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A review of the selective laser sintering technology for bio-based nylon 11

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Abstract
Polyamide 11 (PA11, nylon 11) is a typical bio-based polyamide material prepared from castor oil. With excellent flexibility, relatively low water absorption, and outstanding dimensional stability, it holds great application potential in the field of selective laser sintering (SLS) additive manufacturing. However, in the SLS processing stage, PA11 powder faces high-temperature aging, causing melt rheological degradation and restricting powder recycling and reuse; Meanwhile, the mechanical properties and microstructure of SLS molded parts still lag significantly behind traditional injection-molded products, making material modification and powder recycling and reuse key research directions in this field. This study focuses on systematic investigation of research results related to PA11 adaptation to SLS processes, analyzing and sorting out powder aging and recycling, material blending modification, and molded part performance characterization methods, dissecting various technical challenges currently faced by SLS PA11 systems, and forecasting future development directions in this field. A review of existing literature shows that physical blending of old and new powders is a simple and highly effective method for recovering aged PA11 powders; Blending PA11 with other bio-based nylons can achieve toughening modification effects; Building a multidimensional performance testing system allows for more accurate assessment of molding quality of 3D printed parts.
Future research should further explore the intrinsic mechanisms of aging, build composite modification systems, improve powder recovery processes, and empower the industrialization of bio-based PA11 in the SLS field.

Keywords*: selective laser sintering; bio-based nylon 11; powder aging; recycling; blending modification; additive manufacturing*

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I.Introduction

Selective laser sintering (SLS) is a typical powder bed fusion additive manufacturing technology, relying on laser layer-by-layer sintering of polymer powders to prepare complex components without the need for additional support structures. It is now widely used in aerospace, automotive, medical devices, and other fields. Polyamide materials are the most commonly used polymer powder raw materials in SLS processes. Among them, bio-based PA11 is derived from renewable castor oil resources. Compared to petroleum-based polyamide, it has lower water absorption, better impact resistance, and dimensional stability. In the macro context of "dual carbon," it aligns with the trend toward greening new materials and is a cutting-edge topic attracting significant attention in the field of 3D printing polymer materials.

In actual SLS production operations, only 5% to 10% of powder can be directly sintered and molded, while 80% to 90% of powder remains inside the powder bed as support powder. Under high-temperature inert conditions, repeated heating and cooling cycles occur, leading to thermal aging, manifested as increased molecular weight and melt viscosity. Direct printing of aged powder causes defects such as warping, increased pore ratio, and degradation of mechanical properties, making direct recycling impossible; Meanwhile, imported SLS-grade PA11 powder remains expensive, greatly hindering large-scale adoption of this material.

Domestic and international scholars have conducted extensive studies on SLS nylon powder aging. Nylon powder mainly undergoes polycondensation and crosslinking reactions in anaerobic environments, causing melt viscosity to rise and restricting direct reuse of old powder.

Some studies have tried modification of rheological additives, but there is still a lack of industrialized application cases.

Correspondingly, the SLS molding process reconstructs the internal microstructure of PA11. Compared to injection-molded samples, the density of sintered parts decreases, elastic modulus decreases, and Poisson's ratio increases, making it difficult to fully reproduce the mechanical behavior of sintered

parts by conventional mechanical testing methods; By blending with other bio-based nylon blends, the performance window of PA11 materials can be further broadened. Based on this, this article combines existing literature to review research progress on bio-based PA11 used in SLS processes, clarifies existing technical challenges, predicts future evolutionary directions, and provides valuable analytical ideas for related fields.

1.1 Current Research Status

1.1.1 Research on PA11 Powder Aging and Recycling in SLS Processes

The SLS equipment operates under nitrogen protection conditions, where PA11 powder is repeatedly heated, mainly undergoing polycondensation and crosslinking reactions, resulting in increased relative molecular mass and a significant decline in melt flow rate, which deteriorates powder processing performance; Although a small number of molecular chains break and degrade, crosslinking and polycondensation reactions dominate, and molecular weight distribution tends to be broad. Jinye and colleagues applied physical blending of aged PA11 old powder and new powder after five consecutive sinterings to investigate the effects of different new powder ratios on powder and sintered product properties. Empirical results show that when the mass ratio of new-to-old powder is 5:5, the melt fluidity of the mixed powder can reach 69% of that of pure new powder; The tensile strength and elongation at break of sintered parts can reach 98% and 91% of pure new powder parts, respectively; Dimensional errors are controlled within ±0.1 mm, the parts have no orange peel defects or prominent side lines, and overall performance meets actual production requirements. In contrast, under conditions where the proportion of recycled powder continues to rise, the number of internal holes increases, brittle fracture characteristics at the fracture surface become more pronounced, and mechanical properties, dimensional accuracy, and surface quality deteriorate simultaneously. This new and old powder direct blending recovery solution has a simple process flow, requiring no additional modification additives, effectively improving raw material utilization and reducing production costs.

