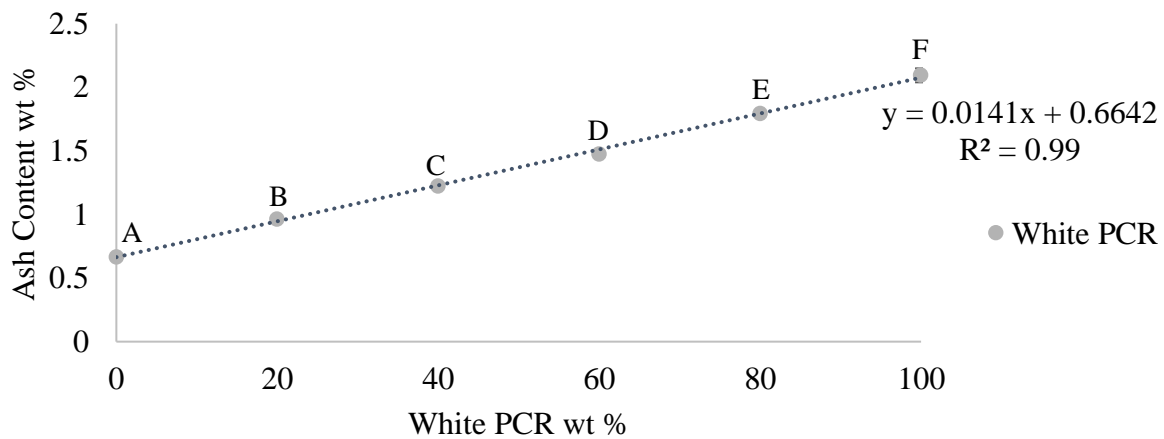
Figure 6. Ash content by white PCR %. Means separated by different letters are significantly different.
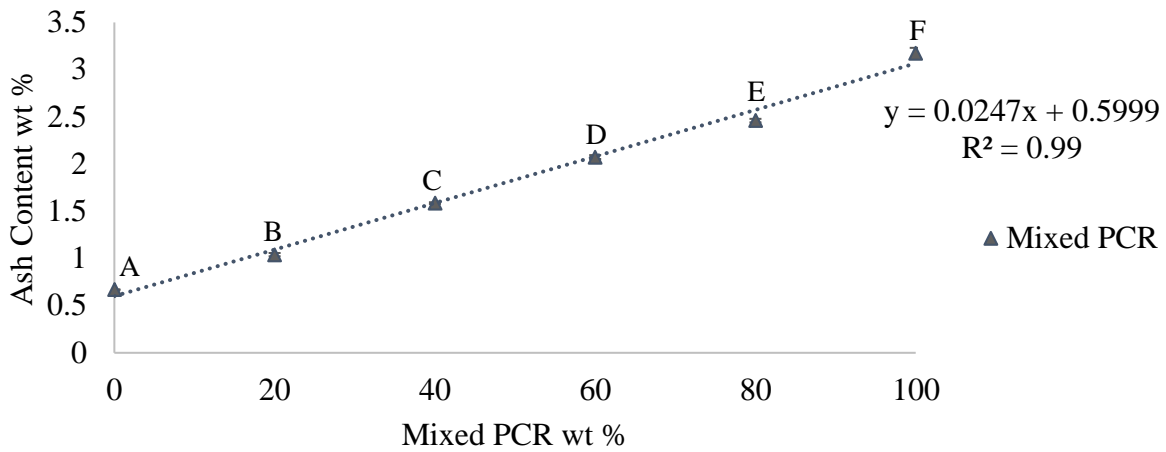

Figure 7. Ash content by mixed PCR %. Means separated by different letters are significantly different.

