



Review

# Degradation and Long-Term Response Evaluation of Polymeric Components Produced by Additive Manufacturing

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## Abstract

Additive manufacturing (AM) has rapidly evolved from a prototyping tool into an effective method for producing end-use components, thanks to its ability to produce complex, lightweight and customised parts. However, this technique requires a thorough understanding of the long-term behaviour and degradation mechanisms of components, especially when polymers are involved in the printing process. Unlike polymer components manufactured using traditional methods, polymers produced through AM exhibit unique microstructures, anisotropies, and interfacial characteristics due to the layer-by-layer fabrication process. These features can affect how these materials respond to thermal, mechanical and environmental stresses over time. Furthermore, technology-specific processing parameters directly govern porosity distribution, crystallinity evolution, interlayer bonding quality, and residual stress development, all of which are key factors for ensuring long-term performance. This review aims to support researchers in the development of durable additively manufactured polymer components by systematically analysing polymer degradation mechanisms, accelerated ageing and lifetime prediction methodologies. Following a PRISMA-based screening process, approximately 160 international standards relevant to polymer durability in additive manufacturing were selected from an initial corpus of about 620 documents for in-depth analysis. Processing–structure–property relationships specific to the AM processing of polymers, including the commonly used FFF (fused filament fabrication), SLA (stereolithography) and SLS (selective laser sintering), are examined in relation to crucial aspects for long-term structural integrity and degradation behaviour. Finally, limitations within the current normative framework are identified, emphasising the absence of process-aware durability assessment protocols and the need for dedicated standards tailored to additively manufactured polymer components.

**Keywords:** accelerated ageing; lifetime prediction; processing–structure–property relationship; long-term durability; components certification



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## 1. Introduction

The industrial relevance of polymeric materials has increased significantly in recent decades due to their low density, chemical resistance, affordability, and design flexibility. These properties have driven their widespread use among others in aerospace, automotive, medical, and consumer goods sectors. As global polymer production has reached record levels [1,2], the need to optimise material usage and reduce waste has become increasingly urgent [3]. In this context, additive manufacturing (AM) [4], particularly for polymers, has emerged as a transformative approach [5–8]. Its ability to produce complex, lightweight, and customised components with minimal material waste offers clear economic and environmental advantages. Moreover, AM enables the fabrication of advanced composite materials, thereby expanding the mechanical performance envelope and functional capabilities of printed components [9]. In addition, AM enables on-demand production through digital inventories. This approach reduces storage and logistics requirements while limiting degradation associated with long-term physical stockpiling [10]. Beyond direct part production, AM is also increasingly integrated into hybrid manufacturing routes, such as rapid investment casting (RIC), where additively manufactured polymer patterns are employed to enhance geometrical complexity, tooling flexibility and process efficiency [11]. Recent studies have demonstrated that the integration of topology optimisation, additive manufacturing, rapid investment casting, and life cycle assessment provides a structured framework for the development of lightweight metal components. This integrated approach ensures structural robustness, manufacturing feasibility, and measurable environmental performance improvements [12].

Despite these advantages, the adoption of AM introduces challenges related to component certification and long-term reliability assessment. Unlike conventionally manufactured polymer parts qualified using established ISO/ASTM standards, AM components exhibit distinct microstructural characteristics, including anisotropy, increased porosity, and reduced interlayer adhesion resulting from the layer-by-layer fabrication process [13,14]. These features strongly influence long-term behaviour under combined environmental and mechanical stressors.

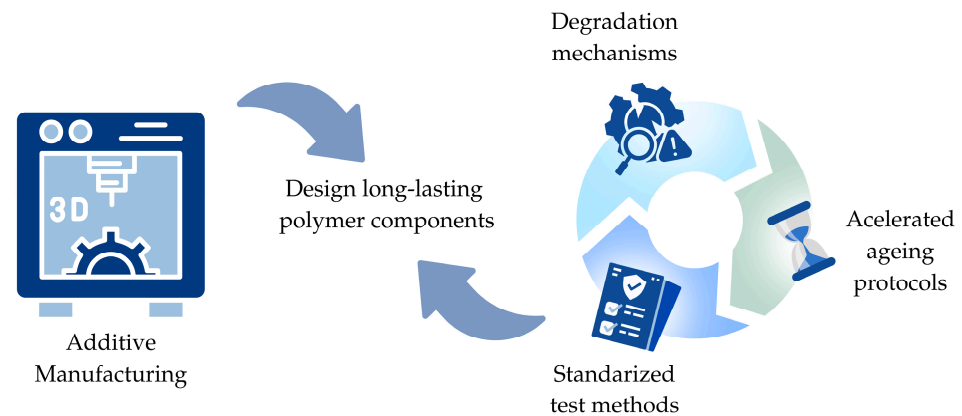
Moreover, AM is not yet fully integrated into existing standardisation and certification frameworks, particularly regarding polymer ageing and long-term durability. Although AM-specific standards are currently under development [15], this lack of harmonised guidelines limits its adoption in critical applications. It further complicates durability comparisons across different AM technologies [16].

Polymers are inherently susceptible to environmental ageing mechanisms such as thermal oxidation, hydrolysis, and photodegradation [17]. However, the interactions between these mechanisms and AM process parameters, including print orientation, layer thickness, infill geometry, and post-processing treatments, remain insufficiently characterised [18]. This gap highlights the need for robust methodologies to assess and predict the service life of additively manufactured components.

Accelerated ageing tests have therefore become essential for components qualification in high-demanding industries like defence or nuclear power. These protocols expose materials to intensified stressors (e.g., temperature, UV radiation, and humidity) to approximate the effects of long-term degradation within practical laboratory timeframes [19–21]. While originally developed for conventional polymers, accelerated life testing methods must be adapted to account for the heterogeneity of AM parts. When combined with predictive models [22,23], these approaches support lifetime estimation and facilitate the early identification of potential failure modes.

In this context, this review aims to provide a comprehensive and structured framework to support researchers in the development of durable additively manufactured polymer

components by integrating the analysis of polymer degradation mechanisms, accelerated ageing methodologies, and predictive modelling approaches relevant to AM systems (Figure 1). In contrast to the existing literature, which commonly treats polymer degradation mechanisms, accelerated ageing protocols, lifetime prediction frameworks, and AM as independent research domains, this review systematically connects and integrates these elements within a unified, process-aware framework specifically tailored to polymer AM.

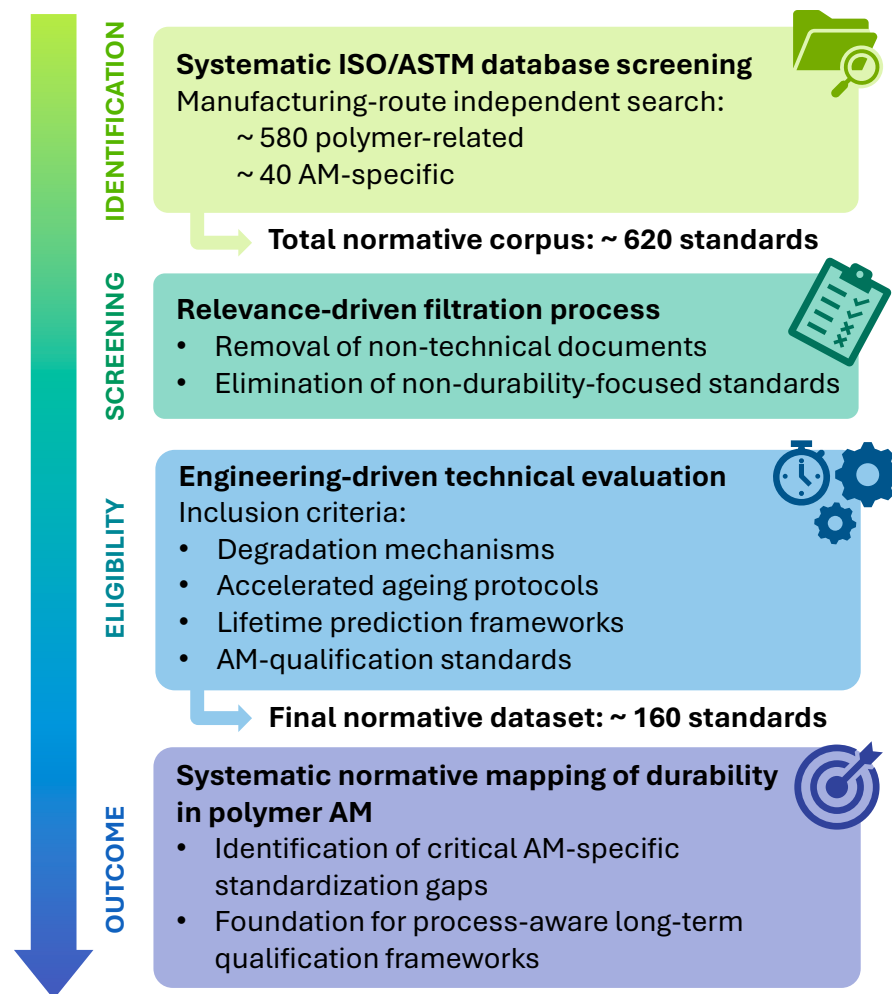


**Figure 1.** Connection between AM processes and the analysis of degradation, accelerated ageing and standardised testing strategies to enable the development of long-lasting polymer components.

