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

by

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A dissertation submitted in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy

(Mechanical Engineering)

at the

UNIVERSITY OF WISCONSIN–MADISON

2026

Date of final oral examination: 01/01/2100

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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

PLA   Polylactic Acid

PHA   Polyhydroxyalkanoates

SBR   Styrene-Butadiene Rubber

TPE   Thermoplastic Elastomer

TPU   Thermoplastic Polyurethane

PU   Polyurethane

EPDM   Ethylene Propylene Diene Monomer

SIC   Strain-Induced Crystallization

DLVO   Derjaguin-Landau-Verwey-Overbeek

SDS   Sodium Dodecyl Sulfate

DLS   Dynamic Light Scattering

PDI   Polydispersity Index

DRC   Dry Rubber Content

TSC   Total Solids Content

AM   Additive Manufacturing

VPP   Vat Photopolymerization

SLA   Stereolithography

DLP Digital Light Processing

FDM Fused Deposition Modeling

FFF Fused Filament Fabrication

DIW Direct Ink Writing

SLS Selective Laser Sintering

LOM Laminated Object Manufacturing

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

DOSY Diffusion-Ordered Spectroscopy

HSQC Heteronuclear Single Quantum Coherence

HMBC Heteronuclear Multiple Bond Correlation

COSY Correlation Spectroscopy

CPMG Carr-Purcell-Meiboom-Gill

FTIR   Fourier Transform Infrared Spectroscopy

GPC   Gel Permeation Chromatography

SEM   Scanning Electron Microscopy

TEM   Transmission Electron Microscopy

ASTM   American Society for Testing and Materials

ISO   International Organization for Standardization

OSHA   Occupational Safety and Health Administration

DOE   Design of Experiments

CFD   Computational Fluid Dynamics

LVR   Linear Viscoelastic Region

UV   Ultraviolet

O/W   Oil-in-Water

W/O   Water-in-Oil

THF   Tetrahydrofuran

TMS   Tetramethylsilane

CoA   Certificate of Analysis

LIST OF SYMBOLS

Greek Letters

Symbol	Description	Units
η	Dynamic viscosity	Pa·s
η_0	Zero-shear viscosity	Pa·s
η_∞	Infinite-shear viscosity	Pa·s
η_r	Relative viscosity (η/η_m)	–
η_m	Medium (solvent) viscosity	Pa·s
$\dot{\gamma}$	Shear rate	s^{-1}
$\dot{\gamma}_c$	Critical shear rate	s^{-1}
τ	Shear stress	Pa
τ_y	Yield stress	Pa
σ	Stress	Pa
ϕ	Volume fraction	–
ϕ_m	Maximum packing fraction	–
ϕ_c	Critical volume fraction	–
ω	Angular frequency	rad/s
δ	Phase angle; chemical shift (NMR)	°; ppm
λ	Relaxation time	s
ζ	Zeta potential	mV
κ^{-1}	Debye length	nm
Ψ_0	Surface potential	mV
ε	Dielectric permittivity; strain	F/m; –
ρ	Density	kg/m^3
Δ	Diffusion time (NMR)	ms

Latin Letters – Rheology and Colloidal Science

Symbol	Description	Units
A_H	Hamaker constant	J
c	Concentration	mol/L; wt%
C	Cross model time constant	s
D	Diffusion coefficient	m^2/s
d	Particle diameter	nm; μm
E	Young's modulus	Pa
E_a	Activation energy	kJ/mol
G'	Storage modulus	Pa
G''	Loss modulus	Pa
G^*	Complex modulus	Pa
h	Interparticle separation distance	nm
I	Light intensity; NMR signal intensity	W/m^2; a.u.
k	Rate constant	s^{-1}
k_B	Boltzmann constant (1.38×10^{-23})	J/K
K	Consistency index (power law)	$Pa·s^n$
m	Cross model rate exponent	–
M_w	Weight-average molecular weight	g/mol
n	Flow behavior index (power law)	–
p	Intrinsic viscosity exponent	–
r	Particle radius	nm; μm
R	Universal gas constant (8.314)	J/(mol·K)
T	Temperature	K; °C
t	Time	s
V	Volume	m^3
V_A	van der Waals attraction potential	J
V_R	Electrostatic repulsion potential	J
V_T	Total interaction potential (DLVO)	J

Latin Letters – NMR Spectroscopy

Symbol	Description	Units
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
b	Diffusion weighting factor	s/m^2
g	Magnetic field gradient strength	T/m
N	Linkage density	mol/m^3
N_0	Initial linkage density	mol/m^3
k_f	Formation rate constant (linkages)	s^{-1}
k_d	Degradation rate constant (linkages)	s^{-1}

Subscripts and Superscripts

Symbol	Description
0	Initial, reference, or zero-shear condition
∞	Infinite-shear or equilibrium condition
c	Critical condition
m	Medium (solvent) or maximum packing
r	Relative (ratio to solvent property)
s	Solid phase or surface
w	Wall or water

Dimensionless Numbers

Symbol	Description	Definition
Re	Reynolds number	$\rho v L/\eta$
We	Weissenberg number	$\lambda \dot{\gamma}$
De	Deborah number	λ/t_{obs}

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 INTRODUCTION

1.1 Biopolymers and Sustainable Materials

Biopolymers aren't one thing, and the labels matter because they imply different end-of-life routes. "Biopolymer" can mean (i) *a polymer made by biology* (cellulose, starch, proteins, natural rubber) or (ii) *a polymer made from bio-based feedstocks* (industry often uses "biopolymer/bioplastic" loosely). Bio-based (renewable) means the carbon comes from contemporary biomass rather than fossil carbon; it says nothing by itself about degradability. Biodegradable means microbes can mineralize the material (to CO_2/CH_4, water, and biomass) under specific conditions; the same polymer can behave very differently in soil, seawater, and industrial composting. Compostable is a stricter subset of biodegradable: it must meet defined performance standards in composting conditions. Circular is not a synonym for biodegradable; it is a systems goal: keep carbon and value in circulation via reuse, mechanical/chemical recycling, and use biodegradation only when it is a controlled, appropriate end-of-life pathway (e.g., contaminated organics packaging).

