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Review

Polyglycerol-Based Polymers for Additive Manufacturing: Thermomechanical Design for Structural Applications

Julie Pearl M. Andal [1], Roxanne R. Navarro [2] and Reymark D. Maalihan [3,*]

[1] College of Engineering and College of Engineering Technology, Batangas State University, Alangilan Campus, Batangas City, 4200 Philippines; juliemarasigan@g.batstate-u.edu.ph
[2] College of Engineering, Batangas State University, Alangilan Campus, Batangas City, 4200 Philippines; roxanne.navarro@g.batstate-u.edu.ph
[3] Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota 58102 United States
* Correspondence: reymark.maalihan@ndsu.edu; reymark.maalihan21@gmail.com

Abstract: Additive manufacturing (AM) is revolutionizing the fabrication of structural components, demanding materials that balance printability with superior thermal and mechanical performance. Polyglycerol-based macromolecular systems have emerged as promising candidates due to their highly tunable chemical architecture. Variations such as linear, hyperbranched, and dendritic topologies significantly influence thermal behavior, elasticity, and mechanical strength. Functional strategies including crosslinking, copolymerization, and additive incorporation enable property enhancement tailored to diverse AM platforms like stereolithography (SLA), digital light processing (DLP), and fused deposition modeling (FDM). While native polyglycerol systems exhibit low thermal stability, chemical modifications and hybridization with fillers like carbon nanotubes, cellulose nanofibers, or graphene oxide improve decomposition temperatures, flame retardancy, and thermal conductivity. Crosslinked derivatives also show increased glass transition and melting points, suitable for moderate-temperature printing and structural applications. However, trade-offs such as brittleness from excessive crosslinking and dispersion challenges with nanofillers remain unresolved. This review critically evaluates the structure–property-processing relationships in polyglycerol-based systems, emphasizing their role in the development of next-generation, multifunctional materials for AM. Emphasis is placed on thermal performance, mechanical optimization, and the integration of environmentally friendly processing strategies.

Keywords: polyglycerol; additive manufacturing; thermal stability; mechanical performance; crosslinking; stereolithography; hybrid composites

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1. Introduction

Additive manufacturing (AM) enables the fabrication of complex geometries with up to 90% material efficiency gains, yet the structural integrity of printed components remains constrained by suboptimal thermomechanical stability [1-3]. However, structural components manufactured through AM are often subjected to demanding conditions—cyclic loading, temperature fluctuations, and long-term mechanical stress [4-7]. As a result, there is a growing need for advanced materials that combine printability with superior thermal and mechanical stability. Current photopolymer resins for vat-based AM often display low glass transition temperatures (Tg), brittle mechanical behavior after curing, and limited biocompatibility, restricting their suitability for load-bearing and medical applications [8-10].

Polyglycerol-based macromolecular systems are attracting growing interest for their potential to address the limitations of current AM materials due to their highly tunable chemical structure.

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This review covers a broad range of PG architectures—including linear, hyperbranched, and dendritic forms—and explores both biomedical and industrial variants. Key derivatives such as poly(glycerol sebacate) (PGS), poly(glycerol sebacate acrylate) (PGSA), polyglycerol diacrylate (PGDA), as well as PG-based urethanes, foams, and acrylates are included, with a focus on their relevance to additive manufacturing. Polyglycerol's polyhydroxylated backbone allows precise tuning of cross-linking, branching, and hydrophilicity—making it well-suited for additive manufacturing techniques such as DLP, FDM, and VAM, where material behavior affects structural accuracy and function. With AM advancing toward more demanding applications, interest in materials offering both printability and enhanced thermomechanical stability is growing. Yet, current reviews often overlook polyglycerol's potential beyond biomedical uses, particularly in structural and industrial AM contexts.

Enhancement of mechanical and thermal behavior in these systems is often achieved through functional modification. Studies have shown that the incorporation of carbon nanotubes (CNTs) into polyglycerol-based matrices can significantly improve mechanical reinforcement and thermal conductivity, making them viable for load-bearing and high-temperature applications [11]. Similarly, the use of plasticizers such as hyperbranched polyglycerols (HPGs) or glycerol has been shown to improve flexibility and toughness without compromising biodegradability [12]. Natural or inorganic fillers like zein and sodium chloride have also demonstrated compatibility with acrylated or norbornene-functionalized polyglycerol systems, further enhancing elastic and thermal behavior [13,14].

The potential of these materials lies not only in their chemical adaptability but also in their compatibility with sustainable and high-resolution printing. Their use in structural components such as lightweight frames, insulation panels, and mechanical supports illustrates the growing relevance of polyglycerol-based materials beyond biomedical applications.

This review provides a comprehensive analysis of polyglycerol-based macromolecular systems for additive manufacturing, emphasizing their thermal and mechanical performance in structural applications. It covers structure–property relationships, thermal stability, mechanical behavior in printed forms, and strategies for structural and functional enhancement. The review also presents case studies across diverse applications and critically discusses current challenges and future opportunities in advancing polyglycerol systems for next-generation AM platforms.

2. Structure–Property Relationships in a Polyglycerol System

Polyglycerol can be synthesized into distinct architectures—linear, hyperbranched, and dendritic—each exhibiting unique physicochemical property. These forms significantly influence the material's physical and chemical properties. Linear polyglycerol (LPG), characterized by regularly spaced hydroxyl functionalities along its backbone, allows for predictable and high-efficiency chemical modification [15,16]. Hyperbranched and dendritic polyglycerols, which feature multiple branching points, influence solubility, intermolecular interactions, and rheological behavior during processing [17,18]. Factors such as molecular weight, branching density, and terminal group composition influence mechanical behavior, elasticity, and thermal transitions [19,20]. Understanding these relationships is crucial for advancing polyglycerol systems in material applications.

2.1. Overview of Linear, Hyperbranched, and Dendritic Architectures

Architectural precision in polyglycerols is achieved through controlled polymerization techniques. Linear polyglycerol (LPG) synthesis employs anionic ring-opening polymerization (AROP) with alkoxide initiators, enforcing linear chain growth and narrow dispersity (Đ typically < 1.1 under controlled AROP conditions). For hyperbranched architectures (HPG), reversible addition-fragmentation chain-transfer (RAFT) polymerization regulates branching density ($DB = 0.4–0.6$) while preserving terminal functionality [21]. Dendritic systems utilize copper-catalyzed azide-alkyne cycloaddition (CuAAC) for defect-free branching ($DB > 0.9$), whereas atom transfer radical polymerization (ATRP) enables precise chain-end functionalization for hybrid architectures. Bottlebrush architectures are often prepared via grafting-through or grafting-from strategies using RAFT-controlled polymerization for side-chain growth. Side-chain engineering at the monomer level plays a critical role in modulating polymer conformation and nanostructure formation, influencing phase behavior and self-organization. Alkyl glycidyl ethers impose steric barriers increasing free volume by thereby affecting chain packing and mobility; carboxyethyl variants introduce ionizable carboxyl groups, enabling stimuli-responsive behavior [15]; and long-chain epoxides confer amphiphilicity to guide self-organization. Macromolecular topology is dictated by core design strategies, where linear chains prioritize sequential monomer addition [22]; cyclic cores employ end-group cyclization [23]; star-brush systems utilize multifunctional initiators [24]; comb topologies employ backbone grafting of linear side chains; and bottlebrush architectures require orthogonal grafting techniques. polyglycerols as promising sustainable materials, though production scaling and recyclability challenges persist. Block versus random architectural control significantly impacts the resulting nanostructure and material performance. Block copolymers, formed via sequential monomer addition, often exhibit microphase separation, which can enhance mechanical strength and thermal stability through distinct domain formation [25]; Hyper-branched-linear block copolymers combine the flexibility of branching with linear segments, offering improved solubility, tunable viscosity, and potential for Tg adjustment depending on segment composition [26]. In contrast, random copolymers, with statistically distributed comonomers, tend to form more homogeneous phases, which may reduce phase separation but can yield materials with broad thermal transitions and improved processability [16].

