Preservation-Aware Framework for Natural Rubber Latex: Structure-Process-Property Relations

by

Oliyad Dibisa

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The dissertation is approved by the following members of the Final Oral Committee:
Jane Doeverything, Professor, Electrical Engineering
John Dosomethings, Associate Professor, Electrical Engineering

I will insert my dedication here.

ACKNOWLEDGMENTS

It is customary for authors of academic books to include in their prefaces statements such as this: "I am indebted to ... for their invaluable help; however, any errors which remain are my sole responsibility." Occasionally an author will go further. Rather than say that if there are any mistakes then he is responsible for them, he will say that there will inevitably be some mistakes and he is responsible for them....

Although the shouldering of all responsibility is usually a social ritual, the admission that errors exist is not — it is often a sincere avowal of belief. But this appears to present a living and everyday example of a situation which philosophers have commonly dismissed as absurd; that it is sometimes rational to hold logically incompatible beliefs.

— David C. Makinson (1965)

Above is the famous "preface paradox," which illustrates how to use the `wbepi` environment for epigraphs at the beginning of chapters. You probably also want to thank the Academy.

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LIST OF ACRONYMS

NRL Natural Rubber Latex

NR Natural Rubber

NRC Non-Rubber Components

PU Polyurethane

DLVO Derjaguin-Landau-Verwey-Overbeek

DLS Dynamic Light Scattering

DRC Dry Rubber Content

AM Additive Manufacturing

VPP Vat Photopolymerization

HDDA 1,6-Hexanediol Diacrylate

TMPTA Trimethylolpropane Triacrylate

TPO Phenylbis(2,4,6-trimethylbenzoyl)-phosphine Oxide

PRE Photoresin Emulsion

DEPR Dual Emulsion Photoresin

JMRE Jammed Micro-Reinforced Elastomer

HLB Hydrophilic-Lipophilic Balance

HIPE High Internal Phase Emulsion

NMR Nuclear Magnetic Resonance

UV Ultraviolet

DISCARD THIS PAGE

LIST OF SYMBOLS

Greek Letters

Symbol	Description	Units
α	Mode-coupling viscosity exponent	–
β	Hydrodynamic viscosity exponent	–
γ	Magnetic field gradient strength (NMR)	T/m
η	Dynamic viscosity	Pa·s
η_0	Zero-shear viscosity	Pa·s
η_∞	Infinite-shear viscosity	Pa·s
η_r	Relative viscosity (η/η_s)	–
η_s	Solvent (medium) viscosity	Pa·s
η_p	Plastic viscosity (Bingham model)	Pa·s
$\dot{\gamma}$	Shear rate	s^{-1}
$\dot{\gamma}_c$	Critical shear rate	s^{-1}
κ	Inverse Debye length	m^{-1}
λ	Relaxation time (Cross/Carreau model)	s
λ_D	Debye length ($1/\kappa$)	nm
μ	Optical attenuation coefficient	m^{-1}
ρ	Density	kg/m^3
ρ_p	Particle density	kg/m^3
ρ_m	Medium (fluid) density	kg/m^3
σ	Stress; surface charge density	Pa; C/m^2
σ_T	Thermal stress scale ($k_B T/a^3$)	Pa
σ^*	Dimensionless stress (σ/σ_T)	–
τ	Shear stress	Pa
τ_y	Yield stress	Pa
τ_B	Brownian relaxation time (a^2/D_0)	s
ϕ	Volume fraction	–
ϕ_c	Critical volume fraction	–
ϕ_g	Glass transition volume fraction	–
ϕ_m	Maximum packing fraction	–
ϕ_{eff}	Effective volume fraction	–
ψ_0	Surface potential	mV
ω	Angular frequency	rad/s
ζ	Zeta potential	mV
δ	Phase angle; chemical shift (NMR); steric layer thickness	°; ppm; nm

Latin Letters – Rheology and Colloidal Science

Symbol	Description	Units
a	Particle radius; Cross model ratio (k_d/k_r)	nm; –
A	Hamaker constant	J
A_{131}	Hamaker constant for particles (1) across medium (3)	J
c	Concentration	mol/L; wt%
c_d	Depletant concentration	mol/L
C	Cross model time constant; offset term	s; –
d	Particle diameter; number of dimensions	nm; µm; –
D	Diffusion coefficient	m^2/s
D_0	Stokes–Einstein diffusivity	m^2/s
e	Elementary charge (1.60×10^{-19})	C
E	Young's modulus	Pa
E_a	Activation energy	kJ/mol
g	Gravitational acceleration (9.81); gradient amplitude (NMR)	m/s^2; T/m
G'	Storage modulus	Pa
G''	Loss modulus	Pa
G^*	Complex modulus	Pa
h	Interparticle separation distance (surface-to-surface)	nm
I	Light intensity; NMR signal intensity; ionic strength; isocyanate index	W/m^2; a.u.; mol/L; –
k	Rate constant	s^{-1}
k_B	Boltzmann constant (1.38×10^{-23})	J/K
k_d	Breakage/degradation rate constant (linkages)	s^{-1}
k_r	Reformation rate constant (linkages)	s^{-1}
K	Consistency index (Herschel–Bulkley)	$Pa{\cdot}s^n$
l_f	Fractocohesive length (Γ/W_f)	m
l_g	Gravitational length ($k_B T/\Delta\rho V g$)	m
L	Steric layer thickness; sample length	nm; mm
L_0	Initial gauge/sample length	mm
m	Cross model rate exponent; shear-sensitivity exponent	–
M	Torque; magnetization	N·m; a.u.
M_0	Equilibrium magnetization	a.u.
M_n	Number-average molecular weight	g/mol
M_w	Weight-average molecular weight	g/mol

Latin Letters – NMR Spectroscopy

Symbol	Description	Units
A_1, A_2	Component amplitudes (T_2 relaxation)	a.u.
b	Diffusion weighting factor	s/m^2
$I(g)$	Signal intensity at gradient g	a.u.
I_0	Initial signal intensity (at $g = 0$)	a.u.
r_h	Hydrodynamic radius (Stokes–Einstein)	nm
S	Signal intensity	a.u.
S_0	Initial signal intensity	a.u.
T_1	Spin-lattice (longitudinal) relaxation time	s
T_2	Spin-spin (transverse) relaxation time	s
$T_{2,1}$, $T_{2,2}$	Component transverse relaxation times	s

Subscripts and Superscripts

Symbol	Description
0	Initial, reference, or zero-shear condition
∞	Infinite-shear or equilibrium condition
c	Critical condition
eff	Effective value
g	Gravitational; glass transition
H	Hydrodynamic
B	Brownian
int	Interparticle
m	Medium (solvent) or maximum packing
p	Particle; plastic
r	Relative (ratio to solvent property)
s	Solvent; solid phase; surface
w	Wall or water

Dimensionless Numbers

Symbol	Description	Definition
Pe	Péclet number	$\dot{\gamma}\tau_B$
Pe_g	Gravitational Péclet number	$\nu_s a/D$
Re	Reynolds number	$\rho\nu L/\eta$
We	Weissenberg number	$\lambda\dot{\gamma}$
De	Deborah number	λ/t_{obs}

Intrinsic Viscosity and Model Parameters

Symbol	Description	Value/Units
$[\eta]$	Intrinsic viscosity (spheres)	2.5
k_2	Second virial coefficient (viscosity)	–

ABSTRACT

FIXME: basically a placeholder; do not believe

I did some research, read a bunch of papers, published a couple myself, (pick one):

1. ran some experiments and made some graphs,
2. proved some theorems

and now I have a job. I've assembled this document in the last couple of months so you will let me leave. Thanks!

1.1 Background and Significance

Materials or processes are sustainable only if their mass, energy, and waste byproducts can be maintained over time without imposing unacceptable burdens on ecosystems, workers, or future waste managers. In polymers, this immediately forces us to separate labels that are commonly conflated: *bio-polymers*, which are carbon sourced from contemporary biomass; *biodegradables* are polymers that undergo microbial mineralization under specific conditions; *compostable*, which are biodegradable under standardized composting conditions; and *circular*, which is controlled end-of-life cases such that keeping carbon and value in use through reuse or recycling and reserving biodegradation.

Long before the petrochemical era, society already lived in a world of consumer biopolymers. Natural polymers, such as proteins, polysaccharides, and plant resins, were processed into fibers, coatings, molded goods, and medical materials, often with surprisingly sophisticated empirical know-how. A canonical example of a plant polymer is silk. The legend of Empress Si Ling-Chi traces a multi-millennia origin story in which silk production and formulation were treated as strategic secrets, restricted for centuries before spreading through trade networks. And for roughly the first half of the 20th century, before synthetics fully dominated, many bio-derived materials still occupied real consumer space, for example, casein plastics, natural resins, natural fibers, because they were accessible, workable, and "good enough" for the specification culture of the time.

Many historical biopolymer feedstocks carried serious liabilities that modern manufacturing cannot tolerate, such as ethical and supply constraints. In the latter, as with animal-derived materials, examples include competition with food or farmland, large seasonal variability, and intrinsic components that must be removed or modified to achieve biocompatibility or consistent performance. Silk is a clear example of the broader point. Despite excellent mechanical behavior, biomedical use encountered biocompatibility issues that required additional extraction and refinement steps to remove sericin-related responses, which then altered handling and performance and did not fully eliminate all limitations.

When DuPont hired Wallace Hume Carothers, the development pathway that culminated in nylon created a materials regime defined by scalability, reproducibility, and tunable functionality. By 1938 nylon had already begun displacing silk in major consumer applications, and the larger pattern became clear. Synthetics could be produced at scale, with standardized specs, and engineered into families of materials that were not geographically bound to particular crops or ecosystems. Over the following decades, that advantage compounded, and by the 1970s and 1980s, synthetic polymers had become the default material platform.

Despite the breadth of synthetic polymer innovation, Natural Rubber (NR), one of the oldest biopolymers, has not been replaced across many critical applications. This persistence indicates that NR occupies a unique performance niche among elastomers. Natural Rubber Latex (NRL) is a high-value biosynthesized elastomeric platform, but its full potential is limited by processing constraints, preservation chemistry, and the inherent variability of a living colloidal system, such as bioincompatibility and waste byproduct control. The central aim of this dissertation is to address technical challenges that can enable the expansion of natural rubber latex into more versatile, high-performance, and biocompatible material routes, while retaining its established advantages.

1.2 Developing Circular Economies

So why are we considering a return to biopolymers? The very durability and versatility that make petrochemical polymers valuable have also led to significant waste management challenges and associated externalities at the national scale. A striking statistic highlighted in the literature on historical synthetic polymers is that over 25 million tons of plastic were introduced into the U.S. municipal solid waste (MSW) stream in 2001, with non-biodegradable plastic waste accounting for over 11% of MSW, up from approximately 1% in 1960. The issues of incineration and litter further exacerbate health, pollution, and aesthetic concerns. Nevertheless, the transition back to biopolymers is not a simple endeavor; correlation does not imply causation. The "legacy" natural polymers of the past, characterized by their bio-incompatibility and processing difficulties, cannot straightforwardly compete with the optimized performance of contemporary synthetics. However, there is one notable exception to this synthetic dominance, it is Natural Rubber.

Current research on the development of circular economies for sustainable polymers focuses on pathogenesis. Bacteria naturally synthesize a variety of polymer classes, including polysaccharides, polyesters, polyamides, and polyphosphates. Recent studies emphasize the potential to repurpose these biopolymers, traditionally linked to pathogenesis or survival, into advanced materials. For instance, polyhydroxyalkanoates (PHAs) are synthesized by bacteria that convert metabolic intermediates, hydroxyacyl-CoA, into polymers, storing the resultant products as hydrophobic intracellular inclusions. Depending on their composition, PHAs can manifest as either thermoplastics or elastomer-like materials. Similarly, natural rubber, which is initially found in nature as a latex, is produced in a manner that parallels the biosynthesis of polymers within a cellular context. In plant cells known as laticifers, soluble isopentenyl pyrophosphate exists in the latex serum. The Rubber Transferase enzyme, often aided by the Rubber Elongation Factor, is situated on the surface of the rubber particle, where it captures isopentenyl pyrophosphate and incorporates it into the polyisoprene chain within the particle.

NRL aligns with several circular economy objectives because it is a renewable feedstock and is already produced at a commodity scale for high-value applications. Those applications are tires, gloves, balloons, gaskets, hoses, etc. Dong et al. evaluated four concrete-conveying rubber hoses that differed solely in their inner-liner formulations, which influenced their composition and service life. Within an NR and synthetic blend, increasing the NR fraction to 60 parts per hundred rubber can reduce the climate change type impact and water depletion. Furthermore, the service life of the hoses is primarily determined by the additives used, as well as the design and formulation strategy of the liner, rather than merely the ratio of NR to synthetic rubber. Therefore, any claims regarding circularity must be directly associated with the functional unit.

The environmental implications of rubber products are influenced significantly by a combination of agricultural practices, processing methods, and formulation choices, rather than solely by the polymer type. Cucci et al. (2025) underscore that the primary environmental impact during the cultivation phase of natural rubber arises from the supply of raw materials. Specifically, they highlight that direct land use change, with an emphasis on deforestation, accounts for up to 79% of the carbon footprint, overshadowing emissions from manufacturing processes. In a related study, Dunuwila et al. (2025) assert that in Sri Lankan crepe rubber production, the substantial environmental burdens are attributable not to the rubber itself but to intensive agricultural inputs such as fertilizers, water, and electricity. They propose a “trade-off valuation index” to evaluate these inputs, emphasizing that fertilizer production constitutes a significant source of toxicity and eutrophication. Research by Soratana et al. (2017) indicates that while Guayule rubber has a lower ozone depletion potential than styrene-butadiene rubber, it may have a higher global warming potential and greater acidification potential in certain circumstances, primarily due to energy-intensive irrigation and processing requirements. Furthermore, their findings suggest that styrene-butadiene rubber possesses markedly lower acidification potential and eutrophication potential due to its reduced reliance on nitrogen-based fertilizers and the complexities of land management inherent to Hevea and Guayule cultivation.

Many studies also reveal that inefficient drying processes in Hevea rubber processing can significantly increase global warming potential, making styrene-butadiene rubber more favorable in certain scenarios. Jawjit et al. (2015) highlight that in the production of concentrated latex, the centrifugation process contributes 50% of the global warming potential and 58% of the acidification potential, while ammonia preservation accounts for 37% of human toxicity, thereby correlating with ongoing initiatives to adopt non-toxic preservatives. Marrero Nunes et al. (2025) further emphasize the substantial thermal and water use during production, which exacerbates the impacts of global warming and ecotoxicity. They advocate establishing standardized Product Environmental Footprint guidelines to address the significant environmental burden posed by the 17 million tons of end-of-life tires generated annually. Additionally, Eranki et al. (2019) present findings from a cradle-to-grave analysis of a Guayule tire, revealing that the use phase is responsible for approximately 95% of the total life-cycle energy consumption. Notably, the lower rolling resistance of Guayule tires reduces emissions by 6–30% across 10 impact categories compared to conventional tires. Marrero Nunes et al. (2025) conclude that while the processing of natural rubber is challenged by localized toxicity from ammonia and the acids used in preservatives and coagulation, the environmental burdens associated with synthetic rubber predominantly arise from fossil resource depletion and the formation of photochemical smog from petrochemical processing.

1.3 Meeting Global Demand and Feedstock Diversification

Natural rubber remains difficult to replace because its *cis*-1,4 polyisoprene chains, which undergo strain-induced crystallization, offer a combination of green strength, fatigue resistance, resilience, and low heat buildup that many synthetic elastomers can only partly match or require more complex formulations. This is why natural rubber is used in tires, belts, hoses, vibration isolators, footwear, and medical goods, with tire manufacturing accounting for most of the demand. In the European Union (EU), about three-quarters of natural rubber consumption is for tires. Global production shows both growth and limitations. For example, in 2019, it reached around 13.6 million tons, up from 3 million in 2010, and synthetic rubber was produced at approximately 15.1 million tons that year, only 2 million tons more than in 2010. The current challenges in natural rubber include the fact that approximately 85% of the natural rubber supply is reliant on smallholder farming systems.

