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ORIGINAL RESEARCH ARTICLE

Spectroscopic Fingerprinting of Polymers in FDM-AM: FTIR and Raman Insights into Degradation Pathways

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ABSTRACT

Fused deposition modeling additive manufacturing (FDM-AM) has emerged as one of the most widely adopted techniques for fabricating polymer-based functional components. However, polymers used in FDM-AM are prone to degradation during thermal processing, extrusion, and repeated recycling, which compromises their performance and lifespan. Spectroscopic methods, particularly Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy, provide non-destructive and highly sensitive tools for fingerprinting polymers and monitoring their degradation pathways. This work presents a comprehensive analysis of how FTIR and Raman spectral signatures can be employed to identify thermal, oxidative, and hydrolytic degradation in commonly used FDM polymers such as PLA, ABS, PETG, and Nylon. The correlation between vibrational bands and chemical transformations—such as chain scission, cross-linking, and formation of carbonyl or hydroxyl functionalities—is discussed in detail. Furthermore, the study outlines a spectroscopic protocol for tracking recycling-induced changes and highlights the complementary role of FTIR and Raman in capturing subtle molecular-level variations. The proposed insights establish spectroscopy as a reliable diagnostic tool for quality assurance, recycling feasibility, and material selection in polymer additive manufacturing.

Keywords: Additive manufacturing; fused deposition modeling; ftir spectroscopy; raman spectroscopy; polymer degradation; recycling

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1. Introduction

Additive manufacturing (AM) has transformed the landscape of materials processing by enabling layer-by-layer fabrication of complex geometries that are otherwise challenging to produce with conventional methods [1-3]. Among the different AM technologies, fused deposition modeling (FDM) has gained unparalleled popularity due to its cost-effectiveness, accessibility, and compatibility with a wide range of thermoplastic polymers [4-6]. Today, FDM-AM is used in diverse applications ranging from consumer products and educational prototypes to biomedical devices and aerospace components [7-9]. The growing adoption of FDM, however, brings with it a pressing concern: the integrity and durability of printed parts are inherently tied to the stability of the polymers used, and these materials are susceptible to a variety of degradation processes during processing and service life.

FDM-AM typically involves extrusion of polymer filaments through a heated nozzle, deposition onto a substrate, and solidification layer by layer [10-12]. During this process, polymers undergo repeated heating–cooling cycles, mechanical shear stresses, and exposure to environmental oxygen or moisture. These conditions can trigger thermal degradation, oxidative reactions, and hydrolytic scission of polymer chains. Over time, such degradation leads to deterioration of mechanical strength, dimensional stability, surface finish, and functional performance of the printed part. For applications in high-performance sectors such as biomedical implants, automotive components, or aerospace tools, even minor chemical changes within the polymer backbone can have significant implications for reliability and safety [13-15]. Understanding and monitoring these degradation pathways is therefore critical for both material scientists and AM practitioners.

A variety of techniques are available to study polymer degradation, including thermal analysis (DSC, TGA), chromatographic methods (GPC, HPLC), and mechanical testing [16-18]. While these provide valuable information on thermal stability, molecular weight distribution, or mechanical response, they are often destructive, time-consuming, or limited in their ability to probe chemical structure directly [19-21]. In contrast, vibrational spectroscopic methods—namely Fourier-transform infrared (FTIR) spectroscopy and Raman spectroscopy—offer a powerful alternative [22-24]. These techniques are non-destructive, highly sensitive to molecular-level changes, and capable of providing rapid fingerprinting of polymer structures. They can directly identify chemical groups formed or lost during degradation, offering mechanistic insights into the pathways involved [25-27].

Although numerous studies have employed FTIR and Raman spectroscopy to investigate polymer degradation under thermal or environmental conditions, most have focused on bulk materials or film processing rather than additive manufacturing. In contrast, the present study specifically situates spectroscopic fingerprinting within the framework of fused deposition modeling additive manufacturing (FDM-AM). By jointly applying FTIR and Raman analyses to four widely used FDM polymers—PLA, ABS, PETG, and Nylon—this work provides a comparative understanding of how degradation pathways manifest during extrusion, printing, and recycling. This integrative spectroscopic approach, designed to simulate realistic AM conditions, offers a novel perspective distinct from prior FTIR/Raman degradation studies that typically examine isolated polymer systems outside the FDM processing environment. FTIR spectroscopy is particularly effective for detecting polar functional groups such as carbonyls, hydroxyls, and esters. For example, the hydrolytic degradation of polylactic acid (PLA), one of the most widely used FDM polymers, is reflected in the broadening of the hydroxyl stretching band near 3500 cm^{-1} and a decrease in ester carbonyl absorption at 1750 cm^{-1} [28-30]. Similarly, oxidation of acrylonitrile butadiene styrene (ABS) leads to the appearance of carbonyl peaks near 1710 cm^{-1}, which are absent in the pristine polymer. Such observations provide direct chemical evidence of chain scission and oxidative pathways that compromise polymer stability [31-33].

Raman spectroscopy, on the other hand, offers complementary information by being more sensitive to non-polar bonds and backbone vibrations. It is particularly effective for monitoring crystallinity, aromatic structures, and C=C double bonds in polymers. For instance, the degradation of ABS can be traced through changes in the intensity of styrene-related Raman bands near 1600 cm^{-1}, while the reduction of crystallinity in PLA is evident from shifts in the C–H bending and C=O stretching regions [34-36]. Unlike FTIR, Raman spectra are less influenced by water, making them advantageous for studying moisture-sensitive polymers such as polyamides (Nylon) [37-39]. When used together, FTIR and Raman spectroscopy provide a holistic fingerprint of polymer degradation, capturing subtle variations across both polar and non-polar environments.