By establishing a clear and systematic guide to the standards currently used for degradation analysis, ageing assessment, and accelerated lifetime testing, this review also examines processing–structure–property relationships specific to AM polymers in relation to long-term structural integrity and degradation behaviour. Moreover, it critically evaluates the adequacy of current ISO/ASTM standards when applied to additively manufactured polymers, identifying key normative gaps and the lack of orientation-dependent and process-sensitive durability qualification protocols. These insights enable the development of durability-oriented design strategies aimed at ensuring the long-term performance of additively manufactured polymer components. Through this integrative and normative perspective, the review contributes to advancing reliability-based design and the future standardisation strategies for polymer AM.

## 2. Methodological Approach for Standards Evaluation

A systematic review methodology based on the principles of PRISMA (preferred reporting items for systematic reviews and meta-analyses) [24] was adopted to analyse the current normative framework addressing the durability assessment and degradation prediction of polymeric materials, with particular emphasis on their applicability to additively manufactured components (Figure 2). An initial comprehensive screening of international standards databases from ISO and ASTM was conducted without restrictions on manufacturing route, resulting in the identification of approximately 580 standards related to polymeric materials overall, covering chemical resistance, mechanical testing, thermal and thermo-oxidative behaviour, accelerated ageing, and long-term performance evaluation. In parallel, an additional set of around 40 standards specifically associated with polymer AM was identified, primarily focused on terminology, feedstock specification, process requirements and quality assurance.



**Figure 2.** PRISMA methodological flowchart describing the systematic identification, relevance-driven screening, engineering-based eligibility assessment, and final mapping of ISO/ASTM standards analysed in this review.

The combined corpus therefore comprised approximately 620 ISO/ASTM standards, which constituted the total normative dataset analysed during the review process. During the screening phase, a relevance-driven filtration process was implemented in order to ensure technical coherence with the objectives of the study. This stage involved the removal of non-technical documents and the elimination of standards not specifically focused on durability-related aspects.

Subsequently, during the eligibility phase, an engineering-driven technical evaluation was conducted based on pre-defined inclusion criteria. Standards were retained only if they explicitly addressed degradation mechanisms, accelerated ageing protocols, lifetime prediction frameworks, or additive manufacturing qualification requirements.

Following this structured selection procedure, a subset of approximately 160 standards was selected for detailed analysis and inclusion in the article. This final selection encompasses well-established polymer durability standards, key accelerated ageing protocols and the limited number of AM-specific documents currently available that can be applied.

Through this exhaustive analysis of the existing normative landscape, the review establishes a direct connection between AM processes and standardised approaches for degradation analysis, accelerated ageing and lifetime prediction methodologies. The resulting dataset enabled a systematic normative mapping of durability in polymer additive manufacturing, supported the identification of critical AM-specific standardisation gaps,

and provided a structured foundation for the development of process-aware long-term qualification frameworks. This integrated perspective provides a structured basis for translating process-dependent material behaviour into durability-informed design strategies, thereby enabling the development of long-lasting polymer components manufactured using additive technologies. For completeness and transparency of the systematic methodology adopted, a detailed PRISMA checklist is provided in the Supplementary Materials.

### 3. Degradation Mechanisms

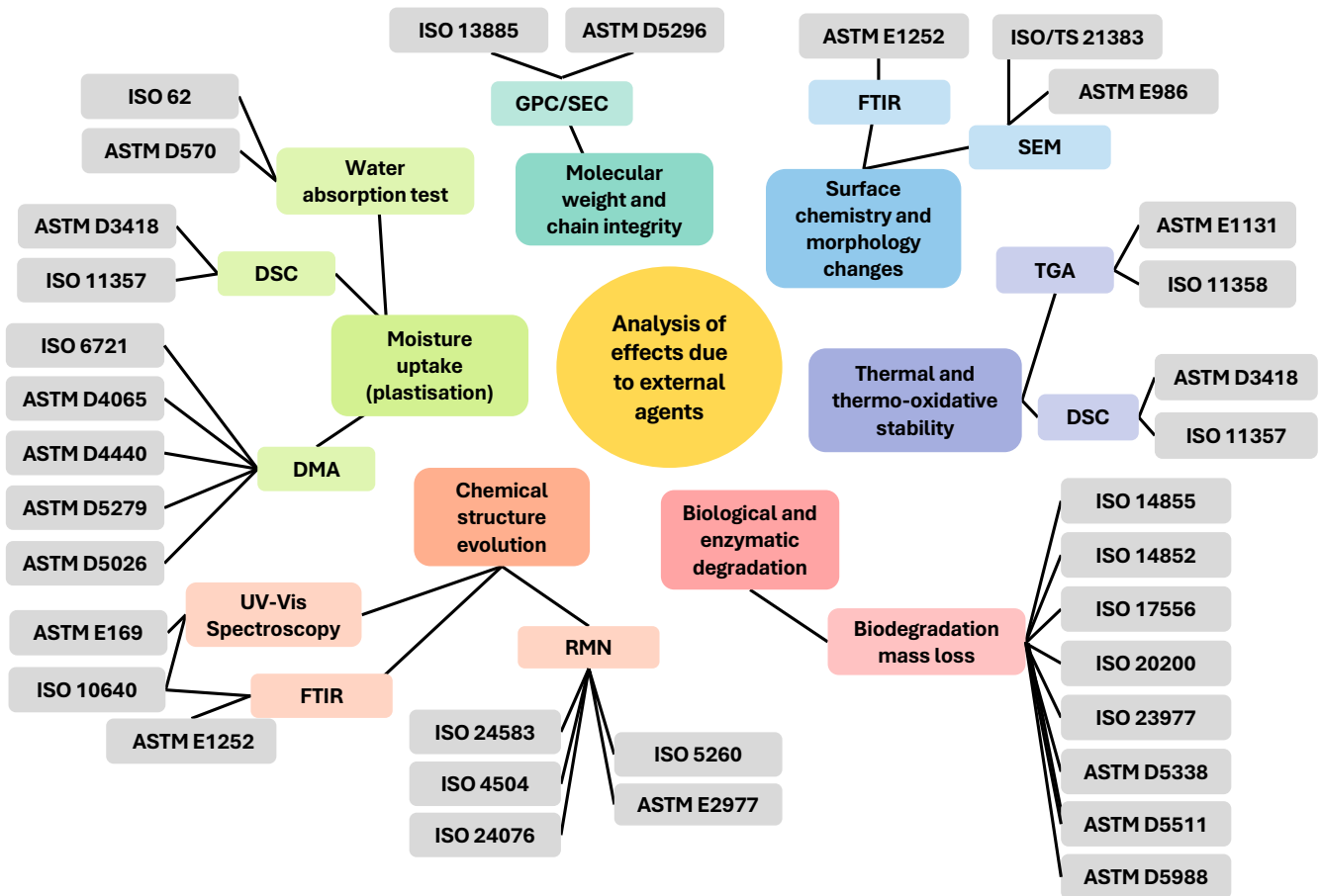
Polymeric materials are inherently sensitive to exposure to common environmental agents, such as atmospheric humidity, precipitation, solar radiation, temperature fluctuations, and oxygen, as well as to a variety of agents they may encounter depending on their specific application, including chemicals, solvents, and acidic or alkaline environments. In addition, polymers may be subjected to different types of mechanical stresses according to their functional requirements. These environmental and/or mechanical loads, which may act independently or synergistically throughout the service life of the polymer, can induce a range of mechanisms that reversibly, but more frequently irreversibly, alter polymer characteristics, collectively referred to as degradation processes [25–27].

Depending on the nature of the external agents involved, polymer degradation can be classified into hydrolysis, thermal degradation, oxidation, thermo-oxidation, photodegradation, photo-oxidation, mechanical degradation, biodegradation, among others. All polymers undergo some degree of degradation during their service life, resulting in a continuous modification and/or reduction in their properties. From a mechanistic standpoint, polymer degradation can be broadly categorised into chemical degradation processes and physical degradation mechanisms. Although these mechanisms are often interrelated, distinguishing between them is essential for a comprehensive understanding of long-term polymer performance and durability.

#### 3.1. Effects of External Agents and Chemical Degradation Mechanisms

The effect of exposure to external agents on polymeric materials is commonly described as chemical degradation. With a few exceptions, chemical degradation involves irreversible molecular transformations that modify the chemical structure of polymer chains, leading to functional deterioration and, in some cases, material failure. These processes may include chain scission, the formation of new chemical bonds, crosslinking reactions, and chain elimination phenomena [28,29].

At the molecular scale, chemical degradation is evidenced through variations in average chain length, molar mass distribution, degree of branching, crosslink density, and the generation of new functional groups. The presence of structural irregularities—such as tertiary carbon atoms, unsaturated moieties, or residual catalyst fragments—plays a critical role in defining degradation initiation sites, particularly under thermal or oxidative conditions [25,27]. An overview of the principal analytical domains employed to assess these processes, based on recognised international standards, is schematically presented in Figure 3. These molecular-scale modifications govern the evolution of macroscopic properties, including mechanical, thermal, dielectric, and optical characteristics, and ultimately determine the long-term reliability of polymeric materials.



**Figure 3.** Schematic overview of the main analytical domains used to assess the effects on polymer materials due to external agents and relevant international reference standards. The figure organises degradation-related phenomena according to key aspects of analysis, together with the corresponding ISO and ASTM standards.