Spectrophotometric analysis of pigmented PCR
In both sample sets, there was an increase in the ultraviolet light absorption. This increase in absorption is attributed to the increased concentration of carbonyl compounds such as aldehydes, ketones, acids, and esters [6]. However, pigment load was not held consistent in all blends and increased in concentration as the PCR content increased. An increase in absorption area was observed as pigment load increased. The area under the absorption curve from 290-400 nm was calculated to account for UVA (315-400 nm) and UVB wavelengths (280-315 nm). These results support previous research by Curtzwiler *et al*. demonstrating an increase in ultraviolet and visible light absorbance as PCR content increases [9, 11, 13]. Unique linear models were identified for both white PCR (Figure 8) and mixed PCR (Figure 9) blends as a result of higher absorption properties of carbon black.
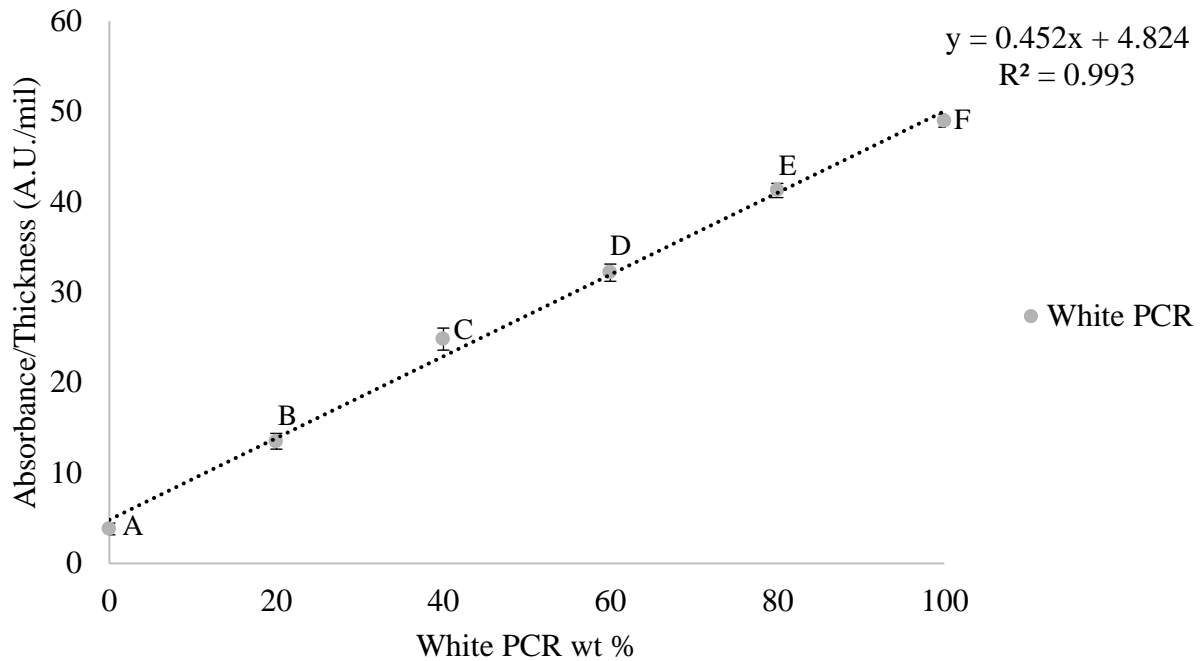
Figure 8. Thickness normalized absorbance area (A.U./mil) for blends containing white PCR. Means separated by different letters are significantly different.
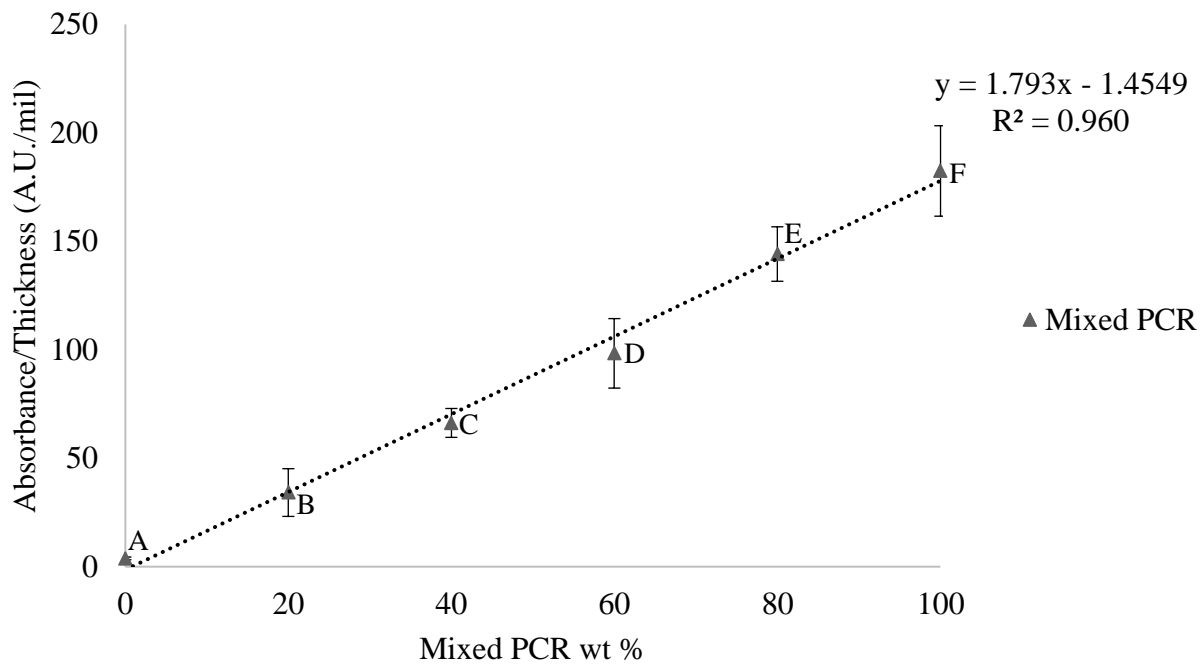

