SCIENTIFIC MONOGRAPH · PREPRINT

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Polymer Engineering of Additive Manufacturing

Materials-Science and Process Fundamentals of Material Extrusion (FDM/FFF) and Vat Photopolymerization (SLA/DLP/MSLA): Theory, Material Behaviour, Metrics and Reproducibility

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Publication metadata

Type: Monograph / Preprint · Version 1.0 · Language: English

Licence: CC BY 4.0 · DOI: assigned on Zenodo upload · March 2026

Subjects: Polymer Science · Additive Manufacturing · Materials Engineering · Manufacturing Technology

Companion volume to the SICHERHEITSWERK safety compendium. This work addresses the materials and process dimension; health and occupational-safety aspects are covered in a separate treatise.

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Abstract

Background. Additive manufacturing of polymeric parts reaches industrial relevance in two process families – material extrusion (FDM/FFF) and vat photopolymerization (SLA/DLP/MSLA). Both yield materials whose properties differ fundamentally from their injection-moulded counterparts.

Objective. This monograph presents the materials-science and process fundamentals of both processes systematically and comparatively, focusing on the physico-chemical mechanisms that govern part properties, the relevant metrics, and the conditions for reproducible manufacturing.

Key findings. The strength of FDM parts is governed by inter-layer diffusion (reptation) across the layer interfaces and is therefore anisotropic; Z-strength typically reaches 40–70 % of the XY strength. SLA parts are largely isotropic owing to continuous covalent crosslinking, but their properties depend strongly on the degree of conversion. Reproducibility in both processes requires control of defined influencing variables.

Keywords: *additive manufacturing; FDM; FFF; stereolithography; reptation; interlayer bonding; anisotropy; photopolymerization; degree of conversion; reproducibility; material properties*

1. Introduction

Additive manufacturing builds parts layer by layer from a feedstock, enabling geometric freedoms unattainable with formative or subtractive processes. For polymeric materials two physically distinct principles dominate: thermally driven material extrusion and light-induced photopolymerization.

Whereas material extrusion relies on solidification of a molten thermoplastic and the welding of adjacent beads through molecular interdiffusion, photopolymerization is based on covalent crosslinking of liquid monomers under light. These different bonding mechanisms produce fundamentally different property profiles, in particular regarding the directional dependence (anisotropy) of mechanical properties. [1]

This monograph aims to present the materials-science basis of both processes at comparable depth. Section 2 addresses the polymer physics of the materials; Sections 3 and 4 the process-specific bonding mechanisms; Section 5 the mechanical properties and their directional dependence; Section 6 the process-property relationships; Section 7 reproducibility and process capability.

2. Polymer-Physical Fundamentals

2.1 Thermoplastics: amorphous and semi-crystalline

Thermoplastics are classified by molecular order into amorphous (e.g. ABS, PETG, PC) and semi-crystalline (e.g. PA, PP) materials. Amorphous polymers lack long-range order and soften continuously above the glass-transition temperature Tg. Semi-crystalline polymers possess crystalline domains with a defined melting point Tm, causing higher shrinkage and warping tendency.

Material	Structure	Tg (°C)	Tm (°C)	Shrinkage
PLA	amorph./semi-cryst.	55–65	150–160	low
PETG	amorphous	78–85	—	low
ABS	amorphous	105	—	medium
PA6	semi-crystalline	45–60	215–220	high
PC	amorphous	145–150	—	medium
PP	semi-crystalline	−10	160–165	very high

2.2 Glass transition and chain mobility

Above Tg the molecular chains gain significant mobility and can diffuse across interfaces. This chain mobility is the prerequisite for inter-layer bonding in material extrusion; without sufficient temperature and dwell time the weld remains incomplete. [2]

2.3 Photopolymers: network structure

Photopolymers are reactive mixtures of monomers, oligomers, photoinitiators and absorbers. Under UV light a three-dimensional covalent network forms (thermoset-like). Unlike thermoplastics this network is not reversibly re-meltable after curing; properties are determined by network density and the degree of conversion.

3. Bonding Mechanism of Material Extrusion

3.1 Phases of bead welding

Welding of adjacent beads proceeds in three phases: (1) surface contact of the beads, (2) neck growth driven by surface tension, and (3) molecular diffusion and entanglement across the interface. Only the third phase establishes the mechanical load-bearing capacity of the bond. [3]

3.2 Reptation theory

Molecular interdiffusion is described by the reptation theory of de Gennes and Doi–Edwards. A polymer chain moves as if within a tube formed by neighbouring chains. The characteristic reptation time τ determines how rapidly chains entangle across the interface and is strongly temperature-dependent:

$$\tau(T) = \tau_0 \cdot \exp(E_a / R \cdot T) \qquad (3.1)$$

with activation energy E_a, gas constant R and absolute temperature T. As interface temperature rises, τ decreases and diffusion proceeds faster and more completely.

3.3 Degree of bonding and weld time

The degree of bonding is defined as the ratio of achieved to maximum attainable interface strength. Models couple reptation-based interdiffusion with the equivalent isothermal weld time obtained by numerical integration of the interface time-temperature history. For semi-crystalline materials the crystallization kinetics superimpose. [4]

3.4 Factors influencing interlayer bonding

Experimental studies identify nozzle temperature, print speed (dwell time), layer height and cooling as the main control variables. Auxiliary heating (preheating, infrared, ultrasound) selectively enhances diffusion; ultrasonic excitation increased the interlayer strength of ABS by up to 10 %. [5]

Recent interface analyses by XPS show that bonding is not purely physical (diffusion, entanglement) but also chemically influenced: oxidation, chain scission and material-specific interface signatures contribute to the observed anisotropy and reduced Z-strength. [6]

4. Bonding Mechanism of Photopolymerization

4.1 Free-radical chain polymerization

The photoinitiator absorbs photons of suitable wavelength (typically < 405 nm) and dissociates into radicals that initiate chain polymerization of the acrylate/methacrylate groups. A crosslinked network forms. Because crosslinking proceeds continuously across layer boundaries, SLA parts are largely isotropic – a fundamental difference from material extrusion.