### 3.1.1. Moisture-Induced Plasticisation

Moisture absorbed into a polymeric material frequently induces plasticization phenomena. Plasticization refers to the process by which low-molecular-weight species, such as water, reduce the weak intermolecular interactions within the polymeric structure, thereby increasing the mobility of polymer chains and rendering the material more flexible. Typical consequences of plasticization include reductions in elastic modulus, glass transition temperature, and creep resistance [28–32]. Once moisture penetrates the polymer, it may be partially removed through drying procedures; consequently, the initial properties of the material can, in principle, be restored, as plasticization does not involve chemical reactions. However, under practical service conditions, complete moisture removal is difficult to achieve, and the reversibility of plasticization effects remains largely theoretical. Moreover, when prolonged moisture exposure is combined with elevated temperatures or sustained mechanical stresses, irreversible degradation pathways may be activated. In condensation polymers, such conditions favour hydrolytic reactions and stress-assisted chain scission, thereby accelerating property deterioration and promoting premature failure [33]. In additively manufactured polymers, process-induced porosity and interlayer interfaces may enhance moisture diffusion, while anisotropic microstructures can promote direction-dependent degradation and non-uniform mechanical response. This phenomenon is particularly critical in medical applications, where AM-components such as surgical guides or customised prosthetic devices may be exposed to body fluids or repeated steam sterilisation cycles (autoclave conditions), leading to temporary or

permanent losses in dimensional accuracy and mechanical stability [34]. Plasticization and moisture uptake are commonly investigated by monitoring reductions in the glass transition temperature using dynamic mechanical analysis (DMA) (ISO 6721 series [35]; ASTM D4065 [36]; ASTM D4440 [37]; ASTM D5279 [38]; ASTM D5026 [39]) and differential scanning calorimetry (DSC) (ASTM D3418 [40]; ISO 11357 [41]), or by directly quantifying absorbed water through water absorption tests (ISO 62 [42]; ASTM D570 [43]).

### 3.1.2. Hydrolytic Degradation

Ageing due to exposure to aqueous environments can induce several degradation processes, primarily hydrolysis and/or plasticisation. Hydrolysis involves the cleavage of chemical (covalent) bonds within the polymeric structure and is therefore an irreversible phenomenon. This mechanism predominantly affects polymers produced by polycondensation, such as polyesters, polyamides, and polycarbonates. In addition, hydrolysis may represent the initial step in the biodegradation of biodegradable polymers, as discussed in subsequent sections. At the molecular level, hydrolysis proceeds through the scission of ester or amide bonds via reactions with water molecules, leading to a progressive decrease in molecular weight accompanied by a loss of mechanical strength and ductility [44–46]. The kinetics of hydrolysis are strongly dependent on polymer morphology, as reactions occur preferentially in amorphous regions that are more readily accessible to water, whereas crystalline domains act as diffusion barriers. Elevated temperatures, acidic or alkaline environments, and residual moisture originating from processing significantly accelerate this degradation mechanism [47]. In additively manufactured polymers, layer-by-layer fabrication may generate interfacial regions and process-induced porosity that facilitate water ingress, potentially accelerating hydrolytic chain scission compared to conventionally processed counterparts. Furthermore, anisotropic microstructures can lead to direction-dependent reductions in molecular weight and mechanical performance [48,49]. Gel permeation chromatography/size exclusion chromatography (GPC/SEC) (ASTM D5296 [50]; ISO 13885 [51]) is widely employed to monitor reductions in molecular weight, while fourier transform infrared spectroscopy (FTIR) (ASTM E1252 [52]; ISO 10640 [53]) enables the identification of chemical changes, such as increases in hydroxyl or carbonyl functionalities associated with hydrolytic chain scission.

### 3.1.3. Photo-Oxidative Degradation

Polymeric materials that perform their function outdoors are simultaneously exposed to radiation and oxygen. Exposure to UV/solar radiation in the presence of oxygen gives rise to photo-oxidation processes, leading to free-radical formation within polymer chains. These radicals trigger chain scission, oxidation reactions, and in some cases even crosslink formation, leading to surface embrittlement, micro crack formation, discolouration, and a progressive loss of mechanical properties [54,55]. Photo-oxidation is primarily a surface-driven process, as oxygen diffusion into the polymer bulk is limited and UV penetration depth is finite [56,57]. At the molecular level, photo-oxidation promotes the formation of oxygen-containing functional groups such as hydroperoxides, ketones, aldehydes, and carboxylic acids, with carbonyl groups acting as both degradation products and secondary UV absorbers that further sensitise the material. This mechanism is of particular concern for additively manufactured automotive and construction components, such as exterior trim elements, facade panels, or lightweight structural components, which are subjected to continuous solar radiation and atmospheric oxygen during service, potentially leading to surface cracking, loss of dimensional stability, and aesthetic fading [58,59]. In addition, photo-oxidative degradation becomes especially critical in applications involving UV-based sterilisation (photo-sterilisation) or extended post-curing processes, where ex-

posure to short-wavelength UV radiation can accelerate chain scission and embrittlement, progressively reducing mechanical performance and compromising the long-term structural reliability of polymer components [60,61]. The chemical and microstructural changes associated with photo-oxidation are typically characterised using a set of spectroscopic techniques, including FTIR (ASTM E1252 [52]; ISO 10640 [53]), ultraviolet-visible (UV-Vis) spectroscopy (ASTM E169 [62]; ISO 10640 [53]), and nuclear magnetic resonance (NMR) spectroscopy (ASTM E2977 [63]; ISO 24583 [64]; ISO 4504 [65]; ISO 24076 [66]; ISO 5260 [67]). Together, these methods enable the identification and quantification of oxidation products, chromophore formation, and polymer chain microstructural evolution.

#### 3.1.4. Thermo-Oxidative Degradation

Most polymers are only marginally affected by moderate temperatures, typically not exceeding 60–80 °C. Nevertheless, exposure to such temperatures can promote the evaporation or migration of low-molecular-weight additives and residual solvents. In contrast, covalent chemical bonds within polymer macromolecules may be cleaved when sufficient energy is supplied, such as at elevated temperatures. Polymer degradation driven exclusively by thermal energy is referred to as thermolysis. With the exception of specific applications, most polymeric materials are exposed to oxygen during their service life. At moderate temperatures, reactions between polymers and oxygen generally proceed at very slow, often negligible, rates. However, when radicals are present within the polymer—such as those previously generated by thermal activation—the reaction between oxygen and these radicals becomes rapid, leading to thermo-oxidative degradation. In thermo-oxidative ageing, thermal energy and oxidative reactions act synergistically [68]. This degradation pathway follows a free-radical mechanism comprising initiation, propagation, branching, and termination steps.

At the molecular level, hydrogen abstraction at labile sites, such as tertiary carbon atoms or branching points, generates radicals that readily react with oxygen to form peroxy radicals and hydroperoxide intermediates. The accumulation and subsequent decomposition of hydroperoxides mark the onset of autocatalytic oxidation, resulting in irreversible changes including embrittlement, increased stiffness, altered failure mechanisms, and, in certain cases, modifications in crystallinity [69–71]. Understanding these effects is essential for aerospace and electronic housing applications, where additively manufactured polymer components frequently operate near their thermal stability limits due to engine proximity, aerodynamic heating, or heat dissipation from internal circuitry, thereby accelerating oxidative chain scission and promoting a progressive loss of mechanical properties and long-term structural reliability [72,73]. Thermogravimetric analysis (TGA) (ISO 11358 [74]; ASTM E1131 [75]) and DSC (ASTM D3418 [40]; ISO 11357 [41]), when conducted under oxidative atmospheres, are commonly employed to assess thermo-oxidative stability and degradation kinetics occurring during both processing and service conditions. In addition, complementary spectroscopic techniques such as UV-Vis, FTIR, and NMR—previously described—are frequently used to monitor the chemical and microstructural evolution associated with thermo-oxidative degradation.