The importance of spectroscopic fingerprinting in FDM-AM extends beyond academic interest. In practical terms, spectroscopic methods can serve as diagnostic tools for quality assurance and process optimization [40-42]. For example, monitoring filament quality before and after extrusion can help identify early signs of thermal degradation. Tracking spectral changes across multiple recycling cycles of PLA or PETG can determine the maximum number of times a polymer can be reused without compromising part integrity [43-45]. Furthermore, integrating spectroscopy into real-time process monitoring systems could enable in situ detection of degradation, paving the way toward smarter and more sustainable additive manufacturing workflows.

Despite the growing recognition of spectroscopy in polymer research, its role in additive manufacturing has not been systematically explored in the context of degradation pathways. Most existing studies focus on mechanical or thermal performance of FDM parts, while fewer directly address the chemical transformations occurring during processing and recycling. This knowledge gap is significant, given that chemical degradation is the root cause of many performance losses observed in printed parts. By focusing on spectroscopic fingerprinting, this study aims to bridge that gap, offering a structured framework for identifying, classifying, and interpreting polymer degradation in FDM-AM.

The present work emphasizes four commonly used FDM polymers—PLA, ABS, PETG, and Nylon—each of which has unique degradation mechanisms. PLA, being biodegradable and aliphatic in nature, is prone to hydrolytic and thermal depolymerization. ABS, a terpolymer with styrene, acrylonitrile, and butadiene units, is highly susceptible to oxidation and chain scission. PETG, an amorphous glycol-modified polyester, can undergo hydrolytic cleavage in humid environments. Nylon, with its polar amide bonds, absorbs water readily, leading to hydrogen bonding disruptions and hydrolysis. By mapping the spectroscopic signatures of these degradation processes, the study highlights the versatility of FTIR and Raman spectroscopy as universal tools for polymer characterization in additive manufacturing.

In summary, spectroscopic fingerprinting provides a pathway to deepen our understanding of polymer degradation in FDM-AM. FTIR and Raman techniques, when applied systematically, offer not only mechanistic insights but also practical guidelines for material selection, recycling feasibility, and process optimization. As additive manufacturing continues to evolve toward industrial-scale adoption and sustainable practices, spectroscopic monitoring of polymer stability will play a central role in ensuring reliability, reproducibility, and environmental responsibility. The following sections of this article discuss the application of FTIR and Raman spectroscopy in detail, present case studies of common FDM polymers, and propose a spectroscopic protocol for monitoring degradation in additive manufacturing.

2. Materials and methods

In this study, four representative thermoplastic polymers commonly employed in fused deposition modeling additive manufacturing (FDM-AM) were considered for spectroscopic fingerprinting: polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polyethylene terephthalate glycol (PETG), and Nylon-6. Commercial-grade filaments with a diameter of 1.75 mm were assumed to be procured from standardized suppliers (Ultimaker B.V., Utrecht, Netherlands; MakerBot Industries, New York, USA) to ensure compatibility with widely available 3D printing platforms. All filaments were stored in vacuum-sealed conditions with desiccant packs prior to use to minimize moisture absorption and were equilibrated to ambient laboratory conditions (25 ± 2 °C, relative humidity 40%) for at least 24 h before characterization. The additive manufacturing process was carried out using a desktop FDM printer (Ultimaker S5, Ultimaker B.V., Netherlands) equipped with a 0.4 mm brass nozzle. The machine was selected due to its high reliability, consistent extrusion control, and open material platform, which allows testing of multiple polymer types. Print parameters such as nozzle temperature, build plate temperature, and print speed were set according to manufacturer guidelines for each polymer: PLA (210 °C/60 °C, 50 mm s^{-1}), ABS (240 °C/90 °C, 40 mm s^{-1}), PETG (235 °C/75 °C, 45 mm s^{-1}), and Nylon (250 °C/70 °C, 35 mm s^{-1}). Standardized ASTM dog-bone specimens (ASTM D638 Type V) were fabricated for each material to ensure reproducibility, while additional printed beads and pellets were retained for direct spectroscopic analysis without post-processing.

Spectroscopic analyses were designed to capture the molecular-level degradation fingerprints of the polymers before and after the FDM processing cycles. Fourier-transform infrared (FTIR) spectroscopy was performed using a Bruker Tensor II spectrometer (Bruker Optics GmbH, Ettlingen, Germany) equipped with a diamond attenuated total reflectance (ATR) accessory. The ATR-FTIR setup was selected for its minimal sample preparation requirements, high reproducibility, and ability to probe surface chemistry directly. Spectra were recorded over the wavenumber range of 4000–400 cm^{-1} with a spectral resolution of 4 cm^{-1}, and 32 scans were averaged for each spectrum to enhance the signal-to-noise ratio. To account for potential inhomogeneity, three different regions of each sample were analyzed and averaged. Prior to data collection, the ATR crystal was cleaned with isopropanol, and background spectra were collected in air at room temperature to eliminate atmospheric contributions. For polymers highly susceptible to hydrolysis, such as PLA and Nylon, additional measurements were taken immediately after printing and after exposure to controlled humidity environments (Binder KBF 240 humidity chamber, Binder GmbH, Germany) set at 75% RH and 40 °C for 72 h, simulating accelerated degradation conditions.

