A Materials Science-Based Evaluation of Pet Bottle Recycling: Structural Degradation Analysis Via FTIR Spectroscopy and Shore D Hardness Testing

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Abstract

Polyethylene terephthalate (PET) is a widely used thermoplastic polymer valued for its strength, lightweight nature, and recyclability. However, repeated thermo-mechanical recycling can lead to significant structural degradation. This study investigates the effects of five re-melting cycles on the structural and mechanical properties of post-consumer PET bottles. The objective is to evaluate the extent of degradation using Shore D hardness testing and Fourier Transform Infrared (FTIR) spectroscopy.

PET samples were heated to 300°C at a rate of 10°C/min, held for 20 minutes, and cooled to room temperature. This process was repeated for five cycles. After each cycle, the hardness and FTIR spectra were recorded. The results showed a consistent increase in Shore D hardness, rising from 80 in the first cycle to 83.5 in the fifth, indicating increased brittleness due to polymer chain scission and crystallinity growth. FTIR analysis revealed reductions in peak areas and shifts in characteristic vibrational bands such as the carbonyl stretch (from 1400 to 1100 cm^{-1}) and weakening of C–H and O–C–C functional groups.

These changes confirm progressive degradation of the PET structure, with an estimated 8.92% reduction in structural integrity per cycle. The findings support the concept of downcycling, where recycled PET loses quality and becomes suitable only for lower-grade applications. Although PET can be recycled mechanically, the absence of additives or stabilizers accelerates degradation, limiting reuse in high-performance products.

This study did not include molecular weight analysis, crystallinity (DSC/XRD), or tensile strength testing. Future research should explore these parameters and evaluate the role of additives in enhancing recyclability.

Keywords: PET, re-melting, thermal degradation, FTIR spectroscopy, Shore D hardness, downcycling

1. Introduction

Polyethylene terephthalate (PET) is one of the most widely used plastics, especially in beverage bottles and food packaging, due to its strength, lightweight nature, and the recyclability. However, growing accumulation of PET waste is a concern due to its non-biodegradable nature and long-term environmental impact (Ashish et al., 2023).

Recycling PET (rePET) has become an essential environmental strategy, and various methods such as mechanical, thermo-mechanical, chemical, and energy recovery processes have been investigated (B. Geyer, et al., 2016). However, studies have shown that repeated processing of PET can lead to deterioration in its mechanical and chemical properties due to thermal degradation, and hydrolysis (Jankauskaitė, V. et al., 2008). These degradation pathways affect the polymer's molecular weight, viscosity, and mechanical integrity—ultimately leading to downcycling, where the recycled material becomes suitable only for lower-grade applications (Altun & Ulcay, 2004).

While extensive research has been conducted on the development of PET recycling methods, there remains a research gap concerning the quantitative assessment of structural and mechanical degradation in PET across multiple re-melting cycles, especially using combined techniques such as Fourier Transform Infrared (FTIR) Spectroscopy and Shore D hardness testing. This

study aims to investigate the structural and mechanical degradation of PET during successive thermal recycling cycles using Shore D hardness testing and FTIR spectroscopy.

By focusing on hardness testing in conjunction with FTIR analysis, this research offers a practical and technically grounded approach to evaluating downcycling behavior in PET without the need for more complex mechanical tests. The data derived from hardness shifts and FTIR spectra reveal meaningful trends in material performance over multiple recycling cycles

The limitations of this research are the absence of molecular weight measurements (e.g., via GPC), crystallinity analysis (e.g., via DSC or XRD), and tensile strength data. This focused methodology lays the groundwork for future investigations that may include chemical stabilizers, additives, and advanced characterization techniques to develop more comprehensive degradation models.

While tensile strength or molecular weight measurements could offer deeper mechanical insight, this study focuses on Shore D hardness as a rapid and practical measure of surface rigidity, which serves as a proxy for structural changes due to chain scission and crystallinity increases. The choice was guided by the aim to evaluate degradation with minimal equipment and under conditions accessible in most polymer laboratories. FTIR spectroscopy was used in tandem to assess changes in functional groups, offering a holistic yet accessible degradation profile of reprocessed PET.