#### 3.1.5. Biological Degradation

A separate discussion is required for biodegradation processes, which occur in certain polymers, namely biodegradable materials. Biodegradation refers to the ability of specific polymers to decompose under the action of living organisms. In this context, microorganisms are capable of breaking down organic substances through physical, chemical, and enzymatic mechanisms. Consequently, both synthetic and bio-based polymers—that is, polymers derived from renewable resources—require the involvement of microorganisms

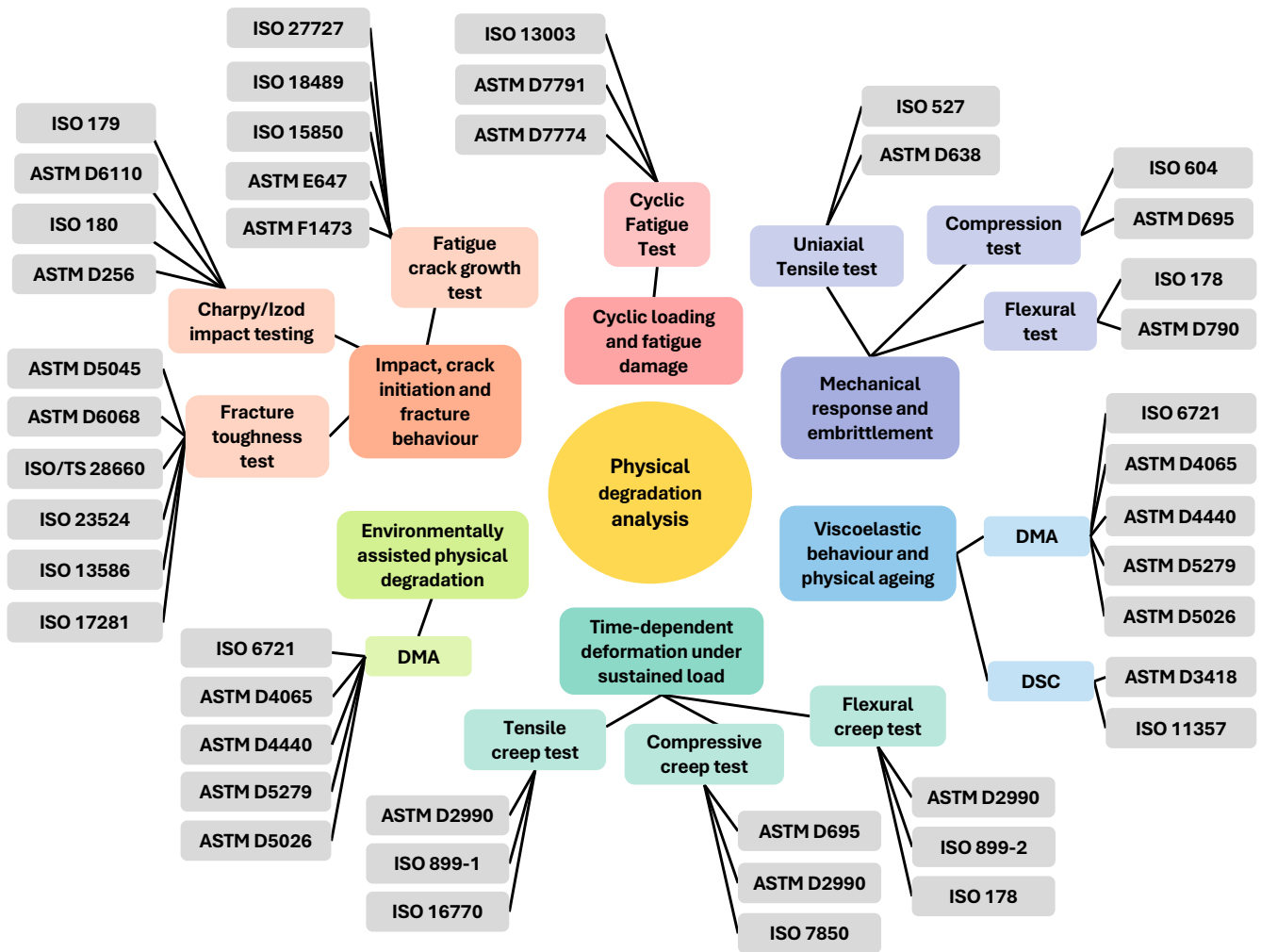
for biodegradation to take place. A major limitation of the biodegradation process is the high molar mass of polymer chains, which prevents their direct transport across microbial cell membranes. Therefore, long polymer chains must first be cleaved into smaller oligomers or monomers before they can cross the cell membrane and be subsequently assimilated by intracellular metabolic pathways. The chemical reactions involved in this initial biodegradation stage, which may occur simultaneously or sequentially, are primarily based on oxidation—typical of polymers with carbon-carbon backbones—or hydrolysis, which is characteristic of condensation polymers. In a subsequent phase, the resulting low-molecular-weight species enter cellular metabolic processes, where they are utilised as carbon and energy sources and ultimately converted into water, carbon dioxide, methane, biomass, and other non-toxic products [25–29]. The macroscopic effects of biodegradation are manifested as mass loss, dimensional or volumetric changes, and deterioration of mechanical properties. This degradation pathway is strongly influenced by polymer chemistry—particularly the presence of hydrolytically or oxidatively labile bonds—as well as polymer structure, crystallinity, and environmental conditions [76–78].

In the context of the growing use of biodegradable materials [76], biological degradation has gained significant relevance. Biodegradable polymers can undergo enzymatic or microbial degradation, where biological agents catalyse chain scission reactions, leading to mass loss and the deterioration of mechanical properties. This degradation pathway is strongly dependent on polymer chemistry, crystallinity, and environmental conditions, and is often coupled with hydrolytic mechanisms [77,78]. Biodegradation is particularly relevant for AM-compostable packaging, agricultural devices, temporary biomedical implants, and marine-deployed polymer systems, where environmental exposure directly governs material lifetime and functional performance [79].

Mass loss associated with biodegradation is commonly quantified using standardised test methods such as ISO 14855 [80], ISO 14852 [81], ISO 17556 [82], ISO 20200 [83], ISO 23977 [84] and ASTM D5338 [85], ASTM D5511 [86], and ASTM D5988 [87]. In addition, changes in molecular weight distribution and morphological features induced by biodegradation are typically characterised using GPC/SEC (ASTM D5296 [50]; ISO 13885 [51]), FTIR (ASTM E1252 [52]), and scanning electron microscopy (SEM) (ISO/TS 21383 [88]; ASTM E986 [89]).

### 3.2. Physical Degradation Mechanisms

In addition to chemical degradation, polymers experience physical degradation mechanisms that do not necessarily involve chemical bond cleavage but nonetheless exert a significant influence on long-term performance [25–28,90–92]. An overview of the main analytical domains used to assess physical degradation phenomena—based on recognised international standards—in polymeric materials is schematically presented in Figure 4.



**Figure 4.** Schematic overview of the main analytical domains used to assess physical degradation in polymeric materials and relevant international reference standards. The figure organises degradation-related phenomena according to key aspects of analysis, together with the corresponding ISO and ASTM standards.

### 3.2.1. Viscoelastic Behaviour and Physical Ageing

Physical ageing represents an intrinsic material response driven by time-dependent molecular rearrangements toward thermodynamic equilibrium and primarily affects polymers in a non-equilibrium glassy state formed during processing [93]. Over time, sub-glass-transition molecular relaxation processes reduce free volume, densify the amorphous phase, and alter chain packing. These processes typically result in increased stiffness and yield stress, accompanied by reduced ductility, impact resistance, creep rate, stress relaxation, and dimensional stability [93–95]. Physical ageing is commonly monitored using DMA (ISO 6721 [35]; ASTM D4065 [36]; ASTM D4440 [37]; ASTM D5279 [38]; ASTM D5026 [39]), which is widely employed to track changes in viscoelastic properties and relaxation spectra. In addition, DSC (ASTM D3418 [40]; ISO 11357 [41]) is frequently used to characterise physical ageing through enthalpy recovery phenomena occurring just above the temperature range of the glass transition process [96]. Furthermore, quasi-static mechanical tests, such as tensile stress-strain tests (ISO 527 [97]; ASTM D638 [98]), compression tests (ISO 604 [99]; ASTM D695 [100]), and flexural tests (ISO 178 [101]; ASTM D790 [102]), are routinely applied to quantify ageing-induced variations in elastic modulus, yield strength, strain-to-failure, and post-yield behaviour.

### 3.2.2. Residual Stress and Relaxation Behaviour

Residual stresses introduced during polymer processing, including injection moulding, extrusion, and additive manufacturing, constitute another critical factor in physical degradation [18,103]. In the specific case of fused filament fabrication (FFF), repeated heating-cooling cycles inherent to the layer-by-layer deposition strategy generate steep thermal gradients, which promote residual stress accumulation and interlayer stress concentration. Rapid cooling, thermal gradients, and constrained shrinkage generate frozen-in stress fields that may persist throughout the service life of polymer components. Thermo-mechanical simulations reported in the literature demonstrate that these stresses are particularly concentrated between the first and second deposited layers, where temperature differences between the extruded filament and the build platform are most pronounced [104,105]. Over time, these residual stresses evolve through viscoelastic relaxation, leading to dimensional instability, warpage, and localised variations in mechanical response [106–108]. Moreover, rapid temperature variations during deposition have been shown to amplify stress concentration and may favour interlaminar delamination, highlighting the strong coupling between process-induced thermal gradients and mechanical integrity in additively manufactured parts [104,105]. The influence of residual stresses on degradation is often assessed through tensile, compressive, or flexural tests performed using a universal testing machine (ISO 527 [97]; ASTM D638 [98]; ISO 604 [99]; ASTM D695 [100]; ISO 178 [101]; ASTM D790 [102]), which may reveal premature yielding, asymmetric deformation, or reduced strength compared to stress-free reference specimens. Residual stress relaxation is commonly characterised using DMA (ISO 6721 [35]; ASTM D4065 [36]; ASTM D4440 [37]; ASTM D5279 [38]; ASTM D5026 [39]).

