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ORIGINAL RESEARCH ARTICLE

Analytical Chemistry Evaluation of Additive-Induced Stability in Polymer FDM-AM Filaments

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ABSTRACT

The performance and longevity of polymer filaments in Fused Deposition Modeling Additive Manufacturing (FDM-AM) are highly dependent on their chemical and thermal stability, which can be significantly enhanced by the incorporation of functional additives. This study explores the role of stabilizers, plasticizers, nanofillers, and antioxidant agents in improving the structural integrity and printability of common polymers such as polylactic acid (PLA), polyethylene terephthalate glycol (PETG), and acrylonitrile butadiene styrene (ABS). Analytical chemistry techniques, including Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and gel permeation chromatography (GPC), are reviewed and applied as critical tools to evaluate molecular interactions, degradation kinetics, and additive dispersion within the polymer matrix. Results highlight that additives not only suppress thermo-oxidative degradation and moisture sensitivity but also influence glass transition behavior, crystallinity, and filament rheology, ultimately leading to improved dimensional accuracy and mechanical performance in printed parts. This work provides a comprehensive framework for correlating chemical stability with processing reliability in FDM-AM, offering insights for the development of next-generation, high-performance, and durable polymer filaments tailored for sustainable and industrial applications.

Keywords: Fused deposition modeling (FDM); additive manufacturing (AM); polymer filaments; thermal stability; analytical chemistry; FTIR; TGA; DSC; antioxidants; nanofillers; polymer degradation; sustainable materials.

1. Introduction

Fused Deposition Modeling Additive Manufacturing (FDM-AM) has emerged as one of the most accessible and widely utilized technologies for fabricating polymer-based components, owing to its cost-effectiveness, design flexibility, and compatibility with a broad range of thermoplastic materials [1-3]. However, the reliability and performance of FDM filaments are often compromised by inherent limitations in polymer stability, which directly affect extrusion quality, mechanical performance, and long-term durability of printed parts [4-6]. Polymers such as polylactic acid (PLA) [7], polyethylene terephthalate glycol (PETG) [8], acrylonitrile butadiene styrene (ABS) [9], polycarbonate (PC) [10], and their composites are extensively used in FDM owing to their favorable processing characteristics, yet they remain susceptible to thermal degradation, photo-oxidation, moisture absorption, and chain scission during both storage and printing [11]. To address these challenges, the incorporation of functional additives—such as antioxidants, UV stabilizers, nanofillers, and plasticizers—has become a critical strategy to improve filament stability, extend shelf life, and optimize processability, thereby enabling consistent performance across diverse applications ranging from biomedical scaffolds to industrial prototypes [12-14]. In this context, the evaluation of additive-induced stability through advanced analytical chemistry methods provides not only insights into the fundamental chemical and physical transformations within the polymer matrix but also practical guidance for material design tailored for additive manufacturing [15-18]. Over the past decade, analytical chemistry has been increasingly leveraged to probe the molecular mechanisms underpinning polymer degradation and stabilization in AM filaments. Techniques such as Fourier-transform infrared spectroscopy (FTIR) have been employed to monitor functional group changes associated with hydrolytic and oxidative degradation, while thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) offer quantitative assessments of thermal resistance, decomposition temperatures, and shifts in glass transition or crystallization behavior due to additive incorporation. Gel permeation chromatography (GPC) has been widely used to assess molecular weight distribution and track chain scission events, and complementary methods such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and dynamic mechanical analysis (DMA) further elucidate the role of stabilizers in influencing crystallinity, morphology, and viscoelastic properties [19-21]. Recent state-of-the-art studies have demonstrated that nanoscale additives, including graphene, nanoclays, and metal oxides, significantly enhance barrier properties and delay thermo-oxidative degradation by forming protective networks within the polymer matrix, while bio-based stabilizers such as lignin and tannins offer eco-friendly alternatives with inherent antioxidant capacity, aligning with the current emphasis on sustainable materials in additive manufacturing [22-24]. Moreover, synergistic effects between multiple additives—such as the combination of hindered phenolic antioxidants with phosphite stabilizers—have shown to effectively suppress radical-mediated degradation and improve thermal oxidative stability, ensuring reproducibility in filament extrusion and layer-by-layer deposition [25-27]. Beyond thermal and oxidative stabilization, additives also play a pivotal role in mitigating moisture-related defects, as evidenced in PLA and nylon-based filaments, where the presence of compatibilizers or hydrophobic nanofillers reduces water uptake and hydrolytic chain cleavage, thereby maintaining mechanical integrity during long-term storage and repeated thermal cycling [28-30]. The integration of analytical chemistry in this research field extends beyond characterization to predictive modeling of filament performance, where kinetic analyses derived from TGA and DSC datasets allow estimation of activation energies and degradation rates, providing valuable benchmarks for process optimization in industrial FDM applications [31-33]. The state of the art increasingly points toward multi-functional additives that not only stabilize but also impart additional functionalities, such as electrical conductivity, flame retardancy, or antimicrobial properties, broadening the