Figure 9. Thickness normalized absorbance area (A.U./mil) by PCR % for Mixed PCR. Means separated by different letters are significantly different.

Further analysis using Fluorescence spectroscopy found significant differences between the virgin samples and blends containing recycled content for both white PCR (Figure 10) and mixed

PCR (Figure 11). This suggests the potential to identify PCR material from virgin material. The resulting model for mixed PCR content and fluorescence intensity was not considered valid due to only explaining 18% ($R^2 = 0.18$) of sample variance. These findings supported previous research conducted by Curtzwiler et al to use fluorescence spectroscopy to determine if a sample contains PCR content, but not quantify PCR content [13].
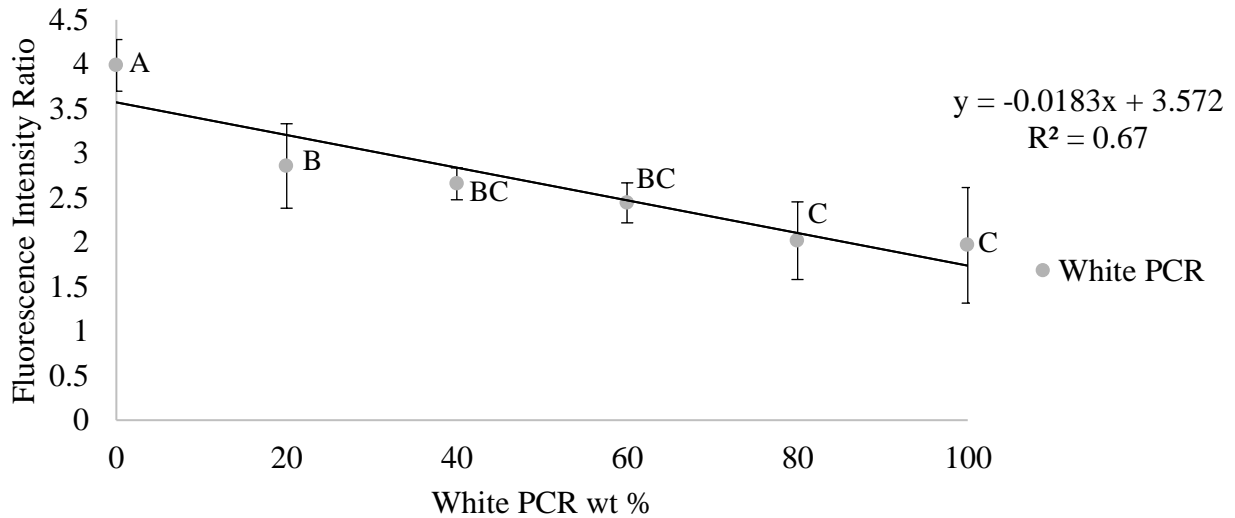

