

Application of Cellulose Nanocrystals (CNCs) in Emulsified Asphalt

by

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Author's Declaration

This thesis consists of material, all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contribution

Parinaz is the sole writer of this thesis and did all methodology, experiments, data analysis, and model development. Professor Tam helped me with the result analysis and final edit of the thesis.

This thesis is partially the product of co-authored publications as follows:

- Ataeian, Parinaz, Rasool Nasser, Alice Tong, and Kam C. Tam. "Effect of Oil Phase Transition on the Stability of Pickering Emulsions Stabilized by Cellulose Nanocrystals." *Langmuir*, 2022, 38, 2737–2745.
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- Parinaz wrote chapter 7, Yashar helped conduct some of the experiments relating to the asphalt residue characterization. Professor Michael K.C. Tam helped in revising the manuscript. Chapter 7 is a pending patent and journal submission.

Abstract

In today's world, transportation infrastructure plays a vital role in global competitiveness and the quality of life in societies. A considerable fraction of taxpayers' money is spent on expanding and maintaining road networks each year. The pavement industry deals with tremendous amounts of construction materials and mathematically speaking, even a tiny improvement in the quality of construction material can lead to significant environmental benefits and reduce the life-cycle cost of road networks. Asphalt cement is an integral part of road pavements, and despite favorable properties at performance temperature, its viscosity should be reduced at the production stage to make it processable. The most common approach used today is to reduce the viscosity by raising the temperature of the asphalt, which is expensive and energy-intensive. The emulsification of asphalt in water using surfactant-based technologies has been used in the pavement industry for decades. Significant modifications have been applied over time, and various formulations have been developed, leading to safer and more environmentally friendly pavement construction and maintenance techniques. The most common applications of asphalt emulsions are cold recycling of asphalt pavement, tack-coat to bind successive layers, soil treatments, and cold surface treatments, such as micro-surfacing, cheap sealing, and fog sealing. However, due to the complicated chemistry and high-temperature sensitivity of the rheological behavior of asphalt cement, emulsified asphalt still suffers from practical limitations in either production, storage, or application. The asphalt cement's significant physical state changes throughout the production and application temperature range imposes strict production, storage, and application conditions. Inevitable deviation of required conditions could lead to loss of stability in the system and material waste. Such practical problems in conjunction with limited rheological properties have limited the application of emulsified asphalt in many applications.

The current asphalt emulsions in the pavement industry use ionic surfactants to stabilize the asphalt particles, and the charge of the surfactants is pH-dependent. When mixed with aggregates, multivalent ions of the aggregates would neutralize these surfactants and destabilize the asphalt emulsions. More importantly, the stability of such systems is extremely sensitive to storage conditions, and any changes will result in the partial or total destabilization of the system. Unlike surfactant-based technologies, the Pickering emulsion stability is achieved through a solid barrier

that prevents the oil droplets from coalescing. Pickering emulsions are less sensitive to the pH of the environment, making them more compatible with mixed aggregates.

Cellulose nanocrystals (CNCs) are nanoscale cellulose in crystalline form produced from the acid hydrolysis of cellulose microfibrils and the removal of the amorphous domains. Several specific features have been attributed to CNCs, including high tensile strength, biodegradability, non-toxic, low cost, and large surface area. As a result of their renewability, low density, nanoscale dimension, non-hazardous nature, and competitive price, CNCs find broad application for a diverse range of products. CNCs have been used successfully as Pickering emulsifying agents mainly in the cosmetic industry due to their amphiphilic properties, low surface charge, and large aspect ratio.

Due to their structural form (nanoscale fiber) and mechanical properties, CNCs have been shown to enhance the mechanical properties of formulations, such as tensile strength, elastic behavior, and ageing. Such properties could also benefit asphalt cement for pavement application by delaying the crack initiation, improving resistance to permanent deformation, and reducing age-related changes.

In this doctoral research, various aspects on the CNC-based asphalt Pickering emulsion preparation were studied. Viable chemical surface treatments on the surface of CNC were performed to enhance and adjust the rheological properties and stability of the resulting emulsified asphalt. The impact of CNC on the rheological and performance properties of asphalt cement was examined.

The partitioning behavior of CNC at the droplet's surface before and after phase transition was analyzed. As a first step, coconut oil and paraffin wax were used as a surrogate to improve laboratory emulsification process control to investigate the physicochemical characteristics of Pickering emulsions prepared using pristine CNC and modified CNC particles throughout the phase transition of the dispersed phase. The partitioning of CNC to the droplet interface during phase transition was monitored and elucidated through fluorescent labelling of CNCs with PAMAM G6 dendrimer and fluorescent microscopy.

Interface tension measurements were performed to evaluate the impact of surface charge on CNC partitioning at the interface. To reduce the interparticle electrostatic repulsion and achieve

better surface coverage, the negative surface charge of CNCs was reduced by adding salt and with four different chemical modifications. The stability of the resulting systems was then evaluated under dynamic loading. A mathematical model for time-associated changes in the dynamic interfacial tension of oil in the presence of various modified and pristine CNCs was developed and used to investigate the surface coverage. The stability of CNC-based systems through the phase transition of the dispersed phase was evaluated and compared with a surfactant-base technology. Using particle size analysis in conjunction with an extensive rheological analysis on both systems through temperature sweep and dynamic loading revealed significantly improved stability for the CNC Pickering emulsions. A mathematical model describing the relationship between particle concentration and resulting droplet size in Pickering emulsions was developed and used to optimize the formulation composition. Complex viscosity measurements were used to compare the resistance of the two systems under dynamic loading.

The 2S2P1D analogical model facilitated the development of complex modulus master curves and rheological analysis of asphalt cement residues. The impact of free and unbound CNC in asphalt residue's rheological properties was compared to the residue of a surfactant-based system. Fundamental change in the rheological behavior was observed due to the free CNCs in the formulation. Phase angle master curve and black-space diagram revealed an elastic return point in the sample with CNC. It was concluded that the remaining CNCs could form a network at low shear strains, and the residue performed as a composite material with improved elastic behavior, especially at a high-performance temperature range. Multiple stress creep recovery tests revealed the improved resistance of CNC-containing samples in the non-linear viscoelastic region.

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Dedication

This thesis is dedicated to my beloved parents Nosrat and Mehdi.

The reason that I became what I am today.

I also dedicate this dissertation to my husband, Yashar, for his love, support, and encouragement and to my daughters Eileen and Celine for being the source of joy in my life

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List of Symbols

AC	Asphalt Concrete
AFM	Atomic Force Microscopy
AGU	Anhydroglucose Unit
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
BBR	Bending Beam Rheometer
BC	Bacterial Cellulose
CCD	Central Composite Design
CCPR	Cold Central Plant Recycling
Cin-CNC	Cinnamoyl-grafted- Cellulose nanocrystal
CIPR	Cold-in-Place Recycling
CNC, NCC	Cellulose Nanocrystal
CNC-PS	Cellulose Nanocrystal Tailored with Polystyrene
CNFs, NFC	Cellulose Nanofibers
DP	Degree of Polymerization
Desulf-CNC	Desulfated Cellulose nanocrystal
DLS	Dynamic Light Scattering
DOE	Design of the Experiment
DSC	Differential Scanning Calorimetry
DSR	Dynamic Shear Rheometer
FDR	Full Depth Reclamation
FIA	Fracture Index Analysis

FTIR	Fourier transforms infrared spectroscopy
GKV	Generalized Kelvin-Voigt Model
GM	Generalized Maxwell model
H&S	Huet-Sayegh Model
HIPR	Hot In-Place Recycling
HMA	Hot Mix Asphalt
IFT	Interfacial Tension
LODP	Level-off Degree of Polymerization
LAS	Linear Amplitude Sweep
LVE	Linear Viscoelastic Region
LCST	Lower Critical Solution Temperature
MCC	Microcrystalline Cellulose
MSCR	Multiple Stress Creep Recovery
MS	Medium Setting
O/W	Oil in Water Emulsion
PSD	Particle Size Distribution
PCL	Poly(caprolactone)
PLA	Poly (lactic acid)
RS	Rapid Setting
RSM	Response Surface Methodology
RV	Rotational Viscosity
SANS	Small Angle Neutron Scattering
SS	Slow Setting

TEMPO-CNC	TEMPO-Oxidized-Cellulose Nanocrystal
TEM	Transmission Electron Microscopy
TTS	Time-Temperature Superposition Principle
2S2P1D	Two Springs, Two Parabolic Elements, One Dashpot
UV-Vis	Ultraviolet-Visible
UCST	Upper Critical Solution Temperature
VTB	Vacuum Tower Bottom
VECD	Viscoelastic Continuum Damage
W/O	Water in Oil Emulsion
W/O/W	Water in Oil in Water Emulsion

CHAPTER 1: INTRODUCTION

1.1. Motivation

With new advances in technology and the general concerns on the environmental and health challenges, finding advanced materials and techniques that have less impact on the environment should be considered. The pavement industry has a significant impact on the environment from various aspects, such as energy consumption and non-renewable materials. Materials and pavement engineers are seeking new technologies to reduce these impacts and provide a more sustainable infrastructure to manage economic and industrial growth.

Canada has over one million kilometers of the road network, around 400,000 km paved with asphalt. Each year over 20,000 km of asphalt pavement require reconstruction and 80,000 km require significant maintenance. Such operation requires at least five million tons of asphalt cement (asphalt) to keep the existing road network in good condition.

To produce asphalt cement that is processable, the viscosity should be reduced significantly. Heating, using organic solvents, and emulsification in water are amongst the most common methods to achieve production range viscosities. The application of asphalt emulsions in road construction and maintenance is increasing remarkably because they cost-effectively reduce the viscosity without any major environmental or safety concerns when compared to alternatives.

Currently, surfactant-based technology is the only practical option for asphalt emulsification in the pavement industry. A wide range of surfactants has been marketed with different ionic charges to produce a wide range of asphalt emulsions for various applications. The produced asphalt emulsion is not only supposed to provide application-related properties, such as viscosity, oil-water ratio, and setting time, but it should be resilient enough to provide a reasonable shelf life through varying storage conditions. Combining various properties in one formulation is not always an easy task. A slight deviation from recommended conditions (either in formulation or through storage and application period) could result in loss of stability in the system, resulting in product loss.

Derived from forest and agri-biomass, cellulose nanocrystals (CNCs) are bio-degradable nanoparticles that possess various interesting physical and chemical properties. As all these properties come with a competitive price, a wide range of commercial products has been

reformulated, and many more have been developed by relying on the CNC's unique properties. Due to high surface area and amphiphilic properties, CNCs exhibit excellent Pickering emulsifying characteristics.

The main motivation of this study is to use emerging CNC Pickering emulsions to improve the rheological and application properties of asphalt emulsions and increase the share of asphalt emulsion in pavement construction. In other words, the global motivation of this study is to encourage the pavement industry to use materials with less impact on the environment. As asphalt emulsions have a wide range of applications that require various rheological and chemical properties, the key question is “how CNC based emulsion formulation can be tailored for each application?” To answer this question, it is necessary to understand the interaction of CNC with asphalt cement and the rheology and physical properties of the resulting emulsions. The chemical tools to improve and adjust asphalt Pickering emulsions and the impact of CNCs on the performance properties and rheology of asphalt residue should be investigated.

1.2. Problem Statement and Research Objectives

The global objective of this research is to improve the asphalt emulsion storage and application properties using CNC as Pickering emulsifier for pavement application. The target emulsion should possess superior properties (compared to conventional surfactants) that could improve current applications or satisfy required properties for applications for which asphalt emulsions are not considered as a viable option yet. In addition, it must be considered that the asphalt residue is considered as the final product, and the remaining CNCs in the asphalt structure would impact the performance and rheological properties, which need to be addressed and studied.

To achieve the goal mentioned above, the interaction of cellulose nanocrystals (CNCs) with asphalt cement in the Pickering emulsion system should be thoroughly understood. Unlike most commercial oils, asphalt cement possesses complex temperature-sensitive viscoelastic behavior. The rheological behavior of asphalt cement could change significantly from an elastic solid at low temperatures to a viscous liquid at high temperatures. The interaction between the aqueous phase, emulsifier, and dispersed phase could be altered throughout this process. Due to the innovative nature of this research and lack of previous examples for paving application, each step of the Pickering emulsification process should be thoroughly investigated. The applied formulation should be adjusted frequently to overcome deficiencies in each step.

The complicated rheological behavior of asphalt cement makes the emulsification process less controllable, especially for laboratory-scale production. Coconut oil and paraffin wax are used as surrogates for asphalt cement to address this problem. Both coconut oil and paraffin wax possess phase inversion; thus, their physical states at production and storage temperatures are different. However, their properties are significantly less temperature-sensitive above the phase transition temperatures, which provides easier control over the emulsification process.

This Ph.D. research is formulated according to the following hypotheses.

- CNC can stabilize emulsions consisting of the oil phase with high viscosity and high melting temperature.
- CNC has irreversible absorption after solidification of oil droplets with different interfacial properties.
- The charge density of CNC affects their diffusion behavior and kinetic barrier absorption at oil droplet interfaces.
- After setting asphalt emulsions, the presence of dispersed CNC in asphalt residue improves asphalt residue's mechanical properties.

The research outcomes of this study are summarized below:

1. The Pickering emulsification with CNCs was optimized for phase-changing oils based on various parameters, including the concentration of CNC and salt, time, and homogenizer speed. The explored emulsification formulation was used for paraffin wax, and asphalt emulsions were used. Then, the irreversible absorption of CNC at the interface of coconut oil droplets before and after oil crystallization was monitored through the fluorescence absorbance of PAMAM-grafted-CNC as an interfacial stabilizer.
2. The CNC diffusion into the oil interface and kinetic adsorption barrier of partitioned CNC at the oil/water interface was evaluated based on the surface charge of the CNCs stabilizer. The different charge density of CNCs particles was designed through salt addition and hydrophobic modification. The measurement of dynamic interfacial tension confirmed that the reduction of negative charge of CNC particles improves their Pickering stabilizer role.
3. The asphalt emulsion stability under cooling at storage and shear force applied under pumping and spraying on the road were simulated through the rheology properties of paraffin wax emulsions. The effect of oil droplets' solidification was analyzed by studying the temperature

sweep of the CNC and SDS-based paraffin wax stabilized. Also, frequency sweep analysis of paraffin wax emulsions evaluates the emulsifier's effect on emulsion stability under loading forces. We observed that the irreversible absorption of CNCs more remarkably enhances paraffin wax's stability than SDS.

4. The applicability of CNC as an interfacing stabilizer of asphalt was evaluated. The results indicated that the asphalt emulsion stabilized with CNC has more stability under different temperatures and applied shear force with lower creaming.
5. Improvement of asphalt properties through polymer or nanomaterial modification is expensive and challenging. We established that CNC as nanofibers improve the mechanical properties of asphalt residue on road pavement while surfactants do not impact asphalt. Therefore, prior modification of asphalt will not be necessary using CNC as a Pickering stabilizer of asphalt.

1.3. Thesis Outlines

This thesis consists of eight chapters, and they are illustrated in Figure 1.1.

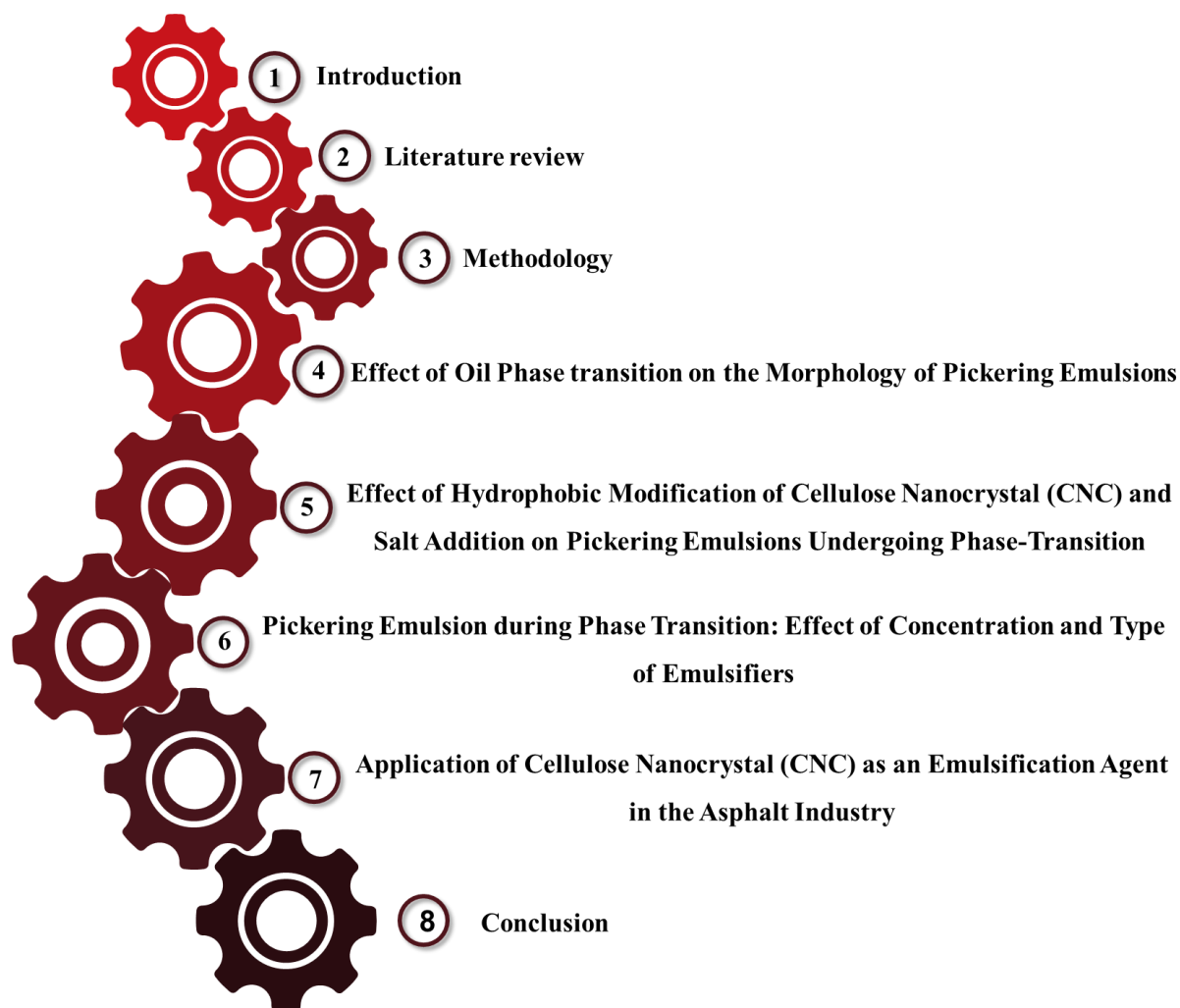


Figure 1.1. General structure and organization of Ph.D. dissertation

Chapter 1: the general aspect of the project and the overall concept of the thesis are provided. The introduction contains an overview (motivation), research objectives (problem statement), and thesis outline.

Chapter 2: The literature review describes the relevant information related to the project, mainly cellulose Nanocrystals, Pickering emulsions, and asphalt emulsion.

Chapter 3: Methodology consists of materials, characterization methods, and data analysis used in the project.

Chapter 4: Effect of Oil Phase transition on the Morphology of Pickering Emulsions

This chapter examines the location of CNC particles as emulsifiers before and after coconut oil crystallization using the fluorescent-labelled CNC with PAMAM-dendrimers. In addition, the

effect of various parameters, such as CNC concentration, water/oil ratio, mixing time and speed on properties and stability of the emulsion, were analyzed and optimized.

Chapter 5: *Effect of Hydrophobic Modification of Cellulose Nanocrystal (CNC) and Salt Addition on Pickering Emulsions Undergoing Phase-Transition*

This chapter covers the effect of surface coverage of droplets by emulsifiers during the droplet phase transition to prevent the rupture and aggregation of the crystalized dispersed phase. The influence of the surface charge of CNC particles on their kinetic and strength adsorption at the oil-water interface was examined. Hydrophobic modification and salt addition were used to modify the density surface charge of CNCs.

Chapter 6: *Pickering Emulsion during Phase Transition: Effect of Concentration and Type of Emulsifiers*

The CNC's capability in stabilizing emulsion during the paraffin wax phase solidification was compared with SDS surfactant. It was shown that the armoring behavior of CNC around oil droplets prevents their aggregation, which was more effective than SDS-based paraffin wax emulsion.

Chapter 7: *Application of Cellulose Nanocrystal (CNC) as an Emulsification Agent in the Asphalt Industry.*

This chapter reports the preparation of novel sustainable CNC-based asphalt emulsions with higher stability. In addition, it was shown that CNC particles in asphalt enhanced the durability and mechanical properties of asphalt residue of broken CNC-based emulsions

Chapter 8: *Conclusion and future studies.*

The conclusions from the doctoral research are summarized in this chapter together with the proposed future studies that will be necessary.

CHAPTER 2: LITERATURE REVIEW

2.1. Introduction

This chapter reviews the literature related to various aspects of the research performed in this thesis. Firstly, cellulose nanocrystals (CNCs) are introduced, where the preparation methods, properties, modification types, and applications of cellulose nanocrystals (CNCs) are discussed. Secondly, the Pickering emulsion is explained and compared with traditional surfactant-based emulsions. The effect of various parameters, especially the phase transition of the dispersed phase, on the stability and rheological properties of emulsions is discussed. Following this, cellulose nanocrystals (CNCs) as interfacial stabilizer is explained in more detail. A review of the fundamentals of rheology and model fitting predictions is presented. Then, a definition of asphalt emulsions is given together with a detailed discussion on properties, production, advantages, challenges, and characterization methods of the asphalt emulsion. Finally, improvement of nanomodified asphalt residue based on previously published studies is described.

2.2. Cellulose and Cellulose Nanocrystal

2.2.1. Cellulose

During the past decades, due to the overuse of fossil fuel and their negative effect on the environment, renewable resources have attracted more interest in daily life^{1,2}. Comparing renewable and biodegradable resources, lignocellulosic biomass is the primary source of natural fibers with lower costs, and it is an environmentally friendly substitute for petroleum products. The lignocellulosic biomass cell wall structure consists of cellulose, hemicellulose, and lignin. Lignin (10-25%) is a binder between cellulose and hemicellulose (20-35%), while cellulose is the primary component in the cell wall²⁻⁴.

Cellulose is the most abundant natural polymer on earth^{1,4-8}. Cellulose was discovered in 1837 by the French chemist Anselme Payen's when he investigated fibers produced from acid hydrolysis of various plant materials^{6,9}. This robust fibrous material has specific properties, such as biodegradability, water dispersibility, and functionality. There are numerous sources of producing cellulose, like bacteria, fungi, algae, and sea animals; however, the primary source of cellulose is a plant^{5,6,10}. Plants, as the primary source of cellulose, are cheap and abundant. Therefore, wool pulp and cotton fibers are the primary sources of cellulose production in industrial

scales¹⁰. By having unique cellulose characteristics, such as renewability, biocompatibility, low density and a wide range of chemical modification, cellulose opens a new path to solving the current industrial environmental and recycling challenges^{1,6,11}.

Cellulose is a linear homopolysaccharide composed of repeating D-glucopyranose ring units linked by β -1,4-glycosidic bonds^{2,6}. Each anhydroglucose unit (AGU) of cellulose contains three hydroxyl groups^{2,6}, and cellobiose is the repeating unit (10000-15000) dependent on the cellulose source^{2,5,6,9}. Each cellulose chain has a "chemically reducing functionality" and a "nonreducing" site. Cellulose is thermodynamically stable by having 4C1 conformation^{4,5,8}. Cellulose contains crystalline and amorphous regions entangled together⁵ (Figure 2.1). The hydroxyl groups on anhydroglucose units lead to various hydrogen bonds on the same or different chains as intramolecular and intermolecular networks. In cellulose, the strong intramolecular hydrogen bond is the reason for the tightly packed crystalline structure leading to cellulose's rigidity and stiffness of the cellulose^{2,6} (Figure 2.2). Cellulose has hydrophobic properties related to its abundant carbon atoms, which affect its solubility⁶. By having various chemical and physical modifications of cellulose, cellulose can be used for different application fields^{3,6}.

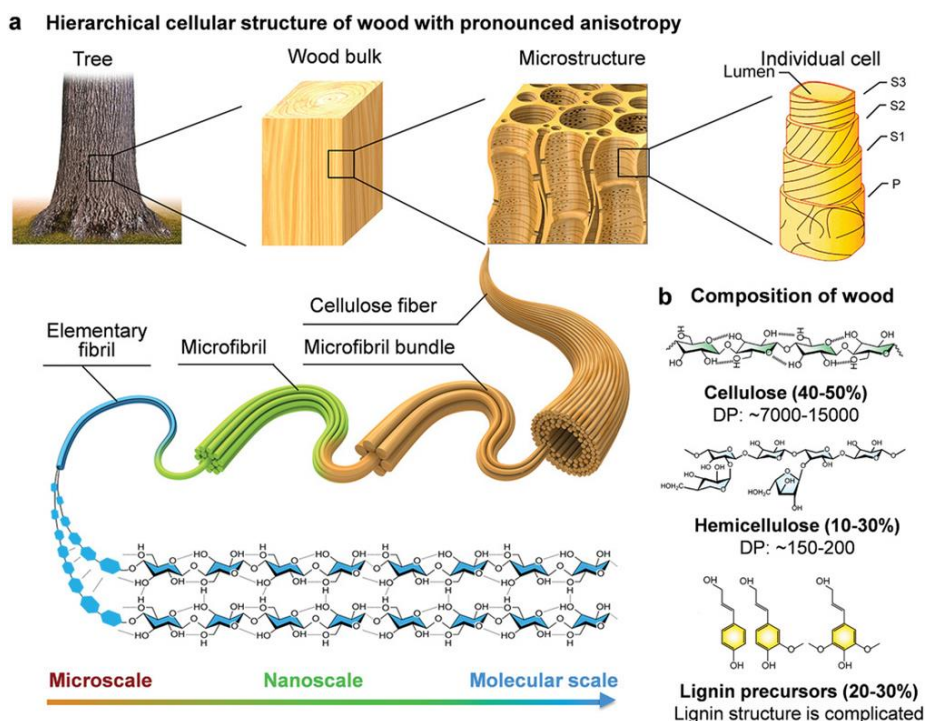


Figure 2. 1. Association of hierarchical cellular structure in the plant cell wall ¹²

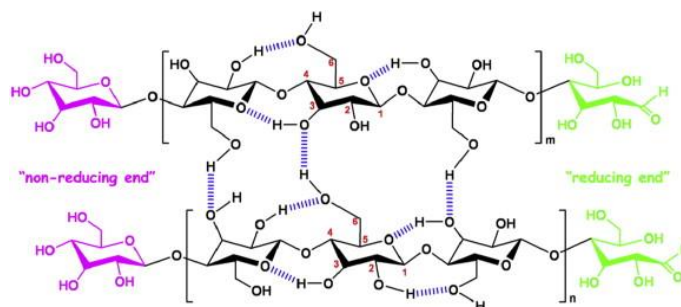


Figure 2.2. Chemical structure of cellulose, intra- and intermolecular hydrogen bond in cellulose chains ¹³

Nanocellulose can be extracted from cellulose by chemical and physical methods. Following the source and production conditions, nanocellulose possesses different dimensions and properties. It is categorized into three groups, including bacterial cellulose (BC), cellulose nanofibers (CNFs, NFC), and cellulose nanocrystal (CNC, NCC) ^{2,5,8,11,14,15}. Nanocellulose is biodegradable and biocompatible with a large surface area and excellent mechanical strength ^{2,5,11,13}. It has distinctive physical, mechanical, and biological properties that are attractive for use in different applications, like cosmetic, pharmaceutical, packaging, and paper coating ^{2,5,11,13–17}.

2.2.2. Cellulose Nanocrystal (CNC)

The rigid rodlike crystals of cellulose nanocrystals (CNC) can be manufactured from cellulose biomass via acid hydrolysis. Cellulose nanocrystals have attracted increasing attention due to their attractive features, such as large surface area, high mechanical performance, renewability, lightweight, nanoscale dimension, and low cost (Figure 2.3) ¹⁰. The annual articles, books and patents publications are continuously increasing ⁷.

In the 1950s, the first cellulose extraction process was developed via the sulfuric acid-catalyzed degradation of cellulose fibers. Later, Nikerson & Habrle ¹⁸ investigated the cellulose structure using transmission electron microscopy (TEM) and reported a rod-shaped structure for cellulose. Battista ¹⁹ produced microcrystalline cellulose (MCC) through hydrochloric acid-assisted cellulose fibers degradation and sonication. Finally, Marchessault et al. optimized the acid hydrolysis conditions to produce cellulose nanocrystals (CNCs) with crystalline structure ²⁰. Various mechanical and chemical extraction procedures of CNCs were reported, including acid hydrolysis, enzymatic degradation, oxidation, and hydrothermal hydrolysis leading to a nanosized, highly crystalline structure with a chiral nematic phase and needle-like shape. ^{21–24}

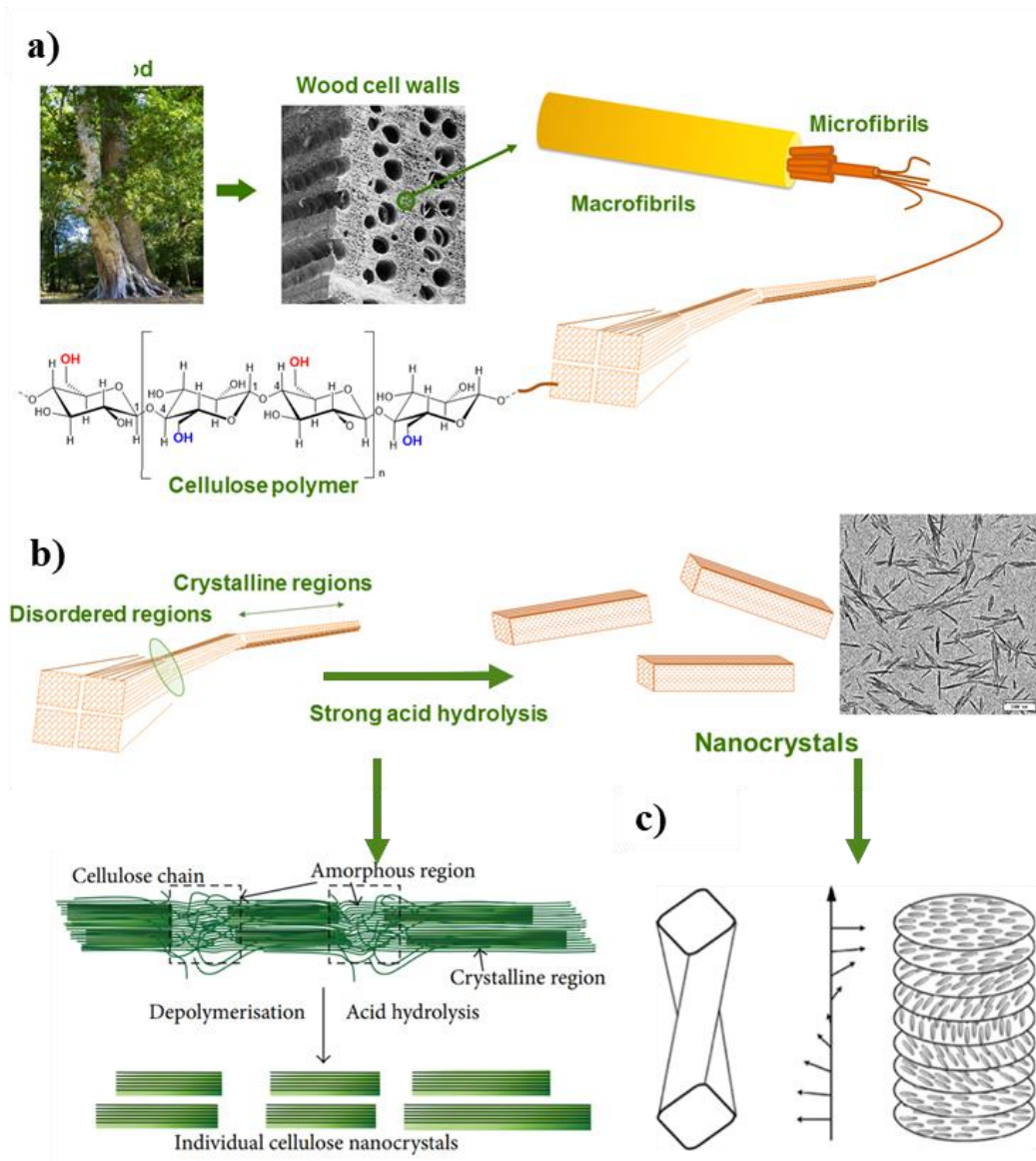


Figure 2.3. (A) Structure of cellulose polymer from the tree, (B) Cellulose nanocrystal prepared by acid hydrolysis, (C) Asymmetric of CNC with anisotropic properties^{25–27}

2.2.2.1. Preparation of Cellulose Nanocrystals (CNCs)

There are various methods for the mechanical production of cellulose, such as high pressure, high-intensity ultrasound, microfluidization, and cryo-crushing. Applying shear force in mechanical processes would disrupt and dissociate the cellulose fibers to produce cellulose microfibrils. Compared to the mechanical method, the chemical processes reduce the energy consumption and yield CNCs with a higher crystallinity^{10,23}. The surface of CNCs can be designed

based on the treatment procedures. For instance, some other alternative procedure has recently led to the grafting of aldehyde or carboxyl groups on the prepared CNCs.^{9,28–32}

Acid hydrolysis is the most widely used method to remove the amorphous region, leaving behind the highly crystalline regions. Different acids, like sulfuric, hydrochloride, phosphoric, and nitric acid, were used for the CNC preparation, with sulfuric acid being the most common. Under acid hydrolysis of cellulose, penetration of strong acid extracts the amorphous region, while the crystalline regions remain unaffected (Figure 2.3).²³ During the boiling of the cellulose in a concentrated acid solution, the degradation of cellulose is limited to a specific size of CNCs. The decrease in the polymerization degree under acid hydrolysis of cellulose is defined as the level-off degree of polymerization (LODP). The LODP value is dependent on the cellulose source and treatment methods.^{10,33,34} The quality and quantity of prepared CNCs under acid hydrolysis depend on the processing time and temperature. For instance, on the design of the processing conditions, finding adequate time is critical to remove all the amorphous regions and avoid a long time to prevent the depolymerization of crystalline domains.^{10,35} Longer hydrolysis time, higher acid concentration and temperature lead to smaller CNC with higher crystallinity degree and lower thermal stability.^{9,36,37} Compared to other processing parameters, the hydrolysis time is more effective than the acid concentration.⁹

The use of negatively-charged sulfuric and phosphoric acid produces CNC particles stabilized by electrostatic repulsion.²³ The preparation of CNC using sulfuric acid compared to phosphoric acid has a more negative surface charge, which improves their dispersibility in polar solvents like water. Sulfuric acid is the most common reagent, which diffuses into the pulp fibres and introduces negative half-ester sulfate groups ($-\text{OSO}_3^-$) with zeta potential around -40 mV on the surface of cellulose nanocrystals^{9,38}. Various CNC preparation methods also used other acids, such as hydrochloric acid^{39,40}, and using a higher acid concentration and hydrolysis over a longer time increases the surface charge of CNC particles.^{36,39,41}

2.2.2.2. Properties of Cellulose Nanocrystals (CNCs)

CNCs possess various advantages, such as biodegradability, renewability, extensive availability, high aspect ratio, lower cost than other nanoparticles, and versatile surface chemistry.^{21,39,42–44} Dispersion of rod-shaped CNC organizes to form chiral nematic structures in solution.^{10,21,43} CNC has an anisotropic structure with a degree of polymerization (DP) of around

500-15000. Depending on the source and extraction method of CNCs, their dimensions are between 100-1000 nm in length, 5-20 nm in diameter with 10-120 aspect ratios^{23,44,45}. Mostly, CNC is reported to have dimensions of 3-20 nm diameter and 100-250 nm length. CNC has a large surface area of 150–250 m²g⁻¹ and a low density of around 1.61 g cm⁻³. The elastic modulus (Young's modulus, E) is reported to be in the range of 110 to 220 GP with tensile strength from 7.5 to 7.7 GPa, similar to carbon nanotubes and nanoclays.^{10,23,43} The crystalline behavior of CNC in dispersion is dependent on their aspect ratio, surface charge, morphology, and alignment ability.^{10,15,23,43}

The dimensions, crystallinity value, shape, chirality, and surface chemistry of CNCs depend on their source and treatment procedures, which affects their application.^{10,24,45,46} For instance, CNCs extracted from tunicate are highly crystalline (85-100%). Increasing the time or processing temperature reduces the dimensions of CNCs.^{9,43,46} The surface charge of CNC can be designed based on the type of acid, temperature and hydrolysis time. Therefore, the negative charge of CNC provides interparticle repulsion to improve their dispersion.¹⁰ Also, the type of acid influences the crystallinity of the CNCs. For instance, sulfuric acid and phosphoric acid provide CNC with the chiral nematic structure, while hydrochloric acid leads to the CNC owing birefringent glassy phase.^{9,10,47} The surface of CNC can be chemically modified due to their abundant hydroxyl groups (0.96–2.65 mmol g⁻¹).^{21,23,43,47}

The rheological properties of CNC are dependent on their aspect ratio and surface charge. CNC suspension possesses shear-thinning behavior at a critical shear rate, and it aligns and forms a nematic structure. The type of acid used in the preparation method alters the surface charge of CNC, leading to different shear-thinning behavior. For instance, the shear-thinning behavior of CNC prepared by sulfuric acid is independent of time. In contrast, hydrochloric acid hydrolysis provides higher shear-thinning behavior, anti-thixotropy at lower concentrations and thixotropy at higher concentrations.^{10,43,48,49}

2.2.2.3. Chemical Modification of Cellulose Nanocrystals (CNCs)

Each of the monomeric glucose units in CNC has three hydroxyl groups with different reactivities. The hydroxyl groups in the second and third positions are directly linked to the alkyl groups on the glucose unit, which has additional steric constraints, and hence their modification requires higher energy. In contrast, the hydroxyl group in the sixth position acts as primary alcohol

with higher reactivity.^{20,50} CNC may possess other functional groups such as sulfate ($-\text{OSO}_3^-$), carboxyl ($-\text{COO}^-$) and acetyl ($-\text{COCH}_3$), aldehyde ($-\text{CHO}$), amino ($-\text{NH}_2$) or thiol ($-\text{SH}$), all of which have different reactivity and can impact the properties of CNC.

CNCs particles are prone to different modifications due to the abundant hydroxyl groups at their surface area. The CNC surface can be modified via covalent (chemical) or noncovalent (adsorption) functionalization to improve its physicochemical properties (like dispersibility and compatibility in various solvents).^{20,21,39,51–53} Noncovalent surface modifications are commonly achieved through adsorption and polymer coating. The interaction between CNC and the modifier may be controlled by electrostatic attraction, hydrogen bonding, or van der Waals forces (Figure 2.4).

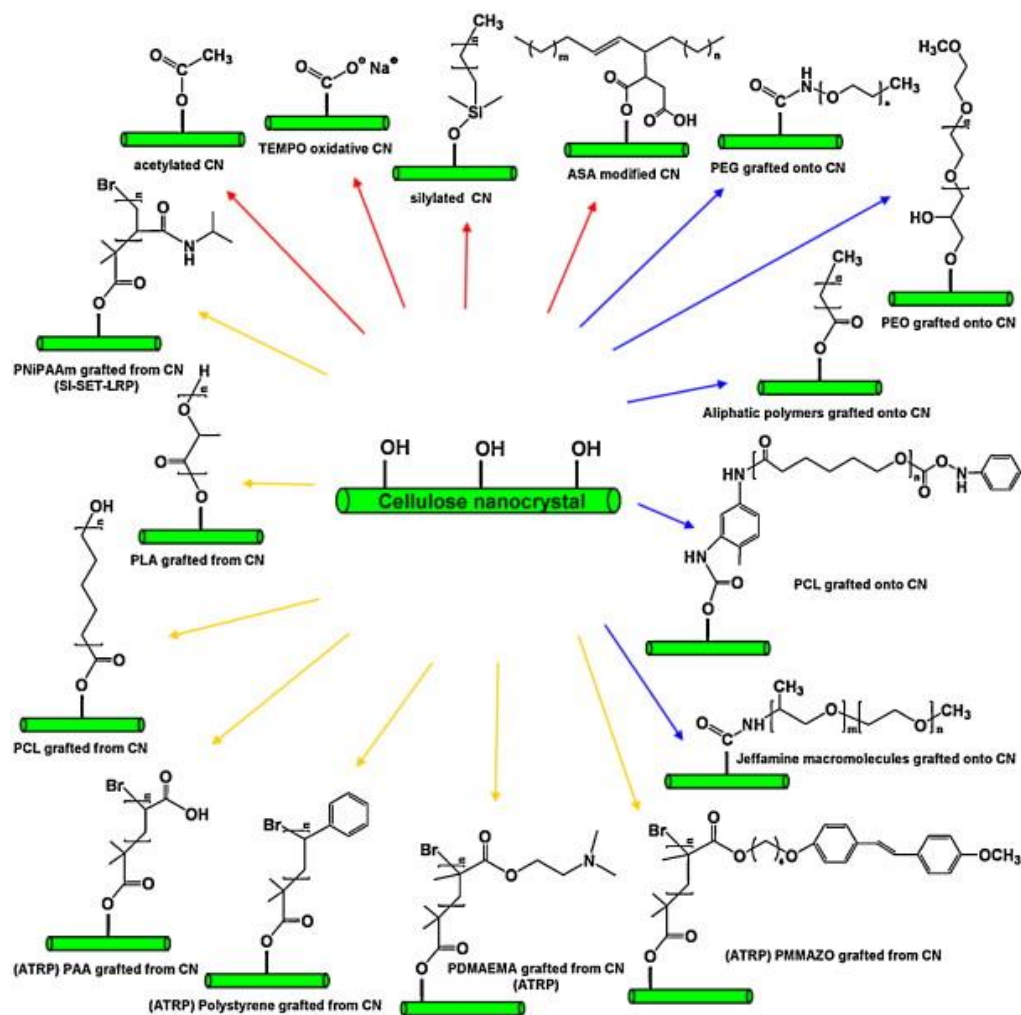


Figure 2.4. Common chemical modification of Cellulose nanocrystals (CNC)⁵⁴

2.2.2.4. Applications of Cellulose Nanocrystals (CNCs)

In the effort toward sustainable advanced functional materials, CNC as a renewable nanomaterial with biocompatibility and low toxicity has recently attracted extensive attention. CNC presents unique mechanical, thermal, and biological properties^{1,5,15,21,23,55}. Also, the prospect of functionalizing cellulose nanocrystals provides high-performance materials with electronic, magnetic, catalytic, fluorescence and optical properties. Generally, the utilization of CNCs for different applications can be categorized into two types, either using unmodified or modified CNC directly and CNCs as reinforcement agents on polymer nanocomposites¹⁰. Therefore, CNC offers new potentials in a wide range of applications, such as catalysis, aerogels and foams, biomedicines, mechanically enhanced nanocomposites, energy-storage devices, paperboard industry, food industry, cosmetics, paints and coatings, pharmaceutical industry such drug delivery, biosensing, biosensors (Figure 2.5)^{1,5,10,20,23,55–59}.