2.2. Molecular Weight, Branching, and Functional Group Influence on Modulus, Toughness, and Glass Transition Temperature

Molecular weight (MW) and branching architecture collectively influence the polymer's entanglement density, crystallinity, and segmental mobility, thereby governing thermal transitions and mechanical behavior. High-MW LPG (>50 kDa) increases chain entanglements, which can elevate the glass transition temperature by up to 50 °C under certain formulations and enhance toughness due to improved energy dissipation during deformation [27]. Cyclic topologies intrinsically restrict chain mobility, increasing glass transition temperature beyond values predicted by MW alone. Star-brush architectures demonstrate branching-dependent crystallization suppression, with compact topologies enhancing elastic modulus by increasing segmental density, though at the expense of crystallinity due to steric hindrance and disrupted packing of regular chains. Functional group distribution plays a critical role in modulating stimuli-responsive behavior. Peripheral ionic groups, such as carboxy and sulfate, influence pH-dependent conformational changes through charge repulsion. Side-chain variations such as bottlebrush and comb architectures affect molecular flexibility and responsiveness. Bulk versus interfacial effects introduce distinct structural and functional dynamics, shaping overall material properties [28]; In bottlebrush architectures, increasing side-chain length generally elevates free volume and softens the backbone, enabling Tg tuning within a 40–60 °C window depending on backbone rigidity and grafting density.; and sulfated HPGs with DB=0.6 optimize biointerfacial responses through steric-ionic balance [29]. Branching architecture influences the spatial orientation and density of hydroxyl groups, thereby modulating hydrogen bonding networks that contribute to cohesive energy density and adhesive performance [30]. In comb-like architectures, the decoupling of rigid backbones from mobile side chains facilitates surface-localized erosion kinetics, especially under hydrophilic or enzymatic environments [31].

2.3. Strategies to Enhance Mechanical Strength: Crosslinking, Copolymerization, and Filler Addition

Enhancing the mechanical strength of polyglycerol-based systems is crucial for their in polyglycerol-based systems requires navigating fundamental trade-offs across crosslinking, copolymerization, and filler addition strategies, compounded by methodological contradictions and

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unresolved gaps in standardization. Crosslinking forms covalent networks that intrinsically increase rigidity but introduces strategy-specific compromises, such as brittleness, cytotoxicity, or incomplete network formation. While enzymatic approaches offer biocompatibility, they suffer kinetic limitations and inconsistent network density due to factors like pH sensitivity, enzyme deactivation at elevated temperatures, and variability in substrate diffusion [32,33]. Chemical agents like methacrylates enhance thermal stability but introduce significant cytotoxicity risks, reducing cell viability substantially in vitro [34,35]. Excessive crosslinking induces brittleness that compromises fracture toughness [36]. Critically, optimal curing durations remain elusive. Extended thermal or UV curing times can increase crosslink density, enhancing modulus, but often reduce elongation at break due to reduced chain mobility or embrittlement [37,38]. A lack of crosslinker–property mapping frameworks impedes the rational design of PG-based networks. Computational screening or in silico modeling approaches could help address this [39].

Copolymerization enables tunable mechanics but may also introduce instability risks depending on material composition. Integrating PEG improves processability yet can accelerate hydrolytic degradation threefold. Additionally, it may provoke immunogenic responses if residual monomers or byproducts persist, particularly in vivo [30,40]. Monomer ratio sensitivity causes significant mechanical fluctuations: in some PG-co-polyester systems, even a ±5% shift in glycerol content can result in a 30–50% change in elastic modulus, highlighting compositional sensitivity [41], while glutamic acid incorporation slows degradation but reduces elasticity by 40% [42]. Hydrophilic components depress Tg by 10–15°C due to increased free volume and plasticization effects from hydrogen bonding with ambient moisture [43], and slow-degrading derivatives risk chronic inflammation if degradation byproducts accumulate in vivo [44]. These inconsistencies stem partly from unstandardized synthesis protocols, where accelerated methods sacrifice crosslinking homogeneity [45].

Filler addition enhances strength but faces intrinsic dispersion-limited efficacy. Nanosilicate reinforcement increases stiffness by 300% but reduces cell viability by 50% at 10 wt% loading [46], while nHA exhibits a strict 3% loading threshold beyond which aggregation induces catastrophic embrittlement [47]. Agglomerates >200 nm create stress concentration points that reduce tensile strength by 35–60% despite filler content [48,49]. Graphene's reinforcement efficiency diminishes by up to 50% in cases of poor exfoliation or re-agglomeration, compromising tensile modulus and fracture strength [50]. Thermally, coefficient of expansion mismatches provokes delamination >80°C particularly at filler–matrix interfaces, where differential thermal expansion introduces shear stresses that exceed interfacial adhesion, leading to delamination above critical processing temperatures [51], while poor filler orientation causes ±30% modulus fluctuations across studies [52].

Synthesizing the strategies reveals context-dependent hierarchies where mechanical reliability favors crosslinking over copolymerization and filler addition due to dispersion variability; long-term stability shows fillers and crosslinking comparable but both superior to copolymerization given hydrolytic sensitivity; biocompatibility risk peaks with chemical crosslinking while fillers and copolymerization exhibit dose-dependent concerns; and thermal resilience ranks crosslinking highest, followed by fillers, with copolymerization last due to monomer-driven Tg depression. No approach universally dominates. Crosslinking suits static implants but fails in dynamic tissues; copolymerization enables drug delivery tunability but sacrifices durability; fillers enhance bone scaffold mechanics but compromise vascularization. Critically, clinical translation remains hampered by unaddressed gaps including inconsistent characterization protocols that obscure cross-study comparisons [45], unpredictable in vivo degradation-mechanics coupling that undermines lab results [53], and scalable synthesis methods that degrade mechanical performance [54]. Optimization must therefore reconcile these trade-offs with application-specific biological and mechanical demands while prioritizing standardized testing, in silico-experimental validation, and accelerated aging studies.

3. Thermal Stability and Processing Considerations

Polyglycerol-based polymers are gaining attraction in additive manufacturing (AM), especially for applications that require high thermal stability and mechanical strength. Their hydroxyl-functionalized polyether backbone provides versatility, allowing for both thermoplastic and thermoset applications [55]. Polyglycerol can be modified to optimize its performance in AM processes such as stereolithography (SLA) and fused deposition modeling (FDM) [21,22].

3.1. Thermal Decomposition Profiles

Thermal stability plays a vital role in determining how well polyglycerol-based materials perform in additive manufacturing (AM), especially in applications that involve elevated temperatures. When compared to traditional thermoplastics like PLA and ABS, polyglycerol systems—particularly those that are crosslinked—tend to show better thermal behavior. Crosslinking helps raise the glass transition temperature (Tg), melting point (Tm), and resistance to thermal breakdown, allowing the materials to maintain their structure and function during processing and use [56,57].

In particular, modified polyglycerol resins used in SLA printing have demonstrated higher thermal degradation onset temperatures after UV curing. UV curing promotes the formation of dense crosslinked networks, increasing both the thermal degradation onset and structural stability during high-temperature post-processing [58,59]. Additional improvements in thermal performance have been observed when reinforcing the base polymer with additives such as cellulose nanofibers, graphene oxide, or sodium silicate—each contributing to increased decomposition temperatures and overall stability [60,61].

As shown in Table 1, a variety of polyglycerol-based systems have been developed with targeted modifiers to improve both thermal and mechanical properties. Whether for environmental cleanup, wound care, or lightweight structural parts, these materials are showing real promise. While the level of improvement depends on the additives and how the material is processed, the general trend is clear: polyglycerol composites are becoming more capable of handling the thermal demands of AM.

Table 1. Thermal Decomposition Profiles of Polyglycerol-Based Systems.