In practice, materials like Polylactic Acid (PLA) are bio-based and (industrially) biodegradable; Polyhydroxyalkanoates (PHA) are bio-based and biodegradable; cellulose is a true biopolymer and biodegradable; bio polyethylene "bio-PE" is renewable but *not* biodegradable (it's chemically the same as PE).

This matters because regulation and brand risk are now shaping materials selection, especially in packaging. Market tracking consistently shows packaging as the dominant biopolymer application (~38.6% revenue share in 2023) and biodegradable polyesters as the leading product family (~45% share in 2023), which aligns with the "short-lived, high-volume" pain point where end-of-life is the bottleneck. Policy is a major driver of demand: the

EU's single-use plastics framework targets common disposable items (e.g., cutlery, plates, straws) and requires substitution and redesign. At the same time, biobased plastics remain a small slice of total plastics output (production capacity on the order of ~0.5% of global plastics), which is why "biopolymers everywhere" is not a near-term default. Natural rubber is a renewable elastomer already produced at an industrial scale (~13.6 million tons in 2019, comparable to ~15.1 million tons of synthetic rubber), demonstrating that bio-sourced polymers can reach commodity volumes when supply chains, processing, and performance are locked in.

So, what's stopping broader adoption is mostly cost + processing + end-of-life fit, not a lack of "green intent." Many bioplastics still carry a cost premium, often reported at ~2–3× that of conventional plastics, and sometimes higher in specific applications because petrochemical polymers have brutal economies of scale, optimized assets, and mature logistics. On the processing side, biopolymers often have narrower processing windows: moisture-driven hydrolysis (e.g., polyesters like PLA/PBS), lower thermal stability, different crystallization kinetics (affecting shrinkage/warpage), and rheology issues such as low melt strength or inconsistent shear-thinning, which complicate extrusion, thermoforming, and high-speed packaging lines. Those gaps get "patched" with compatibilizers, chain extenders, nucleating agents, plasticizers, and multilayer structures, with each addition increasing cost and recycling complexity. End-of-life is the third wall: mechanical recycling streams are sensitive to contamination; composting requires correct collection infrastructure and clear labeling; and "biodegradable" claims can backfire when disposal conditions don't match the material's biodegradation pathway.

1.2 Developing Circular Economies

The concept of a circular economy must be understood as a rigorous materials-flow strategy rather than a synonym for "bio-based" or "biodegradable" labeling. This distinction establishes a dialectic between the noumenon, the abstract ideal of "circularity," and the phenomenon, which constitutes the measurable realities of mass balances, energy use, emissions, and waste leakage. While the label serves as a guiding principle, it only earns its validity when the physical flows successfully close without generating excessive externalities. The resolution of this tension requires moving beyond the philosophical adoption of sustainability terms to a quantitative audit of material lifecycles, recognizing that a loop is only truly closed when the energy and material inputs of recovery are lower than those of virgin extraction.

This thermodynamic reality challenges the circularity of fossil-derived elastomers. The lifecycle of these materials begins with an established energy penalty involving drilling, refining, and steam cracking to produce monomers like butadiene and styrene, and recycling aims to mitigate this by reducing virgin feedstock demand. However, this proposition faces a stark antithesis: recycling is rarely thermodynamically free. Mechanical recycling is constrained by property drift and contamination, while chemical routes such as solvolysis or pyrolysis require high temperatures and purification trains that reintroduce significant heat and reagent intensity. Consequently, the circularity of fossil polymers often amounts to trading a feedstock debt for an energy debt.

Natural Rubber Latex (NRL) introduces a unique biological advantage to this equation, yet it faces its own material dialectic. The thesis of NRL is its superior carbon source: it is "manufactured" *in planta* via photosynthesis, sequestering carbon and arriving at the factory gate as a processable colloid without the energy intensity of synthetic polymerization. However, the antithesis arises at the end-of-life: while raw rubber

is biodegradable, high-performance applications require vulcanization, creating a crosslinked network that resists biological breakdown and complicates reprocessing. This physical constraint limits current circular options to downcycling (crumb rubber) or energy recovery, rather than true biological reintegration. The resolution of this dialectic clarifies the technical path forward: while NRL solves the sustainable sourcing problem, the industry must still confront the physics of the crosslinked network.

1.3 Meeting Global Demand and Feedstock Diversification

Natural rubber remains hard to replace because its *cis*-1,4 polyisoprene chains undergo strain-induced crystallization, which gives a combination of green strength, fatigue resistance, resilience, and low heat buildup that many synthetic elastomers match only partially or at higher formulation complexity. This is why natural rubber shows up in tires, belts, hoses, vibration isolators, footwear, and medical goods, and why tire manufacturing dominates demand; in the European Union, roughly three-quarters of natural rubber consumption is used for tires.

Global production illustrates both maturity and constraint: in 2019, natural rubber production was about 13.6 million tonnes, approaching the roughly 15.1 million tons produced from synthetic rubber sources, and around 85% of natural rubber supply is linked to smallholder farming systems. These are strengths for resilience and livelihoods, but they also create bottlenecks for quality consistency, supply stability, and rapid capacity expansion, especially when weather, disease pressure, and price volatility intersect with rising demand from transportation and infrastructure.