### 3.2.3. Creep Deformation

Creep results from time-dependent molecular relaxation under sustained stress and typically occurs at stress levels well below the short-term yield strength [109,110]. At the molecular scale, creep deformation is governed by segmental motion, chain disentanglement, and viscous flow within the amorphous phase. Creep behaviour is strongly influenced by temperature, moisture, and the physical ageing state of the material [111,112]. In additively manufactured polymers, creep response is strongly affected by process-induced anisotropy, interlayer bonding, and internal porosity. The layer-wise architecture generates direction-dependent load transfer, while weak interfacial adhesion and microvoids may promote interlayer sliding and stress concentration under sustained loading, thereby accelerating creep strain accumulation compared to conventionally processed materials [113]. It is generally evaluated through long-term creep tests conducted under constant load or constant stress conditions (ISO 899-1 [114]; ISO 16770 [115]; ASTM D2990 [116]), often complemented by compressive creep tests (ISO 7850 [117]; ASTM D2990 [116]; ASTM D695 [100]) and flexural creep tests (ISO 899-2 [118]; ISO 178 [101]; ASTM D2990 [116]).

### 3.2.4. Fatigue Degradation, Impact, Crack Initiation and Fracture Behaviour

Fatigue degradation under cyclic loading involves the progressive accumulation of damage driven by repeated stress or strain fluctuations [91,92,119]. At the micro scale, fatigue damage manifests through micro-void nucleation, craze formation, and crack initiation at defects, interfaces, or regions containing residual tensile stresses [120,121]. In additively manufactured polymers, fatigue behaviour is strongly governed by process-induced features. In extrusion-based systems, raster orientation and build direction significantly affect fatigue life, with 45° / -45° configurations generally improving resistance, whereas 0° or 90° orientations promote crack propagation along weaker interlayer boundaries, evidencing pronounced anisotropy [113]. Variations in microstructure, interlayer bonding,

and density lead to different fracture responses, ranging from more ductile behaviour with greater energy absorption to more brittle failure with limited plastic deformation. These differences directly affect fatigue crack growth resistance and load-carrying capacity, particularly under mixed-mode loading conditions. In powder-based systems, improved densification and particle coalescence generally reduce crack nucleation, reinforcing the strong link between processing parameters, resulting morphology, and fatigue performance [122,123]. Overall, fracture resistance in 3D-printed polymers depends not only on material properties but also on notch geometry, loading mode, and crack-tip driving forces, underscoring the need for fracture mechanics-based approaches in fatigue assessment.

Fatigue behaviour is commonly assessed using stress-controlled or strain-controlled cyclic fatigue tests (ASTM D7791 [124]; ASTM D7774 [125]; ASTM D3479 [126]), including tension-tension, tension-compression, and flexural fatigue configurations. Fatigue life is typically quantified using stress-life (S-N) and strain-life ( $\epsilon$ -N) approaches [127,128]. In addition, fatigue crack growth tests based on fracture mechanics principles (ASTM E647 [129]; ASTM F1473 [130]; ISO 27727 [131]; ISO 18489 [132]; ISO 15850 [133]) are employed to characterise crack propagation rates and threshold conditions. Furthermore, fracture toughness tests (ASTM D5045 [134]; ASTM D6068 [135]; ISO/TS 28660 [136]; ISO 23524 [137]; ISO 13586 [138]; ISO 17281 [139]), together with Charpy (ISO 179 [140]; ASTM D6110 [141]) and Izod (ISO 180 [142]; ASTM D256 [143]) impact tests, are used to evaluate impact behaviour, crack initiation, and fracture resistance.

### 3.2.5. Environmentally Assisted Physical Degradation

Environmentally assisted fatigue and creep-fatigue interaction represent particularly severe degradation scenarios, where mechanical loading is combined with aggressive environmental conditions such as elevated temperature, humidity, or oxidative atmospheres [144]. These phenomena are investigated through combined mechanical-environmental tests [144,145], where cyclic or sustained loading is applied under controlled environmental conditions using DMA (ISO 6721 [35]; ASTM D4065 [36]; ASTM D4440 [37]; ASTM D5279 [38]; ASTM D5026 [39]). In addition, tensile testing (ISO 527 [97]; ASTM D638 [98]) and fracture toughness measurements (ASTM D5045 [134]; ASTM D6068 [135]; ISO/TS 28660 [136]; ISO 23524 [137]; ISO 13586 [138]; ISO 17281 [139]) are commonly employed to monitor stiffness degradation, damage accumulation, and the evolution of failure mechanisms.

## 4. Accelerated Ageing and Lifetime Prediction Methodologies

The prediction of long-term durability and service life of polymeric materials remains a major challenge in polymer engineering, as degradation processes typically evolve over timescales far exceeding those accessible through conventional laboratory testing. These processes induce progressive changes in molecular structure, morphology, and macroscopic properties, including chain scission, crosslinking, additive depletion, crystallinity evolution, and physical ageing [21–23]. Under real service conditions, polymers are exposed to combined thermal, photo-oxidative, mechanical, chemical, and biological stressors, as discussed previously [25–29].

Although natural exposure testing provides the most realistic representation of in-service behaviour, its long duration, high cost, and sensitivity to climatic variability severely limit its applicability for material development and qualification. Consequently, accelerated ageing methodologies have become indispensable tools for durability assessment. These tests are inherently conservative and are designed to ensure adequate safety margins by verifying the retention of chemical integrity and thermo-mechanical performance through-



#### 4.1.1. Natural Exposure

Natural exposure testing is generally regarded as the benchmark for durability assessment, particularly when the expected service life is relatively short or when materials operate under severe environmental conditions [148]. General procedures for outdoor exposure of plastics are established in ASTM G7 [149], ASTM D1435 [150], ASTM G24 [151], ISO 877-1 [152] and ISO 877-2 [153], while accelerated natural sunlight exposure using concentrator systems is addressed in ASTM G90 [154], ASTM D4364 [155] and ISO 877-3 [156].

From a lifetime prediction perspective, natural exposure data are rarely used directly for extrapolation; instead, they serve as a reference for determining acceleration factors and validating degradation mechanisms activated during artificial ageing. Correlation between natural and artificial exposure is often established using half-life times or fixed property-retention thresholds [157,158].

#### 4.1.2. Artificial Weathering and Light Exposure

Artificial weathering tests accelerate degradation by controlling spectral distribution, irradiance, temperature, and humidity within laboratory devices [159,160]. Xenon-arc exposure methods, standardised in ASTM G155 [161], ASTM D2565 [162] and ISO 4892-2 [163], simulate the full solar spectrum—including UV, visible, and near-infrared radiation—and are widely applied to plastics, coatings, and elastomers intended for outdoor use. Key control parameters include irradiance (typically 0.35–0.55 W·m<sup>-2</sup> at 340 nm), black-panel temperature (50–80 °C), and relative humidity (ranging from approximately 40% to 95%).

Fluorescent UV methods specified in ASTM D4329 [164], ASTM G154 [165], and ISO 4892-3 [166] emphasise short-wavelength UV radiation and employ programmed cycles of UV irradiation and condensation to promote photo-oxidative and hydrolytic degradation. Carbon-arc methods (ISO 4892-4 [167]; ASTM D1499 [168]), although harsher and less spectrally representative, remain relevant for historical datasets and conservative screening. General practice requirements for artificial weathering—including lamp calibration, irradiance control, black-panel temperature, humidity regulation, and cycle design—are defined in ASTM G151 [169] and ISO 4892-1 [170].

#### 4.1.3. Thermal Ageing, Thermo-Oxidative Stability and Hydrothermal Ageing

Thermal ageing protocols constitute the experimental foundation for most lifetime prediction approaches based on thermally activated degradation [19,20,146,147]. In typical tests, specimens are aged isothermally at elevated temperatures—commonly between 60 and 200 °C—for defined periods and subsequently conditioned under a standard laboratory climate prior to property evaluation [171]. ASTM D3045 [172], ISO 2578 [173], ISO 188 [174] and ISO 11346 [175] establish procedures for long-term thermal ageing of plastics and explicitly permit lifetime extrapolation using Arrhenius-based methods [173].

Property-retention criteria are fundamental for determining the service life “end-point.” Two commonly referenced standards address this topic with different roles and levels of prescriptiveness. ASTM D5870 [176] serves as a guideline, providing general recommendations on property selection, thermal ageing procedures, and the interpretation of ageing data, but it does not define a fixed percentage of property loss as a failure criterion. In contrast, the relative thermal index (RTI) approach defined by Underwriters Laboratories (UL 746B [177]) specifies 50% retention of a critical property as the criterion for establishing the thermal endurance limit.

Thermo-oxidative stability is commonly evaluated through oxidation induction time (OIT) measurements obtained by DSC according to ISO 11357-6 [178] or ASTM D3895 [179]. OIT represents the onset of rapid oxidative degradation and is strongly influenced by antioxidant concentration, dispersion, and depletion kinetics. When measured at multiple

temperatures, OIT values may be treated as failure times and analysed using Arrhenius-type extrapolation to predict oxidation-controlled service life [180,181].

Hydrothermal ageing is considered a specific subset of thermal ageing, where temperature-driven degradation occurs in conjunction with controlled moisture exposure [182,183]. While elevated temperature governs reaction kinetics, the presence of water alters degradation pathways through hydrolysis, plasticisation, and moisture-assisted oxidation [184]. In this context, ASTM D7444 [185] defines a standardised protocol for assessing the durability of oxidatively degradable plastics under combined heat and humidity, complementing conventional dry thermal ageing by capturing synergistic thermal-moisture effects relevant to humid service conditions.

#### 4.1.4. Chemical, Biological and Radiation-Induced Ageing Environments

Accelerated ageing protocols also encompass chemically aggressive environments, including ozone exposure, saline atmospheres, and biological attack. Ozone resistance is commonly evaluated using chamber tests standardised in ASTM D1149 [186], ASTM D1171 [187], and ISO 1431 [188], which quantify crack initiation and crack density under controlled ozone concentrations and applied strain.