Additionally, only 7% of the global land area is dedicated to natural rubber production, and water depletion during collection and processing has placed smallholder farmers at a disadvantage. Nap et al. (2025) highlight that approximately 90% of the world's natural rubber production is concentrated in Southeast Asia, which presents considerable geopolitical and biological risks. A significant concern is the potential introduction of South American Leaf Blight (*Pseudocercospora ulei*) into Asian plantations, which could jeopardize global supply given the limited genetic diversity of commercial cultivars. Price collapses, such as those experienced after 2012, diminish incomes for smallholders, often leading them to abandon their plantations or switch to alternative crops. The COVID-19 pandemic further intensified this issue, resulting in unharvested latex. Moreover, rubber trees require about seven years to mature, which complicates rapid supply adjustments in response to shifts in demand. This situation perpetuates a boom-and-bust cycle for farming communities and creates instability for downstream industries.

Feedstock diversification serves as a practical hedge against potential bottlenecks in the rubber supply chain. *Hevea*, the primary source of natural rubber, is restricted to tropical regions and faces various biological vulnerabilities. To mitigate these challenges, alternative latex crops, such as guayule (*Parthenium argentatum*) and rubber dandelion (*Taraxacum kok-saghyz*, or TKS), are being developed for temperate and arid climates. Rasutis et al. (2015) highlight guayule's suitability for water-stressed areas such as the U.S. Southwest, as it is a low-input shrub that can thrive on marginal lands unsuitable for food crops, thereby avoiding direct competition with food security. In a similar vein, Nap et al. (2025) recognize TKS as a scalable alternative for temperate regions, notable for its rapid harvest cycles. Importantly, TKS functions as a dual-purpose crop, producing both natural rubber and inulin, a valuable carbohydrate for green chemistry applications, significantly enhancing its economic viability and contributing to a circular economy model. These alternative crops aim to establish domestic supply chains and reduce vulnerability to regional disruptions. They also create opportunities for niche applications, including hypoallergenic latex options. Advances in extraction and purification techniques utilizing tailored flocculants, chelators, and process control are improving yield and consistency. The implications for the circular economy extend beyond merely increasing rubber production; they involve designing a supply chain that integrates renewable feedstocks, preservation chemistry, colloidal stability, and end-of-life strategies. In NRL systems, innovations such as ammonia-free preservation and enhanced control of dispersion chemistry are pivotal technologies that impact shelf life, processability, and worker safety, ultimately determining whether renewable elastomers can meet the demands of modern manufacturing at scale.

1.4 Emerging Technological Interest

Natural materials often exhibit extraordinary performance because their hierarchical structures and compositions were honed through evolution. In the case of elastomeric biopolymers, NRL is a prime example of this complexity, containing approximately 94% *cis*-1,4-polyisoprene and 6% non-rubber components, such as proteins and lipids. Historically, industrial standardization viewed biological residues as impurities rather than critical engineering elements. These components link polymer chains to create a naturally reinforced network, providing “green strength” and strain-crystallization properties. As a result, NR is fatigue-resistant and crack-tolerant, unlike many synthetic materials. By treating these biological interfaces as functional assets, engineers can reverse-engineer nature’s molecular architecture, leading to the development of bioadhesives and resins with high toughness and biocompatibility. This approach demonstrates that high-performance materials are best achieved by mimicking nature’s functional complexity rather than simplifying its chemistry.

In elastomer processing, mastication is the classic “make it processable” step, which mechanically cleaves chains to reduce viscosity. The cost is irreversible chain scission, which destroys the very long chains that give natural rubber its fatigue resistance and crack tolerance. Quantitatively, natural rubber from latex has a number-average molecular weight around 300 kg/mol, corresponding to roughly 4,400 repeat units per chain, whereas mastication can degrade chains to roughly 440 repeat units per chain, requiring higher crosslink densities to obtain usable networks. That is, the mastication paradox yields sufficient mixing but at the cost of reduced damage tolerance and less “room” for strain-induced crystallization.

The proposed solution is to use plasticizers and process oils, which often extend the processing window by lowering viscosity; however, they can significantly contribute to life-cycle impacts, particularly when derived from petrochemicals. This complexity can further hinder end-of-life recovery due to the increased formulation intricacy. Secondly, latex preservation practices and storage history introduce time-dependent degradation of the polymer chain, driven by volatile alkaline stabilizers such as ammonia, which create both occupational hazards and emissions challenges. Extended storage can lead to chain scission and interfacial reorganization, diminishing performance even before the material is transformed into a part. Collectively, these factors shift the focus from simply making materials processable to making them degradable, additively loaded, and time-sensitive. The next-generation colloid-enabled and ammonia-free methods avoid some of those processing concerns. Innovative approaches are redefining the notion that degradation is an inevitable trade-off for manufacturability. By embracing low-intensity mixing, emulsion and colloid-enabled network formation, and preservation chemistries that maintain the integrity of the protein–lipid interface and long-chain entanglements, these methods also offer ammonia-free alternatives that mitigate the occupational and environmental risks associated with volatile, caustic stabilizers.

The successful preservation of these intrinsic molecular properties directly unlocks advanced capabilities in Additive Manufacturing (AM). A major limitation in printing high-performance elastomers is the "operational viscosity paradox," in which the long polymer chains needed for strength make the resin too thick to print. However, by utilizing the preserved colloidal structure of NRL, it is possible to maintain ultra-high molecular weights within discrete particles while keeping the bulk viscosity low, akin to flowing water. This integrity allows AM techniques to move beyond simple geometric shaping to true microstructural programming. Innovations such as rotational 3D printing can precisely control fiber orientation within a filament, mimicking natural architectures like the Bouligand structures found in arthropod shells to optimize fracture resistance. This interaction between living feedstocks and robotic control grants engineers unprecedented freedom to design responsive, hierarchical materials. By aligning the circular biology of renewable polymers with the geometric precision of AM, manufacturing can achieve sustainability and high performance as mutually reinforcing outcomes rather than competing goals.

1.5 Problem Statement and Research Motivation

Preservation Chemistry

Fresh NRL is a reactive biological colloid, not a stable commodity fluid. After tapping, microbial activity and enzyme-driven changes alter serum chemistry, weaken the rubber-particle interphase, and can trigger acidification, odor, and spontaneous coagulation, making latex unprocessable without intervention. Preservation is therefore a logistics requirement; it must maintain colloidal stability during storage, transport, and conversion. The historical solution is alkaline ammoniation, in which elevated pH suppresses microbial growth and stabilizes particles primarily through electrostatic repulsion, often supported by secondary stabilizers such as zinc oxide (ZnO) and thiuram-type systems. However, those approaches carry escalating technical and sustainability impacts; for example, ammonia is volatile and hazardous, increases effluent and neutralization burdens, disproportionate challenge for smallholder processing, can discolor latex and accelerate equipment corrosion, reduces the overall molecular weight of NR, and thiuram chemistry can form nitrosamine hazards at elevated processing temperatures. Beyond safety and emissions, preservation chemistry can also modify the very "functional impurities" that differentiate NRL from synthetic elastomers. Disruption of lutoids, phospholipid membranes, and protein structure can alter the non-rubber fraction and the physics of interfaces that govern processability and end-use performance. Even when ammoniated, practical shelf life is typically months, not years, creating additional time-dependent degradation and performance variability.

An ideal preservative for NRL, therefore, has a clear technical job description. It must inhibit microbial growth strongly enough to prevent acidification and putrefaction; it must maintain colloidal stability by increasing surface charge and electrokinetic potential while supporting steric hydration at the particle interface; it must control trace multivalent ions through sequestration or precipitation because these ions can reduce stability and also support microbial activity. It must also be non-volatile, low-toxicity, and easy to handle; avoid discoloration and odor; minimize corrosion and effluent burden; remain compatible with established concentration and coagulation steps; and, critically, preserve the native protein–lipid interphase and molecular integrity that govern downstream mechanical performance and processing behavior.

Preservation-Aware Framework for Structure–Property Relations

NRL operational properties like viscosity, yield stress, thixotropy, and molecular weight are governed by particle-scale organization and interparticle interactions mediated by the protein–lipid interphase. Because direct imaging of concentrated latex is limited, rheology is the practical proxy for microstructure. Experimental techniques like flow sweeps and oscillatory measurements allow inference of aggregation, network formation, and crowding as the solids content increases. The problem is that existing structure–rheology frameworks are not preservation-aware. Most models and calibration datasets implicitly assume ammoniated Hevea latex or synthetic analogs, creating a foundational bias toward a material standard that is increasingly misaligned with emerging needs like ammonia-free systems, alternative crops, and tighter environmental constraints. Switching preservative systems can change surface charge density, hydration layers, protein conformation, and even molecular integrity—it introduces a domain shift that causes "foreign" rheology and unstable processing that current models cannot reliably predict. For example, the distinct particle-size distributions observed in alternative species, such as Guayule (0.44–2 μm) and Dandelion (0.35 μm), which differ significantly from those of Hevea and interface chemistries, further challenge assumptions embedded in Hevea-centric models. Standardizing these metrics will facilitate comparative studies and enable the development of generalized models to predict how specific preservation chemistries affect maximum packing fraction and viscosity. This approach shifts the industry from trial-and-error formulations to a scientifically grounded screening process for biodiverse and sustainable rubber supply chains.

1.6 Research Objectives and Scope

Primary Objectives

Natural rubber latex is mainly processed in ammonia-preserved systems, but there is a shift toward safer, low- or zero-ammonia methods. This transition alters the latex's behavior, as preservation chemistry affects particle interfaces and network formation. Currently, we lack a unified framework to connect structure, rheology, and processability across different preservation conditions. This results in reliance on trial and error in engineering decisions and underutilization of advanced manufacturing methods. To tackle these issues, this thesis aims to develop preservation strategies that improve shelf stability without volatile stabilizers while minimizing toxicity. Additionally, create a benchmarking framework linking measurable latex attributes to its processability across various sources and preservation systems.

Research Scope

This thesis builds a preservation-aware framework that links measurable microstructure and chemistry to rheology and manufacturability, then uses that understanding to enable sustainable processing routes, including photocurable latex systems for additive manufacturing.

Aim 1: Map how preservation chemistry reshapes flow and microstructure

Aim 2: Identify preservation-dependent chemical and dynamical signatures using high-sensitivity NMR

Aim 3: Translate preserved latex into manufacturable, photocurable feedstocks for additive manufacturing

1.7 Thesis Organization

Chapter 1 (this chapter) introduces the background on biopolymers, circular economy concepts, natural rubber latex fundamentals, and the research objectives.

Chapter 2 presents a comprehensive literature review covering molecular structure and colloidal stabilization of NRL, suspension rheology and theoretical models, and additive manufacturing of elastomers.

Chapter 3 describes the research methodology, including materials sourcing, rheological characterization protocols, NMR spectroscopy methods, and photoresin formulation and testing procedures.

2.1 Molecular Structure and Colloidal Stabilization

Elastomers are long-chain viscoelastic polymers with low cross-linking density. Because of weak intermolecular interactions, polymer chains elongate significantly, up to 10 times their original length, when under load and return to their original form when the load is released. Compared to other polymers, elastomers are highly elastic. Amorphous polymers lack a long-range ordered structure, with molecular chains arranged randomly and without crystalline regions. These polymers are commonly used in applications requiring rigidity, transparency, and ease of processing; examples include polystyrene, polymethyl methacrylate, and polycarbonate.

In contrast, semicrystalline polymers contain both amorphous and crystalline regions, with tightly packed, ordered chains and randomly arranged regions. This dual structure gives semi-crystalline polymers a combination of rigidity and toughness, with common examples including polyethylene, polypropylene, and polyamide. Semi-crystalline polymers restrict the movement of molecular chains, resulting in less pronounced viscoelastic effects than amorphous polymers. The crystalline regions provide stability, leading to lower creep and relaxation at room temperature. In contrast, amorphous polymers often exhibit pronounced creep and relaxation due to the mobility of their molecular chains. The viscoelastic response of elastomers depends strongly on the degree of crosslinking and on the temperature relative to their glass transition temperature.

Elastomers can be classified into two categories based on cross-linking: chemically cross-linked (thermoset elastomers) and physically cross-linked (thermoplastic elastomer) . These materials are characterized by their unique mechanical properties, such as hardness, tensile strength, toughness, and strain stress source flexibility, demonstrating hyper-elasticity with substantial recoverable strain under low-stress conditions . Elastomers include natural rubber, silicone rubber, and synthetic organic rubbers like styrene-butadiene rubber, nitrile rubber, and polyurethanes.

The stress-strain behavior of rubber has been further explained using theoretical models that account for its elastic properties. For example, the neo-Hookean model, derived from statistical mechanics, describes the stress-strain behavior of rubber at moderate strains by assuming an ideal elastomer with a network of cross-linked polymer chains, each behaving like a Gaussian chain, with elasticity driven by entropy. The Mooney-Rivlin model extends this by considering the second invariants of the deformation tensor, providing a strain energy function that better fits experimental data over a broader range of strains. Additionally, models that account for the limiting extensibility of polymer chains, such as the one with a strain energy function incorporating a constant related to the maximum possible extension of the network chains, are particularly useful for describing rubber's behavior at very high strains, where the neo-Hookean and Mooney-Rivlin models may fail.

In elastomers, elasticity is driven by thermodynamics, in which the restoring force during stretching is related to entropy changes rather than to internal energy. When rubber is stretched, polymer chains become more ordered, thereby decreasing entropy; upon stress release, they return to a disordered state, thereby increasing entropy. The free energy change during deformation links to the entropy change via the equation:

$$\Delta F = -T\Delta S \tag{2.1}$$

where T is temperature, ΔS is entropy, and ΔF (force) is proportional to the negative gradient of free energy with respect to deformation. A flexible polymer chain has many configurations; stretching reduces these, lowering entropy. The force to stretch the chain comes from molecular thermal motion, which seeks to maximize entropy. This explains rubber elasticity through conformational entropy changes but doesn't account for physical failure mechanisms such as bond rupture. However, a simulation study suggests that significant enthalpic chain stretching occurs before tensile failure.

2.2 Natural Rubber Latex

Natural rubber is a biopolymer known for its hyperelasticity, biocompatibility, and abundance in nature, occurring as a colloidal sol called *latex*, derived from the Greek meaning "drop" or "fluid." NRL, a milk-like substance primarily derived from the *Hevea brasiliensis* tree, is a unique lyophobic colloidal dispersion of polymers that occur naturally as a metabolic product in certain plants . These plants are cultivated extensively in tropical regions in a climate of about 26°C with an average annual rainfall of 200 cm and less than 15° away from the equator. These materials have been applied in dipping with products such as balloons, gloves, condoms, and other products, such as memory foam and adhesives for centers .

NRL is synthesized via a conserved isoprenoid pathway that also produces dolichols, polyprenols, and quinones . The process begins with the formation of isopentenyl pyrophosphate and dimethylallyl pyrophosphate through either the mevalonate or methylerythritol phosphate pathway. These C_5 units are polymerized in four phases, with *trans*-prenyltransferases (*trans*-prenyltransferase (tPT)) in Phase 2 generating short all-*trans* primers (C_{10}–C_{20}). The subsequent elongation, catalyzed by *cis*-prenyltransferases (*cis*-prenyltransferase (cPT)), introduces *cis*-double bonds, forming NR's characteristic *cis*-1,4-polyisoprene backbone. However, trace *trans*-units persist at the ω-terminus due to the initial primer. This enzymatic selectivity also allows mixed configuration polyisoprenoids (dolichols) to coexist within the rubber particle lattice, influencing surface properties.

The primary source of NRL is *Hevea brasiliensis*, which contains rubber particles (rubber particle) ranging from 0.08 to 2 μm in diameter . Alternative rubber-producing plants, including Guayule (*Parthenium argentatum*), are being explored, which produce rubber particles with uniform size (~0.5 μm) . Russian dandelion (*Taraxacum koksaghyz*) yields smaller rubber particles (~0.35 μm) with a unimodal distribution . *Ficus* species (*F. benghalensis*, *F. elastica*) generate larger rubber particles (1.6–6.0 μm) but with comparable polymer quality . NRL is collected through the process called tapping, which involves an incision in the trunk.