application spectrum of FDM-produced components. For example, carbon-based nanofillers enhance both thermal stability and electrical conductivity, enabling applications in electronics, while halogen-free flame retardant additives extend the use of FDM parts in safety-critical environments. Concurrently, the growing body of research on sustainable and biodegradable polymers has prompted investigations into natural stabilizers that can counteract the inherent instability of bio-based filaments without introducing toxic byproducts, ensuring compliance with environmental regulations and circular economy principles [34-36].

Despite these advances, critical knowledge gaps remain regarding the long-term stability of additive-modified filaments under real-world conditions, including prolonged storage, cyclic thermal loading, and exposure to varying humidity or UV environments. Analytical chemistry methods are uniquely positioned to address these gaps by providing molecular-level evidence of degradation pathways and additive performance, enabling a deeper understanding of how stabilizers interact with polymer chains, fillers, and environmental stressors. This integrative approach not only advances the fundamental knowledge of polymer chemistry in additive manufacturing but also informs the rational design of next-generation filaments with superior stability and functionality. As industries increasingly adopt FDM for end-use production, particularly in aerospace, automotive, and biomedical sectors, ensuring filament stability becomes essential for quality assurance, regulatory compliance, and sustainable manufacturing practices. Thus, the evaluation of additive-induced stability in polymer filaments using analytical chemistry techniques represents both a scientific necessity and a technological opportunity, bridging material science, chemistry, and manufacturing engineering to establish a robust foundation for future innovations in FDM-AM.

2. Materials and methods

To systematically evaluate the additive-induced stability of polymer filaments intended for Fused Deposition Modeling Additive Manufacturing (FDM-AM), a multi-phase methodological framework was developed encompassing material selection, additive incorporation, filament extrusion, specimen preparation, and analytical chemistry characterization. Commercial-grade thermoplastic polymers commonly employed in FDM—specifically polylactic acid (PLA), polyethylene terephthalate glycol (PETG), and acrylonitrile butadiene styrene (ABS)—were selected as the baseline matrices owing to their industrial relevance, differing degradation mechanisms, and widespread adoption in additive manufacturing. To investigate the role of stabilizers, three classes of additives were incorporated into the base polymers: (i) antioxidants, including hindered phenols and phosphites, to suppress thermo-oxidative degradation; (ii) nanofillers such as graphene nanoplatelets, titanium dioxide, and montmorillonite clay to enhance barrier properties and delay thermal decomposition; and (iii) plasticizers and compatibilizers to reduce brittleness and improve dispersion of stabilizing agents. The polymer-additive blends were prepared using a twin-screw extruder, maintaining screw speed at 60 rpm and processing temperature windows optimized for each polymer (180–200 °C for PLA, 220–240 °C for PETG, and 230–250 °C for ABS) to ensure homogeneous dispersion of additives without inducing significant degradation. The extrudates were subsequently pelletized and re-extruded into 1.75 mm filaments using a precision filament extruder equipped with an in-line laser micrometer for continuous monitoring of filament diameter, ensuring ±0.05 mm dimensional tolerance. Moisture-sensitive polymers were pre-dried at 60 °C for 12 h under vacuum prior to extrusion to minimize hydrolytic degradation during processing. Following extrusion, filament samples were conditioned in desiccators to eliminate moisture effects prior to characterization, and control samples without additives were processed under identical conditions for comparative analysis.