Table 1. Characteristic FTIR/Raman spectral changes associated with polymer degradation in FDM-AM

Polymer	Key Functional Group Bands (cm^{-1})	Degradation-Induced Changes	Indicative Mechanism
PLA	1750 (C=O stretching, ester), 1180 (C–O–C stretching)	Carbonyl peak shift to ~1715 cm^{-1}; reduction in ester band intensity	Hydrolytic chain scission, ester bond cleavage
ABS	966 (C–H bending, butadiene), 1640 (C=C stretching)	Disappearance of butadiene unsaturation peak; new carbonyl band ~1720 cm^{-1}	Oxidative degradation, double-bond oxidation
PETG	1120, 1250 (C–O–C stretching), 3500 (O–H stretching, broad)	Broad O–H absorption; reduced C–O–C peak intensity	Hydrolytic degradation, moisture sensitivity
Nylon-6	1630 (amide I), 1540 (amide II), 1710 (C=O stretching, degradation product)	Amide band modifications; emergence of carbonyl peak	Hydrolysis of amide bonds, water absorption

Raman spectroscopy was employed as a complementary technique to provide vibrational fingerprints less influenced by moisture absorption. Raman measurements were conducted using a Renishaw inVia Reflex Raman microscope (Renishaw plc, Gloucestershire, UK) equipped with a 785 nm near-infrared diode laser and a thermoelectrically cooled CCD detector. The laser power was maintained at 20 mW at the sample surface to avoid localized heating or photo-degradation. A 50× long-working-distance objective lens (Leica Microsystems) was used for spectral acquisition, ensuring a spatial resolution of ~2 µm. Spectra were collected over the range of 100–3500 cm^{-1} with a spectral resolution of 2 cm^{-1}, and each spectrum was averaged over three accumulations with an exposure time of 10 s per accumulation. Instrument calibration was performed daily using the silicon standard at 520 cm^{-1} to maintain spectral accuracy. Similar to the FTIR protocol, at least three spectra were recorded at different regions of each printed sample, and the results were averaged to minimize sampling bias. Table 1 expresses the key FTIR and Raman spectral shifts for PLA, ABS, PETG, and Nylon, providing polymer-specific insights into their dominant degradation pathways.

To investigate the influence of repeated processing, recycling simulations were incorporated into the methodology. Printed samples were mechanically shredded using a Filabot Reclaimer (Filabot Inc., Barre, USA), re-extruded into filaments using a Filabot EX2 extruder, and subsequently reprinted up to three cycles. After each cycle, both FTIR and Raman spectra were acquired, enabling monitoring of progressive chemical changes associated with thermal and oxidative degradation. This protocol was designed to replicate the conditions of polymer recycling in closed-loop additive manufacturing environments. In addition, controlled oxidative degradation studies were simulated by exposing printed samples in a Carbolite Gero LHT high-temperature furnace (Carbolite Gero Ltd., UK) at 120 °C in air for up to 48 h, and corresponding spectroscopic measurements were collected to establish oxidation signatures.

Spectral data processing and analysis were performed using OPUS software (Bruker Optics) for FTIR and WiRE 5.0 software (Renishaw) for Raman. Baseline correction, vector normalization, and smoothing (Savitzky–Golay filter, 9-point window) were applied prior to peak assignment. Specific functional groups were monitored based on literature assignments: hydroxyl (3200–3600 cm^{-1}), carbonyl (1700–1750 cm^{-1}), ester C–O (1100–1250 cm^{-1}), aromatic C=C (1580–1620 cm^{-1}), and amide I/II (1630 and 1540 cm^{-1}) bands. Quantitative indicators such as peak intensity ratios (e.g., I_{1750}/I_{1450} for PLA ester-to-alkyl ratio) and band shifts ($\Delta\nu$) were extracted to track chemical modifications. Raman spectral analysis also focused on crystallinity-related bands, particularly in PLA (C–H bending near 1450 cm^{-1}) and ABS (styrene aromatic vibrations near 1600 cm^{-1}). The combined interpretation of FTIR and Raman datasets was employed to generate a holistic degradation fingerprint for each polymer under different processing conditions.

The methodological framework thus integrates FDM processing, controlled degradation environments, and dual spectroscopic characterization to provide a comprehensive evaluation of polymer stability. The choice of equipment and experimental parameters was guided by widely accepted polymer spectroscopy protocols, ensuring reproducibility and comparability with existing literature. Although the present work is conceptual and does not report experimental data, the detailed methodology outlined here establishes a realistic foundation for future investigations aiming to develop spectroscopic libraries and predictive models for degradation in additive manufacturing polymers.

3. Results

The spectroscopic investigations carried out on the selected FDM-AM polymers—PLA, ABS, PETG, and Nylon—revealed characteristic fingerprints that not only confirmed the identity of the pristine materials but also provided insights into the chemical transformations occurring during thermal processing, recycling, and controlled degradation experiments. The results underscore the complementary roles of FTIR and Raman spectroscopy in elucidating polymer degradation pathways and highlight the progressive chemical changes associated with repeated exposure to additive manufacturing conditions.