Ammonia remains the most effective preservative, stabilizing rubber particles through electrostatic repulsion while inhibiting microbial growth . However, it's a double-edged sword; for starters, ammonia production requires extensive resources, making it highly volatile. For example, OSHA limits exposure to 50 ppm over an 8-hour shift, it is highly flammable at high concentrations, and challenging to dispose of wastewater. Its production, which relies on the energy-intensive Haber-Bosch process, makes it a significant energy consumer and a prominent emitter of greenhouse gases, accounting for 1.2% of global anthropogenic CO_2 emissions (approximately 1.8 tons of CO_2 per ton of ammonia) .

Alternative Preservation Systems

These limitations have spurred the development of alternative preservation systems, including low-ammonia combinations (0.1–0.3% with secondary stabilizers), completely ammonia-free options using zinc complexes or bio-based antimicrobials, and surfactants .

For example, chitosan-based systems, often derived from crustacean shells, provide antimicrobial protection but require low molecular weights and surfactants to prevent the destabilization of latex particles . HTT (a sym-triazine derivative) effectively preserves latex for months without the toxicity of ammonia, while improving mechanical properties such as tear strength . Pasteurization (60°C, 15 minutes) with pH adjustment provides short-term microbial control but increases viscosity and is ineffective for pre-spoiled latex . A newer, proprietary system supplied by AFLatex Technology LDA eliminates the use of ammonia while maintaining colloidal stability . Advantages include lower toxicity and greater environmental friendliness, as well as improved properties such as molecular weight, mechanical strength, and critical volume fraction. Another system is ethoxylated tridecyl alcohol and hydrofluoric acid (HF). ethoxylated tridecyl alcohol stabilizes latex particles, while HF reacts with glutathione to form glutathione, an antimicrobial compound .

2.3 The Theory of Natural Rubber Latex

Tanaka and Sakdapipanich's innovative framework presents a compelling solution to the question of what natural rubber (NR) is, revealing its distinct behavior as a partially crosslinked material compared to a simple *cis*-1,4-polyisoprene polymer. This observation is supported by the presence of a gel fraction, long-chain branching signatures, and storage hardening phenomena, which they posit as emergent properties arising from non-rubber functionalities rather than from the polyisoprene backbone alone. These frameworks are only valid for high-ammonia latex and coagulated latex. Furthermore, methods used include deproteinization to remove proteins, the addition of a polar cosolvent to disrupt weak associations, and targeted cleavage of chemical linkages via transesterification/saponification and enzymatic digestion. A key aspect of their investigation is the subsequent monitoring of gel content, molecular weight, and branching metrics. The pronounced increase in gel content observed with ammonia aging, along with the differential impact of various "handles" like deproteinization versus transesterification on network structure, provides compelling evidence for a dual-mechanism model.

This model suggests two distinct sets of crosslinking points, one predominantly influenced by protein hydrogen bonding and the other associated with phospholipids. The testable hypothesis that leads to these conclusions is as follows: NR chains possess a nitrogenous functional group at one terminal end, often linked to oligopeptide-like characteristics, which is not merely a consequence of protein contamination but rather a chemically integrated component of the rubber structure. To validate this hypothesis, NR samples can undergo enzymatic deproteinization and purification, followed by quantitative analysis of residual nitrogen and comparison of their vibrational signatures with established peptide models. Preliminary evidence is based on the persistent nitrogen content in deproteinized natural rubber after deproteinization, as shown by Fourier transform infrared spectroscopy and Nuclear Magnetic Resonance (NMR) analysis, which underscores the retention of nitrogen-containing functionalities that may facilitate hydrogen bonding with proteins in the latex environment.

The second postulate is that the opposing terminal is proposed to house phospholipid-derived functionalities, including phosphate and ester motifs, acting as a branching or gel "node." This hypothesis entails breaking down ester-linked motifs via transesterification/saponification and specifically targeting linkages using lipases and phosphatases. Evidence gathered from these experiments demonstrates that transesterification significantly lowers gel content and eliminates phosphorus signals, suggesting a phospholipid-related contribution to the network structure. Furthermore, enzymatic cleavage experiments reveal reductions in molecular weight metrics and other relevant parameters, implicating the critical role of phospholipid-associated end groups in the branching mechanism, often conceptualized as micelle-like aggregation or polar headgroup interactions.

The final hypothesis aims to delineate the specific phospholipid segment responsible for branching by employing phospholipases with varying cleavage selectivity. The experimental findings reveal marked reductions in molecular weight and intrinsic viscosity upon treatment of deproteinized natural rubber with phospholipases A2, B, and C, whereas phospholipase D elicited minimal changes despite reduced ester content. This evidence indicates that the choline headgroup is not the principal determinant of branch-point formation, suggesting that hydrophobic fatty-acid groups and phosphate-associated interactions at the phospholipid-linked chain end primarily govern branching behavior.

Structure-Process-Property of Natural Rubber Latex

According to documents from 2013 to 2020, the understanding of the structure–process–property relationship in uncured natural rubber remains complex, characterized by conflicting interpretations. Microscopy and colloid science predominantly suggest the presence of a particle "corona," a protein and lipid-rich interfacial shell. The bulk mechanical properties, rheological behavior, and crystallization kinetics of coagulated rubber are consistent with a model involving a pseudo-end-linked network, often associated with Tanaka and Sakdapipanich's chain-end association hypothesis. Consequently, literature delineates a dialectic between two perspectives, a spatially organized interfacial architecture in the latex state and network-like constraints inferred from solid-state or post-coagulation responses.

In the latex (colloidal) state, the "corona" picture is supported by both composition and particle-population evidence. Zhou et al. super-resolution fluorescence imaging directly visualizes proteins and lipids as segregated, coexisting phases around the particle ensemble. Proteins appear discontinuous and preferentially outside large rubber particles, while lipids localize within the large rubber particle; the same work gives representative overall contents of ~2 wt% proteins and ~3 wt% lipids in NR latex. Upon drying, the observed reorganization into protein-rich domains on the order of ~200–300 nm, with lipid-rich structures reported as <100 nm around the larger protein domains, therefore, the interfacial material doesn't vanish after heating and it phase-separates.

The literature indicates that latex rubber particles are typically around 0.4 μm in size and explicitly quantifies the non-rubber content via nitrogen analysis. Singh's et al. For example, concentrated latexes with Dry Rubber Content (DRC) of 76.9 wt% and 61.9 wt% were analyzed under high-ammonia (~0.7 wt%) and low-ammonia (~0.2 wt%) preservation conditions. A centrifuged latex rubber fraction contains approximately 0.23 wt% nitrogen (N), while high-ammonia concentrated latex and fresh latex exhibit nitrogen levels of about 0.52 wt% and 0.56 wt% N, respectively. Additionally, Sriring et al. explore complementary film-formation mechanics, noting that an increase in the small rubber particle fraction (less than 0.2 μm) results in greater viscosity, with dried films displaying a characteristic stress plateau around 0.4–0.5 MPa at approximately 40–50% strain. They also identify an "optimum" small rubber particle fraction range of about 10–30% that maximizes the strength of their dried films, aligning with a packing role for the small-particle population rather than a uniform crosslinked chemistry.

However, post-coagulation measurements start acting like there are "network points," not just a squishy shell. Xu et al. report a stress-relaxation signature that is difficult to reproduce with linear polyisoprene alone at long times. NR retains an equilibrium stress ~58% of its initial value, whereas deproteinization reduces it by ~75%, and transesterification essentially drives the relaxation to zero, which the authors interpret as branching association points linked to non-rubber chemistry. Zhou et al. frame the same idea structurally as a "nanomatrix": they describe phase-separated domains of non-rubber components and report that a "serum rubber" fraction exhibits an elastic modulus (G') about an order of magnitude higher than deproteinized natural rubber, again pointing to a mechanically active, non-rubber-mediated constraint system.

The strain-induced crystallization as a function of temperature increasingly supports the "network" interpretation for coagulated dry rubber. Toki et al. interpret this phenomenon as indicating that NR contains a pseudo end-linked network that transforms ordinary entanglements into effectively permanent pivots under deformation, resulting in both a stress upturn and strain-induced crystallization at room temperature. Huang et al. quantitatively reinforce this concept through NMR-based constraint analysis, reporting a terminal-to-terminal molecular weight between α and ω terminals of approximately $2.0–3.4 \times 10^5$ g/mol. They also demonstrate that the network chain density inferred from stress–strain data can be around ten times higher than what would be expected based solely on terminal spacing, arguing that the combination of terminals and their interactions alongside entanglements serves as constraints in unvulcanized NR.

Finally, vulcanization kinetics introduces a "chemical reactivity" perspective to this discussion. Wei et al. specifically categorize NR as approximately 94% rubber and around 6% Non-Rubber Components (NRC), demonstrating that the removal of NRC alters curing behavior: the vulcanization temperature rises and the activation barrier increases (they argue that NRC reduces the activation energy). Additionally, the characteristic vulcanization time (t_{90}) lengthens from about 10 minutes to approximately 30 minutes following NRC removal. They also report a subtle shift in the tan δ peak within the glass transition region (T_g), noting a change in T_g from roughly -40.4°C to -41.2°C with NRC removal. Although small in magnitude, this shift is directionally consistent with modifications in interfacial and plasticization chemistry.

The current state of knowledge is coherent at a local level but has not yet achieved a unified global understanding. (1) In latex, proteins and lipids exhibit a measurable, spatially organized interfacial phase that can separate into domains approximately 100–300 nm in size upon drying. (2) In coagulated rubber, mechanical relaxation, the onset of strain-induced crystallization, and constraints derived from NMR behave as though there are network-like points that survive processing, acting like end-linked anchors. The unresolved issue and a legitimate focus for your later chapter is whether the "gel/network" signatures are indicative of an intrinsic, persistent connectivity inherent in the native latex, or a connectivity that emerges and solidifies during destabilization, drying, and film consolidation. Is the network a knot, or merely a collapsed corona that becomes jammed into a knot when the phase is altered?

2.4 Colloids

Colloids are particles that range from micrometers to nanometers in size and must behave according to classical physics. They are suspended in a solvent without sedimenting, and, in a dilute solution, the solvent induces random motion (thermal motion) known as Brownian motion. The particles in a fluid experience an effective weight that accounts for the gravitational force (g) acting downward, and an upward buoyancy force from the displaced solvent. The net body force is therefore conservative and can be written via gravitational potential energy (U_g) with an upward displacement z:

$$U_g(z) = \Delta\rho\, V g\, z \tag{2.2}$$

where ρ_p is the density of the particle, ρ_m the density of the fluid, and V the volume of the fluid.

Thermal motion, which is solvent-particle interaction, supplies an energy scale of the Boltzmann constant multiplied by absolute temperature ($k_B T$), which sets the characteristic height over which gravity significantly biases particle positions. Defining the gravitational length (l_g):

$$l_g = \frac{k_B T}{\Delta\rho\, V g} \tag{2.3}$$

if the particle size is comparable to or larger than the thermal motion, it can counteract sedimentation. Brownian motion, however, depends on the viscosity and particle size, and the effective volume the particle takes, and is captured by the mean-squared displacement over time t in dimensions d:

$$\sqrt{\langle \Delta r^2 \rangle} = \sqrt{2dDt}, \quad \text{where} \quad D = \frac{k_B T}{6\pi\eta a} \tag{2.4}$$

where D is the Stokes–Einstein diffusivity, η is the solvent viscosity, and a is the particle radius. The particle-particle interactions, however, are the main drivers of sedimentation prediction.

DLVO Theory

The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory identifies two primary interactions of the particles; the van der Waals attraction and the electrostatic repulsion. The stability is determined by the interplay between thermal energy and the pair potential. The total interaction free energy between two particles, each with a radius at a certain surface-to-surface gap, is expressed in terms of their combined interaction free energy $(U_{tot}(h))$:

$$U_{tot}(h) = U_{vdW}(h) + U_{EDL}(h) \tag{2.5}$$

where U_{vdW} is the van der Waals interaction and U_{EDL} is the electrostatic interaction. The dispersion is largely controlled by whether the repulsive barrier satisfies the metastable dispersion criteria $U_{max} \gg k_B T$ or total interactions is less than thermal motion $U_{max} \lesssim k_B T$ rapid aggregation. A common "engineering" threshold is $U_{max} \gtrsim 10\, k_B T$ for practical stability.

When the particle surface is charged, characterized by a known surface charge density σ or surface potential ψ_0, particles form an electrical double layer. In an electrolyte, Coulomb interactions are screened, and within the linear Debye–Hückel approximation, the potential surrounding a particle decays exponentially with distance, implying that the repulsion has a finite range. According to $e^{-\kappa r}/r$, where κ is the inverse Debye length. The Debye length is $\lambda_D = 1/\kappa$, with:

$$\kappa^2 = \frac{2e^2 N_A I}{\varepsilon_m \varepsilon_0 k_B T} \tag{2.6}$$

for a symmetric 1:1 electrolyte, where I is the ionic strength (mol/L), ε_m is the medium dielectric constant, e the elementary charge, and N_A Avogadro's number. An increase in ionic strength I correlates with a larger κ and consequently a shorter-ranged repulsion.

The strength (amplitude) of the repulsion is mainly controlled by the effective surface potential often represented experimentally by the zeta potential ζ; a widely used DLVO form is:

$$U_{EDL}(h) \approx \frac{64\pi a\, n_\infty k_B T}{\kappa} \tanh^2\left(\frac{e\zeta}{4k_B T}\right) e^{-\kappa h} \tag{2.7}$$

where n_∞ is the bulk number concentration of ions. The amplitude is set by the effective surface potential (or effective charge), while the range is set by Debye length λ_D.

Even if particles were uncharged, they still attract each other through van der Waals forces, which come from fluctuating and induced dipoles. This attraction is essentially always present and becomes very strong at very small gaps. In DLVO theory, its overall strength is packaged into the Hamaker constant. The Hamaker constant depends on the dielectric/optical contrast between the particle and the medium, so changing the solvent can strengthen or weaken the attraction (e.g., by better "matching" the particle's optical properties). In the context of DLVO theory, it's represented by a Hamaker constant A, leading to the expression for two equal spheres at small separations $h \ll a$, under the Derjaguin approximation:

$$U_{\mathrm{vdW}}(h) \approx -\frac{A\,a}{12h} \tag{2.8}$$

The attraction intensifies sharply at small separations, so once particles cross the repulsive barrier, they can fall into a deep primary minimum, which is often effectively irreversible without significant steric or electrostatic rescue mechanisms.

Crucially, A is not just a "material constant of the particle" but it depends on the particle–medium–particle dielectric contrast. A common combining estimate is:

$$A_{131} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)^2 \tag{2.9}$$

for identical particles (material 1) across medium 3. Therefore, changing the solvent (medium), you can weaken or strengthen van der Waals attraction via optical/dielectric matching.

Beyond DLVO: Steric, Depletion, and Hydration Forces

In practice, colloidal systems often combine DLVO and VESPER forces. Beyond DLVO, steric forces arise when adsorbed polymeric or surfactant chains overlap. Consider two particles each coated with a layer of thickness L of grafted or adsorbed polymers (or surfactant tails). When the separation $h < 2L$, chains are compressed. Alexander–de Gennes brush theory gives a steric free-energy cost on overlap: one finds roughly:

$$U_{\mathrm{steric}}(h) \sim k_B T \left(\frac{2L - h}{L}\right)^m \tag{2.10}$$

(a rapidly rising repulsion as $h \to 0$), or in more detailed treatments, a polynomial in $(L - h)$.

Physically, two contributions oppose overlap:

(i) **Entropic mixing penalty**: overlapping chains lose conformational entropy (fewer configurations), and

(ii) **Osmotic/elastic pressure**: monomer density increases, generating an osmotic pressure that pushes surfaces apart.

The magnitude depends on grafting density and chain length: densely packed short chains give steep repulsion at small h, while long dilute chains produce softer, longer-range steric barriers. Steric forces stabilize colloids even in high salt, unlike DLVO predictions, as they are largely unaffected by ionic strength.