4.2 Degree of conversion

The degree of conversion (DoC) denotes the fraction of reacted reactive groups. As-printed green parts have an incomplete DoC; post-curing raises it. DoC governs strength, hardness, glass transition and residual-monomer content:

$$DoC = (C_0 - C_t) / C_0 \qquad (4.1)$$

with initial concentration of reactive groups C_0 and remaining concentration C_t. Too low a DoC means soft parts and high residual monomer; too high a DoC leads to embrittlement and yellowing.

4.3 Cure depth and resolution

The cure depth per exposure follows approximately a logarithmic relationship to exposure dose (the Jacobs equation of stereolithography): cured depth grows with the logarithm of energy density, scaled by the material-specific penetration depth Dp. Absorbers selectively limit Dp and thereby increase Z-resolution. [7]

$$C^d = Dp \cdot ln(E / Ec) \qquad (4.2)$$

with cure depth C^d, penetration depth Dp, exposure dose E and critical energy Ec (gel point).

5. Mechanical Properties and Anisotropy

5.1 Properties compared

Material/Process	Tensile MPa	E-mod. GPa	Elong. %	Character
FDM PLA	45–65	3.5–4.0	2–6	stiff, brittle
FDM PETG	50–65	2.0–2.8	8–20	tough
FDM ABS	40–60	1.8–2.4	6–20	impact-resistant
FDM PA-CF	80–120	5.0–8.0	2–5	stiff, strong
SLA Standard	45–65	2.5–3.5	2–5	fine, brittle
SLA Tough	45–70	2.0–2.8	8–20	tough

5.2 Anisotropy of material extrusion

FDM parts exhibit pronounced mechanical anisotropy: strength in the build direction (Z) is reduced relative to the print plane (X/Y), because Z-strength is borne solely by interlayer diffusion while in-plane the continuous bead carries the load. Typical Z-values are 40–70 % of the XY-values. [8]

Orientation	Rel. tensile strength	Load mechanism
XY (in-plane)	100 % (reference)	continuous bead

Orientation	Rel. tensile strength	Load mechanism
XZ / on-edge	often maximum	bead + favourable direction
Z (build direction)	40–70 %	interface diffusion only

5.3 Isotropy of photopolymerization

SLA/DLP/MSLA parts are nearly isotropic owing to continuous covalent crosslinking. The small remaining directional dependence results from exposure gradients and layer-wise post-curing, not from a weak interface as in FDM.

6. Process-Property Relationships

6.1 FDM: parameter effects

Parameter	Effect on Z-strength	Mechanism
Nozzle temp. ↑	increases	τ decreases, more diffusion
Print speed ↑	decreases	shorter dwell time
Layer height ↓	slightly increases	more interfaces, better contact
Cooling ↑	decreases	faster drop below Tg
Annealing	increases	recrystallization, stress relief

6.2 SLA: parameter effects

Parameter	Effect	Mechanism
Exposure time ↑	DoC ↑ to saturation	more radicals, more crosslinking
Post-cure ↑	strength/hardness ↑	DoC increase
Resin temp. ↑	reactivity ↑	faster kinetics
Absorber content ↑	Z-resolution ↑	Dp decreases

6.3 Annealing as post-treatment

For semi-crystalline FDM materials, annealing above Tg increases crystallinity and thus stiffness and heat-deflection temperature, while relieving residual stresses. Localized methods (microwave, induction, ultrasonic welding) selectively improve interlayer bonding and reduce anisotropy. [9]

7. Reproducibility and Process Capability

7.1 Influencing variables

Reproducible properties require control of all significant influencing variables, which differ by process:

FDM	SLA
Filament tolerance, residual moisture	Resin batch, ageing, sedimentation
Nozzle wear (CF/GF)	FEP film clouding/wear
Bed calibration (mesh)	LCD-display ageing (transmission)
Ambient temperature	Resin temperature, room climate
Profile/batch management	Exposure validation per batch

7.2 Process capability

For serial production, statistical assessment of process capability (Cp/Cpk) over critical dimensions and samples is recommended. First-article inspection per new part and archiving of print records (profile, batch, machine, date) are prerequisites for traceability and quality evidence.

Conditions for reproducible manufacturing (synthesis)

Defined, documented parameter profiles per material and machine.
Batch management of feedstock including drying/ageing status.
Regular validation (exposure test for SLA, calibration objects for FDM).

Wear-part management (nozzle, FEP film, LCD).
Statistical process control of critical dimensions (Cpk).

8. Conclusion

The two dominant processes of polymeric additive manufacturing rely on fundamentally different bonding mechanisms: thermally driven interdiffusion (FDM) versus light-induced covalent crosslinking (SLA). This produces their characteristic property profiles – the pronounced anisotropy of material extrusion versus the near-isotropy of photopolymerization. Understanding these mechanisms is the basis for material-appropriate design, targeted parameter selection and reproducible manufacturing. Key control variables are interface temperature and dwell time for FDM, and degree of conversion for SLA.

Declarations

Conflict of interest

The author operates Schichtwerk, a service company in additive manufacturing. This work was prepared without external funding and reflects the published state of the art.

Data availability

This work is based on published literature and manufacturer data; no new primary data were collected. Property values are reference figures and do not replace material-specific testing in individual cases.

Suggested citation

[Nachname] T. Polymer Engineering of Additive Manufacturing: Materials-Science and Process Fundamentals. Preprint, Version 1.0. Zenodo; 2026.

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