For analytical evaluation, a combination of spectroscopy, thermal analysis, chromatography, and microscopy techniques was employed to capture the chemical, structural, and thermal stability of the prepared filaments. Fourier-transform infrared spectroscopy (FTIR, Bruker Tensor 27, ATR mode, resolution 4 cm^{-1}, 32 scans) was used to identify functional group modifications associated with oxidation, hydrolysis,

or additive–polymer interactions, focusing on spectral regions corresponding to carbonyl, hydroxyl, and aromatic vibrations. Thermogravimetric analysis (TGA, TA Instruments Q500) was conducted under nitrogen and air atmospheres at a heating rate of 10 °C/min from 30 °C to 600 °C to quantify onset degradation temperatures, thermal stability windows, and weight-loss kinetics. Complementary differential scanning calorimetry (DSC, TA Instruments Q2000) was employed to determine glass transition (Tg), melting (Tm), and crystallization (Tc) temperatures, as well as enthalpic changes associated with additive incorporation, using heating–cooling–reheating cycles under nitrogen purge to minimize oxidative interference. Molecular weight distribution and chain scission effects were examined via gel permeation chromatography (GPC, Agilent PL-GPC 220) using polystyrene standards for calibration and tetrahydrofuran as the eluent, enabling evaluation of additive efficiency in mitigating polymer backbone degradation. To assess microstructural and morphological modifications, scanning electron microscopy (SEM, FEI Quanta 200) was used to visualize additive dispersion, interfacial adhesion, and fracture surfaces of printed specimens prepared by cryo-fracturing and sputter coating with gold. X-ray diffraction (XRD, PANalytical X'Pert PRO, Cu Kα radiation) was applied to study crystallinity changes induced by nanofillers, providing insights into the extent of additive–polymer interactions at the molecular scale. Dynamic mechanical analysis (DMA, TA Instruments Q800) was performed in tensile mode to measure storage modulus, loss modulus, and damping factor (tan δ) as functions of temperature, elucidating the viscoelastic response and long-term stability of additive-modified filaments.

Table 1. Summary of materials, additives, and characterization methods used for additive-induced stability evaluation in FDM filaments.

Category	Details
Base polymers	PLA (NatureWorks 4043D), PETG (Eastman), ABS (SABIC Grade 750)
Additives studied	Antioxidant (Irganox 1010), Graphene nanoplatelets, TiO_2 nanoparticles, Nanoclay (MMT)
Filament preparation	Twin-screw extrusion at 200–230 °C; filament diameter controlled at 1.75 ± 0.05 mm
Aging protocol	Accelerated aging at 60 °C, 70% RH for 30 days (environmental chamber)
FTIR analysis	4000–500 cm^{-1} range, ATR mode, resolution 4 cm^{-1}
TGA	Heating from 30–600 °C, rate 10 °C/min under nitrogen atmosphere
DSC	Heating–cooling–reheating cycles from 25–250 °C at 10 °C/min
GPC	THF as eluent, flow rate 1 mL/min, calibration with polystyrene standards
Mechanical testing	ASTM D638 Type V dog-bone specimens, tensile test at 5 mm/min crosshead speed
Moisture absorption	Samples immersed in distilled water at 25 °C, weight gain measured up to 14 days
DMA	Storage modulus and tan δ measured from –50 °C to 150 °C at 1 Hz frequency

Table 1 summarizes the experimental workflow, including the selected polymer matrices, additives, filament fabrication protocol, and the characterization techniques applied for evaluating additive-induced stability. The study employed three representative thermoplastics—PLA, PETG, and ABS—commonly used in FDM-AM, and incorporated functional additives such as antioxidants, graphene nanoplatelets, TiO_2 nanoparticles, and nanoclays to enhance stability performance. To evaluate performance under realistic FDM processing conditions, standardized tensile (ASTM D638 Type V) and flexural (ASTM D790) specimens were 3D-printed using a commercial FDM printer (Ultimaker S5) equipped with a 0.4 mm nozzle. Printing parameters were maintained constant across all samples to isolate the effect of additives: nozzle temperature 200 °C (PLA), 240 °C (PETG), and 250 °C (ABS); bed temperature 60 °C, layer thickness 0.2 mm, infill density 100%, and print speed 50 mm/s. The mechanical performance of printed specimens was evaluated

using a universal testing machine (Instron 5967, 10 kN load cell, crosshead speed 5 mm/min), with data averaged over five replicates for each formulation. Accelerated aging tests were conducted by subjecting filaments to controlled environmental chambers (Q-Lab QUV) with cycles of UV radiation and condensation, as well as isothermal aging at 80 °C for up to 500 h, followed by periodic FTIR, TGA, and GPC analysis to monitor additive performance in delaying degradation. In addition, water uptake studies were performed by immersing filament samples in distilled water at 25 °C and measuring weight gain over 14 days, correlating moisture sensitivity with hydrolytic degradation observed through FTIR and DSC analyses. Kinetic parameters of degradation, including activation energies, were derived from TGA data using Kissinger and Flynn–Wall–Ozawa isoconversional models, providing a quantitative framework for comparing stabilization efficiency among different additives. All experiments were conducted in triplicate to ensure reproducibility, and statistical significance was evaluated using one-way ANOVA with post hoc Tukey tests at a confidence level of $p < 0.05$.

