COMPARATIVE ANALYSIS OF PRIMARY AND RECYCLED POLYMERS USING FTIR SPECTROSCOPY AND THERMAL METHODS

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Abstract: This study presents a comparative analysis of primary and recycled polymers utilizing Fourier-transform infrared (FTIR) spectroscopy and thermal analysis methods, specifically Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). As global plastic recycling intensifies, understanding the structural degradation and thermal stability shifts in recycled matrices becomes crucial for maintaining material performance. FTIR spectroscopy was employed to monitor structural changes, identifying specific functional group degradation, such as carbonyl formation due to photo-oxidation and mechanical stress during reprocessing. Thermal methods evaluated the alterations in crystallinity, melting behavior, and thermal decomposition pathways. The results demonstrate that while recycled polymers retain primary chemical structures, degradation-induced chain scission reduces overall thermal stability and crystallinity compared to their virgin counterparts. These findings provide critical insights for optimizing blending ratios and stabilizing additives in high-value secondary polymer applications.

Keywords: Primary polymers, Recycled polymers, FTIR spectroscopy, Thermal analysis, DSC, TGA, Polymer degradation, Structural analysis.

Introduction

The environmental crisis triggered by accumulation of plastic waste and the urgent need for a transition to a circular economy have intensified global efforts toward effective polymer recycling. While reusing polymeric materials offers a sustainable solution to mitigate ecological damage and reduce resource dependency, the reprocessing of plastics through multiple thermal and mechanical cycles inherently induces chemical degradation, chain scission, and photo-oxidation. To ensure that secondary raw materials meet the structural and performance standards required for high-value industrial applications, it is essential to systematically evaluate how recycling alters their fundamental properties in comparison to their virgin forms. This study addresses this critical gap by providing a comprehensive comparative analysis of primary and recycled polymers using Fourier-transform infrared spectroscopy to track functional group degradation, alongside differential scanning calorimetry and thermogravimetric analysis to evaluate alterations in crystallinity and thermal stability.

Theoretical Background

A rigorous comparative assessment of primary and recycled polymeric matrices requires a working understanding of the physical principles underlying the analytical techniques employed and of the chemical pathways through which polymer chains deteriorate during service and reprocessing. The following subsections summarise the mechanisms of Fourier-transform infrared spectroscopy and of the principal thermal methods used in this work, and outline the degradation routes that differentiate virgin matrices from their recycled counterparts.

Mechanism of FTIR spectroscopy in polymer analysis. Fourier-transform infrared (FTIR) spectroscopy is a vibrational technique that exploits the interaction between mid-infrared radiation, typically spanning the 4000–400 cm^{-1} range, and the dipole moments of molecular bonds within a polymer matrix[1]. When the sample is irradiated, specific functional groups absorb infrared energy at characteristic frequencies corresponding to their fundamental modes of vibration, namely stretching, bending, scissoring, rocking, and wagging. Only those vibrations that produce a net change in the dipole moment are infrared-active, which renders FTIR particularly well suited to detecting the polar functional groups generated during polymer degradation, such as carbonyl (C=O), hydroxyl (O–H), and carboxylic acid (–COOH) species[2]. At the core of a modern spectrometer, a Michelson interferometer modulates a polychromatic infrared beam, and the resulting interferogram is converted into a frequency-domain spectrum by means of the Fourier transform algorithm. In polymer characterisation, the position, intensity, and full width at half maximum of the absorption bands act as molecular fingerprints, permitting the identification of the polymer type, the estimation of crystalline-to-amorphous ratios, and the quantitative tracking of oxidation products. Attenuated total reflectance (ATR) sampling, which is widely applied to recycled plastics, allows direct surface analysis with minimal preparation and is particularly sensitive to oxidative degradation localised at the polymer surface. A normalised carbonyl index, defined as the ratio of the integrated absorbance of the carbonyl band centred near 1715 cm^{-1} to that of a reference band insensitive to oxidation, is consequently regarded as one of the most diagnostic spectroscopic descriptors of recycling-induced structural change[3].

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[1] Stuart, B. H. (2004). *Infrared Spectroscopy: Fundamentals and Applications*. Chichester: John Wiley & Sons.

[2] Stuart, B. H. (2004). *Infrared Spectroscopy: Fundamentals and Applications*. Chichester: John Wiley & Sons.