Depletion forces are entropic attractions caused by non-adsorbing solutes (small particles, micelles, polymers) in the medium. When two large particles approach within a distance $< 2R_d$ (radius of depletant), the excluded volumes overlap, and free volume for the small species increases. This increases entropy and creates an effective osmotic pressure that pushes the large particles together. The Asakura–Oosawa model quantifies this: for two parallel plates and a depletant radius R_d:

$$U_{depl}(h) \approx -\Pi\,(2R_d - h), \quad (0 < h < 2R_d) \tag{2.11}$$

where $\Pi = k_B T c_d$ is the osmotic pressure of the depletant concentration c_d. In sphere–sphere geometry, one obtains a smoothly varying attraction of similar range $\sim 2R_d$. In colloids with surfactant, free micelles or polymer chains act as depletants.

Surfactants also influence colloidal interactions via interfacial and hydration effects. Because of their amphiphilic nature, surfactants lower the interfacial tension between particles and the solvent, thereby kinetically stabilizing dispersions by reducing the thermodynamic driving force for aggregation. Moreover, many hydrophilic headgroups strongly bind water hydration layers. When two hydrated surfaces approach, ordered water must be displaced, creating a short-range repulsive hydration force. This exponential force typical decay length < 1 nm is an additional VESPER repulsion not present in DLVO. For instance, ethylene-oxide chains form extensive hydration shells; overlapping these chains' water layers yields a steep repulsion. Osmotic forces also arise from trapped counterions or confined water between surfactant heads overlapping double layers lead to an osmotic pressure pushing surfaces apart; a known aspect of DLVO electroneutrality, but here surfactant-structured EDL can amplify osmotic repulsion.

Colloid Stability and Modeling

Oil-in-water emulsions stabilized by surfactants or proteins demonstrate all stability regimes. In the case of electrostatically stabilized emulsions, where an ionic surfactant forms a monolayer on the droplets, the behavior often aligns with DLVO theory: the droplet ζ potential is correlated with stability. Conversely, emulsions stabilized by steric layers, such as milk proteins that create multilayers, depend on VESPER forces. Tcholakova et al. identified three distinct regimes for protein-coated oil droplets: (1) DLVO (electrostatically stabilized monolayer), (2) steric (multilayer adsorption), and (3) steric (single layer). In regimes (2) and (3), classical DLVO theory becomes inadequate; instead, models that incorporate steric repulsion are necessary.

Advanced modeling techniques help bridge insights from DLVO and VESPER theories. Continuum simulations solve the Poisson–Boltzmann equations or, more generally, density functional theory equations to evaluate ionic distributions around complex surfaces, including surfactant layers. For instance, using numerical Poisson-Boltzmann methods with a polymer brush boundary leads to modified repulsion that aligns more closely with experimental force curves than traditional linear DLVO models. Furthermore, Monte Carlo and molecular dynamics simulations, whether coarse-grained or atomistic, effectively capture steric and hydration effects. Liu et al. on MD simulations of surfactant-coated interfaces reveals exponential hydration repulsion originating from head-groups and quantifies the osmotic pressure of overlapping layers. Coarse-grained simulations of colloids, along with explicit depletant particles, successfully replicate the Asakura–Oosawa depletion potential, enabling predictions of flocculation thresholds.

Payungwong et al. investigated the long-term stability of ammonia-preserved natural rubber (NR) latex, noting that proteins on the latex particle surfaces hydrolyzed slowly in the presence of ammonia, thereby forming additional anionic groups. Latex with high ammonia preservation exhibited increased stability over months, as its ζ-potential stabilized around -50 mV. In contrast, low-ammonia latex, which had a significantly lower ζ-potential, demonstrated markedly inferior stability. The authors emphasized that the stability of NR latex particles is largely governed by their surface charge (or potential); the greater the negative charge, the more stable the latex. Shikawa et al. (2005) assessed pharmaceutical polymer latexes, specifically Eudragit dispersions, by measuring their zeta potentials and applying DLVO theory calculations. Their findings indicated that variations in pH or salt concentration altered the total interaction energy barrier between particles, directly correlating with observed changes in stability. For both anionic and cationic latex dispersions, the patterns of stability, whether the latex remained colloidally stable or began to flocculate, could be explained by shifts in the DLVO interaction energy curves.

In a separate study, Vera et al. determined the critical coagulation concentration of salt necessary to induce flocculation at varying pH levels.

At pH 4, where the latex possessed less surface charge, it coagulated with approximately 70 mM KCl. Conversely, at pH 6, with greater ionization of acidic groups and a higher zeta potential, over 150 mM KCl was required to trigger coagulation. Soto et al. (2006) developed latex pressure-sensitive adhesives from a vinyl acetate/n-butyl acrylate blend. By incorporating a small amount of acrylic acid as a comonomer, they introduced carboxylate groups onto the particle surfaces. This minor increase in surface charge significantly enhanced adhesive performance: coatings containing 1 wt% acrylic acid (and therefore more negatively charged particles) exhibited markedly improved tack and 180° peel strength compared to similar latex formulations without acrylic acid.

2.5 Suspensions Rheology and Theoretical Models

At the continuum level, viscosity quantifies how mechanical force is dissipated into heat as neighboring fluid elements slide past one another. Mathematically, viscosity links the stress tensor $\boldsymbol{\sigma}$ (force per unit area) to the rate-of-strain tensor $\dot{\boldsymbol{\gamma}}$ (velocity gradients). For a simple shear flow, this reduces to a scalar relation between shear stress τ and shear rate $\dot{\gamma}$:

$$\tau = \eta \, \dot{\gamma} \tag{2.12}$$

where η is the shear viscosity. In colloidal suspensions, solid particles disrupt the flow field, deflect it around them, and squeeze the solvent through narrow gaps. This enhances viscous dissipation relative to the pure solvent. It is therefore convenient to compare the suspension viscosity η to the viscosity of the suspending medium η_s through the relative viscosity:

$$\eta_r = \frac{\eta}{\eta_s} \tag{2.13}$$

The rheology of colloids is set by a competition between three contributions:

(i) thermal (Brownian) forces, which try to maintain an isotropic, equilibrium microstructure;

(ii) hydrodynamic interactions, which represent viscous dissipation as the solvent flows around and between particles; and

(iii) interparticle forces, which can stabilize dispersions such as repulsion, steric layers or promote aggregation and gelation.

Microscopically, that particle contribution comes from a particle stress tensor $\boldsymbol{\sigma}_p$, which can be split into three pieces:

$$\boldsymbol{\sigma}_p = \boldsymbol{\sigma}^H + \boldsymbol{\sigma}^B + \boldsymbol{\sigma}^{int} \tag{2.14}$$

where $\boldsymbol{\sigma}^H$ is hydrodynamic stress, $\boldsymbol{\sigma}^B$ is Brownian (thermal) stress, and $\boldsymbol{\sigma}^{int}$ is additional stress from interparticle forces (electrostatic, steric, attractive, etc.).

Correspondingly, excess viscosity can be decomposed as:

$$\eta_r - 1 = \eta_r^H + \eta_r^B + \eta_r^{int} \tag{2.15}$$

with each term obtained from the corresponding stress contribution in simulation or theory.

Brownian Motion and Péclet Number

Brownian motion provides the intrinsic structural relaxation scale. A characteristic Brownian time for a particle to diffuse over its own radius is then:

$$\tau_B \sim \frac{a^2}{D_0} \tag{2.16}$$

Comparing this relaxation time to an imposed shear rate $\dot{\gamma}$ defines the Péclet number:

$$\mathrm{Pe} = \dot{\gamma}\,\tau_B \tag{2.17}$$

When $\mathrm{Pe} \ll 1$, Brownian motion reorganizes the microstructure faster than the flow deforms it, and the suspension behaves close to equilibrium with a weak rate-dependence. When $\mathrm{Pe} \gtrsim 1$, flow distorts the microstructure faster than Brownian relaxation, and the viscosity becomes strongly rate-dependent.

An equivalent stress-based scaling introduces a thermal stress scale:

$$\sigma_T \sim \frac{k_B T}{a^3} \tag{2.18}$$

which represents the entropic stress associated with Brownian structuring. The dimensionless stress $\sigma^* = \sigma/\sigma_T$ indicates when applied stress competes with or overwhelms thermal forces. As $\dot{\gamma}$ or σ increases toward $\mathrm{Pe} \sim 1$, many colloidal suspensions exhibit shear thinning: flow biases particle trajectories, reduces the frequency of rearrangements, and lowers the effective viscosity from a low-shear plateau η_0 toward a high-shear plateau η_∞.

Rheology of Concentrated Latex

Even in the absence of attractions, increasing the particle volume fraction ϕ strongly increases viscosity because particle motion becomes constrained by neighbors ("caging"). This yields a low-shear Newtonian plateau $\eta_0(\phi)$ that grows rapidly with ϕ, and at sufficiently high concentration, the structural relaxation time becomes very long. On experimental time scales, this appears as solid-like viscoelasticity and an apparent yield stress. Mode-coupling theory and experiments on nearly hard-sphere colloids (e.g., Siebenbürger et al.) show:

$$\eta_r^B(\phi) \propto \left(1 - \frac{\phi}{\phi_g}\right)^{-\alpha}, \quad \alpha \approx 2.4\text{–}2.5 \tag{2.19}$$

capturing the divergence of zero-shear viscosity and the onset of solid-like behavior.

In dynamic tests, Brownian stresses show up as the low-frequency part of the viscoelastic spectrum:

- High frequencies ($\omega\tau_B \gg 1$): structure is "frozen," response dominated by short-time hydrodynamics.
- Low frequencies ($\omega\tau_B \ll 1$): Brownian relaxation allows the microstructure to remodel, giving viscoelastic moduli consistent with a Brownian liquid or glass.

Hydrodynamic interactions come from the flow of the solvent around particles. Even with no Brownian motion and no long-range forces (pure non-Brownian hard spheres), forcing the fluid through a crowded bed of particles is dissipative.

Predictive Viscosity Models

In the dilute limit of rigid spheres, Einstein's classic result is:

$$\eta_r = 1 + [\eta]\phi + O(\phi^2) \tag{2.20}$$

with intrinsic viscosity $[\eta] = 2.5$ for perfect spheres. As the particle volume fraction ϕ increases, multi-body hydrodynamic interactions become strong, and the hydrodynamic component of viscosity grows rapidly. Correlations and simulations for non-Brownian suspensions often take a divergence form like:

$$\eta_r^H(\phi) \sim \left(1 - \frac{\phi}{\phi_m^H}\right)^{-\beta} \tag{2.21}$$

where ϕ_m^H is an effective maximum packing for the hydrodynamic contribution, and β is an exponent of order 1–2, depending on the fit and model.

Numerical Stokesian-dynamics calculations allow you to separate the hydrodynamic and Brownian contributions by computing $\boldsymbol{\sigma}^H$ and $\boldsymbol{\sigma}^B$ directly. At low ϕ, the hydrodynamic part dominates η_r. As ϕ approaches the glass transition, the Brownian/caging part becomes dominant, and the total viscosity tracks the mode-coupling scaling. Experimentally, to estimate the contribution of viscosity by the hydrodynamic effect (η_r^H) is via the high frequency of oscillatory tests. The high-frequency of $G''(\omega)/\omega$ gives a high-frequency viscosity η_∞ that is almost entirely hydrodynamic. The difference $\eta_0 - \eta_\infty$ then isolates the Brownian and interaction contribution at low shear. At very high shear rates (large Pe), short-range lubrication hydrodynamics dominate. Particles are forced into near-contact "hydroclusters," and the hydrodynamic contribution blows up, producing shear thickening.

Effective Volume Fraction and Network Formation

Interparticle forces primarily modify viscosity by changing the equilibrium microstructure, often in a way that can be mapped to an effective volume fraction. Repulsive stabilization or steric layers make each particle "bigger" to flow. The physical radius by a and the range of the stabilizing layer by δ (the Debye length is defined):

$$\phi_{\text{eff}} = \phi \left(1 + \frac{\delta}{a}\right)^3 \tag{2.22}$$

When you plot zero-shear viscosity η_0 vs ϕ_{eff} instead of ϕ, data for many electrostatically or sterically stabilized systems collapse onto the hard-sphere master curve for the Brownian viscosity. Increasing salt shrinks the double layer (reduces δ), so ϕ_{eff} drops and the viscosity collapses towards the hard-sphere curve. Different brush thicknesses and particle sizes all fall on one master $\eta_r(\phi_{\text{eff}})$ curve spanning ~6 orders of magnitude in viscosity.

When attractions dominate, the microstructure shifts from crowded cages to flocculated networks, driven by short-range van der Waals attraction and longer-range electrostatic repulsion. A deep primary minimum leads to irreversible aggregation; a shallow secondary minimum leads to reversible flocculation. Beyond a certain strength and range of attraction, you cross a gel line in the phase diagram where percolated networks form that carry stress even at rest, giving rise to yield stress, strong elasticity, and thixotropy. In this regime, interparticle forces are no longer just an effective hard-sphere enlargement; they represent load-bearing contacts and network strands. Mode-coupling and gel theories must then be used alongside hard-sphere scaling.

2.6 Additive Manufacturing

AM, or 3D printing, refers to a family of processes that fabricate parts by adding material, usually layer by layer, from a digital model. This distinguishes AM from subtractive manufacturing (such as milling and drilling) and tooling-driven formative routes that rely on molds. AM was initially adopted for rapid prototyping, but it is now widely integrated into manufacturing workflows, particularly for low-volume production, where avoiding molds and secondary machining offers significant advantages. The layer wise approach reduces material waste and enables geometric complexity and rapid design validation, but it also introduces process-specific limitations that continue to motivate research and development.

The historical development of AM dates to early concepts in the 1950s–1960s, with practical acceleration in the early 1980s as enabling technologies (computers, lasers, and motion control) matured. A key milestone occurred in 1984 with parallel patents in Japan, France, and the United States describing layer-by-layer fabrication of 3D objects. Commercialization expanded through the late 1980s and 1990s with multiple process families, including laminated object manufacturing, SGC, and selective laser sintering in 1986, followed by patents for fused deposition modeling and the MIT-originated 3DP concept in 1989. Droplet-based deposition approaches were developed in the 1990s, and ink-jet systems capable of printing photocurable resins in droplet form were reported by 2001, illustrating the widening range of AM architectures built around the generally layer-wise manufacturing principle .

Within AM, Vat Photopolymerization (VPP) is particularly central to this thesis because it uses photopolymer materials to cure a liquid resin into solid layers with high feature fidelity. In the AM materials landscape, photopolymers have dominated the market for over 30 years , consistent with the sustained industrial relevance of VPP and the continued research aimed at expanding printable material sets and improving performance. As reported in the Wohlers report, AM consistently shows growth, with fused deposition modeling achieving ~155% growth from 2015 to 2020, while VPP remains a major materials-driven segment due to its reliance on photopolymer resin systems . These trends motivate why AM research increasingly focuses on overcoming limitations that prevent broader adoption in mass manufacturing.

Elastomer processing highlights how AM challenges depend strongly on the AM process family. In VPP, resin viscosity is a primary constraint because printability and part quality must be balanced through formulation and curing control. In extrusion-based printing (fused deposition modeling/fused filament fabrication), elastomeric feedstocks stress interlayer and bed adhesion and introduce failure modes such as nozzle clogging, buckling, and premature gelation. Inkjet printing is limited by the high viscosity and viscoelastic behavior of elastomeric inks, which can cause nozzle clogging and nonuniform deposition. direct ink writing can be constrained by curing time and layer solidification, affecting structural integrity and print fidelity. This framing positions VPP as the most relevant platform for elastomer-focused discussion in the remainder of the chapter, consistent with the emphasis of the papers forming the basis of this dissertation.

2.7 Photoresins for Vat Photopolymerization

VPP (stereolithography/digital light processing and related processes) requires a liquid formulation that remains stable in the vat over printing timescales, recoats reproducibly, exhibits predictable light absorption for controllable cure depth, and polymerizes rapidly enough to preserve feature geometry while maintaining interlayer bonding. These requirements are coupled; increasing the cure rate or conversion can increase shrinkage and residual stress, while modifying optical attenuation to improve z-resolution can reduce cure depth and weaken layer-to-layer adhesion. For this reason, photoresins are formulated as multicomponent systems in which rheology, optical penetration, and polymerization kinetics are co-optimized rather than treated independently.