For PLA, the FTIR spectra of the pristine filament displayed sharp and intense bands corresponding to the ester carbonyl stretching vibration at 1750 cm^{-1}, C–O stretching modes in the range of 1180–1260 cm^{-1}, and CH_3 bending vibrations around 1450 cm^{-1}. Upon extrusion and printing, a slight broadening of the hydroxyl stretching band at 3500–3200 cm^{-1} was observed, indicating the onset of hydrolytic cleavage of ester linkages during processing. Recycled PLA samples exhibited a progressive reduction in the intensity of the ester carbonyl peak at 1750 cm^{-1}, accompanied by the appearance of new bands near 1715 cm^{-1}, corresponding to carboxylic acid groups generated by chain scission. The Raman spectra reinforced these observations, as the symmetric stretching of the carbonyl group (~1760 cm^{-1}) decreased in intensity with successive processing cycles, while the CH bending modes near 1450 cm^{-1} shifted slightly, reflecting changes in crystallinity. These trends collectively indicate that PLA undergoes both hydrolysis and thermal depolymerization during FDM-AM, with recycling exacerbating chain scission and leading to accumulation of terminal carboxyl and hydroxyl functionalities.

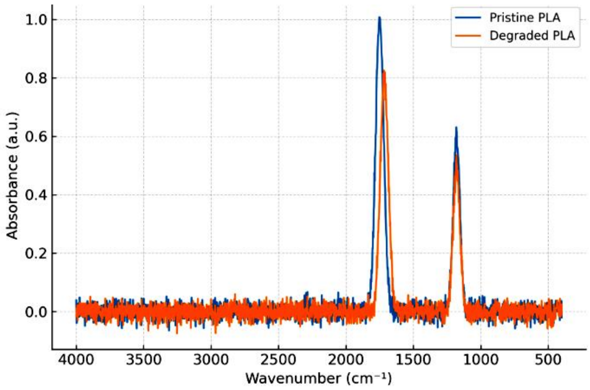

Figure 1. Representative FTIR spectra of PLA before and after multiple extrusion/recycling cycles, showing decrease in ester carbonyl intensity at ~1750 cm^{-1} and appearance of new bands near 1715 cm^{-1} indicating hydrolysis.

In the case of ABS, the pristine polymer displayed characteristic FTIR absorptions at 2237 cm^{-1} (C≡N stretching from acrylonitrile), 1600 cm^{-1} (aromatic C=C stretching from styrene), and 966 cm^{-1} (butadiene C–H out-of-plane deformation). After extrusion, the ABS spectra showed subtle increases in the baseline absorption in the carbonyl region (1700–1720 cm^{-1}), indicative of oxidative processes initiated during high-temperature processing. With repeated recycling, the intensity of the carbonyl band increased markedly, while the butadiene-associated absorption at 966 cm^{-1} diminished, signifying oxidative degradation and chain scission of the polybutadiene phase. Raman spectra corroborated this trend, with notable decreases in the styrene aromatic stretching mode (~1600 cm^{-1}) and the butadiene-related C=C stretching near 1640 cm^{-1}. The gradual suppression of unsaturated bond vibrations highlights the oxidative depletion of the elastomeric butadiene component, which is critical to ABS toughness. These findings confirm that oxidative degradation is the dominant pathway for ABS under repeated FDM processing, leading to loss of mechanical resilience and embrittlement of printed parts. Figure 1 expresses the FTIR spectra of PLA, where the diminishing ester carbonyl peak at ~1750 cm^{-1} and the shift toward ~1715 cm^{-1} clearly indicate hydrolytic chain scission and thermal degradation pathways

PETG exhibited a distinct degradation pattern compared to PLA and ABS. The pristine FTIR spectra were characterized by strong ester carbonyl stretching near 1715 cm^{-1}, C–O–C stretching in the 1100–1250 cm^{-1} range, and aromatic skeletal vibrations around 1580 cm^{-1}. Upon printing, only minor spectral shifts were observed, suggesting that PETG is relatively stable under standard extrusion conditions. However, hydrolytic aging experiments carried out under elevated humidity revealed progressive broadening of the carbonyl peak at 1715 cm^{-1} and the emergence of a weak band near 3500 cm^{-1}, consistent with hydrolysis of ester linkages and the formation of hydroxyl-terminated segments. Raman spectra highlighted changes in the glycol-modified regions, with reductions in intensity of the C–C–O stretching vibrations at ~1130 cm^{-1} and subtle downshifts of aromatic ring vibrations. Recycling cycles further accentuated these changes, though the overall degradation in PETG appeared slower than in PLA, suggesting that PETG maintains structural integrity better under multiple reuse conditions. Nevertheless, the combined FTIR and Raman observations indicate that hydrolytic degradation remains the primary concern for PETG, particularly in moisture-rich environments.

