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Not Finished, But Abandoned

by

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the requirements for the degree of

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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.

CONTENTS

Contents iii

List of Tables iv

List of Figures v

LIST OF ACRONYMS vi

LIST OF SYMBOLS vii

Abstract xii

1 Introduction 1

- 1.1 *Biopolymers and Sustainable Materials* 1
- 1.2 *Developing Circular Economies* 2
- 1.3 *Meeting Global Demand and Feedstock Diversification* 4
- 1.4 *Emerging Technological Interest* 5
- 1.5 *Problem Statement and Research Motivation* 6
- 1.6 *Research Objectives and Scope* 9
- 1.7 *Thesis Organization* 10

2 Literature Review 11

- 2.1 *Molecular Structure and Colloidal Stabilization* 11
- 2.2 *Colloids* 15
- 2.3 *The Theory of Natural Rubber Latex* 16
- 2.4 *Suspensions Rheology and Theoretical Models* 18
- 2.5 *Additive Manufacturing* 21

3 Research Methodology 26

3.1	<i>Sourcing, Traceability, and Rationale: Natural Rubber Latex Preservation Systems</i>	26
3.2	<i>Spectroscopic and Analytical Reagents</i>	29
3.3	<i>Rheological Characterization</i>	30
3.4	<i>Nuclear Magnetic Resonance (NMR)</i>	32
3.5	<i>Components and Protocols of NRL Photoresin Formulation</i>	35
3.6	<i>Material Characterizations</i>	37
3.7	<i>Mechanical Characterizations</i>	38
3.8	<i>DLP 3D Printing</i>	40
	Colophon	42

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS

FEM	Finite Element Method
FDM	Finite Difference Method
FVM	Finite Volume Method
CFD	Computational Fluid Dynamics
DNS	Direct Numerical Simulation
LES	Large Eddy Simulation
RANS	Reynolds-Averaged Navier-Stokes
EOS	Equation of State
LTE	Local Thermodynamic Equilibrium
HTC	Heat Transfer Coefficient
RVE	Representative Volume Element
PDE	Partial Differential Equation
ODE	Ordinary Differential Equation
BVP	Boundary Value Problem
IVP	Initial Value Problem
SMA	Shape Memory Alloy
FRP	Fiber Reinforced Polymer

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LIST OF SYMBOLS

Greek Letters

Symbol	Description	Units
α	Thermal diffusivity	m^2/s
β	Coefficient of thermal expansion	$1/\text{K}$
γ	Specific heat ratio (c_p/c_v)	–
δ	Boundary layer thickness; Kronecker delta	m ; –
ε	Strain tensor; emissivity	–; –
$\dot{\varepsilon}$	Strain rate	$1/\text{s}$
ζ	Damping ratio	–
η	Dynamic viscosity (alternative notation)	$\text{Pa}\cdot\text{s}$
θ	Temperature (dimensionless); angular coordinate	–; rad
κ	Thermal conductivity; bulk modulus	$\text{W}/(\text{m}\cdot\text{K})$; Pa
λ	Lamé's first parameter; wavelength	Pa; m
μ	Dynamic viscosity; Lamé's second parameter (shear modulus)	$\text{Pa}\cdot\text{s}$; Pa
ν	Kinematic viscosity; Poisson's ratio	m^2/s ; –
ξ	Dimensionless coordinate	–
ρ	Density	kg/m^3
σ	Stress tensor; Stefan-Boltzmann constant	Pa; $\text{W}/(\text{m}^2\cdot\text{K}^4)$
τ	Shear stress; time constant	Pa; s
ϕ	Scalar potential; porosity; angle	various; –; rad
ψ	Stream function	m^2/s
ω	Angular velocity; vorticity	rad/s ; $1/\text{s}$
Γ	Boundary; circulation	–; m^2/s
Δ	Difference operator	–
Ω	Domain; angular velocity (rotation rate)	–; rad/s
∇	Gradient operator (nabla)	$1/\text{m}$