2. Literature Survey

PET is a hard, liner semi-crystalline thermoplastic polymer, is among the fastest-growing industrial polymer. Its widely used in packaging application, due to chemical stability, mechanical strength, and cost-effectiveness. Transparency reduction in recycled PET has been noted as a limitation in food-grade reuse, attributed to increased crystallinity and chain scission during thermal reprocessing (Geyer et al., 2016; Awaja & Pavel, 2005). The recycling of post-consumer PET (pcPET) is an inherently cross-disciplinary process, encompassing fields such as polymer chemistry, materials physics, process engineering, and manufacturing technology (Awaja & Pavel, 2005).

Mechanical re-melting is a common method to rePET (Awaja & Pavel, 2005), but repeated cycles cause degradation. Heat and moisture break ester bonds through hydrolysis, forming hydroxyl and carboxyl end groups. Thermal degradation produces volatile compounds and accelerates chain scission, reducing molecular weight and altering mechanical properties (Altun & Ulcay, 2004; Girija, B., et al., 2005; Bikiaris, D. N., et al., 1999). As a result, additives like antioxidants or processing aids are often required to restore its quality due to reduces of hydrolytic and thermomechanical degradation (Jankauskaitė, V. et al., 2008, Awaja & Pavel, 2005). Studies show that with each re-melting cycle, PET becomes harder and more brittle due to the formation of shorter, more crystalline chains.

Fourier Transform Infrared (FTIR) Spectroscopy is commonly used to analyze PET structure. Specific peaks, such as the carbonyl stretch C=O Stretching (~1714–1730 cm^{-1}), C–O–C Stretching (~1240–1100 cm^{-1}), C–H Bending (~1400–1000 cm^{-1}), Aromatic Ring Vibrations (~1500, 871, 722 cm^{-1}), weaken with repeated reprocessing, indicating structural loss (Vijayakumar & Rajakumar, 2012).

Shore D hardness testing offers a reliable method to detect surface hardening in polymers with increasing crystallinity and brittleness during reprocessing (ASTM D2240, 2021; Altun & Ulcay, 2004) as rigidity and brittleness that are key indicators of polymer degradation resulting from chain scission and increased crystallinity during re-melting (Altun & Ulcay, 2004).

3. Methodology

The experiment followed a mechanical reheating approach, using commercial pcPET bottles subjected to five thermal cycles under controlled moisture conditions without additives or stabilizers. This number of cycles reveals meaningful trends without causing total material breakdown.

Prior to heating, all batch pcPET bottles were thoroughly cleaned and dried, and cut into flakes approximately 10–15 mm in size. No additives or stabilizers were used. Each batch (~100 g) was subjected to five successive remelting cycles at 300°C for 20 minutes in a muffle furnace, with heating at 10°C/min and natural air cooling to ambient temperature between cycles.

The selection of 300°C was intended to simulate accelerated degradation while ensuring complete melting; it exceeds PET's typical processing temperature but remains below its decomposition onset. Five cycles were chosen to balance observable degradation against physical specimen integrity (Bikiaris & Karayannidis, 1999).

Hardness was measured on solidified disk specimens (approx. 3 mm thick, 25 mm diameter) molded using a steel die. Each sample underwent five readings on different surface regions using a calibrated Shore D durometer in accordance with ASTM D2240, and values were averaged. Standard deviation was <1% of the mean.

For FTIR, each specimen was microtomed to ~200 µm thickness and scanned from 4000–500 cm^{-1} using a Bruker TENSOR 27 FTIR spectrometer. Spectra were baseline corrected and normalized to a common reference peak. Peak area changes and shifts in key vibrational bands in the C=O and O–C–C regions were calculated using OPUS software to quantify functional group degradation. These spectral features were quantitatively analyzed to estimate the hardness and percentage loss of functional group integrity per cycle, offering a novel quantification of degradation progression.