The increasing demand for cellulose nanocrystals (CNCs) in industrial applications is dependent on CNC production on an industrial scale. Currently, the ton-per-day production of CNCs is available in many countries around the world like Japan, the US, Canada, etc.^{22,23,60}. The functionalized or unfunctionalized CNCs have been utilized directly on various applications, such as drug carriers, antimicrobial materials, biosensing agents, pH-sensors, Pickering emulsion stabilizers, barrier films, etc., binders in food packaging, and biomedical applications (Figure 2.5)^{10,57,59}.

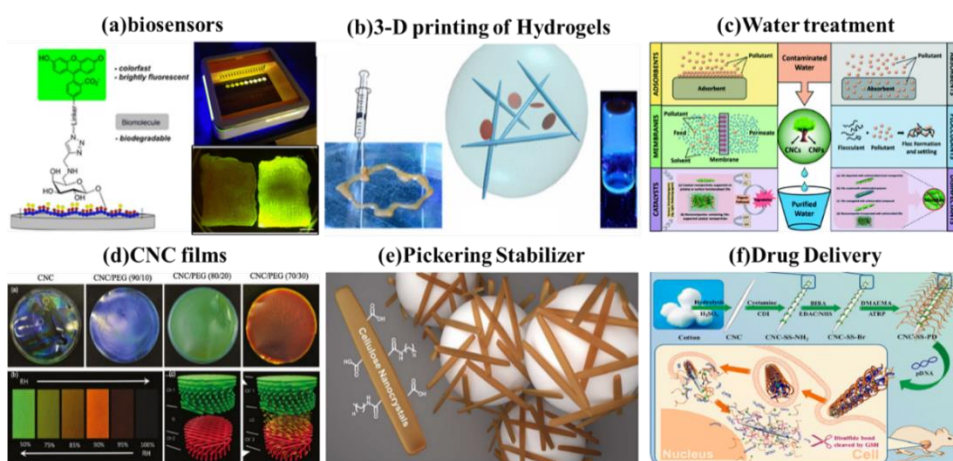


Figure 2.5. Applications of cellulose nanocrystals (CNCs) in (a)Biosensors⁶¹, (b)Hydrogels⁶², (c)Water treatment⁶³, (d)Film preparation^{64,65}, (e) Pickering stabilizer⁶⁶, (f) Drug delivery systems⁶⁷

2.3. Pickering Emulsion

The emulsion as a colloidal system is a stable mixture of two immiscible liquids of oil and water, where one (dispersed phase) is usually dispersed in another (continuous phase).^{68,69} As the two liquids are immiscible, emulsification agents (emulsifiers) are needed to stabilize the oil-water interface. Amphiphilic emulsifiers (having an affinity to both aqueous and oil phases) are usually employed to provide stability in the emulsions.^{69,70} The lipophilic phase of emulsifiers adheres to the lipid phase, while the hydrophilic segment partitions to the water phase, reducing the surface tension. The electrostatic repulsion of emulsifiers reduces the contact of the lipid phase, preventing the coalescence of the oil droplets.^{71,72} Traditional emulsions stabilized with conventional surfactants have been used in different food, medical, agriculture, and petrochemical industries. The application of conventional ionic surfactants has some limitations due to their ionic character, high cost, and toxicity. Ionic surfactants are more sensitive to electrolytes and may lose their ability to provide stability for the mixture. Hence, nonionic surfactants are more desirable as they can provide more stability by reducing flocculation and coalescence.⁷³

At the beginning of the 20th century, an emulsification technique was reported for stabilizing two immiscible phases using solid particles. This type of emulsion stabilization is called "Pickering emulsion," named after Spencer Umfreville Pickering.^{68,72,74–76} However, the interfacial phenomenon reduces the surface tension through the adsorption of solid particles on the oil-water interface was first reported by Ramsden (1904).⁷⁷ Pickering emulsion stabilization occurs by partitioning particles at the droplet interface, which have an affinity to both phases and can wet both the liquid phases.⁷⁸

The mechanism of emulsion stabilization with surfactants is defined based on reducing the interfacial tension. In comparison, Pickering emulsions are stabilized according to the partitioning of nanoparticles with high adsorption energy at droplet interface and formation of physical barrier between the oil droplets (Figure 2.6). As the particle adsorption at the droplet's surface is irreversible, they provide higher stability and display more resistance to coagulation and coalescence than traditional surfactant stabilized emulsions.^{15,18,71,75,76,78–83} Therefore, two main advantages of Pickering emulsion over classical surfactant-based emulsions are their lower toxicity and higher stability.^{9,15,75} Spherical and non-spherical particles with different sizes and aspect

ratios can stabilize Pickering emulsions.^{76,84–87} The adsorption of solid nanoparticles compared to surfactant provide emulsions with larger droplet size

S.⁹

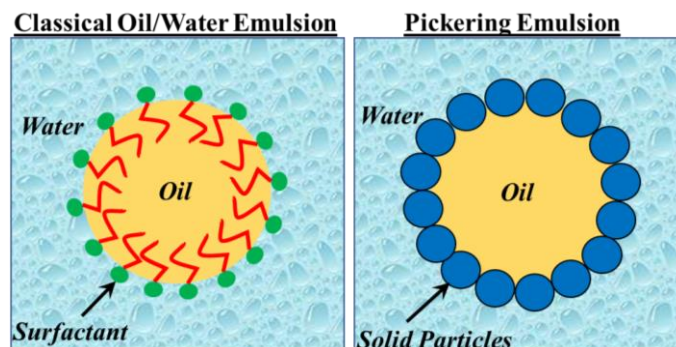


Figure 2.6. Emulsification mechanisms by classical (surfactants) and Pickering method (solid particles)⁷¹

Creaming occurs due to the different densities of the continuous and dispersed phases, separating the emulsion into two regions, including the concentrated and continuous phases. Slow creaming with a low percentage of separated phases enhances the emulsion's stability. Increasing the viscosity of the continuous phase, decreasing the droplet size, or reducing the density difference between the two phases would reduce the creaming. In Pickering emulsions, the surface coverage of droplets with adsorbed particles can change the density of droplets and reduce creaming. Also, the interconnected network between nanoparticles at the oil/water interface increases the emulsion's viscosity, leading to lower creaming values.^{9,88} Sometimes, no creaming occurs in the Pickering emulsion by manipulating the neutrally buoyant condition by balancing droplet surface coverage and density.^{80,89}

Compared to traditional emulsions, the highly stable Pickering emulsion attracts more attention in the food, cosmetics, pharmacy, and farming industries. Different nanoparticles have been used to stabilize Pickering emulsions based on their required application.^{84,90–92} Various inorganic or petrochemical-based particles, such as silica, clay, carbon graphite, calcium carbonate, montmorillonite, polystyrene, and various latexes, are the most common commercially available emulsification agents for Pickering emulsions.^{75,92–96} Recent studies to develop environmental-friendly renewable materials for Pickering emulsion examined biomass-derived particles as environmentally friendly materials. The naturally derived particles have recently

attracted more attention to stabilizing green Pickering emulsions, such as natural minerals, polysaccharides, biodegradable polymers, and protein nanoparticles.^{15,84,97}

According to the applications, the effect of the emulsion stabilizer on health should be evaluated.⁹⁸ Toxicity and carcinogenic effect of conventional surfactants limit their use in food and cosmetic industries.⁹⁹ However, the low toxicity of biodegradable nanoparticles as Pickering stabilizers improves their applications in the food, pharmaceutical and cosmetic industries. Also, the use of nanoparticles with specific characteristics, such as conductivity and antimicrobial properties, widens their application in new fields.^{9,100–102} In addition, the use of Pickering emulsions over traditional emulsions reduces the non-environmentally friendly impact of surfactants and improves the stability of emulsions.^{103,104}

Other types of nanoparticles, such as nanoclay, have been used for emulsion stabilization in some applications, like oil extraction and catalysis.^{104–107} Recently, biodegradable polymer particles stabilized Pickering emulsions such as poly(lactic acid) (PLA) and poly(caprolactone) (PCL), lignin was used as a stabilizer in the drug delivery and paper industry.^{108–111} The amphoteric properties of biodegradable protein provide a dual advantage in stabilizing Pickering emulsions.¹¹² Compared to other biological stabilizers, protein provides the option of pH and salt responsive emulsions.^{113,114}

During the development of renewable materials as an emulsifier, the application of various cellulose particles, like bacterial cellulose and cellulose derivatives, cellulose fibrils, and cellulose nanocrystals, have been reported.^{15,115,116} Polysaccharide nanoparticles, such as cellulose, chitin, and chitosan nanoparticles with biocompatibility and biodegradability^{8,15,84} have been used in food, healthcare, and water treatment.^{117–121} Cellulose and chitosan are abundant biopolymers on the planet⁴ that they can adsorb at the oil-water interface as stabilizers in Pickering emulsions.^{68,122–125} Biocompatible and biodegradable polysaccharide particles have the potential of modification to modulate their surface charge by reducing the coalescence and Ostwald Ripening and improving the stability of Pickering emulsions.^{39,52,126}

2.3.1. Pickering Stabilizer's Properties

The stability and droplet size of emulsions is dependent on the properties of stabilizing particles, such as size, shape, wettability, surface chemistry, aspect ratio, and concentration as explained as follows:^{9,15,76,127}

2.3.1.1. Particles' Wettability

The required detachment energy determines the strength of the mechanical barrier to displace the particles from the surface. The robust partitioning of the barrier particles to the interface in Pickering emulsions results in higher emulsion stability.^{71,76,128} The required energy to detach the solid particles at the droplet interface depends on the particle size, three-phase contact angle (θ_{ow}), and the interface tension value of oil and water (γ_{ow}). Therefore, the detachment energy of spherical particles is defined by the radius of particles (r in the range of 10-30 nm) described in Eq. (2. 1):¹²⁸

$$\Delta E = \pi r^2 \gamma_{ow} (1 \pm \cos \theta_{ow})^2 \quad (2. 1)$$

Also, the energy to desorb the rode-like particles is explained based on the length (l) and the width (b) of the particles at the oil/water interfaces on Eq. (2.2).^{129,130}

$$\Delta E = lb \gamma_{ow} (1 \pm \cos \theta_{ow}) \quad (2.2)$$

The emulsions are defined as oil-in-water or water-in-oil systems. Hydrophilic particles stabilize the oil-in-water emulsions with more water affinity, and hydrophobic particles can stabilize the water-in-oil emulsions. The adherence tendency and position of particles at the oil/water interface are defined according to their hydrophilic/hydrophobic properties. The sign of $\cos \theta_w$ is negative for removing the particle to the water phase and positive for removing the particle to the oil phase.

The wettability characteristic of particles can be calculated from the three-phase contact angle, which is described by Young's equation (Eq. (2.3)):

$$\cos \theta = (\gamma_{po} - \gamma_{pw})/\gamma_{ow} \quad (2.3)$$

where γ_{po} , γ_{pw} , γ_{ow} are surface energies of particle-oil, particle-water, and oil-water.

Pickering emulsions can be classified into three categories based on the nature of the dominant phase, such as oil-in-water (O/W), water-in-oil (W/O), and water-in-oil-in-water

(W/O/W). The ratio between the components affects the formation of each of the three types of emulsions as well as the types and amounts of emulsification agents (Figure 2.7 (a)).^{71,128} The solid particles with a contact angle of $0^\circ < \theta < 90^\circ$, and $90^\circ < \theta < 180^\circ$ give rise to oil-in-water and water-in-oil emulsions respectively (shown in Figure 2.7(b)).^{73,79,128} Hydrophobic or hydrophilic modification of particles can change the type and stability of the emulsion, leading to very large or small contact angles, respectively. Particles with intermediate wettability and a contact angle close to 90° provide stable Pickering emulsions¹²⁸. The optimum contact angle to stabilize the oil/water and water/oil emulsions was reported at around 70° and 110° .^{80,127,131}

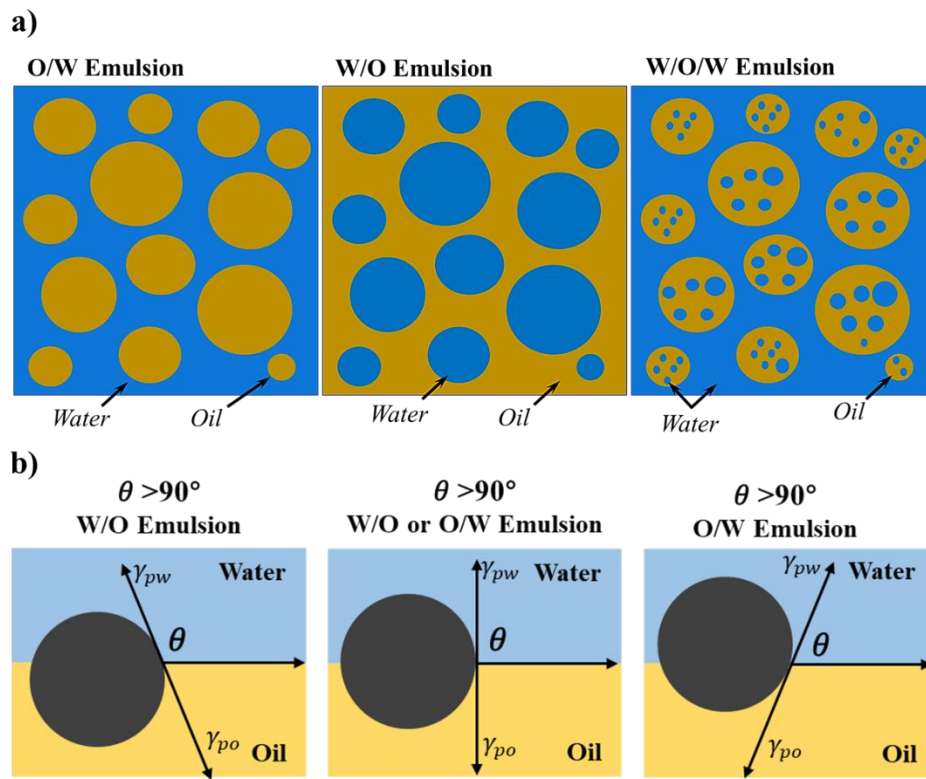


Figure 2.7. (a) Three types of the emulsion; oil in water, water in oil, and water in oil in water, (b) Contact angle of solid particles at the O/W interface¹³²

2.3.1.2. Particles' Shape and Size

Particles with cylindrical or elliptical shapes contribute to the packed network at the interface, with a larger aspect ratio having a more significant effect. The capillary force between adsorbed particles increases the emulsion stability of spherical particles.^{76,133} The smaller particles adsorb faster at the interface than larger ones, giving a smaller dropper size.⁷⁶ Also, the size of

particles should be at least be one order of magnitude smaller than the droplet of the emulsion to provide proper interface layers and stabilize emulsion^{127,134,135}

The adsorption energy of small size particles and surfactants (<1 nm) is approximately equal to 10 kBT (Boltzmann constant is $1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$). Therefore, the low detachment energy of particles decreases the stability of emulsions¹²⁷. In comparison, larger particles (>10 nm) greatly exceed the thermal energy (up to 104 kBT),¹¹⁵; hence these nanoparticles and rodlike particles at the oil/water interface with considerable desorption energy are considered to adsorb irreversibly. Strongly adsorbed particles at the Pickering emulsion interface provide higher stability compared to surfactant-based emulsions.^{9,15,117}

In addition to particle properties, environmental conditions, such as surface modification of particles, salt, and changes in pH affect steric and electrostatic interaction between droplets, which can influence the stability of emulsions.⁹

2.3.2. Oil's Properties

The emulsions' stability and droplet size depend on the emulsified oil's properties, such as polarity, water-solubility, surface tensions, viscosity, and physical state. For instance, oils with high viscosity or high polarity lead to emulsions with larger droplet sizes and lower emulsion stability.^{82,86,92,136–138} The droplet size and stability of the emulsions are dependent on the ratio of oil to water. Capron and Cathala (2013) prepared HIPE emulsions using CNC as a Pickering emulsifier and found a large oil-to-water ratio results in larger droplets and lower stability due to insufficient emulsifiers covering the droplet surfaces.¹³⁹

Recently, emulsions with different physical properties have attracted attention in applications, such as food and pharmaceutical industries.^{140–145} Emulsifying oil with high viscosity or melting point is challenging due to the mixing challenges with the water phase. Usually, high temperature has been used to improve the preparation of the emulsion. As the storage temperature is low, emulsion cooling would result in solidification or an increase in the viscosity of the oil phase, which affects the stability and droplet size of the emulsion.

The phase transition of the dispersed phase alters the interfacial tension, wettability, and emulsifiers at the oil/water, resulting in lower stability of the Pickering emulsion.^{145–153} In addition, oil solidification impacts the spherical shape of the droplets, altering the partitioning of the

emulsifiers at the interface of the droplet. Therefore, changing the surface coverage of droplets leads to droplet aggregation and emulsion destabilization.^{146–150,152,154} During the cooling of the emulsion, the oil phase partially crystallizes, and the crystallized oil droplets interact with the oil phase resulting in coalescence, which destabilizes the emulsion. The crystallized oil droplets penetrate the interface of neighboring liquid droplets and bridge the droplets leading to coalescence and demulsification.^{102,105,142,146,150} The emulsion destabilization of the crystallized dispersed phase depends on the parameters, such as oil and emulsifier types.

Rayner et al. (2014) used quinoa starch granules as Pickering emulsifiers in the oil-water emulsion. They confirmed that the armored coverage in Pickering emulsions could significantly prevent droplets coalescence and interface coverage rupture during phase transition of dispersed phase compared to surfactant-based system¹⁰². The ability of the emulsifier to form a thick layer at the interface of the droplets improves their resistance to rupture during phase inversion preventing droplet aggregation and emulsion instability.^{48,105,142,155}

2.3.3. Rheological Properties

Rheological characterization of the emulsion is critical to examine their flow properties in the production process, such as mixing and pumping and in the application, such as food, cosmetics, inks, asphalt emulsion, and paper coating. For example, it is essential to evaluate the dependency of the flow behavior of asphalt emulsion on factors such as temperature, time, and frequency. The rheology of the emulsion depends mainly on three components: the continuous phase composition, dispersed phase, and emulsifier's characteristics. The impact of the continuous phase composition on the rheology of the emulsion is related to their density, viscosity, salinity, and pH.^{156,157}

2.3.3.1. Effect of Oil Phase

One of the controlling parameters on the rheology of emulsions is the volume fraction of the dispersed phase. All Pickering emulsions and surfactant-stabilized emulsions possess viscoelastic properties after achieving a specific ratio of dispersed phase to the continuous phase. Increasing the percentage of the dispersed phase enhances the elastic properties of the emulsion. The greater elasticity is achieved due to work done to deform and break the droplets into smaller sizes of higher surface area.^{80,158,159}

Droplet size and distribution considerably impact the rheology profile of the emulsion. The effect of droplet deformation under shear force is more sensitive for emulsions with larger droplet sizes, and the deformation of tiny droplets is negligible. The smaller droplet size results in a higher viscosity emulsion due to lower deformability and distribution. Also, the droplet size affects the thermal properties of the oil phase, which is dependent on the type and concentration of the emulsifier.^{80,156,157} The viscosity of the dispersed droplets is another vital factor influencing the rheological properties of the emulsion. The droplet deformation under shear depends on the viscosity of the droplets and the layer of emulsifiers around the droplets.¹⁵⁹

The physical properties of the droplets impact the rheology properties of the emulsion. At O/W emulsion, crystallized oils migrate to the oil and water interface, altering the interfacial properties. Crystallized oils deform the spherical shape droplets, affecting the adsorption of the emulsifiers at the interface of the oil droplets. The structure of oil crystals at the interface produces a network between droplet interfaces, and solid droplets behave differently under deformation under the applied shear force affects the rheological properties of the emulsion.¹⁵⁶

2.3.3.2. Effect of Pickering Stabilizer

The emulsifier's type and concentration impact the emulsion's rheology, which can be evaluated from the temperature and frequency sweep rheological tests. The chemical properties of emulsifiers adsorb at the interface affect the viscosity of the emulsion, and the shear force impacts the partitioning at the interface.⁸⁰ In Pickering emulsions, excess emulsifiers in the continuous phase would produce an inter-particle network leading to the bridging of the droplets to form a gel. The percolation network provides filler behavior of connected droplets that increases the emulsion's elasticity and solid behavior.⁸⁷ Therefore, the concentration of emulsifiers as solid particles has a critical role in the emulsion rheology, while the elastic properties of surfactant-based emulsions are not dependent on the amounts of surfactants.^{80,158,159}

2.3.4. Cellulose Nanocrystal as Pickering Stabilizer

The application of particles derived from biomass, such as cellulose particles (microcrystalline cellulose, CNCs, BNC), is preferred as interfacial stabilizers in Pickering emulsions.^{15,68,70,101,139,160} Compared to other cellulose-based particles, such as cellulose nanofibers, CNC has more controllable morphology, dimensions, and surface chemistry, and it is

proven to be more efficient in stabilizing Pickering emulsions.^{83,129,161–163} The use of CNC prepared from bacterial cellulose as a Pickering stabilizer was first reported in 2011^{68,164}. The self-assembly of CNC at the interface of oil and water to stabilize Pickering Emulsion attracts significant attention due to their low toxicity and biocompatibility.^{15,101,165,166} CNCs with intermediate wettability and rodlike structure with a high aspect ratio provide the potential of producing highly stable surfactant-free emulsions with several environmental and economic benefits.^{9,15,163,167} CNC as a green interfacial stabilizer is an efficient replacement for non-renewable surfactants used in the traditional emulsion that may display toxic effects in the gastrointestinal (GI) tract.^{9,15,92}

The orientation of crystalline cellulose planes containing hydrophilic hydroxyl groups and (200) β /(220) α hydrophobic crystalline edge (glucopyranose) exposing hydrophobic –CH groups of CNC imparts amphiphilic character to the nanoparticle (presented in Figure 2.8).^{15,87,129,165,168,169} The mechanism of CNC adsorption at the oil/water interface is defined by their diffusion to the interface and the charge-induced kinetic adsorption barrier, which is dependent on CNC particles' surface charge.^{15,167,170,171} Moreover, adsorbed CNCs at droplet interfaces can create an interfacial network that improves emulsion stability. Also, CNC as Pickering agents improves the creaming resistance of stabilized emulsions.^{70,101} The interface behavior of CNC particles around the droplets is dependent on different parameters, such as processing condition of CNC preparation, shape, size, concentration and the surface chemistry and charge of CNCs, pH and ionic strength of emulsion, temperature, oil type and oil to water ratios, the preparation method of CNCs.^{9,15,169}

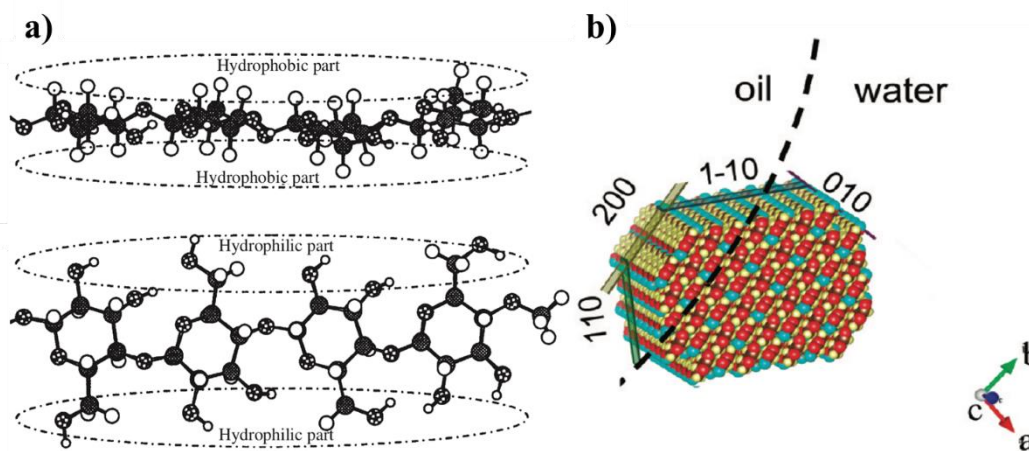


Figure 2.8. (a)Hydrophilic plane and hydrophobic edge, (b) The orientation of (200) β /(220) α hydrophobic crystalline edge of CNCs particles

2.3.4.1. Effect of Cellulose Nanocrystal Concentration

The droplet size and stability of the emulsion are dependent on the amounts of CNC. Higher CNC concentration provides more available CNC leading to smaller droplet size, lower aggregation rate, and better emulsion stability. Emulsion preparation with a low concentration of CNC tends to flocculate and aggregate.^{9,83,162,172–174} The droplet size of emulsions at the low range of CNC concentration is dependent mainly on the CNC concentration, while at high values of CNC concentration, it is dependent on the disruptive forces in the homogenizer.^{9,173} Increasing the concentration of CNC decreases the inter-particle distance, and the van der Waals forces can dominate, leading to the aggregate in the dispersion.^{87,175}

2.3.4.2. Effect of the Shape and Size of Cellulose Nanocrystal

Stability of emulsion depends on the size and shape of CNC^{9,15,165,168} Firstly; microcrystalline cellulose stabilized the Pickering emulsions with better stability than surfactant stabilized emulsions. However, their long length produces a network of droplets rather than the individual droplet.^{70,92} Then, hydrophobically modified fibrillated cellulose with smaller size was introduced to prepare Pickering emulsions. Unmodified CNC particles as emulsifiers stabilize Pickering emulsion with long-lasting stability. shows the effect of the aspect ratio of CNC prepared from two different cellulose sources (i.e. cotton, bacterial cellulose) on the stability of the Pickering emulsions.^{15,92} Kalashnikova et al. (2013) evaluated the dependency of emulsion stability on the size and shape of the CNC. They found that the aspect ratio of CNC was the dominant factor in establishing the surface coverage of oil droplets (Figure 2.9) ⁷⁰.

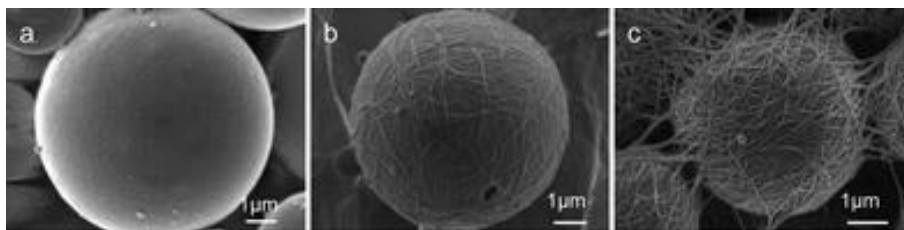


Figure 2.9. SEM images of interface coverage of Pickering emulsion stabilized via (a) Cotton (CCN), (b) Bacterial cellulose (BCN) and (c) Cladophora (ClacN) ⁷⁰

The droplet size, surface rheology of droplets, and CNC configuration at the interface depend on the shape, size, and aspect ratio of CNC, surface charge density, or oil type affecting emulsion stabilization.^{9,15,176} Due to the partitioning of CNC at the interface, the size of CNC

nanoparticles should be much smaller than the droplet size of emulsion.^{9,134} One of the limitations of using CNC as an interfacial stabilizer is that the smallest droplets are relatively large (2 μm) and cannot be used for some applications.^{68,70,83,138,168,177} The aspect ratio of CNC depends on the CNC morphology, such as spherical, rodlike, elliptical, or cylindrical structures that significantly affect the emulsion stability. Fibrillated cellulose particles with a larger aspect ratio enhance emulsion stability due to the interconnection network between droplets^{15,133,176,178}. Due to the large surface area of CNC, only 40% of droplets covered with CNCs can form stable emulsions⁹. Therefore, CNCs with high aspect ratios are good candidates for improving the surface coverage and stabilizing the Pickering emulsions.

2.3.4.3. Effect of Cellulose Nanocrystal's Electrostatic Forces

CNCs particles contain abundant hydroxyl groups, which are predominantly hydrophilic.^{70,129,179} The balance between the adsorption energy and kinetic barrier of CNC adsorption at the droplet interfaces defines the surface coverage of droplet, which is dependent on the surface charge density of the CNC particles.^{82,167,170} The charge and surface chemistry of CNC particles plays an essential role in their diffusion behavior and the required interfacial barrier.⁹ The electrostatic repulsion between particles improves their dispersion, provides a barrier against their accumulation at the oil/water interface and affects the emulsion stability. The higher surface charge of CNC increases the required amount of CNC for emulsion stabilization. Droplet aggregation is dependent on the balance of attractive and repulsion forces between CNC particles.

Cellulose nanocrystals (CNC) extracted with sulfuric acid have a surface charge density of 0.033 e/nm² leading to the electrostatic repulsion that provides the energy barrier against interface adsorption of particles stabilize the emulsion.^{68,87,92,139,165,168} CNC extracted from hydrochloric acid hydrolysis is uncharged, removing interparticle repulsion.^{68,164} However, it reduces their water dispersity and causes the agglomeration of CNC particles.^{28,60} CNC with a surface charge lower than 0.03 e/nm² can stabilize the emulsions.¹⁶⁵ Consequently, repulsion between negatively charged CNC particles leads to a loose monolayer coverage around the oil droplets and form an emulsion system with low stability.^{167,170,171,180–182} Therefore, through the various techniques, like introducing electrolytes or surface modification of CNC, the surface charge density can be adjusted to control the surface packing density and enhance the emulsion stability.^{87,164,167,170,183} CNC

particles with lower surface charge are more dependent on the diffusion forces than the kinetic barrier leading to the more intense coverage of droplet interfaces.^{9,51,167,170,171,181,184}

The thickness of the CNC layer around the droplet can be assessed using a small-angle neutron scattering (SANS). It is reported that increasing the CNC concentration was observed as different thickness from 7 nm for charged CNCs at low ionic strength to 18 nm for low charge density of CNC or high ionic strength (Figure 2.10). Also, at high CNC concentration, the thickness would not change and interface densification is related to the alignment of the anisotropic shape of CNCs.¹²²

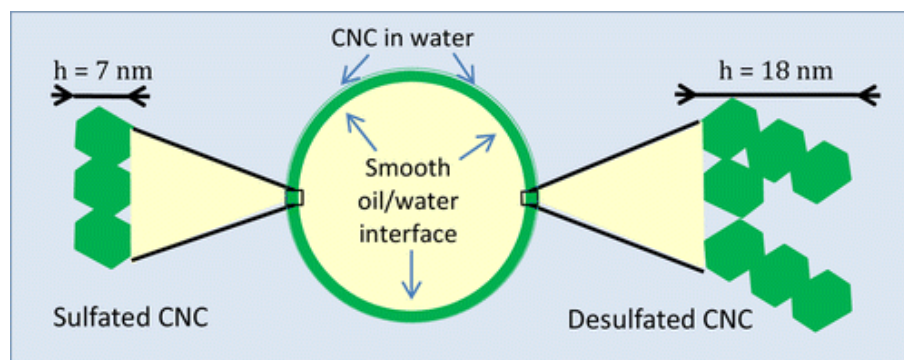


Figure 2.10. Schematic illustration of thickness coverage of charged and uncharged CNC particles at the oil and water interface¹²²

2.3.4.3.1. Salt Addition

The reduction of charge density of CNC in conformity with the salt addition reduces the Debye length and electrostatic interparticle repulsions, which facilitates the CNC to migrate and adsorb onto the oil/water interface. Therefore, adding salt reduces the required CNC to stabilize the emulsion.^{87,164,168} Varanasi et al. (2018) reported that the reduction of surface charge of CNC (0.033 e/nm^2) by adding salts (NaCl or CaCl_2) reduced the required amount of CNC to stabilize the Pickering emulsion⁸⁷. Varanasi et al. evaluated the stabilization effect of 0.1wt.% CNC under different concentrations of salt (3-200 mM). The results indicated that 0.1 wt.% CNC stabilized the emulsion even with 3 mM NaCl, but adding 20-50 mM of salt increased the stability remarkably.⁸⁷ The dependency of self-assembly of CNC as a lyotropic liquid crystal on the types of counterions affects the stabilizing capabilities of CNCs.^{26,164,185} The addition of the salt changes the ionic strength of the stabilizer until it reaches an optimum value that enhances the emulsion stability. While, at low salt concentration, the repulsion overcomes the van der Waals interactions,

a high concentration of salt decreases the net surface charge of the emulsion, leading to the van der Waals interactions exceeding the repulsive forces and droplets aggregation occurs.^{9,86,172,186} The problem of high salt addition is related to their effect on the density of the water phase, increasing the creaming and droplet aggregates.

2.3.4.3.2. Surface Modification

The CNC adsorption mechanism on the oil and water interface is explained based on the diffusion of CNCs to the interface and their kinetic adsorption barrier. The kinetic adsorption barrier of unmodified CNCs causes a lag phase which can be reduced based on the hydrophobic modification of CNCs. The chemical and physical modification can change the amphiphilicity and charge density of CNC to formulate Pickering emulsions for various applications. Therefore, functionalized CNC particles with lower surface charge can lead to faster adsorption with greater surface coverage and surface pressure.^{9,51,179,187} The abundance of hydroxyl groups on CNC provides avenues for surface treatment and adjustment of the surface charge density and wettability of CNC. Reducing the repulsion between modified CNC particles increases the intensity coverage and emulsion stability.^{51,122} The Pickering emulsions stabilized with CNC are designed according to the modification on the surface of CNC. For instance, hydrophobic modification of CNC enhances the affinity of CNC to the oil phase and even leads to water production in oil emulsions.⁹ Therefore, based on the CNC modification, emulsions type can be changed between oil-in-water and water-in-oil emulsions. Surface modification of CNC can enhance the stability of emulsions containing oils with high viscosity.^{66,68,92,122}

2.4. Rheology

Rheology has been defined as the study of materials' flow or deformation behavior of fluids or solids where Hook's law is not valid. While Hook's law can explain the deformation of perfectly elastic solids, a wide range of solids displays a combination of elastic (instantaneously recoverable) and viscous or plastic behavior.^{188,189} Deformation of viscous material is not instantaneously recovered after removing the applied force. The deformation of such materials depends on the magnitude of load and time of loading.

While deformation in fluids could be explained by viscosity (η), Hook's law represents the relationship between stress and strain in elastic solids (Eq.(2.4) and (2.5)).¹⁸⁸

$$\eta = \tau / \dot{\gamma} \quad (2.4)$$

$$E = \frac{\sigma}{\varepsilon} \quad (2.5)$$

where η is the shear viscosity, τ is the shear stress, $\dot{\gamma}$ is the shear rate, E is the elastic modulus, σ is axial stress, and ε is axial strain.

Fluids could be categorized as Newtonian (linear relationship between applied shear stress and shear strain rate) and non-Newtonian fluids based on their flow properties. Non-Newtonian fluids can also be classified into time-independent and time-dependent fluids^{188,190–193}. Time-independent fluids are categorized into shear-thinning and shear-thickening. Shear-thinning fluids have a pseudo-plastic behavior where the viscosity decreases as the shear rate increases. As shown in Figure 2.11, at low shear rates, viscosity approaches a maximum value of η_o . By the increase in shear rate, viscosity drops till it reaches its minimum value for excessively high shear rates¹⁸⁸. Shear-thinning behavior is expected in emulsions and suspensions due to the rearrangement of droplets, polymers or particles.¹⁸⁸ In contrast, the viscosity of some materials increases under applying the shear force or shear rate (shear-thickening) mainly due to clustering.

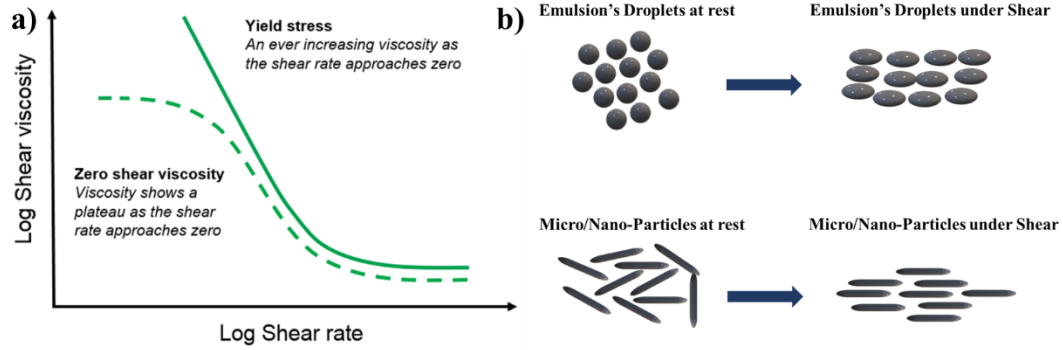


Figure 2.11. Shear-thinning behavior of non-Newtonian fluids¹⁸⁸

Viscoelastic Materials

The behavior of viscoelastic materials can be modelled using a combination of spring and dashpot in which springs would represent ideal elastic behavior, and dashpots for Newtonian fluids: ideal solid spring and dashpot, respectively^{188,191,194}.

The complex modulus (E^*) is the best parameter that explains the response of viscoelastic material under any combination of load and time of loading^{188,192,194}. Complex modulus consists of storage (elastic) and loss (viscous) components (E' & E''), which are graphically explained in

Figure 2.12. The phase angle (δ) expresses the contribution of each component in the total stiffness¹⁸⁸. Complex viscosity η^* can also explain the deformation of viscoelastic material and is related to shear complex modulus (G^*) and loading frequency (ω) by Eq.(2.6):

$$\eta^* = G^* / \omega \quad (2.6)$$

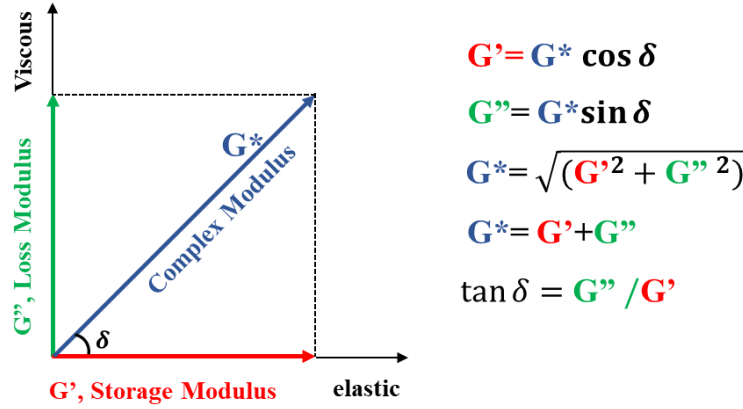


Figure 2.12. Relation between G^* and $\tan \delta$ with G' and G'' ^{188,194}

2.4.1. Linear Viscoelastic Region (LVER)

The complex modulus is independent of the magnitude of the load at low strain levels, and the stress and strain are proportional. However, passing the linear viscoelastic region (LVE), the increased applied load would result in varying complex modulus and other rheological parameters. Strain amplitude sweep test can be used to determine the LVE range for any combination of loading frequency and temperature. When $G' > G''$, samples are solid or gel-like with viscoelastic solid properties. When $G' < G''$, the samples are fluid-structure and viscoelastic liquid (Figure 2.13).¹⁸⁸

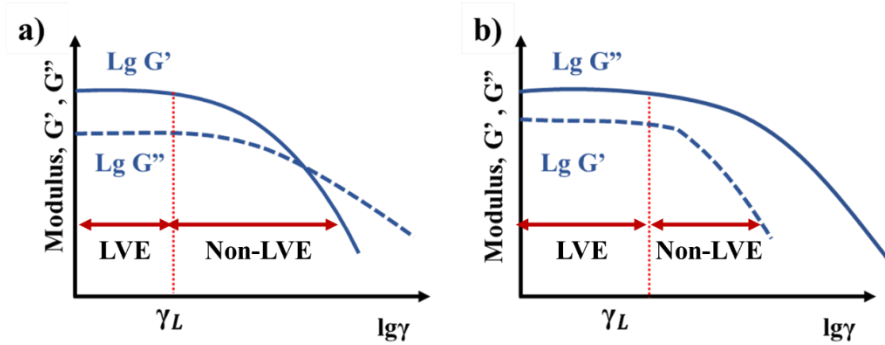


Figure 2.13. LVE region as a function of G' and G'' with (a) Solid or gel-like structure, (b) Liquid structure^{188,194}

2.4.2. Rheological Characterization

A wide range of rheological tests can investigate flow properties in different applications requiring different rheological behavior. For most rheological tests, keeping the shear strain within the LVE range (low deformation) is mandatory to avoid unnecessary complexity. However, there are instances where the material's response under large deformation is of the question, and the test setup should be carefully designed. For liquid state, rotational and oscillatory modes could be used for viscometry, while each would characterize the viscosity for different applications. If the viscosity of a liquid under pumping and mixing is of interest, the rotational measurement would be more appropriate. However, there are instances such as storage where oscillatory measurements could come in handy. Rheological tests can be designed as stress or strain (or strain rate) control modes. Sweep tests (temperature, stress, strain, or strain rate) are usually employed to map the viscoelastic material over a wide range of test parameters.