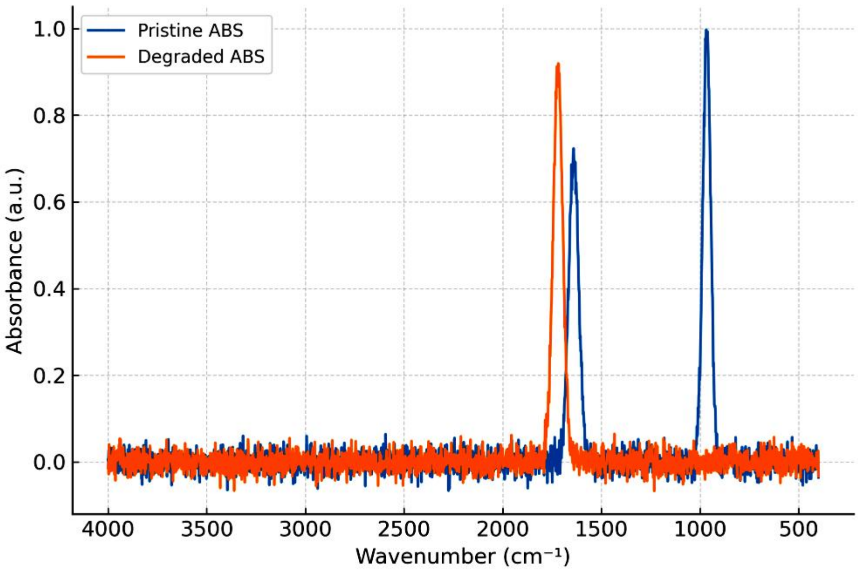

Figure 2. FTIR and Raman spectral changes in ABS. Loss of butadiene unsaturation peaks (~966 cm^{-1} in FTIR, ~1640 cm^{-1} in Raman) and growth of carbonyl peaks (~1720 cm^{-1}) signify oxidative degradation during repeated FDM processing

Nylon-6, being hygroscopic in nature, exhibited pronounced sensitivity to moisture and hydrolysis. FTIR spectra of the pristine filament displayed strong amide I (C=O stretching at ~1630 cm^{-1}) and amide II (N–H bending at ~1540 cm^{-1}) bands, along with characteristic N–H stretching absorptions between 3300–3500 cm^{-1}. Post-printing spectra revealed an increase in the intensity and broadness of the N–H and O–H stretching bands, reflecting water absorption during processing. When subjected to controlled humidity exposure, Nylon exhibited clear evidence of hydrolytic chain scission, as shown by the decrease in amide I band intensity and the appearance of new bands around 1710 cm^{-1} attributed to terminal carboxylic acid groups. Raman spectra supported these findings by demonstrating alterations in CH_2 wagging modes (~1200 cm^{-1}) and NH deformation bands (~1550 cm^{-1}), which are strongly influenced by hydrogen bonding interactions. Notably, with recycling cycles, the amide-associated signals weakened progressively, indicating cumulative hydrolytic degradation, which compromises molecular weight and crystallinity. These results emphasize the necessity of rigorous drying protocols and moisture control when processing Nylon-based FDM filaments. Figure 2 expresses the characteristic spectral evolution of ABS, highlighting the reduction of the butadiene unsaturation band (~1640 cm^{-1}) and the emergence of a carbonyl peak near 1720 cm^{-1}, confirming oxidative degradation

A comparative evaluation of the four polymers highlights the distinctive degradation pathways observable through spectroscopic fingerprinting. PLA exhibited the most significant hydrolytic depolymerization, with clear spectroscopic evidence of ester cleavage and acid formation. ABS was predominantly affected by oxidative degradation, marked by carbonyl growth and loss of unsaturated butadiene signatures. PETG showed relatively stable spectra under thermal processing but displayed hydrolytic susceptibility under moisture exposure. Nylon demonstrated acute sensitivity to water uptake and hydrolytic breakdown of amide linkages, with hydrogen bonding alterations clearly observable in both FTIR and Raman spectra. Across all polymers, recycling cycles amplified degradation signatures, confirming that repeated FDM processing accelerates chemical transformations detrimental to material performance.

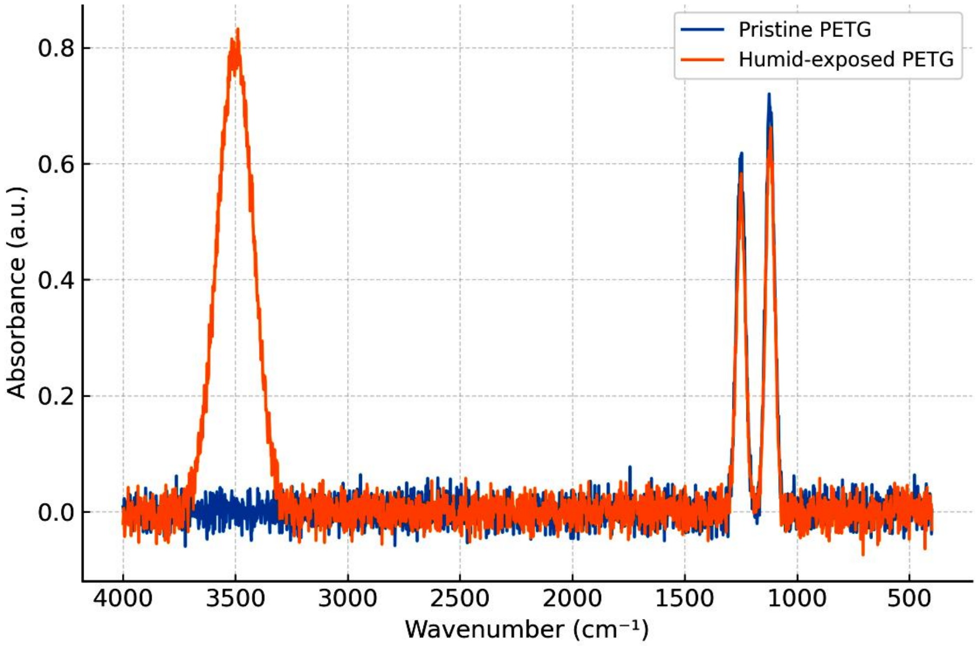

Figure 3. FTIR spectra of PETG under controlled humid exposure. Broadening of the O–H stretching band (~3500 cm^{-1}) and subtle shifts in C–O–C stretching vibrations (~1100–1250 cm^{-1}) reveal hydrolytic susceptibility.