PG Type	Modifier	Thermal Indicator	Observed Change	Application
Poly(glycerol tartrate) hydrogel	Cellulose nanofibers	T_5% (onset of 5 % weight loss): increased from ~230 °C (PGT alone) to ~250 °C with CNF	+20 °C — improved thermal stability and adsorption	Heavy metal adsorption, environmental cleanup [62-64]
Poly(glycerol sebacate) electrospun fiber	Chitin-lignin sol–gel + 15 % PGS	T_m decreased from 9.6 °C to ~66 °C (peak attributed to sol–gel), T_c ~49.7 °C; mechanical strength ↑ from ~1.2 MPa to ~3.1 MPa	Slight reduction in melting/crystallization temps; mechanical and antibacterial boost	Wound-healing scaffolds [65,66]
Polyglycerol-based polyurethane adhesive	Sodium silicate (waterglass)	Thermally stable below ~260 °C with T_m ~280 °C	+~40 °C early strength stability; flame resistance	Grouting & structural adhesives [67]

		(TGA onset ≈ 260 °C)		
PGS biodegradable composite with gelatin + GO	Gelatin, graphene oxide	T_5% increased from ~250 °C to ~270–280 °C	+20–30 °C; enhanced thermal & mechanical performance	Tissue engineering scaffolds [68]
Polynorbornene network	Crosslinked polynorbornene	T_m/GTT >310 K (≈37 °C); decomposition of blends at ≳320 °C	High thermal stability; decomposition onset >320 °C	Shape-memory; damping materials [69-71]
PEG-PG diacrylate network	Poly(ethylene glycol) diacrylate	T_5% >360 °C in semi-IPN/hydrogel networks	Strong network thermal stability (T_5% ≳360 °C)	PEMs, tissue engineering [72,73]
Polyglycerol urethane foam	Rigid PU foam from polyglycerol polyol	Multi-stage T_5% ~250–350 °C; second stage ~400–600 °C	Typical PU thermogram; urethane bonds decompose at ≳ 250 °C	Thermal insulation, lightweight bio-foam [74-76]
Polyglycerol dodecanedioate	Poly(glycerol dodecanedioate) (PGD)	Shape memory T_trans ≈ 37 °C; degradation onset ~200–250 °C	Transition near body temp; thermally stable for biomedical use	Minimally invasive devices, SMPs [60, 77-80]

To enhance thermal properties, hybrid systems that combine polyglycerol with functional materials such as nanoparticles, fibers, and bio-based polymers have been actively investigated. Hybrid composites combining polyglycerol with nanofillers (e.g., CNTs, graphene oxide, cellulose) exhibit enhanced thermal stability due to increased phonon scattering and interfacial thermal resistance, which reduce chain mobility and delay thermal decomposition [60]. For example, incorporating carbon nanotubes (CNTs) into polyglycerol-based composites leads to an increase in thermal conductivity, making these materials ideal for high-performance applications in industries such as aerospace and automotive [11,56,61,81-83]. Additionally, polyglycerol-modified composites reinforced with natural fibers offer both superior mechanical performance and enhanced sustainability, positioning them as eco-friendly alternatives in sectors like construction and automotive [84,85].

The glass transition temperature (Tg), melting points (Tm), and thermal conductivity of polyglycerol-based systems are vital to their suitability for AM. Crosslinking polyglycerol derivatives increases Tg and improves thermal stability, which is critical for maintaining dimensional accuracy and load-bearing capacity at elevated temperatures [60,86,87]. Similarly, crosslinking with various monomers increases Tm, allowing the material to maintain mechanical integrity at elevated temperatures, making them appropriate for industrial and automotive uses [37,88].

Regarding thermal conductivity, polyglycerol-based systems typically exhibit low to moderate conductivity [89]. While native polyglycerol systems exhibit low thermal conductivity (~0.2 W/m·K), incorporation of graphene or CNTs forms conductive networks that improve heat dissipation. However, filler percolation thresholds and dispersion quality are critical—excessive loading or agglomeration may reduce mechanical performance despite thermal gains [83,90].

3.2. Suitability for High-Temperature Printing Platforms

Native polyglycerol-based polymers, such as poly(glycerol sebacate) (PGS), exhibit softening transitions and rubbery behavior near physiological temperatures (~37 °C), limiting their use in high-temperature extrusion platforms like FDM, which require melt-processing temperatures

>200 °C [60]. However, due to their hydroxyl-rich backbone, polyglycerols can be easily functionalized with acrylate, methacrylate, or norbornene groups, enabling photocuring via SLA and DLP techniques [91,92]. When appropriately modified, these resins show potential for use in industries operating within moderate thermal ranges (40–120 °C), such as patient-specific biomedical devices, soft robotic components, or cosmetic automotive interior parts. Recent studies also suggest their adaptability to non-layered processes like Volumetric Additive Manufacturing (VAM), where bulk photopolymerization benefits from rapid curing kinetics and material transparency [93-95].

3.3. Fire Retardancy and Insulation Potential

Another significant advantage of polyglycerol-based systems is their fire retardancy and insulation potential. The hydroxyl-rich structure promotes char formation upon thermal degradation, which can marginally delay ignition, though native polyglycerols are not intrinsically flame-retardant without modification. This can be further enhanced by incorporating inorganic fillers, such as phosphorus-based compounds or intumescent additives, which improve the material's ability to resist ignition and slow the spread of flames [96,97]. These modifications make polyglycerol-based systems potentially suitable for low-voltage electronic enclosures or interior automotive components where moderate flame retardancy is sufficient.

Polyglycerol-based polymers inherently possess low thermal conductivity, making them suitable for thermal insulation applications due to their amorphous structure and high free volume, which limit phonon and electron transport. The incorporation of insulating fillers, such as glass fibers or ceramic particles, can further enhance the thermal barrier properties of polyglycerol-based polymers. These fillers act as thermal barriers by reflecting or dissipating heat through low-conductivity pathways, thereby improving insulation performance while preserving the material's mechanical integrity [20]. However, due to the limited thermal stability of the base polymer, these composites are more appropriate for applications involving low to moderate temperatures rather than high-temperature environments.

4. Mechanical Performance in 3D Printed Forms

4.1. Mechanical Properties in AM

Polyglycerol-based polymers enable tunable mechanical properties for 3D printed biomedical applications. Photocurable PGSA systems, depending on crosslink density and UV dosage, show tensile strengths from 0.5–2 MPa and elongation at break exceeding 200%, which enables tissue compliance and durability **[**98**]**, **while PGS-coated 3D printed scaffolds match trabecular bone strength (5–20 MPa)** [38]**. Electrospun PGS/PCL blends mimic cardiac tissue (0.5–6 MPa tensile strength)** [99]**. HPG bioinks allow stiffness tuning** [100]**, and light-assisted curing improves interlayer bonding** [101]**, though extrusion-based printing may still exhibit anisotropy** which limits mechanical uniformity in load-bearing implants or pressure-bearing medical devices **[**102**]**. **These materials balance flexibility, strength, and biocompatibility for tissue engineering.**

4.2. Influence of Printing Parameters on Anisotropy and Layer Bonding

Printing parameters (speed, nozzle temperature, layer height) affect anisotropy and interlayer bonding in polyglycerol systems. Excessive nozzle temperatures (>180 °C) can cause backbone scission or oxidation in polyglycerol derivatives, leading to molecular weight loss and compromised mechanical integrity. [103-106]. Print orientation impacts anisotropy, with higher strength along the print direction (0°) versus perpendicular (90°) due to interlayer bonding limitations [107,108].

Thinner layers (50–100 μm) reduce voids, improving bonding but increasing print time [109,110]. Non-planar printing reduces anisotropy by aligning deposition with stress flow [111].

Multi-objective optimization (e.g., Grey Relational Analysis [GRA], a statistical optimization tool often employed to balance competing AM parameters such as strength, adhesion, and print resolution) balances parameters for optimal strength and bonding [112]. Chemical modifications (surface-segregating additives) enhance interfacial adhesion, reducing anisotropy [113].

4.3. Comparative Performance with PLA, PCL, PEGDA, and Other Polymers

Polyglycerol systems differ mechanically, thermally, and biologically from PLA, PCL, and PEGDA (Table 2).

Table 2. Quantitative comparison of mechanical, thermal, degradation, and processing-related properties of polyglycerol derivatives versus conventional AM polymers.

