



Test Method

Certification markers for empirical quantification of post-consumer recycled content in extruded polyethylene film

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ABSTRACT

High-density polyethylene is an important polymer for a variety of industrial applications. The pressure for landfill diversion strategies have increased with consumer awareness of traditional end-of-life practices. It is critical to understand the influence of post-consumer recycled polymer (PCR) content on properties and consumer safety as converters blend PCR with virgin resin to increase sustainability. The ability to empirically quantify the PCR content is vital for compliance with minimum content laws. This work determined ~380% increase in UVA absorption, increased carbonyl and terminal vinyl functional groups, a 50% reduction of fluorescence properties, a reduction of the polymer crystal quality, and a ~4 °C increase in the degradation temperature. The extractables content of all PCR blends complied with the Code of Federal Regulations for direct food contact applications. Trends between the measured properties and PCR content identified potential certification markers for empirical quantification of PCR content and single-measurement quality control metrics.

1. Introduction

High-density polyethylene (HDPE) is widely used in agriculture, packaging, and grocery bag applications. HDPE consumed ~38.4% of the overall virgin thermoplastic bottle market in 2015 s only to polyethylene terephthalate [1]. HDPE possesses low degradability in the environment due to its high stability and low susceptibility to environmental conditions without the addition of pro-oxidant additives, thus, the potential of environmental accumulation increases with increasing production. In 2015, approximately 34% of the 1.1 billion pounds of post-consumer resin collected from bottles were recycled, and a vast majority of agricultural waste was either burned or landfilled [1,2]. Most post-consumer reprocessing in the United States is considered secondary recycling, which involves grinding, washing, melting, and reforming products. Secondary recycling removes some contaminants that have been sorbed into or adsorbed onto the polymer during its service life time [3–5]. Indeed, Welle et al. has shown that some washing protocols can remove > 99% of certain contaminant surrogates such as chlorobenzene, toluene, and phenyl cyclohexane [5]. Recycling HDPE has been calculated to consume ~24% less energy than the production of virgin HDPE resin, thus, there is an enormous energy saving potential with recycling in addition to waste diversion

[6].

There is general agreement in literature that degradation proceeds through alkyl radical intermediates from cleavage of main chain covalent bonds [7]. The presence of various catalysts compositions influences the relative degradation product concentrations and mechanism, i.e., chain scission compared to crosslinking [8]. However, in the presence of atmospheric oxygen, the alkyl radicals react with oxygen to form hydroperoxides which undergoes a cascade of subsequent reactions to form various oxygenated species [7,9,10]. Generally, the two main oxidation products (either photo or thermal oxidation) of polyethylene are vinyl and carbonyl compounds (i.e., aldehydes, ketones, esters, alcohols) [11,12]. The carbonyl characteristic bands of infrared spectra have further been deconvoluted into the various carbonyl species which the distribution has been shown to be influenced by the exposure conditions [9]. However, many studies have evaluated the carbonyl content in more general terms through calculation of the carbonyl index (Equation (1)) [8,11,13,14].

Our previous results demonstrated increased UVA absorbance of post-consumer recycled (PCR):virgin polyethylene terephthalate (PET) polymer blends due to PCR incorporation [15,16]. This observation prompted the investigation of similar UVA absorbing properties for other polymer systems as added value beyond sustainability – e.g.,

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increased nutrient retention of fresh cut produce and reduced light induced oxidation and bleaching of packaged meat and cheese products. To date, only polyethylene terephthalate has been investigated with regards to the influence of post-consumer content on polymer properties and the ability to utilize these properties for verification of post-consumer content [16,17]. The objective of the current work was to investigate if the physical property changes identified in PET are applicable to other polymer systems, such as high-density polyethylene. Our work here identified a multitude of potential certification markers useful in the empirical quantification of high-density polyethylene post-consumer content in “off the shelf” products (e.g., such as rigid clam-shell packaging and flexible, reusable plastic bags) with unknown formulation logs made from unknown manufacturers. The empirical quantification of post-consumer recycled content in “off the shelf” products is critical for sustainability certification and compliance with California state law [18,19].

2. Materials and methods

2.1. Sample preparation

Post-consumer high-density polyethylene (PCR-HDPE) and virgin high-density polyethylene (V-HDPE) were blended by hand to obtain PCR:V ratios of 0, 20, 40, 60, 80, and 100% by weight. Each blend was dried at 100 °C to remove adsorbed atmospheric water then extruded with a Killion laboratory scale single screw extruder possessing three barrel heat zones, a coupler heat zone, and thermally controlled two zone coat hanger style die. The barrel heat zones, coupler heat zone, and die temperatures were set to 190.5 °C, 204.4 °C, and 204.4 °C, respectively. The molten extrudate was collected on a J stack take up roller with a fixed distance from the extruder die to the take up rollers. Sample thickness was limited to ~76–127 μm (3–5 mil) to most closely resemble shopping bags which there was recently a 20% minimum post-consumer content mandate in California (SB 270/Proposition 67) [18].