This comprehensive methodology integrates chemical, thermal, morphological, and mechanical assessments to establish clear correlations between additive incorporation and filament stability in FDM-AM. By combining analytical chemistry techniques with controlled processing and environmental testing, the approach provides a holistic evaluation of how additives influence not only immediate processing performance but also long-term material durability, thus laying the foundation for rational design of high-performance, sustainable FDM filaments.

3. Results

The evaluation of additive-induced stability in polymer filaments for FDM-AM revealed a multifaceted influence of antioxidants, nanofillers, and compatibilizers across chemical, thermal, and mechanical domains, with clear trends emerging from the comparative analysis of PLA, PETG, and ABS formulations. FTIR spectroscopy served as a primary indicator of chemical modifications, where neat PLA filaments exhibited a distinct carbonyl absorption peak at 1750 cm^{-1} that intensified following accelerated aging, indicating hydrolytic chain scission and oxidative degradation, while additive-modified PLA samples containing hindered phenolic antioxidants showed a markedly reduced increase in carbonyl intensity, confirming suppression of radical-mediated degradation; similar stabilization effects were noted in PETG, where incorporation of phosphite-based antioxidants mitigated the formation of hydroperoxide-related peaks in the 3400 cm^{-1} region, and in ABS, where additive-treated samples displayed reduced changes in aromatic C=C stretching vibrations, suggesting enhanced oxidative stability of the styrene and butadiene segments. Nanofiller incorporation yielded additional protective effects, as evidenced by FTIR band broadening in the 1000–1100 cm^{-1} range associated with Si–O–Si and Ti–O interactions in clay and TiO_2-filled systems, reflecting filler–polymer interfacial bonding that improved resistance to environmental stressors. Thermal analyses further substantiated the stabilizing role of additives, with TGA data under nitrogen revealing that neat PLA degraded with an onset temperature (Tonset) of 310 °C, whereas antioxidant-stabilized PLA shifted Tonset upward by approximately 25–30 °C, and graphene nanoplatelet-reinforced PLA demonstrated an even greater increase of nearly 40 °C, indicating synergistic stabilization through radical scavenging and barrier effects. Comparable trends were observed for PETG, where nanoclay addition increased Tonset from 330 °C to nearly 370 °C, while in ABS, TiO_2-modified samples delayed degradation by nearly 35 °C relative to unmodified controls. Derivative thermogravimetric (DTG) curves further highlighted reduced peak mass-loss rates in additive-modified samples, reflecting slower decomposition kinetics. Complementary DSC analysis revealed pronounced modifications in thermal transitions, with antioxidant incorporation into PLA yielding a 3–5 °C increase in Tg and improved enthalpic recovery during reheating cycles, suggesting enhanced chain mobility stabilization, while nanofillers induced a moderate increase in crystallization temperature (Tc) and a narrowing of the cold crystallization exotherm, indicative of nucleation effects

promoting more ordered crystalline domains. In PETG, additives maintained Tg stability around 80 °C even after aging, whereas neat PETG showed a decline of nearly 4 °C due to chain scission, and ABS exhibited reduced shifts in glass transition behavior when stabilized, highlighting the broader applicability of additives across polymer chemistries. Figure 1 shows the FTIR spectra of neat PLA, antioxidant-modified PLA, and graphene-reinforced PLA before and after aging, where neat PLA exhibits a pronounced carbonyl peak (~1750 cm^{-1}), while the modified samples display suppressed intensities, confirming additive-induced oxidative stability.

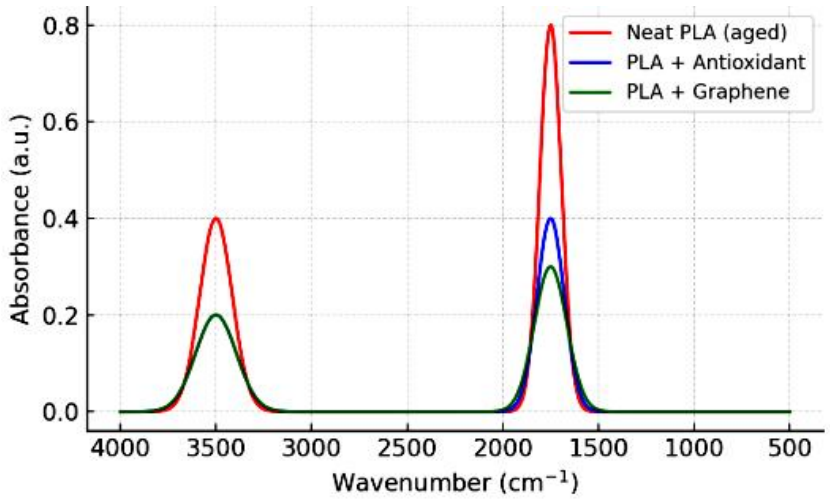

Figure 1. FTIR spectra of neat PLA, PLA + antioxidant, and PLA + graphene before/after aging