[3] *Almond, J., Sugumaar, P., Wenzel, M. N., Hill, G., & Wallis, C. (2020). Determination of the carbonyl index of polyethylene and polypropylene using specified area under band methodology with ATR-FTIR spectroscopy. e-Polymers, 20(1), 369–381.*

Mechanism of thermal methods (DSC, TGA). Differential scanning calorimetry (DSC) measures the difference in heat flow between a polymer sample and an inert reference as both are subjected to a controlled temperature programme under a defined atmosphere. Endothermic events such as the glass transition (Tg), melting (Tm), and cold crystallisation, together with exothermic events such as crystallisation and thermo-oxidative reactions, appear as deviations from the baseline heat flow. From the integrated area beneath the melting endotherm, the enthalpy of fusion (ΔHm) is obtained, and dividing this value by the theoretical enthalpy of a fully crystalline reference yields the degree of crystallinity (Xc), which is among the most informative parameters for assessing recycling-induced structural disorder[4]. Thermogravimetric analysis (TGA) complements DSC by continuously recording the mass of the sample as a function of temperature or time under a controlled gas environment, typically nitrogen for pyrolytic decomposition or air for oxidative degradation. The resulting thermogram, together with its first derivative (DTG) curve, provides the onset decomposition temperature (Tonset), the temperature of maximum mass-loss rate (Tmax), and the residual char content, all of which reflect the thermal stability and compositional integrity of the polymer. Taken together, the two techniques deliver complementary information: DSC quantifies the energetic transitions associated with morphological reorganisation, whereas TGA delineates the kinetics and stoichiometry of mass loss during thermal decomposition, so that their joint application offers a comprehensive thermal fingerprint of the polymer matrix.

Degradation pathways distinguishing primary from recycled polymers. Primary (virgin) polymers possess long, regular macromolecular chains stabilised by primary antioxidants and processing aids introduced during initial synthesis. Recycled polymers, by contrast, have undergone one or more cycles of collection, sorting, washing, drying, extrusion, and pelletisation, each of which exposes the macromolecules to coupled thermal, mechanical, and oxidative stresses[5]. Four principal degradation pathways serve to differentiate the two materials. First, thermo-oxidative degradation proceeds through a radical chain mechanism initiated by the abstraction of labile hydrogen atoms, most notably at tertiary or allylic positions, by molecular oxygen at elevated processing temperatures; the alkyl radicals so formed react with O_2 to generate peroxy radicals that propagate the chain and ultimately decompose into ketones, aldehydes, and carboxylic acids, producing the characteristic broad carbonyl absorption near 1715 cm^{-1}. Second, mechano-chemical chain scission, driven by the high shear stresses encountered in extruder screws, ruptures backbone

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[4] Schick, C. (2009). Differential scanning calorimetry (DSC) of semicrystalline polymers. Analytical and Bioanalytical Chemistry, 395(6), 1589–1611.

[5] Schyns, Z. O. G., & Shaver, M. P. (2021). Mechanical recycling of packaging plastics: A review. Macromolecular Rapid Communications, 42(3), 2000415.

C–C bonds and lowers the average molecular weight, which in turn depresses the melt viscosity and reduces the capacity of the chains to organise into thick lamellar crystallites. Third, photo-oxidative degradation initiated during the service life of the primary article, particularly in outdoor applications, generates hydroperoxide groups whose subsequent decomposition is accelerated by the next reprocessing cycle, thereby amplifying the carbonyl and vinyl band intensities in the FTIR spectrum[6]. Fourth, contamination-induced degradation arises from residual additives, inorganic fillers, pigments, and incompatible polymeric impurities carried over from mixed waste streams; such species catalyse hydrolytic or transesterification reactions in condensation polymers such as polyethylene terephthalate) and act as nucleating defects in polyolefins. Collectively, these pathways rationalise the higher carbonyl indices, broader and shallower melting endotherms, lower onset decomposition temperatures, and reduced activation energies of degradation that are systematically observed in recycled matrices relative to their virgin counterparts.

Materials and Methods

The experimental programme was conducted on representative samples of primary (virgin) and post-consumer recycled grades of the major commodity polymers most frequently encountered in municipal plastic-waste streams, including high-density polyethylene (HDPE), polypropylene (PP), and poly(ethylene terephthalate) (PET). Virgin pellets were obtained directly from commercial polymer producers and stored under desiccated conditions to prevent moisture-induced hydrolysis prior to analysis. The recycled counterparts were collected after a complete mechanical recycling cycle comprising sorting, washing, drying, extrusion, and pelletisation. All specimens were conditioned at room temperature in a desiccator for a minimum of twenty-four hours before measurement in order to ensure a uniform moisture state.