Property	PLA	PCL	PEGDA	Polyglycerol (PGS)
Tensile Modulus	2000-3000 MPa [114]	300-400 MPa [115]	1-10 MPa [116]	0.05-1.5 MPa [12]
Elongation at Break	4-10% [114]	300-1000% [114]	5-15% [116]	200-450% [12]
Glass Transition (Tg)	55-65°C [114]	(-65)-(-60)°C [114]	(-20)-0°C [116]	(-40)-(-10)°C [116]
Degradation Rate*	12-24 months [114]	24-36 months [114]	PEGDA is typically non-degradable under physiological conditions, though degradable variants have been synthesized through labile linkers.	1-6 months [12]
AM Printability	Excellent [114]	Good [115]	Excellent [116]	Moderate-Good [12]

PGS has lower stiffness (0.05–1.5 MPa tensile modulus). The wide tensile modulus range reflects sensitivity to degree of crosslinking, copolymerization content, and processing conditions. PGS has higher elasticity (200–450% elongation) than PLA/PCL, making it ideal for flexible scaffolds. Although PEGDA blending improves processability, its incomplete photopolymerization may induce cytotoxicity in vivo, necessitating careful dosage and post-curing validation [38,98]. PGS has moderate-to-good printability due to viscosity and curing limitations.

Thermally, PLA/PCL have higher Tg than PGS, but modifications (crosslinking, blending) enhance PGS stability (Table 3). PGS degrades faster (1–6 months) than PLA/PCL under physiological conditions, with tunable hydrolysis rates [117]. Its hydrophilicity minimizes protein adsorption, offering superior biocompatibility [118].

Table 3. Tunable thermal properties of polyglycerol systems via chemical and architectural modifications.

Material Modification	Glass Transition Temperature (ΔTg) vs. Baseline	Maximum Service Temperature	Key Effect
Unmodified PGS (baseline)	Tg ≈ −20°C to −10°C [88,119]	40-50°C [88,119]	Reference
Citrate crosslinking	+15-20°C (Tg ≈ −5°C to +10°C) [88]	60-70°C [88]	Enhanced thermal resistance
Norbornene functionalization	+10-15°C (Tg ≈ 0°C to +5°C) [120]	55-65°C [120]	Improved UV curability
PCL blending (20-40 wt%)	+5-10°C (Tg ≈ −15°C to 0°C) [121]	50-60°C [121]	Balanced elasticity

Hybrid systems (PGS-PLA, PGS-PCL) improve hydrophilicity, degradation control, and osteogenic activity [122,123]. This gap significantly limits design confidence in dynamic-load-bearing biomedical or robotic applications.

Table 4 shows a comparison of shape-memory and creep performance across PLA/PCL blends, PEGDA systems, and polyglycerol-based materials. Polyglycerol systems stand out with full shape recovery (100%) and lower creep strain (3–8%), making them promising for applications that require long-term flexibility and stability. While PLA/PCL blends offer higher recovery stress, their creep resistance is lower. These results highlight the potential of combining rigid and flexible components—like PLA with PGS—to create balanced, high-performing materials for AM-based biomedical devices

Table 4. Functional behavior comparison: Shape-memory and creep performance.

Property	PLA/PCL Blends	PEGDA Systems	Polyglycerol Systems
Shape-recovery ratio	94-99% [124]	75-90% [125]	100% [126]
Creep strain	6-10% [127]	10-18% [128]	3-8% [126]
Recovery stress (MPa)	12.85 [124]	Not reported	0.180-0.250 [79]

These hybrid systems synergistically merge the rigidity of PLA/PCL with PGS's flexibility and biofunctionality, broadening the material design space for AM-fabricated biomedical devices [27]. Future work should prioritize quantitative characterization of polyglycerol-based shape-memory effects and long-term creep behavior.

4.4. Shape Retention, Creep Resistance, and Dynamic Loading Performance

PGS and its derivatives demonstrate minimal permanent deformation (<3% strain under cyclic compression for 1,000 cycles at 20% strain), attributed to their covalently crosslinked network structure, though exact residual strain values were not explicitly quantified. Higher crosslink density reduces creep strain, enhancing dimensional stability [129]. Dynamic mechanical analysis (DMA) of PGS scaffolds reveals storage modulus stability and low hysteresis (<5% energy loss per cycle) under cyclic loading (0.1–10 Hz), indicating resilience under physiological strain rates [130]. Post-printing UV or thermal curing can increase crosslink density by up to 2–3× (compared to non-post-cured samples), enhancing fatigue resistance and dimensional stability over time. [131].

5. Structural and Functional Enhancements

5.1. Reinforcement with Inorganic Filler

5.1.1. Silica Reinforcement

Adding silica to polyglycerol-based resins increases glass transition temperature (Tg) and thermal conductivity, making them potentially suitable for moderate-temperature components, such as casings or housings in automotive and aerospace subassemblies, where operational temperatures remain below 200–250 °C [88,132-137]. Silica nanoparticles improve crosslinking efficiency, enhance the surface area for interaction, and promote better layer bonding in 3D-printed structures likely due to increased surface area and hydrogen bonding sites that facilitate radical polymerization or crosslink propagation during curing [44,132]. Silica-functionalized polyglycerol resins combine high-temperature stability with enhanced mechanical strength and interlayer bonding, making them promising candidates for structural components in advanced manufacturing technologies.

5.1.2. Graphene Reinforcement

Graphene has emerged as a multifunctional nanofiller that significantly enhances the mechanical strength, electrical conductivity, and thermal stability of polyglycerol-based composites. Incorporation of 0.5–2 wt% graphene oxide has shown up to 20-45% increase in tensile strength and 2× fracture toughness compared to unreinforced PG-based systems [138-142]. Its high intrinsic thermal conductivity (~3000–5000 W/m·K) enables efficient heat dissipation, making it ideal for thermal management in electronics. Studies have demonstrated that GO-based composites significantly reduce hotspot temperatures and improve thermal management performance in electronic systems. Additionally, the incorporation of GO into polymer matrices leads to the formation of percolated filler networks, which enhance structural rigidity while maintaining flexibility. This synergistic effect is particularly advantageous in load-bearing applications such as aerospace and automotive components, where a high strength-to-weight ratio and mechanical resilience are critical [143-145]. These improvements parallel the performance gains observed in stereolithography-printed methacrylate/chitin nanowhisker composites, where nanofiller addition enhanced both mechanical and thermal behavior [146]. Graphene-based systems provide multifunctionality—including electrical conductivity, EMI shielding, and heat dissipation—that surpass silica and nanoclay reinforcements in active or smart device contexts.

5.1.3. Nanoclay Reinforcement

Nanoclays such as montmorillonite and kaolinite enhance mechanical reinforcement and barrier performance in polyglycerol-based systems by forming nanostructured networks within the polymer matrix. Incorporating 3–5 wt% of these fillers has been shown to increase stiffness and tensile strength while significantly improving thermal stability [147]. Studies report a rise in decomposition onset temperatures by 40–50 °C and a reduction in peak heat release rates by up to 35%, indicating enhanced flame retardancy. [148-151]. These improvements make nanoclay-reinforced PG composites well-suited for high-performance applications [149,152,153].

5.1.4. Effects of Hybrid Reinforcement

Hybrid reinforcement strategies that combine multiple inorganic fillers—such as silica–graphene or clay–carbon nanocomposites—can synergistically enhance the multifunctional properties of polyglycerol-based systems. Synergistic effects arise when distinct fillers contribute complementary mechanisms: graphene enhances conductivity and tensile strength, while silica or nanoclays improve thermal stability and dimensional rigidity. While studies specific to polyglycerol composites are still emerging, research on similar polymer systems has demonstrated that combining graphene and silica can significantly improve flexural strength and thermal resistance. Nanoclays, in particular, are well-recognized for enhancing barrier properties and mechanical toughness [154].

Building on these findings, recent research continues to focus on optimizing filler type, concentration, and dispersion techniques to further advance the performance of polyglycerol-based composites. As industries increasingly demand lightweight, multifunctional, and printable materials, polyglycerol-based composites—especially when reinforced with optimized inorganic hybrids—offer a promising platform that balances sustainability, printability, and performance.