Latin Letters

Symbol	Description	Units
A	Area; Helmholtz free energy	m^2 ; J
\mathbf{b}	Body force per unit mass	m/s^2
c	Specific heat; speed of sound	$\text{J}/(\text{kg}\cdot\text{K})$; m/s
c_p	Specific heat at constant pressure	$\text{J}/(\text{kg}\cdot\text{K})$
c_v	Specific heat at constant volume	$\text{J}/(\text{kg}\cdot\text{K})$
\mathbf{C}	Right Cauchy-Green deformation tensor	–
\mathbb{C}	Fourth-order elasticity tensor	Pa
D	Diameter; diffusion coefficient	m ; m^2/s
\mathbf{D}	Rate of deformation tensor	$1/\text{s}$
e	Specific internal energy	J/kg
E	Young's modulus; total energy	Pa; J
\mathbf{F}	Deformation gradient; force vector	–; N
G	Shear modulus; Gibbs free energy	Pa; J
h	Specific enthalpy; heat transfer coefficient; height	J/kg ; $\text{W}/(\text{m}^2\cdot\text{K})$; m
H	Enthalpy	J
\mathbf{I}	Identity tensor	–
J	Jacobian determinant	–
k	Thermal conductivity; turbulent kinetic energy	$\text{W}/(\text{m}\cdot\text{K})$; m^2/s^2
K	Bulk modulus	Pa
L	Characteristic length	m
\mathbf{L}	Velocity gradient tensor	$1/\text{s}$
m	Mass	kg
\dot{m}	Mass flow rate	kg/s
M	Molar mass; Mach number	kg/mol ; –
\mathbf{n}	Normal direction (unit vector)	–
\mathbf{n}	Outward unit normal vector	–
p	Pressure	Pa
\mathbf{P}	First Piola-Kirchhoff stress tensor	Pa
q	Heat flux (scalar)	W/m^2
\mathbf{q}	Heat flux vector	W/m^2
Q	Heat; volumetric flow rate	J; m^3/s
\dot{Q}	Heat transfer rate	W
r	Radial coordinate; specific gas constant	m ; $\text{J}/(\text{kg}\cdot\text{K})$
R	Universal gas constant	$\text{J}/(\text{mol}\cdot\text{K})$

Dimensionless Numbers

Symbol	Description
Bi	Biot number (hL/k) – ratio of internal to surface thermal resistance
Fo	Fourier number ($\alpha t/L^2$) – dimensionless time for heat conduction
Gr	Grashof number ($g\beta\Delta TL^3/\nu^2$) – ratio of buoyancy to viscous forces
Ma	Mach number (V/c) – ratio of flow velocity to speed of sound
Nu	Nusselt number (hL/k) – ratio of convective to conductive heat transfer
Pe	Péclet number (VL/α) – ratio of advective to diffusive transport
Pr	Prandtl number (ν/α) – ratio of momentum to thermal diffusivity
Ra	Rayleigh number ($Gr \cdot Pr$) – buoyancy-driven flow parameter
Re	Reynolds number ($\rho VL/\mu$) – ratio of inertial to viscous forces
St	Stanton number ($Nu/(Re \cdot Pr)$) – heat transfer coefficient

Subscripts and Superscripts

Symbol	Description
$(\cdot)_0$	Reference state; initial condition
$(\cdot)_\infty$	Free stream condition; far-field value
$(\cdot)_{\text{avg}}$	Average value
$(\cdot)_{\text{crit}}$	Critical value
$(\cdot)_{\text{eff}}$	Effective value
$(\cdot)_{\text{eq}}$	Equilibrium value
$(\cdot)_f$	Fluid property; final state
$(\cdot)_i, (\cdot)_j, (\cdot)_k$	Tensor indices
$(\cdot)_{\text{in}}$	Inlet condition
$(\cdot)_{\text{max}}$	Maximum value
$(\cdot)_{\text{min}}$	Minimum value
$(\cdot)_{\text{out}}$	Outlet condition
$(\cdot)_s$	Solid property; surface value
$(\cdot)_w$	Wall value
$(\cdot)^*$	Dimensionless quantity; critical/sonic condition
$(\cdot)'$	Fluctuating component; derivative
$\overline{(\cdot)}$	Time-averaged quantity
$\dot{(\cdot)}$	Time derivative (rate)
$\ddot{(\cdot)}$	Second time derivative (acceleration)