2.4.2.1. 3 Intervals Thixotropy Test, 3ITT

Thixotropy is time-dependent shear-thinning in gels or liquids, mainly due to microstructure rearrangement. After removing the shear rate, the microstructure could regain its initial structure, and viscosity would be restored. The thixotropic behavior of liquids can be evaluated using the three intervals thixotropy test (3ITT). In this test, viscosity measurement is performed before and after applying a temporary high shear rate (Figure 2.14). The required time to recover 90% of initial viscosity after interruption (the rebuild time) could characterize the thixotropy.¹⁸⁸

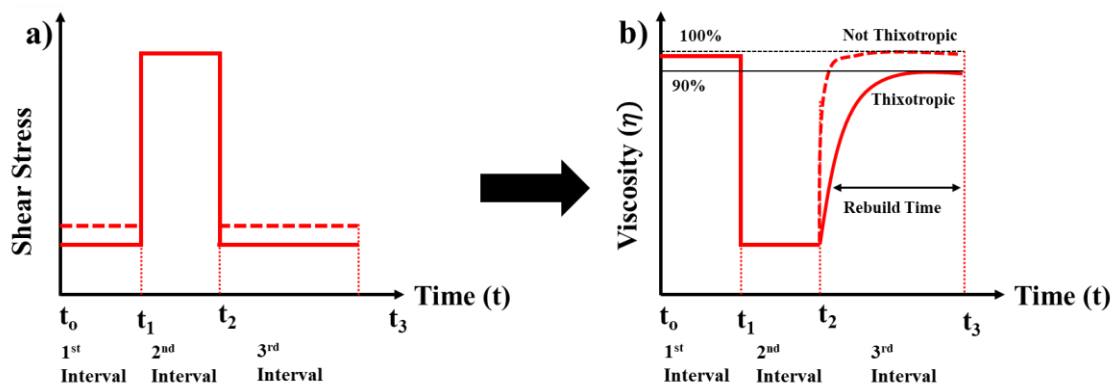


Figure 2.14. Thixotropy behavior with recoverable viscosity (a) Applying different values of shear rate under time, (b) Non-thixotropic and thixotropic response¹⁹⁵

2.4.2.2. Creep Test

To evaluate the creep properties of a viscoelastic material, a set of load and rest periods would apply to the material, and recoverable and non-recoverable deformation would be measured. Multiple stress creep recovery test is an example of creep test in which several cycles of 0.1 s loading and 0.9 s rest period would be applied on a disc shape sample, and creep compliance (J_{nr}) would be calculated by dividing non-recovered part of deformation to the applied load (Figure 2.15).

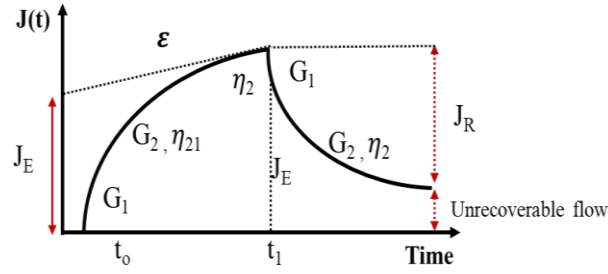


Figure 2.15. The Viscoelastic behavior based on the burger model ¹⁸⁸

2.4.3. Time and Temperature Dependency of Viscoelastic Materials

The behavior of viscoelastic materials to applied load is the time of loading and temperature-dependent. The time-temperature superposition principle (TTS) explains that the effect of loading time and temperature are interchangeable in that lowering the loading time has the same impact on the material, and the increase in temperature can compensate for it. ^{194,196–200}

Based on the time-temperature superposition principle (TTS), the rheological properties of materials at one temperature and loading time can be moved into another set of temperature and loading time. Therefore, replacing the temperature from T_1 to T_2 can be achieved by scaling the loading time from t_1 to t_2 . TTS principle can be used to convert frequency sweep test results at various temperatures into the desired reference temperature by applying the shift factor (a_T) using Eq.(2.7) to develop a complex modulus master curve that represents the rheological behavior of the material within a wide range of loading time (Figure 2.16) ^{194,196–198,200}.

$$E(T_1, t_1) = E\left(T_r, t_1/a_T\right) \quad (2.7)$$

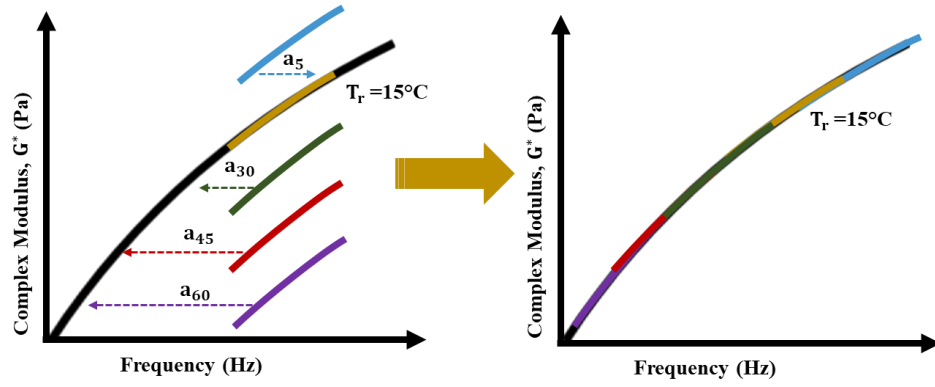


Figure 2.16. Schematic illustration of the master curve using time-temperature superposition shift factors as a function of time for different temperatures ^{194,198}

To convert the results from temperatures below the T_r , the shift-factor (a_T) has to be between 0 and 1, and values greater than one could be used to convert results from temperatures higher than T_r .²⁰⁰ The relationship between shift-factor and temperature is an intrinsic material property, and various equations William-Landel-Ferry (WLF) (Eq.(2.8)), Arrhenius equation (Eq. (2.9)), modified Arrhenius equation, and the polynomial equations (Eq.(2.10) and (2.11)) has been used to explain this relationship. ^{194,197,199}

$$\log a_T = -\frac{C_1(T-T_r)}{C_2(T-T_r)} \quad (2.8)$$

$$\log a_T = -\frac{E_a}{2.303R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \quad (2.9)$$

$$\log a_T = C_1(T_r - T) + C_2(T_r - T)^2 \quad (2.10)$$

$$\log a_T = 10^{C_1} \left(\frac{1}{T^{C_2}} - \frac{1}{T_r^{C_2}} \right) \quad (2.11)$$

where $\log a_T$ is the decadic logarithm of the TTS shift factor, T is the test temperature, T_r is the reference temperature, C_1 and C_2 are material specific constants, E_a is the activation energy (J/mol), and R is gas constant (8.314 J/mol. K).

2.4.3.1. Complex Modulus Master Curve Development

To develop a master curve of a viscoelastic material, it is necessary to conduct a frequency sweep test over a wide temperature range. Rheological models can then be used in conjunction with the selected time-temperature superposition model to convert the measurements at different

temperatures to the desired reference temperature. Rheological models can be divided into analogical and mathematical models. Mathematical models are usually consisted of a set of two equations (one to explain the changes in complex modulus value and the other for phase angle), while analogical models try to combine a set of elastic, viscous, or plastic elements in a configuration that is more appropriate for a specific material. A mathematical explanation of such models is usually in complex numbers system to obtain the complex modulus. Curve fitting techniques are used to calibrate the rheological and TTS model parameters on the laboratory results. The frequency sweep test result and rheological modelling could be developed by loss and storage moduli master curves and Black-space and Cole-cole diagrams.^{194,201,202}

2.4.3.2. Basic Viscoelastic Models

The simplest rheological models for viscoelastic materials combine one spring and one dashpot in series (Maxwell model) or parallel (Kelvin-Voigt model).^{194,201,202} The Maxwell model can explain material creep behavior but does not consider relaxation and delayed elastic behavior. On the other side, Kelvin–Voigt configuration is blind to creep and explains all deformation as elastic and delayed elastic.²⁰¹ The viscoelastic behavior of asphalt cement is more complex that can be explained by either of these models. The Generalization of Maxwell (GM) and the Kelvin–Voigt (GKV) models are better fitted for practical purposes.^{194,201–203} The Burgers model combines Maxwell and Kelvin-Voigt model in series and has been successfully used to explain the rheological properties of asphalt mixtures.^{188,203} Huet used a combination of one spring and two parabolic creep elements in series to explain the rheological behavior of asphalt cement.²⁰⁰ Huet-Sayegh is a reconfigured form of Huet model to explain the behavior of asphalt mixtures.²⁰⁰ Olard and Di-Benedetto (2003) modified the Huet-Sayegh model by combining two springs, two parabolic elements, and one dashpot in the 2S2P1D model to be used with asphalt cement and asphalt mix (Figure 2.17, Eq.(2.10)).

$$E^*(i\omega\tau) = E_0 + \frac{E_\infty - E_0}{1 + \delta(i\omega\tau)^{-K} + (i\omega\tau)^{-h} + (i\omega\beta\tau)^{-1}} \quad (2.10)$$

where h and k are parabolic elements parameters ($0 < k < h < 1$), E_∞ is the maximum complex modulus value, E_0 is the minimum complex modulus value, δ is shape parameter, and β is a dimensionless parameter.^{202,204}

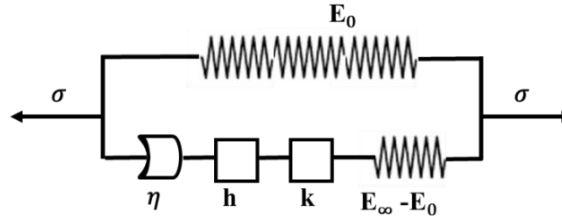


Figure 2.17. Schematic Representation of the 2S2P1D model²⁰²

2.5. Asphalt and Asphalt Emulsion

2.5.1. Asphalt Cement

Asphalt is defined as black, sticky with high viscosity hydrocarbons obtained naturally or as a petroleum distillation residue.^{205,206} The pavement comprises an agglomerate of precisely graded aggregates (as the primary pavement structure) held together by a binder. The primary role of asphalt (70%) is as a binder to act as adhesive for the aggregates to yield a durable pavement on road construction.^{193,205,207,208} Asphalt is also known as bitumen in the European definition. We will use asphalt cement to avoid confusion, which is more common in North America.²⁰⁹ The role of asphalt cement is to act as adhesive for the aggregates to yield a durable pavement. Asphalt cement¹ and Portland cement are the two significant binders for pavement applications, with asphalt commanding 80 percent of the market share^{193,208}.

Although asphalt cement looks like solid at room temperature, it can be categorized as viscoelastic sol/gel material, and the stiffness is highly dependent on temperature and loading time. At very low temperatures (or very low loading time, which has the same effect on asphalt properties), asphalt acts as a viscoelastic solid. In contrast, it behaves as a viscoelastic liquid at a high temperature (or very long loading time). The stiffness is highly dependent on temperature and loading time. At low temperatures (or low loading time, which has the same effect on asphalt properties), asphalt acts as a viscoelastic solid. Asphalt is a complex material, and even if it contains polar compounds, its overall character is nonpolar. In contrast, it behaves as a viscoelastic liquid at a high temperature (or very long loading time). Depending on the source of crude and chemical structure of asphalt, the properties of asphalt-like viscosity would vary.^{205–209}

¹ Terms “asphalt cement” and “asphalt binder” are more popular in North-America, while term “asphalt” is more popular in Europe and other places. In some old references term “tar” is also used for the same material, though the source and mechanical properties are different from coal tar. Here we use “Asphalt” to prevent any confusion between “Asphalt cement” and “Asphalt Mix”

Asphalt is classified into two groups asphaltenes and maltenes. Maltene is composed of three groups saturates, aromatics and resins. Asphalt is a colloidal system with a discontinuous phase (aromatic) of asphaltenes dispersed in the continuous phase of maltenes (Figure 2.18).^{193,206,208,209}

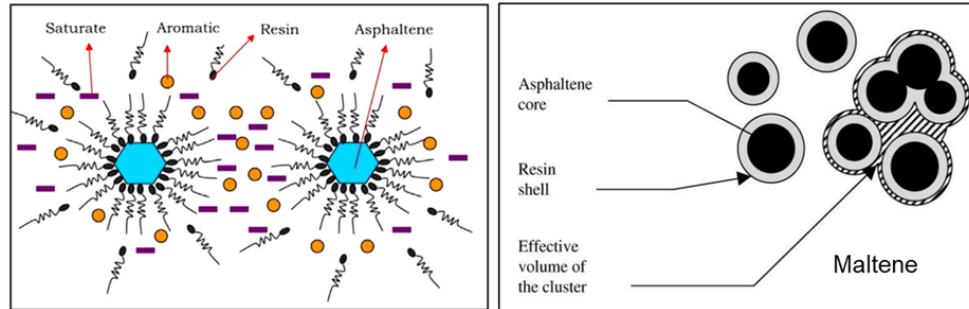


Figure 2.18. Composition of asphalt^{209,210}

2.5.2. Pavement Layers

Highway pavements consist of different layers; each requires other mechanical properties. Therefore, asphalt cement can be used in each or between these layers (See Figure 2.19). Asphalt is primarily used as a binder for aggregates in the pavement surface and granular material treatment (of much lower quantity than the first two layers). It can be used as a prime coat (to increase the bond between granular and asphalt mix layers) or as a tack-coat (to strengthen the bond between two consecutive asphalt layers).²¹¹ The first layer, or asphalt mix layers, is the main structural part of the pavement that contains two or more asphalt layers. This layer comprises aggregate (~95% wt.) and asphalt cement (~5% wt.), and it is responsible for distributing the traffic load to the acceptable level for the following layers. The second general layer is aggregate base and subbase, which distributes the transferred loads from top layers to the acceptable level of subgrade soil that may be treated with binders. The third layer, subgrade soil, is prepared using available natural material.

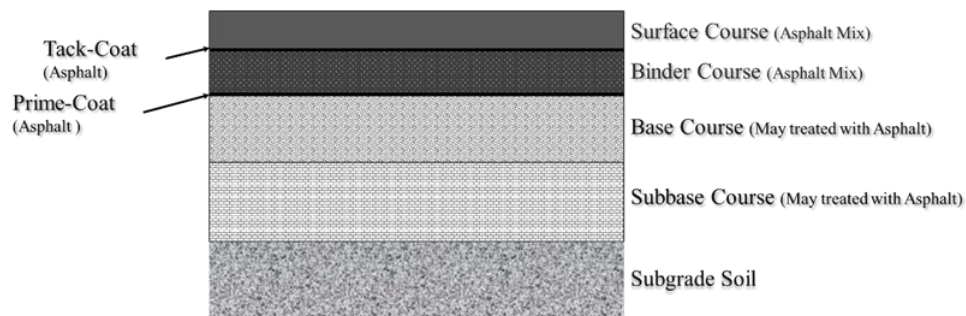


Figure 2.19. Typical flexible pavement structure

2.5.3. Rheology Properties of Asphalt

Asphalt is a viscoelastic material, meaning they have both partially elastic and viscous properties. The viscoelastic behavior of asphalt depends on its viscoelastic nature, temperature, and loading time. Therefore, understanding the viscoelastic behavior of asphalt cement is critical for designing asphalt applications. It is crucial to analyze the rheology properties of asphalt cement and evaluate the relationship between stress and deformation.^{193,194,196–200,212} For instance, asphalt at low temperatures or high frequencies is more elastic with high modulus, and at high temperatures, low frequencies, it behaves as a viscous material with low modulus. The viscosity of asphalt will change depending on the pressure and temperature.^{188,190–193} Asphalt can have Newtonian or non-Newtonian behavior depending on the applied shear rates or shear stresses, and it generally possesses a Newtonian behavior at high temperatures. However, asphalt with elastic behavior at low temperatures cannot be a Newtonian material;^{193,212} however, primarily unmodified asphalt has Newtonian behavior at very high temperatures or low shear rates. Asphalt in high temperature or long loading time behaves as a viscous liquid and in low temperatures or short loading time as an elastic solid.^{193,212} The rheology properties of asphalt binder greatly influence the pavement structure. It is crucial to analyze the rheology properties of materials to evaluate the relationship between stress and their deformation.

2.5.4. Asphalt Durability

The durability of asphalt defines the change of its properties because of ageing, where the viscosity increases and becomes more brittle and stiffer. Ageing is classified as short-term and long-term ageing. Short-term ageing occurs when mixing asphalt cement with hot aggregates, and long-term ageing occurs after HMA pavement construction due to environmental conditions and loading. Various parameters affect the durability of asphalt, such as environmental conditions, temperature and humidity, construction procedure of applying asphalt mixture, aggregates and asphalt cement properties and their gradation relationship.

Main Asphalt Distress Modes are rutting and fatigue cracking.

2.5.4.1. Rutting Resistance

Rutting is known as one of the most severe pavement distress forms. Rutting occurs due to permanent deformation of the asphalt surface that accumulates in the wheel paths (Figure 2.20).

Rutting failure develops from repetitious wheel loading, leading to high shear failure at high temperatures. It is of the most significant challenges in the early and mid-life of pavement structures.^{213–216} Stiffer asphalt has a higher value of G^* , leading to minor deformation. Also, elastic asphalt residue has a low phase angle to regain its original formation after applying loading forces.

Sirin et al. (2008) performed a field study on the resistance of mixes prepared with unmodified and SBS modified asphalt cement and correlated their findings with asphalt pavement analyzer (APA) rut depth. They found strong correlation between APA rut depth and field performance. Significant improvement in polymer modified mixes' rutting resistance was observed in laboratory (APA) results and field evaluation²¹⁷.



Figure 2.20. Pavement rutting in the wheel paths ²¹⁸

2.5.4.2. Fatigue Cracking

Fatigue cracking is one of the most significant concerns in the late life of the pavement. Distribution loading of various asphalt types over the subgrade level of pavement structures causes different levels of fatigue cracking. Prevention of fatigue cracking occurs while asphalt is elastic to disperse energy and prevent cracking. Also, asphalt should not be too stiff to deform instead of cracking (Figure 2.21(a)). Therefore, the ratio $G^*/\sin\delta$ should be a minimum to deform without considerable stress and regain their original shapes without dissipating work.^{214,219,220} Flexible asphalt materials distribute the loading over a smaller area transmitting to the subgrade levels.

In contrast, rigid ones with high stiffness values dissipate the repeating loading force over a broad subgrade area. The fatigue damage rate depends on various parameters such as environmental conditions, aggregate characteristics, and chemical properties of asphalt. Asphalt cement has the most effect on the fatigue behavior of asphalt pavement. During the traffic cycle, work loading deforms the surface of the pavement. Part of this deformation can be recovered,

while some are dispersed in heating formation, leading to permanent distortion and pavement cracking. As a result, lower dissipated energy leads to less fatigue cracking. Having lower G^* asphalt is less stiff and will be deformable without causing high stress. Besides, lower δ values make asphalt more elastic able to reinstate its original condition without dissipating work.

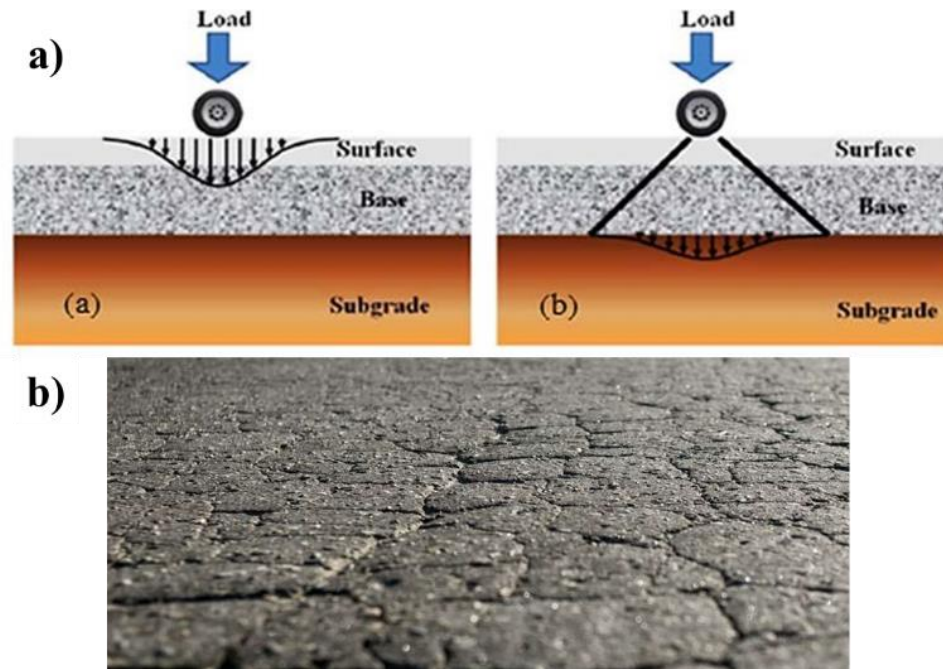


**Figure 2.21. Fatigue cracking (a) According to load distribution on flexible and rigid pavement²²¹,
(b) Alligator structure of cracks²¹⁴**

Aurilio et al. (2021) used continuum damage and fracture mechanics to evaluate the fatigue resistance of SBS modified asphalt cement. They compared fatigue resistance energy index (FREI) and viscoelastic continuum damage (VECD) number of load repetition to failure from linear amplitude sweep test (LAS) in predicting fatigue resistance of unmodified and SBS modified with various concentrations and concluded that the number of load repetition from VECD showed a better correlation with the fatigue life of samples²²².

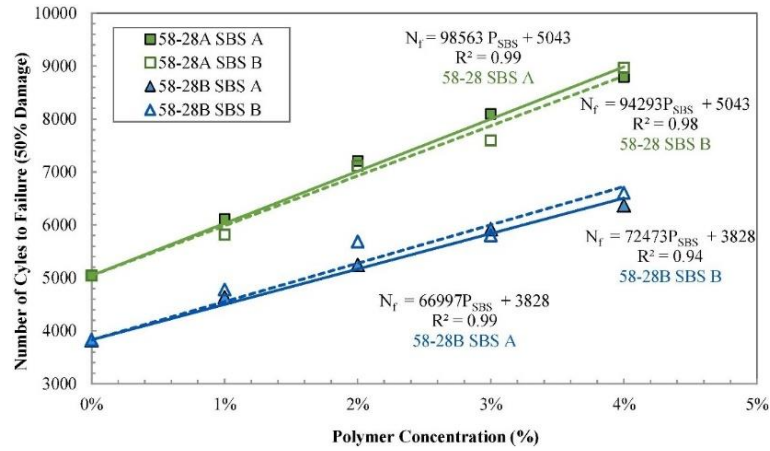


Figure 2.22. Number of load repetition to failure in VECD analysis on LAS test for control and SBS modified asphalt cement²²²

2.5.5. Asphalt Characterization

Several characterization methods can be used to evaluate asphalt viscoelastic properties, such as creep and oscillatory tests. The rheological properties of asphalt determine through bending beam rheometer (BBR), rotational viscosity (RV), dynamic shear rheometer (DSR), and linear amplitude sweep (LAS).

2.5.5.1. Dynamic Shear Rheometer (DSR)

Dynamic shear rheometer (DSR) test evaluates the asphalt's viscous and elastic behavior under medium to high temperatures.²²³ DSR measures the complex shear modulus (G^*) as a resistance deformation factor under repeated applied shear, and phase angle (δ) as the lag between applied stress and final strain.²²⁴ The rutting and fatigue cracking resistance of asphalt residue on pavement structure are predicted through G^* and δ measurements. At $\delta = 0$ degrees, the material is entirely elastic, and $\delta = 90$ degrees is viscous. In early life pavement, rutting is the primary concern, while in later life of pavement fatigue cracking becomes the primary concern.

2.5.5.2. Linear Amplitude Sweep (LAS)

Linear amplitude sweep (LAS) assesses the fatigue performance of asphalt through applied cyclic loading at increasing the amplitudes. LAS contains two steps: a frequency sweep to evaluate the rheological properties and an amplitude sweep to analyze the damage characteristics.^{225,226} The results of LAS tests can be analyzed with Viscoelastic Continuum Damage (VECD) model principles, where it predicts the fatigue damage of asphalt.

2.5.5.3. Multiple Stress Creep Recovery (MSCR)

The rutting performance of asphalt at high temperatures can be evaluated through the multiple stress creep-recovery test (MSCR). The elastic response of asphalt can be measured according to the AASHTO TP70 and MP19. The accumulated strain in the asphalt is recorded with time under two low- and high-stress levels. MSCR testing determines the amount of dissipated energy in viscous compounds. The MSCR test contains two-step 1-second creep loading at 0.1 kPa creep loading followed by a 9-second recovery under a 3.2 kPa stress level. The MSCR test data evaluate the permanent deformation of material based on the non-recoverable compliance (J_{nr} , kPa^{-1}) factor is to identify the rutting resistance of asphalt. The non-recoverable compliance (J_{nr} , kPa^{-1}) is measured according to Eq.(2.11):

$$J_{nr} = \epsilon_{nr} / \sigma \quad (2.11)$$

where ϵ_{nr} is the non-recovered strain at each three-level of applied creep stress and recovery, σ is the applied stress. Higher rutting resistance is achieved according to the lower J_{nr} value. In addition, J_{nr} , Diff, or the percentage recovery (%R) can be used to evaluate asphalt's sensitivity under varying stress levels. $J_{nr, \text{Diff}}$ is defined as the percent difference in the non-recoverable compliance (J_{nr}) calculated at 0.1 and 3.2kPa (Eq.(2.12)).

$$J_{nr, \text{Diff}} = [(J_{nr, 3.2} - J_{nr, 0.1}) / J_{nr, 0.1}] * 100 \quad (2.12)$$

Asphalt with lower stress sensitivity has a lower J_{nr} Diff value. The slope of curves changes through increasing the applied stress level.

2.5.6. Reduction of Asphalt's Viscosity

Only up to 8 percent by weight of the asphalt mixture is asphalt cement, and all other ingredients aggregates, fillers, and any other additives. The preparation of homogenous asphalt mix can be prepared by reducing the viscosity of asphalt. Various methods are introduced to reduce the viscosity of asphalt. The viscosity of asphalt should reduce (0.5–10 Poise at 60°C) for properly mixing with aggregates on producing asphalt mixture. The reduction of asphalt's viscosity can be obtained through one of the following techniques (presented in Table 2. 1):²²⁷

1. **Heating:** requires heating asphalt and aggregates to around 135-160°C, which displays Newtonian fluid behaviors.

2. **Organic solvents** (cut-back asphalt): dissolving in organic solvents; nonenvironmental friendly
3. **Foaming**: injection of water and air into the hot asphalt at high pressure
4. **Emulsification**: by emulsifying asphalt in water (O/W)

Each method of reducing viscosity is suitable for some applications according to their advantages and disadvantages (Table 2. 1). Asphalt emulsions and cut-back asphalts have various applications, such as tack- and prime-coating, dust palliation, chip sealing, micro-surfacing, and so forth. Despite the practical approach of using solvents as viscosity-reducing agents, their serious environmental and safety concerns limit their application. Therefore, many regulatory agencies in Canada (like the Ministry of Transportation of Ontario MTO) seek to ban its application, leading to various initiatives to explore asphalt emulsions as economical, environmentally friendly, and viable options for pavement applications.

Table 2. 1. Comparison between various techniques for reducing the viscosity

Viscosity Reducing Technique	Application			Hazards and Workplace safety	Energy Consumption
	Asphalt Aggregate Mix	Surface Treatment	Bonding Layer		
Heating	✓	✓		✓✓✓	✓✓✓✓
Warm-Mix additives ²	✓	✓		✓✓	✓✓✓
Foaming ³	✓	✓			✓
Emulsification ⁴	✓	✓	✓		✓
Cut-Back ⁵	✓	✓	✓	✓✓✓✓	✓

² Addition of some chemicals (such as waxes) can reduce the asphalt viscosity to some extent without altering performance temperature range properties ³⁵²

³ Foamed asphalt or expanded asphalt is produced by a process in which water is injected into the hot asphalt resulting in spontaneous foaming ³⁵³

⁴ Asphalt dispersed in water and stabilized by surface active agent (surfactant) ²²⁹

⁵ These are products whose viscosity has been reduced by addition of volatile solvents, such as naphtha, white spirit, kerosene, or gas oil

2.5.7. Asphalt Emulsions

Asphalt emulsions are a mixture of asphalt and water stabilized by emulsifiers.²⁰⁶ They are produced through mixing asphalt, water and additives with a high-shear mill that disperses the asphalt into droplets of size between 0.1 to 50 μm .²²⁸ Typically, an asphalt emulsion is an O/W type containing 40-75% asphalt, 25-60% water phase, and 0.1-2.5% emulsifier. Due to osmotic pressure, water is drawn into the asphalt causes W/O/W emulsion and increases the emulsion viscosity. Adding salt like calcium and sodium chloride (0.1%–0.2%) reduces water osmosis to minimize the viscosity changes.^{206,207,229}

These small asphalt particles will remain in suspension induced by electrostatic repulsion of emulsifiers, such as surfactants. As the charge on the emulsifier head group defines the charge on the asphalt droplets, asphalt emulsions are categorized into cationic (with a positive charge) and anionic (with a negative charge) emulsions (see Figure 2.23).

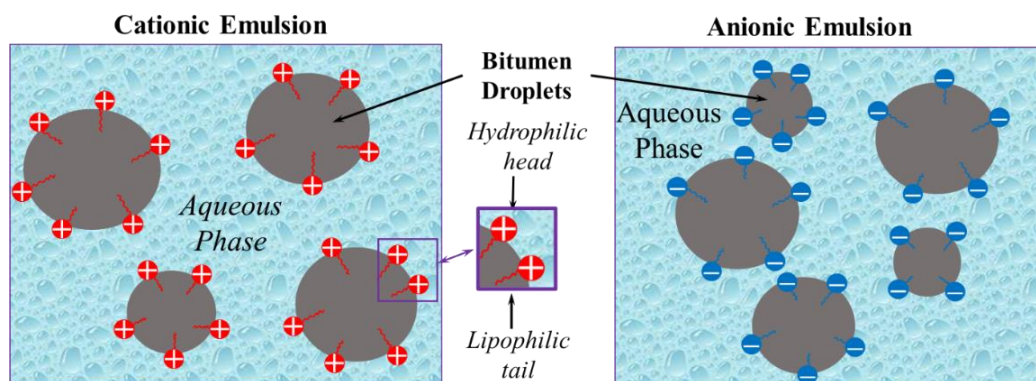


Figure 2.23. Repulsion between charged asphalt particle according to the charge of emulsifier

Van Westrum (1906) patented the first asphalt emulsion for road application.²³⁰ Initially, mechanical mixing is the main factor in preparing asphalt emulsions, and the similar specific gravity of asphalt and water helps stabilize the emulsion for a short period. Subsequently, various researchers developed other emulsification agents to stabilize the asphalt droplets. The first effort to chemically stabilize the asphalt droplets in emulsion consisted of adding sodium or potassium hydroxide to the aqueous phase that led to anionic emulsion²²⁸. Since the significant aggregate type used in the pavement industry is limestone, using anionic emulsions produced a poor aggregate coating with low durability. By introducing cationic emulsifiers in the 1950s, such as amines, amidoamines, and imidazoline, asphalt emulsions gained more popularity due to the high

affinity of cationic emulsions to the surface of calcareous materials.^{206,231} However, the amine class of surfactants is the most commonly used surfactant and is not soluble in water.

2.5.7.1. Chemical Properties of Emulsifiers

The emulsifiers play two prominent roles in asphalt emulsion, where the surface-active agent stays at the interface of water and asphalt by orientating their polar group to the water phase and the nonpolar group to the oil interface to reduce the energy required for emulsification to prevent coalescence.^{205,206,231} Asphalt cannot easily disperse in the water phase, and the emulsifier stabilizes the system by decreasing the interfacial tension energy. Secondly, emulsifiers, such as surfactants stabilize the emulsion by preventing coalescence of asphalt droplets via electrostatic repulsion (Figure 2.24).^{206,229}

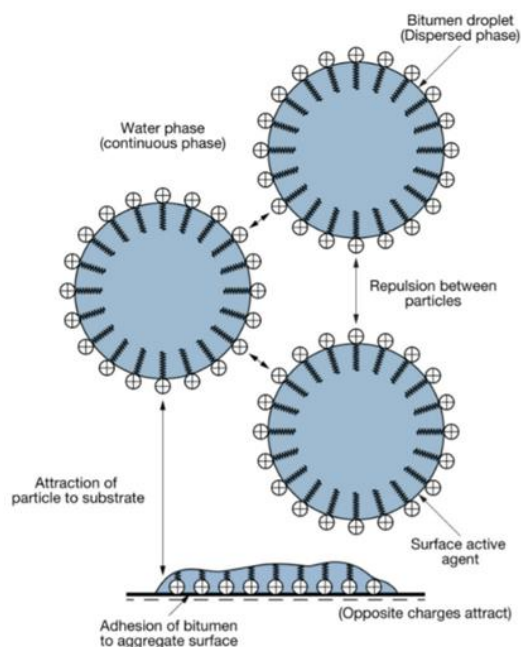


Figure 2.24. Role of emulsifier on asphalt emulsion²²⁸

As the emulsifier is the most crucial component in any asphalt emulsion, extreme care should be taken to achieve the desired properties, such as storage stability and setting properties. Most importantly, the emulsifier should be amphiphilic with an affinity for water and asphalt phases. For instance, typical commercial surfactants in asphalt emulsions possess a lipophilic chain consisting of hydrocarbon with 8 to 22 carbon atoms and a hydrophilic segment with anionic or cationic charge.^{205,206} Emulsifiers are anionic, cationic, and nonionic according to their polar head group's pH-dependent charge.^{207,232–235} The water solubility of surfactant can be improved by the

addition of acid (Hydrochloric acid and phosphoric acid) or base (sodium and potassium hydroxide) is required to prepare cationic or anionic emulsions.^{227,231,236} Commonly anionic or cationic surfactants have been used to prepare asphalt emulsion. Adding salt (NaCl) leads to a smaller droplet size on the emulsion and increases the viscosity. If excess salt is used, they destabilize the emulsion.

The emulsifier type determines the polarity of prepared emulsions. Choosing a suitable emulsifier is critical to achieving the desired properties of asphalt emulsion for a particular application. Charge interactions can be induced by selecting the appropriate surfactants to achieve the desired characteristics of the emulsion, such as adhesive properties to the surface of the solid material (aggregate) if the aggregates have a slightly negative charge (such as limestone). In that case, cationic surfactants will be more suitable, while for aggregates with a more positive charge (like basalt), one should select an anionic emulsifier (Figure 2.25).

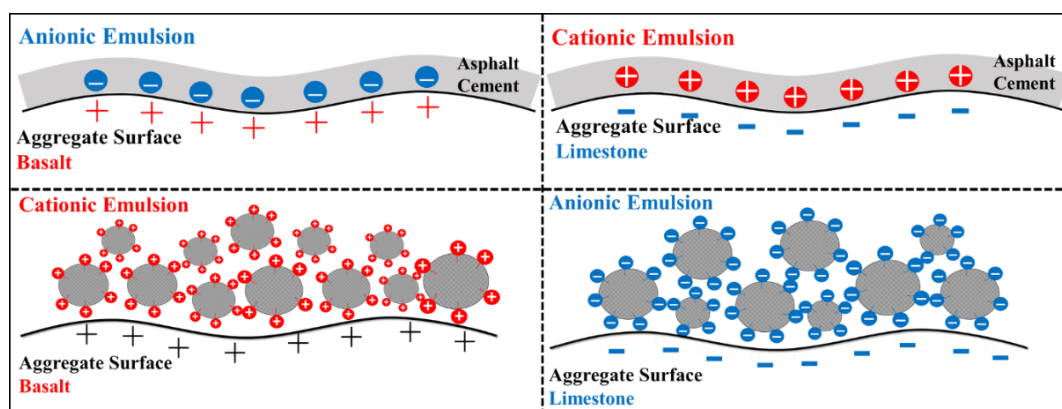


Figure 2.25. The importance of selecting correct surfactant to obtain appropriate compatibility of emulsion with aggregates

Compared to different emulsifier types, cationic emulsifiers are more prevalent in the pavement industry. Cationic emulsifiers are usually produced from one or a combination of primary, secondary or tertiary amines compounds with positive nitrogen (N) atoms.^{207,232–234} As most cationic emulsifiers are produced in neutral or basic conditions, acid treatment (usually hydrochloric acid) is required to activate these emulsifiers and make them water-soluble. As a result, cationic emulsions are acidic with a pH of less than 7.²³⁶ The polar group should be protonated (usually hydrochloric acid) to carry a positive charge and be water-soluble. Therefore, cationic emulsions can be used under acidic pH of less than 7. The most aggregate used on pavement structure is between siliceous aggregates found in nature, and they possess a negative

charge. Therefore, the cationic emulsifier is more prevalent in the pavement industry. One of the main challenges of using cationic emulsions is that it increases the pH of the mixture, which can be as high as 13. Also, aggregates with opposite surface charges like cement neutralize the acids content of cationic emulsions resulting in demulsification.^{207,236}

Anionic emulsifiers are also widely used to produce asphalt emulsions with negatively charged oxygen (O) atoms, such as sulfonate groups.^{206,235,237} They should be deprotonated using alkali, such as sodium hydroxide, to raise a negative charge on their polar head and make them water-soluble. Usually, anionic surfactant-containing sodium naphthenic groups have been used in asphalt emulsion. The application of anionic emulsions is limited due to the released ions of Ca^{2+} ions from aggregates (cement) with anionic emulsifiers leading to emulsion destabilization. Some other surfactants like quaternary ammonium compounds and alkylbenzenesulphonates are water-soluble, and they do not react with acid or base. These surfactants, like nonionic emulsifiers, can be used at neutral pH for emulsification. The emulsion droplets stabilized with nonionic usually have a slightly negative charge and are used in slow-setting asphalt emulsions. Nonionic emulsifiers are active and do not need to be protonated or deprotonated.^{206,237}

2.5.7.2. Classification and Naming of Emulsions

There are two classifications of asphalt emulsion according to their surface charge of droplets and breaking time.^{206,227}

Surface Charge of Asphalt Droplets

The surface charge of emulsion droplets is dependent on the charge on the emulsifier head group. Therefore, asphalt emulsions are cationic (with a positive charge), anionic (with a negative charge) and nonionic. Droplets carry positive and negative charges in cationic and anionic emulsions, respectively. In contrast, nonionic emulsions have droplets with low surface charge and compatibility with different aggregates.

Setting Time of Asphalt Emulsion

Breaking of asphalt emulsion is time-dependent, and asphalt emulsions can be categorized according to their set time after being applied on the road. The curing time of asphalt emulsions can be designed according to environmental conditions and emulsification conditions such as emulsifier type and concentration. Therefore, based on the required time for phase separation and

coalescence of asphalt emulsion, emulsions are classified into three groups rapid setting, medium setting, and slow setting.²²⁹

Rapid-setting (RS) emulsions destabilize quickly in contact with aggregates and can be used on the surface treatment, tack coat, and chip seals (surface dressings). RS emulsions are reactive and can be mixed with low reactive aggregates.²²⁹

Medium-setting (MS) emulsions are slow settings, allowing sufficient time to mix with aggregates. MS emulsions can be prepared using the same emulsifiers in RS type but containing higher concentrations.²²⁹

Slow-setting (SS) emulsions usually contain higher emulsifier concentrations and result in emulsions with smaller particle sizes than RS grades. Unreactive SS emulsions are mixable with reactive aggregates,²²⁹ and they have been used in the cold asphalt mix and slurry seal process.