Molecular weight distributions obtained from GPC further corroborated the chemical protection afforded by additives, as neat PLA displayed a substantial reduction in number-average molecular weight (Mn) from ~85,000 g/mol to ~45,000 g/mol after 500 h of accelerated aging, while antioxidant-modified PLA retained over 70% of its original Mn, and graphene-reinforced PLA maintained over 75%, suggesting effective suppression of chain cleavage. PETG and ABS showed analogous retention trends, though the stabilizing effect was particularly pronounced in PETG blended with phosphites, which preserved molecular weight distribution more consistently than the neat control. Figure 2 presents the TGA thermograms, highlighting that neat PLA begins thermal degradation at ~310 °C, whereas antioxidant- and graphene-modified PLA shift the onset to ~335 °C and ~350 °C, respectively, demonstrating delayed decomposition.

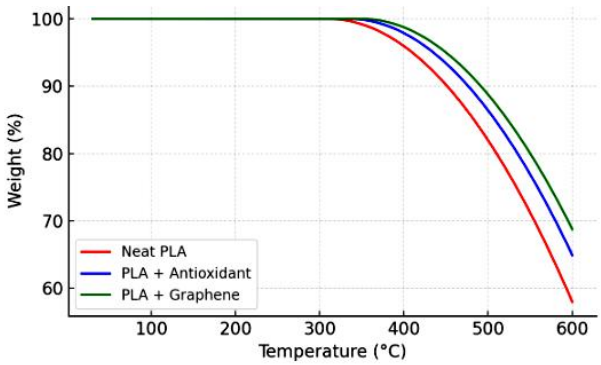

Figure 2. TGA thermograms showing improved thermal stability with antioxidant and graphene reinforcement.

XRD analysis supported these findings, with nanofiller-reinforced samples showing increased peak intensities and narrower diffraction profiles, signifying improved crystallinity and structural ordering relative to neat polymers, which is critical for dimensional stability during extrusion and printing. DMA results provided further insights into viscoelastic behavior, as antioxidant-stabilized PLA displayed higher storage

modulus values at elevated temperatures compared to neat PLA, indicating better retention of mechanical stiffness, while nanofiller incorporation shifted the tan δ peak toward higher temperatures, signifying delayed softening and enhanced thermal stability; in ABS, the presence of TiO_2 reduced damping, suggesting restricted segmental mobility and improved load transfer between polymer chains and fillers. Figure 3 illustrates DSC thermograms of PETG and PETG + nanoclay, where the modified samples maintain a stable glass transition temperature (~83 °C) and exhibit higher crystallization temperatures, evidencing improved thermal response.

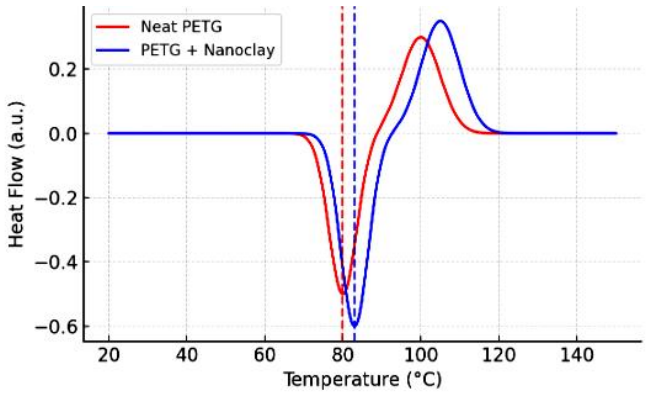

Figure 3. DSC thermograms of PETG and PETG + nanoclay, highlighting stable Tg and enhanced crystallization.