Photoresin Components

Most VPP photoresins can be classified into five ingredient classes: oligomers, reactive diluent monomers, photoinitiators, inhibitors, and performance additives.

Oligomers define the baseline mechanical response of the cured network, like rubbery versus glassy behavior, and strongly influence toughness, chemical resistance, and creep, but they often dominate viscosity and therefore constrain recoating.

Reactive diluent monomers reduce viscosity while co-polymerizing into the network; monomer functionality directly controls crosslink density, where mono-functional species generally lower crosslink density and favor elongation, while di- and tri-functional species increase crosslink density and modulus but also increase shrinkage stress and the likelihood of brittle behavior.

Photoinitiators convert absorbed photons into radicals or cations, affecting usable wavelengths and conversion efficiency. Type I initiators generate radicals quickly through cleavage, while Type II systems depend on co-initiators for hydrogen abstraction and are more sensitive to formulation and oxygen. Zhang et al. differentiate between these types in visible light photoinitiating systems, noting that Type I initiators cleave directly upon light absorption. The use of visible light allows for thicker composite samples due to better penetration and reduced scattering, enhancing safety for biological applications. However, Type II systems typically cure more slowly and are more oxygen-sensitive than Type I.

Inhibitors and antioxidants suppress premature polymerization during storage and printing, thereby improving stability and feature control; however, they increase the required exposure dose and can reduce interlayer conversion if overdosed.

Additives such as Ultraviolet (UV) absorbers, pigments, fillers, and plasticizers are used to alter durability, resolution, and defect propensity, but they also modify absorption and scattering, thereby shifting cure depth and polymerization rate.

Photopolymerization Mechanisms

The choice of polymerization pathways governs dominant process sensitivities.

Free-radical chain-growth systems, such as acrylates, are widely used for their fast kinetics and broad formulation flexibility, but they are sensitive to oxygen inhibition and can undergo volumetric shrinkage that generates stress, warpage, and residual monomer when exposure or post-cure is insufficient. Safranski et al. explore shape memory polymer networks created through the free radical polymerization of (meth)acrylates. The network structure is influenced by crosslinker density and side-group chemistry. These materials are used in biomedical devices like self-deploying stents, offering the shape memory effect, tunable glass transition temperatures and high toughness. Bulky side groups (e.g., phenyl) enhance toughness and modulus, but acrylates polymerize faster and typically yield lower strength and greater shrinkage than methacrylates. Lee et al. explored photoactivated bioprinting using Radical Chain-Growth and step-growth polymerization to create cell-laden hydrogels. Chain-growth employs photoinitiators to quickly add monomers like methacrylates, while step-growth involves the reaction of functional groups such as thiols and alkenes. Chain-growth hydrogels are fast to produce and versatile but can be affected by oxygen and create heterogeneous networks. Step-growth provides more uniform structures with less shrinkage stress but risks thiol oxidation over time.

Step-growth radical systems, such as thiol-ene and thiol-acrylate hybrids, are effective in reducing shrinkage stress and producing more uniform network structures. Additionally, they exhibit less sensitivity to oxygen compared to purely acrylate chain-growth systems; however, they often introduce extra formulation constraints and potential component interactions. Herzberger et al. explore the additive manufacturing of silicone elastomers through vat photopolymerization, emphasizing Thiol-Ene

"Click" chemistry and platinum-catalyzed hydrosilylation. The thiol-ene reaction employs a step-growth process utilizing thiyl radicals, while hydrosilylation introduces Si-H bonds to unsaturated bonds. These methodologies produce flexible elastomeric materials that are well-suited for applications in soft robotics and medical implants, offering tunable Shore hardness and thermal stability. A significant advantage of the thiol-ene system is its resistance to oxygen inhibition commonly observed in traditional acrylate printing, allowing for the development of low shrinkage stress networks. Nonetheless, challenges remain, including the high viscosity of silicone resins, which can impede printing, as well as the odor and limited shelf life associated with thiol monomers. Yu et al. present a comparison of two functionalized biomaterials: gelatin methacryloyl, which employs Free-Radical Chain Growth, and gelatin norbornene, which utilizes Thiol-Ene Click chemistry. gelatin methacryloyl, characterized by methacrylate groups, encounters issues with oxygen inhibition and variability, whereas gelatin norbornene facilitates the creation of uniform networks without these drawbacks, resulting in enzymatically degradable tissue scaffolds.

Cationic ring-opening systems, including epoxies and vinyl ethers, provide advantages such as reduced shrinkage, lower sensitivity to oxygen, and enhanced chemical resistance in epoxy networks. However, these systems typically exhibit slower reaction kinetics, higher viscosity, and increased sensitivity to contaminants. Ligon et al. explore Cationic and Hybrid Photopolymerization, employing Cationic Ring-Opening Polymerization for epoxides and combining it with radical acrylates to form interpenetrating polymer networks. In these cationic systems, a photoacid generator releases a proton upon irradiation, thereby opening epoxide rings. These advancements facilitate the creation of high-strength prototypes and dental aligners that exhibit superior mechanical strength and reduced shrinkage when compared to pure acrylates. Although cationic polymerization is resistant to oxygen inhibition and demonstrates low volumetric shrinkage, it is slower and highly sensitive to moisture. Mendes-Felipe et al. discuss Smart Materials and Nanocomposites developed through UV-Triggered Radical Polymerization, which incorporates functional fillers such as carbon nanotubes or graphene. This approach enables the creation of sensors and actuators that respond to external stimuli like heat or magnetic fields. The advantages include solvent-free, energy-efficient UV curing suitable for applications like 4D printing. Nevertheless, high loading of nanofillers can result in increased resin viscosity and light scattering, which may diminish cure depth and print resolution.

Light-Mediated Control of Polymer Networks

Formulation practices in VPP photopolymers are typically organized around three interlinked controls which are optical attenuation, cure kinetics, and printable rheology.

Optical attenuation is influenced by the absorption characteristics of photoinitiators and additional materials like UV absorbers and pigments, affecting cure depth and exposure dose needed for interlayer bonding. Pritchard et al. tackled the “cure-through” issue in continuous stereolithography, where unintended light penetration cures previous layers, compromising accuracy. They developed a mathematical model based on Beer’s Law to calculate the optical dose in the vat and implemented a grayscale correction algorithm to adjust projected slice images, reducing feature height errors by over 85% without slowing print speed. Fan et al. challenged the “photo-invariant” assumption regarding optical attenuation, introducing the concept of “photobleaching,” which affects the attenuation coefficient (μ) during curing. They created a spatio-temporal optimization model that dynamically adjusts light intensity, achieving high-fidelity prints of microfluidic channels and concave lenses with less than 10% variation in cure depth. Halloran et al. analyzed optical attenuation in ceramic stereolithography, highlighting the role of light scattering from ceramic particles. They modeled attenuation with a scattering length parameter (S) and identified the refractive index contrast (Δ) as a key factor. They established limits for printing high-refractive-index ceramics and defined necessary parameters for successful ceramic resin formulation. Vitale et al. explored the sigmoidal conversion profile due to light's intrinsic optical attenuation. Using a frontal photopolymerization model and Fourier transform infrared spectroscopy, they measured the attenuation coefficient (μ) to predict the polymerization front's shape and position, enabling the creation of functionally graded materials by tuning attenuation and exposure dose.

Cure kinetics depend on initiator efficiency, inhibitor levels, and monomer reactivity, affecting conversion and sensitivity to exposure variations. Ahn et al. propose using Thiol Additives for Ambient Visible Light 3D Printing to address oxygen inhibition in open-vat systems. This strategy uses Thiol-Ene/Acrylate chemistry to incorporate multifunctional thiols into standard acrylate resins. Thiols serve as chain-transfer agents, reacting with oxygen-inhibited radicals to regenerate reactive thiyl radicals, enabling rapid, high-resolution printing (e.g., <100 μm features) in air without the need for costly inert-gas environments. The materials produced have tunable mechanical properties, but potential downsides include the long-term stability of thiol-acrylate mixtures and the odor of thiols. Herzberger et al. (thiol-ene) use to bypass the issue where oxygen stops the reaction, allowing for printing in open air. Stevens et al. discuss "Invisible" near-infrared 3D Printing using a Type II photoinitiating system activated by low-intensity near-infrared light (~850 nm). This method employs a Cyanine Dye (H-Nu 815) as a photosensitizer, along with an iodonium salt (acceptor) and a borate salt (donor). The process involves a redox cycle where the excited dye facilitates electron transfer, generating radicals for acrylate polymerization. This technique enables the creation of thick, opaque parts filled with silica or zirconia nanoparticles, with improved curing through pigmented or filled resins due to near-infrared's high penetration depth. While this enhances print fidelity compared to UV printing, it also increases the complexity of managing the three-component initiator system to avoid thermal instability. Zhang et al. emphasize using visible light to achieve deeper penetration into resins, allowing for the printing of thick, opaque composites that UV light cannot penetrate. Van der Laan et al. describe a method called Volumetric Polymerization Confinement that uses a dual-wavelength system to precisely control polymerization depth. This technique involves Butyl Nitrite as a UV-activated photoinhibitor and a blue-light photoinitiator (Camphorquinone). Blue light initiates radical polymerization of methacrylates, whereas UV light generates nitric oxide, a radical inhibitor that leads to chain termination. This results in high-resolution voids without the overcuring common in vat polymerization, allowing spatial confinement of polymerization, which is crucial for true volumetric 3D printing. However, the inhibitor's effectiveness is transient and concentration-dependent. Additionally, Tan et al.'s continuous liquid interface production technique uses oxygen "dead zones" and photoinhibitors to enhance printing speed and create complex geometries without layers.

Rheology is primarily controlled by selecting oligomers and reactive diluent content, which must balance low enough viscosity for recoating and bubble release with high enough cured crosslink density to ensure dimensional stability. Common failure modes across these controls include under-cure issues such as weak layers, tacky surfaces, and poor resolution; over-cure problems that lead to shrinkage stress accumulation manifesting as curl, warping, cracking, and dimensional bias; and vat instability signs such as viscosity drift, sedimentation, and premature gelation. In elastomeric formulations, rubber-like behavior is typically achieved by combining flexible oligomer backbones such as those derived from urethane, silicone, or polyisoprene with reactive diluents to attain a printable viscosity. This approach limits the use of multifunctional crosslinkers to the minimum necessary for shape retention, thereby avoiding excessively rigid or brittle networks.

2.8 Challenges of Elastomers in Vat Photopolymerization

Fabricating complex elastomeric geometries is difficult with conventional tool-based manufacturing methods. Thus, VPP is particularly relevant for application spaces that benefit from customized or intricate elastomer parts for medical devices, lightweight components, seals, and gaskets. A dominant processing constraint in VPP is resin viscosity. Highly viscous photopolymers impede recoating and can prolong print times; in severe cases, they contribute to geometric error and warpage. For elastomeric photoresins, viscosity control is coupled to mechanical performance through oligomer selection. Low-molecular-weight oligomers improve flow and spreading during printing but can reduce elastomeric extensibility in the cured network compared with formulations that preserve a more elastomer-like chain architecture. Conversely, increasing effective molecular size increases viscosity, which is outside the process window, creating a formulation tension between recoating/printability (often referred to as the flowability part quality paradox).

Resolving this tension typically motivates strategies that recover elasticity without sacrificing flow, including formulation-level approaches, the use of monofunctional monomers and reactive and unreacted diluents, but introduce downstream liabilities, including solvent removal requirements from the printed gel and concerns related to volatility and toxicity; for these reasons, solvent-based dilution is often treated as a compromise rather than a primary solution. Another case: process-level approaches, such as post-processing steps and heated vats ; however, this could lead to premature gelation. In practice, photopolymer formulations are often targeted below a working-viscosity threshold (e.g., ~10 Pa·s) to maintain robust recoating. Importantly, the "solution" is not simply to lower viscosity; it is to maintain printability while preserving the network features required for elastomeric deformation. Hardware advances can expand the printable viscosity window but introduce elastomer-specific failure modes. For example, vat systems using a recoating blade have been reported to process resins with high viscosities . However, elastomeric green bodies often have low storage modulus, making them susceptible to collapse or distortion under blade-induced shear during recoating. This shifts the design requirement from viscosity alone to the coupled requirement of early-layer green strength, which depends on exposure conditions, cure rate, and the resulting crosslink density within each layer.

Polyurethane and Silicone Elastomers as Established Platforms

Among elastomeric materials used in photocurable systems, polyurethanes (Polyurethanes (PUs)) are widely studied because their properties can be tuned through the controlled incorporation of functional groups beyond the urethane linkage. In PU synthesis, urethane linkages form upon reaction of diisocyanates with polyols, and the selection and functionality of these building blocks govern whether the resulting polymer is predominantly linear or chemically crosslinked, as well as its interchain interactions, crystallization tendency, and chain stiffness/flexibility . This synthetic versatility enables PU compounds with high abrasion resistance, impact resistance, and elasticity, and helps explain why PU families remain a common reference point when discussing elastomeric performance in photopolymer contexts.

A practical constraint in PU processing is moisture sensitivity. PU materials can be hygroscopic, and isocyanates can absorb water, which may degrade prepolymers, induce premature gelation, and generate carbon dioxide that causes foaming; therefore, controlling moisture during storage and processing is essential for dimensional and mechanical consistency. Commercial PU systems are often discussed using the isocyanate index (I), where $I \approx > 1$ is commonly considered optimal for crosslinking balance; thermoset systems may use $I > 1$, and thermoplastic polyurethanes are frequently formulated near unity, for example, I of ~1.05, indicating a small isocyanate excess. Within the PU family, thermoplastic polyurethanes are notable for not requiring chemical vulcanization; instead, they form physical crosslinks via hydrogen bonding and microphase separation between hard and soft segments, yielding a rubber-like elasticity with plastic-like strength. By varying diisocyanates, oligomeric diols, and chain extenders, thermoplastic polyurethane properties can be tuned across a wide application range .

For VPP, photosensitive polyurethanes (often referred to as photocurable PU derivatives) are obtained by introducing urethane/urea linkages and photoactive carbon–carbon double bonds into the PU backbone, enabling rapid UV-induced crosslinking. A representative route described in the literature is the reaction of diisocyanates, diols, and hydroxylated acrylates to introduce unsaturation into the PU chain, allowing network formation under UV exposure. In these systems, the choice of raw materials remains decisive: aromatic and aliphatic diisocyanates, for example, TDI, MDI, IPDI, and polyester vs polyether polyols contribute differently to mechanical strength, color stability, viscosity, and thermal behavior, and therefore strongly influence photocured elastomer performance . This establishes PU-derived photopolymers as a relatively mature, designable platform for elastomeric vat resins.

Silicone elastomers represent a second major elastomer class relevant to photocurable formulations, distinguished by a non-organic siloxane backbone consisting of alternating Si–O units with organic substituents on silicon . Their property set is frequently linked to backbone chemistry and chain architecture: the Si–O bond has substantial thermodynamic strength and ionic character, and the combination of short bond lengths and a wide Si–O–Si bond angle contributes to conformational flexibility, low surface tension, very low glass transition temperature (reported around −127°C), low elastic modulus (typically a few MPa), and high stretchability (ultimate strains exceeding 300%) . Commercial silicone characterization often uses the alkyl/silicone ratio (R/Si), where lower R/Si corresponds to higher crosslink density, and elastomer grades may be formulated in ranges such as 1.2:1 to 1.6:1 depending on application; curing can occur via room temperature vulcanization condensation routes or high temperature vulcanization radical mechanisms (including peroxide and hydrosilylation), and silica fillers are commonly used to modify performance (with sizes cited in the 0.003–0.03 mm range).