Figure 10. Fluorescence intensity ratio (395 nm/515 nm excited at 300 nm) for white PCR. Means separated by different letters are significantly different (P<0.05).
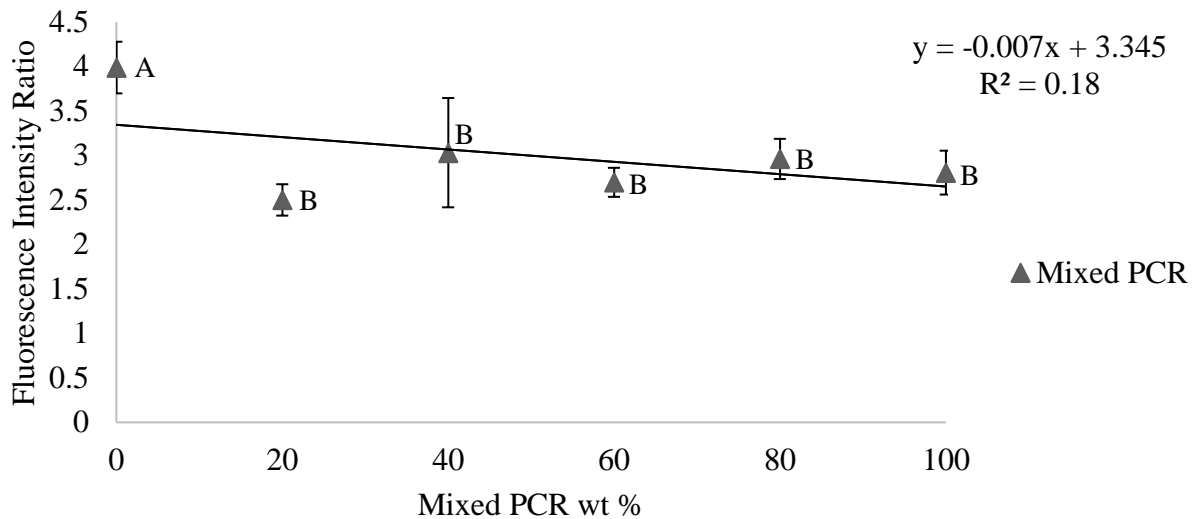

Figure 11. Fluorescence intensity ratio (395 nm/515 nm excited at 300 nm) for mixed PCR. Means separated by different letters are significantly different.

Extractive analysis for regulatory compliance
Total extractives for the white and mixed PCR blends were below the 5.5% limit in n-hexane (Figure 12) and 11.3% limit in xylene (Figure 13) for direct food holding. All blends were below

the 2.6% limit for food holding during cooking (Figure 12) with virgin, 60%, and 100% PCR samples not exceeding the extractives limits for either application. It was assumed that all remaining blends would also fall within the limits because they contained less recycled material than the 100% PCR blends. These results support the use of post-consumer recycled material in food contact applications without compromising safety.
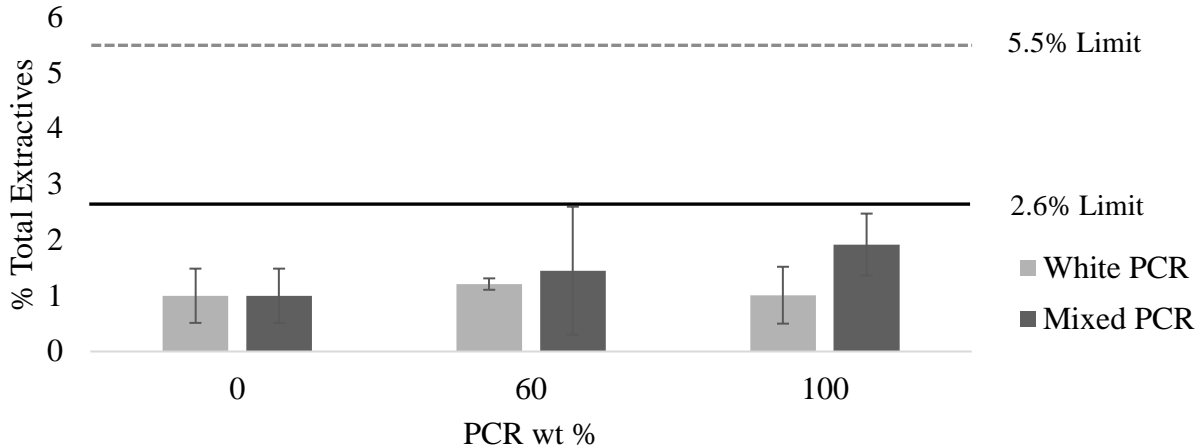