5.2. Dual-Network Systems (DNS) and Interpenetrating Polymer Networks (IPNs)

A dual-network system (DNS) consists of two distinct polymer networks: one soft and elastic and the other stiff and rigid. This combination optimizes fracture resistance and impact strength while maintaining stiffness. In polyglycerol-based systems, DNS enhances the strength from the rigid phase and toughness from the elastic phase [155]. For example, a polyglycerol-based resin combined with a crosslinked thermoplastic elastomer exhibits tensile strengths up to 12MPa and elongation at break above 500% in optimized formulations[38,116,155,156], making it suitable for moderate-load applications.

Polyglycerol-based systems have the potential to form interpenetrating polymer networks (IPNs) with other crosslinked polymers such as polyurethane (PU) or epoxy resins. While direct studies on such systems are limited, existing research on similar polymer matrices suggests that IPN architectures can enhance load-bearing capacity and fracture resistance. The IPNs leverage phase interpenetration and molecular entanglements to distribute applied stress across interfaces, thereby delaying crack propagation and enhancing load-bearing behavior [157].

The incorporation of nanofillers into DNS or IPN architectures reinforces interfacial bonding and constrains polymer chain mobility, thereby increasing tensile modulus by 2-4× and shifting thermal decomposition onset temperatures by 20-40 °C [157]. This makes them ideal for high-temperature applications.

5.3. Mechanically Adaptive Polyglycerol Networks

Mechanically adaptive polyglycerol (PG) networks are typically formed by crosslinking polyglycerol-based resins with reactive monomers or multifunctional crosslinkers to create flexible yet robust polymer structures. These networks allow for elastic deformation and partial recovery when external forces are removed. Depending on the formulation, PG networks can respond to environmental stimuli such as temperature, light, or moisture, resulting in changes to their mechanical properties including stiffness, elasticity, or shape-memory behavior.

Several studies suggest that temperature-responsive PG networks are capable of shape-memory effects, showing thermally induced deformation and partial shape recovery while maintaining high mechanical integrity [158-160]. Although most of these studies focus on model systems or modified analogs rather than native polyglycerol, they support the broader potential of PG-based materials for adaptive applications such as smart scaffolds and responsive packaging.

The adaptability of these networks is further enhanced through polymer blending strategies. For instance, combining PG with polymers like polycaprolactone (PCL) or polyethylene glycol (PEG) has been shown to improve mechanical resilience and shape retention under deformation [49,161,162]. These hybrid networks offer tunable recovery characteristics and are under investigation for use in soft actuators, biomedical stents, and packaging that requires conformability and dynamic response. While PEG improves hydrophilicity and elasticity, it may lower thermal resistance, while PCL can delay response times due to slow crystallization dynamics.

Shape-memory polymers (SMPs) represent an important subclass of adaptive materials. They are capable of temporarily fixing a deformed shape and then returning to their original configuration upon stimulation by heat, light, or moisture [80,163,164]. While there is currently limited direct evidence of shape-memory effects in PG systems, related studies in other DCB-enabled polymers suggest that polyglycerol could be engineered to exhibit dual- or multi-shape transitions refer to polymers capable of fixing and recovering more than two temporary shapes via sequential thermal triggers, often enabled by distinct phase-segmented architectures [165-167]. Developing SMPG (Shape Memory Polyglycerol) networks typically involves introducing dynamic covalent chemistries such as esters, imines, or disulfides—bonds known to undergo reversible reactions under heat or chemical stimuli [165-167]. The abundant hydroxyl groups on PG chains provide multiple sites for such modifications, enabling the design of thermally responsive and potentially reversible networks. Though Peng et al. (2022) and Roh et al. (2024) focus on other polymer classes, their findings lend conceptual support to the future development of SMP behavior in polyglycerol matrices.

Applications of these networks in additive manufacturing (AM) are promising due to PG's chemical versatility and compatibility with photopolymerization. For example, poly(glycerol dodecanedioate) (PGD), a thermoset polyester, has demonstrated shape-memory characteristics suitable for resorbable stents and implants [168]. Additionally, studies indicate that PG–urethane foams can exhibit shape fixity and recovery above 99%, albeit with relatively long recovery times (~2400 seconds) under compressive stimuli [169], making them more appropriate for cushioning or slow-release structural components which may be unsuitable for fast-response actuators but acceptable for packaging cushions or delayed-release biomedical devices.

While UV-cured polyglycerol diacrylate (PGDA) systems have been explored as photoreactive resins, their shape-memory performance remains under-characterized. Saunoryte et al. (2024) demonstrated light-induced actuation of glycerol-acrylate photopolymers using UV/vis irradiation at 310 mW/cm^2, achieving full recovery of the original shape in approximately 5 seconds upon reheating above glass transition—but they did not report quantitative metrics for shape fixity, strain recovery ratio, or actuation durability over multiple cycles. [170].

Table 5 highlights the shape-memory and mechanical recovery capabilities of selected polyglycerol-based networks under various stimuli. PGS elastomers demonstrate strong shape-memory behavior with high shape fixing (98%) and recovery (97%) at moderate temperatures, making them suitable for biomedical uses [171]. When reinforced with silica nanoparticles, PGS shows even greater performance—achieving full shape recovery (~100%) within approximately 20 seconds at 60 °C [172]. Polynorbornene-modified networks also display effective memory behavior, with over 99% fixing and over 90% recovery at 45 °C [70]. Polyglycerol urethane foams exhibit excellent fixity and recovery (above 99%) but respond more slowly, with recovery times around 40 minutes (2400 seconds) [169], making them ideal for structural applications that require gradual shape adaptation. Although PEG–polyglycerol diacrylate networks are UV-responsive, further data are needed to evaluate their shape-memory performance [173]. Overall, these systems illustrate the tunability of polyglycerol-based networks for responsive, high-performance applications in medical, structural, and adaptive technologies.

Table 5. Shape Memory and Mechanical Recovery Performance of Selected Polyglycerol-Based Networks.

Sample	System	Trigger Stimulus	Recovery Time (s)	Shape Fixing Ratio (%)	Shape Recovery Ratio (%)
PGS Elastomer	Poly(glycerol sebacate)	Heat (50 °C)	Not reported	98%	97%
PGS/Silica Nanocomposite	PGS + Silica Nanoparticles	Heat (60 °C)	~20	Not reported	100%
Polynorbornene Network	Norbornene-modified Polymer	Heat (45 °C)	Not reported	>99%	>90%
PEG-PG Diacrylate	Polyglycerol Diacrylate Network	UV (365 nm)	Not reported	Not reported	Not reported
Polyglycerol Urethane Foam	Polyglycerol–Isocyanate Foam	Compressive Release	~2400	99.2% ± 0.2%	99.3% ± 0.8%

5.4. Interface Engineering in Multi-Material Printing

In multi-material 3D printing, forming a strong and stable interface between different materials is essential to ensure the durability and performance of the final product. When adhesion at the interface is weak, it can lead to problems such as interfacial delamination, microcrack propagation, and reduced tensile shear strength—typically lowering the effective strength of multi-material assemblies by 40–70%, depending on the material pairing and print conditions [174,175].To address this, interface engineering must consider not only compatibility at the macro level but also interactions happening at the molecular scale.

Polyglycerol-based systems bring unique advantages when it comes to interface design because of their abundance of hydroxyl groups. These functional groups can engage in hydrogen bonding or react chemically through reactions such as isocyanate-based urethane linkages, anhydride ring openings, or base-catalyzed transesterification with neighboring acrylate or lactide groups [176-178].

Surface energy and adhesion forces are also critical factors in determining how well different materials bond together. While surface modification of polyglycerol hasn't been studied extensively, research on similar polymers shows that adding functional groups like amines, carboxyls, or epoxides can improve bonding by making the surface more reactive or polar. Functionalization with amines and carboxylic acids increases polar surface energy, improving wettability and adhesive strength, especially in hydrophilic–hydrophobic polymer blends [179-181]. For example, polymers modified with amine groups have shown better adhesion to materials like epoxy and polyurethane, suggesting that similar approaches might work for polyglycerol too.