Mathematical Operators

Symbol	Description
$\nabla(\cdot)$	Gradient of a scalar field
$\nabla \cdot (\cdot)$	Divergence of a vector field
$\nabla \times (\cdot)$	Curl of a vector field
$\nabla^2(\cdot)$	Laplacian operator
$\frac{D(\cdot)}{Dt}$	Material (substantial) derivative
$\frac{\partial(\cdot)}{\partial t}$	Partial derivative with respect to time
$\text{tr}(\cdot)$	Trace of a tensor
$\det(\cdot)$	Determinant of a tensor
$(\cdot)^T$	Transpose of a tensor
$(\cdot)^{-1}$	Inverse of a tensor
$(\cdot) : (\cdot)$	Double contraction of tensors
$(\cdot) \otimes (\cdot)$	Tensor (dyadic) product

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 CO₂/CH₄, 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 **PLA!** (**PLA!**) are bio-based and (industrially) biodegradable; **PHA!** (**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 $\sim 0.5\%$ 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 $\sim 2\text{--}3\times$ 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—each adding 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 “biodegrad-

able” 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—drilling, refining, and steam cracking to produce monomers like butadiene and styrene—which recycling aims to mitigate 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.

NRL! (**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 (*Parthenium 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 **SIC!** (**SIC!**) to do its job.

The successful preservation of these intrinsic molecular properties directly unlocks advanced capabilities in **AM!** (**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—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”—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:

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

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

lcbel=(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 (**TPE!** (**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 **SBR!** (**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.

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:

$$\Delta F = -T\Delta S \quad (2.1)$$

where T is temperature, ΔS is entropy, and ΔF (force) is proportional to the negative gradient of free energy with respect to deformation.

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 C₅ units are polymerized in four phases, with *trans*-prenyltransferases (tPTs) in Phase 2 generating short all-*trans* primers (C₁₀–C₂₀). 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 CO₂ emissions (approximately 1.8 tons of CO₂ 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 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 and the buoyancy force due to the solvent.

Once particles enter the Brownian regime, their subsequent behavior—whether they remain dispersed, weakly flocculate, or irreversibly aggregate—is governed by their interparticle potentials. The **DLVO!** (**DLVO!**) theory identifies two main interactions:

1. **Electrostatics:** Particles typically have surface charge density (σ), so in a vacuum they interact through a bare Coulomb potential represented by $1/(4\pi\epsilon_0)$. In a solvent, this prefactor changes to $1/(4\pi\epsilon_m)$ because the medium's dielectric permittivity (ϵ_m) screens the electric fields. When dissolved ions create an ionic atmosphere known as a double layer, it “dresses” the particle charges, transforming the Coulomb interaction into a screened-Coulomb (Debye–Hückel/Yukawa) form. The Debye length (κ) determines the range—higher ionic strength leads to a shorter Debye length.
2. **Van der Waals attraction:** Fluctuating and induced dipoles create an always-present attraction. When summed for all molecules in two bodies, this interaction is captured by the Hamaker constant (A). Importantly, the Hamaker constant depends on the dielectric contrast between the particle and the medium.

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.

Surfactant Stabilization Mechanisms

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

- label=(i) **Ionic surfactants** contribute to electrostatic stabilization. Anionic **SDS!** (**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.
- lbbel=(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.
- lcbel=(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.

2.3 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 testable hypothesis is 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. 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.”

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. Consequently, literature delineates a dialectic between two perspectives:

label=(i) a spatially organized interfacial architecture in the latex state,

lbel=(ii) network-like constraints inferred from solid-state or post-coagulation responses.

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.

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

label=(i) thermal forces that randomize structure,

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

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

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

$$D_0 = \frac{k_B T}{6\pi\eta_s a} \quad (2.2)$$

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):

$$Pe = \dot{\gamma}\tau_B \quad (2.3)$$

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:

$$\eta_r \equiv \frac{\eta}{\eta_s} = 1 + [\eta]\phi = 1 + 2.5\phi \quad (2.4)$$

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:

$$\eta_r = 1 + 2.5\phi + k_2\phi^2 + \dots \quad (2.5)$$

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:

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \quad (2.6)$$

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—it resists like a weak solid. The simplest yield-stress constitutive model is Bingham:

$$\tau = \tau_y + \eta_p \dot{\gamma} \quad (2.7)$$

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

$$\tau = \tau_y + K\dot{\gamma}^n \quad (0 < n < 1 \text{ for shear thinning}) \quad (2.8)$$

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

$$\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\lambda\dot{\gamma})^m} \quad (2.9)$$

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

$$\eta(\dot{\gamma}) = \eta_\infty + (\eta_0 - \eta_\infty) [1 + (\lambda\dot{\gamma})^a]^{(n-1)/a} \quad (2.10)$$

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 **LOM!** (**LOM!**), **SGC**, and **SLS!** (**SLS!**) in 1986, followed by patents for Finite Difference Method (FDM) and the MIT-originated 3DP concept in 1989.