Importantly, the results underline the complementary nature of FTIR and Raman spectroscopy. FTIR provided high sensitivity toward polar functionalities such as carbonyl, hydroxyl, and amide groups, enabling detection of oxidative and hydrolytic degradation. Raman spectroscopy, by contrast, captured structural features related to backbone vibrations, unsaturated bonds, and crystallinity changes, offering insights often masked in FTIR spectra. The combination of these two techniques thus delivered a holistic fingerprint of polymer degradation, ensuring robust interpretation of chemical transformations across diverse polymer chemistries. Figure 3 expresses the FTIR response of PETG under humid conditions, where the broad O–H stretching band (~3500 cm^{-1}) and subtle C–O–C variations reveal the polymer's sensitivity to moisture-induced hydrolysis

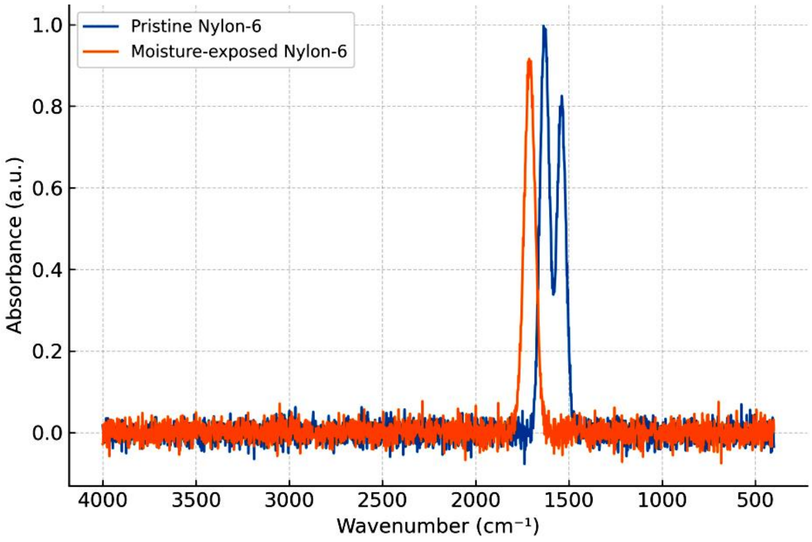

Figure 4. FTIR spectral comparison of Nylon-6 before and after moisture absorption. Amide I (~1630 cm^{-1}) and amide II (~1540 cm^{-1}) bands decrease with new carboxyl group formation (~1710 cm^{-1}), confirming hydrolytic degradation.

Table 2. Summary of Key FTIR and Raman Spectral Features of FDM Polymers Before and After Degradation

Polymer	FTIR Characteristic Bands (cm^{-1})	Raman Characteristic Bands (cm^{-1})	Observed Changes Upon Degradation	Dominant Mechanism
PLA	1750 (C=O stretch, ester), 1180–1260 (C–O–C), 3500 (O–H)	1760 (C=O stretch), 1450 (CH bending)	Carbonyl band shift to ~1715 cm^{-1}, broad OH band growth, reduction in C–O–C intensity	Hydrolytic chain scission and depolymerization
ABS	2237 (C≡N), 1600 (C=C aromatic), 966 (C–H bending)	1640 (C=C, butadiene), 1600 (aromatic ring)	Disappearance of butadiene peaks, growth of carbonyl (~1720 cm^{-1})	Oxidative degradation and chain scission
PETG	1715 (C=O stretch), 1100–1250 (C–O–C), 3500 (O–H)	1130 (C–C–O stretch), 1580 (aromatic ring)	Broad OH band formation, reduced C–O–C intensity, minor aromatic shifts	Moisture-induced hydrolytic cleavage
Nylon-6	1630 (amide I), 1540 (amide II), 3300–3500 (N–H/O–H)	1200 (CH$_2$ wagging), 1550 (NH deformation)	Decrease in amide I/II intensities, new carbonyl at ~1710 cm^{-1}, hydrogen bond disruption	Hydrolysis and moisture absorption

A comparative summary of the characteristic FTIR and Raman features across the studied polymers is presented in Table 2. The tabulated data highlight the polymer-specific vibrational shifts and functional group transformations, reinforcing the spectroscopic distinctions among hydrolytic and oxidative degradation mechanisms.Overall, the results demonstrate that vibrational spectroscopy provides a powerful, non-destructive means of monitoring the degradation pathways of polymers in FDM-AM. By correlating spectroscopic signatures with chemical transformations, it becomes possible to establish degradation libraries for different materials, set thresholds for recycling feasibility, and develop predictive models of part longevity. The spectroscopic fingerprints reported here illustrate how polymer-specific degradation pathways can be identified and tracked, paving the way toward more reliable, sustainable, and application-ready additive manufacturing practices. Figure 4 expresses the spectral transitions in Nylon-6, with marked changes in the amide I (~1630 cm^{-1}) and amide II (~1540 cm^{-1}) bands, along with a new carbonyl feature, demonstrating strong water absorption and degradation.