2.5.7.3. Advantages and Disadvantageous of Asphalt Emulsion

According to the hot mix asphalt (HMA), aggregates, fillers, and other additives should be preheated at high temperatures (at 180-250°C). So, hot mix asphalt (HMA) preparation requires many fuels. For instance, the production of 1-ton HMA requires about 9 L of fuel-burning.^{206,207,211} During the last decades, various techniques have been used to lower the effect of asphalt on the depletion of natural resources and environmental issues. First, warm mix asphalt (115- 140°C preparation temperature) was used to replace HMA that higher the energy conservation by about 20-30%. Then, cold mix asphalt obtained by mixing asphalt emulsion and aggregates has attracted considerable attention because of its lower environmental impact, higher energy saving (90%) and more cost-effectiveness.^{206,207,211} The viscosity of asphalt emulsions (0.5–10 Poise at 60°C) is considerably lower than asphalt alone (100–4,000 Poise), making it processable at lower temperatures. Low-temperature techniques have several advantages, including reducing emission and energy consumption with lower asphalt oxidation, which is more economical and environmentally friendly.

Asphalt emulsion can be applied without heating, drying, and haulage of aggregates, reducing emissions. The use of cold techniques such as asphalt emulsion decreases the energy consumption to approximately half the required energy for the hot-mix asphalt (HMA) process. Due to the low-temperature processing steps, the oxidation and ageing of asphalt decrease

remarkably. Finally, cold techniques are less hazardous, more economical, and environmentally friendly. However, there are some challenges on the suitable setting time of applied asphalt emulsions. For instance, asphalt emulsions usually have a low setting time for water evaporation and adhesion of asphalt to aggregates. If breaking happens fast, in comparison to HMA, the aggregates would not bind strongly with asphalt materials with high porosity. Also, the presence of water would increase the concern of moisture damage and durability. Therefore, cold mix asphalt has not been used to a large extent as a structural layer for heavy-duty pavements.

2.5.7.4. Manufacturing of Asphalt Emulsions

In asphalt emulsion production facility, a continuous process comprising a rotor-stator colloid mill is commonly used to disperse asphalt particles in water. The gap between the rotor and stator is adjusted at 0.25 to 0.50 mm, with the rotor revolving at 15 to 100 revs/sec. Heated asphalt and emulsifier solution (usually called soap) are fed simultaneously using separate feeding lines into the high-shear mill (Figure 2.26). The temperatures of both components play a vital role in the final formulation. Practical considerations limit the viscosity of asphalt to conveyed through the mill, which should not exceed 200 mPa.s. Heating asphalt in the range of 100 to 140°C⁶ provides the required viscosity range. Therefore, the temperature of the water phase should be adjusted to below its boiling point (usually, the temperature of the product should not exceed 90°C).^{206,229} The formulation of proper asphalt emulsion should consider critical factors, such as the salinity and pH of the continuous phase, structure asphalt, asphalt EVT (asphalt temperature), temperature of soap based on emulsifier chemistry, the rotational viscosity profile of asphalt, the ratio between water and asphalt, and surfactant concentration and type, the equipment with the intensity of mixing and emulsion preparation procedure.

⁶ This minimum temperature is highly asphalt grade dependent, as various asphalts with various stiffness is used for different conditions such as average temperature and traffic loading. In cold region such as Canada, softer asphalt is used comparing to tropical areas.

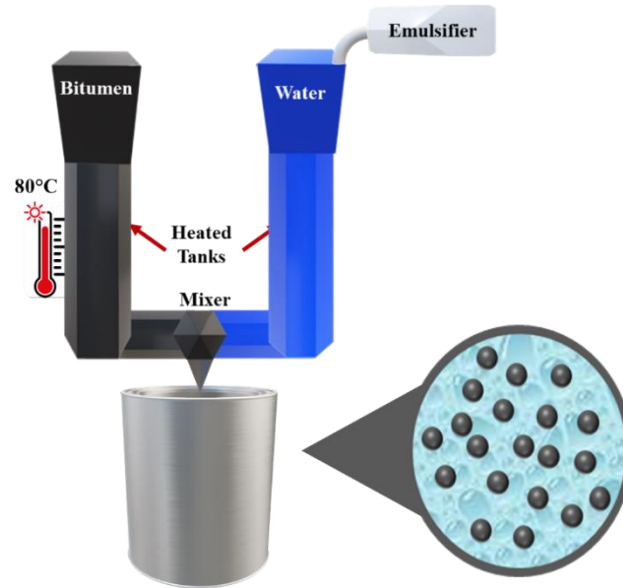


Figure 2.26. Manufacture of asphalt emulsion

2.5.7.5. Breaking of Emulsion

The emulsified asphalts are required to mix the asphalt and aggregates, where the asphalt can penetrate between the aggregates (See Figure 2.27), and the emulsion breaking causes the asphalt to separate from the water and binds the aggregates.^{227,238,239}

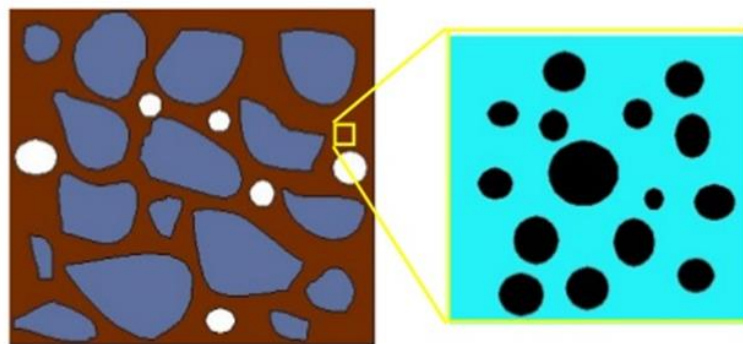


Figure 2.27. Dispersion of asphalt in aggregates as a binder²²⁷

After applying the asphalt emulsion mixture, phase separation occurs through water separation, and the asphalt residue acts as a binder between the aggregates. The setting time or breaking time of asphalt emulsion is dependent on various parameters such as ratio percentages of aggregates and emulsion, the content of asphalt, type and concentration of emulsifier, environmental conditions, temperature and pH. The emulsion must be stable during storage,

transportation, and application on the road. However, according to the required application setting time of emulsions should be designable.

During storage time, the destabilization process of asphalt emulsion consists of sedimentation, flocculation, and coalescence of droplets (Figure 2.28). The rate of droplet coalescence determines the stability of the emulsion. Therefore, the lower rate of coalescence leads to a more stable emulsion.^{238–240}

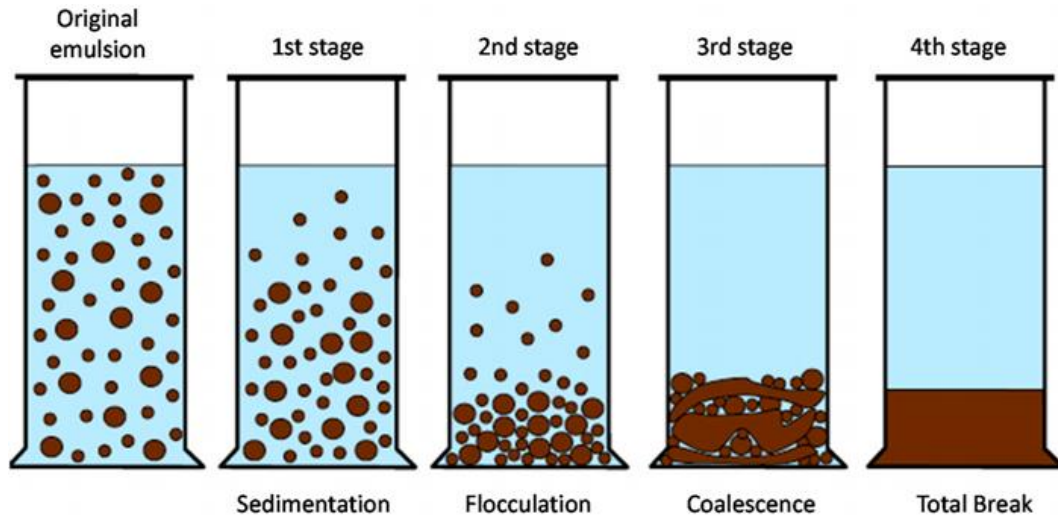


Figure 2.28. Breaking of asphalt emulsion during storage²⁴¹

Mechanism of Emulsion Breaking

There are four mechanisms of demulsification: evaporation of the water (drying), pH change, adhesion of droplets to the aggregate surfaces, and destabilization effect of minerals in aggregates. The water evaporation mechanism is time-consuming and is dependent on environmental conditions. The mechanism of water evaporation is for slow-setting emulsions.^{206,229} Charged aggregates such as lime can deactivate the extra acid in cationic emulsion, altering the pH and destabilizing the emulsion. Also, some aggregates react with hydrogen ions leading to pH change and destabilizing emulsions. In addition, aggregates like limestones release the ion with positive charges (Calcium, magnesium), neutralizing the anionic emulsions.²²⁹ In addition, asphalt droplets with low surface charge can adsorb into aggregates' surface, inducing aggregation and emulsion destabilization (Figure 2.29).²²⁹ The fourth mechanism is the adsorption of emulsifiers on the mineral aggregate leading to the depletion of the droplet surface and coalescence. As the covered

surface of aggregates with emulsifiers become hydrophobic, liberated hydrophobic asphalt settles on the surface of aggregates (Figure 2.29).^{206,227,229,239,240}

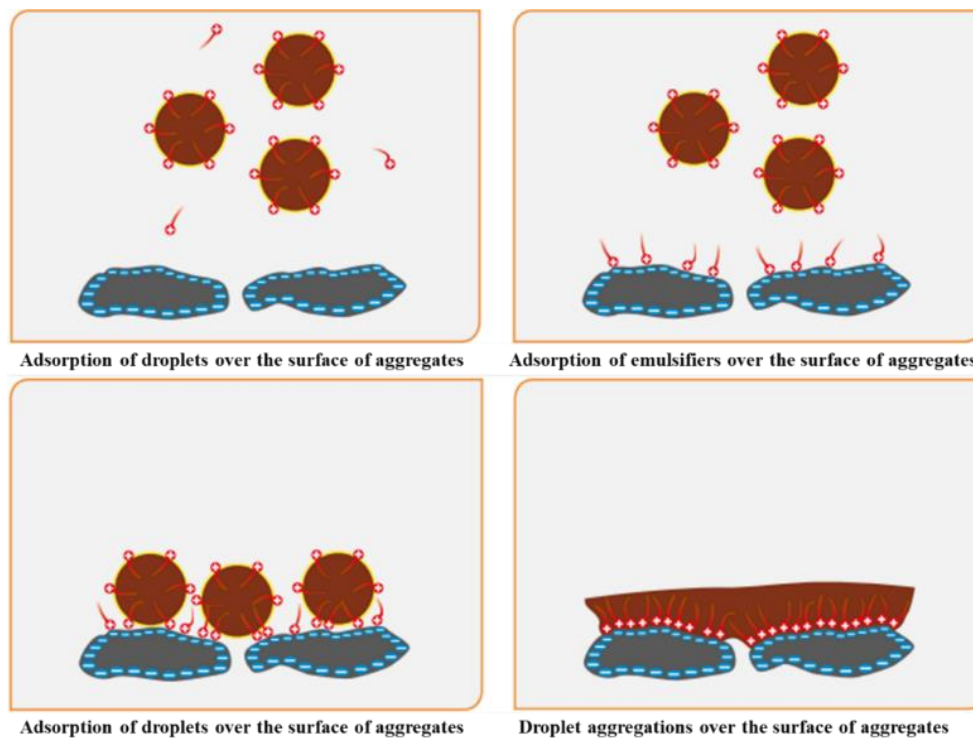


Figure 2.29. Mechanism of the demulsifying behavior of asphalt emulsion mixed with solid²²⁹

2.5.7.6. Applications on Asphalt Emulsion

Asphalt emulsions have wide applications due to their low viscosity at lower temperatures. They can be used for surface treatment, such as tack coat, chip seal, slurry seals, and micro surfacing. Also, asphalt emulsions have been used for structural treatment like cold in-place recycling or full-depth reclamation.²²⁹ Therefore, it can be used to properly replace hot molten asphalt in road maintenance and construction work. The viscosity of asphalt emulsion may vary during storage. Asphalt emulsions have been mainly used in cold road construction like tack coats, chip seals, Fog seal, prime coat, slurry seal and micro surfacing, asphalt emulsion mixtures, cold mix, full depth reclamation, hot in-place recycling, cold in-place recycling, dust palliatives, ultrathin bonded wearing course, and driveway sealers.^{206,229}

Tack coat application is defined as spraying the emulsion to provide adhesion between the different layers of pavement structures (Figure 2.30 (a)). Also, the final layer of sprayed asphalt emulsion on-road enhances the fatigue life of the paving structure.^{229,242,243} As surface treatments

designed to provide long-term pavement performance sprayed asphalt emulsion on the pavement and covered it with a layer of chips (Figure 2.30 (b)). Rapid setting asphalt emulsions should be used on-chip seal application to expose the traffic immediately after construction.^{229,244,245} In the slurry seal application, the emulsion and aggregates would be mixed and applied on the road to provide a uniform outer layer on the pavement structure and improve fatigue resistance (Figure 2.30 (c)).^{229,246} Full depth reclamation (FDR) recovers the cracked first pavement layer and provides a new base layer. FDR is a cost-effective method for treating severe distress without heating requirements, and it conserves non-renewable resources by reducing the cost and energy usage (Figure 2.30 (d)).^{247,248}

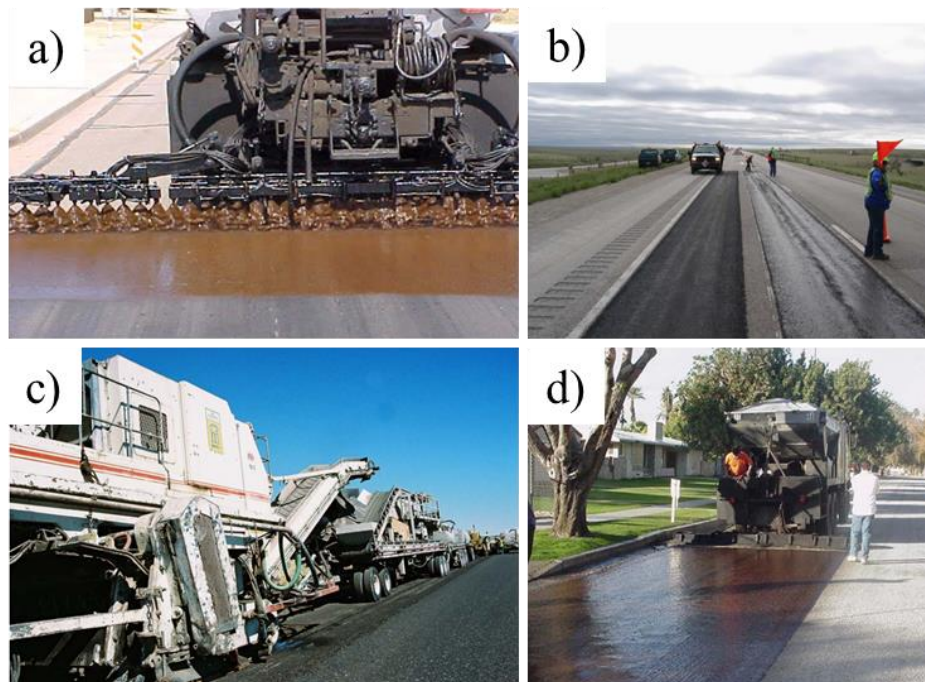


Figure 2.30. (a) Tack Coat, (b) Microsurfacing, (c) Cold in-Place Recycling, (d) Slurry Seal²⁰⁶

Recycling the asphalt pavement without heating is called cold recycling, categorized as cold in-place recycling (CIPR) and cold central plant recycling (CCPR). Cold in-place recycling (CIPR) rehabilitates the deteriorated pavement road, minimizing transportation costs and new materials. CIPR reuse of the remaining asphalt materials on the existing pavement surface. Therefore, CIPR has various advantages, such as lower energy usage and conservation of non-renewable resources. CIPR removes cracks and minor rutting without disrupting the base and subgrade of the pavement structure. CIPR allows quick access to traffic by lowering air pollution shorter working days.^{229,248,249}

2.5.7.7. Limitation of Current Commercial Surfactant on Asphalt Emulsion

Emulsifiers are often insoluble in water and should be anionic or cationic, where it can become water-soluble form by adding acid or base, respectively. Cationic surfactants must be protonated by an acid, thus gaining a positive charge. A base is also required to prepare the deprotonated anionic surfactants with a negative surface charge. In contrast, the head group of nonionic emulsifiers is permanent, and the addition of acid or base would not affect their charges.^{206,207,236} The emulsifier charge determines the charge of the asphalt droplets therefore asphalt droplets' surface charge depends on the pH and salinity concentration. Asphalt emulsions have limited mixing compatibility with aggregates having opposite charges. Multivalent ions of aggregates neutralize the cationic and anionic emulsions leading to the asphalt emulsion destabilization. The interfacial tension of ionic surfactants is pH-dependent; hence a suitable pH range is critical to control the stability of the emulsion. For anionic emulsion, alkaline $\text{pH} > 7$ and cationic emulsion $\text{pH} < 7$ are required. As pH is extremely sensitive to the environment, keeping it constant is challenging. Also, the mixing of different emulsions with the ionic charge of the asphalt droplets is limited. If anionic and cationic emulsions are mixed, droplets aggregates, and emulsion will break.

Pinto and Buss (2020) investigated the stability of asphalt emulsion and found a strong correlation between the stability of the system with ζ potential of emulsion. By titrating aggregates into the emulsion, they observed that the change in ζ potential caused by the change in ionic strength is significantly less important than the addition of aggregates²⁵⁰.

Khan et al. (2016) investigated the impact of premature coalescence on the aggregate surface and developed an experimental visual-base test method to examine the coalescence of asphalt droplets in the surfactant-based environment (Figure 2.31). Their method placed two millimeter scales of various grades asphalt droplets in various aqueous phases and evaluated the relaxation time required for droplets to fully merge²⁵¹.

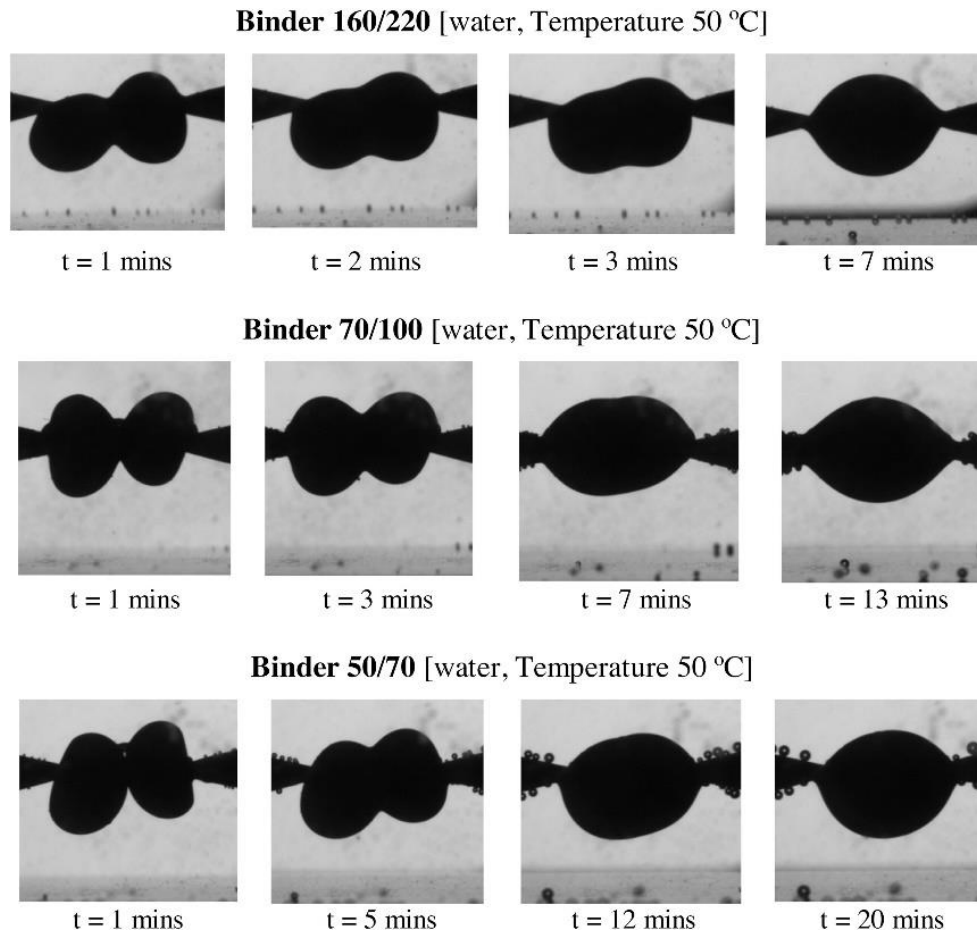


Figure 2.31. Droplet aggregation of emulsified asphalt on three different ratios of asphalt and water²⁵¹

Alvarado, Howard and et al. (2017) investigated the impact of compatibility between selected asphalt emulsion and aggregates in chip shealing. They concluded that the combination of aggregates and emulsion should be seen as a system instead of relying solely on each ingredient specification. They reported various aggregate retention mass for similar surfactant-based emulsions for aggregates with various petrology²⁵².

You et al. (2020) studied the impact of alkali and acidic environments on emulsion stability and rutting resistance of resulting cold mixed asphalt (Figure 2.32). They found higher storage stability and moisture retention at the expense of loss of permanent deformation resistance of the resulting mix²⁵³.

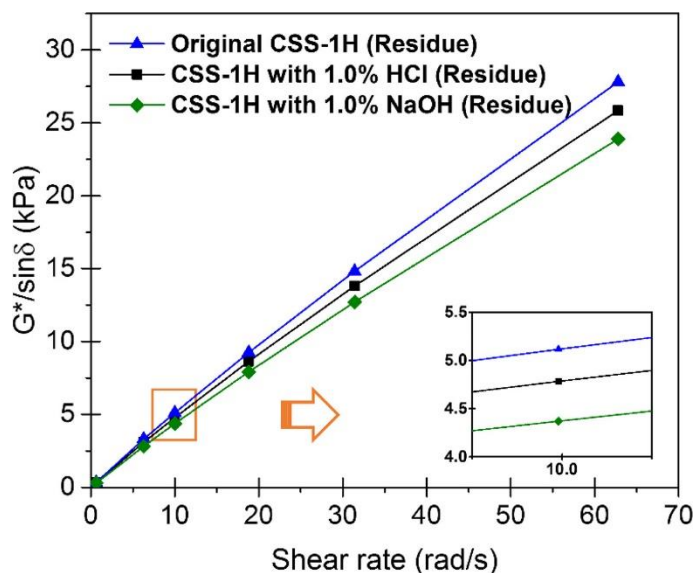


Figure 2.32. $G^*/\sin \delta$ results at 58°C used as a measure of rutting resistance for residues²⁵³

2.5.8. Nanomodification of Asphalt

In the last years, besides environmental factors, increasing the traffic loading contributes to the gradual distress propagation in the pavement structure, high maintenance, and construction costs. These factors make the need to improve the durability, safety, and efficiency of asphalt pavement, and this can be done through utilizing the asphalt modification. Although bituminous materials are mainly used in large quantities for large-scale road constructions, the macroscopic mechanical behavior of these materials depends mainly on the extent of microstructure and physical properties at the micro and nanoscale. The use of nanomaterials in asphalt indicates their potential for improvement in pavement's mechanical and physical properties.^{216,226,254-258}

Some research shows that the application of nanomaterials in the pavement industry can satisfy the current shortcomings. Due to the lack of the operational requirements of the current pavement materials, safety, reliability, and mechanical performance are in high demand.²²⁶ In previous studies, some modifiers like crumb rubber and fibers were used to improve the pavement properties. The novel properties of nanomaterials provide the required properties for existing highway pavement. The addition of nanomaterial to asphalt improves the mechanical performance of the transportation network with higher durability, viscoelasticity, resistance to ageing, fatigue damage with more environmentally friendly features.^{256,259,260} Nanoscale particles attracted many research interest in modifying the structure of asphalt. (See Figure 2.33).^{216,226,255,256,260}



Figure 2.33. The mixture of modified asphalt and aggregates ²⁵⁵

Various nanomaterials have been used in asphalt modification which improves properties of asphalt, such as ageing resistance, rutting prevention, and cracks resistance.

2.5.8.1. Rutting Prevention

Intercalated and exfoliated structures of nanomaterials dispersed in asphalt structure improve nanomodified asphalt's physical and mechanical properties (Figure 2.34). The nanomaterials' exfoliated structure increases the interaction areas leading to higher G^* , lower phase angle (δ). Therefore, the softening point of the structure increased, which enhanced the high-temperature performance, and the rutting resistance of the modified asphalt was improved. ^{213,261–268}

Two different nano-clay modified asphalt as nano-clay (NMN) asphalt and polymer modified nano-clay (PMN) asphalt had improved the thermal and mechanical properties of the exfoliated structure. ^{255,261,269} As presented in Figure 2.34 (a), the addition of bentonite clay (BT) and organically modified bentonite (OBT) increased the complex modulus values and softening point of asphalt, leading to higher rutting resistance. ²⁶¹

Carbon nanoparticles in milligram-scale quantities are available in tonnes per year. They have been used to improve the rheological properties of asphalt. ^{216,226} Also, Yang et al. reported that asphalt/CNT nanocomposite compared to asphalt show greater rutting resistance. As presented in Figure 2.34 (b), the addition of CNTs to asphalt increased the G^* , implying greater stiffness and elastic behavior. ²⁶⁵

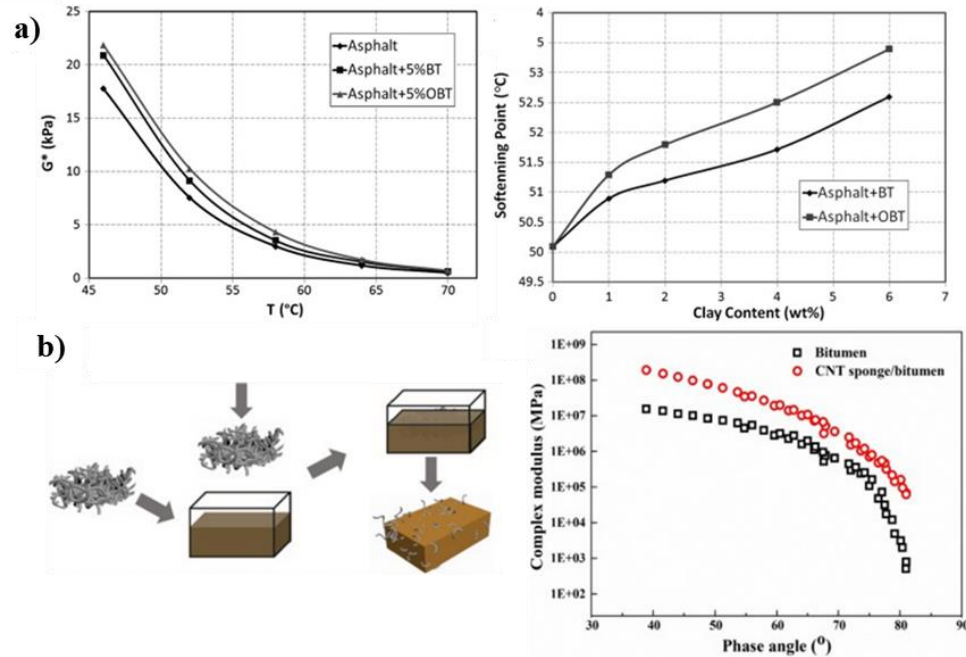


Figure 2.34. Properties of asphalt, modified asphalt with (a) Bentonite clay (BT) and organically modified bentonite (OBT) based on complex modulus (G^*) against temperature and a softening point against the concentration of clay²¹³, (b) Presentation of CNT /asphalt composite, and rutting resistance comparison of asphalt and CNTs-modified asphalt²⁶⁵

2.5.8.2. Ageing Resistance

Dispersion of nanomaterial in composite creates tortuosity path that increases the path length in asphalt, creating a physical obstacle to the diffusion and permeation of molecules. As a result, asphalt modification provides an effective barrier to oxygen and water and improves the ageing resistance of asphalt (Figure 2.35).^{261,263,270}

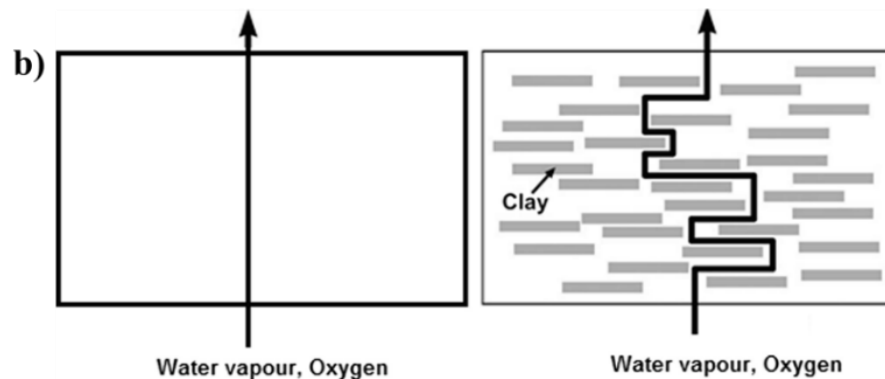


Figure 2.35. Tortuosity path effect of nano-clay on asphalt²⁶¹

2.5.8.3. Crack Resistance

Proper interfacial interaction between the asphalt and nanomaterial can prevent microcrack growth. Carbon nanofibers (CNF) as nanosized particles with large surface areas can have great interfacial attachment ability to create a network named as "bridging effect" with the matrix (Figure 2.36). Also, CNF has a high tensile modulus which improves their strength against high vehicle loading. It was presented a reinforced zone containing CNT can prevent the crack development.^{271,272}

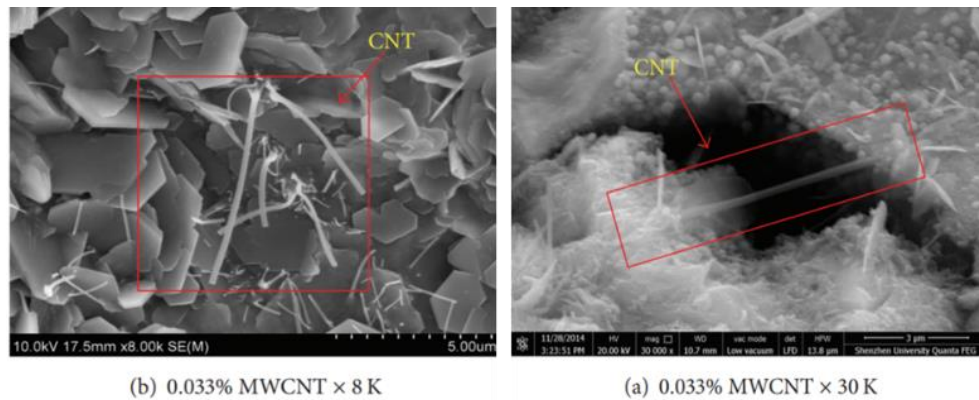


Figure 2.36. Bridge effect of CNTs on cement structure²⁷¹

Johnson et al. (2021) investigated the impact of untreated nano-clay and cellulose nanocrystals on performance properties of asphalt mixes prepared with PG64 -28 asphalt cement using IDEAL-CT (indirect tension asphalt cracking test) and observed 47 to 114% increase in crack resistance of resulting mixes²⁷³.

2.5.8.4. Limitations and Challenges of Nano modified Asphalt

Nanotechnology in pavement structure is defined based on three categories. Firstly, the science of chemistry and physics concerns the composition, structure, and interrelationships of matter. Then, engineering concerns apply these principles to the design and manufacture on a large scale. Finally, pavement engineering deals with the design of roads with the highest potential benefit/cost ratio and quality of life.²⁷⁴ Some challenges limit the application of nanomaterials on asphalt.

Large-scale application of nanomaterials should be considered to improve the properties of asphalt in practical pavement engineering. Hence, it is critical to evaluate the preparation cost of nanomaterials on a large scale.²⁷⁴ For instance, in applying carbon nanotubes (CNTs) as fibers in

fiber-reinforced concrete, 52 kg of CNTs is expected to pave 1 km concrete. Thus, for 10 to 100 km of road, a typical pavement project requires 520 to 5,200 kg of CNTs, which is not appropriate due to the high cost. Also, as nanomaterials properties vary when supplied at a large scale, the effect of nanomaterials on the environment is currently a main major concern. Pavements are applied in the open areas, so all the ingredients should minimize their impact on the natural environment. Therefore, the leaching of nanomaterials into groundwater and release into the air through dust generation on unpaved roads can expose dangerous materials under construction and maintenance operations.²⁷⁴

In addition, the properties improvement of modified asphalt depends on the effective dispersion of the nanomaterial into the asphalt. However, agglomeration of nanomaterials in asphalt usually leads to a clump structure. Finding a proper mixing method to guarantee the homogenous dispersion of nanomaterials is challenging.^{220,226,274} There are two mixing techniques to disperse the nanomaterials in asphalt, namely the dry blending method and the solvent blending method. Increasing the mixing temperature decreases the asphalt viscosity, efficiently improving nanomaterial dispersion. However, high temperature accelerates the ageing rate and deteriorates the durability of asphalt. Also, a longer mixing time enhances the dispersion of the asphalt particles, resulting in high energy consumption.

Xie et al. (2018) studied the challenges of implementing CNC in nanocomposite polymers and reported high agglomeration of CNC occurred mainly due to abundant hydroxyl groups on its surface. The low homogeneous dispersion was found to limit the tensile reinforcement of the resulting modified polymer ¹.

2.6. Summary of the Literature Review

This chapter reviewed the background of cellulose nanocrystal (CNC), properties, and applications in preparing Pickering emulsions. Pickering emulsions according to their advantages and properties is discussed. The stabilization capability of CNCs on Pickering emulsions is described in detail based on the CNC's properties. Also, a comprehensive review of the rheological characterization of viscoelastic materials was performed. Asphalt emulsion's definition and properties, their advantages and shortcomings were reviewed. Finally, the advantages and challenges of asphalt modification on the durability enhancement of asphalt residue are reviewed.

Some examples of previous works related to the higher mechanical properties of CNC-based composite are listed.

From the review of the literature, the following shortcomings of the conventional asphalt emulsions are identified.

- Low storage stability is usually addressed by increased alkalinity or acidity of the emulsions which could inversely affect the properties of the residue asphalt cement and compromise performance properties, such as rutting and fatigue resistance
- Extreme sensitivity of surfactant-based emulsions to the surface charge of aggregates could cause premature breaking and low aggregate coverage and higher moisture sensitivity
- The sensitivity of surfactant-based emulsions to phase transition of the dispersed oil caused by fracture at the interface has reported in literature to reduce the stability of the system at lower storage temperatures

Based on this literature review, it can be concluded that the strong absorbance of CNC particles as an interfacial stabilizer can prepare stable Pickering emulsion after oil phase transition. Our goal is to utilize CNCs as an environmentally friendly stabilizer to prepare asphalt emulsions with higher stability and interesting properties. In addition, characterize the physical and mechanical properties of asphalt residue modified with CNC particles.

CHAPTER 3: METHODOLOGY

3.1. Materials

Celluforce Inc supplied the CNCs used in this project. The commercial coconut oil sample was procured from a local market. Asphalt cement (PG 58-28 supplied by CAE), and a commercial-grade surfactant were provided by CoCo Paving company. All other chemicals used in this research were analytical grade and they were purchased from Sigma-Aldrich and used without further purification. These include potassium bromide (KBr), sodium chloride (NaCl), 2,2,6,6-tetramethyl-1-piperidinyloxyradical (TEMPO), sodium bromide (NaBr), sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium hypochlorite (NaClO), ethanol (C₂H₆O), 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid sodium salt (HEPES), polyamidoamine dendrimer generation 6 (5 wt.% solution in methanol) (G6-PAMAM), N-hydroxysuccinimide (NHS), N-(3-Dimethylaminopropyl)-N'-ethyl-carbodiimide hydrochloride (EDC), sodium dodecyl sulfate (SDS), dimethyl-aminopyridine (DMAP), triethylamine (TEA), cinnamoyl chloride (trans-3-phenylacryloyl chloride), N-dimethyl formamide (DMF, anhydrous 99.8%), tetrahydrofuran (THF, anhydrous 99.9%), sodium cyanoborohydride (NaBH₃ reagent grade, 95%), hydroxylamine hydrochloride (NH₂OH.HCl reagent grade, 98%), amine-terminated polystyrene (PS NH₂), toluene (anhydrous 99.8%), Heptane (anhydrous 99%), paraffin wax.

Milli-Q (MQ) water (resistivity 18.2 MΩ) obtained from Millipore Direct-Q5 was used for all aqueous solution preparation.

3.2. Characterization Methods

The surface charge and size of particles were measured using the Malvern Instrument Zetasizer Nano Series. The average zeta potential of twelve measurements of three different runs of each 0.04wt% diluted samples were reported.

Fourier transform infrared spectra of CNCs and functionalized CNCs particles were recorded using the Bruker Tensor 27 spectrometer FT-IR spectrometer. Each measurement was comprised of an accumulated 32 scans over the wavelength range of 4000 to 400 cm⁻¹. Freeze-dried sample (1wt.%) was mixed with KBr, grounded, and pressed into FTIR pellets.

The contact angle of unmodified and modified CNCs were measured based a sessile drop method using an optical tensiometer and ImageJ software to analyze the contact angle. Each sample (4.0 wt%) was dispersed in water, coated on a glass slide, and dried in the oven. The contact angle results were reported as the average of three μl DI water droplets using a NE-1010 higher pressure syringe pump (NewEra Pump Systems Inc.) on the surface of the resulting films.

The carboxyl and amine groups on the surface of TEMPO-CNC and PAMAM-CNC were measured using the Metrohm 809 Titrand auto-titrator. Typically, 30 ml of modified CNCs dispersed in water at pH three were stirred gently, and 0.01M NaOH was added at the rate of 0.05ml/min.

UV-visible spectrometer (model Carey 100 Bio) was used to determine the grafting ratio of Cinnamate groups on the surface of CNCs.

Thermal properties of paraffin wax in emulsions were determined using differential scanning calorimetry (DSC, TA Q2000 equipment). DSC measurements were performed by injecting 0.038 mM samples into an aluminum pan, while other reference cells filed with Millipore water. The analysis of thermal properties was set in the range of 25-80° under cooling and heating at ten °C/min rate and purged with nitrogen at a 30 ml/min flow rate throughout the test.

The interfacial tension of the samples was measured using a VCA 2500 XE system (AST Products, Billerica, MA). According to the axisymmetric drop shape, a pendant drop of CNC dispersion was suspended from a stainless-steel needle tip inside the cuvette containing two ml of the oil phase. To prevent droplet evaporation, the cuvette's cap was covered with a parafilm. Continuous pendant droplet images were recorded at a frame rate of five shots per minute for 1200 seconds for dynamic interfacial tension analysis using a high-speed CCD camera at room temperature. The Laplace equation was utilized for the study of each image.

The morphology of emulsions was observed using a Nikon Elipse Ti-S optical microscope (model Agilent Cary Eclipse) equipped with a CCD camera (QImaging ReTIGA 2000R). The oil droplets were visualized by adding one droplet of 10 times diluted samples on a glass slide.

The maximum excitation and emission of fluorescent modified CNCs were determined using a Carey Eclipse fluorescence spectrometer equipped with a digital CCD camera.

The partitioning behavior of fluorescent modified CNCs at the interface of oil droplets was observed using an Inverted Microscope Leica DM IL LED equipped with a three-position fluorescence slider. LAS X software was used to analyze the recorded images. The creaming index of the emulsion was determined through the images taken 24 hr after storage at room temperature.

The droplet size and size distribution of prepared emulsions were measured using the laser-diffraction particle size analyzer (Anton Paar, Model PSA 1190). Samples dropwise were added slowly to the 500 ml water until they reached the 5-30% concentration. Then, the droplet size was reported as the average of three continuous measurements.

The rheological characterization of samples was performed by a Kinexus Ultra+ Malvern rheometer that used a cup and bob geometry to characterize the samples. A double gap system provided a larger contact area and higher torque resolution. Samples with higher viscosities were evaluated with a Kinexus Ultra+ and a cone and plate geometry sensor (20-mm diameter) using a 1mm gap distance. The solvent trap was used to prevent water evaporation for testing at high temperatures. Raw results were then analyzed using the rSpace-for-Kinexus-Pro1.3 software.

3.3. Data Analysis

Analysis of variance (ANOVA) examined the optimum emulsion stability based on different parameters statically.

The 2S2P1D (two springs, two parabolic, and one dashpot) model developed complex modulus and phase angle master curves, black space, and Cole-Cole diagrams to correlate the rheological properties with the asphalt formulations.

CHAPTER 4: EFFECT OF OIL PHASE TRANSITION ON THE STABILITY OF PICKERING EMULSIONS STABILIZED BY CELLULOSE NANOCRYSTALS

Abstract

Emulsifier design is one of the key strategies in interfacial engineering for emulsion stability. In this study, cellulose nanocrystal (CNC) was used as an interfacial stabilizer to improve the stability of coconut oil (CO) in water emulsions. Pickering emulsion consisting of coconut oil and water was optimized based on four parameters using the response surface methodology (RSM) and the central composite design (CCD). The droplet coverage remained stable during the crystallization of the oil phase when the temperature was reduced below the melting temperature of CO. Fluorescent-labelled CNC was used to monitor the partitioning of CNC at the O/W interface during the crystallization of CO. PAMAM G6 dendrimer covalently grafted on the surface of CNC was used as an intrinsic fluorescent dye. Since it displayed similar properties as the emulsifier, it could be used to monitor the CNC coverage on the oil droplets at various temperatures. The fluorescence micrographs showed that the emission of PAMAM-CNC at the O/W interface remained on both the liquid and solid CO droplets, confirming that oil crystallization did not affect the fluorescent CNC coverage on the oil droplets.