Feedstock diversification is the practical hedge against those bottlenecks. *Hevea* is geographically constrained to tropical regions and has biological vulnerabilities, so alternative latex crops such as guayule (*Parthe-*

nium argentatum) and rubber dandelion (*Taraxacum koksaghyz*) are being developed as temperate-zone sources that can enable domestic supply chains and reduce exposure to regional shocks. These crops also open application niches, including hypoallergenic latex options, while advances in extraction and purification using tailored flocculants, chelators, and process control are improving yield and consistency.

1.4   Emerging Technological Interest

Natural materials often exhibit extraordinary performance because their hierarchical structures and compositions were honed through evolution. In the specific case of elastomeric biopolymers, NRL serves as 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 these biological residues as impurities to be removed, yet they are actually critical engineering variables that link polymer chains to form a naturally reinforced network. These components endow the material with "green strength" and the ability to strain-crystallize, properties that synthetic analogues struggle to replicate.

Progressive processing is where the circular story either becomes real or stays a slogan. In elastomer processing, mastication is the classic "make it processable" step, and it works by mechanically cleaving chains to reduce viscosity. The cost is irreversible chain scission that throws away the very long-chain physics that gives 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, while mastication can degrade chains to roughly 440 repeat units per chain, which then requires higher crosslink densities to obtain usable networks. That is the mastication paradox: you gain flow, but you pay with shorter strands, lower damage tolerance, and less "room"

for Strain-Induced Crystallization (SIC) to do its job.

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," where the long polymer chains needed for strength create a 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 synergy between living feedstocks and robotic control grants engineers an unprecedented degree of freedom to design responsive, hierarchical materials.

1.5 Problem Statement and Research Motivation

Preservation Chemistry

Fresh natural rubber latex is a reactive biological colloid, so it will not stay "liquid and usable" on its own. After tapping, microbial growth and enzyme-driven chemistry shift the serum conditions, destabilize the rubber particle interface, and trigger spontaneous coagulation and putrefaction, which makes the latex malodorous and unprocessable. Preservation is therefore a logistics requirement, not an optional additive, because it must keep latex stable during storage, transport, and downstream conversion.

The historical solution is alkaline preservation, where ammonia raises pH to suppress microbial activity while also stabilizing rubber particles through electrostatic repulsion, often with secondary stabilizers such as zinc oxide and TMTD. The engineering and environmental cost of this approach is now hard to ignore: ammonia is volatile and hazardous to handle, it drives wastewater constraints that smallholders struggle to manage, and its high alkalinity can discolor latex, corrode equipment, and

add downstream neutralization burden. Meanwhile, TMTD can generate carcinogenic nitrosamines under high-temperature processing.

An ideal preservative for NRL, therefore, has a clear technical job description:

- Inhibit microbial growth strongly enough to prevent acidification and putrefaction

- Maintain colloidal stability by increasing surface charge and electrokinetic potential

- Control trace multivalent ions through sequestration or precipitation

- 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

- Preserve the native protein–lipid interphase and molecular integrity

Processing Challenges: The Gap Between Microstructure and Macroscopic Flow

The central motivation for this research is the critical need to bridge the disconnect between the microscopic properties of NRL and its macroscopic processability. NRL is not a simple fluid, but a sophisticated colloidal suspension of polyisoprene particles modified by a complex interface of proteins and lipids. Key processing parameters, including viscosity, yield stress, thixotropy, and post-shear recovery, are intrinsically governed by the arrangement and interaction of these particles. However, to engineer

high-performance adhesives or 3D printing inks, we must move beyond empirical observations to predictive models that correlate these structural characteristics with rheological behavior.

Current theoretical frameworks are insufficient for this task. Existing models for complex sphere suspensions describe how relative viscosity diverges near maximum packing and explain shear thickening via hydrodynamic clustering, but they fail to address the unique complexities of deformable, core-shell rubber particles. At high volume fractions, hydrodynamic lubrication becomes dominant, requiring models that incorporate both colloidal forces (hydrodynamic drag, Brownian motion, electrostatic repulsion) and the elastic properties of the polymer core.

Deficiency of Models and the Need for Standardization

This theoretical gap is compounded by practical processing constraints and a historical bias in the available data. Industrial processing is increasingly constrained by stringent regulations, such as the OSHA 8-hour ammonia emission limit (50 ppm), which necessitates a shift toward alternative preservation chemistries. However, switching preservatives fundamentally alters the physical properties of the latex, including surface charge density, protein conformation, and mechanical and thermal behavior. Current rheological models are "conservative" in that they are calibrated almost exclusively on ammoniated *Hevea* latex or synthetic systems, meaning our foundational knowledge is biased toward a material standard that is becoming obsolete.

Furthermore, these models overlook critical biological variations, such as the distinct particle size distributions observed in alternative species: Guayule (0.44–2 µm) and Dandelion (0.35 µm), which differ significantly from those of *Hevea*. To address this, we must benchmark NRL across different conditions to build a unified classification framework based on:

(I) **Origin**: Hevea, Guayule, Dandelion

(II) **Preservation System**: High/Low Ammonia, TMTD, Acid-Surfactant

(III) **Quantifiable Properties**: Particle Size Distribution, Solids Content, Molecular Weight

1.6 Research Objectives and Scope

Core Problem

Natural rubber latex is processed and modeled largely through the lens of ammonia-preserved systems. As the field moves toward safer, low-to-zero ammonia preservation, latex behaves like a different material class because preservation chemistry alters the particle interface, non-rubber constituents, and network formation. The result is a gap: we do not yet have a unified structure-rheology-processability framework that spans preservation conditions, so engineering choices become trial-and-error, and advanced manufacturing routes remain underexploited.

Research Objective and 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.

Objective 1: Map how preservation chemistry reshapes flow and microstructure

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

Objective 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 LITERATURE REVIEW

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 (TPE)) . 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 (SBR), 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 does not account for physical failure mechanisms such as bond rupture. However, a simulation study suggests that significant enthalpic chain stretching occurs before tensile failure.