Another way to strengthen interfaces is by using coupling agents or stabilizers. Silane coupling agents, for instance, can form strong siloxane bonds with silica particles and at the same time attach to polyglycerol's hydroxyl groups. For instance, treating silica fillers with 1 wt% 3-methacryloxypropyltrimethoxysilane (3-MPS) forms covalent bridges between polyglycerol and silica, boosting interfacial shear strength by approximately 90%—from ~10 MPa to ~19 MPa—in hybrid composites [182,183]. Graphene oxide (GO), with its many oxygen-containing groups, can create hydrogen bonds, van der Waals forces, and even π–π stacking with certain polymers. These interactions can help transfer stress more effectively across the interface and improve the overall toughness of the material [52,183].

Post-processing methods like UV curing and thermal annealing also play a role in reinforcing interfaces UV curing activates residual acrylate/methacrylate groups at the interface, increasing crosslink density by up to 30 %, while thermal annealing enhances polymer chain mobility and interdiffusion at the interfacial zone, improving toughness and modulus by 25-40% [184-186]. That said, the success of these processes depends on matching them to the thermal behavior of the polyglycerol system.

Creating multi-phase composites by combining polyglycerol with nanomaterials such as graphene, silica, or carbon nanotubes may further improve interface quality. These tiny fillers can anchor to the polymer matrix at the nanoscale and create a mix of covalent, electrostatic, and dispersion forces that help hold everything together. While such enhancements have been proven in other polymer systems, their specific use with polyglycerol is still being explored [187].

Further experimental studies should focus on: (1) quantifying interfacial adhesion using peel or lap-shear tests, (2) mapping surface energy profiles of functionalized PG films, and (3) using molecular dynamics simulations to model interfacial interaction energies between PG and common AM polymers.

6. Case Studies and Applications

6.1. Printed Structural Scaffolds with Load-Bearing Potential

Recent advances in 3D printing of polyglycerol-based materials have enabled the fabrication of structural scaffolds with tailored mechanical properties for load-bearing applications [12,188]. Photocurable poly(glycerol sebacate) (PGS) formulations have been successfully printed via stereolithography, producing elastomeric scaffolds with modulus tunable between 0.1–1.5 MPa via crosslink density control that match the mechanical properties of soft load-bearing tissues [12]. Further development of poly(glycerol sebacate) acrylate (PGSA) inks for digital light processing has yielded porous tubular scaffolds with enhanced mechanical strength (compressive modulus up to 12 MPa) and controllable degradation profiles [188].

Hybrid approaches combining polyglycerol derivatives with reinforcing materials show particular promise for bone tissue engineering. Gupta et al. (2023) developed a triple-layered gel/PCL/gel scaffold inspired by natural bone architecture, achieving compressive strengths (40-80 MPa) comparable to cortical bone while maintaining the bioactivity and degradability benefits of polyglycerol-based materials. This performance approaches that of high-strength ceramic scaffolds offers competitive performance to certain polymer-ceramic hybrids while enabling superior biointegration.

6.2. PG-based thermal insulating panels

While no direct literature exists on 3D-printed polyglycerol (PG)-based thermal insulating panels, evidence from related systems suggests PG holds significant promise for this emerging application. Studies demonstrate that PG-derived rigid polyurethane foams achieve thermal conductivities as low as 0.0258-0.0326 W/m·K [146], rivaling conventional petroleum-based insulators. PG's chemical versatility enables it to stabilize phase change materials through hydrogen bonding [189-191], a trait adaptable to dynamic thermal regulation in printed panels. Additionally, PG polyester polyols enhance mechanical strength in composites by over 58% [192], addressing a critical need for durable insulation structures. Crucially, PG-based elastomers (e.g., polyglycerol sebacate acrylate) have been successfully 3D-printed via digital light processing for biomedical scaffolds [12], confirming compatibility with additive manufacturing. To realize PG-based printed insulation, future work should prioritize: (1) hybrid ink formulations integrating PG with nano-insulators (e.g., silica aerogels), (2) bio-inspired cellular geometries (e.g., Voronoi architectures) to minimize thermal bridging, and (3) encapsulation of PCMs within PG matrices. This convergence of PG's thermal performance, mechanical robustness, and proven printability positions it as a compelling bio-based candidate for next-generation sustainable insulation panels.

6.3. Soft Robotics and Actuators Requiring Elasticity and Temperature Resilience

The UV-curable PGSI elastomer demonstrates tunable mechanical properties through controlled UV exposure, with elastic modulus adjustable between 0.1 and 1.5 MPa and elongation exceeding 200%, making it suitable for compliant actuator designs [193]. The ester-rich composition of this poly(glycerol sebacate) derivative suggests thermal limitations consistent with PGS materials, though comprehensive thermal characterization was not performed in the present study. Future testing should include: (1) glass transition temperature (Tg) determination by DSC (reported PGS $T_g \approx -15°C$ [194]), (2) thermo-mechanical stability assessment via DMA (exhibiting 50% storage modulus reduction above 50°C [195]), and (3) degradation profiling by TGA (showing 5% mass loss at ~220°C [196]). For implementation in thermally variable environments, the material would require systematic evaluation under thermal cycling conditions and potential modification with stabilizers to maintain performance across operational temperature ranges while preserving its elastic properties and environmentally benign degradation characteristics.

6.4. Printable Adhesives and Damping Components

Recent advances in hyperbranched polyglycerols (HPG) have demonstrated their potential as sustainable materials for printable adhesives and damping applications [152,197]. Research has established HPGs as effective rheology modifiers for water-based printing inks that improve performance while reducing environmental impact [198]. For electronics applications, polyglycerol methacrylates have been shown to enhance photoresist adhesion on copper substrates by 40-60%

[197]. Significant advances in 3D printing have been achieved using biobased polyglycerol acrylic monomers, reporting a 35% reduction in carbon footprint compared to traditional acrylates [11,199]. While HPGs degrade into benign byproducts, their life-cycle impacts remain influenced by purification energy requirements [11,198]. These developments position polyglycerols as promising sustainable materials, though production scaling and recyclability challenges persist due to purification energy intensity and low solvent recovery rates in HPG synthesis.

7. Challenges and Opportunities

The development of polyglycerol-based macromolecular systems for additive manufacturing (AM) presents multifaceted challenges and emerging opportunities. Key concerns include processing–performance tradeoffs, limited thermal conductivity, difficulty in controlling crystallinity, and the need for accelerated material discovery. Addressing these issues is essential to fully realize their potential in high-performance sectors such as biomedicine, aerospace, and soft robotics.

7.1. Processing–Performance Tradeoffs

Optimizing the interplay between printability and material performance remains a persistent challenge. For example, increased viscosity in UV-curable polyglycerol (PG) networks can elevate tensile strength to ~1.8 MPa, but this also reduces flowability, hindering extrusion and layer resolution [12,13,60,186]. Similarly, crosslinking enhances thermal degradation resistance—raising T_5% to over 350 °C in some systems [12,53,56,84,186,200]—but frequently leads to embrittlement, lowering elongation at break to under 10%.

7.2. Poor Thermal Conductivity vs. Insulation Needs

Polyglycerol-based systems typically exhibit thermal conductivities ranging from 0.03 to 0.06 W/m·K, which is insufficient for heat-dissipating applications such as electronic packaging or automotive housings. Incorporating conductive fillers like graphene or multi-walled carbon nanotubes (MWCNTs) at loadings of 5 wt.% can improve thermal conductivity by 1.5–2× without significantly degrading tensile strength [201]. Conversely, this intrinsic low conductivity is advantageous for insulation, particularly in building components and thermal barrier coatings. The addition of insulating fillers such as silica aerogels or hollow glass microspheres has demonstrated thermal conductivities below 0.03 W/m·K in polymer matrices, making them suitable for passive thermal insulation [202].