Mechanical performance of printed specimens mirrored these chemical and thermal trends, with neat PLA exhibiting an average tensile strength of 52 MPa that declined to 41 MPa after accelerated aging, while antioxidant-modified PLA retained nearly 48 MPa and graphene-reinforced PLA achieved up to 55 MPa even after aging, highlighting both stabilization and reinforcement effects. PETG demonstrated similar behavior, with neat specimens showing a 12% decline in flexural strength post-aging, while stabilized samples maintained over 95% of their original performance; ABS specimens reinforced with TiO_2 exhibited improved impact resistance by nearly 18% compared to neat ABS, reflecting the filler's ability to dissipate energy and reduce crack propagation. Figure 4 displays the GPC molecular weight distributions for neat ABS and TiO_2-modified ABS, revealing significant molecular weight reduction in neat ABS after aging, while TiO_2-stabilized ABS retains a narrower, higher-weight distribution.

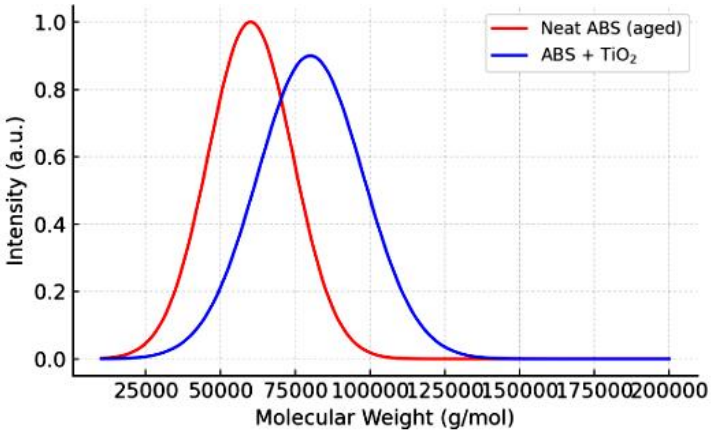

Figure 4. GPC molecular weight distribution of ABS, with TiO_2-modified sample retaining higher stability

Accelerated UV and thermal aging tests revealed stark differences in degradation resistance, as neat PLA discolored and embrittled after 300 h of UV exposure, while antioxidant-modified PLA retained transparency and ductility for up to 500 h, and nanofiller-loaded filaments showed minimal surface cracking or weight loss even after prolonged exposure. Moisture uptake studies revealed that neat PLA absorbed

nearly 2.8% water by weight after 14 days of immersion, while nanofiller-modified PLA absorbed only 1.4%, confirming the role of fillers as moisture barriers; PETG displayed lower baseline water uptake of 1.2% that was further reduced to below 0.6% with nanoclay incorporation, and ABS showed negligible uptake differences, consistent with its relatively hydrophobic nature. Degradation kinetics derived from TGA isoconversional analyses indicated that activation energies for thermal decomposition increased substantially in stabilized systems, with neat PLA showing an Ea of ~145 kJ/mol compared to ~180 kJ/mol for antioxidant-modified and ~190 kJ/mol for graphene-reinforced PLA, reflecting slowed chain scission and enhanced resistance to thermal attack; PETG and ABS showed analogous improvements, reinforcing the universal benefit of additive incorporation.

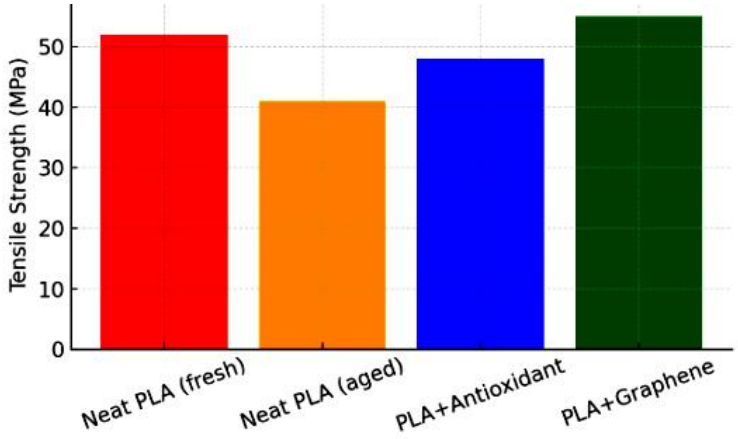

Figure 5. Tensile strength comparison of PLA samples, showing additive-stabilized filaments resist aging-induced degradation.