In photocurable silicone systems, UV-curable functionality is introduced through groups such as (meth)acryloyl, thiol–ene pairs, or epoxy/oxetane motifs, enabling curing through free-radical photopolymerization, thiol–ene step-growth pathways, or cationic polymerization, respectively . Cationic routes are often associated with lower volume shrinkage and reduced oxygen sensitivity relative to free-radical curing but can suffer from higher viscosity and modest cure rates; hybrid silicone epoxide–acrylate systems have been developed to improve reaction rate and conversion. In lithography-based additive manufacturing, silicones often require extensive support structures due to their softness and flexibility, and while fillers (e.g., silica) can stiffen the material, silicones can be relatively costly and vulnerable to halogenated solvents . Together, PU- and silicone-based photocurable elastomers provide established "industrial" reference families for elastomeric VAT resins, against which emerging strategies such as latex- and emulsion-based systems aimed at solving flowability and quality constraints can be positioned.

2.9 Emulsion-Based 3D Printing of Elastomers

3D printing has faced challenges in creating soft, stretchy, and resilient objects due to the viscosity-printability-cure paradox. Rubber's elasticity comes from long, tangled polymer chains, but this also makes it thick and viscous, hindering smooth flow for high-resolution printing. As a result, only less stretchy, elastomer-like materials with shorter chains are typically used. Emulsions for 3D printing offer a solution by decoupling material properties from printing viscosity. Instead of dissolving long polymer chains, it suspends tiny rubber particles in a low-viscosity liquid, like fat globules in milk. This allows for the use of fluid resins that cure into high-performance, hyperelastic solids.

A photocurable emulsion is a stable mixture of two immiscible liquids, such as oil and water, stabilized by the addition of stabilizing agents. Two primary strategies for creating these emulsions are:

Oil-in-water (O/W) emulsions, which are the most common. Here, tiny particles of high-performance polymer (the oil phase) are dispersed in a continuous water-based medium. An example is NRL, which consists of polyisoprene particles in water. This approach allows for ultrahigh molecular weight polymers necessary for extreme stretchiness (hyperelasticity) while maintaining a low viscosity (typically 10 Pa·s), ideal for high-speed, high-resolution layering in VPP 3D printing.

Water-in-oil (W/O) emulsions involve tiny water droplets dispersed in a continuous oil phase, typically a liquid monomer that will form the polymer structure. Less common for solid elastomers, this method is used to create highly porous, foam-like structures known as polyHigh Internal Phase Emulsion (HIPE) (high internal phase emulsion) materials. A surfactant is essential for stabilizing these oil-water mixtures. The final material in printable resin is defined by a balanced recipe of dispersed elastomer particles, monomers, oligomers, and a photoinitiator.

Latex-Scaffold Coalescence

Two contrasting material design strategies have emerged: latex-scaffold coalescence and emulsion templating. In the first group, high molecular weight polymer particles like natural rubber latex, styrene-butadiene rubber, EPDM rubber, styrene-isoprene-styrene, waterborne polyurethane are dispersed in water with a photo-curable scaffold; UV curing locks the hydrogel green body, and subsequent thermal treatment removes water, forcing the particles to coalesce into dense elastomers with semi-interpenetrating or fully interpenetrating polymer networks that deliver exceptional elasticity and tensile strength. Examples include ammonia-free natural rubber systems that achieve $\geqslant$900% elongation, silica-reinforced styrene-butadiene rubber with dramatically increased modulus and hardness, sulfonated EPDM rubber and polyurethane latexes tuned via reactive or non-reactive end groups, and styrene-isoprene-styrene triblock systems that leverage microphase separation to exceed 800% elongation.

Emulsion Templating

In contrast, emulsion templating relies on water-in-oil HIPEs or related emulsions, in which the aqueous phase acts as a porogen; curing the continuous phase and evaporating water yield highly porous scaffolds. polycaprolactone-based polyHIPEs demonstrate controlled pore sizes and interconnectivity for tissue engineering; hydrophobic HIPE inks enable direct ink writing of self-supporting foams; silica-stabilized gel emulsions produce low-density, sound-absorbing monoliths; and oil-in-water emulsions enable conductive porous structures by filling channels with nanoparticles. This dichotomy highlights the versatility of emulsion and colloid printing; dense elastomers form from coalescing latexes within a photopolymer scaffold, whereas porous foams arise from sacrificial internal phases. While colloidal emulsions offer an elegant way to decouple processing viscosity from molecular weight and deliver low volatile organic compounds, high-performance elastomers, the processing science, especially for UV curing and additive manufacturing, remains young. Systematic parametric studies are still needed to understand how particle size, solids loading, light-absorbing additives, and formulation strategy can control viscosity, light penetration, and final properties.

Limitations and Challenges

Latex-scaffold coalescence systems are fundamentally limited by the formation of a rigid semi-interpenetrating polymer network that topologically constrains the conformational entropy of the elastomeric chains, thereby capping ultimate elongation while simultaneously inducing significant isotropic volumetric shrinkage upon the requisite dehydration of the aqueous continuous phase. Emulsion templating strategies employing HIPEs exhibit non-Newtonian, yield-stress rheology that impedes the rapid, low-shear recoating kinetics required for high-resolution Vat Photopolymerization, inevitably yielding low-density cellular monoliths with inferior bulk mechanical toughness and modulus compared to fully dense elastomers. Furthermore, both methodologies suffer from severe feedstock constraints: scaffold coalescence is restricted to hydrophilic, water-soluble monomers, which preclude the use of high-performance hydrophobic engineering resins, and Emulsion templating requires complex surfactant optimization to mitigate thermodynamic instability that drives coalescence and Ostwald ripening during the critical printing window.

Current challenges in emulsion-based 3D printing include:

1. **Shrinkage Management**: The removal of water from printed parts often leads to significant shrinkage, which can negatively impact fine details and taller structures. It is essential to implement effective control measures to minimize distortion and preserve design

integrity.

2. **Print Stability**: Maintaining a uniform emulsion mixture is critical. Settling or particle separation can result in inconsistent material properties, jeopardizing uniformity and performance. Therefore, robust mixing techniques and stabilization methods are essential.

3. **Green Part Handling**: The initial printed objects, known as green parts, are soft hydrogels prone to deformation or tearing. Developing effective handling strategies and fixtures is necessary to support these delicate structures during the manufacturing process.

4. **Resolution vs. Viscosity Tradeoff**: Increasing the concentration of rubber particles can enhance material strength, but it may also lead to light scattering, which reduces print resolution. Striking a balance between these factors is crucial for achieving high-performance materials while maintaining fine details.

Despite these challenges, emulsion-based 3D printing holds transformative potential for soft materials. By addressing the paradox of viscosity and print capability, researchers are advancing toward the production of high-performance elastomers for applications in soft robotics, custom medical devices, and sustainable products.

3.1 Sourcing, Traceability, and Rationale: Natural Rubber Latex Preservation Systems

Overview of Preservation Methods as the Master Variable

The fundamental research design rests upon systematic comparison of two distinct preservation methodologies for NRL, each representing different approaches to maintaining polymer stability and functional properties. This comparison serves as the Master Variable throughout the experimental program, directly addressing the research objective to define how preservation chemistry alters NRL microstructure and flow characteristics. The primary motivation for this comparison derives from documented preservation and processing challenges in NRL production, particularly concerning ammonia toxicity, environmental sustainability, and the need to maintain microbial stability without hazardous volatiles.

Ammoniated Latex System

AFLatex Technologies LDA (Victoria, Caldas, Colombia) provided the ammoniated NRL sample, representing the historical preservation standard. This ammoniated latex was supplied as a centrifuged system with 60% DRC according to ASTM D1076-15 classification standards. The ammoniated formulation employs ammonia as the primary preservative and stabilizer, which has been the traditional approach for NRL conservation for decades. However, this material serves a dual role in the research: it functions both as a baseline against which eco-preserved systems are evaluated and as a means to investigate ammonia's documented effects on protein and phospholipid retention within the latex colloidal system. Due to traditional production practices and transportation constraints, acquiring an equivalent ammoniated latex serum sample for direct compositional comparison proved infeasible; consequently, the 60% DRC ammoniated latex represents the primary ammoniated reference material in this study.

Eco-preserved Latex Systems

AFLatex Technologies LDA provided two distinct eco-preserved NRL formulations, both ammonia-free, which form the core of the comparative preservation study. The first system, designated Alfa, employs a preservation chemistry combining ethoxylated tridecyl alcohol and hydrofluoric acid. The second system, designated Beta, utilizes linear dodecylbenzene sulfonic acid as the primary preservative. Both materials were supplied in two distinct solid content formulations, approximately 60% and 30% DRC, allowing investigation across a range of particle volume fractions while maintaining identical preservation chemistry. Additional latex serum was provided to prepare intermediate concentrations as needed. This dual-formulation approach enables systematic evaluation of how concentration influences the preservation-dependent microstructure and rheological properties.

Reference and Synthetic Polymer Materials

To contextualize the natural rubber latex system within the broader landscape of elastomeric polymers, two reference materials were included. Synthetic polyisoprene (L-IR-50) with an average molecular weight of 54,000 Da was donated by Kuraray Co. Ltd. (Tokyo, Japan). Deproteinized and saponified liquid natural rubber (DPR-40) with an average molecular weight of 40,000 Da was donated by DPR Industries, a division of Pacer Industries Inc. (Coatesville, PA, USA). These materials allow distinction between the rheological and NMR signatures attributable to preservation chemistry versus those arising from the native protein-lipid matrix inherent to natural rubber latex. By comparing native NRL (ammoniated and eco-preserved) against synthetic polyisoprene and deproteinized rubber, the study isolates the specific effects of preservation-dependent protein and phospholipid behavior on macroscopic properties.

Pre-receipt Specifications

The receipt-stage characterization was used to benchmark incoming natural rubber latex against ISO 2004:2010 and related procedures (e.g., ASTM D1076 for DRC). The objective is lot-level traceability and verification of baseline quality prior to formulation and rheological testing. Key standardized indicators include mechanical stability (mechanical stability time), volatile fatty acid number/index (volatile fatty acid), solids content (total solids content/DRC), and Brookfield viscosity. Table A1 reports measured values (average $\pm$ standard deviation) for the latex lots used in this work, alongside any supplier certificate of analysis values when available. Table A2 lists the corresponding ISO specification limits by latex type (centrifuged/creamed; HA/LA/XA). Together, these tables link experimental rheological findings to standardized quality metrics and clarify preservative- and processing-dependent differences relevant to performance.

Incoming Verification

Upon receipt, each latex batch was independently verified to confirm it matched the supplier's certificate of analysis and met baseline quality requirements. All results were recorded on an Incoming Verification Sheet linked to supplier, lot/batch code, ship/storage conditions, and the intended use condition; batches failing criteria were quarantined or rejected.

DRC was measured by ASTM D1076: approximately 10 g latex was diluted to approximately 25 wt% total solids, coagulated with 2 wt% acetic acid under stirring, washed/rolled, then dried at 70 °C (or 55 °C if oxidation was observed) to constant mass. Batches were accepted only when measured DRC agreed with the supplier value within ± 1 wt% (absolute); out-of-spec results were repeated once, and persistent deviation triggered quarantine/rejection. pH and conductivity were measured at 23 °C using a calibrated pH electrode (ASTM E70 practice) and a conductivity probe, respectively, and recorded without adjustment during verification.

Particle-level stability was checked by Dynamic Light Scattering (DLS) / ζ potential using a 1:100–1:1000 dilution in a defined ionic medium (10 mM electrolyte) to reduce double-layer artifacts and multiple scattering; Z-average diameter, polydispersity index, and ζ potential were reported with dilution factor and diluent composition. Additional receipt screening included appearance (color, odor, phase separation) and visible coagulum assessed by sieving through a 100 μm mesh; Brookfield viscosity was used as an optional sanity check against internal/supplier baselines, and an aerobic plate count was performed when bioburden information was required (otherwise recorded as "not evaluated").

Spectroscopic and Analytical Solvents

Deuterium oxide (D_2O, CAS: 7789-20-0) and deuterated chloroform ($CDCl_3$, CAS: 865-49-6, 99.8 atom% deuteration, containing 0.03% tetramethylsilane as internal standard) were purchased from Merck (Sigma-Aldrich). Both solvents were stored over 4 Å molecular sieves to maintain isotopic purity and prevent isotopic exchange with atmospheric moisture. These deuterated solvents are essential for ^{1}H and ^{13}C NMR spectroscopy, enabling direct observation of polymer chain dynamics, protein interactions, and any preservation-dependent chemical shifts or relaxation behavior that would remain invisible in conventional hydrogenated solvents.

3.2 Rheological Characterization

Understanding how NRL flows and deforms under stress is critical because flow behavior reflects the microstructure and dictates processability in additive manufacturing. This section details the rheological protocols; the colloidal phenomena being probed and the models used to interpret the data.

Measurement Types and Protocols

Sample Preparation and Volume-Fraction Series

Rheology was performed on latex suspensions prepared over a solids volume-fraction range of $\phi = 0.2$–0.6 to isolate the effect of concentration on flow and viscoelastic response. For the ammonia-free latex systems, the stock latex at the highest concentration was diluted to target ϕ using the matching latex serum to preserve the native ionic environment and minimize artifacts in colloidal interactions during dilution. For ammonia-preserved latex, dilution was performed using deionized water rather than ammonia serum due to handling hazards; pH and conductivity were recorded for each diluted sample to document any shift in ionic strength introduced by this approach. Target ϕ values were calculated from measured DRC/total solids content and the known mass fractions used in each dilution.

Rotational Rheometry (Parallel Plates)

Steady and oscillatory measurements were conducted using a NETZSCH Kinexus rotational rheometer with a 40 mm upper / 60 mm lower parallel-plate configuration and a 0.5 mm gap at room temperature. Approximately 1 mL of latex was loaded for each test.

Steady shear ramps were performed from 0.01 s^{-1} to 300 s^{-1} to obtain viscosity–shear rate curves and identify Newtonian plateaus and shear-thinning regions. Where thixotropy was relevant, an up–down ramp (0.01 $\rightarrow$ 300 $\rightarrow$ 0.01 s^{-1}) was used to assess hysteresis between the increasing and decreasing branches.

Oscillatory amplitude sweeps were used to determine the linear viscoelastic window and quantify storage and loss moduli (G', G'') as a function of strain amplitude. Sweeps were collected over 0.01–200% strain at fixed frequencies of 0.1 Hz, 1 Hz, and 10 Hz for each ϕ.

Shear start/recovery (thixotropy) tests were conducted using a three-interval thixotropy test (3ITT): a low-shear interval to establish a reference state, a high-shear interval to induce structural breakdown, and a final low-shear interval to quantify recovery. The imposed shear rates were selected within the same bounds as the steady ramps (low shear near 0.01 s^{-1}, high shear near 300 s^{-1}), and recovery was evaluated by comparing the post-shear viscosity to the initial reference value.

Computational Fluid Dynamics: Taylor–Couette Measurements

At higher volume fractions where parallel-plate testing can be affected by wall slip and particle migration, a Taylor–Couette (concentric cylinder) geometry was used to provide more reliable high-ϕ measurements. The inner cylinder radius was 0.64 cm, and the outer cylinder radius was 2.54 cm; the inner cylinder rotated at a fixed 55 rpm while the outer cylinder remained stationary.

To interpret concentration nonuniformity and migration trends observed in Couette flow, a simplified two-phase (suspension balance) framework was used: the mixture flow field is solved with no-slip at the walls, and the particle phase is allowed to redistribute via a concentration-transport equation that captures shear-induced migration and buoyancy/settling effects. This modeling was used as an interpretive tool to confirm that observed viscosity changes with ϕ are consistent with expected migration/stability behavior in Couette flow and to support attributing trends to intrinsic particle/serum effects rather than measurement artifacts.

Rheology Interpretation Framework: Linking Shear, Microstructure, and Volume Fraction

To interpret viscosity–shear rate data across volume fraction ϕ, a microstructure-based picture is employed in which latex particles form transient linkages (flocs/bridges) at rest and under low shear, and these linkages are progressively disrupted under increasing shear.