4.1. Introduction

An emulsion is a dispersion system produced by mixing two immiscible liquids, where one liquid is dispersed in a continuous phase of the other.^{69,275} In the absence of a stabilizing agent, this dispersed system is unstable, and the two phases would eventually separate. Amphiphilic surfactants are commonly used to stabilize the emulsions used for agricultural, medical, food, and petrochemical industries. Another system used to stabilize emulsions is solid particles that provide a barrier on the surface of the dispersed phase droplets, which prevent coalescence.^{71,75,276} Such emulsions are termed Pickering emulsions^{74,77} and they are usually more stable than traditional surfactant-based emulsions. Amphiphilic surfactants typically adsorb and desorb from interfaces with a rapid time scale, whereas solid particles with appropriate wettability remain irreversibly adsorbed at the interface.²⁷⁷ Therefore, a lower emulsifier concentration is required to stabilize the emulsion with solid particles. With the growing global interest in adopting renewable and environmentally friendly products, particle-stabilized emulsions are gaining more attention in applications like bio-medicines and cosmetic products.^{71,79,278,279}

The behavior of Pickering emulsion depends on the wettability of solid particles, which control the characteristics of the particles at the oil/water interface.^{79,96,128} The combined analysis of the energy required for the particle removal from interface and the maximum capillary pressure of thin liquid film between the emulsion droplets, revealed that if the emulsion is stabilized by a single layer of solid particles, the oil-in-water emulsion will be stable, where the contact angle (CA) of particles at the interface is between 15° and 90°, while water-in-oil emulsions are stable when the CA is between 90° and 165°. ^{131,280} Moreover, the shape of the solid particles plays a vital role in the physicochemical properties of the emulsion. Emulsions stabilized by cylindrical or elliptical particles exhibit higher stability than those prepared by spherical particles due to the ability of elongated particles to form a network structure at the interface.^{133,135} Other factors, such as surface properties and particle concentration, are also critical in determining the dispersed phase droplet size and the stability of the emulsion system.⁷⁶

The effectiveness of various inorganic particles, such as silica, calcium carbonate, and montmorillonite as emulsifiers for Pickering emulsions was previously reported.^{281–286} Cellulose nanocrystals (CNCs) have recently been investigated to replace inorganic emulsifiers in Pickering emulsions.^{70,115,287} Besides having amphiphilic properties,¹⁶⁸ CNC possesses other unique characteristics, including desirable wettability, high surface area, biocompatibility, and high

tensile strength, making it an ideal emulsifier.^{68,115,139} However, acid-hydrolyzed-CNCs possess negative sulfate ester groups that induce electrostatic repulsion between CNC particles at the oil-water interface.^{43,185} Modification of the CNC surface or the addition of salt reduces the repulsion and facilitates the adsorption of CNC on the surface of oil droplets.¹⁶⁸ Moreover, the ease of chemical modification offers many possibilities to develop functional CNCs suitable for specialized applications.^{288,289} The capability of CNCs to produce various emulsion types, including oil-in-water, water-in-oil, water-in-water, and complex emulsions, has been reported for applications, such as food, cosmetics, and pharmaceuticals.^{44,115,132}

Phase change materials (PCMs) can adsorb and release their latent heat during the phase change. Nano-encapsulation is an effective way to isolate PCM from its surrounding environment and enhance the thermophysical properties of the PCM.²⁹⁰ That is why in recent years, the emulsification of PCMs by solid particles has attracted significant attention in food^{141–144} and pharmaceutical applications.¹⁴⁵ Few studies have reported on the stability of these emulsions at the phase transition of the dispersed phase from liquid to solid or vice versa. For the emulsification of a highly viscous oil or high melting liquid, it is necessary to reduce the viscosity to a practical level for emulsion production, for instance by increasing the temperature. Since emulsions are stored at ambient conditions, the dispersed phase turns into a solid or a viscous liquid. Thus, the capability of the emulsifier to stabilize the emulsion over a broad temperature range covering the production to storage and application is of paramount importance. Solidification of the oil phase alters the properties of the emulsion and may destabilize the system due to various factors.¹⁵¹ The wettability of the oil phase during the solidification process may alter the partitioning of the emulsifiers at the oil/water interface.^{145,152,153} Additionally, the spherical droplets of emulsion may deform when the liquid oil solidifies, affecting the surface coverage of the droplets by the emulsifiers. Lack of strong attachment of emulsifier to the oil droplets may reduce the surface coverage, causing the droplets to coalesce or the emulsion to break.¹⁵² Therefore, in order for emulsion to remain stable when the dispersed phase experiences a phase transition from liquid to solid, the emulsifier should preserve the droplets coverage and prevent the coalescence of the oil droplets.¹⁵⁴

This study investigates the use of CNC to stabilize Pickering emulsion over the phase transition temperature of the dispersed phase. Food grade coconut oil was selected as the phase change

material and was emulsified in water using CNC as the emulsifier. The resulting emulsion was used as the model system to investigate emulsion behavior during the phase transition.

The first step is to optimize the formulation of CO Pickering emulsion stabilized by CNCs. The design of experiment (DOE) strategy was employed for the parameter optimization based on the Response Surface Methodology (RSM). A mathematical model was obtained to describe the relationship between the parameters and responses.^{291,292} The model was used to determine the optimum conditions and the parametric effect on the stability of the emulsions, after which the optimum emulsion was analyzed over the phase transition region.^{293–295}

Secondly, the CNC was covalently labelled with Generation 6 polyamidoamine (G6-PAMAM) dendrimer as a tracer dye to visualize the CNC at the oil/water interface. The intrinsic fluorescent G6 PAMAM dendrimer was grafted to the oxidized-CNC imparting fluorescent emission to the CNCs.²⁹⁶ The emulsions were imaged using a fluorescence microscope at different temperatures to examine the effect of phase transition of oil droplets on the stability of CNCs at the oil/water interface and droplet coalescence. Nile red was used as a fluorescent marker for CO to track the PAMAM-CNC at the oil-water interface. Fluorescence spectroscopy studies indicated that dyed CNCs were stable at the oil/water interface even after the phase transition confirming the potential of using CNC as the emulsifier in the Pickering emulsion systems with a phase transition.

4.2. Experimental

4.2.1. Materials

The chemicals used, such as potassium bromide (KBr), sodium chloride (NaCl), 2,2,6,6-tetramethyl-1-piperidinyloxyradical (TEMPO), sodium bromide (NaBr), sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium hypochlorite (NaClO), ethanol (C₂H₆O), 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid sodium salt (HEPES), sodium hydroxide (NaOH), polyamidoamine dendrimer generation 6 (5 wt.% solution in methanol) (G6-PAMAM), N-hydroxysuccinimide (NHS), sodium dodecyl sulfate (SDS), and N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) were purchased from Sigma-Aldrich. Celluforce Inc. kindly supplied the CNCs. The commercial coconut oil sample was procured from a local market. In the sample preparation, Milli-Q water was used for all the aqueous solutions preparation.

4.2.2. Preparation of Coconut Oil in water Pickering Emulsion

All the CO emulsions were prepared by sonication of pre-heated CO in the aqueous phase. An ultrasonic probe (Misonix Microscon-XL2000) was used to prepare the emulsions. The resulting emulsions were stored at room temperature for further analysis.

4.2.3. Optimization of Coconut Oil/water Emulsion

The optimum conditions for the stability of Pickering emulsion were determined using the Response Surface Methodology (RSM) and Central Composite Design (CCD). Through the RSM, the optimum emulsion stability was analyzed, and a model based on different factors was identified. The Central Composite Design (CCD) was used to determine the minimum number of experiments. The number of designed experiments were calculated based on equation $n = 2^k + 2k + N_0$, where n is the number of experiments, k is the number of parameters ($k=4$), 2^k is the factorial portion, the $2K$ is the number of face-centered points, and the N_0 is the number of experiments at the center point ($N_0=6$).

Thirty experiments were chosen randomly based on four factors, namely, CNC concentration, water/CO volumetric ratio, sonication time and amplitude of sonication (Table 4.1). Table 4.2 summarizes the values of factors for the 30 samples.

Table 4.1. Range of parameters used in the Experimental Design.

Factor	Unit	Low (–)	High (+)
Time	min	1	4
Amplitude	percentage	20%	35%
Volumetric W/O ratio	-	1	4
C _{CNC}	mg/ml	3	6

Table 4.2. Experimental results and their associated parameters.

Run	A: time (min)	B: Amplitude (%)	C: W/O (Volumetric)	D: C _{CNC} (mg/ml)	Particle size (μm)	
					without NaCl	with NaCl
1	1.0	35.0	4.0	6.00	11.00	2.06
2	1.0	35.0	1.0	3.00	12.28	2.74
3	2.5	27.5	2.5	4.50	10.86	1.76
4	2.5	27.5	2.5	4.45	12.91	1.84
5	2.5	27.5	2.5	4.45	12.21	1.69
6	1.0	27.5	2.5	4.45	11.47	2.22
7	4.0	27.5	2.5	6.00	14.27	1.33
8	4.0	35.0	4.0	4.45	13.41	1.02
9	4.0	20.0	1.0	6.00	9.16	2.10
10	1.0	20.0	4.0	3.00	11.83	2.08
11	2.5	27.5	4.0	4.45	13.10	1.61
12	4.0	20.0	4.0	3.00	11.36	1.50
13	1.0	20.0	1.0	6.00	13.32	2.40
14	1.0	20.0	4.0	6.00	14.92	2.11
15	2.5	27.5	2.5	4.45	9.67	1.64
16	4.0	20.0	4.0	6.00	11.78	2.09
17	2.5	20.0	2.5	4.45	12.49	1.83
18	2.5	27.5	2.5	6.00	9.75	2.82
19	1.0	20.0	1.0	3.00	8.30	2.37

20	2.5	27.5	2.5	3.00	12.25	1.44
21	2.5	35.0	2.5	4.45	10.93	1.54
22	2.5	27.5	2.5	4.45	12.28	1.78
23	4.0	35.0	1.0	3.00	14.66	1.80
24	1.0	35.0	1.0	6.00	11.34	1.29
25	4.0	35.0	4.0	3.00	11.60	1.66
26	2.5	27.5	2.5	4.45	10.13	1.47
27	4.0	20.0	1.0	3.00	8.60	2.23
28	2.5	27.5	1.0	4.45	10.76	1.38
29	4.0	35.0	1.0	6.00	13.15	1.86
30	1.0	35.0	4.0	3.00	11.26	2.09

The droplet size, being one of the most vital parameters on the emulsion's creaming and coalescence, was used to characterize the stability of emulsion.^{123,297,298} The experimental design (DOE) results were statistically analyzed using the analysis of variance (ANOVA). The effect of factors was presented with two and three-dimensional graphs. Also, a mathematical model was determined to predict the highest possible stability of emulsion from the optimum values of the four parameters. The model with the best fit revealed the impact of each variable and their interactions on the droplet size.

Since the coconut oil (CO) melts at 24 °C, the emulsification was performed above the melting point of CO, at 30 °C. The Pickering emulsion was prepared by sonicating 2 ml hot CO in 8 ml deionized water containing CNC and NaCl. Thirty emulsions were prepared randomly based on their defined parameters at the constant sodium chloride concentration (0.5wt.%) Figure 4.1. The particle size of freshly prepared samples was measured using optical microscopy.

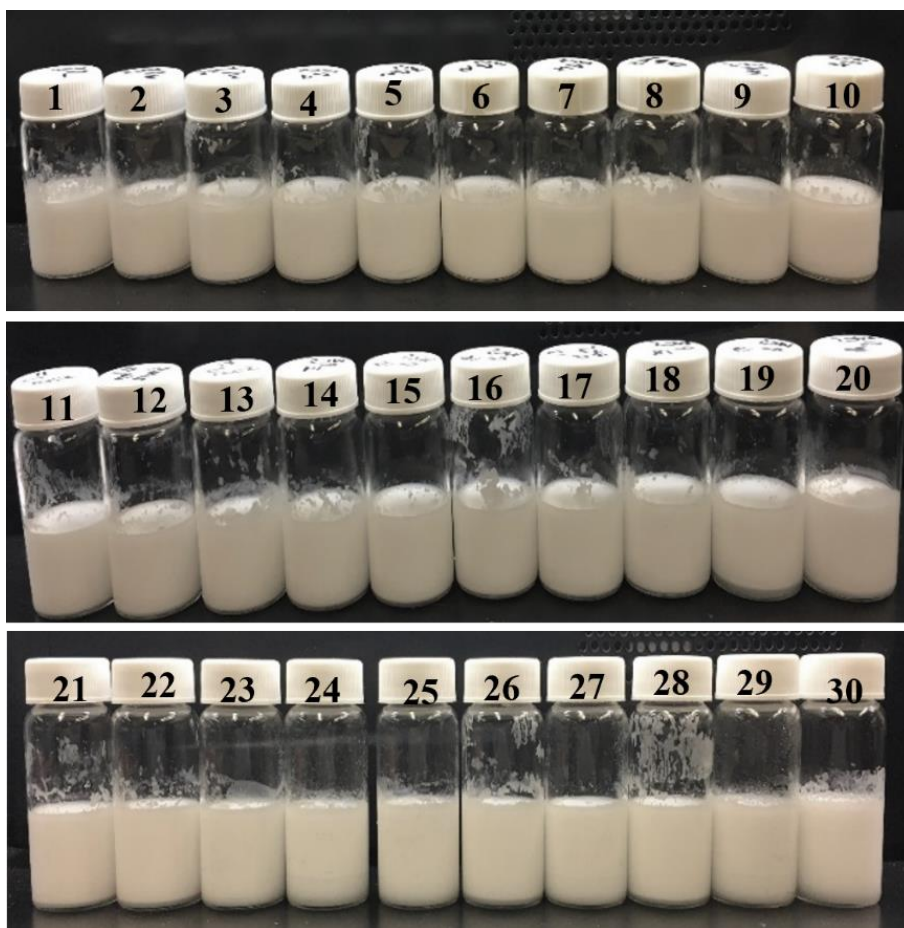
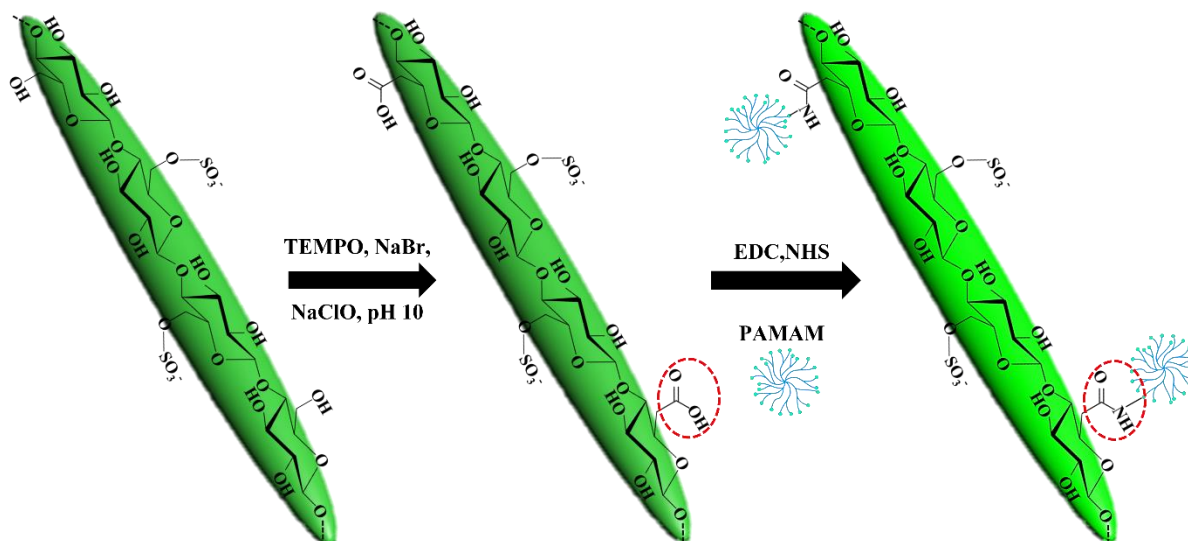


Figure4.1. Phase behavior of CNC-stabilized emulsions after 24 Hr.

4.2.4. Synthesis of PAMAM-CNC

CNC (5 gr) was dispersed in 375 mL distilled water and oxidized with 0.0125 g TEMPO and 0.0125 g sodium bromide. The mixture was vigorously stirred and sonicated for 15 min before it turned highly viscous. It was then mechanically stirred while 50 mg sodium hypochlorite (NaClO) was added. The pH was adjusted to 10 using NaOH and kept for 4 hours. After the oxidation, 5 mL of ethanol was added to deactivate the unreacted TEMPO, and the pH was adjusted to 7 using HCl. The precipitate was dispersed in distilled water and centrifuged three times at 8,000 rpm for 5 min to remove excess acid, inorganic salt, and TEMPO. The oxidized CNC was then freeze-dried.^{299,300} An amount of 0.06 g (25 mM) HEPES buffer was dispersed in 100 ml water, and by adding HCl, the pH was adjusted to 6.5. Freeze-dried Oxidized-CNC (50 mg) was dispersed in the HEPES buffer and sonicated for 10 min. Then 100 mg EDC and 100 mg NHS were slowly added to the Oxidized-CNC. The reaction was stirred for 2 hours, and the G6 PAMAM dendrimer was

added dropwise under sonicating. The mixture was stirred for 24 hours and purified for three days by dialyzing it against water (scheme 4.1).²⁹⁶²⁹⁶



scheme 4.1.Synthesis of PAMAM-CNC

4.2.5. Characterization

Zeta Potential. The zeta potential of pristine and modified CNCs was determined using the Malvern Zetasizer Nano Series. The average zeta potential of 12 measurements of three different runs was reported.

FTIR Characterization. Fourier transforms infrared spectroscopy (FTIR) was performed to confirm the reactions using the Bruker Tensor 27 spectrometer FT-IR spectrometer. A total of 32 scans were accumulated over the wavelength range of 4000 to 400 cm^{-1} . The FTIR pellets were prepared by mixing, grinding, and pressing the freeze-dried samples with KBr.

Conductometric Titration. The amount of the carboxyl and amine groups was determined via conductometric titrations using a Metrohm 809 Titrando auto-titrator (Switzerland). Suspension of functionalized CNCs in water (2 mg/mL) was prepared, and the pH was adjusted to 3 using 1M HCl, and the dispersion was stirred overnight. The suspensions were then titrated with NaOH. First, a strong acid (HCl) and then carboxylic acid, amine, and amide functional groups as weak acids were neutralized. Based on the volume of NaOH required to neutralize the weak acids, Eq. (4.1) was used to estimate the amounts of carboxyl, amine, and amide groups on the surface of CNC.

$$\text{amount of functional group} \left(\frac{\text{mol}}{\text{g}} \right) = \frac{C_{\text{NaOH}} \times \Delta V_{\text{NaOH}}}{m(\text{g})} \quad (4.1)$$

where ΔV is the volume of NaOH (mL) needed for the neutralization of the weak acid, C_{NaOH} is the concentration of NaOH solution ($\frac{\text{mol}}{\text{L}}$), and m is the mass of the functionalized CNCs used in the titration.

Contact Angle. Contact angle tests were performed on the CNC and modified CNC using a goniometer, and software ImageJ was used to determine the contact angle. A dispersion of each sample (4.0 wt%) in water was coated on a glass slide and dried in an oven. The contact angle measurement was performed by adding 3 μL DI of water droplets with a NE-1010 high pressure syringe pump on the surface of the coated films.^{301,302}

Optical Microscopy. The morphology of the oil droplets was observed through a Nikon Elipse Ti-S optical microscope (Agilent Cary Eclipse) equipped with a CCD camera (QImaging ReTIGA 2000R). One emulsion droplet that was ten times diluted was placed on a glass slide to visualize the emulsion in the microscope. The average diameter of the droplets was reported as the average of at least 100 measurements of three images captured by the microscope.

Fluorescence Characterization. Fluorescence spectroscopic measurements were performed on dyed CO emulsions containing fluorescent-labelled CNCs. The maximum excitation and emission of PAMAM grafted on CNC, and Nile red was measured using a Carey Eclipse fluorescence spectrometer equipped with a digital CCD camera. Oil-in-water emulsions were prepared at 30°C with either pure CO or dyed CO with Nile Red using the optimum parameters. Before the emulsion preparation, Nile red was mixed with the CO, where 5 mg Nile Red was added to hot CO liquid and stirred overnight in the dark, and excess Nile red was removed by centrifugation.

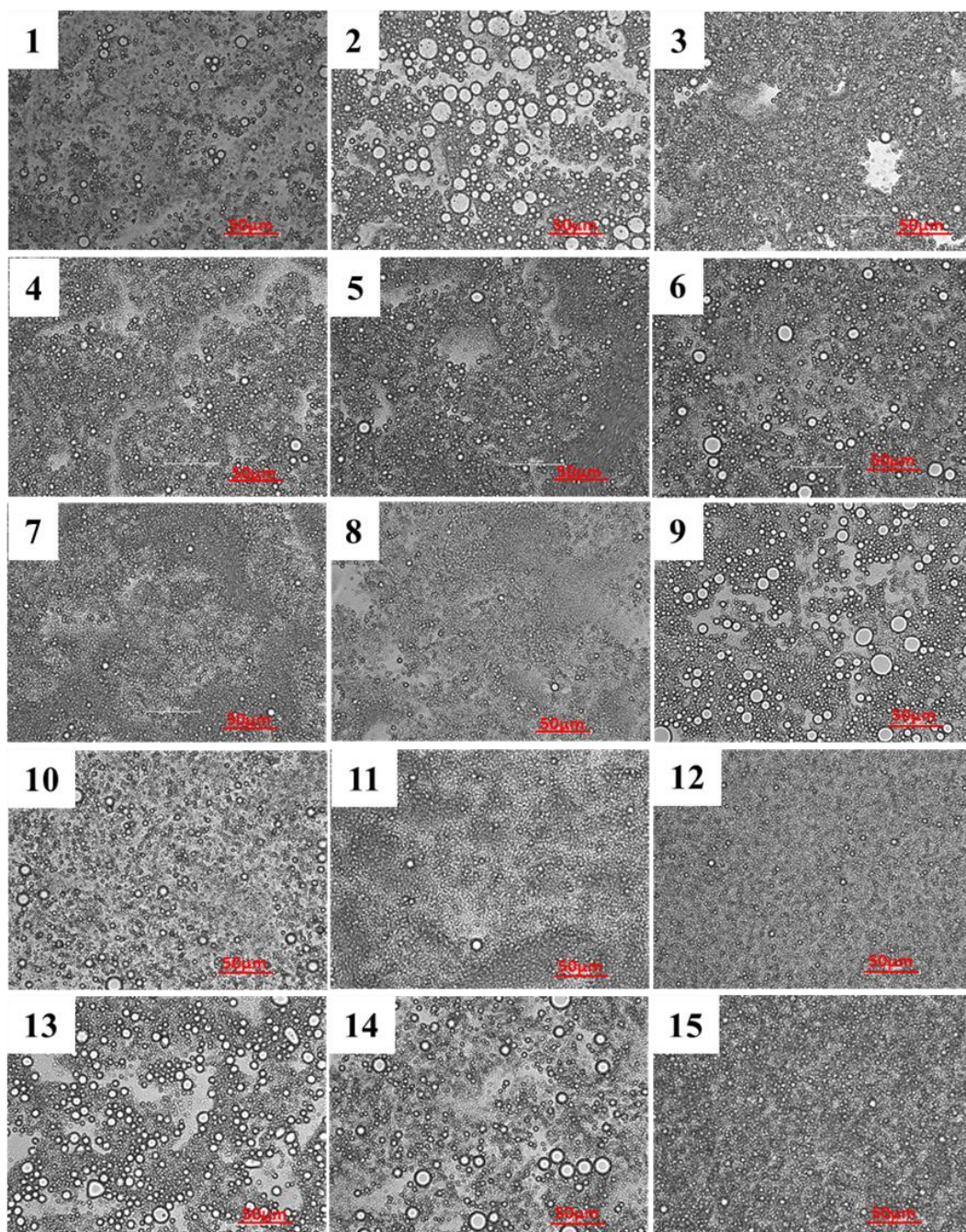
Fluorescence microscopy was used to monitor the emulsifier behavior at the oil/water interfaces. The location of PAMAM-CNC on coconut oil droplets at different temperatures (below and above the phase transition of coconut oil droplets) was visualized using the Inverted Microscope Leica DM IL LED equipped with a three-position fluorescence slider. Images were recorded and merged using the LAS X software.

Rheological Analysis. Temperature sweep oscillatory tests were performed at 1 Hz (0.5% strain) over a temperature range of 50 to 15°C at a cooling rate of 2 °C/min using a concentric cylinder geometry. The storage modulus (G'), and the loss modulus (G'') of coconut oil emulsions stabilized with CNC and SDS were compared.

4.3. Results and discussion

4.3.1. Statistical Analysis of Coconut Oil Emulsion

The optimization process was performed on coconut oil emulsions stabilized with CNC in the presence of sodium chloride. The electrostatic repulsion of negatively charged CNCs affects their adsorption to the surface of the oil droplets, which reduces the emulsion stability. In this study, sodium chloride was added to shield the negative charge of the CNCs, which reduced the electrostatic repulsion. Consequently, the higher amphiphilicity of CNCs improved their adsorption on the oil droplets. Microscopic images of all 30 prepared emulsions were recorded and summarized in Figure 4.2. The effect of different parameters on the droplet size of the emulsion could be observed by comparing images where all parameters except one remained the same. For instance, by comparing Figures 4.2-1 and 4.2-14 one could conclude that increasing the amplitude of sonication decreased the droplet size. The effect of increasing the W/O volumetric ratio on the reduction of the droplet size could be inferred from comparing Figure 4.2-13 and Figure 4.2-14.



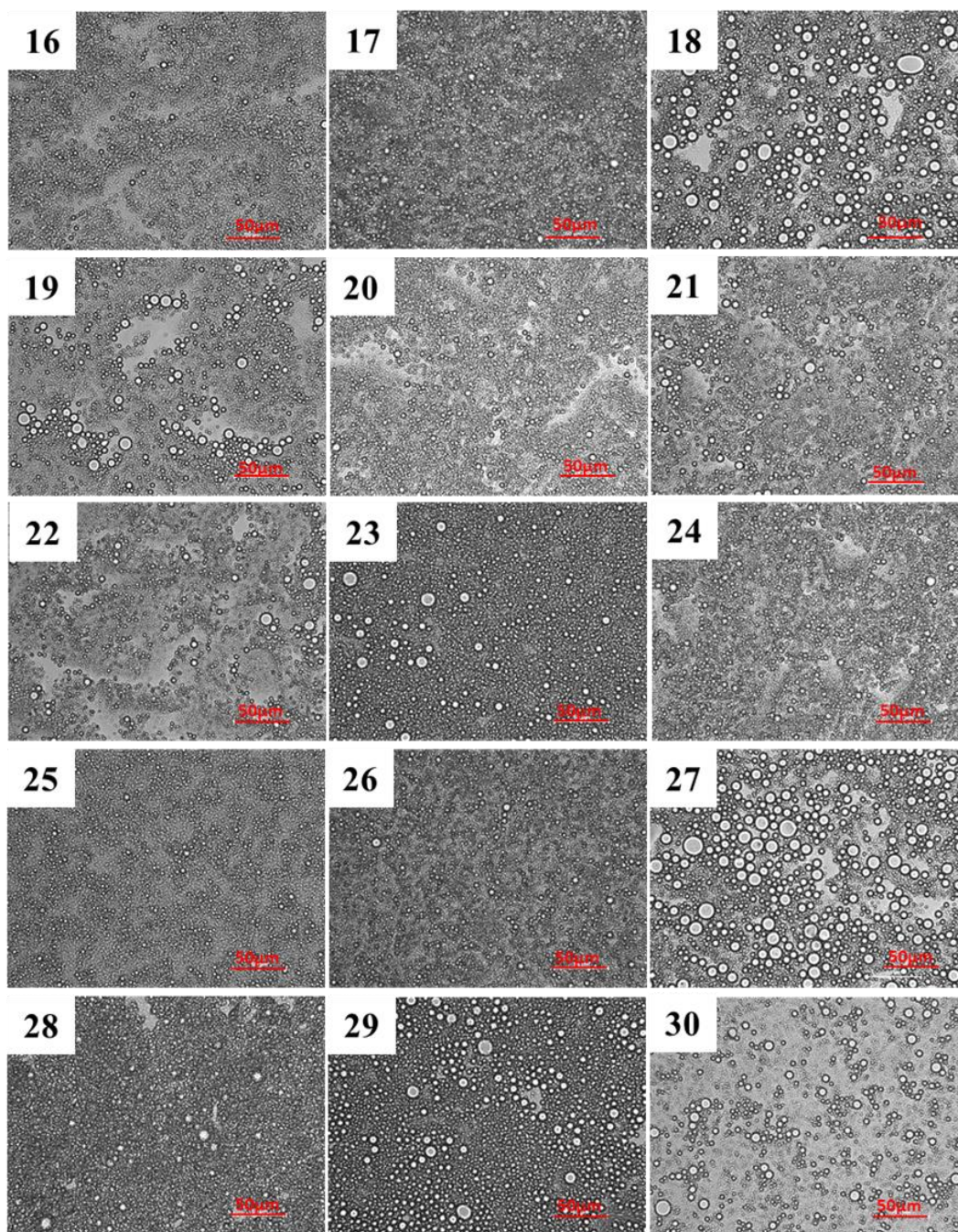


Figure 4.2. Optical microscopy images of thirty coconut oil emulsions based on four factors including, time and amplitude speed of mixing, water/oil ratio, and CNC concentration.

Figure 4.3(A) shows the effect of each variable on the oil droplet size displayed on a perturbation diagram. The interaction between CNC concentration and W/O volumetric ratio is presented in Figure 4.3(B). The increase of the three parameters, mixing time (A), amplitude of sonication (B), and W/O volumetric ratio (C) decreased the oil droplet sizes. While, increasing the concentration

of CNC (D) first decreased the droplet size, and after optimum CNC concentration was reached, increased the droplet size.

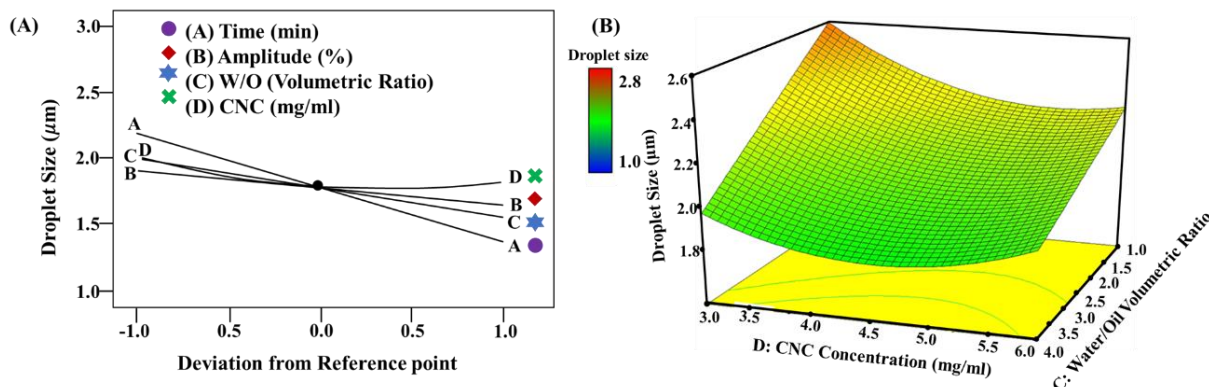


Figure 4.3. (A) Perturbation diagram of influencing parameters on droplet size of emulsions stabilized by CNC, (B) 3D-graph of response surface of particles size as a function of CNC concentration and water/oil ratio.

4.3.2. Optimization of Coconut oil emulsion

A mathematical model based on a quadratic polynomial equation was used to predict the oil droplet size as a function of four independent parameters. Eq.(4.2) shows the effect of selected variables on the average particle size.

$$R_p = 1.75 - 0.38A - 0.14B - 0.21C - 0.08D + 0.069CD + 0.13D^2 \quad (4.2)$$

where R_p is the average radius of oil droplets, A is mixing time, B is amplitude of sonication, C is the water/oil volumetric ratio, and D is emulsifier concentration. The coefficient of determination (R-Squared) was 0.89.

Figure 4.4 summarizes the optimum values of each parameter determining the stability of the emulsions. Each line presents the range of each factor, and the optimum value was identified with a circle. Analysis of variance (ANOVA) was used to examine the quadratic model of the response (Table 4.3). As presented in Figure 4.4, the optimum formulation of the emulsion was achieved with the following parameters: time: 4 min; sonication amplitude: 35%; water/oil volumetric ratio: 4; and 4.45 mg/ml (0.44 wt.%) CNC. As mentioned in the characterization section, the average diameter of the droplets was reported as the average of at least 100 droplets in three images captured by the microscope. The droplet size of the emulsion stabilized based on optimum parameters, was also measured using the Anton Paar particle size analyzer (PSA 1190 model), and

the average of three measurements were reported (Table 4.4). The results were the same as droplet size determined from microscopic images, and they were within the experimental errors.

Table 4.3. Analysis of variance (ANOVA) for model of emulsion stability.

Sources of Variations	Sum of Squares (SS)	Degree of Freedom (DF)	Mean Squares (MS)	F-Value	Probability (P>F)
Model	0.409	6	0.68	29.56	<0.0001
Residual	0.53	23	0.023		
Corrected total	4.62	29			

$R^2 = 0.8852$

Adjusted $R^2 = 0.8553$

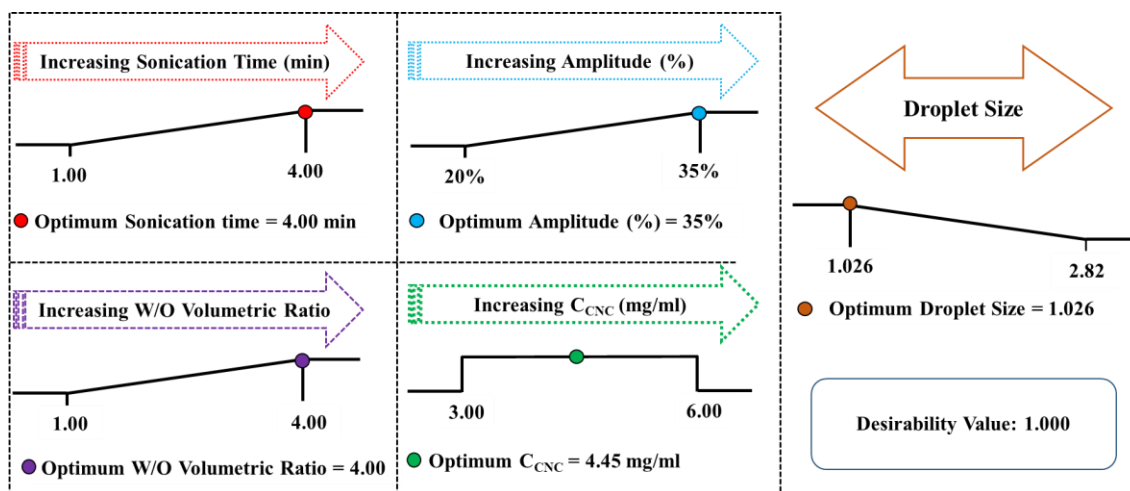


Figure 4.4. Optimum conditions for minimum particle size of Pickering emulsion.

Table 4.4. Mean droplet size of coconut oil stabilized based on optimum parameters.

0.5CNC,0.5NaCl,2.8	D10 volume	D50 volume	D90 volume	Mean size volume	Span
1 st Run	0.549	0.959	1.657	1.099	1.155
2 nd Run	0.464	0.899	1.567	1.028	1.226
3 rd Run	0.392	0.847	1.477	0.962	1.282
Mean droplet size of three measurements			1.029		

The results indicated that increasing the CNC concentration first decreased the droplet size, and after optimum CNC concentration was reached, increased the droplet size. At the optimum CNC concentration, the oil droplets were entirely covered by CNCs, therefore, excess CNC had minimal impact on the droplet size of the oil. Besides, the addition of NaCl reduced the repulsion between the CNCs, resulting in the partitioning of CNCs at the oil/water interface that enhanced the stability of the emulsion. The effect of salt on emulsion stability was evaluated by preparing thirty emulsion samples stabilized by CNC in the absence of salt (Table 4.2). All the prepared emulsions without salt addition were unstable after 24 hrs, and the separated coconut oil crystallized was observed at room temperature (Figure 4.5-A). while the emulsions stabilized with CNC and salt remained stable (Figure 4.5-C). The emulsions prepared outside the optimum condition creamed after one week (Figure 4.5-B), while emulsion prepared at the optimum conditions presented a slight recoverable creaming even after one year of storage Figure 4.5-D, and Figure 4.5-E).

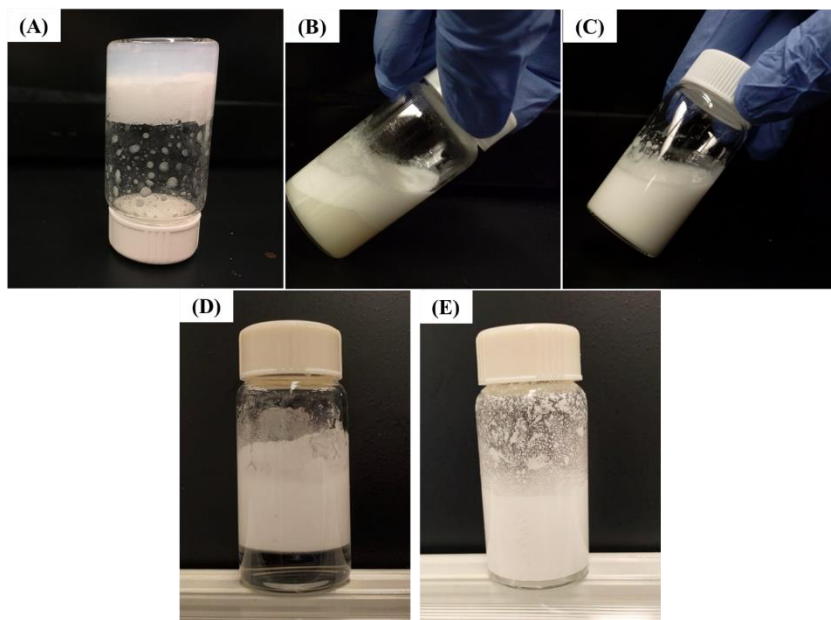


Figure4.5. (A) Phase separated coconut oil in water emulsion stabilized with CNC without salt addition, (B) Creaming of coconut oil in water emulsion stabilized with CNC prepared outside the optimum values of parameters (C) Coconut oil in water stabilized with CNC prepared at the optimum values of parameters, (D) Slight creaming of coconut oil in water emulsion prepared at the optimum values of four parameters after one year storage at room temperature, (E) Coconut oil

in water emulsion prepared at the optimum values of four parameters stored one year in room temperature, after slight shaking.

4.3.3. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectroscopy confirmed the modification of the CNC surface as shown in Figure 4.6. Pristine CNC possessed the following peaks: 3350 cm^{-1} for the O-H stretching, 2910 cm^{-1} for C-H stretching and 1065 to 1165 cm^{-1} for the glucose ring bands. New peaks of C=O stretching indicated the presence of carboxyl groups on Oxidized-CNC at 1725 cm^{-1} . PAMAM-CNC spectra confirmed the grafting PAMAM dendrimer on the surface of CNC by the appearance of C=O stretching at 1647 cm^{-1} , C-N stretching at 1385 cm^{-1} .

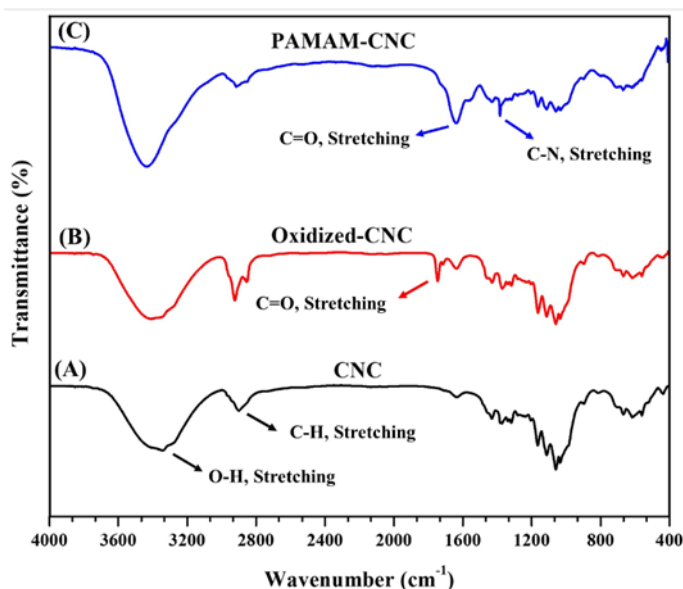


Figure 4.6. FT-IR spectra of (A) Pristine CNCs, (B) Oxidized -CNC, (C) PAMAM-CNC (E).