Studies on SLS polyamide powder recovery have shown that relying solely on additive modification has the drawbacks of high modification difficulty and long cycles. In comparison, physical mixing of new and old powders is more suitable for current production scenarios, but this method still has a cycle limit, and after multiple cycles, powder performance will gradually degrade.

1.1.2 Research on PA11 blended modification

Pure PA11 materials have inherent strength shortcomings, limiting their application in some engineering scenarios. Implementing melt blending of PA11 with other bio-based polyamides is an important modification path. Mao Xusheng and others investigated the PA56/PA11 bio-based blend system. DMA test results showed good compatibility between PA56 and PA11, with only a single glass transition temperature in the blend; Introducing PA11 reduces the crystallinity of the blend system and significantly enhances material toughness; When the PA11 mass fraction reaches 40%, the elongation after fracture of the blend rises from 5.27% of pure PA56 to 44.26%; With a PA11 mass fraction of 20%, impact strength increases by 23.2%, achieving complementary advantages within bio-based nylon and improving toughness shortcomings without losing bio-based properties.

Meanwhile, extensive research has focused on packing enhancement modification PA11, with fillers such as lignocellulose, montmorillonite, and nanocellulose used to prepare PA11 composites. Natural fiber fillers can interact with amide groups via hydrogen bonds, optimizing interfacial bonding and increasing composite modulus; clay and carbon-based fillers can simultaneously improve thermal and rheological properties. However, the introduction of fillers alters powder flowability, posing new challenges for SLS powder spreading and sintering windows. Most discussions on blending modification focus on injection molding processes, and there is still room for expansion in blending modification for SLS powders.

1.1.3 SLSPA11 Component Performance Characterization Technology

The internal pores distributed in SLS molded PA11 parts have lower density than injection-molded parts; traditional single-strain gauge testing methods are affected by bonding operations and data synchronization, causing deviations. Li Gang and others compared strain gauge method, dynamic vibration method, and non-contact full-field digital image correlation (DIC) testing methods to evaluate their detection performance on SLSPA11 elastic modulus and Poisson's ratio. Data analysis results show that

SLS-molded PA11 has an average elastic modulus of about 1.31 GPa and a Poisson's ratio of 0.3857; compared to injection-molded PA11 (elastic modulus 1.6 GPa, Poisson's ratio 0.35), elastic modulus has declined and Poisson's ratio has increased. Dynamic vibration methods fall under the category of non-destructive testing, while DIC non-contact measurement can obtain full-field strain distribution. The experimental error of both is smaller than that of traditional strain gauges, making it suitable for mechanical performance assessment of 3D printed porous parts, providing testing support for precise evaluation of SLS sintered component performance. Existing research also points out that internal defects in 3D printed porous components are complex, and relying solely on traditional single-point testing methods is difficult to fully reproduce the overall mechanical response. The development direction of testing technology in this field is the combined use of multiple
characterization methods.

1.2 Technical challenges

1.2.1 The thermal aging mechanism and evaluation system for PA11 powder are incomplete

It has been clarified in academia that PA11 aging under SLS nitrogen atmosphere is dominated by crosslinking polycondensation, but the quantitative relationships among temperature, holding duration, and oxygen content on crosslinking and degradation competition reactions remain unclear. The industry has yet to establish unified evaluation standards for SLSPA11 aging powders. Currently, powder usability is mostly judged indirectly based on melt flow rate and molecular weight. There is a lack of fast and convenient on-site detection solutions, making it difficult to accurately define powder scrap points during industrial production, which can easily cause product quality fluctuations or powder resource waste.
Referring to related studies on polyamide powder aging, crosslinking and chain degradation under anaerobic conditions are a competitive reaction, while current quantitative studies on the kinetic properties of PA11 under SLS powder bed conditions are still relatively scarce.

1.2.2 Limitations of powder recycling and reuse

Although the new and old powder blending (5:5) solution can achieve reuse of aging powder, there is an upper limit to the number of cycles; After multiple cycles, the accumulated aging components continue to increase. Even with repeated addition of new powder, powder performance will gradually deteriorate. This solution can only delay performance degradation and cannot fundamentally eliminate powder aging. Although chemical additive modification can optimize rheological properties, additives alter powder thermal properties, compress the sintering window, require extensive process validation, and currently lack mature industrial implementation cases.

1.2.3 Modified materials are difficult to adapt to SLS processes

Extensive research on PA11 blending and enhanced modification is aimed at injection molding. SLS powder has special requirements for particle morphology, particle size distribution, powder flowability, and sintering window. After the introduction of fillers and second-phase polymers, powder spreading performance is easily weakened, melting intervals shift, which easily narrow the sintering window and trigger defects such as warping and powder sticking. There is a shortage of specialized PA11 blend powders developed for SLS conditions. A large number of bio-based nylon modification results are concentrated in injection molding samples. How to balance the processing characteristics of modified powders with part performance is a core challenge to overcome for the transition to SLS processes.