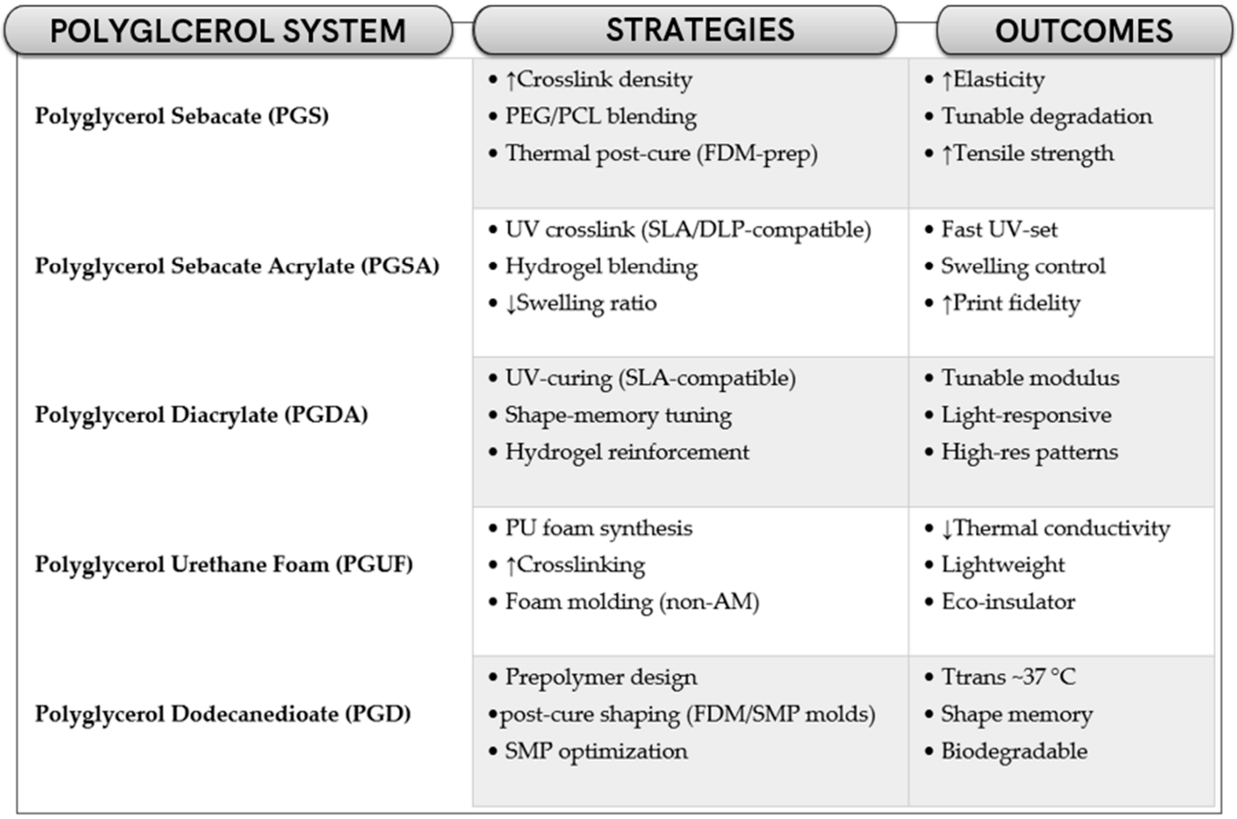
7.3. Engineering Crystallinity or Semi-Crystalline Domains

Polyglycerol's inherently amorphous backbone poses challenges for establishing semi-crystalline structures, which are often desirable for improving dimensional stability and load-bearing capacity. Incorporating crystalline co-polymers like PEG or PCL can yield phase-separated domains that enhance modulus and thermal stability. For example, PEG-PG blends have shown increased crystallinity index (~20%) and melting transitions above 50 °C, compared to <10% for native PG systems [56]. However, over-crystallization may compromise toughness and ductility, necessitating fine-tuned control over formulation and curing parameters.

7.4. Summary of Design Strategies and Pathways

To systematically understand how polyglycerol-based systems are tailored for additive manufacturing, this section maps the relationships between molecular architecture, property enhancement strategies, and targeted functional outcomes. The following figures provide a visual synthesis of these interdependencies, highlighting both the design logic and the developmental challenges associated with implementing polyglycerol-derived materials in AM platforms.

Figure 1 presents a design map of polyglycerol-based macromolecular systems tailored for additive manufacturing (AM), detailing their core architectures, enhancement strategies, and functional outcomes. Each system varies in its compatibility with AM platforms, processing demands, and application performance, reflecting trade-offs that must be considered during material selection.



POLYGLCEROL SYSTEM	STRATEGIES	OUTCOMES
Polyglycerol Sebacate (PGS)	• ↑Crosslink density • PEG/PCL blending • Thermal post-cure (FDM-prep)	• ↑Elasticity • Tunable degradation • ↑Tensile strength
Polyglycerol Sebacate Acrylate (PGSA)	• UV crosslink (SLA/DLP-compatible) • Hydrogel blending • ↓Swelling ratio	• Fast UV-set • Swelling control • ↑Print fidelity
Polyglycerol Diacrylate (PGDA)	• UV-curing (SLA-compatible) • Shape-memory tuning • Hydrogel reinforcement	• Tunable modulus • Light-responsive • High-res patterns
Polyglycerol Urethane Foam (PGUF)	• PU foam synthesis • ↑Crosslinking • Foam molding (non-AM)	• ↓Thermal conductivity • Lightweight • Eco-insulator
Polyglycerol Dodecanedioate (PGD)	• Prepolymer design •post-cure shaping (FDM/SMP molds) • SMP optimization	• Ttrans ~37 °C • Shape memory • Biodegradable

Figure 1. Design map of polyglycerol-based macromolecular systems used in additive manufacturing. Left: polymer architectures derived from glycerol. Middle: strategies for property enhancement. Right: resulting functional outcomes such as elasticity, biofunctionality, and printability.

Polyglycerol Sebacate (PGS) is a thermally crosslinked elastomer known for its elasticity and biodegradability, often used in soft tissue applications [38]. While blending with PEG or PCL can improve mechanical performance and degradation rate, its reliance on high-temperature curing (~120–150 °C) constrains its integration into photopolymer-based AM systems like SLA or DLP [45,53]. As a result, its use is better suited for mold-based or indirect AM workflows (e.g., FDM molds).

Polyglycerol Sebacate Acrylate (PGSA), an acrylated variant of PGS, addresses this limitation through UV-curable chemistry, enabling compatibility with SLA/DLP platforms [203,204]. Studies demonstrate PGSA's ability to form robust, biofunctional hydrogels under light exposure [205,206]. However, its performance is highly sensitive to formulation viscosity, photo-initiator concentration, and layer thickness—factors that can impact dimensional fidelity and swelling control in printed structures.

Polyglycerol Diacrylate (PGDA) offers tunable stiffness and shape-memory characteristics, making it a promising candidate for high-resolution photopatterning [207,208]. Saunoryte et al. (2024) reported its potential in responsive microstructures, though its mechanical performance under repeated actuation or hydration remains underexplored [170]. Compared to PGSA, PGDA shows higher modulus and lower elongation, making it better suited for structural rather than soft applications.

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Polyglycerol Urethane Foam (PGUF) is typically synthesized via polyol–isocyanate chemistry and exhibits low thermal conductivity and lightweight structure, suitable for insulation [209,210]. However, its limited compatibility with direct AM techniques poses challenges. While foams can be shaped using printed molds, issues such as foaming consistency, dimensional accuracy, and batch-to-batch variation remain obstacles to scale-up [74,211].

Polyglycerol Dodecanedioate (PGD) exhibits shape-memory behavior around 37 °C, aligning well with biomedical device requirements [80,212]. Although it is not a direct candidate for SLA or FDM, PGD can be processed through molding or extrusion-assisted techniques. However, ensuring consistent recovery behavior and structural integrity in printed geometries remains a key area for further development.

PGSA and PGDA show strong potential for light-based AM due to their photoreactivity and tunable properties, materials like PGS, PGUF, and PGD may require hybrid processing approaches or serve as complementary components within AM-integrated workflows. The successful integration of polyglycerol systems in AM depends on balancing architecture, processing feasibility, and application-specific performance.

Figure 2 illustrates the development pathway of polyglycerol-based macromolecular systems, moving from the molecular structure of the polymers through enhancement strategies, intended applications, and the challenges faced in additive manufacturing (AM) integration.