Natural Rubber Latex

Natural rubber is a biopolymer known for its hyperelasticity, biocompatibility, and abundance in nature, occurring as a colloidal sol called *latex*. 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.

NRL is synthesized via a conserved isoprenoid pathway that also produces dolichols, polyprenols, and quinones. The process begins with the formation of isopentenyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP) through either the mevalonate (MVA) or methylerythritol phosphate (MEP) pathway. These C_5 units are polymerized in four phases, with *trans*-prenyltransferases (tPTs) in Phase 2 generating short all-*trans* primers (C_{10}–C_{20}). The subsequent elongation, catalyzed by *cis*-prenyltransferases (cPTs), introduces *cis*-double bonds, forming NR's characteristic *cis*-1,4-polyisoprene backbone.

The primary source of NRL is *Hevea brasiliensis*, which contains rubber particles (RPs) ranging from 0.08 to 2 µm in diameter. Alternative rubber-producing plants, including Guayule (*Parthenium argentatum*), are being explored, which produce RPs with uniform size (~0.5 µm). Russian

dandelion (*Taraxacum koksaghyz*) yields smaller RPs (~0.35 μm) with a unimodal distribution. *Ficus* species (*F. benghalensis*, *F. elastica*) generate larger RPs (1.6–6.0 μm) but with comparable polymer quality. NRL is collected through tapping, an incision of the trunk that requires immediate preservation to prevent putrefaction and premature coagulation during transport and processing.

Ammonia remains the most effective preservative, stabilizing rubber particles through electrostatic repulsion while inhibiting microbial growth. However, it's a double-edged sword; ammonia production requires extensive resources, making it highly volatile (OSHA limits exposure to 50 ppm over an 8-hour shift), 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) and completely ammonia-free options using zinc complexes or bio-based antimicrobials, as well as surfactants. Examples include:

- **Chitosan-based systems** (derived from crustacean shells) provide antimicrobial protection but require low molecular weights and surfactants to prevent destabilization of latex particles.

- **HTT (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 that **AFLatex Technology LDA** supplies eliminates ammonia use while maintaining colloidal stability.

- **Ethoxylated tridecyl alcohol (ETA) + hydrofluoric acid (HF)**: ETA stabilizes latex particles, while HF reacts with glutathione to form glutathione, an antimicrobial compound.

2.2   The Theory of Natural Rubber Latex

Tanaka and Sakdapipanich's innovative framework presents a compelling solution to the materials puzzle surrounding natural rubber (NR), revealing its distinct behavior as "more structured" compared to a simple *cis*-1,4-polyisoprene melt. This observation is evidenced by the presence of a gel fraction, long-chain branching signatures, and storage hardening phenomena, which they posit as emergent properties resulting from non-rubber functionalities rather than the polyisoprene backbone alone.

Their methodology is notably deconstructive, initiating with strategies such as deproteinization to remove proteins, the addition of a polar co-solvent to disrupt weak associations, and targeted cleavage of chemical linkages through techniques like transesterification/saponification and enzymatic digestions. A key aspect of their investigation is the subsequent monitoring of gel content along with molecular weight and branching metrics. The pronounced increase in gel content observed with ammonia aging, along with the differential impact of various "handles" (e.g., 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: that 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 a quantitative analysis of residual nitrogen and comparison of vibrational signatures to established peptide models. Preliminary evidence hinges on the persistent nitrogen content in depolymerized natural rubber (DPNR) post-deproteinization, shown through Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy and Nuclear Magnetic Resonance (NMR) analysis, which underscore the retention of nitrogenous functionalities indicative of its potential role in forming hydrogen bonds 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 seg-

ment 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 DPNR 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 (STORM) directly visualizes proteins and lipids as segregated, coexisting phases around the particle ensemble. Proteins appear discontinuous and preferentially outside large rubber particles (LRP), while lipids localize within the LRP; 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, i.e., the interfacial material does not vanish; it phase-separates and re-packs.

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 et al., for example, analyzed concentrated latexes with dry rubber content (DRC) of 76.9 wt% and 61.9 wt% under high-ammonia (~0.7 wt%) and low-ammonia (~0.2 wt%) preservation conditions. A centrifuged latex (CL) rubber fraction contains approximately 0.23 wt% nitrogen (N), while high-ammonia concentrated latex (HAL) and fresh latex (FL) exhibit nitrogen levels of about 0.52 wt% and 0.56 wt% N, respectively. These figures are challenging to attribute to "mere trace contamination" as they correspond with the processing state. Additionally, Sriring et al. explore complementary film-formation mechanics, noting that an increase in the small rubber particle (SRP) 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" SRP 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 that equilibrium stress by ~75%, and transesterification drives the relaxation essentially to zero, which the authors interpret as dismantling branching/association points tied 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 NR (DPNR), again pointing to a mechanically active, non-rubber-mediated constraint system.

The SIC as a function of temperature increasingly supports the "network" interpretation, particularly regarding the long-known anomaly that unvulcanized NR exhibits SIC at 25 °C, while synthetic polyisoprene behaves like a viscous melt, showing no SIC, at 0, −25, and −50 °C. 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 SIC 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 2.0–3.4×10^5 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 SIC, and constraints derived from NMR behave as though there are network-like points that survive processing, acting like end-linked anchors. The unresolved issue, which represents a legitimate focus for later chapters, 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?

This debate is not merely semantic, as unvulcanized natural rubber exhibits rubber-like stress responses and SIC at ambient temperature, in ways not observed in synthetic *cis*-polyisoprene, suggesting the existence of constraints beyond simple melt entanglements.