Biological resistance of polymeric materials is evaluated through exposure to fungal and bacterial species under growth-favourable conditions. ISO 846 [189] and ASTM G21 [190] define standardised procedures for evaluating biodeterioration based on mass loss, surface colonisation, and changes in mechanical properties.

Resistance to liquid chemical reagents is commonly evaluated through standardised immersion and exposure tests designed to assess the effects of chemicals on the physical and mechanical properties of plastics. In this context, ASTM D543 [191] and ISO 175 [192] establish standard practices for determining changes in mass, dimensions, appearance, and mechanical performance following controlled exposure to a wide range of chemical reagents, including acids, bases, solvents, and oils. These methods provide comparative data on chemical compatibility and are frequently used to support material selection and durability assessment in chemically aggressive service environments, complementing accelerated ageing protocols involving gaseous, saline, or biological agents.

In addition to chemical and biological stressors, ionising radiation represents a major degradation factor for polymeric components intended for nuclear applications. Gamma radiation induces chain scission, crosslinking, and oxidative degradation, leading to embrittlement, reduced ductility, and changes in electrical and mechanical properties. Consequently, radiation ageing tests are essential for qualifying polymeric materials and components operating in radiation-controlled environments. Two standards mainly govern the environmental qualification of safety-related equipment for nuclear power plants, IEEE 323 [193] and Regulatory Guide 1.89 Rev.2 [194]. These standards define integrated qualification methodologies combining gamma irradiation, thermal ageing, humidity, and mechanical loading to ensure long-term functional integrity under normal operation and design-basis accident scenarios.

#### 4.1.5. Mechanical-Environmental Accelerated Ageing

Mechanical-environmental accelerated ageing protocols aim to characterise synergistic degradation mechanisms arising from the combined action of mechanical stress and environmental agents, which frequently govern premature failure in polymeric materials [195,196]. Time-dependent deformation under sustained load or constant stress is commonly evaluated using tensile, compressive, or flexural creep tests, as described in the preceding sections. In addition, cyclic mechanical loading under environmental exposure is typically assessed in accordance with ASTM D7791 [124], ASTM D7774 [125],

ASTM D3479 [126] and ISO 13003 [197]. Environmental factors such as elevated temperature, humidity, or chemical exposure are introduced to accelerate damage mechanisms beyond those observed under purely mechanical loading conditions.

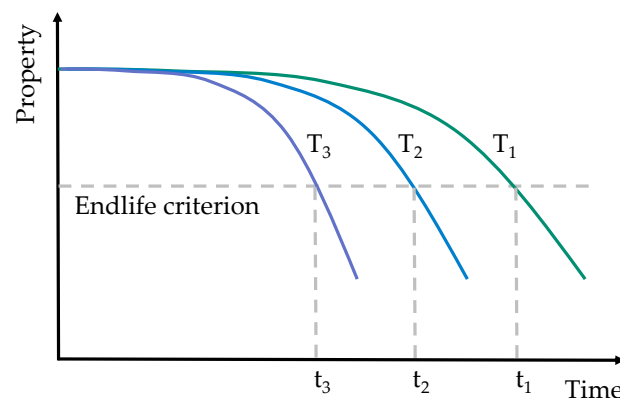
A particularly critical degradation mode is environmental stress cracking (ESC) [198], in which mechanical stress and chemically aggressive media act simultaneously to induce brittle failure at stress levels significantly below the nominal material strength. ESC behaviour in plastics is specifically addressed by the ISO/AWI 22088 series [199], while resistance to stress cracking in polyethylenes is most commonly evaluated using the full notch creep test (FNCT) [200], standardised in ISO 16770 [115].

#### 4.2. Lifetime Prediction Frameworks Based on Accelerated Ageing Data

Lifetime prediction frameworks establish a quantitative relationship between time-dependent property changes observed during accelerated ageing and the anticipated evolution of material performance under service conditions [19,23,201]. These frameworks differ in their underlying assumptions regarding degradation kinetics, the influence of temperature and other stressors, and the complexity of the degradation mechanisms involved.

##### 4.2.1. Arrhenius-Based Lifetime Prediction Model

The Arrhenius model is the most widely used approach for predicting the lifetime of polymeric materials subjected to thermally activated degradation processes [202,203]. This model assumes that degradation is controlled by a single dominant reaction mechanism and that the reaction rate increases exponentially with temperature (Figure 6).



**Figure 6.** Change in property with time at three different temperatures  $T_1 < T_2 < T_3$ .

The Arrhenius equation is expressed as Equation (1):

$$k = A \cdot e^{\left(-\frac{E_a}{RT}\right)} \quad (1)$$

where  $k$  represents the degradation rate constant,  $A$  is the pre-exponential or frequency factor associated with the frequency of molecular events leading to degradation,  $E_a$  denotes the activation energy of the degradation process expressed in joules per mole ( $\text{J} \cdot \text{mol}^{-1}$ ),  $R$  is the universal gas constant (with a value of  $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ), and  $T$  is the absolute temperature.

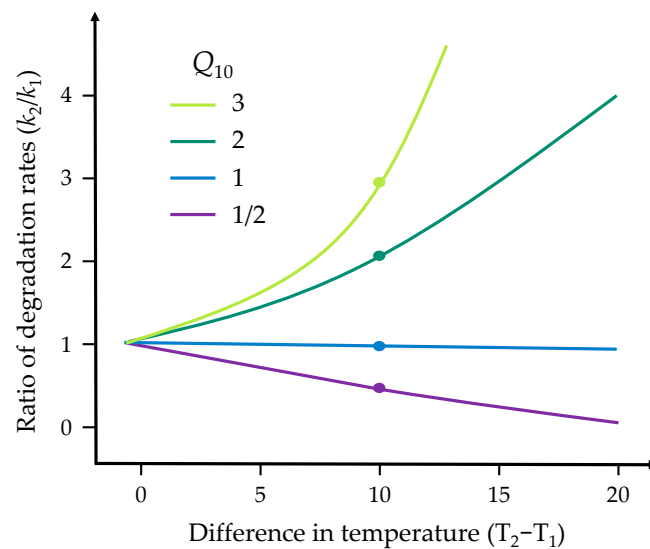
This methodology is formally established in ISO 2578 [173] and is widely applied to thermal ageing data obtained under standardised conditions such as ISO 11346 [175], ASTM D3045 [172], and ISO 188 [174]. Arrhenius-based analysis is frequently used to interpret oxidation induction time (OIT) data measured according to ISO 11357-6 [178] or ASTM D3895 [179]. Under appropriate conditions, Arrhenius extrapolation provides reliable lifetime predictions for oxidation-controlled degradation processes occurring at temperatures well below the melting point and in the absence of diffusion limitations.

In practice, the validity of the Arrhenius model may be restricted, as semicrystalline polymers often exhibit non-linear Arrhenius behaviour when the temperature range crosses the glass transition temperature ( $T_g$ ). This deviation is attributed to changes in molecular mobility, diffusion, and degradation mechanisms. Consequently, extrapolation across  $T_g$  can introduce significant errors, requiring segmented Arrhenius analysis or alternative modelling approaches for accurate lifetime prediction.

#### 4.2.2. Empirical $Q_{10}$ Rule

The  $Q_{10}$  rule is a simplified empirical approach for estimating the effect of temperature on the degradation rate of polymeric materials. It is commonly applied when available experimental data are insufficient to support more rigorous kinetic models such as Arrhenius-based formulations [204–206]. This methodology has been adopted in standards such as ASTM D3045 [172], particularly for practical lifetime estimation and comparative material evaluations.

The  $Q_{10}$  model assumes that the degradation rate increases by a constant factor for every 10 °C rise in temperature (Figure 7).



**Figure 7.** Schematic illustration of the dependence on temperature of the degradation rates for several different  $Q_{10}$  temperature coefficients.

The relationship between degradation rates  $k_1$  and  $k_2$  at temperatures  $T_1$  and  $T_2$ , respectively, is expressed by Equation (2):

$$\frac{k_2}{k_1} = Q_{10}^{\left(\frac{T_2 - T_1}{10}\right)} \quad (2)$$

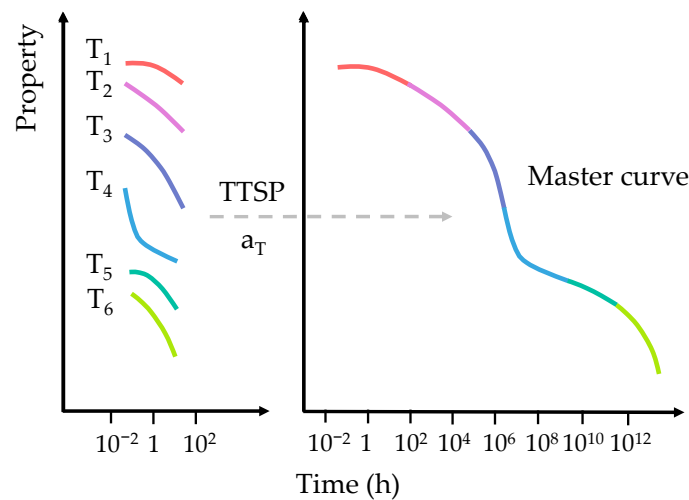
where  $Q_{10}$  is a dimensionless empirical coefficient representing the thermal acceleration factor, typically ranging between 2 and 3 for most polymeric materials. This formulation enables rapid estimation of relative changes in degradation rate and, by extension, service life when materials are exposed to temperatures different from nominal operating conditions.