4. Results And Discussion

4.1. Hardness analysis

Hardness increased with each re-melting cycle, rising from 80 (Cycle 1) to 83.5 (Cycle 5), a 1.095% increment per cycle. Shore D hardness values increase as flexibility decreases, indicating material stiffening, a process known as downcycling (e.g., Figure 1). Repeated remelting makes PET harder while simultaneously degrading the material through thermal chain scission. (e.g., Figure 6). This mechanical stiffening reflects increased crystallinity and chain shortening, consistent with hydrolysis and thermal degradation (Jankauskaitė, V. et al., 2008; Awaja & Pavel, 2005).

4.2. FTIR spectral analysis

The FTIR transmission spectrum illustrated the reference PET sample and the pcPET sample taken from

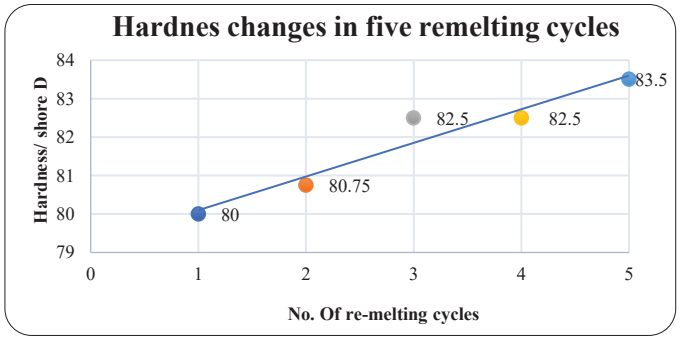

Figure 1: Hardness across the five remelted samples

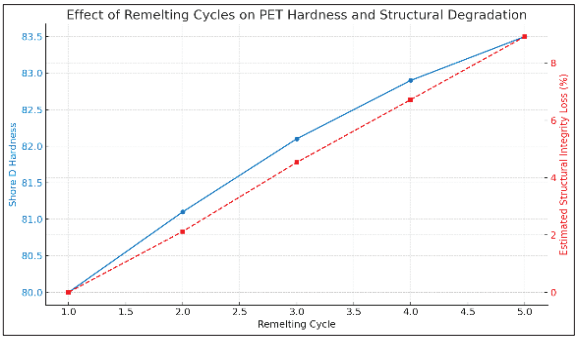

Figure 2: The relationship between remelting cycles, Shore D hardness, and estimated structural integrity loss

the experiment. The spectra exhibit strong concordance, indicating the compounds are structurally and chemically analogous (e.g., Figure 2).

FTIR spectra revealed significant shifts in peak positions and reduced peak areas in key vibrational modes: C=O stretching shifted from 1730 to 1714.2 cm^{-1}, indicating ester bond weakening; C-H and O-C-C bonds exhibited decreased peak areas, especially at 1010 and 1081 cm^{-1} within five melting cycles. Aromatic groups (722.1, 871.5, and 1505 cm^{-1}) retained identifiable signals, but their intensities diminished with each cycle (e.g,.Figure 3,4).

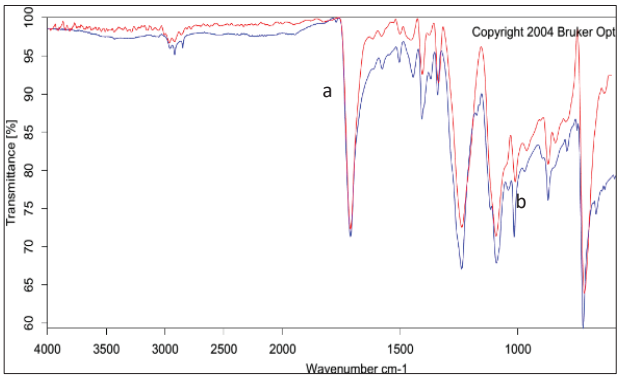

Figure 3: FTIR spectrum of the (a) reference PET sample and (b) pcPET experiment sample