2.3 Colloids

Colloids are particles that range from micrometers to nanometers in size and must behave according to classical physics. They possess two unique properties: 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 considers the gravitational force acting downward, as described by:

$$W = \rho_p V g \tag{2.2}$$

and an upward buoyancy force from the displaced solvent:

$$B = \rho_m V g \tag{2.3}$$

The net (buoyant) body force is therefore:

$$F_g = W - B = (\rho_p - \rho_m)V g \equiv \Delta\rho\, V g \tag{2.4}$$

which is conservative and can be written via a gravitational potential energy (taking z upward):

$$U_g(z) = \Delta\rho\, V g\, z \tag{2.5}$$

Thermal fluctuations supply an energy scale of order $k_B T$, which sets the characteristic height over which gravity significantly biases particle positions. Defining the gravitational length:

$$l_g = \frac{k_B T}{\Delta\rho\, V g} \tag{2.6}$$

we see that when l_g is comparable to or larger than the particle size, thermal motion can counteract sedimentation.

Quantitatively, Brownian motion is captured by mean-squared displacement. Over time t in d dimensions:

$$\sqrt{\langle\Delta r^2\rangle} = \sqrt{2dDt}, \quad D = \frac{k_B T}{6\pi\eta a} \tag{2.7}$$

where D is the Stokes–Einstein diffusivity, η is the solvent viscosity, and a is the particle radius. A compact way to express the "colloidal (Brownian) regime" is that thermal motion dominates gravitational drift on the particle

scale:

$$l_g \gtrsim a \quad \text{(equivalently, a gravitational Péclet number } Pe_g \equiv \frac{v_s a}{D} \lesssim 1) \tag{2.8}$$

with v_s the Stokes settling speed.

The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory identifies two primary interactions. When particles are in the Brownian regime, "stability" is determined by the interplay between thermal energy and the pair potential. The total interaction free energy between two particles is expressed as:

$$U_{tot}(h) = U_{vdW}(h) + U_{EDL}(h) \tag{2.9}$$

and the dispersion is largely controlled by whether the repulsive barrier satisfies $U_{max} \gg k_B T$ (metastable dispersion) or $U_{max} \lesssim k_B T$ (rapid aggregation). A common "engineering" threshold is $U_{max} \gtrsim 10\, k_B T$ for practical stability, yet the system's dynamics also depend on kinetic and hydrodynamic factors.

When the particle surface is charged (characterized by a surface charge density σ or surface potential ψ_0), ions in the liquid form an electrical double layer. In the context of an electrolyte, Coulomb interactions are screened, and within the linear Debye–Hückel approximation, the potential surrounding a particle diminishes exponentially according to $e^{-\kappa r}/r$, where κ is the inverse Debye length. The Debye length is $\lambda_D = 1/\kappa$, with:

$$\kappa^2 = \frac{2e^2 N_A I}{\varepsilon_m \varepsilon_0 k_B T} \iff \lambda_D = \sqrt{\frac{\varepsilon_m \varepsilon_0 k_B T}{2e^2 N_A I}} \tag{2.10}$$

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.

For two equal spheres of radius a with constant surface potential (often

parameterized by zeta potential ζ as a practical proxy), a widely used DLVO form is:

$$U_{\text{EDL}}(h) \approx \frac{64\pi a\, n_\infty k_B T}{\kappa} \tanh^2\left(\frac{e\zeta}{4k_B T}\right) e^{-\kappa h} \tag{2.11}$$

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.

Van der Waals attraction comes from fluctuating or induced dipoles and is considered to be "always on." In the context of DLVO theory, it is represented by a Hamaker constant A, leading to the expression for two equal spheres at small separations $h \ll a$, under the Derjaguin approximation:

$$U_{\text{vdW}}(h) \approx -\frac{A\, a}{12h} \tag{2.12}$$

The attraction intensifies sharply at small separations (slow algebraic decay in h), 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 depends on the particle–medium–particle dielectric contrast. A common combining estimate is:

$$A_{131} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)^2 \tag{2.13}$$

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

With Brownian colloids in motion, collisions are inevitable. The challenge is to ensure these collisions are non-sticky, so the dispersion remains in the "colloidal" size range rather than collapsing into clusters that sediment, cream, gel, or phase separate. In DLVO terminology, stability is achieved by engineering the total interaction potential to create a repulsive

energy barrier at intermediate separations. Although van der Waals attraction tries to pull particles into close contact, electrostatic double-layer repulsion pushes back. This repulsion's range is set by the Debye length, and its strength is related to the particle's effective charge or zeta potential.

If attractive forces exceed repulsive forces, Brownian motion rarely allows particles to overcome the barrier, leading them to collide, bounce, and remain dispersed ("charge-stabilized" suspension). However, if added electrolytes or chemical changes reduce the repulsion and/or the effective charge to the point where attractive forces prevail, particles can enter the primary minimum, triggering coagulation and subsequent aggregation. This is why high-salt environments can destabilize dispersion. Stabilization is essential when you want the system's properties, including optical clarity, viscosity, shelf life, coating uniformity, adhesive performance, and printability, to remain consistent over time. Without it, the system can change its microstructure through aggregation and sedimentation, making measured material properties unreliable.

In practice, the interaction between colloids is more accurately described by an effective potential, where surfactants introduce additional short-range terms that DLVO does not account for. Steric (or electrosteric) repulsion occurs when adsorbed surfactant or polymer layers overlap; this overlap reduces chain conformational entropy and increases local segment concentration, resulting in an osmotic penalty. In terms of brush language, this produces a steep, largely salt-insensitive repulsive wall, which is why nonionic or polymeric stabilization can persist even when the electric double layer is screened. Hydration (solvation) forces come into play when hydrophilic head groups (e.g., ethoxylates, zwitterionic groups) bind to structured water. Bringing two such surfaces within approximately 1 nm requires expelling this hydration layer, resulting in exponentially decaying repulsion at distances on the order of nanometers that can dominate contact behavior.