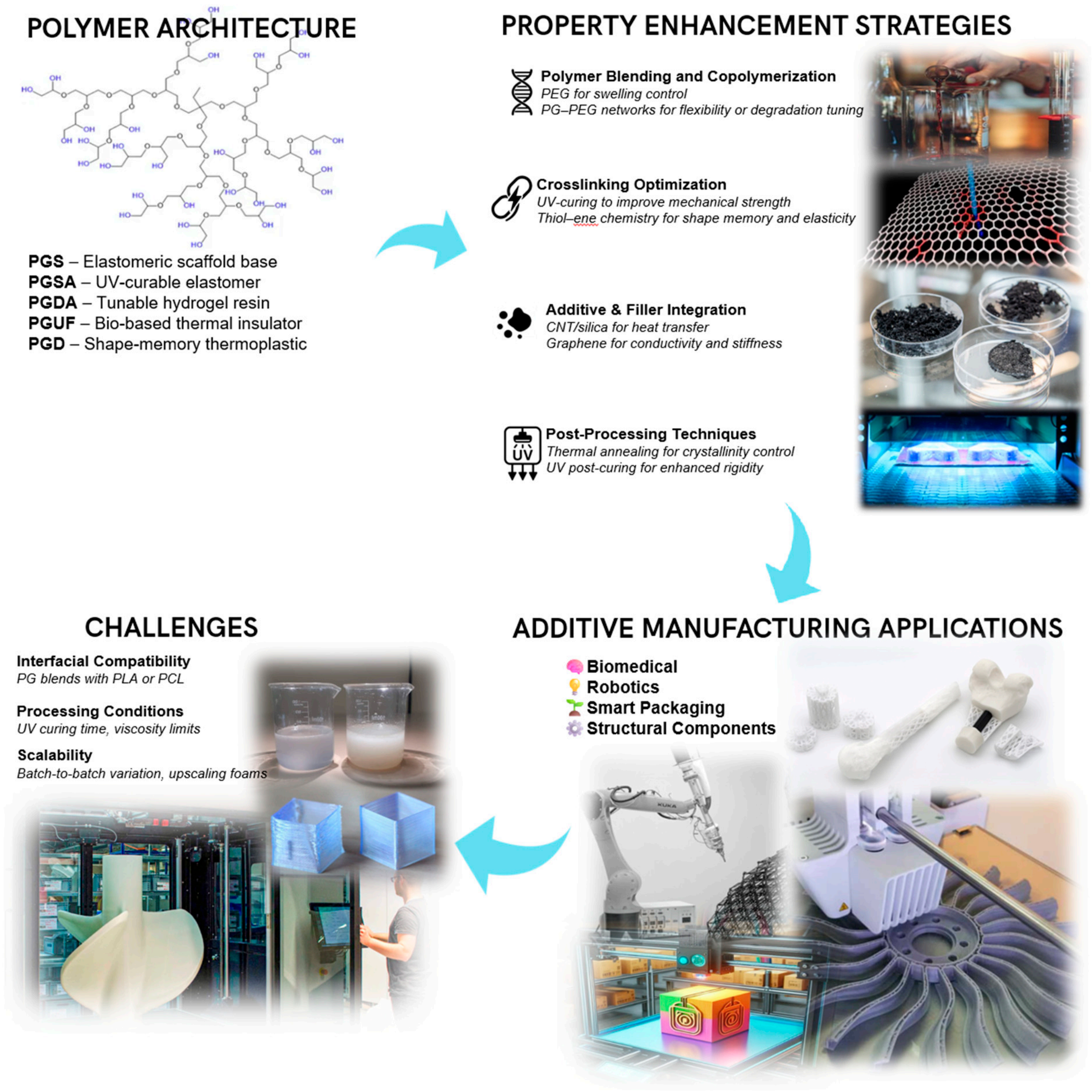

Figure 2. Development Pathway of Polyglycerol-Based Macromolecular Systems: From Polymer Architecture to Additive Manufacturing Applications and Associated Challenges.

The core polymer architectures derived from glycerol—such as PGS, PGSA, PGDA, PGUF, and PGD—which form the foundation for further material modification. These base structures are chosen not only for their chemical versatility but also for their potential to support specialized functions like elasticity, shape-memory, or thermal insulation, depending on the target application.

Building on this foundation, the figure maps out four main strategies used to improve material performance: polymer blending and copolymerization, crosslinking optimization, additive or filler integration, and post-processing techniques. These methods are critical in tuning the thermal, mechanical, and processing behavior of the materials. Still, each strategy comes with trade-offs—for example, while crosslinking can improve stiffness, it may reduce flexibility; and filler addition might enhance conductivity but also increase viscosity, complicating printability.

The pathway continues toward various AM applications, including biomedical scaffolds, robotic components, smart packaging, and structural parts. These sectors are attracted to polyglycerol systems because of their biodegradability, tunability, and processing potential.

However, realizing these applications requires more than just good material properties—it also demands alignment with the specific requirements of AM platforms like SLA, DLP, or FDM.

The figure identifies three core challenges that often emerge in the transition from lab to production: interfacial compatibility, processing conditions, and scalability. These are not minor issues. For example, poor interaction between PG and other polymers like PLA or PCL can lead to phase separation, while narrow UV-curing windows or high material viscosity can limit success in light-based printing. Scalability remains a broader hurdle, particularly when moving from small-batch lab synthesis to consistent, large-scale foam production.

This pathway highlights that the successful integration of polyglycerol-based systems in additive manufacturing is not a straightforward or linear process—it is conditional, shaped by the dynamic interplay between molecular design, engineering strategies, processing limitations, and specific application requirements.

7.5. Future Directions: High-Throughput Synthesis, Computational Design, and Hybrid Architectures

High-throughput platforms now enable the parallel synthesis and screening of 50–200 polymer variants per cycle, drastically shortening development timelines. Integrated real-time analytics (e.g., inline FTIR or UV-Vis spectroscopy) further accelerate formulation feedback loops by 5–10× compared to manual approaches [213]

Computational modeling, including molecular dynamics for predicting polymer glass transitions and finite element analysis (FEA) for flow behavior under extrusion—has become routine in AM development. Additionally, **machine learning** models trained on formulation–performance datasets (~10^3–10^4 data points) can predict target properties (e.g., tensile strength, modulus, viscosity) with mean absolute errors of 5–10%, significantly reducing experimental rounds [214] . For example, in polymer composite research, ML has been successfully applied to forecast multi-layer mechanical and thermal performance across varying filler ratios and cure conditions

Hybrid architectures embedding conductive fillers—such as multi-walled carbon nanotubes (CNTs) or graphene nanoplatelets—have achieved dramatic improvements in thermal conductivity. At loading levels of just 0.5–10 wt.%, thermal conductivity increases by 2×–10× over baseline polymers. For instance, graphene/PVDF composites reached ~2.06 W/m·K (≈10× over the pure polymer) at 20 wt.% loading [201]; similarly, continuous CNT networks at 10 wt.% in polyimide attained 1.9 W/m·K (≈7× improvement) . Single-wall CNT fillers further contribute dramatic heat transport at the nanoscale—individual conductivity values exceed 3,000 W/m·K [82,83]

8. Conclusion

This review synthesized current advances in polyglycerol-based macromolecular systems for additive manufacturing, emphasizing their tunable thermal and mechanical properties. Structural variants—linear, hyperbranched, and dendritic—allow systematic control over elasticity, stability, and strength. Enhancement strategies such as crosslinking, copolymerization, and incorporation of nanofillers (e.g., silica, CNTs) significantly improve performance by reinforcing networks and modulating thermal conductivity. While crosslinking increases dimensional stability, it often reduces ductility, necessitating tradeoff optimization. Low inherent thermal conductivity limits heat dissipation, though this property becomes advantageous in insulating applications. Persistent challenges include weak interfacial adhesion in multi-material systems, limited scalability of synthesis, and incomplete structure–property modeling. Moving forward, integrating high-throughput formulation screening with multiscale computational modeling may accelerate material discovery. Hybrid strategies such as dual-network architectures could reconcile mechanical toughness with biodegradability, making polyglycerol derivatives suitable for medical, aerospace, packaging, and robotic applications. With continued research, these versatile, biocompatible, and sustainable materials may become foundational to next-generation additive manufacturing platforms.

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