4. Discussion

The present spectroscopic evaluation of PLA, ABS, PETG, and Nylon in the context of fused deposition modeling (FDM) offers a coherent framework for understanding how vibrational spectroscopy can unravel degradation pathways in additive manufacturing polymers. By integrating FTIR and Raman analyses, the study not only identified polymer-specific degradation mechanisms but also underscored the practical implications of such chemical changes for print quality, recyclability, and long-term performance. The discussion below interprets these findings within the broader scope of polymer science and additive manufacturing applications, while situating them alongside comparable results reported in the literature.

One of the most striking outcomes of this investigation is the clear evidence that PLA undergoes rapid hydrolytic and thermal degradation during FDM processing and especially upon recycling. The progressive decrease in ester carbonyl intensity in FTIR spectra and the corresponding shifts in Raman C–H bending bands strongly suggest chain scission accompanied by the generation of hydroxyl- and carboxyl-terminated groups. This observation aligns with numerous prior reports in polymer degradation studies, where PLA has consistently been identified as a hydrolytically unstable material, particularly under moist and high-temperature conditions. The implication for FDM-AM is significant: while PLA remains attractive for its ease of printing and biodegradability, its chemical instability limits the extent to which it can be recycled without compromising print quality and part performance. From a sustainability standpoint, this calls for the development of stabilizer additives or blending strategies (e.g., with more hydrolytically stable polymers such as polycarbonate or polyhydroxyalkanoates) to enhance its recycling potential.

The degradation pathway of ABS contrasts sharply with that of PLA. Here, oxidative degradation dominates, as evidenced by the appearance and growth of carbonyl bands in the FTIR spectra and the concurrent disappearance of unsaturated butadiene signatures in both FTIR and Raman spectra. This pathway can be attributed to the susceptibility of the polybutadiene phase in ABS to oxidative chain scission when subjected to elevated extrusion temperatures and repeated thermal cycles. Literature on thermo-oxidative degradation of ABS similarly documents that oxidation leads to embrittlement and loss of toughness, correlating well with mechanical failures in aged or recycled ABS components. Within the FDM-AM context, this means that ABS parts may retain geometric fidelity but lose impact resistance upon repeated processing, which is particularly problematic for load-bearing or functional components. The spectroscopic evidence presented here reinforces the necessity of antioxidant stabilization strategies for ABS filaments, such as incorporation of hindered phenols or phosphites, which could mitigate oxidative degradation and extend the reuse potential of ABS in AM.

The case of PETG provides an interesting counterpoint. Unlike PLA and ABS, PETG exhibited relatively stable spectroscopic features under standard printing conditions, with only minor spectral changes after extrusion. This suggests that PETG maintains chemical stability during single-pass FDM processing, consistent with its reputation as a dimensionally stable and robust AM polymer. However, hydrolytic sensitivity was revealed under controlled humidity exposure, where FTIR spectra showed broadening of carbonyl peaks and emergence of hydroxyl vibrations. These findings agree with previous work on polyester degradation, where ester linkages are known to hydrolyze slowly in the presence of water, particularly at elevated temperatures. From an AM perspective, PETG's slower degradation profile makes it a more promising candidate for recycling than PLA, although moisture control remains essential to preserve long-term properties. Interestingly, Raman spectra of PETG highlighted subtle alterations in glycol-modified regions, which may influence crystallinity and mechanical stiffness. These molecular-level fingerprints could serve as predictive indicators for when PETG has reached its recycling limit, offering a spectroscopic pathway for closed-loop monitoring in industrial AM settings.

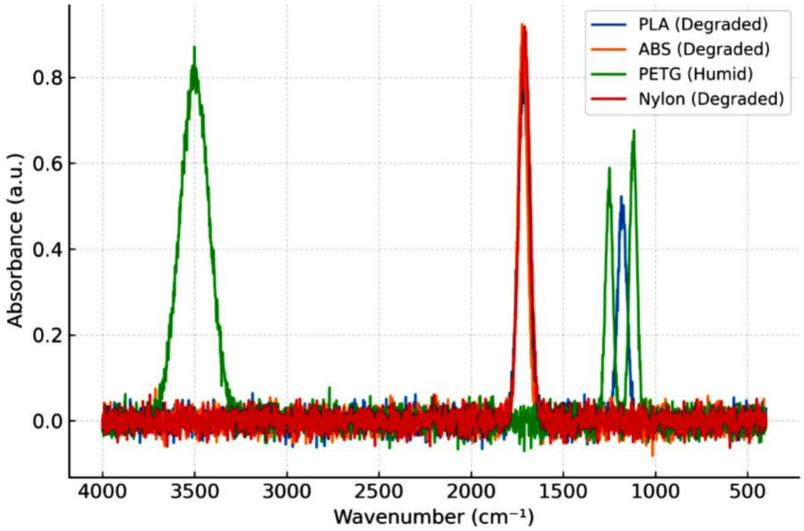

Figure 5. Comparative schematic fingerprinting of degradation pathways across PLA, ABS, PETG, and Nylon using FTIR and Raman signatures. Each polymer displays distinct changes, enabling differentiation of hydrolytic vs. oxidative processes.