4.3.4. Zeta-potential

Modification of CNC with different functional groups alters the surface charge of the CNCs, and zeta potential can be used to confirm the success of the grafting. By changing the surface charge, the property of the emulsifier can be manipulated. The goal of fluorescent labelling of CNC was to track the location of CNCs at the oil/water interface. The labelling of the CNC with fluorescent molecules did not significantly alter the capability of CNC to stabilize the oil-in-water emulsion (Figure 4.9).

Zeta potential (ZP) results (Table 4.5) at different pHs further confirmed the successful modification of the CNC. The zeta potential of fluorescent-labelled CNCs at neutral pH remained within the range observed for pristine CNC, thus, similar emulsification properties were expected.

However, the ZP of PAMAM-CNC was positive in acidic pH due to the protonation of the amines on PAMAM.

Table 4.5. The zeta potential (in mV) of CNC nanoparticles

Sample	PAMAM-CNC	TEMPO-CNC	Pristine CNC
pH 7	-34.3	-40.7	-55.0
pH 5	17.4	-32.8	-47.6
pH 3	37.9	-30.5	-38.4

4.3.5. Potentiometric and Conductometric Titrations

The amounts of carboxyl, amine, and amide groups on the functionalized CNCs could be used to determine the efficiency of the fluorescent labelling. Figure 4.7 shows the titration curves along with the amounts of carboxyl, amine, and amide groups grafted on the surface of Oxidized-CNC and PAMAM-CNC. As presented in Figure 4.7(A), the curve is divided into three regions that corresponded to neutralization of (A) excess HCl, (B) weak acid (carboxyl group) on CNCs, and (C) addition of excess NaOH. The amounts of carboxyl groups on Oxidized-CNC is determined to be 0.27 mol/gr.

Also, five regions (A-E) shown in Figure 4.7(B) are related to the neutralization of (A) strong acid (HCl), (B) unreacted carboxylic groups (-COOH), (C) primary amine (-NH₂) and amide (-NH-) groups, and (D) addition of excess strong base (NaOH). The amounts of unreacted carboxyl, primary amine and amide groups on PAMAM-CNC were determined to be 0.011 mol/gr, 0.127 mol/gr, and 0.0133 mol/gr, respectively.

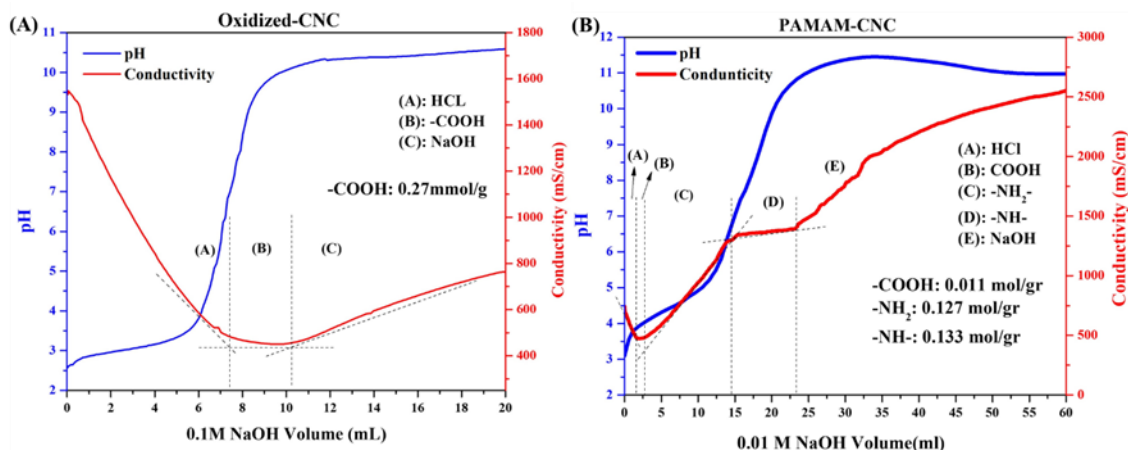


Figure 4.7. Conductometric and potentiometric titration curves of (A) Oxidized-CNC and (B) PAMAM-CNC.

4.3.6. Contact Angle

To evaluate the effect of modification on wettability, the contact angle of water on modified CNCs were compared with pristine CNC. As presented in Figure 4.8, at pH 7 the contact angles of water on pristine CNC and PAMAM-CNC were determined to be 51.1° and 60.8°, respectively. The results indicated that PAMAM-CNC and CNC have quite similar wettability and amphiphilic properties providing them with approximately similar emulsification behavior around the oil droplets.

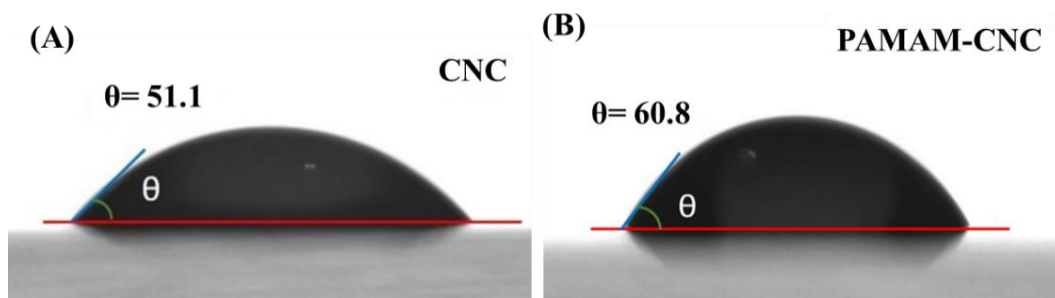


Figure4.8. Images of contact angles of (A) CNC, (B) PAMAM-CNC.

4.3.7. Optical Microscopy

Optical microscopy was used to monitor the morphology of emulsions and their average droplet size to compare the emulsion stabilized with pristine CNC and PAMAM-CNC. Droplet size of emulsions stabilized by CNC and PAMAM-CNC were compared after preparation and after one-month storage at room temperature. The droplet size of emulsions stabilized by CNC and PAMAM-CNC slightly increased (Table 4.6). Figure 4.9 presents microscopy images of fresh and stored CNC, and PAMAM-CNC stabilized emulsions.

Table 4.6. Mean droplet size of Co emulsions stabilized by CNC and PAMAM after preparation and storage for one month.

Emulsifier	Fresh/Stored Emulsion	Average droplet size (μm)
CNC	Fresh	1.03
PAMAM-CNC		3.84
CNC	One month stored	2.71
PAMAM-CNC		3.97

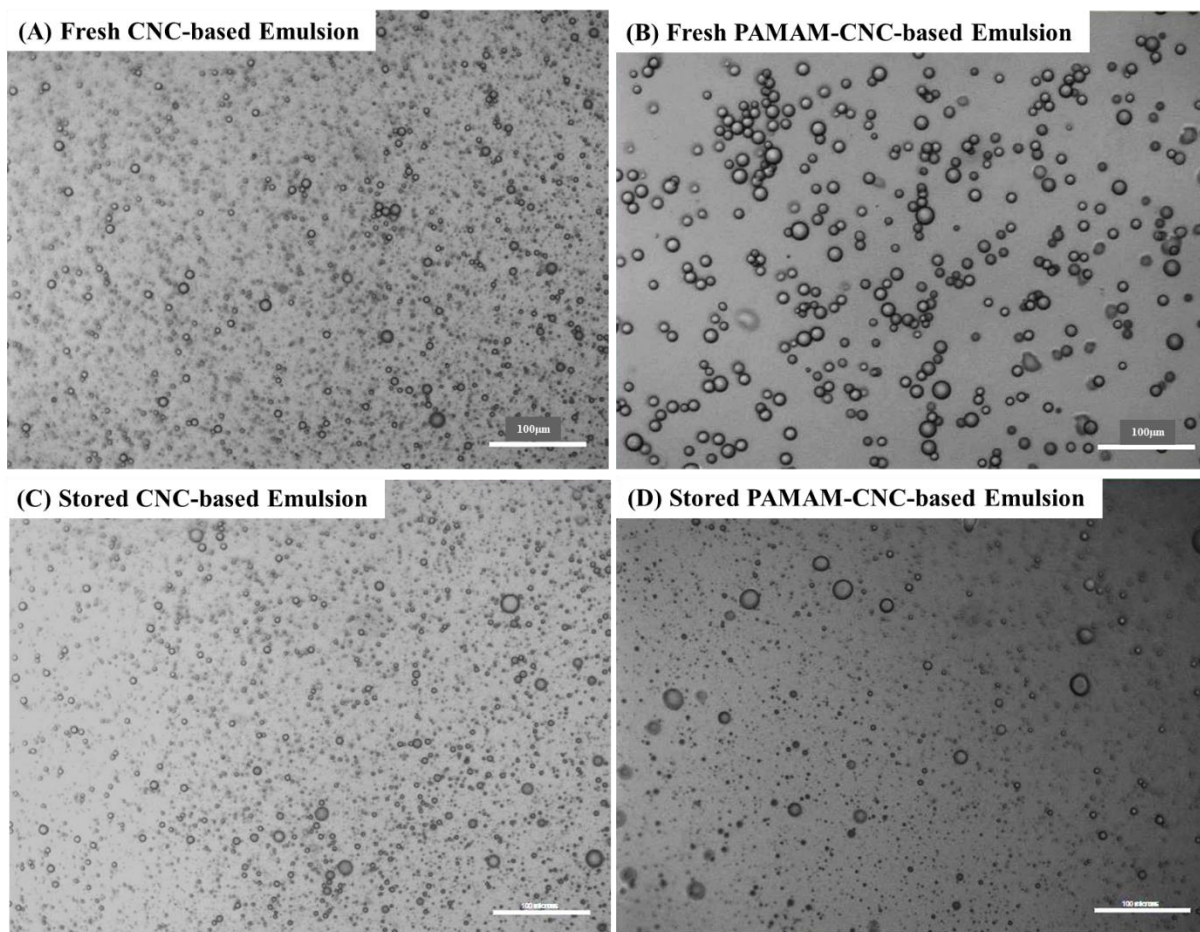


Figure 4.9. Optical microscopy images of coconut oil in water Pickering emulsion stabilized by CNC (A) after preparation, and (C) after one month storage. Optical microscopy images of coconut oil in water Pickering emulsion stabilized by PAMAM-CNC (B) after preparation, and (D) after one month storage.

4.3.8. Fluorescence Characterization

To measure the fluorescence property of PAMAM and Nile red, the excitation was set at 420 nm and 552 nm, respectively. The maximum excitation and emission of PAMAM and Nile red were measured using the Carey Eclipse fluorescence spectrometer, as shown in Figure 4.10 and Table 4.7.

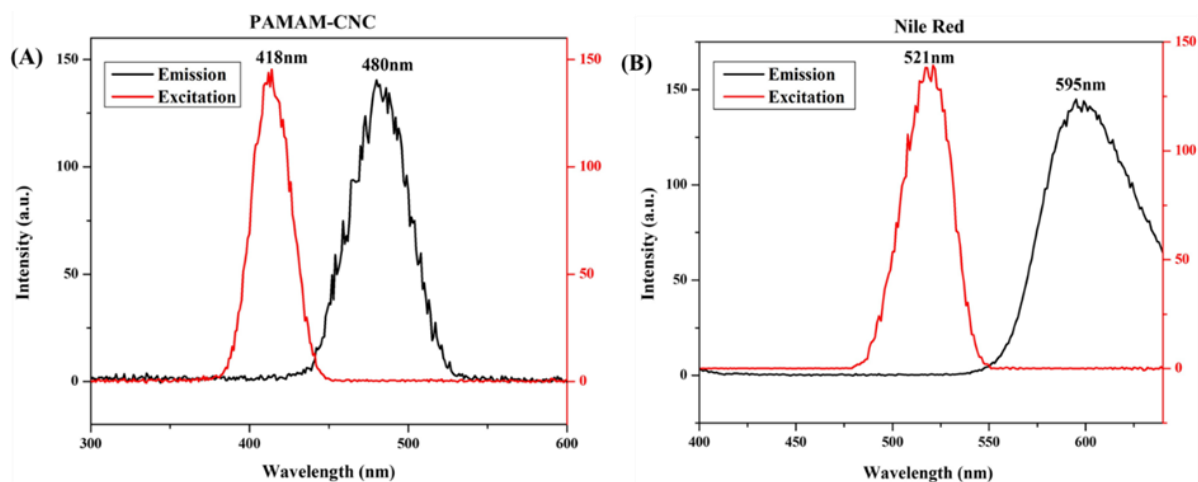


Figure 4.10. Excitation and emission fluorescence spectra of (A) PAMAM on CNC (B) Nile red on coconut oil Pickering emulsion.

Table 4.7. Excitation and Emission spectra of PAMAM-CNC and Nile red.

Sample	Absorption maximum (nm)	Fluorescence maximum (nm)
PAMAM-CNC	418	480
Nile Red	521	595

Fluorescence microscopy was employed to examine the stabilization of the fluorescent-labelled CNCs at the oil/water interface. As shown in Figure 4.11, PAMAM-CNCs were partitioned around coconut oil droplets and remained stable before and after the phase transition (crystallization). As a result, emulsion remained stable after phase transition during the storage at room temperature.

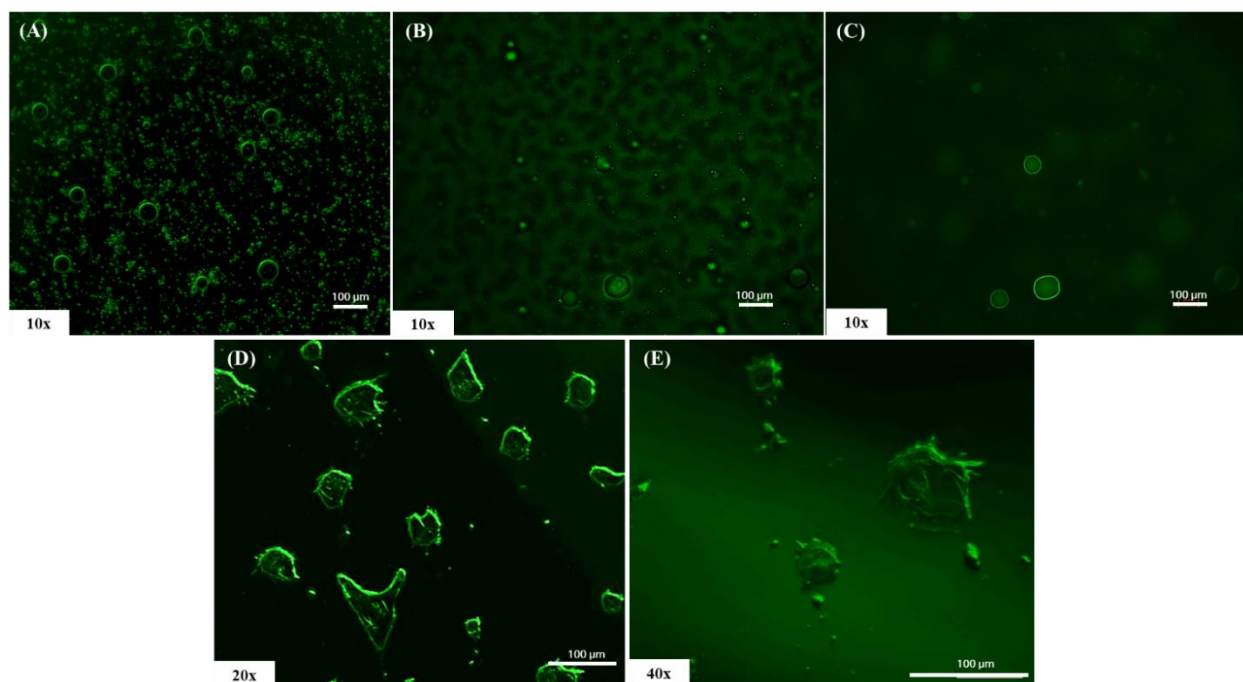


Figure 4.11. Fluorescent microscopic images of coconut oil in water Pickering emulsions showing the partitioning of PAMAM-CNC at the oil/water interface during phase transition. (A, B, C) Liquid oil droplets of emulsions at 30°C at 10X, (D) Crystallized oil droplets of emulsions at room temperature at 20X, (E) Crystallized oil droplets of emulsions at room temperature at 40X.

The location of CNC was tracked more clearly by the addition of Nile red as a label for the oil phase. When the samples were illuminated, PAMAM-CNCs were present at the surface of oil droplets, and due to the presence of Nile red, the oil droplets displayed a red emission. The fluorescence microscopy images of labelled CNCs and dyed oil droplets were merged using the ImageJ software,³⁰³ and presented in Figure 4.12 and Figure 4.13.

The fluorescence microscopic images during oil crystallization revealed that despite the changes in the shape of the droplets (from spherical to irregular shape), partitioning of the labelled CNCs at the oil/water interface inhibited the coalescence of the droplets. Therefore, fluorescence microscopy studies indicated that CNCs provided long-term stability for oil in water emulsions even after the phase transition of the oil.

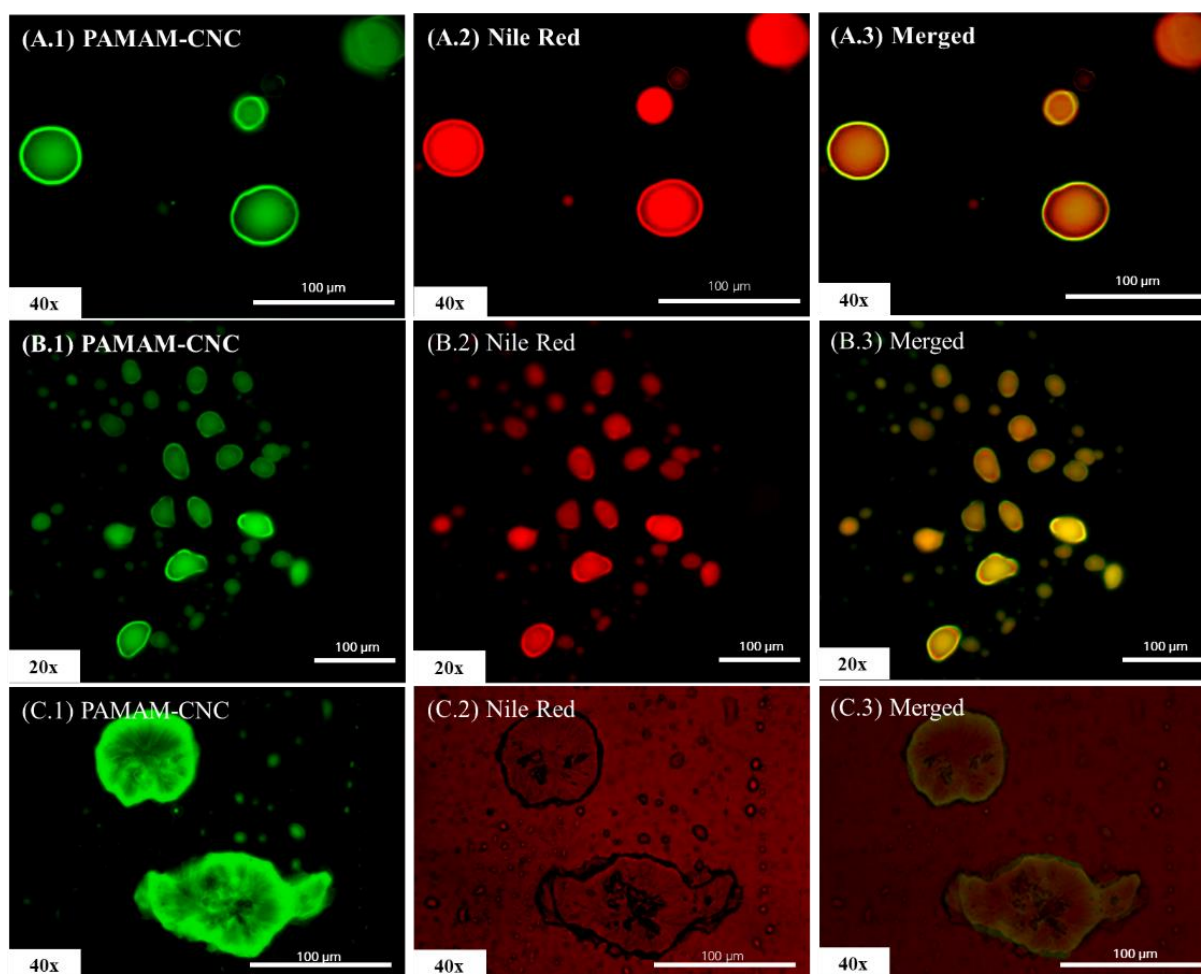


Figure 4.12. Fluorescence microscopy images of dyed coconut oil in water Pickering emulsion stabilized by PAMAM-CNCs (A) at a temperature above the crystallization with the magnification of 40X. (B) at the temperature of crystallization with the magnification of 20X, (C) at a temperature below the crystallization with the magnification of 40X.

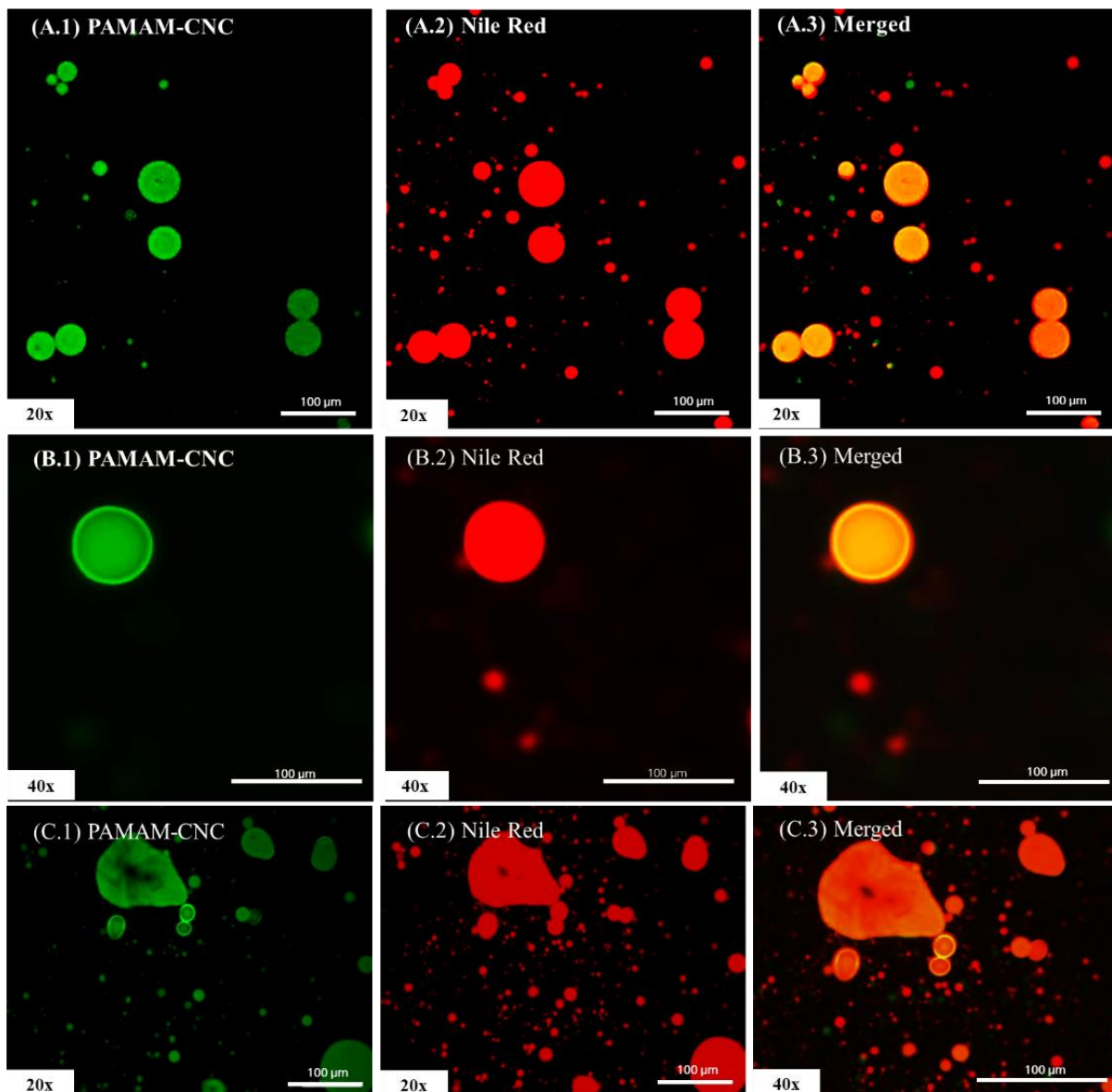


Figure 4.13. Fluorescence microscopy images of dyed coconut oil in water Pickering emulsion stabilized by PAMAM-CNCs (A) at a temperature above the crystallization with the magnification of 20X. (B) at the temperature of crystallization with the magnification of 40X, (C) at the temperature below the crystallization. The magnification is 20X for C.1 and C.2, and 40X for C.3

4.3.9. Rheological Properties

Rheology was employed to compare the stability of coconut oil in water emulsions during the phase transition of oil for emulsions stabilized by CNCs and by a conventional surfactant, SDS. The storage and loss modulus of two coconut oil emulsions stabilized with CNCs and SDS as a function of temperature are shown Figure 4.14. The network between CNC particles at the droplet

interface creates a bridge between droplets that led to a strong gel structure. CNC-based emulsions displayed higher storage modulus (G') and loss modulus (G'') values compared to emulsions prepared with SDS, indicating a more robust gel structure in the emulsions containing CNC. Irreversible adsorption of CNC around the oil droplets and the formation of a strong gel structure via hydrogen bonding among the droplets, led to the stability of emulsion even at low temperatures below the melting point of coconut oil. At temperatures lower than the melting point of coconut oil, the G' of the emulsion was much higher than G'' indicating the formation of gel network and solid-like behavior. Rapid adsorption/desorption of SDS at the interface and greater mobility of droplets covered with SDS presented a weaker structure in emulsions stabilized by SDS and lower G' and G'' compared to CNC stabilized emulsion. As the temperature decreased, the storage modulus of emulsion increased. Crystallization of the oil changed the droplet shape and interfacial properties resulting in the expulsion of surfactant molecules from the oil/water interface leading to droplet aggregation. Therefore, G' increased sharply due to the forming of a three-dimensional gel network associated with the aggregation of the droplets from the depleted oil/water interface. The strong adsorption of CNC at different temperatures improved the dynamical and elastic properties of the emulsion, contributing to the ability of CNC to stabilize the emulsion.^{304,305}

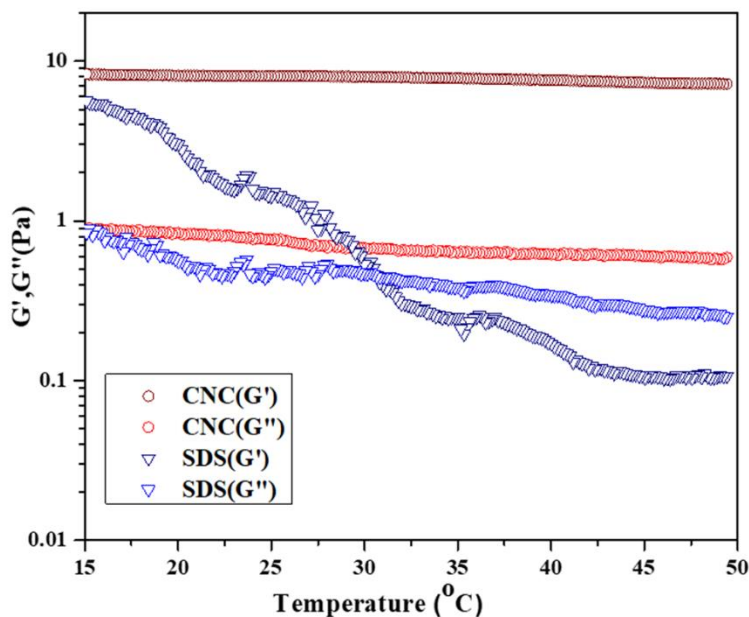


Figure 4.14. Effect of phase transition of coconut oil on the complex viscosity of coconut oil in water emulsion stabilized with CNCs and SDS.

4.4. Conclusions

The solidification of the dispersed phase reduced the surfactant coverage of the emulsion droplets and destabilized the emulsion. In this study, CNC, a renewable solid nanoparticle was used to prepare coconut oil Pickering emulsion and the stability of the emulsion was evaluated during the phase transition of the coconut oil. A design of experiments (DOE) was used to examine the effect of four parameters, namely CNC concentration, water/coconut oil volumetric ratio, sonication time, and sonication amplitude, on the stability of the emulsion. A model based on the RSM and CCD yielded the optimum conditions for the highest emulsion stability based on the analysis of the four parameters.

CNC was covalently labelled with Generation 6 polyamidoamine (G6-PAMAM) dendrimer as a tracer dye to visualize the CNC at the water/oil interface. FTIR and titration results confirmed the modification of CNC with G6-PAMAM. Contact angle and zeta potential measurements at pH 7 revealed a slight change in the wettability and amphiphilicity of PAMAM-CNC compared to CNC. The coconut oil was emulsified at the optimum condition using PAMAM-CNC as the emulsifier. Fluorescence microscopic images showed that the PAMAM-CNCs were adsorbed irreversibly at the water/oil interface even after the crystallization of oil at temperatures below its melting point. Therefore, the emulsion remained stable even after the crystallization of the oil phase. The irreversible adsorption of CNC at the water/oil interface was also confirmed by comparison of the storage and loss moduli versus temperature of emulsion stabilized with CNC and SDS. Crystallization of the oil changed the droplet shape and interfacial properties resulting in the expulsion of SDS molecules from the water/oil interface leading to droplet aggregation and increase of storage modulus below the melting point of the oil. Storage modulus of emulsion stabilized by CNC remained stable over the entire temperature range.

Acknowledgement

The authors would like to acknowledge Celluforce Inc. for providing the cellulose nanocrystals. KCT acknowledges the financial support from NSERC and CFI.

CHAPTER 5: EFFECT OF HYDROPHOBIC MODIFICATION OF CELLULOSE NANOCRYSTAL (CNC) AND SALT ADDITION ON PICKERING EMULSIONS UNDERGOING PHASE-TRANSITION

Abstract

The charge density of emulsifiers determines the thermodynamics and kinetics adsorption properties at the oil-water interface of an emulsion. This study examines the rupture resistance and stability of the crystallized dispersed phase based on the partitioning capability of cellulose nanocrystals (CNCs) with different surface charges. The charge density of CNC particles was designed through salt addition and hydrophobic modification. The measurement of dynamic interfacial tension confirmed that the reduction of negative charge of CNC particles improves their Pickering stabilizer role. We observed that the interfacial tension displayed a sigmoidal profile with increasing time. The dynamic stability of the emulsion during phase transition of the oil phase was enhanced by increasing the interfacial particle accumulation via the reduction of surface charge of CNC. The results indicated based on surface charge adjustment, a balance between diffusion rate and kinetic barrier adsorption of particles is required to achieve optimum system stability.

5.1. Introduction

Compared to surfactant-based systems, emulsions stabilized with nanoparticles (Pickering emulsion) display higher stability and longer shelf-life. Unlike surfactant-based emulsions, which rely on electrostatic repulsion to stabilize incompatible liquids, solid particles are used to provide a shield-like coating that prevents coalescence in Pickering emulsions. Numerous inorganic materials (e.g. silica, clay, laponite, calcium carbonate, graphite), and organic compounds (polystyrene microgels and latexes), have been used as Pickering emulsifiers^{132,169}.

Since cellulose nanocrystal (CNC) possesses the desired dimension and physical properties, it is an attractive system to prepare Pickering emulsion^{70,82,168}. CNC is produced via the acid hydrolysis of cellulose fibers, and it is considered sustainable since it is biodegradable, biocompatible, and renewable^{20,51,287,306,307}. Sulfuric acid hydrolysis is the most common method to produce CNCs from various plant sources. This process introduces sulfur ester groups to the CNC surfaces with a charge density of about 0.03 e/nm^2 ^{70,82,115,168}.

Recently, the application of CNC as a stabilizing agent in various Pickering emulsions has been widely explored⁹. The abundance of hydroxyl groups on the surface of the crystalline structure of CNCs provides an overall hydrophilic character, and the hydrophobic (200) β crystalline edges containing CH groups impart hydrophobicity. This property facilitates the adsorption at the oil-water interface, where the hydrophobic edge aligns with the oil phase, and the hydrophilic domains are exposed to water^{70,129,179}. CNCs can be effectively partitioned to the oil-water interface, resulting in a dense interfacial network. However, the successful utilization of CNCs depends on the unique combination of several properties, such as high aspect ratio, intermediate wettability, nanoscale size, and anisotropic characteristics^{167,170}. Moreover, the amphiphilic properties of CNC play a vital role in the success of CNC as a Pickering emulsion stabilizer.

The nanoparticle adsorption to the oil/water interface occurs in two steps: (i) nanoparticles diffusion to the vicinity of the interface and (ii) nanoparticles partitioning at the interface^{68,167,170,171}. The electrostatic repulsion between CNC particles improves their dispersion in the aqueous phase and their diffusion rate. However, the high negative charge density of CNC particles provides a barrier against their partitioning at the oil/water interface and limits the surface coverage of droplets. Therefore, depending on the surface charge of CNC particles, the balance between the

diffusion rate of CNCs to the interface and their kinetic adsorption barrier define emulsion's stability.^{9,15,82,87,167,170,171,308,309}

The diffusion and interfacial adsorption of CNC particles to the interface depends on their amphiphilic properties, such as surface charge and functionality, which can be evaluated by measuring the contact angle and interfacial tension. As shown in Eq.(5.1), the particles' adsorption energy depends on the contact angle that describes the stability of the resulting emulsion.

$$\Delta G_{\text{rod}} = -lb\gamma(1-\cos\theta) \quad (5.1)$$

where l and b are the length and width of the rod-shaped particle at the interface, and θ is the contact angle. The higher contact angle value increases the adsorption energy signifying a more stable emulsion. Particles with a contact angle of 90° have the same affinity to both phases, displaying the highest detachment energy that imparts the maximum stability to the system.

The surface charge of CNCs depends on various factors, such as materials source and processing conditions (acid type and concentration, time, and temperature)^{129,167,170}. The strong interparticle electrostatic repulsion limits the adsorption density and formation of a weak monolayer coverage with low surface density and reduced stability^{87,167,170,171,182,310}. The repulsion between CNC particles can be reduced by introducing electrolytes or hydrophobic surface modification. As reported by Cherhal et al., a lower surface charge of modified CNCs particles leads to a thicker layer of CNC adsorbed at the droplet interface¹²². These methods could alter the CNC's interfacial properties by lowering the surface charge^{164,311}. The abundance of hydroxyl groups on CNC allows for the surface treatment and adjustment of surface charge density and wettability. By lowering surface charge, the kinetic barrier would be reduced, and diffusion forces would control the adsorption of CNC particles, and higher surface densities could be achieved^{167,170,171}. Improvement in the stability of Pickering emulsions via surface treatment or salt addition has recently been reported^{115,122}.

Emulsion preparation comprises applying a high shear force to generate tiny oil droplets resulting in a large interfacial area, and coalescence of the droplets can be prevented using an emulsifier. Thus, the dynamics of the emulsifier's adsorption to the interface are of paramount importance for the stability and properties of the system. Dynamic interface tension modelling can be utilized to analyze surface coverage and emulsion stability^{167,170}.

Phase transition of the dispersed phase from liquid to solid or vice versa would impact its interfacial tension and wettability characteristics, subsequently affecting the partitioning of solid

particles at the oil-water interface ^{146,148,312}. In addition, during cooling the emulsion, the crystallized dispersed phase ruptures the interface of droplets and penetrates the neighbouring liquid droplets' interface, leading to droplet aggregation. Rayner and coworkers (2014) presented that compared to surfactant-based emulsions, solid particles as Pickering emulsifiers enhance coverage rupture of the crystallized dispersed phase ¹⁰². As the emulsifier's resistance to interface rupture of droplets during phase inversion is a critical parameter, the higher surface coverage of emulsifiers at the oil and water interface improves emulsion's stability throughout the phase inversion process. ^{48,105,142}

This research examines salt addition and hydrophobic modification of CNCs on the strength and dynamic of CNC partitioning at the oil-water interface. The reduction in the electrostatic repulsion between the CNC particles and its effect on the stability of the Pickering emulsion was evaluated using zeta potential, contact angle, and interfacial tension. The hydroxymethyl groups of polysaccharides on CNC are more reactive than the secondary hydroxyl groups ⁵¹. Therefore, four surface modification methods were used to increase the hydrophobicity of CNCs to enhance the emulsion stability. In the first modification, sodium hydroxide was used to partially remove the sulfur ester groups, which would enhance the amphiphilic properties of the CNC. The second modification was performed by substituting C6-hydroxyl groups with C6-carboxyl groups on the CNC surface. In the third modification, the hydrophobicity was enhanced by grafting polystyrene chain on the surface of the CNC (CNC-PS). Finally, cinnamoyl chloride was used to substitute sulfate groups on CNC with cinnamate groups ^{299,313–318}.

As the hydrophobicity of the dispersed phase impacts the adsorption of CNC at the oil-water interface, the effect of oil type was also examined, and toluene and heptane were selected and tested with the modified CNCs. All the CNC modifications were subjected to various analytical techniques, such as Fourier transform infrared spectroscopy (FTIR), Zeta potential, conductometric titration, UV-Vis spectroscopy, contact angle, and interfacial tension measurements. Dynamic interfacial tension was used to study the migration and adsorption of CNCs to the oil/ water interface. In addition, the effectiveness of each modification in improving the stability of the oil-water emulsions was investigated using morphological and rheological techniques and particle size distribution and stability tests such as creaming index on the paraffin wax oil-in-water emulsions.

5.2. Experimental section

5.2.1. Materials

Celluforce Inc. supplied the CNCs used in this study with 100-300 nm, 3-5 nm diameter, and surface charge density of $0.29 \pm 0.01 \text{ e/nm}^2$). All the chemicals used in this research were Sigma-Aldrich analytical grade and used without further purification. The main chemicals are sodium chloride (NaCl), 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO), 1-ethyl-3-(3(dimethylamino)propyl) carbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS), sodium bromide (NaBr), sodium hypochlorite solution (NaOCl), hydrochloric acid (HCl), sodium hydroxide (NaOH), dimethyl-aminopyridine (DMAP), triethylamine (TEA), cinnamoyl chloride, tetrahydrofuran (THF, anhydrous 99.9%), N-dimethyl formamide (DMF, anhydrous 99.8%), sodium cyanoborohydride (NaBH_3 reagent grade, 95%), hydroxylamine hydrochloride (reagent grade, 98%), amine-terminated polystyrene (M_n of 5000 or 10,000 Da), toluene (anhydrous 99.8%), hexadecane (anhydrous 99%), paraffin wax, and potassium bromide (KBr). Milli-Q (MQ) water (resistivity $18.2 \text{ M}\Omega$) was used to prepare CNC dispersions and the oil-water emulsions.

5.2.2. Surface Modification of CNCs

5.2.2.1. Preparation of Desulfated CNC (Desulf-CNC)

To remove the sulfate groups on the surface of CNCs, 3% w/w CNC suspension (270 ml) was treated with 1M NaOH (10.8g). The mixture was mechanically stirred for five (5) hrs. until it turned yellow. The CNC particles slowly agglomerated due to the gradual removal of the sulphate groups. The reaction was terminated after five hours, and the mixture was centrifuged at 7000 rpm for five minutes. It was then dialyzed against DI water and purified for five days with regular changes of DI water (Figure 5.1(A))^{314,315}.

5.2.2.2. Preparation of TEMPO-CNC as Carboxylated Cellulose Nanocrystals (CNC)

CNCs (0.5 g) was sonicated in 375 mL distilled water and oxidized in the presence of 4-acetamido-2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) (0.0125 g) and sodium bromide (0.125 g). The mixture was vigorously stirred and sonicated for 15 min, and 50 mg sodium hypochlorite (NaClO) solution was added, yielding a highly viscous solution. The pH of the mixture was adjusted to 10 using 0.1M of NaOH and stirred for four hours. After the oxidation process, 5 mL ethanol was added to stop the reaction, and the pH was then adjusted to 7 using 0.1M hydrochloric acid. The reaction product was dispersed in distilled water and centrifuged at 8,000 rpm three times for 5 min to remove unreacted acid, inorganic salt, and TEMPO reagent.

The oxidized CNC was freeze-dried and stored in the refrigerator for further analysis (Figure 5.1 (B))^{299,313}.

5.2.2.3. Preparation of Polystyrene Grafted CNC (CNC-PS)

Polystyrene functionalized CNC was prepared by grafting the amine-functionalized PS chain on the reducing ends of CNC. The CNC dispersion (1 g) in DMF (100 ml) was sonicated for 10 minutes. Next, PS-NH₂ (100mg) was added, and the mixture was subjected to mechanical stirring at 600 rpm for 30 min. The mixture was then degassed using nitrogen (N₂) for 20 min, and sodium cyanoborohydride solution (10mg) in DMF (10ml) was added, and the reaction mixture was stirred at 70 °C for three days. The purification was performed via a triple centrifugation step in THF followed by additional centrifugation in acetone. The dispersion was then dialyzed against Millipore water for three days (Figure 5.1 (C))³¹⁸.