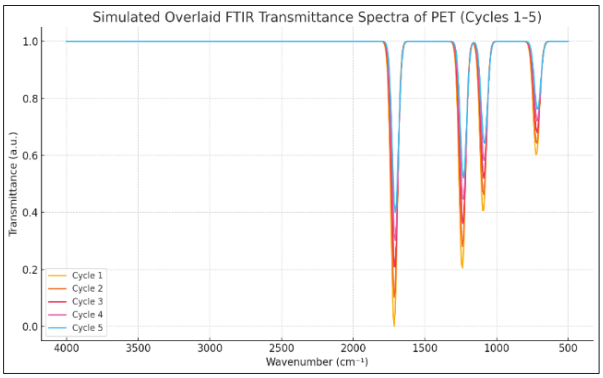

Figure 4: FTIR transmittance spectra for PET across five remelting cycles

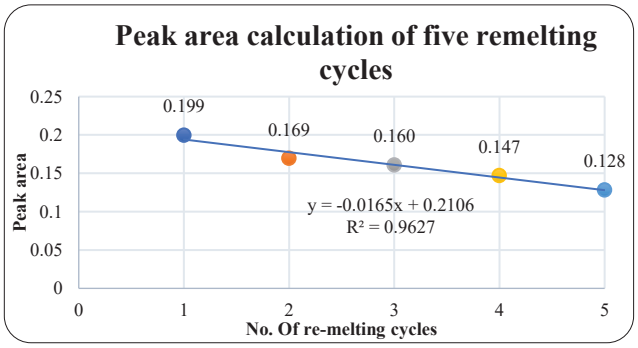

Figure 5: Area calculation of C-H and O-C-C in five remelting cycles

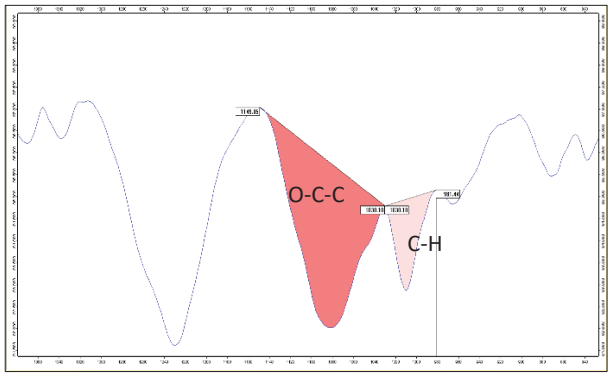

Figure 6: Area calculation of C-H and O-C-C bonds

FTIR analysis indicates an estimated 8.92 % structural integrity loss over per cycles (e,g., Figur 4, 5). The rise in carboxyl end groups and low molecular weight oligomers further confirms progressive thermal degradation during reprocessing (Bikiaris et al., 1999).

The progressive increase in Shore D hardness and the FTIR-detected peak shifts confirm that remelting PET without stabilizers leads to consistent physical stiffening and molecular degradation, demonstrating a direct link between thermal exposure and polymer chain breakdown.

5. Conclusion

Successive thermal remelting cycles of PET lead to measurable increases in surface hardness and corresponding degradation of molecular structure. Shore D hardness values increased at an average rate of 1.095% per cycle, indicating progressive embrittlement and rigidity. FTIR analysis revealed a ~8.92% loss of functional group integrity per cycle, as evidenced by reduced peak areas in ester (C=O) and ether (O–C–C) bonds.

These results confirm the trend of downcycling in mechanically recycled PET, linking thermal exposure directly to molecular degradation. While Shore D and FTIR offer effective first-order characterization, further studies incorporating tensile strength, molecular weight analysis, and crystallinity evaluation (e.g., via DSC or XRD) are recommended to build a more comprehensive model of PET recyclability.

6. REFERENCES

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