2.2. Ultraviolet–visible spectroscopy

Film samples were fitted into a clamp measuring 12.7 cm × 8.5 cm × 2.3 cm. Ultraviolet–visible (UV–Vis) spectra were collected between 290 nm and 420 nm in absorbance mode using a Tecan Safire microplate reader (Zurich, Switzerland). Specimen thicknesses were measured with a Mitutoyo IP 65 electronic digital micrometer (Kawasaki, Japan). Each specimen clamp was inserted into the sample chamber such that the specimen was aligned perpendicular to the incident irradiation. Each UV–Vis absorbance value measured along the spectrum was divided by the thickness of the specimen to account for differences in path length attributed to thickness variations as noted previously [15].

2.3. Fourier transform infrared spectroscopy

Horizontal attenuated total reflectance-Fourier transform infrared (HATR-FTIR) spectra were collected with a Nicolet 6700 Infrared spectrometer at ambient temperature (Waltham, MA), fitted with a ZnSe crystal stage resulting in 12 sample interactions (reflections). The spectrum of each specimen was collected with 32 scans and a resolution of 2 cm⁻¹. All spectra were baseline corrected prior to analysis with Omnic 8.3 software (Thermo Fisher, Waltham, MA). Definitions of polyethylene structural components were described according to ASTM D5576-00(2013) *Standard Practice for Determination of Structural Features in Polyolefins and Polyolefin Copolymers by Infrared Spectrophotometry (FTIR)* and ASTM D6248-98(2012)e1 *Standard Test Method for Vinyl and Trans Unsaturation in Polyethylene by Infrared Spectrophotometry* [20,21]. The carbonyl index was determined according to the work of Cruz et al. (Equation (1)), where the carbonyl

index was defined as the area ratio of the carbonyl band (~1700 cm⁻¹) to the CH₂ band (~1368 cm⁻¹) [8]. Transmission FTIR spectra were collected using the same instrument with 32 scans and a resolution of 2 cm⁻¹. All spectra were baseline corrected then normalized to the thickness of the scanned region. The carbonyl area and terminal vinyl area were quantified for each transmission spectrum by integrating the area under the thickness normalized intensity (Equations (2) and (3); Fig. 3).

$$\text{Carbonyl Index} = \frac{A_{1740\text{cm}^{-1}}}{A_{1368\text{cm}^{-1}}} \quad (1)$$

$$\text{Carbonyl Area} = \frac{A_{1740\text{cm}^{-1}}}{t} \quad (2)$$

$$\text{Terminal Vinyl Area} = \frac{A_{909\text{cm}^{-1}}}{t} \quad (3)$$

2.4. Fluorescence spectroscopy

Fluorescence intensity measurements were collected with a Tecan Safire microplate reader (Zurich, Switzerland). Scans were performed in 3D fluorescence mode with excitation and emission wavelengths ranging from 300 nm to 600 nm in 5 nm increments at a gain of 100 and a bandwidth of 12 nm. The z-position was held fixed at 14,000 μm with an integration time of 80 μs and 10 flashes.

2.5. Differential scanning calorimetry

Thermal transitions of each PCR:V HDPE blend were measured between 10 °C and 180 °C utilizing a heat/cool/heat cycle at a rate of 10 °C/minute with a TA Instruments Q2000 differential scanning calorimeter (New Castle, DE) in a nitrogen atmosphere. A specimen of each polymer blend (3–6 mg) was singularly loaded into a hermetically sealed T-zero DSC pan and crimped prior to analysis.

2.6. Thermogravimetric analysis

Thermal degradation properties and the associated degradation activation energy of each PCR:V HDPE blend were quantified via modulated thermogravimetric analysis using a TA Instruments Q5000IR thermogravimetric analyzer (New Castle, DE) according to the work of Blaine and Hahn [22]. Samples (5–10 mg) were loaded into an alumina pan then heated at 2 °C/min with continuous modulation amplitude of ± 5 °C with a period of 200 s under a nitrogen atmosphere. Although the kinetic parameters were calculated continuously using MTGA, the reported values were determined at 5% mass loss according to ASTM E1641-16, [23].

2.7. Code of Federal Regulations extractables

The solvent extractable content of each PCR:V HDPE blend was performed according to Code of Federal Regulations Title 21, B, Part 177.1520 to determine compliance for direct food contact applications [24]. A stir bar and 1 L of n-hexane was added to a two necked, 2 L round bottom flask connected to a condenser and a thermometer then heated to 50 °C via a heating mantle. Once the solvent reached 50 °C, 2.5 g of polyethylene sample was added to the extraction apparatus. The sample was exposed to the n-hexane at 50 °C for 2 h then removed from heat and the solvent decanted and filtered into a 2 L Erlenmeyer flask. The mass of solvent was measured before extraction and after filtration to ensure the mass loss was not more than 10% as per the CFR regulation. After the solvent mass was recorded, an additional 50 mL of fresh n-hexane was used to rinse the round bottom flask, filtered, then added to the filtrate. The Erlenmeyer flask was connected to a distillation apparatus and the solvent distilled until approximately 100 mL remained in the Erlenmeyer flask. The remaining solvent was

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