5.2.2.4. Preparation of Cinnamate-functionalized CNC (Cin-CNC)

The acylation of CNCs with cinnamoyl chloride was conducted using TEA and DMAP as the catalyst. First, the CNC dispersion (1 g) in DMF (80 mL) was prepared. TEA (2.58 mL, 18.5 mmol) and DMAP (1.13 g, 9.3 mmol) were then introduced, and the mixture was stirred for 30 min. Next, a cinnamoyl chloride solution (3.3 g, 20 mmol) in DMF (20 mL) was prepared and added dropwise to the system. The mixture was stirred at 600 rpm for 24 hours. The Cin-CNC was purified via triple centrifugation in THF followed by additional centrifugation with acetone. Dialysis was then performed for five days with a constant water change. The synthesis procedure of CNC is schematically shown in Figure 5.1 (D)^{316,317}.

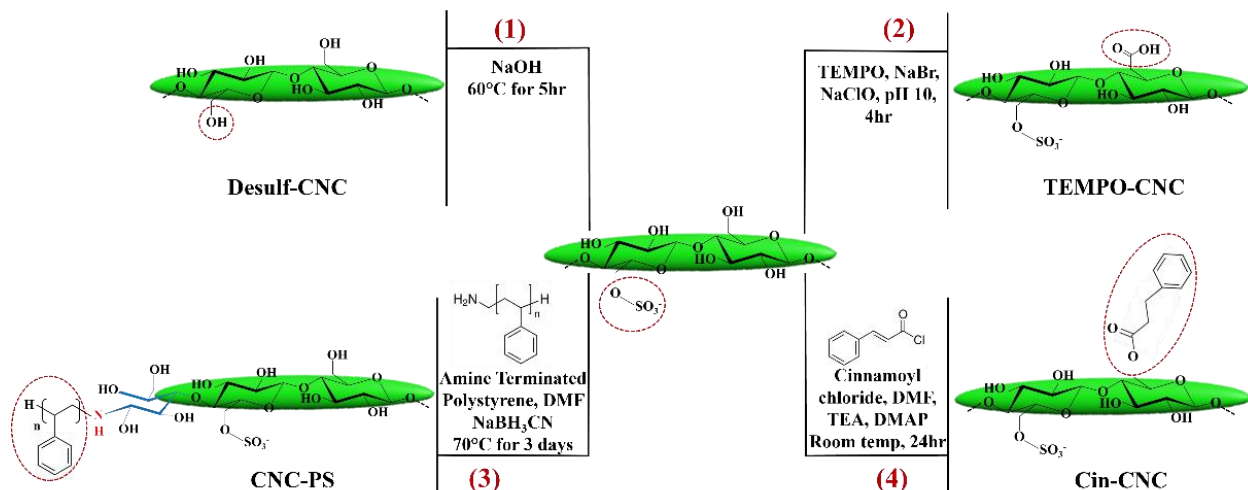


Figure 5.1. Preparation procedures of (A) Desulf-CNC by removing sulfate groups, (B) TEMPO-CNC by TEMPO-mediated oxidation of CNC, (C) CNC-PS by reducing end of CNC with polystyrene, (D) Cin-CNC by acylation of CNC with cinnamoyl chloride.

5.2.3. Preparation of Pickering Emulsion

To investigate the effect of phase transition on the behavior of CNC-stabilized Pickering emulsions, paraffin wax with a liquid-solid transition temperature of approximately 58-60°C was used. The paraffin wax emulsions were prepared in an oil-to-water ratio of 4:6 by volume with unmodified and modified CNC (0.6wt.% in aqueous phase) in 85.5 mM NaCl solutions (0.5wt.% in aqueous phase). The emulsification was performed on the paraffin wax-water mixture at 70°C. The required shear force was applied using a sonication probe for four minutes at 36% amplitude speed with a Misonix Microcon-XL2000 ultrasound system.

5.2.4. Characterization of Modified CNCs

The Fourier transform infrared spectroscopy (FTIR) on modified CNCs was performed using a Bruker Tensor 27 spectrometer. Samples were freeze-dried and grounded with potassium bromide (KBr) using a mortar and compressed into pellets. The FTIR spectra were recorded from 4000 to 400 cm⁻¹ with 32 scans and a resolution of 4 cm⁻¹.

The size and zeta potentials of 0.04 wt.% modified and unmodified CNCs were quantified using the Malvern Zetasizer Nano series. The results were reported as the average of 3 measurements consisting of 12 repeated runs per measurement.

The carboxyl content of samples was measured using potentiometric and conductometric titrations with a Metrohm 809 Titrando autotitrator. A dispersion of TEMPO-CNCs in water (0.2

mg/mL, 30 ml) was prepared, and the pH of the solution was adjusted to 3 using 0.1M hydrochloric acid (overnight stirring). The resulting suspension was then titrated with 0.01 M sodium hydroxide, and the amounts of carboxyl groups on the surface of TEMPO-CNCs were determined from Eq. ((5.2))²⁹⁹.

$$\text{Carboxylic acid } \left(\frac{\text{mmol}}{\text{g}} \right) = \frac{C_{\text{NaOH}} \times \Delta V_{\text{NaOH}}}{m(\text{g})} \quad (5.2)$$

In this equation, ΔV NaOH is the total volume of sodium hydroxide used to neutralize the carboxylic acids, where C_{NaOH} is the concentration of sodium hydroxide in the solution (M), and m is the mass of the TEMPO-CNCs (0.006 g).

The grafting ratio of cinnamate groups on the surface of CNCs was determined through UV absorption spectra measured using a Varian (Cary 100 Bio) UV-visible spectrometer at room temperature. The zero (0% Transmittance) and baseline correction (100% Transmittance) were performed using Milli-Q water. Cinnamoyl chloride has the maximum UV absorbance at around 280 cm^{-1} , while the UV absorbance of CNC was close to zero. The maximum absorbance of samples containing different concentrations of cinnamoyl chloride was measured. The calibration curve resulting from the linear relation between the UV absorbance and concentration of cinnamoyl groups was used to measure the amount of cinnamoyl grafted on CNC.

The wettability of unmodified and chemically modified CNC' was evaluated from the contact angle measured using a sessile drop method in an optical tensiometer. Dispersions of modified and unmodified CNCs were prepared at 4% (by weight) and coated on a glass slide via drop-casting. A NE-1010 high- pressure syringe pump (NewEra Pump Systems Inc.) dispensed three μL DI of water droplets on the coated surface. An average of three measurements was reported as contact angle for each sample.

The shape analysis of an axisymmetric drop was performed to examine the adsorption properties of modified and unmodified CNCs at the oil-water interfaces. The interfacial tension of the samples was measured using a VCA 2500 XE system (AST Products, Billerica, MA) based on the pendant drop technique. In the pendant droplet method, the surface tension is related to the geometry of the droplet. While gravity seeks to elongate the droplet, the surface tension energy counteracts to restore the spherical shape of the droplet. For this purpose, a pendant drop of 0.5 wt.% modified and unmodified CNC dispersion was suspended from a stainless-steel needle tip inside the cuvette containing 2 ml of the oil phase. The cuvette was then sealed with a parafilm to

minimize droplet evaporation, and the syringe needle was immersed through a small hole on the parafilm. Toluene and heptane were used as the oil phases to investigate the effect of the oil phase.

The evolution of the interfacial tension of unmodified and modified CNCs over time was evaluated by monitoring the dynamic interfacial tension at the toluene interface over 120 minutes. Continuous pendant droplet images were recorded at a frame rate of five frames per minute for 1200 seconds for dynamic interfacial tension analysis using a high-speed CCD camera at room temperature. The Laplace equation was utilized to analyze each image.³¹⁹ The fractional interface coverage (η) was calculated, based on the Eq. (5.5), which was derived from Eq. (5.3) and (5.4)^{129,320}.

$$\Delta E = -lb\gamma_{ow}(1 - |\cos \theta|) \quad (5.3)$$

$$\Delta E = [-(\gamma_0 - \gamma)lb]/\eta \quad (5.4)$$

$$\eta = \frac{(\gamma_0 - \gamma)}{\gamma_{ow}(1 - |\cos \theta|)} \quad (5.5)$$

Where ΔE is adsorption energy, γ_{ow} is pristine interface tension of oil and water, θ is contact angle, γ_0 is the initial interface, γ is measured interfacial tension, lb is the area the area is covered up by one particle, and η is the fraction of the interface covered.

5.2.5. Characterization of Prepared Emulsions

Creaming is defined as the migration of oil droplets (without coalescence) due to differences in densities of the water and oil phases. The bottom layer consisted of the water phase-separated from the emulsion system, and the top layer corresponded to the concentrated emulsion. The creaming stability index was determined from images of samples after one-week storage at room temperature using a visual technique described by Eq. ((5.6))³²¹.

$$\text{Creaming Stability Index}(\%) = \frac{h_{\text{Emulsion}}}{h_{\text{Total}}} \quad (5.6)$$

The rheology of prepared paraffin wax emulsions was investigated using the Kinexus Ultra+ (Malvern Instruments) rheometer. A cup and bob with a double gap system geometry were used for viscosity measurements. A solvent trap was used to prevent water evaporation during the experiments, and the raw data were then analyzed using the rSpace-for-Kinexus-Pro1.3 software. The complex viscosity of paraffin wax emulsions was evaluated by conducting temperature sweep studies. A temperature sweep was performed from 80 to 20 °C at the cooling rate of 2 °C/min at 1% strain and 1 Hz. For this purpose, paraffin wax emulsions containing oil to water volumetric

ratio of 4 to 6 were stabilized with 0.5 wt.% unmodified CNC, TEMPO-CNC, CNC-PS, Desulf-CNC, and Cin-CNC. The aqueous phase of all emulsions contained 0.5wt.% NaCl.

Optical microscopy on diluted emulsion samples was conducted with a Nikon Elipse Ti-S (Agilent Cary Eclipse) equipped with a CCD camera (QImaging ReTIGA 2000R). An Anton Paar PSA 1190 particle size analyzer was used to determine the paraffin wax droplet size and distribution, and the data were reported as an average of three measurements. To evaluate the impact of hydrophobic modification of CNC on the stability of paraffin emulsions, particle size analyses were performed before and after shear loading subjected to a frequency of 1 Hz. All the emulsions were prepared with a paraffin wax/water ratio of 4/6 and 0.7wt.% modified or unmodified CNCs in 0.5wt.% NaCl. The samples were then subjected to particle size analysis before and after applying the oscillatory shear testing (1 Hz) under temperature sweep mode (within 80 to 20°C and cooling rate of 2°C/min).

5.3.Results and Discussion

5.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to confirm the grafting of hydrophobic moieties on the surface of CNC (Figure 5.2(A)). The spectra of pristine CNC possessed peaks at 3350 cm^{-1} for O-H stretching, 2910 cm^{-1} for C-H bending, and 1065 cm^{-1} to 1165 cm^{-1} for glucose ring bands. The stronger absorption band at 1600 cm^{-1} resulting from the enhanced vibration in OH stretching confirmed the successful desulfation of the CNC (Desulf-CNC, Figure 5.2(B)). The new peaks in the TEMPO-oxidized CNC at 1748 and 2857 cm^{-1} corresponded to the stretching band of carboxylate (C=O) and hydroxyl (O-H) functional groups, confirming the successful introduction of carboxylate groups on the surface CNC (TEMPO-CNC, Figure 5.2(C)). The appearance of peaks at 1745 cm^{-1} and 2856 cm^{-1} corresponding to the alkene band stretching on the benzene ring (C=C) and the C-H bonds respectively confirmed the grafting of polystyrene (CNC-PS, Figure 5.2(D)). The grafting of cinnamate groups on CNCs was confirmed by the observation of a new vibration band at 1716, 1636, and 769 cm^{-1} , representing the carboxyl stretching (C=O), alkene stretching (C=C), and C-H bending at out-of-plane aromatic, respectively (Cin-CNC, Figure 5.2(E)).

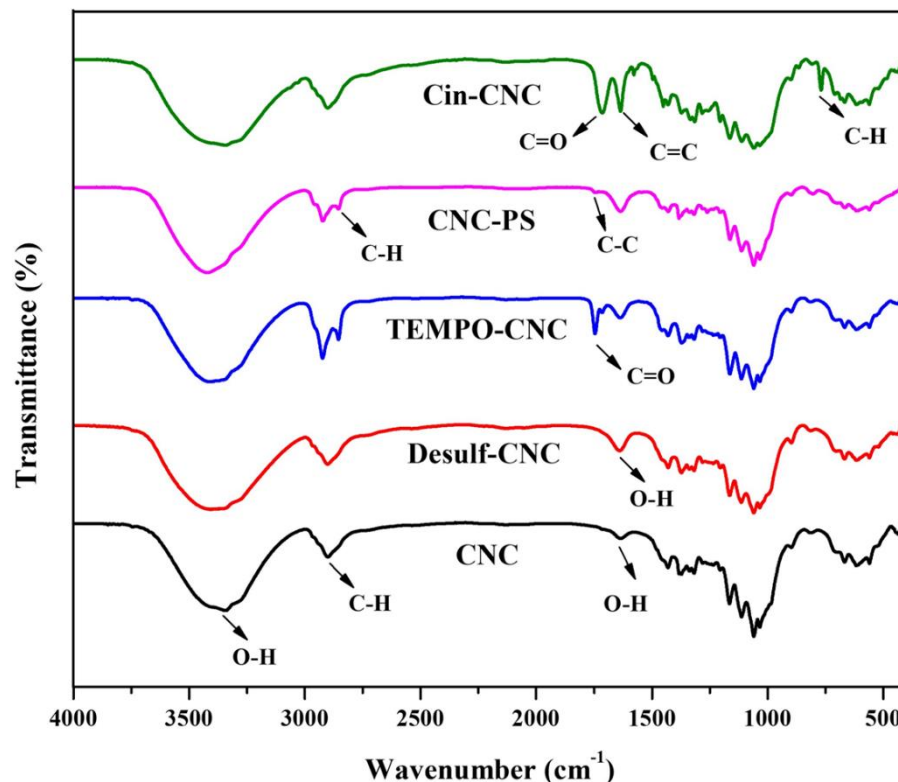


Figure 5.2. FTIR spectra of (A) pristine CNC, (B) Desulf-CNC, (C) TEMPO-CNC, (D) CNC-PS, (E) Cin-CNC.

5.3.2. Dynamic Light Scattering (DLS) and ζ -potential

The zeta potential and particle size of CNC were determined for the various hydrophobic modifications, i.e., TEMPO-CNC, CNC-PS, Desulf-CNC, and Cin-CNC. The surface charge of CNC was influenced by the modification and the grafting ratio of functional groups (See Table 5.1). The effect of the functional groups on the CNC surface charge altered the dispersion and aggregation properties of CNCs, then the modified CNC particle sizes, shown in Table 5.1. Cin-CNC possessed the least negative zeta potential and largest particle size compared to other modified CNCs, which is attributed to the more hydrophobic character of the nanoparticle. The zeta-potential was measured at different pH conditions to determine the presence of carboxyl groups on the surface of TEMPO-CNC. The protonation of the carboxyl groups in the acidic environment (pH 3) reduced the negative surface charge compared to neutral conditions (pH 6.5) (Table 5.2).

Table 5.1. The average size, the zeta potential of the nanoparticles

Nanoparticles	Average size (nm)	Zeta potential (ζ) (mV)	Contact Angle
CNC	90.7	-36.0	51.1
TEMPO-CNC	92.0	-40.1	51.3
CNC-PS	96.9	-33.8	56.3
Desulf-CNC	103.7	-24.6	58.6
Cin-CNC	168.4	-8.3	83.5

Table 5.2. The zeta potential of the TEMPO-CNC at different pH values

TEMPO-CNC	pH 1	pH 3	pH 5	pH 7	pH 9	pH11
Zeta potential, ζ (mV)	-14.7	-23.0	-38.2	-46.6	-48.2	-51.9

5.3.3. Potentiometric and Conductometric Titrations

The required amount of NaOH to neutralize the carboxylic groups on the surface of CNCs was determined through the titration curve, and the amounts of carboxyl groups grafted on the surface of TEMPO-CNC, determined to be 3.75 mol/g (shown in Figure 5.3)

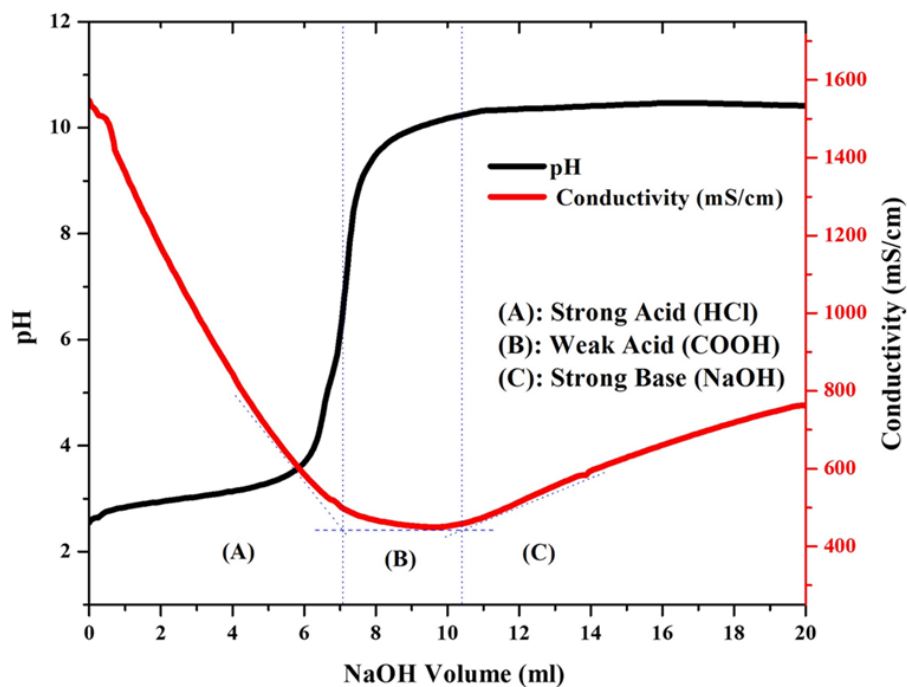


Figure 5.3. Conductometric-potentiometric titration of TEMPO-CNC.

5.3.4. UV-Vis Absorption

A gradual increase in the UV absorbance of cinnamoyl was observed with increasing cinnamoyl chloride concentration (range of 0.0011-0.0019 wt.%) (presented in Figure 5.4(A)). The linear relationship between the maximum absorbance and concentration of cinnamoyl chloride resulting from the calibration curve is described by Eq. ((5.7)) and shown in Figure 5.4(B). The absorbance of CNC suspension as a blank sample and Cin-CNC (0.04wt.%) was measured. UV absorbance of Cin-CNC was subtracted from the absorbance of CNC in the absence of cinnamoyl. The cinnamoyl concentration grafted on CNC was determined using the linear calibration curve equation correlated cinnamoyl absorbance (1.68) and concentration. The grafting ratio of 3.84 % (the weight of grafted cinnamoyl over the total weight of Cin-CNC) was obtained from Eq. ((5.8)).

$$y = 1107.5x - 0.023 \quad (5.7)$$

$$\text{Grafting ratio} = \left(\frac{C_{\text{Cin}}}{C_{\text{Cin-CNC}}} \right) \times 100\% \quad (5.8)$$

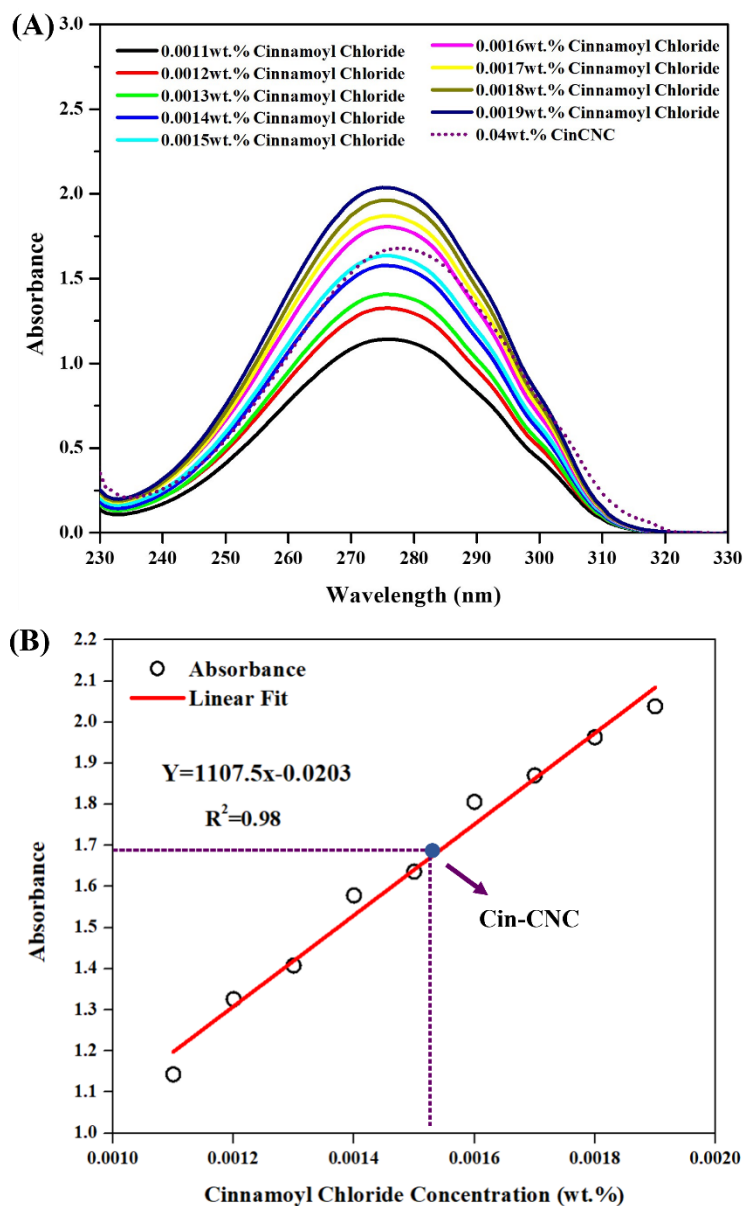


Figure 5.4. UV absorbance of cinnamoyl chloride with concentrations, and Cin-CNC, a (B) calibration curve of absorbance vs. concentrations of cinnamoyl group

5.3.5. Contact Angle Measurements

The effect of modifications on the wettability of CNCs was observed through Contact angle measurements. The contact angle of pristine CNC and modified CNCs are summarized in Table 5.1 and Figure 5.5, confirming that hydrophobic modification of CNCs increased the contact angle. Cinnamoyl modified CNC (Cin-CNC) displayed a contact angle of 83.5° that corresponded to the highest hydrophobic properties.

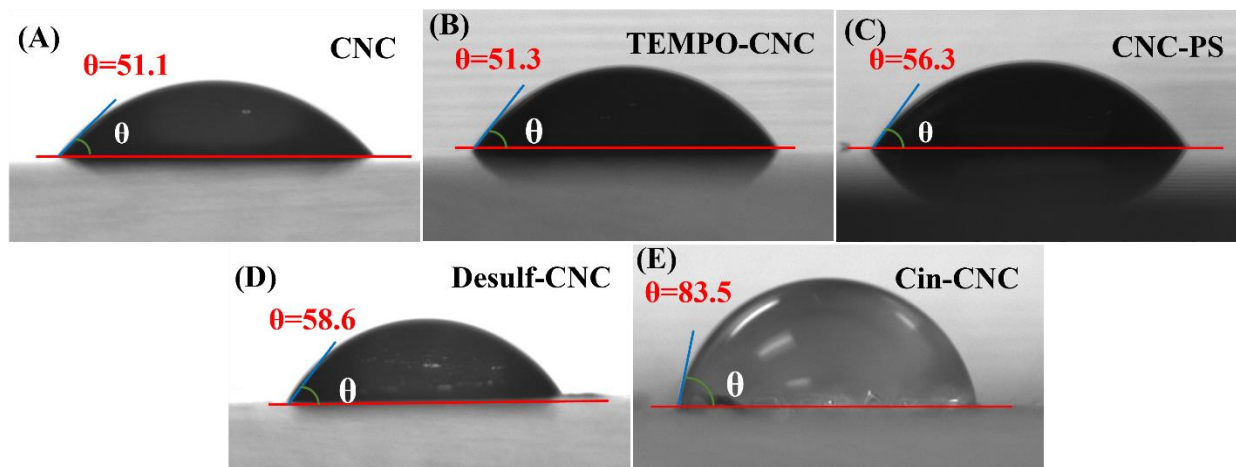


Figure 5.5. Images of contact angles of (A) pristine CNC, (B) TEMPO-CNC, (C) CNC-PS, (D) Desulf-CNC, (E) Cin-CNC.

5.3.6. Interfacial Tension Measurements (IFT)

The effect of various modifications on the interfacial tension of CNC was evaluated using the interfacial tension measurements. The surface tension of the water droplet was performed in air, and it had a value of 72.40 mN.m^{-1} . The interface tension of water was also measured in toluene and heptane and found to be 39.56 and 49.1 mN.m^{-1} , respectively. The results showed that pristine CNC did not affect the surface tension of water in the air. However, due to toluene and heptane's lower hydrophobicity than air, the interface tension at the oil-water interface was reduced. Furthermore, increasing the CNC concentration resulted in a more significant reduction of the interfacial tension to a critical point where the maximum interface coverage with CNC was achieved. The interfacial measurements of CNC in two different organic liquids (toluene and heptane) showed the dependency of interfacial surface tension on the types of the organic phase. Due to the similar affinity of CNC to both oil phases, increasing the concentration of CNC or salt displayed the interfacial reduction with the same slope. (Figure 5.6(A)).

The repulsion between the negative surface charge of CNC will impact the values of interface tension. Comparison of unmodified and modified CNC interfacial tension in toluene and heptane revealed that the hydrophobic modification of CNCs enhanced the partitioning properties of CNC at both the air-water and oil-water interfaces (Figure 5.6(B), (C)). As shown in Figure 5.6(B), lowering the surface charge of CNCs through modification enhanced the oil wettability characteristics of CNC that promoted their partitioning to the interface. Among all the modifications, grafting cinnamoyl to CNC (Cin-CNC) was the most effective approach to reduce

the interfacial tension due to the more hydrophobic character of Cin-CNC. Cin-CNC has π - π interaction with phenyl groups on toluene, resulting in a larger interface tension reduction than heptane. The droplet images and interfacial tension values are shown in Figure 5.7 and Table 5.3. The surface tension measurements of CNC and Cin-CNC at the air-water interface revealed the effect of the more hydrophobic Cin-CNC, showing a more considerable reduction in the surface tension (Figure 5.6(C)).

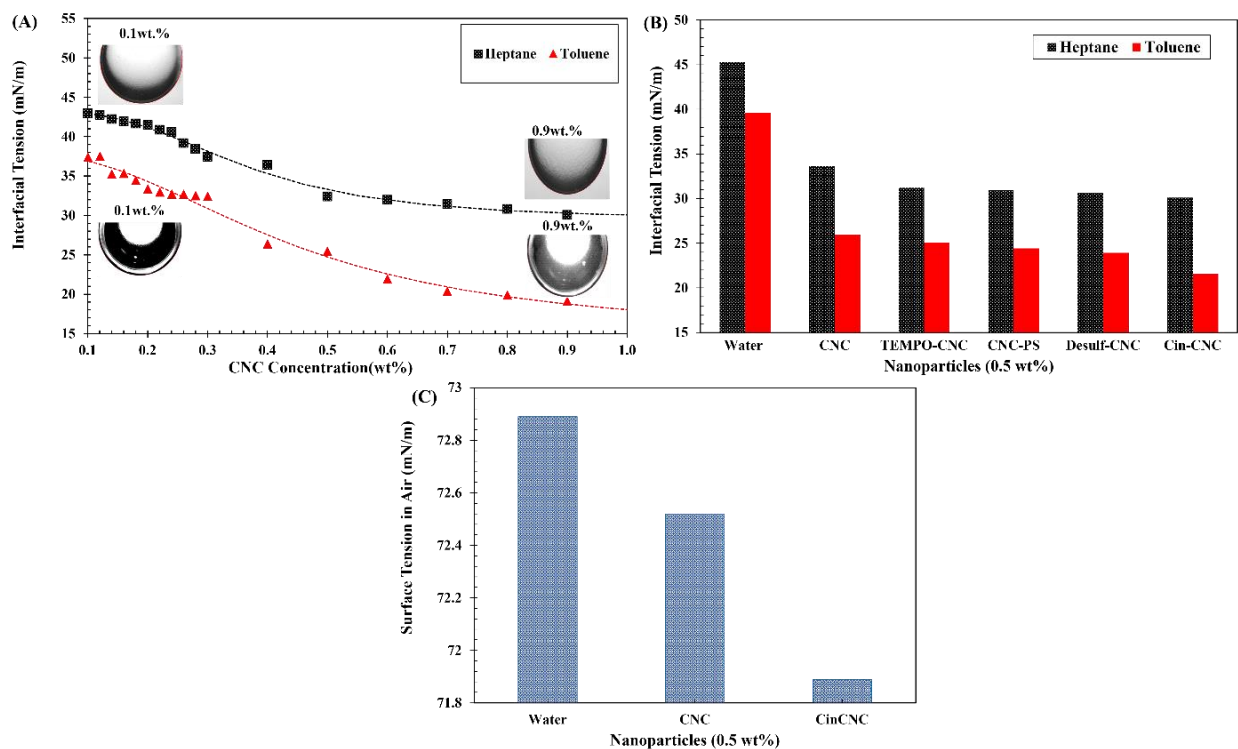


Figure 5.6. (A) Variation in interfacial tension between toluene/heptane and aqueous CNC dispersion with concentration CNCs, (B) Interfacial variation of water, CNC and modified-CNCs including TEMPO-CNC, CNC-PS, Desulf-CNC, and Cin-CNC, (C) Surface tension of CNC, and Cin-CNC.

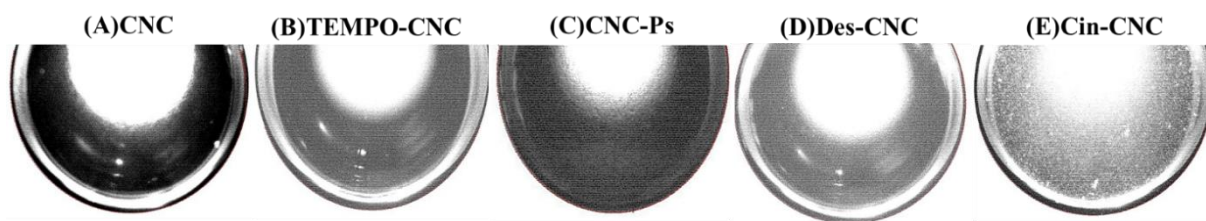


Figure 5.7. Pendant Droplet Photographs of Interfacial tension measurements of (A) CNC, (B) TEMPO-CNC, (C) CNC-PS, (D) Desulf-CNC, and (E) Cin-CNC in Toluene

Table 5.3. Interfacial tension values of Water, CNC, TEMPO-CNC, CNC-PS, Desulf-CNC, Cin-CNC in Toluene

Sample(0.5wt%)	toluene	Heptane
Water	39.56	45.31
CNC	25.99	33.65
TEMPO-CNC	25.04	31.19
CNC-PS	24.43	30.95
Desulf-CNC	23.94	30.69
Cin-CNC	21.61	30.11

Using the same methodology, the impact of salt on the interfacial tension at the oil-water interface was evaluated. For this purpose, the interfacial tension of 0.5% (by weight) of CNC dispersion in different salt (NaCl) content was measured in toluene and heptane (Figure 5.8(A)). The reduction in the interfacial tension was observed for both oil phases with an increasing salt concentration in the aqueous phase. A similar salt effect was observed on the surface tension at the air-water interface ((Figure 5.8(B)).

Cin-CNC and CNC partitioning properties at the air-water interface were compared with and without salt. In the presence of Cin-CNC, the surface tension decreased more than CNC due to the hydrophobic cinnamoyl groups. The effect of salt addition to reducing the repulsion between particles was presented according to the comparison of CNC and Cin-CNC (Figure 5.8(C)). The salt addition on the CNC partitioning was significant more effective than Cin-CNC due to the higher negative charge density of CNC particles. The image of CNC and Cin-CNC droplets and interfacial tension values with and without NaCl addition is shown in Figure 5.9 and Table 5.4).

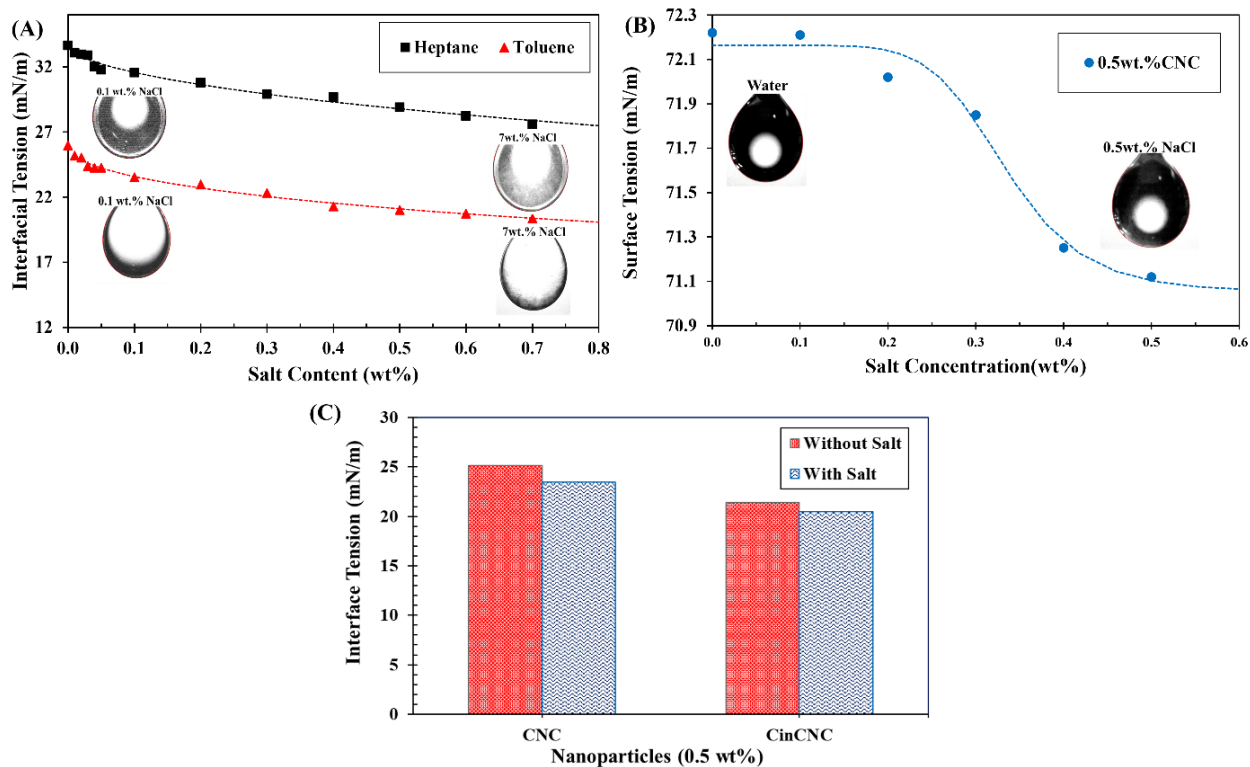


Figure 5.8. (A) Interfacial tension of CNC in different salt concentrations, (B) Surface tension of CNCs as a function of salt concentration, (C) Surface tension of CNC and Cin-CNC with and without salt added.

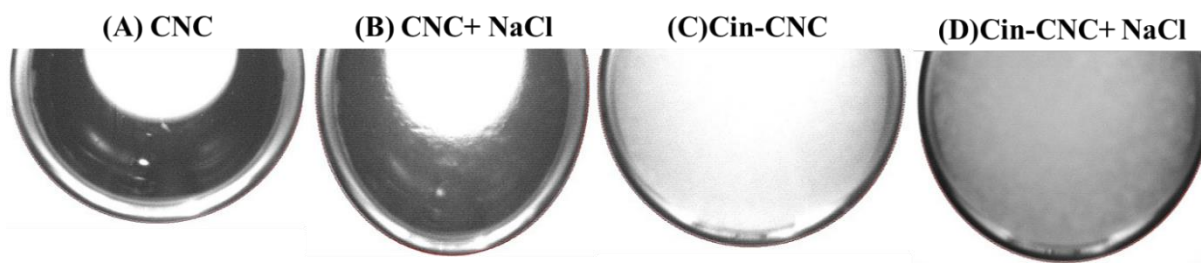


Figure 5.9. Photographs of Interfacial tension measurements of (A) CNC dispersion's droplet, (B) CNC dispersion's droplet with 0.5wt.% NaCl, (C) Cin-CNC dispersion's droplet, (D) Cin-CNC dispersion's droplet with 0.5wt.% NaCl in Toluene

Table 5.4. Interfacial tension values of CNC, CNC+ NaCl, Cin-CNC, Cin-CNC+ NaCl in Toluene

Emulsifier (0.5wt.%)	NaCl (wt.%)	Interfacial Tension (mN/m)
CNC	-	25.15
CNC	0.5	23.48
Cin-CNC	-	21.38
Cin-CNC	0.5	20.49

5.3.7. Dynamic Interfacial Tension Measurements

The dynamic interfacial tension (IFT) of pristine cellulose nanocrystals (CNCs) with and without salt and various chemically modified CNCs were analyzed (Figure 5.10). Lower interparticle repulsion was observed for samples with lower surface charge (Cin-CNC and Desulf-CNC), which reduced the kinetic adsorption barrier. The dynamic interfacial tension data were fitted to a sigmoidal equation (Eq. (5.9)) to examine the evolution of interfacial tension over time. The initial and final interfacial tension values were fitted, and the model parameters were used to evaluate the effect of various CNC systems (Eq.(5.9)).

$$\gamma = \frac{\gamma_0 - \gamma_\infty}{1 + a \cdot t^p} + \gamma_\infty \quad (5.9)$$

where γ_0 represents initial interfacial tension (at time zero), γ_∞ is the model prediction for final interfacial tension, t is time in seconds, and a and p are the shape parameters (a mainly controls the horizontal location of the curve and p governs the slope of reduction in interfacial tension curve in the semi-log graph).

Sigmoidal Model Parameters for Dynamic Interfacial Tension Measurements are presented in Table 5.5. Eq. (5.3) was used to calculate the interface coverage (η) at various times base on dynamic interfacial tension measurements for laboratory results and model predictions. As shown in Figure 5.10, the interface tension values decreased sharply at the beginning due to the rapid absorption of the CNCs to the unoccupied oil-water interfaces. The generation of diffusion barrier and steric hindrance of the adsorbed particles reduces the adsorption rate¹⁷⁰. The TEMPO-CNC sample exhibited very slow initial adsorption (compared to pristine CNC). However, due to the

lower kinetic barrier, interfacial tension reduction reaches lower interfacial tension values compared with pristine CNC. By having the lowest surface charge and the hydrophobic interaction between cinnamoyl functional groups and toluene, the use of Cin-CNC resulted in the highest drop in interfacial tension amongst all chemically modified CNCs. Lowering the electrostatic repulsion by introducing salt into the system significantly affected particle adsorption in terms of calculated interface coverage. The predicted terminal interfacial tension of pristine CNC in the presence of salt was the lowest among all samples.