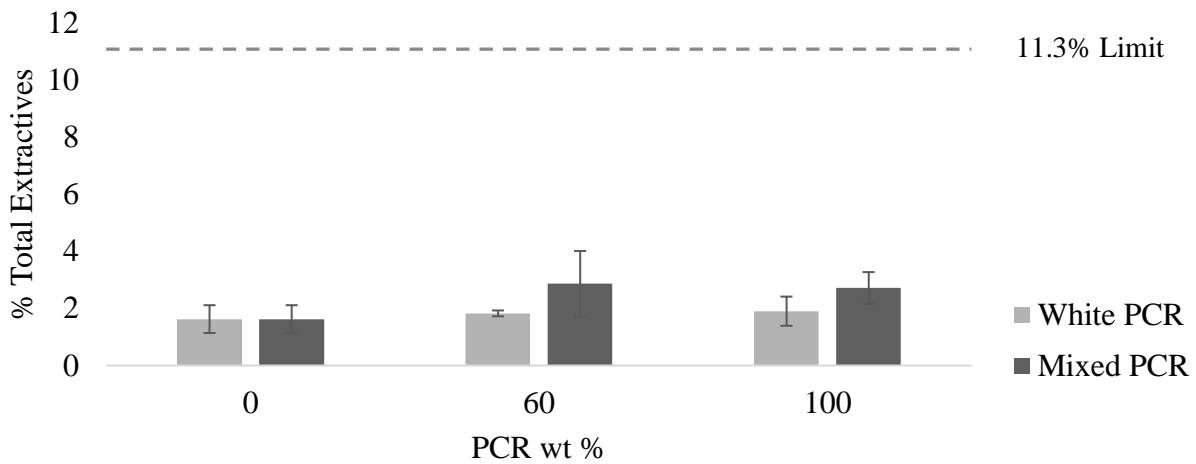Figure 12. Total Extractives in n-hexane for white and mixed PCR

Figure 13. Total Extractives in Xylene for White and Mixed PCR

Conclusion

Linear relationships were observed for PCR content and absorbance, fluorescence intensity ratio, and 5% weight loss temperature. Relationships were not consistent or valid for both white and mixed PCR blends with the exception of UV absorbance between 280 and 400 nm. The results of this study suggest the potential for PCR modeling for polyethylene, particularly using ultraviolet spectroscopy. These results suggest that there are measurable differences between the lower content PCR blends and the higher content PCR blends for both white and mixed PCR. However, determining the differences for the blends mixed between 40-80% PCR/Virgin still poses a challenge. Initially stratification was hypothesized to have interfered in blend characterization. Stratification can be visually observed in feedstock with different size, shape,

and bulk densities such as blending flake and pellet. Results of the research did not see a significant impact from stratification due to the use of uniform pellet feedstocks and efficient mixing by blend, as previously discussed using ash content in Figures 6 and 7. Controlling for stratification during extrusion and investigating linear, non-linear, and mixed modeling methods are necessary to find robust predictive models. A simple model cannot be uniformly applied to all recycled polyethylene blends due to the different effect of pigments and fillers on polyethylene properties. More analysis is needed to evaluate the impact of pigment and PCR individually. Pigment concentration may have impacted these results and needs to be controlled in future studies. The extractions demonstrated that post-consumer recycled material may be safely incorporated into products that have direct food contact applications for holding, packing, and cooking in package. Additional analysis is needed to fully evaluate performance of PCR polyethylene in packaging and product applications including seal strength, tensile strength, and barrier properties.

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