Unlike Arrhenius-based models, the  $Q_{10}$  rule does not require activation energy or detailed thermodynamic parameters. However its validity is limited by the assumption of uniform degradation behaviour over the temperature range. Consequently, it is best suited for moderate temperatures, preliminary design evaluations, and conservative lifetime estimates, and should be applied with caution for long-term or extreme thermal extrapolation due to its empirical nature [207].

#### 4.2.3. Time–Temperature Superposition Principle

The time–temperature superposition principle (TTSP) is a fundamental framework for accelerated experimental methodologies applied to polymeric materials. It enables the prediction of long-term viscoelastic behaviour and mechanically driven degradation from short-term tests conducted at elevated temperatures. However, it is necessary to ensure that exposure to high temperatures does not induce chemical reactions in the polymer material.

The principle relies on the empirical assumption of time–temperature equivalence, which states that the effect of increasing temperature on a viscoelastic response is equivalent to extending the observation time at a lower reference temperature. Under this assumption, isothermal response curves obtained at different temperatures can be horizontally shifted along the logarithmic time axis to construct a single master curve referenced to a chosen temperature (Figure 8) [208–210]. The application of TTSP is described in ISO 18437-6 [211].



**Figure 8.** Schematic illustration of creating a master curve through the time–temperature superposition (TTSP) method.

The temperature dependence of the horizontal shift factor is commonly described by an Arrhenius-type relationship, expressed in Equation (3):

$$\log a_T = -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \quad (3)$$

where  $a_T$  is the time–temperature shift factor,  $E_a$  is an apparent activation energy associated with the viscoelastic relaxation process,  $R$  is the universal gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ),  $T$  is the absolute temperature, and  $T_0$  is the reference temperature at which the master curve is constructed.

TTSP enables extrapolation of creep compliance, modulus, and failure times over multiple decades, provided that the governing viscoelastic mechanisms remain unchanged across the investigated temperature range. Its applicability is therefore limited to conditions where physical ageing, moisture effects, or damage accumulation do not alter the underlying deformation and relaxation processes, thereby invalidating the assumption of time–temperature equivalence.

#### 4.2.4. Williams–Landel–Ferry Model

The Williams–Landel–Ferry (WLF) model is a specific form of time–temperature superposition particularly suited for polymeric materials near the glass transition temperature, where viscoelastic behaviour is governed by cooperative segmental chain mobility [212,213]. Unlike Arrhenius-based approaches, the WLF model is derived from free-volume the-

ory and accounts for the non-linear temperature dependence observed near  $T_g$ , where small temperature variations produce large changes in molecular mobility and relaxation times [214–217]. By explicitly incorporating these effects, the WLF formulation is more appropriate than Arrhenius-type relations for constructing master curves in the vicinity of the glass transition. Its application in accelerated ageing and temperature-dependent mechanical behaviour is referenced in ISO 11346 [175].

The temperature dependence of the time–temperature shift factor is expressed by the WLF equation (Equation (4)):

$$\log a_T = -\frac{C_1(T - T_r)}{C_2 + (T - T_r)} \quad (4)$$

where  $a_T$  is the shift factor,  $T$  is the absolute temperature, and  $T_r$  is the reference temperature, typically selected close to the glass transition temperature. The material constants  $C_1$  and  $C_2$  reflect the sensitivity of molecular mobility to temperature and the available free volume within the polymer matrix.

The WLF model is generally valid from approximately  $T_g$  to about  $T_g + 100$  °C, where viscoelastic behaviour is governed by cooperative segmental motions. Outside this range, secondary relaxations, chain slippage, diffusion effects, or the onset of physical or chemical degradation reduce the predictive reliability of the model. These conditions require alternative models for accurate lifetime assessment.

## 5. Normative Framework for the Assessment of Degradation and Durability in Additively Manufactured Polymer Components

Following the description of the chemical and physical degradation mechanisms governing the long-term performance of polymeric materials, it is essential to examine the current normative framework available for the characterisation and qualification of polymer components manufactured by AM. Although the degradation phenomena affecting additively manufactured polymers are, at a fundamental level, comparable to those observed in conventionally processed materials, the inherent features of AM—such as layer-by-layer fabrication, microstructural anisotropy, process-induced porosity, interlayer bonding quality, and complex thermal histories—pose additional challenges beyond the scope of existing standards [13–15,218].

In recent years, a growing set of ISO/ASTM standards has been developed specifically for additive manufacturing. These standards primarily address terminology, design guidelines, feedstock material specification and characterisation, process requirements, system qualification, and quality assurance (Table 1).

This normative framework is essential for ensuring process consistency, repeatability, and baseline mechanical performance of AM components. However, its scope remains primarily focused on manufacturing and design aspects, rather than on the evaluation of long-term degradation and durability. Polymer AM standards remain largely limited to the systematic detection, classification, and acceptance criteria for defects within printed components.

**Table 1.** Classification of ISO/ASTM and ASTM standards relevant to polymer AM.

AM Domain	Standards	Scope/Purpose
Terminology and general principles	ISO/ASTM 52900 (General) [219] ISO/ASTM 52901 (General) [220] ISO/ASTM 52920 (Production Sites) [221] ISO/ASTM 52927 (General) [222] ISO/ASTM 52939 (Infrastructure) [223] ASTM F3572 (Aviation) [224] ASTM F3674 (Automotive) [225] ISO 5092 (Medicine) [226]	Establish a unified terminology and classification of AM processes and define general requirements for quality, documentation, and communication across AM supply chains.
Design for Additive Manufacturing and build orientation	ISO/ASTM 52910 (General) [227] ISO/ASTM 52911-2 (Powder bed fusion) [228] ISO 17295 (General) [229] ISO/ASTM 52915 (General) [230] ASTM F3488 (General) [231] ASTM F3529 (Material extrusion) [232] ASTM WK83109 (Vat photopolymerization) [233]	Specify requirements and characterization methods for polymer feedstocks to control material consistency, thermal stability, and reuse-induced degradation in AM processes.
Feedstock material specification and characterization	ISO/ASTM 52903-1 (Material extrusion) [234] ISO/ASTM 52925 (Powder bed fusion) [235] ASTM F3606 (Powder bed fusion) [236] ASTM F3456 (Powder bed fusion/Medicine) [237]	Specify requirements and characterization methods for polymer feedstock materials, supporting control of material consistency, thermal stability, and reuse-related degradation in AM processes.
Process-specific requirements by AM technology	ISO/ASTM 52903-2 (Material extrusion) [238] ASTM F3489 (Material extrusion) [239] ASTM F3091/F3091M (Powder bed fusion) [240]	Define technology-specific process requirements and qualification principles linking process control to part quality and performance.
Quality assurance, system qualification, and process performance	ISO/ASTM 52902 (General) [241] ISO/ASTM 52920 (General) [221] ISO/ASTM 52924 (General) [242] ISO/ASTM 52936-1 (Powder bed fusion) [243]	Address process performance, repeatability, system qualification, and geometric capability to ensure consistent AM manufacturing quality.

While comprehensive guidelines for defect identification, inspection, and quality assessment have been developed for metal AM (ISO/ASTM TR 52905 [244]; ISO/ASTM TR 52906 [245]; ISO/ASTM 52909 [246]; ISO/ASTM 52928 [247]), equivalent polymer-specific standards are largely absent.

At present, there is a lack of ISO or ASTM standards specifically designed to evaluate chemical degradation mechanisms, such as oxidation, hydrolysis, photo-degradation, or molecular weight evolution, in polymer components produced by AM. Similarly, no dedicated AM-specific standards exist for the systematic assessment of physical degradation phenomena, including physical ageing, creep, fatigue, residual stress relaxation, or environmentally assisted damage under service-relevant conditions. Consequently, the durability of additively manufactured polymer parts is typically evaluated using conventional polymer testing standards originally developed for injection-moulded or extruded materials, which are subsequently adapted for use with AM specimens [248,249].

While this combined approach—integrating AM-specific process standards with established polymer characterisation and durability tests—is widely accepted within the scientific literature, it presents inherent limitations. Conventional testing methodologies often fail to capture AM-specific features such as build orientation effects, interlayer adhesion quality, and spatial heterogeneity of properties, all of which play a critical role in long-term performance and failure mechanisms. As a result, extrapolating durability data obtained using non-AM-specific standards to real service conditions remains uncertain [16,250,251].

The absence of a unified and AM-specific normative framework for the assessment of physical and chemical degradation constitutes a major barrier to the widespread adoption of additively manufactured polymer components in long-life or safety-critical applications. Addressing this limitation will require either the development of new standards specifically aimed at evaluating degradation and durability in AM polymer parts, or the inclusion of dedicated technical annexes to existing polymer and AM standards to explicitly address testing requirements and conditions associated with additive manufacturing.