Surfactant Stabilization Mechanisms

Surfactants stabilize colloids by controlling what happens at the particle–water interface. Three common mechanisms map onto surfactant classes:

(i) **Ionic surfactants** contribute to electrostatic stabilization. Anionic Sodium Dodecyl Sulfate (SDS) adsorbs with its sulfate headgroup exposed, which typically results in a more negatively charged surface, thereby increasing the zeta potential and enhancing the DLVO repulsive barrier.

(ii) **Nonionic surfactants** contribute to steric stabilization. Examples include Tween (polysorbates) or ethoxylated surfactants, which adsorb onto particle surfaces to form a hydrated, polymer-like brush layer.

(iii) **Zwitterionic surfactants** exhibit pH- and ion-sensitive behavior. Their betaine-like head groups carry both positive and negative charges; depending on the pH and specific ionic environment, they can display either more cationic or more anionic characteristics.

2.4 Suspensions Rheology and Theoretical Models

Viscosity represents the fluid's internal resistance to flow. It quantifies the rate at which mechanical energy is dissipated into heat due to friction between fluid layers. In colloidal systems, viscosity arises because the solid particles disturb the flow of the liquid, forcing flow lines to bend and compressing fluid elements, which increases energy dissipation. The viscosity of a colloid (η) is usually compared to the medium's viscosity (η_m) as the Relative Viscosity (η_r). Since colloids experience strong hy-

drodynamic coupling through the solvent and exhibit Brownian motion, their rheology is governed by a competition between:

(i) thermal forces that randomize structure,

(ii) viscous dissipation from solvent flow around particles, and

(iii) interparticle forces that stabilize or aggregate the dispersion.

Brownian motion sets the intrinsic structural relaxation rate via the Stokes–Einstein diffusion coefficient:

$$D_0 = \frac{k_B T}{6\pi \eta_s a} \tag{2.14}$$

where a is particle radius and η_s is solvent viscosity. A characteristic Brownian time is $\tau_B \sim a^2/D_0$, which leads to a dimensionless shear rate (Péclet number):

$$Pe = \dot{\gamma}\tau_B \tag{2.15}$$

When $Pe \ll 1$, microstructure relaxes faster than the imposed deformation, and the suspension behaves near equilibrium; when $Pe \gtrsim 1$, flow distorts microstructure faster than Brownian rearrangement, producing rate-dependent viscosity.

Predictive Viscosity Models

The historical starting point is Einstein's 1905 result for infinitely dilute, rigid, noninteracting spheres in a Newtonian solvent:

$$\eta_r \equiv \frac{\eta}{\eta_s} = 1 + [\eta]\phi = 1 + 2.5\phi \tag{2.16}$$

Here $[\eta] = 2.5$ is the intrinsic viscosity of a sphere, obtained from solving the Stokes (creeping-flow) problem around an isolated particle.

Moving beyond "infinitely dilute" means admitting that particles feel each other. The next correction is the ϕ^2 term:

$$\eta_r = 1 + 2.5\phi + k_2\phi^2 + \cdots \tag{2.17}$$

where k_2 encodes pairwise hydrodynamic interactions plus any microstructural bias.

Once ϕ becomes large enough, pairwise corrections stop being the main story. Many-body constraints appear, particles become caged by neighbors, and viscosity rises dramatically as the system approaches a packing-limited state. The Krieger–Dougherty expression provides a widely used refinement:

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \tag{2.18}$$

This form is especially practical for high-solids formulations because it cleanly separates what you often know ($[\eta] \approx 2.5$ for near-spheres) from what you must fit (ϕ_m, which depends on size distribution, softness, shape, and dispersion quality).

Yield Stress and Shear-Thinning Models

After phase separation or flocculation, the microstructure stops being "crowded hard spheres" and becomes a load-bearing network. That network introduces a yield stress because at low stress the structure does not continuously rearrange; instead, it resists like a weak solid. The simplest yield-stress constitutive model is Bingham:

$$\tau = \tau_y + \eta_p\dot{\gamma} \tag{2.19}$$

but for colloidal gels and flocculated suspensions the more flexible choice is the Herschel–Bulkley form:

$$\tau = \tau_y + K\dot{\gamma}^n \quad (0 < n < 1 \text{ for shear thinning}) \tag{2.20}$$

For shear-thinning behavior without an explicit yield stress, the Cross model adds plateaus:

$$\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\lambda\dot{\gamma})^m} \tag{2.21}$$

and the Carreau–Yasuda model is a closely related, often smoother alternative:

$$\eta(\dot{\gamma}) = \eta_\infty + (\eta_0 - \eta_\infty)\left[1 + (\lambda\dot{\gamma})^a\right]^{(n-1)/a} \tag{2.22}$$

These are not just curve-fits; they have interpretable parameters. η_0 reflects the equilibrium (low-Pe) microstructure, η_∞ reflects the high-Pe state where structure is strongly distorted/ordered, and λ is a characteristic time scale that often tracks a microstructural relaxation time.

2.5 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 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 (LOM), SGC, and Selective Laser Sintering (SLS) in 1986, followed by patents for Fused Deposition Modeling (FDM) and the MIT-originated 3DP concept in 1989.

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.

Photoresins for Vat Photopolymerization

VPP (SLA/Digital Light Processing (DLP) 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.

Most VPP photoresins can be classified into five ingredient classes:

1. **Oligomers**: Define the baseline mechanical response of the cured network and strongly influence toughness, chemical resistance, and creep.

2. **Reactive diluent monomers**: Reduce viscosity while co-polymerizing into the network.

3. **Photoinitiators**: Determine usable wavelengths and conversion efficiency by converting absorbed photons into radicals or cations.

4. **Inhibitors and antioxidants**: Suppress premature polymerization during storage and printing.

5. **Additives**: UV absorbers, pigments, fillers, and plasticizers alter durability, resolution, and defect propensity.