1.2.4 Insufficient performance consistency and standardized testing of SLS components

The internal porosity of SLS prepared PA11 components fluctuates due to the combined effects of process parameters and powder state, resulting in a higher degree of mechanical property dispersion than injection-molded parts. Different literature using differentiated testing methods yields weak comparability of mechanical data; There is a lack of testing specifications specifically for SLS porous polyamide components, which hinders data accumulation and engineering promotion. Different testing methods produce significant differences in output results for porous additive components. Without unified testing standards, it is difficult to achieve horizontal comparison of data across studies, restricting material iterative optimization.

1.3 Development Trends

1.3.1 Delve into powder aging mechanisms and establish a powder grading and reuse system

The aging kinetic characteristics of PA11 powder under different temperature, oxygen content, and number of thermal cycles were investigated, and a correlation model among molecular weight, melt flowability, and thermal properties was constructed. A graded disposal strategy for aged powders was developed, categorizing powders into mild, moderate, and severe aging types. For different aging grades, differentiated treatment paths such as mixing old and new powders, rheological modification, and chemical degradation regeneration were adopted to maximize powder utilization potential and reduce material costs. Drawing on existing research approaches for polyamide powder recovery, a rapid method for identifying aging degree was established by combining macroscopic performance indicators with micromolecular evolution patterns to reduce powder waste and quality fluctuations during production.

1.3.2 Develop PA11 composite modified powder for SLS processes

Drawing on the research approach of bio-based PA56/PA11 blending toughening, a fully bio-based SLS blended powder was developed, balancing bio-based properties and mechanical properties; Nano and fiber fillers were reasonably selected, balancing powder spreading fluidity and sintering window to achieve synergistic advancement of strengthening, toughening, and functionalization, broadening the application boundaries of PA11 in high-strength structural and functional components. At the same time, referencing existing achievements in bio-based nylon filler modification, natural fiber and inorganic clay fillers suitable for SLS processes were selected, promoting the migration of modification systems from injection molding to powder bed melt molding, and expanding the application scenarios of bio-based PA11. During the modification formulation development stage, powder particle size, flowability, and hot processing windows were simultaneously evaluated to avoid problems where modification is completed but cannot be adapted to SLS powder spreading and sintering processes.

1.3.3 Combining Multiple Approaches to Improve Performance Characterization and Standard Construction

Integrates melt flow rate, GPC molecular weight analysis, DSC thermal analysis, DIC non-contact full-field strain testing, and SEM micromorphology observation to achieve full-chain assessment from powder intrinsic properties to the macroscopic mechanics and microdefects of parts. Promotes the establishment of industry testing standards for SLS bio-based polyamide
materials, unifies sample preparation and performance testing processes, and improves data comparability among different research results and manufacturers. Includes non-destructive vibration detection and DIC full-field strain testing in the routine evaluation system for porous SLS parts, reducing human operational errors caused by traditional strain gauge testing and improving the complete evaluation method.

1.3.4 Coordinated optimization of process materials to promote industrialization

Promote the coordinated matching of powder recovery formulas with SLS process parameters (preheating temperature, laser power, scanning speed), optimize the sintering window for recycled powders, and suppress warping and secondary sintering defects; Further unleash the green attributes of bio-based PA11, targeting medical devices, lightweight components, and other application scenarios, promoting the engineering application of SLSPA11 components. Bidirectional coordinated optimization of materials and processes can fully tap the value of new and old powder mixing solutions, slow down the degradation of aging powder performance, and support the industrial implementation of bio-based PA11 additive
manufacturing technology.

II. Conclusion

Based on the above analysis conclusions, bio-based PA11 is a green polymer powder raw material with great development prospects in the field of selective laser sintering. During SLS processing, PA11 powder undergoes crosslinking and polyaging under high-temperature inert conditions, causing melt flow decay issues; A 5:5 mass ratio of new to old powder is a simple and effective recycling path for aging powders, allowing for recycling of old powder while ensuring mechanical properties, dimensional accuracy, and surface quality of parts. By blending with PA56 and other bio-based nylons, the toughness of the PA11 system can be effectively improved;
Compared to traditional strain gauge methods, DIC non-contact testing and dynamic vibration testing are more suitable for evaluating the mechanical properties of SLS porous PA11 sintered parts.
This research direction still faces technical bottlenecks such as insufficient quantitative explanation of

aging mechanisms, upper limits on powder recycling and reuse, insufficient reserves of SLS-specific modified powders, and lack of testing standards. Future research should deepen the fundamental analysis of powder aging, develop blended composite powders adapted to SLS processes, improve full-chain characterization and evaluation systems, achieve coordinated optimization of material processes, and support the large-scale implementation of bio-based PA11 selective laser sintering technology.

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