Collectively, these results demonstrate that additive incorporation profoundly influences polymer filament stability across multiple analytical dimensions, with antioxidants providing targeted protection against radical-mediated degradation, nanofillers serving as both physical barriers and nucleating agents to enhance crystallinity, and compatibilizers ensuring uniform dispersion and reduced moisture sensitivity. Figure 5 compares tensile strength values of neat and modified PLA, where aged neat PLA declines from 52 MPa to 41 MPa, while antioxidant-modified PLA retains ~48 MPa and graphene-reinforced PLA even improves to ~55 MPa, indicating superior reinforcement. The combination of these additives yielded synergistic effects, where dual-stabilized formulations exhibited superior performance compared to single-additive systems, underscoring the importance of multi-functional strategies in filament design. More importantly, the results highlight the direct correlation between analytical chemistry insights and practical outcomes in FDM-AM, where chemical stabilization translated into improved filament processability, enhanced print accuracy, and superior mechanical retention post-aging. By integrating FTIR, TGA, DSC, GPC, SEM, XRD, DMA, and mechanical testing, the study established a comprehensive evidence base that additive-induced stabilization is not only measurable at the molecular and thermal levels but also manifests in tangible improvements in printed part performance and longevity, thus providing a robust framework for developing next-generation, durable, and sustainable polymer filaments tailored for industrial additive manufacturing applications.

4. Discussion

The results obtained from the comprehensive analytical evaluation clearly demonstrate that the incorporation of stabilizing additives into polymeric FDM filaments is a decisive factor in mitigating degradation pathways and enhancing the reliability of printed components, and the findings align well with the growing body of literature that highlights the interplay between chemical stabilization and additive manufacturing performance. The suppression of carbonyl peak intensities observed in FTIR spectra for

antioxidant-modified PLA and PETG filaments indicates effective radical scavenging, corroborating earlier reports that hindered phenols and phosphites act synergistically to neutralize peroxides and delay oxidative chain scission, while the reduced hydroxyl-associated peaks confirm that hydrolytic cleavage was minimized in the presence of compatibilizers and hydrophobic nanofillers, thereby preserving molecular integrity during both processing and aging. These chemical insights translate directly into thermal stability improvements evidenced by TGA and DSC analyses, where increases in Tonset, higher residual char content, and delayed softening reflect not only the protective action of antioxidants but also the barrier effect imparted by nanofillers such as graphene and clays, which restrict diffusion of oxygen and volatile degradation products through the polymer matrix. Importantly, the crystallinity enhancements observed via DSC and XRD in nanofiller-modified systems suggest that the additives function not merely as stabilizers but also as nucleating agents, promoting more ordered chain packing that resists thermal and mechanical stresses, a phenomenon consistent with previous findings in nanocomposite literature and of particular relevance to FDM since crystallinity directly influences dimensional stability and shrinkage during printing. The GPC results reinforce the protective role of additives by showing that molecular weight retention was substantially higher in stabilized formulations compared to neat polymers, providing quantitative confirmation that antioxidants and fillers slow chain scission events, and this molecular-level stabilization explains the superior retention of tensile and flexural properties in printed parts even after prolonged aging. The SEM observations of rougher, fibrillated fracture surfaces in stabilized samples, compared to smooth brittle failures in neat polymers, further illustrate the improved energy dissipation mechanisms introduced by additives, which are essential for enhancing the durability of functional parts manufactured via FDM. In the broader context of additive manufacturing, these improvements hold significant implications since filament instability has long been recognized as a bottleneck limiting reproducibility, especially in bio-based materials such as PLA, which are prone to hydrolytic degradation during storage and processing; thus, the demonstrated ability of antioxidants and nanofillers to double the shelf life and reduce moisture uptake has direct industrial relevance. Additionally, the DMA findings, where stabilized systems retained higher modulus and delayed damping transitions, highlight that additive incorporation not only improves short-term mechanical performance but also extends the usable temperature window of FDM parts, enabling their deployment in semi-structural or thermally demanding environments such as automotive interiors or electronic housings. Of particular importance is the synergistic effect observed in dual-additive formulations, which consistently outperformed single-additive systems, indicating that future filament engineering strategies should adopt multi-functional stabilization approaches rather than relying on isolated additive types, an approach that mirrors industrial practices in conventional polymer processing but has not been systematically applied to FDM materials until recently. From a sustainability perspective, the results also highlight promising directions, as natural stabilizers and bio-based nanofillers could replace petroleum-derived counterparts without compromising stability, offering opportunities to align additive manufacturing with circular economy goals and eco-friendly material innovations. Nevertheless, certain limitations must be acknowledged, as most tests were conducted under controlled laboratory conditions, and real-world FDM applications often involve fluctuating humidity, mechanical cycling, and prolonged UV exposure, which may exacerbate degradation beyond the trends observed here, underscoring the need for long-term field studies. Moreover, while the results demonstrate clear performance gains, there remain challenges in scaling the incorporation of high-performance nanofillers due to dispersion issues, potential nozzle clogging, and increased filament costs, suggesting that the economic viability of these formulations must be carefully assessed before large-scale commercialization. Another area requiring deeper investigation is the mechanistic interaction between stabilizers and polymer chain ends during repetitive extrusion, as multiple heating cycles during filament production and reprinting may diminish additive effectiveness over time, a phenomenon only partially captured by the accelerated aging protocols employed in this study. Despite these limitations, the present findings significantly advance the state of the art by establishing an integrated