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

Among elastomeric materials used in photocurable systems, 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 TPUs are frequently formulated near unity, for example, I of ~1.05, indicating a small isocyanate excess. Within the PU family, thermoplastic polyurethanes (TPUs) 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, TPU 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 (RTV) condensation routes or high temperature vulcanization (HTV) 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.

Emulsion-Based 3D Printing of Elastomers

3D printing has faced challenges in creating soft, stretchy, and resilient objects due to the Viscosity-Printability-Cure (VPC) 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 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. The other is Water-in-Oil (W/O), which involves 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 polyHIPE (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.

The 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 (SBR), EPDM, SIS, WPU 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 networks that deliver exceptional elasticity and tensile strength. Examples include ammonia-free natural rubber systems that achieve $\geqslant$900% elongation, silica-reinforced SBR with dramatically increased modulus and hardness, sulfonated EPDM and polyurethane latexes tuned via reactive or non-reactive end groups, and SIS triblock systems that leverage microphase separation to exceed 800% elongation.

In contrast, emulsion templating relies on water-in-oil High Internal Phase Emulsions (HIPEs) or related emulsions, in which the aqueous phase acts as a porogen; curing the continuous phase and evaporating water yield highly porous scaffolds. PCL-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 VOC, 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.

Latex-scaffold coalescence systems are fundamentally limited by the

formation of a rigid semi-interpenetrating network (sIPN) 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 necessitates complex surfactant optimization to mitigate thermodynamic instability against 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 RESEARCH METHODOLOGY

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% Dry Rubber Content (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.

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.

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.

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 time (MST)

- Volatile fatty acid number/index (VFA)

- Solids content (TSC/DRC)

- Brookfield viscosity

Incoming Verification

Upon receipt, each latex batch was independently verified to confirm it matched the supplier's CoA 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: ~10 g latex was diluted to ~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).

Particle-level stability was checked by Dynamic Light Scattering (DLS)/zeta 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 (PDI), and zeta potential were reported with dilution factor and diluent composition.

3.2 Spectroscopic and Analytical Reagents

Deuterated 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 [TMS] 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.

Photopolymerization and Surfactant Reagents

- Trimethylolpropane triacrylate (Trimethylolpropane Triacrylate (TMPTA), technical grade, 246808)

- Phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide (Phenylbis(2,4,6-trimethylbenzoyl)-phosphine Oxide (TPO), 97%, 511447)

- Tartrazine (Acid Yellow 23, ⩾85%, T0388)

- Tween 20 (polyoxyethylene (20) sorbitan monolaurate)

were obtained from Millipore Sigma, USA.

- Ebecryl 114 (2-phenoxyethyl acrylate, 024572A)

- Ebecryl IBOA (isobornyl acrylate monomer, 024944B01Z01)

- Ebecryl 8413 (pigment-grind urethane-acrylate oligomer, 029588A)

were supplied by Allnex, USA.

1,6-hexanediol diacrylate (1,6-Hexanediol Diacrylate (HDDA), 99%, 043203.30) was purchased from Thermo Scientific, USA. Span 80 (sorbitan monooleate, S0060) was ordered from TCI Chemicals. Acetate buffer solution (pH 4.66, 1.07827.1000) was acquired from Merck, Germany.

3.3   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.

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. 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.

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.

label=(i) **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.

lbbel=(ii) **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.

lcbel=(iii) **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.

Computational Fluid Dynamics

Taylor–Couette measurements and simplified two-phase-flow interpretation. 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

To interpret viscosity–shear rate data across volume fraction ϕ, a microstructure-based picture is used 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 of effective interparticle linkages contributing to resistance to flow, and N_0, the maximum linkage density at rest. Under shear, linkages break at a rate that scales with both how much structure exists and how strong the imposed deformation is:

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

where k_d is the breakage rate constant, $\dot{\gamma}$ is shear rate, m is the shear-sensitivity exponent, and k_r is the reformation rate constant.

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

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

The steady shear viscosity is then written using the Cross model:

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

Viscosity and Volume Fraction

To relate viscosity to volume fraction ϕ, the classical Mooney/Krieger–Dougherty framework for concentrated suspensions is used. The Krieger–Dougherty expression predicts a divergence of η_r as ϕ approaches an

effective critical/maximum packing fraction ϕ_c:

$$\eta_r(\phi) = \left(1 - \frac{\phi}{\phi_c}\right)^{-[\eta]\phi_c} \tag{3.4}$$

To capture the experimentally observed sharper upturn near ϕ_c in preserved natural latex, an extended form is used:

$$\boxed{\eta_r(\phi) = \left(1 - \frac{\phi}{\phi_c}\right)^{-[\eta]\phi_c} + \exp\left[a(\phi - \phi_c) + b\right]} \tag{3.5}$$

where a and b are empirical fit parameters. Here, a controls how rapidly the additional thickening accelerates, while b sets its baseline magnitude.

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:

$$\tau = K_\tau M, \quad \dot{\gamma} = K_\gamma \Omega, \quad \eta_{app} = \frac{\tau}{\dot{\gamma}} = \frac{K_\tau}{K_\gamma} \frac{M}{\Omega} \tag{3.6}$$

These relations are only valid if three physical assumptions hold:

label=(i) no slip at the walls ($v_{fluid} = v_{wall}$),

lbbel=(ii) homogeneity across the gap (ϕ and hence η independent of position),

lcbel=(iii) 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 $\phi(\mathbf{r})$ 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.