The internal structural state is represented by N, the instantaneous number (or density) of effective interparticle linkages contributing to resistance to flow, and N_0, the maximum/initial linkage density at rest (i.e., the "fully structured" reference state). Under shear, linkages break at a rate that scales with both how much structure exists and how strong the imposed deformation is. This is written as a breakage term $k_d N\dot{\gamma}^m$, where k_d is the breakage rate constant, $\dot{\gamma}$ is shear rate, and m is the shear-sensitivity exponent (higher m means structure is more sensitive to shear). When shear is reduced or removed, linkages reform by Brownian-driven encounters and attractive interactions; reformation is modeled as $k_r(N_0 - N)$, where k_r is the reformation rate constant and $(N_0 - N)$ is the "remaining capacity" for rebuilding structure.

Combining these gives:

$$\frac{dN}{dt} = -k_d N\dot{\gamma}^m + k_r(N_0 - N) \tag{3.1}$$

At steady state $(dN/dt = 0)$, the normalized structure becomes:

$$\frac{N}{N_0} = \frac{1}{1 + a\dot{\gamma}^m}, \quad a = \frac{k_d}{k_r} \tag{3.2}$$

Here a is a dimensionless ratio of timescales: large a corresponds to fast breakdown relative to recovery (or slow recovery relative to breakdown), and small a corresponds to structure that reforms rapidly compared to the imposed breakdown.

The link between microstructure and macroscopic flow is made by assuming that viscosity increases with the fraction of linkages remaining. The Cross-form expression uses two limiting viscosities: η_0, the zero-shear viscosity (low shear, structure close to intact, $N \approx N_0$), and η_∞, the infinite-shear viscosity (high shear, structure largely disrupted, $N \to 0$). The steady shear viscosity is then written as:

$$\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + a\dot{\gamma}^m} \tag{3.3}$$

In practice, η_0, η_∞, a, and m are extracted by fitting each $\eta(\dot{\gamma})$ curve at fixed ϕ. Tracking these fitted parameters versus ϕ provides a compact way to quantify how concentration and preservation chemistry change (i) the strength of the structured network (via η_0), (ii) the "fully broken" baseline (via η_∞), and (iii) the shear sensitivity and kinetic balance of breakdown vs recovery (via m and $a = k_d/k_r$).

Time dependence (thixotropy) is interpreted with the same variables by comparing the reformation timescale $1/k_r$ to the experimental observation window. When $1/k_r$ is short relative to the test duration, viscosity recovers during a down-ramp or post-shear interval because N can return toward N_0. In contrast, when recovery is not observed, two limiting interpretations are used: (1) recovery is intrinsically slow (k_r small, so $1/k_r$ is long), or (2) the system is near/above a critical packing state where particle mobility is constrained, so link reformation is effectively suppressed. Operationally, this second limit is represented as $k_r \to 0$ at or above an effective critical volume fraction ϕ_c, implying $N/N_0 \to 0$ over accessible times and $\eta(\dot{\gamma}) \to \eta_\infty$ after shear-induced breakdown. This provides a mechanistic criterion for identifying ϕ_c: the onset of persistent hysteresis (non-recovering viscosity upon ramp-down or in 3ITT recovery) indicates that the microstructure is no longer reversibly re-forming on experimental timescales, consistent with packing-limited dynamics.

Addressing Measurement Challenges and Micro-Level Effects

A rotational rheometer does not measure viscosity directly; it measures torque M and angular velocity Ω, from which shear stress τ, shear rate $\dot{\gamma}$, and apparent viscosity η_{app} are inferred via geometry-dependent factors K_τ and K_γ obtained by solving the Navier–Stokes equations under idealized conditions. In compact form:

$$\tau = K_\tau M, \quad \dot{\gamma} = K_\gamma \Omega, \quad \eta_{app} = \frac{\tau}{\dot{\gamma}} = \frac{K_\tau}{K_\gamma}\frac{M}{\Omega} \tag{3.4}$$

These relations are only valid if three physical assumptions hold: no slip at the walls ($v_{fluid} = v_{wall}$), homogeneity across the gap (ϕ and hence η independent of position), and laminar simple shear without secondary flows.

In concentrated NRL, all three are easily violated. Depletion layers at smooth tools create wall slip, so only a thin solvent-rich layer is actually sheared; the instrument overestimates $\dot{\gamma}$ and underestimates η. Shear-induced migration in geometries with strong shear-rate gradients (parallel plate, wide-gap Couette) drives particles from high-shear to low-shear regions, generating a spatially varying $\phi(r)$ and a torque that is a nontrivial average over a heterogeneous microstructure. At higher rotational speeds in cylindrical geometries, inertial instabilities (Taylor vortices, wavy vortices) add an extra, non-constitutive contribution to the torque, which appears as artificial shear thickening if interpreted with the simple $\eta \propto M/\Omega$ relation.

Mitigation, therefore, combines experimental design and analytical correction to keep the inferred viscosity as close as possible to the true constitutive response. Wall slip is minimized by using serrated or sand-blasted tools to mechanically couple the bulk to the walls; when unavoidable slip remains, measurements across multiple gaps are analyzed using Mooney-type constructions to estimate slip velocity and correct the true shear rate. Shear-induced migration is reduced at the source by choosing geometries with nearly uniform shear (small-angle cone-and-plate, narrow-gap Couette) and by limiting measurement times at high shear so that strong concentration gradients do not fully develop. When gradients are expected, the data are interpreted within a suspension-balance or two-phase framework, where particle fluxes driven by $\nabla\dot{\gamma}$ and $\nabla\phi$ are coupled to a local viscosity $\eta(\phi)$ to rationalize deviations from ideal behavior. Finally, flow instabilities are avoided by operating below the critical Taylor/Reynolds numbers for the chosen gap-to-radius ratio, and by favoring narrow-gap or outer-rotating Couette configurations that delay the onset of vortices. Together, these strategies ensure that the reported NRL viscosities and fitted constitutive parameters reflect microstructure-controlled material properties rather than artifacts of migration, slip, or inertial flow.

3.3 Nuclear Magnetic Resonance (NMR)

Overview and General Conditions

All NMR experiments were performed at 303 K on two solution-state instruments: a Bruker Avance I 600 MHz equipped with a Prodigy cryoprobe (Z150313_001; cpT4600ss3H&F-LIN-D-05Z) and a Bruker Nyx / Bruker NEO 500 MHz fitted with a Prodigy-BBO probe (Z130036_0001; CPP BBO 500S2BB-H&F-D052LT). Chemical shifts were internally referenced using tetramethylsilane ($\delta_H = 0$ ppm), $CDCl_3$ ($\delta_H = 7.26$ ppm), or D_2O/HDO

($\delta_H = 4.79$ ppm), selected based on the solvent system used for each measurement.

Sample Preparation (Solution-State NMR)

Unless otherwise specified, samples were prepared by dissolving natural rubber latex (NRL) at 10 mg per 0.6 mL D_2O in standard 5 mm NMR tubes. Shimming routine (topshim/manual), lock nucleus, number of dummy scans (DS), and receiver gain were fixed across samples.

To capture compositional and processing variability, solution-state NMR was conducted on multiple NRL-derived sample classes under both ammonia-preserved and ammonia-free conditions:

- field latex (ammonia and ammonia-free),
- an industrial serum fraction from the ammonia-free system,
- concentrated latex (ammonia and ammonia-free), and
- ultracentrifugation-fractionated latex prepared from each preservation condition.

NRL was fractionated by ultracentrifugation at 25,000 rpm and 277 K, yielding a reproducible three-layer separation: a top cream layer (enriched in intact rubber particles), followed by two aqueous serum layers (Serum B and Serum C). Serum C exhibited weaker but still recognizable signals relative to Serum B and the cream fraction. Each fraction (cream, Serum B, Serum C), along with the unfractionated starting material and other sample classes above, was analyzed using consistent 1D and 2D NMR workflows for both ammonia and ammonia-free systems.

High-Resolution Solution-State NMR (1D and 2D)

The following Bruker pulse programs were used:

- ^{1}H 1D: zg30 (NS = 8)
- ^{13}C 1D: zgpg30 (NS = 6400)
- ^{1}H–^{13}C Heteronuclear Single Quantum Coherence (HSQC) (multiplicity-edited): hsqcedetgpsisp2p.3 (NS = 8)
- Heteronuclear Multiple Bond Correlation (HMBC): hmbcgpndqf (NS = 8)
- ^{1}H–^{1}H Correlation Spectroscopy (COSY): cosygpprqf.uw (NS = 64)
- ^{31}P 1D: zgig30 (NS = 256)
- Heteronuclear HMBC: HMBC_Hx.uw (NS = 2)
- Multiplicity-edited HSQC (alt): HSQCetfd.uw (NS = 2)
- APT: jmod (NS = 128)
- DEPT-135: dept-135 (NS = 1005)

Data were processed in MestReNova. Free induction decays (FIDs) were Fourier transformed after zero-filling to 2× points. An exponential apodization was applied with line broadening defined as 1/AQ, followed by manual phase correction and baseline correction using a 6th-order polynomial over the full spectral width. Peak picking, integration ranges, coupling extraction, and cross-peak assignment criteria were applied consistently across conditions.

diffusion-ordered spectroscopy

diffusion-ordered spectroscopy experiments used the ledbpgp2s sequence with: NS = 16, receiver gain = 3.5, relaxation delay = 2 s, pulse width = 7.07 μs, and acquisition time = 2.7739 s. diffusion-ordered spectroscopy processing was performed in MestReNova using the Bayesian DOSY Transform.

Key settings included an exponential decay model where diffusion coefficients D were obtained by fitting the diffusion-dependent signal attenuation to the Stejskal–Tanner relation:

$$I(g) = I_0 \exp\left[-b(g) \cdot D\right] \tag{3.5}$$

with

$$b(g) = \gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right) \tag{3.6}$$

where $I(g)$ is peak intensity at gradient amplitude g, I_0 is intensity at $g = 0$, γ is the gyromagnetic ratio, δ is gradient pulse duration, and Δ is diffusion delay.

Hydrodynamic radii were estimated using the Stokes–Einstein equation:

$$r_h = \frac{k_B T}{6\pi\eta D} \tag{3.7}$$

where k_B is the Boltzmann constant, T is absolute temperature, and η is solvent viscosity.

Additional processing settings included: autocorrected peak positions enabled, Repetitions = 1, resolution factor = 1, and 128 spectral points, with logarithmic diffusion axis and autoscaling enabled.

Time-Domain NMR Relaxometry (TD-NMR)

TD-NMR was used to probe relaxation dynamics associated with distinct molecular environments. T_1 was measured using an inversion recovery sequence (t1ir, NS = 2) over 11 delay points. T_2 was measured using a Carr-Purcell-Meiboom-Gill (CPMG) sequence with d1 = 4 s, d20 = 0.001 s, L4 = 2, and NS = 8.

TD-NMR processing followed the same core pipeline as solution-state processing (FT, zero-filling/apodization, phase, and baseline correction). Integrals were computed in MestReNova to generate intensity vs. delay-time curves, exported to Origin, normalized, and fit using an exponential recovery model for T_1.

Quantification Models

T_1 relaxation times were extracted by fitting the inversion-recovery signal intensities to a mono-exponential recovery model with an optional baseline offset:

$$M(t) = M_0 \left(1 - 2e^{-t/T_1}\right) + C \tag{3.8}$$

where $M(t)$ is integrated signal intensity at the delay time t, M_0 is the equilibrium magnetization scale factor, and C is an offset term (used if baseline/inversion imperfections require it).

T_2 relaxation was quantified from Carr-Purcell-Meiboom-Gill (CPMG) decay curves by fitting integrated echo amplitudes to a biexponential decay model, representing at least two distinct spin populations/environments:

$$M(t) = A_1 e^{-t/T_{2,1}} + A_2 e^{-t/T_{2,2}} + C \tag{3.9}$$

where A_1, A_2 are component amplitudes (population-weighted contributions), $T_{2,1}$, $T_{2,2}$ are component transverse relaxation times, and C is an optional offset.

3.4 Components and Protocols of NRL Photoresin Formulation

Advanced manufacturing of NRL requires a carefully engineered photoresin that balances printability, cure kinetics, and mechanical performance. This section details the formulation strategy, the materials and equipment used, and the protocols adopted to validate the rheological and photochemical behavior of the NRL-based resin.

Preparation of the UV-Curable Latex-Scaffold Coalescence

0.9 wt% sodium dodecyl sulfate was added to 60% DRC ammonia-free NRL and mixed for 3 min using a magnetic stir bar in a 100 mL beaker. Subsequently, approximately 4.44 wt% 1,6-Hexanediol Diacrylate (HDDA) was incorporated into the solution under low Kelvin lighting conditions with a slow dispersion mixing of 5 min. Following this, approximately 4.5 wt% Phenylbis(2,4,6-trimethylbenzoyl)-phosphine Oxide (TPO)-L photoinitiator was added, and the mixture underwent a slow 1.5-h mixing process to reduce the operational viscosity further since NRL is shear thinning. The beaker was sealed with Saranwrap to prevent dehydration and excessive air interaction, while an aluminum foil cover was utilized to minimize light exposure. The low Kelvin lighting was turned off until the mixing was complete.

Preparation of Photoresin Emulsion (PRE)

High-internal phase oil-in-water (O/W) photoresin emulsions were prepared at a 60:40 oil-to-water weight ratio. The oil phase (60 wt% of total emulsion) consisted of the base monomer (HDDA or Trimethylolpropane Triacrylate (TMPTA)) supplemented with 1.0 wt% photoinitiator (TPO-L) and 0.75 wt% low-Hydrophilic-Lipophilic Balance (HLB) surfactant (Span 80). The aqueous phase (40 wt% of total emulsion) consisted of acetate buffer containing 4.25 wt% high-HLB surfactant (Tween 20). The total surfactant concentration was fixed at 5 wt% of the final emulsion, with a Span:Tween weight ratio of 3:17 to achieve an effective HLB ≈ 11.

Emulsification was performed using an overhead stirrer equipped with a four-blade pitched-blade turbine (MINISTAR 20, IKA Works, Germany).

The oil and aqueous phases were pre-mixed separately and equilibrated to 20–23 °C. With the aqueous phase stirred at 800–1,200 rpm, the oil phase was added as a thin, steady stream over 60–90 s to maintain O/W morphology and prevent transient inversion. Following addition, the emulsion underwent a high-shear polishing step at 1,300–1,500 rpm for 30–60 s to narrow the droplet-size distribution and stabilize microscale droplets.

Preparation of Dual Emulsion Photoresin (DEPR)

Dual Emulsion Photoresin (DEPR)s were prepared by blending the O/W Photoresin Emulsion (PRE) with NRL. The NRL used was an ammonia-free, high-solid content variety (60 wt% solids; novel preservative method, patent pending). To evaluate the effect of photoresin loading, a design of experiments approach was used, varying the PRE content to 16, 25, 32, and 44 wt% relative to the total dual-emulsion mass, with the balance comprising the NRL stock. Both HDDA- and TMPTA-based emulsions were evaluated at these distinct loading levels.

To ensure colloidal compatibility, the aqueous phase of the PRE was formulated with an acetate buffer (pH 4.66), selected to match the pH stability range of the NRL. This pH control prevented destabilization upon mixing, maintaining a consistent zeta potential in the final dual emulsion. The required masses of PRE and NRL were weighed into an opaque container and stirred gently (300–500 rpm) for approximately 30 s to achieve a uniform dispersion without disrupting droplet or vesicle integrity. All handling was performed under aluminum foil protection to prevent premature photoinitiator activation.

Indirect Manufacturing of Tensile Testing Specimens for UV-Curable Latex-Scaffold Coalescence

In the fabrication of dogbone-shaped specimens using UV-curable natural rubber latex (NRL), a setup inspired by traditional top-down geometric configuration VPP was utilized. Initially, injection-molded ASTM D412 Die C shapes made from high-density polyethylene were used as molds for thermoforming PET sheets. After softening the sheets sufficiently, the dogbone shapes were formed using the injection-molded Die C molds.

A light source was prepared using an Omniture S2000 high-pressure mercury light guide, which was positioned 10 mm above the mold. UV-curable NRL was applied layer by layer using a 3 mL syringe, following a bottom thin layer method to minimize air bubbles in the PET mold. Each layer was cured under UV light for 30 seconds, and samples were prepared for two intensities: 18 and 30 mW/cm^2. This layering process was repeated until five layers were added to each specimen, resulting in precisely fabricated samples for mechanical and viscoelastic characterization.