Such normative developments should explicitly account for the influence of build orientation, interlayer bonding quality, process-induced porosity, and the complex interaction between multiple, often concurrent, degradation mechanisms. In addition, they should incorporate the inherent anisotropy and microstructural heterogeneity characteristic of additively manufactured polymers, which strongly affect damage initiation, crack propagation, and time-dependent mechanical response. Until such dedicated standards are fully established and validated, reliable long-term qualification of additively manufactured polymer components will necessarily rely on hybrid assessment strategies. These approaches must combine AM process standards with conventional polymer ageing protocols, mechanical characterisation methods, and durability testing procedures, thereby enabling a pragmatic yet robust evaluation of long-term performance while bridging the gap between emerging AM-specific requirements and existing qualification frameworks.

## 6. Processing–Structure–Property Relationships in Polymer AM

Degradation and the progressive loss of mechanical performance in polymeric components produced by additive manufacturing are intrinsically governed by processing–structure–property (P-S-P) relationships, where printing parameters function as primary microstructural design variables rather than secondary manufacturing settings [252–254]. Unlike conventional polymer processing routes, additive manufacturing technologies impose highly localised and process-specific thermal, mechanical, or photochemical histories that directly define the material's internal architecture. Consequently, the long-term stability of additively manufactured polymers cannot be decoupled from processing, as degradation pathways and damage accumulation mechanisms are fundamentally rooted in the microstructures generated during fabrication.

Across fused filament fabrication (FFF) [255–257], stereolithography (SLA) [258,259], and selective laser sintering (SLS) [260,261], printing parameters govern critical microstructural attributes such as porosity morphology, interlayer bonding quality, crosslink density gradients, crystallinity, and residual stress distributions. These structural features govern not only the initial mechanical response—stiffness, strength, and anisotropy—but also the evolution of these properties under environmental, thermal, and mechanical ageing. In particular, processing-induced microstructural heterogeneities act as preferential sites for damage initiation, thereby accelerating degradation mechanisms such as crack nucleation, interfacial debonding, molecular scission, viscoelastic creep, and environmentally assisted damage. From this perspective, processing parameters must be regarded as durability-defining parameters, as relatively small variations during fabrication can lead to substantial differences in degradation kinetics, fatigue resistance, creep behaviour, and ultimately service life [61,262,263].

Table 2 synthesises the dominant processing-induced structural features observed across the main polymer AM technologies and explicitly links them to critical degradation mechanisms governing long-term performance. Rather than considering degradation as an external or post-processing phenomenon, the table highlights how process-controlled microstructural attributes act as primary enablers of damage initiation and property deteri-

oration throughout service life. In this sense, degradation is an intrinsic consequence of the fabrication process itself rather than an independent in-service phenomenon.

**Table 2.** Process-controlled microstructural features and their implications for degradation-driven failure and reliability of additively manufactured polymer components.

AM Technology	Processing-Induced Structural and Molecular Features	Critical Degradation Consequences for Long-Term Performance	Reference
FFF	Low infill density and positive air gaps promote the formation of interconnected porosity.	Accelerated moisture uptake enhances polymer plasticization and induces early stiffness loss, reducing load-bearing capability.	[264–266]
	Insufficient extrusion temperature or excessive layer thickness restrict polymer chain interdiffusion across layers, resulting in weak interlayer bonding.	Interlayer interfaces act as preferential failure sites under cyclic and promoting delamination-controlled failure.	[267–270]
	Build orientation imposes pronounced mechanical anisotropy and defines preferential crack propagation paths.	Direction-dependent durability leads to unpredictable mechanical performance and reduced service life.	[271–273]
SLA	Under-curing results in low crosslink density networks and heterogeneities across printed layers.	Moisture-sensitive under-cured regions undergo premature mechanical degradation.	[274–277]
	Over-curing or aggressive post-curing increase crosslink density and generate high residual stress levels.	Brittle fracture behavior and accelerated crack growth occur under thermal or UV exposure.	[278–280]
	Large layer thicknesses promote cure gradients and lead to the accumulation of internal stresses.	Reduced fatigue resistance and shortened service life under sustained or cyclic mechanical loading.	[281–283]
SLS	Inadequate bed temperature leads to crystallinity gradients.	Progressive stress relaxation, creep deformation and microcrack development.	[284–286]
	Excessive energy input induces polymer chain degradation and high residual stress accumulation.	Accelerated loss of strength and ductility during service and thermal ageing.	[262,284,287,288]
	Repeated powder reuse causes cumulative feedstock ageing, altering molecular weight distribution and crystallinity.	Increased variability and uncertainty in long-term mechanical stability.	[289–292]

Consequently, durability and long-term performance cannot be reliably assessed using generic polymer qualification approaches developed for conventional manufacturing routes. The strong coupling between processing parameters, microstructural heterogeneity, and degradation behaviour underscores the need for technology-specific standards tailored to each AM process. Such standards must explicitly account for the unique process-structure interactions inherent to each technology in order to enable meaningful durability assessment and comparison across material systems.

As polymer AM is increasingly adopted for load-bearing and safety-critical components across multiple industrial sectors, the development of process-aware durability and ageing standards are essential to ensure reliable performance and accurate lifetime prediction. This requirement is particularly critical for certification, qualification, and long-term design of additively manufactured polymer components intended for demanding service environments.

## 7. Future Directions

The transition of polymer additive manufacturing from prototyping to structurally demanding and safety-critical applications requires a fundamental redefinition of durability assessment methodologies. As demonstrated throughout this review, the intrinsic layer-wise fabrication strategy generates anisotropic mechanical behaviour, spatially heterogeneous porosity distributions, interlayer bonding variability, and residual thermal

stresses that cannot be adequately captured by qualification frameworks developed for conventionally processed polymers. These process-induced features directly influence diffusion-controlled oxidation, moisture-assisted degradation, viscoelastic relaxation, creep deformation, and fatigue crack initiation and propagation, thereby redefining the governing mechanisms of long-term failure.

Future research efforts should therefore focus on establishing AM-specific degradation and lifetime qualification protocols in which specimen preparation, property evaluation, and failure criteria are explicitly process-aware. Orientation-dependent mechanical characterisation, interfacial strength assessment, and porosity-sensitive damage metrics must be incorporated into standardised procedures to ensure conservative and reproducible lifetime extrapolation. Without such adaptations, classical Arrhenius-based models, Q10 approximations, and time–temperature superposition methodologies may yield inaccurate predictions when applied to microstructurally heterogeneous AM components.

Furthermore, accelerated ageing methodologies must evolve toward synergistic multi-stressor protocols that replicate realistic operational envelopes. Combined thermo-mechanical loading, hydrothermal exposure under sustained stress, environmentally assisted fatigue, and creep-fatigue interaction should be treated as coupled degradation phenomena rather than isolated mechanisms. This integrated approach is particularly critical for load-bearing AM components intended for aerospace, automotive, medical, defence, and energy systems.

Embedding durability considerations within processing–structure–property optimisation strategies represents a final but essential step. Printing parameters should be regarded as structural design variables governing long-term damage tolerance and degradation kinetics, thereby enabling durability-driven process optimisation. Advancing in this direction will be decisive for achieving standardised, certification-ready, reliability-based deployment of polymer additive manufacturing technologies.

## 8. Conclusions

This review integrates the analysis of polymer degradation mechanisms, standardised characterisation techniques, and accelerated ageing and lifetime prediction methodologies with a process-oriented evaluation of processing–structure–property relationships in polymer additive manufacturing. By critically examining the current normative framework, the study demonstrates that existing durability and lifetime assessment standards—largely developed for conventionally processed polymers—do not adequately capture the process-induced heterogeneity inherent to additive manufacturing.

The principal conclusions derived from this work are:

- Current durability and lifetime assessment standards, largely developed for conventionally processed polymers, are not fully suitable for capturing the anisotropy and spatial heterogeneity inherent to polymer additive manufacturing.
- Printing parameters act as durability-defining variables, as they govern the formation of microstructural features that control degradation kinetics, damage accumulation, and long-term mechanical response across FFF, SLA, and SLS technologies.
- Long-term qualification of AM polymer components requires process-aware evaluation methodologies explicitly linking fabrication parameters with microstructural architecture and service-life performance.

Overall, the results establish that lifetime prediction and certification of additively manufactured polymer components are fundamentally process-dependent, as fabrication parameters dictate the microstructural architecture that ultimately controls long-term degradation, damage tolerance and structural reliability.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/jmmp10030102/s1>. In this Supplementary Information, the PRISMA-based methodology used for the systematic identification, classification, and screening of ISO and ASTM standards related to polymer durability and additive manufacturing can be found, including Table S1 summarizing the distribution of the identified standards.

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## Abbreviations

The following abbreviations are used in this manuscript:

AM	Additive manufacturing
PRISMA	Preferred reporting items for systematic reviews and meta-analyses
FFF	Fused filament fabrication
SLA	Stereolithography
SLS	Selective laser sintering
ISO	International organisation for standardisation
ASTM	American society for testing and materials
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
FTIR	Fourier transform infrared spectroscopy
UV-Vis	Ultraviolet-visible
NMR	Nuclear magnetic resonance
GPC/SEC	Gel permeation chromatography/Size exclusion chromatography
SEM	Scanning electron microscopy
OIT	Oxidation induction time
ESC	Environmental stress cracking
FNCT	Full notch creep test
RTI	Relative thermal index
TTSP	Time–temperature superposition principle
WLF	Williams–Landel–Ferry
Tg	Glass transition temperature

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