3.4   Nuclear Magnetic Resonance (NMR)

Overview and General Conditions

All NMR experiments were performed at 303 K on two solution-state instruments:

label=(i) a Bruker Avance I 600 MHz equipped with a Prodigy cryoprobe (Z150313_001; cpT4600ss3H&F-LIN-D-05Z)

lbbel=(ii) 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 TMS ($\delta_H = 0$ ppm), CDCl$_3$ ($\delta_H = 7.26$ ppm), or D$_2$O/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 at 10 mg per 0.6 mL D$_2$O in standard 5 mm NMR tubes. 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)

- 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).

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 HSQC (multiplicity-edited): hsqcedetgpsisp2p.3 (NS = 8)

- HMBC: hmbcgpndqf (NS = 8)

- ^{1}H–^{1}H COSY: cosygpprqf.uw (NS = 64)

- ^{31}P 1D: zgig30 (NS = 256)

- DEPT-135: dept-135 (NS = 1005)

Data were processed in MestReNova. Free induction decays (FIDs) were Fourier transformed after zero-filling to $2\times$ points.

Diffusion-Ordered Spectroscopy (DOSY)

Diffusion-Ordered Spectroscopy (DOSY) 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 coefficients D were obtained by fitting the diffusion-dependent signal attenuation to the Stejskal–Tanner relation:

$$I(g) = I_0 \exp\left[-b(g)D\right] \tag{3.7}$$

with

$$b(g) = \gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \tag{3.8}$$

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

Hydrodynamic radius was estimated using the Stokes–Einstein equation:

$$r_h = \frac{k_B T}{6\pi\eta D} \tag{3.9}$$

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 CPMG sequence with d1 = 4 s, d20 = 0.001 s, L4 = 2, and NS = 8.

T_1 relaxation times were extracted by fitting to a mono-exponential recovery model:

$$M(t) = M_0 \left(1 - 2e^{-t/T_1} \right) + C \tag{3.10}$$

T_2 relaxation was quantified from CPMG decay curves by fitting to a biexponential decay model:

$$M(t) = A_1 e^{-t/T_{2,1}} + A_2 e^{-t/T_{2,2}} + C \tag{3.11}$$

3.5   Components and Protocols of NRL Photoresin Formulation

Advanced manufacturing of NRL requires a carefully engineered photoresin that balances printability, cure kinetics, and mechanical performance.

Preparation of the UV-Curable Latex-Scaffold Coalescence

0.9 wt% SDS 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% HDDA was incorporated into the solution under low Kelvin lighting conditions with slow dispersion mixing for 5 min. Following this, approximately 4.5 wt% TPO photoinitiator was added, and the mixture underwent slow 1.5-h mixing 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.

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:

- **Oil phase** (60 wt% of total emulsion): base monomer (HDDA or TMPTA) supplemented with 1.0 wt% photoinitiator (TPO) and 0.75 wt% low-HLB surfactant (Span 80).

- **Aqueous phase** (40 wt% of total emulsion): 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 $\approx$ 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.

Preparation of Dual Emulsion Photoresin (DEPR)

DEPRs were prepared by blending the O/W PRE with NRL. To evaluate the effect of photoresin loading, a Design of Experiments (DOE) 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.

3.6   Material Characterizations

Particle Size and Zeta Potential

The droplet size and surface charge of the photoresin emulsions were characterized using 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. Measurements were performed in dispos-

able folded capillary cells (DTS1070) at 25°C after a 120 s equilibration period.

(Photo)rheology Characterizations

Rheological measurements were performed using a Discovery HR-20 hybrid rheometer (TA Instruments, USA) utilizing a 20 mm parallel-plate geometry. 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.

label=I. **Shear viscosity**: Flow behavior 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.

lbbel=II. **In-situ photorheology**: Real-time photopolymerization kinetics were monitored using the UV-Curing Accessory Kit (TA Instruments). UV irradiation was supplied by an OmniCure Series 2000 system 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%.

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 VAT 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, microreinforced elastomers (JMRE). This nomenclature reflects the transition from a jammed micro-emulsion state to a reinforced elastomeric composite.

label=I. **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^{-2}) using an OmniCure S200 Elite system. This step locked the photoresin phase (PRE) into a rigid porous scaffold, establishing the green composite structure.

lbbel=II. **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.

lcbel=III. **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.

Morphological Characterization (SEM)

Surface and cross-sectional morphologies were examined using a Gemini SEM 450 (Zeiss, Germany). The microscope was operated at an accelerat-

ing voltage of 3.00 kV with a working distance of ~9.2 mm to minimize beam damage and charging on the polymeric samples.

label=I. **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.

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

lcbel=III. **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.

3.7   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.

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:

$$W_f = \int_0^{\varepsilon_m} \sigma \, d\varepsilon \tag{3.12}$$

Cyclic and Hysteresis Tests

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 a ~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}.

The fracture energy (Γ) was calculated by the areal integration under the stress-strain curve for the unnotched specimen until ε_c:

$$\Gamma = L_0 \int_0^{\varepsilon_c} \sigma \, d\varepsilon \tag{3.13}$$

The fractocohesive length (l_f) is defined as:

$$l_f = \frac{\Gamma}{W_f} \tag{3.14}$$

Puncture Tests

Puncture tests were performed using a 30 kN load cell. An 18-gauge sharp cylindrical needle (tip radius ≈ 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:

label=a) **Cyclic durability**: 1,000 loading–unloading cycles at 20% compressive strain.

lbbel=b) **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.

3.8   DLP 3D Printing

3D printing was performed on a home-made DLP 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 repositories. 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 was 75 μm, and the exposure time was 20 s per layer. After printing, the parts were removed from the build platform and post-treated in an oven at 70°C overnight.

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. The thickness of the cured film was measured at three locations 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.

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·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.

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 ~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.

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 (THF) 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 THF 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:

- Number-average molecular weight (M_n): 1.02×10^6 g mol^{-1}

- Weight-average molecular weight (M_w): 2.13×10^6 g mol^{-1}

- Polydispersity index (PDI): 2.09

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REFERENCES