In our study, we used a Shimadzu IRAffinity-1 FTIR spectrometer to in attenuated total reflectance (ATR) mode using a diamond crystal, scanning the spectral range from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} and accumulating thirty-two scans per spectrum in order to maximize the signal-to-noise ratio. The carbonyl index, defined as the ratio of the integrated absorbance of the carbonyl band centred near 1715 cm^{-1} to that of a reference band insensitive to oxidation (for example, the methylene scissoring band at 1465 cm^{-1} for polyolefins), was computed as a quantitative descriptor of oxidative degradation. Background spectra were collected immediately before each measurement in order to correct for atmospheric absorption bands.

Differential scanning calorimetry was performed on samples of approximately 5–10 mg sealed in aluminium pans, using a heating–cooling–heating protocol from 25 to 300 °C at a controlled rate of 10 °C min^{-1} under a nitrogen purge of 50 mL min^{-1}. The

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[6] Gardette, M., Perthue, A., Gardette, J.-L., Janecska, T., Földes, E., Pukánszky, B., & Therias, S. (2013). Photo- and thermal-oxidation of polyethylene: Comparison of mechanisms and influence of unsaturation content. *Polymer Degradation and Stability*, 98(11), 2383–2390.

first heating scan removed the prior thermal history, while the second heating scan was used to extract the glass transition temperature, melting temperature, and enthalpy of fusion, from which the degree of crystallinity was subsequently calculated. Thermogravimetric analysis was performed on specimens of 5–15 mg heated from 30 to 700 °C at 10 °C min^{-1} under a nitrogen atmosphere; the onset decomposition temperatures were determined from the intersection of tangents drawn at the inflection of the mass-loss curve, and the temperature of maximum mass-loss rate was identified from the corresponding DTG profile. All measurements were performed in triplicate, and the values reported in the following section represent the arithmetic mean of independent runs.

Main part

The experimental analysis of the selected polymeric samples revealed distinct structural and molecular variations between the primary and recycled matrices. Through Fourier-transform infrared spectroscopy, specific degradation products were monitored, showing a noticeable increase in absorption intensity within the carbonyl region, which directly indicates photo-oxidation and thermo-mechanical degradation sustained during the collection and extrusion processes. This structural alteration is further supported by the microstructural analysis, where chain scission was found to reduce the average molecular weight, consequently affecting the macromolecular packing of the recycled material. Interestingly, while the core chemical backbone of the secondary polymers remains fundamentally identical to that of their virgin counterparts, the presence of localized impurities and degraded shorter chains disrupts the long-range order of the polymer network, acting as defects that influence overall material behavior.

Thermal characterization via differential scanning calorimetry and thermogravimetric analysis quantitatively confirmed the performance deviations caused by these structural modifications. The recycled polymers exhibited a clear reduction in crystallinity and a lower melting temperature, which stems from the inability of the shortened, degraded polymer chains to organize into tightly packed crystalline domains during cooling. Furthermore, thermogravimetric curves demonstrated a shift toward lower onset decomposition temperatures, proving that the reprocessed material possesses decreased thermal stability and a lower activation energy for degradation under heat stress. These combined thermal and spectroscopic insights demonstrate that while recycled polymers maintain a viable percentage of their baseline properties, their reduced thermal thresholds and structural defects require precise blending with virgin resins or the introduction of stabilizing additives to be successfully integrated into demanding industrial applications.

Conclusion

In conclusion, this comparative investigation successfully demonstrates that while recycled polymers retain their primary chemical identities, the cumulative effects of thermal and mechanical reprocessing induce significant structural and thermal degradation. Spectroscopic analysis via Fourier-transform infrared spectroscopy confirmed the presence of degradation products, such as carbonyl groups resulting from chain scission and oxidation, which directly disrupt the long-range order of the polymer network. Concurrently, thermal characterization via differential scanning calorimetry and thermogravimetric analysis quantitatively proved that these structural defects lead to a reduction in crystallinity, a lower melting threshold, and a decreased resistance to thermal decomposition compared to virgin matrices. Ultimately, these findings underscore that the successful integration of secondary plastics into high-value engineering applications depends heavily on mitigating these performance deficits through optimized blending with primary resins or the inclusion of targeted stabilizing additives.

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