Within **AM!**, **VPP!** (**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/**DLP!** (**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).

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.

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%).

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.

Two primary strategies for creating these emulsions are:

1. **Oil-in-Water emulsions:** 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.
2. **Water-in-Oil (W/O):** 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 materials.

Current challenges in emulsion-based 3D printing include:

1. **Shrinkage Management:** The removal of water from printed parts often leads to significant shrinkage.
2. **Print Stability:** Maintaining a uniform emulsion mixture is critical.

3. **Green Part Handling:** The initial printed objects are soft hydrogels prone to deformation.
4. **Resolution vs. Viscosity Tradeoff:** Increasing rubber particle concentration can enhance material strength but may reduce print resolution due to light scattering.

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% **DRC!** (**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 **DLS!** (**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, **PDI!** (**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 (**TMPTA!** (**TMPTA!**), technical grade, 246808)
- Phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide (**TPO!** (**TPO!**), 97%, 511447)
- Tartrazine (Acid Yellow 23, $\geq 85\%$, 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 (**HDDA!** (**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 ($0.01 \rightarrow 300 \rightarrow 0.01 \text{ s}^{-1}$) was used to assess hysteresis.

- lbel=(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.
- lbel=(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.

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:

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

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:

$$\frac{N}{N_0} = \frac{1}{1 + \alpha \dot{\gamma}^m}, \quad \alpha = \frac{k_d}{k_r} \quad (3.2)$$

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

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

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 :

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

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

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

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

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 ($\delta_{\text{H}} = 0$ ppm), CDCl_3 ($\delta_{\text{H}} = 7.26$ ppm), or $\text{D}_2\text{O}/\text{HDO}$ ($\delta_{\text{H}} = 4.79$ 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_2O 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:

- ^1H 1D: zg30 (NS = 8)

- ^{13}C 1D: zgpg30 (NS = 6400)
- ^1H – ^{13}C HSQC (multiplicity-edited): hsqcedetgpsi2p.3 (NS = 8)
- HMBC: hmbcgpndqf (NS = 8)
- ^1H – ^1H 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)

DOSY! (**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:

$$I(g) = I_0 \exp [-b(g)D] \quad (3.6)$$

with

$$b(g) = \gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \quad (3.7)$$

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:

$$r_h = \frac{k_B T}{6\pi\eta D} \quad (3.8)$$

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:

$$M(t) = M_0 (1 - 2e^{-t/T_1}) + C \quad (3.9)$$

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

$$M(t) = A_1 e^{-t/T_{2,1}} + A_2 e^{-t/T_{2,2}} + C \quad (3.10)$$

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% **HDHA** 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 disposable 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.

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%.

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 ($n = 4\text{--}5$). 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:

$$W_f = \int_0^{\varepsilon_m} \sigma \, d\varepsilon \quad (3.11)$$

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 $\sim 2\text{-mm}$ (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 :

$$\Gamma = L_0 \int_0^{\varepsilon_c} \sigma \, d\varepsilon \quad (3.12)$$

The fractocohesive length (l_f) is defined as:

$$l_f = \frac{\Gamma}{W_f} \quad (3.13)$$

Puncture Tests

Puncture tests were performed using a 30 kN load cell. An 18-gauge sharp cylindrical needle (tip radius $\approx 0.2 \text{ mm}$) 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.

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 $75 \text{ }\mu\text{m}$, 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 ($75 \text{ mm} \times 25 \text{ mm}$) 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.

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): $1.02 \times 10^6 \text{ g mol}^{-1}$
- Weight-average molecular weight (M_w): $2.13 \times 10^6 \text{ g mol}^{-1}$
- Polydispersity index (**PDI**): 2.09

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