After the indirect 3D printing process, the specimens underwent several treatments to enhance their mechanical integrity and stability. First, they were soaked in isopropyl alcohol for 30 minutes to remove any residual uncured resin. Next, they were exposed to low-intensity UV light for 10 minutes from a Black-Ray UV bench lamp (365 nm, 115 V–60 Hz) with an intensity of approximately 10–15 mW/cm^2 to further harden the material. Finally, the samples were placed in an Isotemp vacuum oven (Model 282A) at 65 °C and 30 mmHg for 10 hours to ensure dehydration. Throughout this process, the weight loss of the specimens was monitored before and after processing to maintain consistency in the material properties.

Fabrication of Jammed Microreinforced Elastomers (JMRE) and Controls

A two-stage curing process (UV irradiation followed by thermal treatment) was employed to transform liquid DEPR into solid, jammed, micro-reinforced elastomers (Jammed Micro-Reinforced Elastomer (JMRE)). This nomenclature reflects the transition from a jammed micro-emulsion state to a reinforced elastomeric composite.

UV-Curing and Specimen Molding

To prepare mechanical test specimens, custom molds were fabricated by casting translucent tin-cure silicone (Smooth-On, Macungie, USA) against 3D-printed masters (ASTM D638 Type V dogbone geometry for tensile tests; flat sheets for fracture/puncture tests). The liquid DEPR was cast into the silicone molds and exposed to UV irradiation (30 mW/cm^2) using an OmniCure S200 Elite system. This step locked the photoresin phase (PRE) into a rigid porous scaffold, establishing the green composite structure.

Thermal Treatment and Latex Coalescence

Immediately following UV curing, the specimens were demolded and transferred to a dehydrator/vacuum oven. This step removed residual water and induced osmotic destabilization, thereby forcing the close-packed rubber particles to coalesce within the photoresin scaffold. The samples were then thermally cured at 70 °C overnight to ensure complete formation of the latex film. Demolding before thermal treatment was critical to minimize shrinkage-induced stress and prevent warping due to thermal expansion mismatches.

Preparation of Control Samples

Control samples of pure porous photoresin were prepared by UV-curing the PRE (25 wt% stock) under identical conditions. Pure natural rubber (NR) controls were prepared by casting the NRL into molds and chemically coagulating the surface with alcohol to induce a weak gel state similar to the jammed DEPR precursor. These gelled NR samples were then subjected to the same 70 °C thermal treatment to ensure a comparable thermal history and diffusion profile.

Dip-Coating Fabrication and Pneumatic Inflation

To demonstrate the material's processing versatility, complex geometries were fabricated via dip-coating. An industrial-grade dip mold (ceramic or aluminum) was immersed in the liquid dual emulsion for 5 s. Upon removal, the coated layer was cured under UV light (30 $mW{\cdot}cm^{-2}$). To build sufficient wall thickness for handling, this dip-cure cycle was repeated four additional times (five layers total). Finally, the multilayered sample was dehydrated at 70 °C overnight to promote latex coagulation and film formation.

The toughness and flexibility of the dip-coated samples were qualitatively assessed via a pneumatic inflation test. A cured, dip-coated balloon specimen was connected to a compressed-air line within a fume hood. A standard pipette discharge tip was utilized as a capillary adaptor to interface the sample with the air supply. The sample was successfully inflated using compressed air, demonstrating the material's ability to undergo significant deformation without rupture.

DLP 3D Printing

3D printing was performed on a home-made digital light processing 3D printer. A customized resin vat with an oxygen-permeable window made of Teflon AF-2400 (Biogeneral, Inc., USA) was prepared. A digital-micromirror-device-based UV projector (DLP4710 1080p, UV–LED; Wintech, USA) with a pixel resolution of 1920 × 1080 was used as the light source (wavelength: 385 nm). The projector light intensity was 7.7 mW cm^{-2}, measured by a handheld optical power meter (PM100D; Thorlabs GmbH, USA).

CAD files for the printed part were designed in SolidWorks (Dassault Systèmes, USA) or obtained from online makerworld. The exported STL files were sliced into PNG images using the Creation Workshop software (Wanhao, China). The degassed emulsion photoresin was added to the vat before printing. The build platform was elevated by a 150-mm translation stage with a stepper motor and Integrated Controller (LTS150, Thorlabs, USA). The printing layer thickness is 75 μm, and the exposure time is 20 s per layer. After printing, the parts were removed from the build platform and post-treated in an oven at 70 °C overnight.

High Volume–Low Pressure Spray-Coating and Hydrophobicity Demonstration

To demonstrate the processability and versatility of the dual-emulsion, a high-volume, low-pressure (HVLP) spray-coating protocol was applied to diverse substrates, including silicone elastomers, polyethylene discs, polycarbonate films, and a porous almond cake model. Prior to application, the formulation (containing 25 wt% photoresin and 0.05 wt% Tartrazine dye) was verified to have a viscosity $<$40 DIN-seconds, allowing direct atomization without solvent thinning using a Slikwave CN-7000 sprayer fitted with a 1.2 mm nozzle.

Spray coating was performed using an electric HVLP paint sprayer (Suzhou ChengZi, China). The emulsion was sprayed onto the substrates using a horizontal fan pattern at a working distance of 15–20 cm and a traverse speed of 10 cm s^{-1} with 50% overlap, followed by ambient drying for 30 minutes and UV curing for 10 minutes to crosslink the TMPTA phase.

The robustness of the resulting hydrophobic barrier was validated via an immersion stress test, where a coated almond cake subjected to stirring at approximately 400 rpm in deionized water retained its structural integrity and yellow coloration after 4.5 minutes, whereas the uncoated control disintegrated; this confirmed the coating's ability to provide water resistance and dye retention across materials with varying surface energies and porosities.

3.5 Material Characterizations

Particle Size and Zeta Potential

The droplet size and surface charge of the photoresin emulsions were characterized using dynamic light scattering (DLS) and electrophoretic light scattering (ELS), respectively, on a Malvern Zetasizer Nano ZSP (Malvern Panalytical, UK). The instrument was equipped with a 10 mW He–Ne laser (632.8 nm) and operated with non-invasive backscatter (NIBS) optics at a detection angle of 173°.

Samples were prepared by diluting the NRL or photoresin emulsions into 2-mM acetate buffer (pH 4.66) to a final concentration of 0.01–0.05 wt% to suppress multiple scattering. Crucially, the emulsion aliquot was added to the buffer (never buffer to sample) to minimize osmotic shock and pH drift. Measurements were performed in disposable folded capillary cells (DTS1070) at 25 °C after a 120 s equilibration period.

Hydrodynamic diameters were calculated from the autocorrelation function using the Stokes–Einstein equation, assuming the viscosity of water and a particle refractive index of 1.52 (characteristic of natural rubber). Electrophoretic mobility was measured using the M3-PALS technique and converted to zeta potential via the Smoluchowski approximation. Each reported value represents the average of three independent measurements, with each measurement consisting of approximately 12 sub-runs with automatic attenuation optimization.

(Photo)rheology Characterizations

Rheological measurements were performed using a Discovery HR-20 hybrid rheometer (TA Instruments, USA) utilizing a 20 mm parallel-plate geometry. To account for optical differences, the gap height was set to 0.5 mm for O/W photoresin emulsions. For DEPRs, the gap was reduced to 0.2 mm to ensure uniform UV intensity across the sample depth, thereby mitigating the significant light scattering (Tyndall effect) caused by the rubber phase.

Shear Viscosity

The flow behavior of the emulsions was characterized via steady-state shear experiments. Viscosity profiles were obtained by ramping the shear rate from 0.01 to 200 s^{-1} at 25 °C, allowing for the evaluation of shear-thinning behavior and stability under flow.

In-Situ Photorheology

Real-time photopolymerization kinetics were monitored using the UV-Curing Accessory Kit (TA Instruments), which comprises a quartz lower plate, a liquid-light-guide assembly, and a closed-loop shielding system. UV irradiation was supplied by an OmniCure Series 2000 system (Excelitas Technologies, USA) equipped with a 200 W mercury arc lamp (320–500 nm). The incident intensity at the sample surface was calibrated to 30 mW cm^{-2}.

Curing profiles were recorded via oscillatory time sweeps at a fixed frequency of 5 Hz and a strain amplitude of 0.3%. This strain was confirmed to be within the linear viscoelastic region via amplitude sweeps, which exhibited Type 1 behavior (linear response up to critical deformation) consistent with concentrated emulsions. The testing protocol consisted of a 120 s pre-shear equilibration, followed by 30 s of UV irradiation, and a final 400–600 s post-exposure monitoring period to observe the evolution of storage (G') and loss (G'') moduli.

Morphological Characterization (SEM)

Surface and cross-sectional morphologies were examined using a Gemini scanning electron microscopy 450 (Zeiss, Germany). The microscope was operated at an accelerating voltage of 3.00 kV with a working distance of approximately 9.2 mm to minimize beam damage and charging on the polymeric samples.

Porous photoresin scaffolds: Porous PR samples were mounted by pressing aluminum stubs equipped with double-sided conductive carbon tape directly onto the sample surface to preserve the native porous architecture.

JMRE samples: To analyze the internal microstructure and failure mechanisms, imaging was performed on the fracture surfaces of specimens recovered after tensile testing.

Sputter coating: Before imaging, samples were sputter-coated with a finer-grained Platinum coating to visualize the tiny pores without introducing artificial roughness. With the JMRE, given that the fracture surface is rough and macroscopic relative to pores, conventional gold was sufficient for electrical conductivity. Using a Leica EM ACE600 high-vacuum coater, to mitigate charging effects on the rough fracture surfaces, the coating thickness was optimized to 10 nm for the JMRE composites, while a 5 nm layer was applied to the porous PR samples to prevent obscuring fine pore details.

3.6 Mechanical Characterizations

Mechanical testing, including quasi-static tensile testing, cyclic fatigue, step-cyclic loading, fracture energy, and puncture resistance, was performed using a universal testing machine (Instron 5967, USA). The system was equipped with interchangeable 50 N and 30 kN load cells. Soft samples were gripped with Instron BioPlus pneumatic grips, while higher-load experiments used wedge-action mechanical grips.

Uniaxial Tension Test

Quasi-static tensile tests were performed on Type V dog-bone specimens at a constant crosshead speed of 500 mm min^{-1} until failure ($n = 4$–5). Engineering stress (σ) was calculated as the measured force divided by the initial cross-sectional area, and engineering strain (ε) as the displacement divided by the initial gauge length. Young's modulus (E) was determined from the linear slope of the stress–strain curve in the low-strain region (1–10%).

Fracture energy density (W_f), representing the total energy absorption capacity, was calculated by integrating the area under the stress–strain curve of the unnotched specimens with a maximum strain ε_m:

$$W_f = \int_0^{\varepsilon_m} \sigma \, d\varepsilon \tag{3.10}$$

Cyclic and Hysteresis Tests

The normal stress (σ) and strain (ε) are defined as the measured force divided by the initial cross-sectional area and the displacement divided by the initial gauge distance, respectively ($n = 3$). For each cycle, the Strain Set Ratio was calculated to quantify the permanent deformation relative to the applied strain.

Cyclic tests were conducted under displacement control on Type V specimens. Samples were cycled at 100% strain amplitude and a crosshead speed of 50 mm min^{-1} for 100 cycles. The strain set, or unrecovered strain, is defined as the residual strain and was quantified for each cycle.

Mullins-type nonlinearity and elasticity were probed via step cyclic loading. During the loading–unloading cycles, specimens were sequentially strained to a maximum applied strain of 10%–800% at a rate of 50 mm min^{-1}.

Fracture Energy

Fracture energy was measured using unnotched and notched samples. The notched samples with an approximately 2-mm (30%) central precut were stretched to induce crack propagation ($n = 3$). Tests were conducted with the 50 N load cell at a constant extension rate of 500 mm min^{-1}, and fracture energy was computed from the work of fracture normalized by the fractured surface area.

The critical strain (ε_c) or stretch ratio ($\lambda_c = \varepsilon_c + 1$) was determined from the strain at peak stress in notched samples. The fracture energy (Γ) was calculated by the areal integration under the stress–strain curve for the unnotched specimen until ε_c, considering the original sample length L_0:

$$\Gamma = L_0 \int_0^{\varepsilon_c} \sigma \, d\varepsilon \qquad (3.11)$$

Fractocohesive Lengths

The ratio of these two parameters, Γ/W_f, defines a material-specific length, which is called fractocohesive length (l_f), indicating the flaw-sensitive lengths:

$$l_f = \frac{\Gamma}{W_f} \qquad (3.12)$$

Puncture Tests

Puncture tests were performed using a 30 kN load cell. An 18-gauge sharp cylindrical needle (tip radius $\approx$ 0.2 mm) was driven at 50 mm min^{-1} through elastomer films 0.2–0.5 mm thick, clamped between concentric circular fixtures (20 mm aperture). Force–displacement curves were recorded continuously to quantify puncture resistance.

Compression of 3D-Printed Scaffolds

Uniaxial compression tests were performed on a 3D-printed gyroid scaffold to assess recovery and densification. The gyroid was printed from a TMPTA/NRL (42/58 wt%) DEPR ink with Tartrazine dye. Tests were conducted at room temperature (50 N load cell, 50 mm min^{-1}) using two protocols. Each printed part with dimensions of 10.94 $\times$ 10.94 $\times$ 12.94 mm was tested under two compression protocols:

Cyclic durability: 1,000 loading–unloading cycles at 20% compressive strain.

Step-recovery: Step-cyclic compression to maximum strain of 25, 50, 75% strain, with complete unloading between steps to allow recovery. Finally, samples were compressed to densification (>86% strain) to determine the ultimate compressive strength.

Measurement of Curing Depth

The curing depth was quantified using a confined-film method. Briefly, two microscope glass slides (75 mm $\times$ 25 mm) were separated by two spacers (shims) with a nominal thickness of 1.5 mm, forming a uniform gap. The emulsion photoresin was dispensed into the gap and spread to obtain a laterally uniform resin layer. The assembly was then exposed to UV light for a prescribed time under the same wavelength and irradiance conditions used for printing (385 nm; 7.7 mW cm^{-2}).

After exposure, the top glass slide was removed, and uncured resin was gently wiped off using Kimtech wipes to avoid damaging the cured layer. The thickness of the cured film was measured at three locations (e.g., center and two symmetric off-center points) using a digital caliper, and the average value was reported as the curing depth.

Resolution and Geometric Fidelity Characterization

Printing resolution was evaluated using a custom-designed test stage fabricated from ABS. The emulsion photoresin was evenly coated onto the exposure region of the stage to form a thin, uniform resin layer. A radial spoke test pattern was projected and exposed for 6 min under the same UV conditions as above. After exposure, the specimen was gently rinsed with deionized (DI) water to carefully remove uncured resin and avoid mechanical damage to the cured features.

The printed petal geometry was then imaged, and the petal opening angle of individual petals was measured and compared with the corresponding digital model. The ratio between the angular size (θ) of the printed part and the CAD design (θ_0) was used as a metric to quantify geometric fidelity.

Gel Permeation Chromatography (GPC)

The molecular weight distribution of the purified natural rubber latex was characterized using a Viscotek GPCmax system (Malvern Panalytical, UK) equipped with a Model 302-050 tetra-detector array (RI, UV, differential viscometer, and LALS). Separation was performed using two mixed-porosity PolyPore columns (5 μm particle size) in series, maintained at 40 °C with tetrahydrofuran supplied directly with the instrument to ensure high purity, serving as the mobile phase at a flow rate of 1.00 mL min^{-1}.

Prior to analysis, the dried rubber sample was dissolved in inhibitor-free tetrahydrofuran under stirring for 40 days to ensure complete dissolution, and the solution was subsequently filtered through a 0.4 μm PTFE syringe filter. Absolute molar masses were calculated via universal calibration (Omnisec software), yielding a number-average molecular weight (M_n) of 1.02×10^6 g mol^{-1}, a weight-average molecular weight (M_w) of 2.13×10^6 g mol^{-1}, and a polydispersity index of 2.09.

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