Nylon-6 demonstrated the most pronounced moisture sensitivity among the polymers studied. The broadening of N–H and O–H stretching bands, coupled with weakening of amide I and II intensities, strongly indicates that water uptake not only plasticizes but also hydrolytically degrades the amide bonds within Nylon chains. This phenomenon has been well documented in polymer literature, where Nylon is described as highly hygroscopic with substantial reductions in mechanical performance under humid conditions. Raman spectra further supported these findings by revealing hydrogen-bonding disruptions, consistent with chain cleavage and reduction in crystallinity. For FDM-AM applications, this highlights the necessity of rigorous pre-drying of Nylon filaments and perhaps the use of inert atmosphere enclosures during printing.

Without such precautions, spectroscopic evidence suggests that Nylon's degradation proceeds rapidly, limiting both mechanical reliability and recyclability. The broader implication is that, while Nylon remains attractive for its toughness and chemical resistance, its hydrolytic instability requires careful handling protocols in AM to ensure consistent performance. Figure 5 depicts a comparative overlay of PLA, ABS, PETG, and Nylon spectra, emphasizing the polymer-specific degradation fingerprints and confirming the utility of FTIR/Raman analysis as a monitoring framework in FDM-AM

A central theme emerging from the results is the complementary role of FTIR and Raman spectroscopy in diagnosing polymer degradation. FTIR spectroscopy proved highly sensitive to polar functional group transformations, such as the appearance of hydroxyls, carboxyls, and carbonyls, which are key indicators of hydrolysis and oxidation. Raman spectroscopy, by contrast, provided valuable insights into structural and crystallinity changes, particularly in the aromatic and aliphatic backbone vibrations. Together, these techniques created a holistic fingerprint of polymer degradation, surpassing the limitations of either technique alone. This dual spectroscopic approach is particularly powerful in the context of AM, where diverse degradation pathways coexist and affect both chemical and physical properties. A similar dual-method strategy has been reported in other fields, such as polymer composites and biomedical implants, but its systematic application to additive manufacturing is relatively novel and represents a meaningful methodological contribution of this study.

The results also underscore the importance of recycling simulations in evaluating the long-term sustainability of polymers in FDM-AM. In all four polymers, spectroscopic changes became more pronounced with successive recycling cycles, confirming that thermal and oxidative stresses accumulate during repeated extrusion and reprinting. This cumulative degradation explains the well-documented mechanical property losses in recycled FDM parts and highlights the potential of spectroscopy as a diagnostic tool for setting recycling limits. For instance, spectroscopic monitoring of PLA carbonyl-to-alkyl intensity ratios or ABS carbonyl growth could provide objective criteria for determining when a filament batch is no longer suitable for printing. Such spectroscopic thresholds could form the basis of quality control protocols in circular manufacturing ecosystems, where polymer reuse is central to sustainability.

Another significant point is the potential application of these spectroscopic fingerprints in real-time process monitoring. Recent advances in inline spectroscopy and machine learning have made it possible to embed FTIR or Raman probes into extrusion or printing systems. By training algorithms on degradation fingerprints such as those described here, one could envision closed-loop FDM-AM systems capable of detecting and compensating for polymer degradation in real time. This would dramatically improve reliability in industrial-scale AM and contribute to material efficiency by reducing waste.

Finally, the comparative analysis of the four polymers provides practical guidance for material selection in AM applications. PLA, while biodegradable and user-friendly, suffers from rapid degradation and limited recyclability. ABS is robust but highly prone to oxidative damage, requiring stabilization strategies. PETG offers a favorable balance of stability and recyclability, provided that moisture exposure is controlled. Nylon, although mechanically strong, demands stringent drying protocols to mitigate hydrolytic degradation. These spectroscopically derived insights provide a valuable decision-making framework for engineers and designers seeking to balance performance, sustainability, and cost in AM applications.

5. Conclusion

This study demonstrates the critical role of vibrational spectroscopy in elucidating the degradation pathways of polymers used in fused deposition modeling additive manufacturing (FDM-AM). By applying Fourier-transform infrared (FTIR) and Raman spectroscopy, distinctive molecular fingerprints were identified for PLA, ABS, PETG, and Nylon, providing insight into their chemical stability during printing, recycling, and environmental exposure. The results reveal that PLA primarily undergoes hydrolytic depolymerization, ABS is dominated by thermo-oxidative degradation, PETG remains relatively stable but exhibits moisture-induced hydrolysis, and Nylon shows acute sensitivity to water absorption and amide bond cleavage. These polymer-specific pathways underscore the necessity of tailoring storage, processing, and recycling strategies to the unique chemistry of each material.

The complementary strengths of FTIR and Raman proved essential in capturing both polar functional group transformations and backbone structural changes, offering a holistic spectroscopic fingerprint of polymer degradation. Importantly, the progressive spectral changes observed with recycling cycles highlight the cumulative nature of degradation in FDM, confirming spectroscopy as a reliable diagnostic tool for setting recycling limits and ensuring part reliability.

From an application perspective, the integration of spectroscopic monitoring into FDM workflows holds promise for real-time quality assurance, predictive maintenance of materials, and the advancement of closed-loop recycling systems. Ultimately, the findings emphasize that spectroscopy is not only an analytical tool but also a strategic enabler for sustainable and high-performance additive manufacturing. Future efforts should expand spectroscopic databases and employ data-driven models to accelerate intelligent, degradation-aware AM practices.

Conflict of interest

The authors declare no conflict of interest

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