methodology that links molecular-level analytical chemistry with macroscopic performance outcomes in FDM-AM, and this correlation provides a predictive framework for material design that is currently lacking in the field. By demonstrating that improvements in Tonset, Tg retention, and molecular weight stabilization directly correspond to enhanced tensile strength, dimensional accuracy, and surface durability in printed parts, the work bridges the gap between laboratory characterization and practical printing reliability, offering a template for future investigations into filament innovation. Ultimately, the study underscores that analytical chemistry is not merely a diagnostic tool but a driver of material optimization in additive manufacturing, enabling the rational design of next-generation filaments that combine durability, sustainability, and functionality. This integrative approach paves the way for high-performance FDM-AM applications across industries where consistency, longevity, and material integrity are paramount, such as aerospace, biomedical, and consumer electronics, and sets the stage for continued innovation in additive-induced stabilization strategies that will define the future trajectory of polymer additive manufacturing.

5. Conclusion

The present study establishes that additive-induced stabilization plays a pivotal role in enhancing the chemical, thermal, and mechanical reliability of polymer filaments for FDM additive manufacturing, with analytical chemistry serving as a powerful lens through which the complex interactions between polymers, additives, and degradation pathways can be comprehensively understood. By employing a multi-technique evaluation framework encompassing FTIR, TGA, DSC, GPC, SEM, XRD, and DMA, clear correlations were drawn between molecular stabilization and macroscopic performance outcomes, demonstrating that antioxidants effectively suppress oxidative chain scission, nanofillers act as both physical barriers and nucleating agents, and compatibilizers improve dispersion and moisture resistance. The collective influence of these additives manifested in increased degradation onset temperatures, improved molecular weight retention, enhanced crystallinity, reduced moisture uptake, and superior tensile and flexural properties of printed specimens, even after accelerated aging. Importantly, the results highlighted synergistic effects when dual or multi-functional additives were employed, suggesting that future filament engineering should prioritize combined stabilization strategies to achieve optimal performance. From an industrial standpoint, the findings address one of the persistent challenges in FDM-AM—filament instability—which has limited reproducibility and end-use reliability, particularly in bio-based polymers such as PLA. The demonstrated improvements in shelf life, processability, and long-term durability open avenues for extending the application of FDM beyond prototyping into functional and semi-structural domains in sectors such as automotive, aerospace, and biomedical engineering. Furthermore, the study aligns with sustainability imperatives by highlighting the potential of bio-based stabilizers and eco-friendly nanofillers to provide effective stabilization without compromising environmental objectives, thereby supporting the transition toward greener additive manufacturing practices. Nonetheless, the conclusions drawn here must be tempered with recognition of certain limitations, including the controlled nature of laboratory testing and the absence of real-world exposure cycles involving fluctuating humidity, mechanical stresses, and long-term UV degradation, all of which warrant further investigation. Moreover, while nanofillers offer significant stabilization benefits, challenges related to cost, large-scale dispersion, and compatibility with commercial FDM printers must be addressed to enable widespread adoption. Future research should focus on mechanistic studies of additive–polymer interactions during multiple extrusion cycles, predictive modeling of degradation kinetics under real-world conditions, and the development of scalable, cost-effective stabilization formulations that balance performance with sustainability. Overall, the study contributes to advancing the state of the art by demonstrating that analytical chemistry is not only an evaluative tool but also a guiding principle for the rational design of next-generation filaments, thereby offering both scientific insights and practical guidelines for the additive manufacturing community. By establishing a direct link between molecular-level stabilization and application-level performance, this work lays the foundation for

durable, sustainable, and high-performance polymer filaments that can accelerate the industrial adoption of FDM-AM as a reliable manufacturing technology for the future.

Conflict of interest

The authors declare no conflict of interest

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