The highest interface coverage was calculated for the pristine CNC in the presence of salt in the system, while Cin-CNC provided the lowest interface coverage (Figure 5.10). Calculated values for pristine CNC, TEMPO-CNC, and Desulf-CNC showed similar surface coverage. The lowest calculated surface coverage for the Cin-CNC sample is mainly due to having a significantly higher contact angle than other variants. Moreover, due to the low surface charge of Cin-CNC and lack of strong interparticle repulsion, agglomeration was observed at the steady-state condition. The images of droplets containing pristine CNC and Cin-CNC at initial and steady-state are presented in **Figure 5.11**

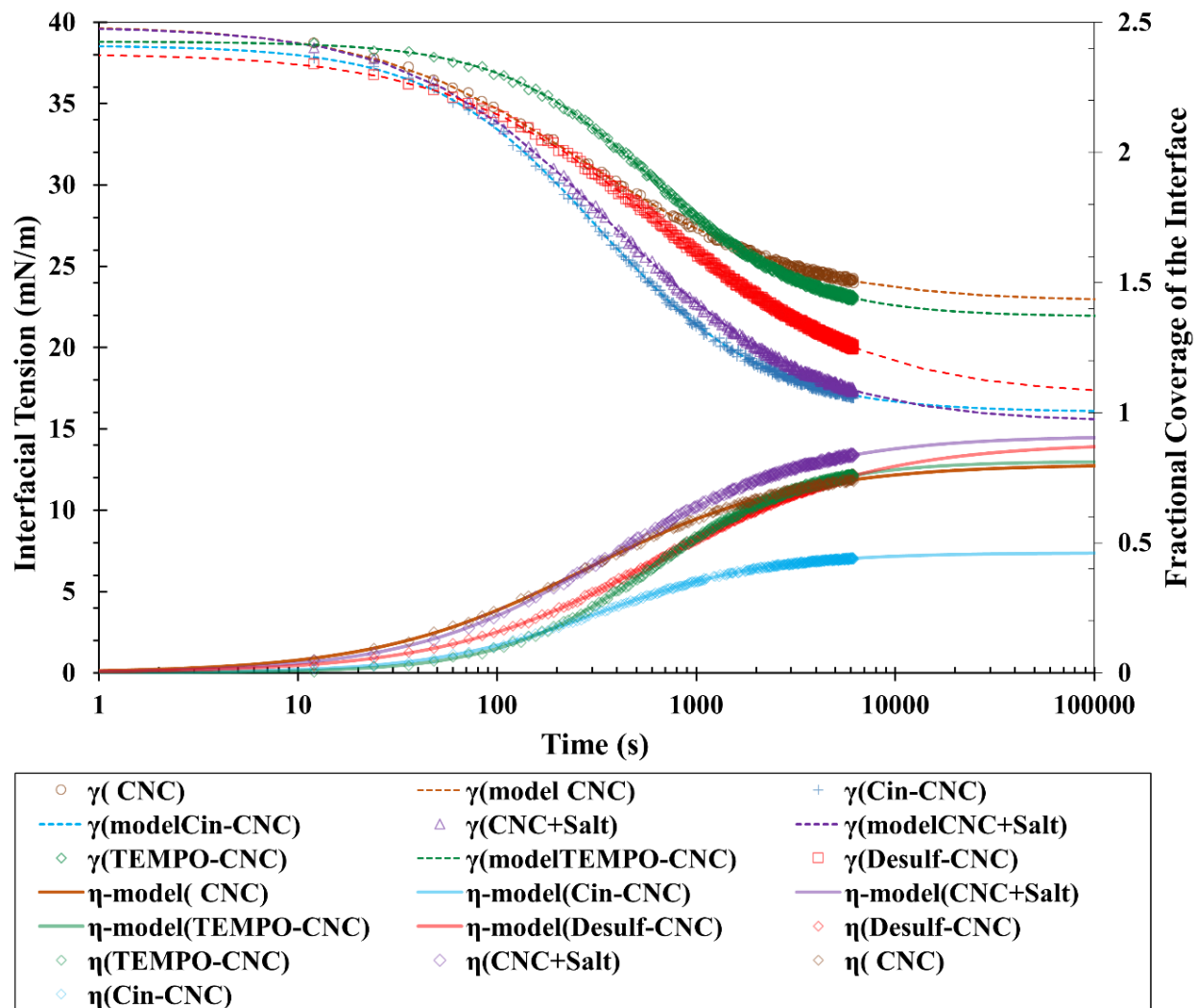


Figure 5.10. Dynamic interfacial tension at toluene-water system with 0.5 wt.% CNC nanoparticles.

Table 5.5. Sigmoidal Model Parameters for Dynamic Interfacial Tension Measurements.

Sample	γ_0	γ_∞	a	p
CNC	31.87	17.97	0.019	0.67
TEMPO-CNC	31.60	17.71	0.006	0.87
Desalt-CNC	24.99	17.79	0.001	1.12
Cin-CNC	27.99	16.35	0.010	0.71
CNC,NaCl	25.71	7.85	0.030	0.39

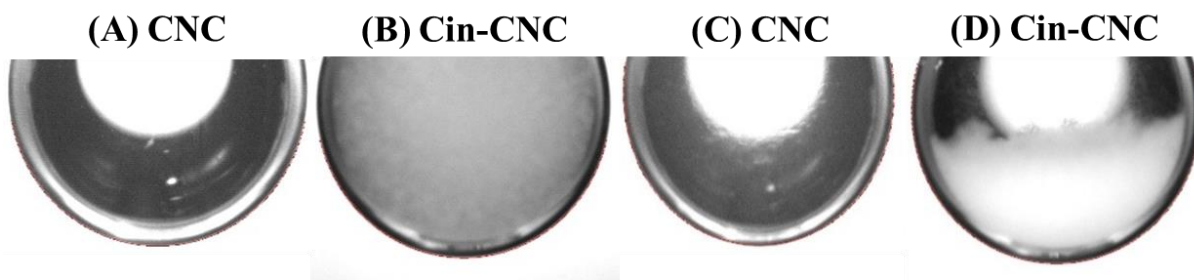


Figure 5.11. Photographs of Interfacial tension measurements of (A) CNC dispersion's droplet at the initial stage, (B) Cin-CNC dispersion's droplet at the initial stage, (C) CNC dispersion's droplet at the steady stage, (D) Cin-CNC dispersion's droplet at the steady stage in Toluene.

5.3.8. Creaming Index

Higher surface coverage decreases the creaming behavior of emulsion. Also, the network of interconnected particles at the oil/water interface increases the viscosity of emulsion, leading to lower creaming values^{9,88}. As presented in Figure5.12, it was observed that modified CNCs displayed a slight increase in the creaming stability index relating to the greater surface coverage of droplets. The Cin-CNC sample with a lower surface charge results in a more droplet network, implying a significantly higher creaming index (Figure5.12(B)).

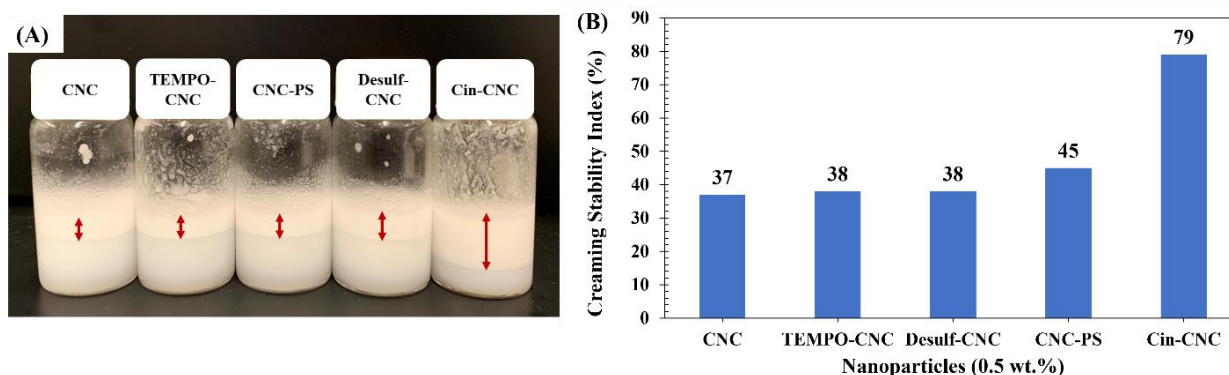


Figure5.12. (A) Visual images of creaming stability, and (B) Creaming index percentages of emulsions prepared with 0.5wt.% emulsifiers including CNC, TEMPO-CNC, CNC-PS, Desulf-CNC, Cin-CNC.

5.3.9. Rheological Properties

The complex viscosity of paraffin wax emulsions stabilized by modified and unmodified CNCs was examined (Figure 5.13). The effect of phase transition of the oil phase on the viscosity profiles could be identified by a sharp transition at the liquid-solid (around 55-56°C) and solid-solid (around 37-38°C) transition of the paraffin wax that corresponded to the thermal transitions of paraffin wax shown in Figure 5.15.³²² during the cooling process, the bridge network formation between droplets results in a higher complex modulus of emulsions. The lower surface charge of modified CNC on the droplet interface provides more significant values of droplet interconnection; therefore, emulsions stabilized via modified CNC present larger values of complex viscosity. The low repulsion between droplets covered with the low surface charge of Cin-CNC particles leads to aggregation. So, the aggregation of solidified droplets stabilized by Cin-CNC yielded a sharp viscosity rise at 55°C, which agrees with previous results of low surface coverage of Cin-CNC presented in Figure 5.10.

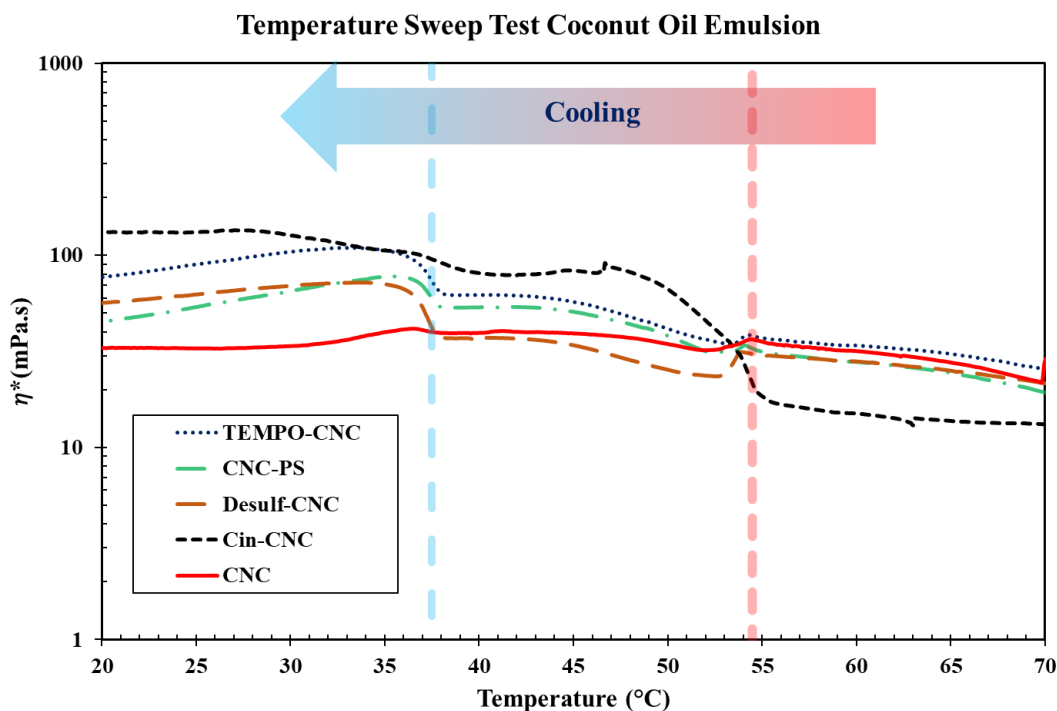


Figure 5.13. Changes in complex modulus of paraffin wax emulsions prepared with 0.5wt.% unmodified and modified CNCs as a function of temperature.

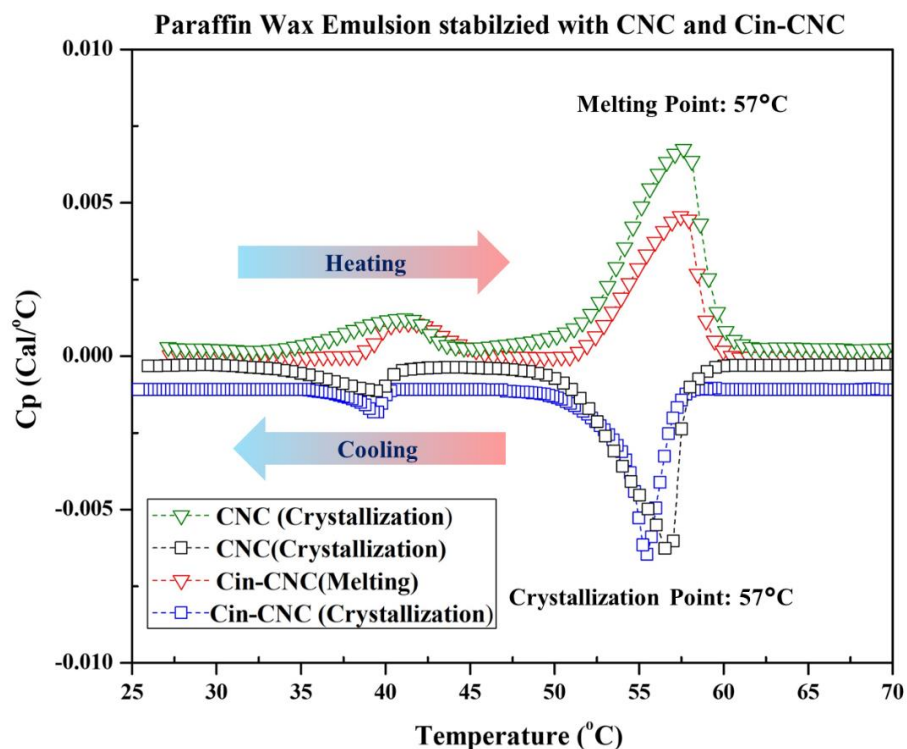


Figure5.14. Differential Scanning Calorimetry (DSC) paraffin wax emulsion stabilized via CNC and Cin-CNC as emulsifier

5.3.10. Particle Size and Distribution

The droplet size of emulsions stabilized by CNC and modified CNC particles (except Cin-CNC) possessed similar droplet sizes. The agglomeration of the low-charged Cin-CNC particles in water reduces their diffusion speed, leading to a larger droplet than other paraffin wax emulsions. Figure5.15(A) shows that except for Cin-CNC, emulsions stabilized with other modified CNCs possessed approximately the same sizes before and after shear loading. Emulsions containing TEMPO-CNC displayed only a 3.72% increase in diameter, imparting the highest stability. However, the relative increase in the particle size of the emulsions prepared with Cin-CNC was lower than pristine CNC. The particle size analysis indicated that sheared CNC-based emulsion possessed a significantly larger droplet size (43.1% increase).

The effect of salt on the stability of the Cin-CNC sample was also examined and compared with the emulsion prepared without salt (NaCl) (Figure5.15 (B)). The optical microscopic images of paraffin wax stabilized with different CNC concentrations and Cin-CNC with and without NaCl are shown in Figure5.16 and Figure5.17). Sheared droplets connect partially, leading to aggregation by having low repulsion between droplets. The results revealed that In the presence

of NaCl, the relative increase in droplet size under applied shear force was higher than emulsion without NaCl. This was due to the lower long-range repulsion of hydrophobic Cin-CNC particles containing NaCl, resulting in droplet aggregation.

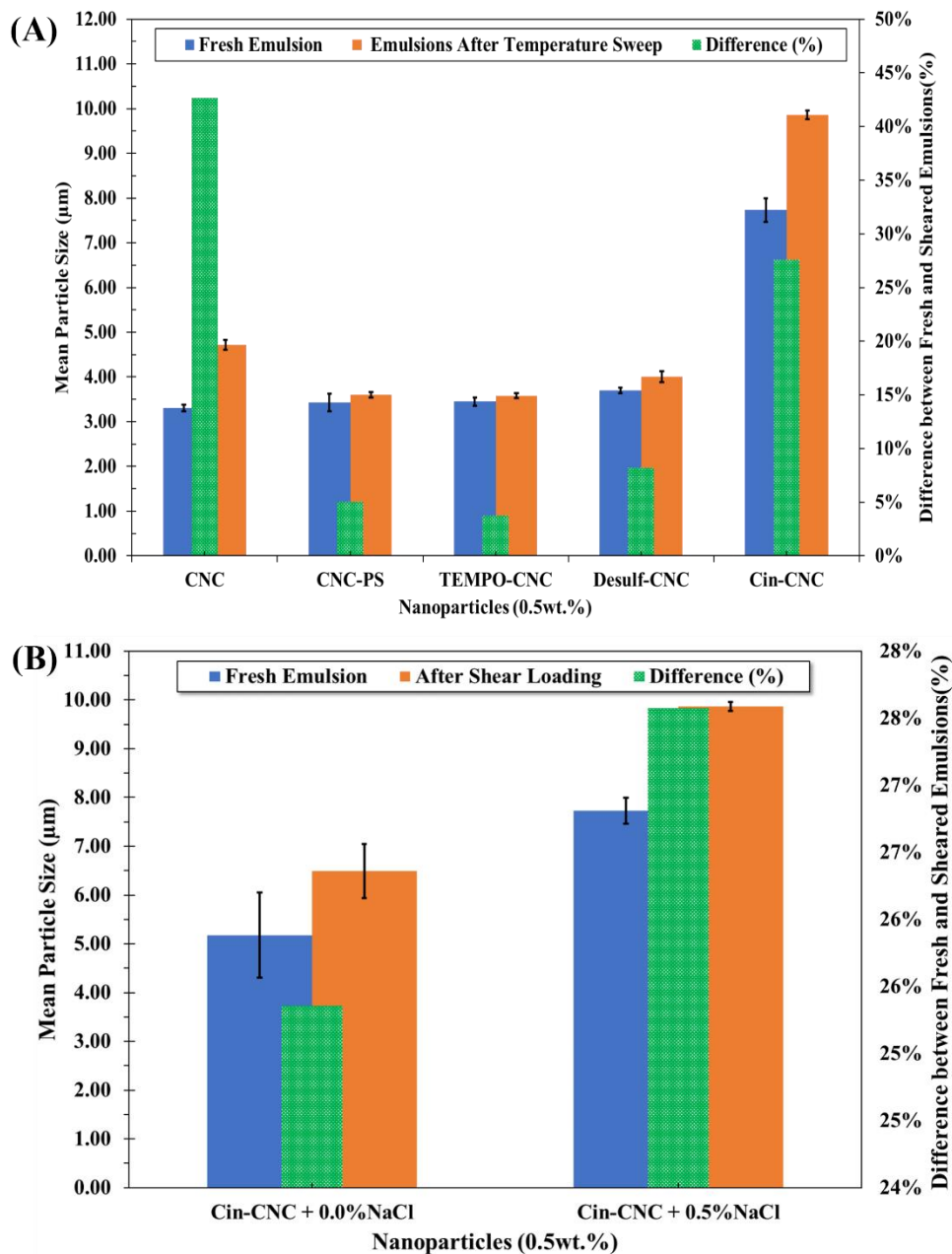


Figure 5.15. The droplet size distributions of paraffin wax emulsions, (A) Stabilized with 0.5 wt. % unmodified and modified CNCs as fresh and after temperature sweep test, (B) Stabilized via Cin-CNC with and without 0.7wt.% NaCl addition.

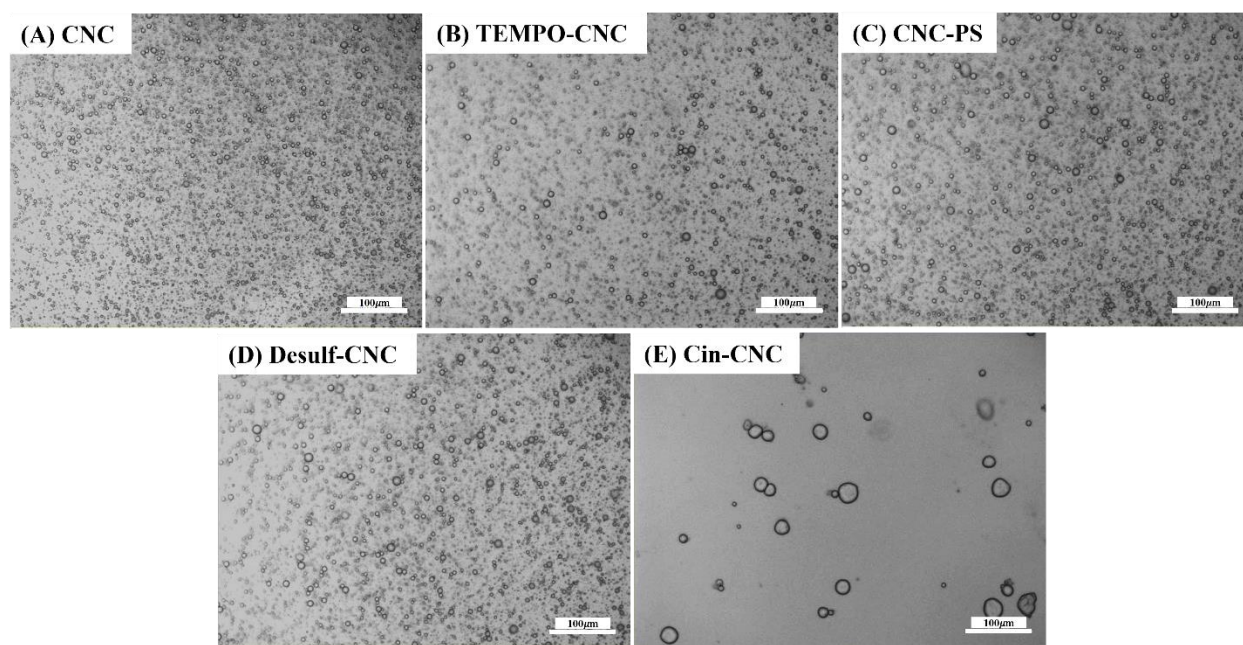


Figure 5.16. Optical microscopy of paraffin wax emulsions stabilized with 0.5wt (A) CNC, (B) TEMPO-CNC, (C) CNC-PS, (D) Desulf-CNC, and (E) Cin-CNC

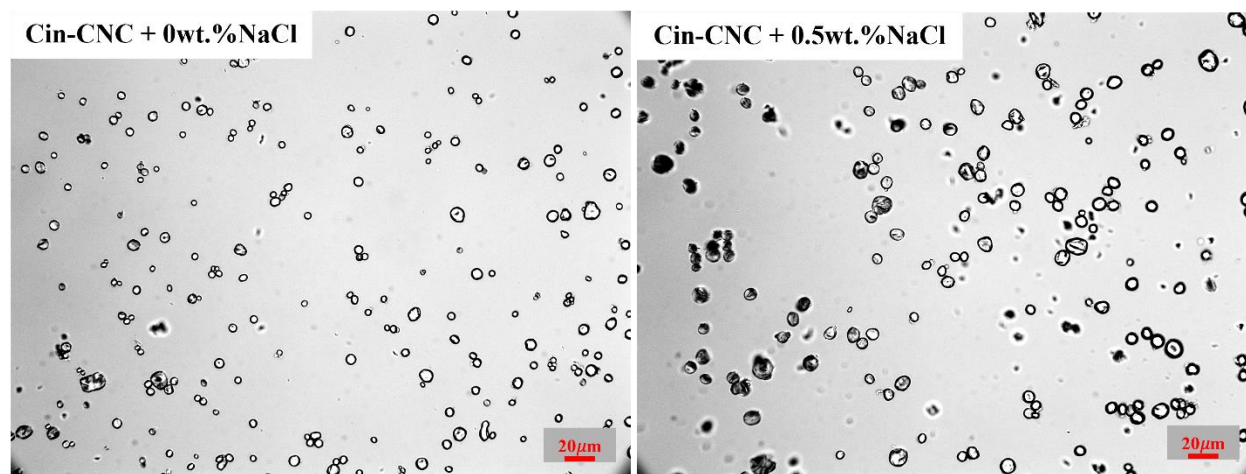


Figure 5.17. Optical microscopy images of emulsions stabilized with 0.5wt.% Cin-CNC containing (A) 0.0 wt.% NaCl, (B) 0.5 wt.% NaCl

5.4. Conclusions

The impact of the reduction in electrostatic repulsion of CNC nanoparticles either by introducing salt to the system or hydrophobic modification of CNCs (TEMPO-, Desulf-, PS-, and Cin-) was evaluated. With the exemption of TEMPO-CNC that showed similar zeta potential and contact angle as pristine CNC, all hydrophobic modifications lowered the zeta potential and increased contact angle. The Cin-CNC variant exhibited a low negative zeta-potential (-8.3 mV) while showing the highest contact angle of 83.5°.

Continuous interfacial tension reduction following the increasing the CNC concentration confirmed the enhancement of CNC partitioning and surface coverage. In addition, the results of the interface tension confirmed the reduction in surface charge and improved interface coverage as a result of partial neutralization of interparticle electrostatic repulsions by sodium ions of NaCl. The dependency of minimum interface tension on the surface charge of particles was confirmed by comparing pristine CNC with modified CNCs. Cin-CNC possessed the lowest surface charge, yielding the lowest interface and surface tension. At the same time, TEMPO-CNC showed the lowest change in interfacial tension compared to pristine CNC. This observation was confirmed by zeta-potential and contact angle measurements. The effect of the oil type was evaluated by using Cin-CNC for toluene and heptane. The higher affinity of phenyl groups in cinnamyl for toluene resulted in more reduction in interface tension of toluene compared to heptane.

The dynamic interfacial tension showed that except for TEMPO-CNC, all the modifications reduced the final interfacial tension. In comparison, Cin-CNC and CNC in a salt-treated environment possessed the lowest surface charge and repulsion, leading to the lowest interface tension values. Visual analysis of the creaming index showed the highest creaming index for Cin-CNC emulsions. The rheological profiles of emulsions confirmed the effect of the surface charge of CNC on the interparticle network in the continuous phase and interface of the dispersed phase. Except for Cin-CNC that showed significantly larger particle size, no significant difference was observed for modified CNCs. The comparison of particle size before and after dynamic loading indicated the importance of reduction in interparticle electrostatic repulsion and interface coverage in the stability of the resulting system through the phase transition of the dispersed phase.

The aggregation of droplets under phase transition depends on the balance of attractive and repulsion forces between CNC particles. This work presented the optimum surface charge of CNC

is required to reduce interparticle repulsion, improve the surface coverage of droplets, and provide sufficient repulsion between droplets.

Credit authorship contribution statement

Parinaz Ataeian: Conceptualization; Data curation; Formal analysis; Methodology; Software; Validation; Visualization Writing - original draft; Writing - review & editing.

Qingyue Shi: Investigation

Mario Ioannidis: Resources, discussion of data and results

Kam C. Tam: Funding acquisition; Supervision; Project administration; Resources; Writing - review & editing

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CHAPTER 6: EMULSIONS UNDERGOING PHASE TRANSITION: EFFECT OF CONCENTRATION AND EMULSIFIER TYPE

Abstract

Pickering emulsion stabilized by cellulose nanocrystals (CNC) during the phase transition of the dispersed oil is poorly understood. We investigated the CNC capability in stabilizing Pickering emulsions during the temperature-induced phase transition. Paraffin wax emulsions stabilized by sodium dodecyl sulfate (SDS) were less stable than CNC stabilized emulsions. The relationship between droplet size and emulsifier content was examined, and a new model describing this relationship was proposed. The droplet size of CNC-based systems was not affected by temperature variation, even at low CNC concentrations. The minimum CNC content required to stabilize paraffin wax emulsion was lower than SDS. DSC results indicated that higher droplet surface coverage with emulsifiers enhanced the deformation resistance of the crystallized droplets, which enhanced the emulsion stability. Temperature sweep viscosity measurements showed that the stability of CNC-based systems was not significantly affected by the phase transition of paraffin wax. Amplitude sweep rheological analysis indicated that emulsions above the melting point of paraffin wax were more stable at all strain levels. However, the SDS-based systems exhibited substantial heterogeneity after the liquid-solid transition. Frequency sweep tests revealed that CNC-stabilized emulsions were more stable than SDS-stabilized emulsions.

6.1.Introduction

Emulsions are thermodynamically unstable systems due to the tendency of liquids to reduce their surface area. The addition of surfactants with amphiphilic characteristics would stabilize the system by reducing the interfacial tension at the oil-water interface.¹⁶⁹ Pickering emulsions stabilized by nanoparticles at the oil-water interface are more stable and popular. Unlike surfactant-based emulsion, the adsorption of solid nanoparticles at the oil-water interface is irreversible, enhancing the emulsion's stability.^{323,324} Various organic and inorganic nanoparticles have been used to stabilize Pickering emulsions, including carbon nanotube, laponite, montmorillonite, silica nanoparticles, and calcium carbonate (CaCO_3).^{71,285,325–328} Both flocculation and coalescence of particles can be reduced by increasing the droplets' repulsion. Enhance repulsion can be achieved by dense absorption of solid particles on the droplets' surface, and some commercial products have benefitted from the increased stability.^{115,329}

CNCs with rod-shaped crystalline structures are derived via the acid hydrolysis of renewable sources, such as wood, cotton, tunicin, algae, and other plant sources. High aspect ratio, high elastic modulus, low density, and thermal stability are amongst the properties of CNCs that promote their applications in many industrial sectors.^{330,331} Having distinctive properties, such as intermediate wettability and nanometric size, makes CNC an ideal system for stabilizing Pickering emulsions. The hydrophobic edge and the hydrophilic face of CNC render the nanoparticle with amphiphilic characteristics⁹, and the large aspect ratio of CNC improves the emulsifying performance of CNCs in stabilizing the emulsion^{9,332}. The hydrophilicity of CNCs is due to the abundant hydroxyl groups with a charge density of 0.03 e/nm^2 and an air-water contact angle of 20° . The surface charge of CNCs plays an essential role in emulsion stability.¹⁶⁸ The sulfuric acid hydrolysis of CNC imparts significant negative charges consisting of sulfur half-ester groups, which hinders the partitioning of the CNCs at the interface. To enhance the coverage of CNC particles on the surface of droplets and improve the emulsion's stability, the hydrophobicity of CNCs should be introduced and enhanced through the addition of salts or surface modification.^{87,101,172} Various studies examined the effect of different counterions such as NaCl and CaCl_2 on the electrostatic screening of CNC particles. Divalent ions such as CaCl_2 were more efficient in screening the electrostatic repulsion of CNC than monovalent ions like NaCl. However, Prathapan et al. observed that the electrolyte effect of Na^+ on the zeta potential of CNC was not significant in both acidic and basic conditions.³³³ Also, Cao et al. reported that the lower electrophoretic mobility of divalent ions increased the

required salt concentration to reduce the repulsion of CNC particles and improved surface coverage of droplets.³³⁴

Surfactant-based emulsions are stabilized via electrostatic repulsion between the droplets. Various studies reported that salt addition to emulsions neutralizes the charged surfactant, resulting in droplet aggregation. The addition of NaCl increased creaming and droplet aggregation of SDS-based emulsions.^{335–337}

The size and aspect ratio of emulsifiers influence the surface coverage of droplets. Also, the minimum emulsifier required to stabilize emulsion significantly depends on the emulsifier aspect ratio. The aspect ratio of CNC influences the stability of the Pickering emulsions.^{15,83,92} Kalashnikova et al. evaluated the dependency of emulsion stability on the size and shape of the CNC. They found that the aspect ratio of CNC was the dominant factor in establishing the surface coverage of oil droplets. For instance, long *Cladophora* nanocrystals stabilize emulsion through 40% surface coverage. While CNC prepared from bacterial cellulose and cotton with medium and low aspect ratio stabilize emulsions by 60% and 80% surface coverage, respectively. It was shown that shorter CNC particles provide a denser layer around the droplets to prevent aggregation, and the longer CNC stabilizes emulsion with low surface coverage relating to the interconnected network of CNC particles at the interface of droplets.⁷⁰ Therefore, compared to surfactants, the large surface area of CNC results in the lower minimum amount of CNC particles required to provide stable emulsion.

The physical state and dynamics of both continuous and dispersed phases affect the emulsion stability and rheology, where the phase transition of the dispersed phase significantly affects the system's rheology and stability.^{148,150,338} When the temperature is reduced, partial crystallization of the dispersed phase will occur. In oil/water emulsions, the crystalline form of the oils is more prone to be wetted by the liquid oil rather than the aqueous phase. Rayner et al. reported that the crystalline portions of the oil would protrude and interact with the liquid oil of the neighbouring droplets.¹³² The bridging of oil droplets induces coalescence that destabilizes the emulsion. However, coalescence due to crystallization is not instantaneous, and factors, such as oil composition and content, emulsifier type, droplet size, thermal profile, and applied shear rate would determine the kinetics of the destabilization process. The emulsifier's resistance to rupture or detachment during phase inversion is critical in isolating the droplets to form a stable emulsion.

The higher surface coverage of emulsifiers at the oil and water interface leads to more rupture resistance, improving the emulsion's stability throughout the phase inversion process.^{132,142}

For any combination of oil and emulsifier, a minimum emulsifier concentration (ρ_{emin}) is required to provide adequate stability. At lower emulsifier concentrations (ρ_e), the interface coverage would be inadequate to prevent droplet coalescence. The interface lifetime is a crucial factor in determining the final droplet size. Bai et al. reported that the addition of higher emulsifier content provided sufficient emulsifier for the surface coverage of droplets, leading to smaller droplet size and higher stability. On the other hand, reducing the droplet size increases the interfacial surface area, and more emulsifiers would be required to cover the droplet interfaces.^{174,339} Also, Chen et al. compared other emulsifiers, and an increase in the CNC concentration enhanced the bridging between droplets without aggregation, resulting in less creaming and better emulsion stability.³⁴⁰

The droplet size in an emulsion plays a vital role in the emulsion properties, such as viscosity and stability, and the final droplet size distribution is governed by the type and concentration of the emulsifier. Regardless of the emulsifier's impact on the droplet size, the type and concentration can affect the rheology of the emulsion. Such effects can be investigated by examining the temperature and frequency dependence of the rheological parameters.³⁴¹

Miao et al. reported that the hydrogen bond between CNC particles at the oil-water interface of droplets led to the bridging 3D network formation between droplets that impacted the rheological and stability of the Pickering emulsions. Also, strong interaction between free CNC particles in the continuous phase increased the viscosity and stiffness of the emulsion.³³⁷ They observed that the emulsions' stiffness was associated with the bridging effect of CNC surrounding the oil droplets, which could be enhanced through the surface modification CNCs. Pandey et al. reported that reducing electrostatic repulsion between CNC particles through desulfation of the CNCs improved the bridging network between droplets and gave rise to higher storage modulus values and stiffer emulsions.³²⁹ Also, the adsorption of bovine serum albumin (BSA) on the surface of CNC enhanced the gel-like behaviors of emulsions, as demonstrated by Liu and coworkers.³⁴²

In addition, the combination of these factors influences the thermodynamics of the system, where the differential scanning calorimeter (DSC) can be used to probe the thermal properties of the dispersed phase.^{322,343–345}

This study examines the effect of emulsifier type and concentration on the paraffin wax emulsion characteristics undergoing phase transitions. Two types of emulsifiers, CNC used in Pickering emulsion and SDS used in the conventional surfactant-based emulsion, were evaluated. The role of emulsifier type and concentration on the droplet size, thermal properties, and rheological behavior of paraffin wax emulsions were examined.

6.2. Experimental

6.2.1. Materials

In this study, water with a resistivity of 18.2 MΩ was prepared with the MilliQ system to prepare the aqueous phase. The CNCs were donated by Celluforce Inc, and all the chemicals, including paraffin wax, sodium dodecyl sulfate (SDS), sodium chloride (NaCl), were analytical grades purchased from Sigma-Aldrich and used without further purification.

6.2.2. Emulsion Preparation

To examine the effect of emulsifiers, the Pickering emulsion produced with CNC was compared with the emulsion prepared using an anionic surfactant, sodium dodecyl sulfate (SDS). CNC emulsions were prepared from 0.2wt% CNC up to 0.9wt% CNC, with paraffin wax/water volumetric ratio fixed at 4:6 and NaCl concentration at 85 mM. The sodium chloride (85 mM) was added to water dispersion containing CNC to enhance the adsorption of emulsifiers by shielding the charge repulsion between the CNC particles. SDS-based emulsions were stabilized using SDS in 0.4wt.% 1.4wt.% concentration range (and named as such), with a fixed volumetric ratio of paraffin wax/water at 4:6. Since paraffin wax is solid at room temperature, the mixture was heated to 70°C in the oven prior to emulsification. An ultrasound probe (Misonix Microscon-XL2000) was used, and the mixture was sonicated for 4 min at 36% amplitude speed. The prepared emulsions were stored for 24 hours at room temperature prior to further characterization. All samples are named based on their emulsifier concentration.

6.2.3. Emulsion Characterization

The distribution of the emulsion droplets was measured using a laser-diffraction droplet size analyzer (Anton Paar Model PSA 1190). The average of three measurements was recorded to yield the mean droplet size for each sample. Fraunhofer diffraction model was used to calculate volume-weighted diameter $d_{4,3}$ (Eq. ((6.1))).

$$d_{4,3} = \sum n_i d_i^4 / \sum n_i d_i^3 \quad (6.1)$$

where n_i is the number of particles at each size, and d_i is the diameter of droplets.

Optical microscopy was used to observe the morphology of emulsions using a Nikon Elipse Ti-S (Agilent Cary Eclipse) equipped with a CCD camera (QImaging ReTIGA 2000R). The effect of emulsifier content on the thermal properties of the oil phase was evaluated using a differential scanning calorimeter (DSC), a TA Q2000 analyzer. Each sample (0.038 mM, 0.0518 ml) was added to an aluminum pan, and water was placed in the reference cell. The test was performed between 20 to 80°C and subject to cooling and heating at 10°C/min rate with the system purged with nitrogen at 30 ml/min.

The rheological properties of the emulsions were determined using a Kinexus Ultra+ rheometer (Malvern Instruments) coupled with rSpace Pro 1.3 software for data analysis. Viscosity measurements were performed using a double gap bob and cup geometry for higher sensitivity for torque detection. A solvent trap was used to prevent the loss of the aqueous phase due to evaporation for tests performed at elevated temperatures. The linear viscoelastic region (LVE) of paraffin wax emulsion was determined using the strain sweep test in the oscillatory loading mode (1 Hz) within a shear strain of 0.1 to 100% at three different temperatures of 30, 50, and 70 °C. The test temperatures were selected according to the DSC test data to represent suspension (oil phase is solid), the combination of suspension and emulsion (mixture of solid and liquid for the oil phase), and emulsion (oil phase is liquid). The effect of the phase transition of the dispersed phase on the rheology of the emulsions was investigated using the complex viscosity measurements under strain-controlled temperature sweep in oscillatory mode within the LVE region. The cooling temperature sweep tests were performed from 80 to 20°C at the rate of 2°C/min, at the constant shear strain amplitude of 0.1% at 1 Hz. The complex viscosity (η^*) of oil in water was measured over a wide range of frequencies (from 0.1 to 100 Hz) at two different temperatures of 35 and 75°C (representing liquid and solid states for the dispersed phase). The applied strain was kept at 0.1% strain (within the LVE range).

6.3. Results and Discussion

6.3.1. Phase behavior of Emulsions

Phase behavior of paraffin wax emulsions stabilized by CNC and SDS were compared after 24 storage at room temperature (Figure 6.1). The images presenting paraffin wax emulsions stabilized by (A) different concentrations of CNC containing 0.5wt.% NaCl (85 mM), (B) different concentrations of SDS, and (C) CNC (0.5wt.%) using different concentration of NaCl (0, 17, 34, 51, 68, 85, 102, 119, 136, 171 mM).

By comparing the results with SDS, a lower concentration of CNC was needed to stabilize the paraffin wax emulsion. All the CNC-based emulsions displayed low creaming behaviour, while oil separation was observed in emulsions with less than 0.8 wt.% SDS (Fig.S1.). As shown in Fig.S1., emulsions containing less than 68 mM NaCl were not stable after 24 hr storage. In comparison, salt addition exceeding 85 mM NaCl improved the adsorption of CNC on the oil droplets, which enhanced the emulsion storage stability.

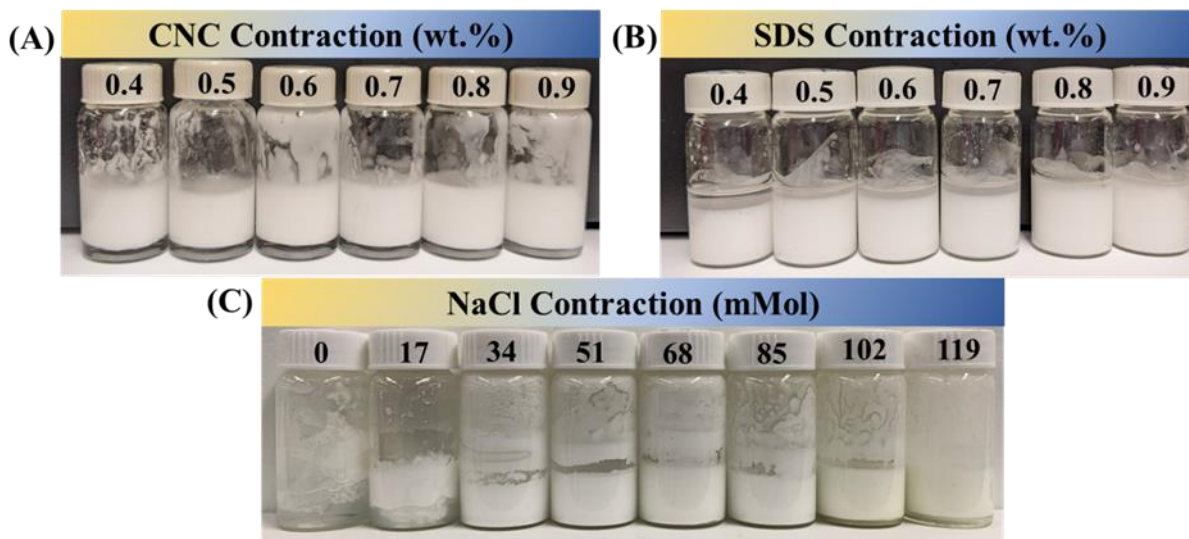


Figure 6.1. Images of paraffin wax emulsions stabilized by (A) different concentrations of CNC containing 0.5wt.% (85 mM) NaCl, (B) different concentrations of SDS, (C) CNC (0.5wt.%) containing different concentration of NaCl, after 24 storage.

6.3.2. Optical Microscopy of Emulsions

The morphology of fresh paraffin wax emulsions stabilized by CNC and SDS were compared in the optical microscopic images (Figure 6.2 and Figure 6.3). The optical microscopic images of emulsions after one-hour storage at room temperature containing crystallized paraffin wax droplets (Melting point: 55-57°C) are shown in Figure 6.4 and Figure 6.5. The results confirmed that the solid adsorption of CNC around the droplets increased the deformation resistance of crystallized paraffin wax droplets leading to higher emulsion stability (Figure 6.4). In comparison, the irregular shape of droplets stabilized by SDS ruptured at the droplet interfaces resulting in aggregation (Figure 6.5). Also, the morphology of CNC-based emulsions was evaluated after 24 hours of storage, indicating that the irreversible absorption of CNC inhibited the droplet coalescence (Figure 6.6).

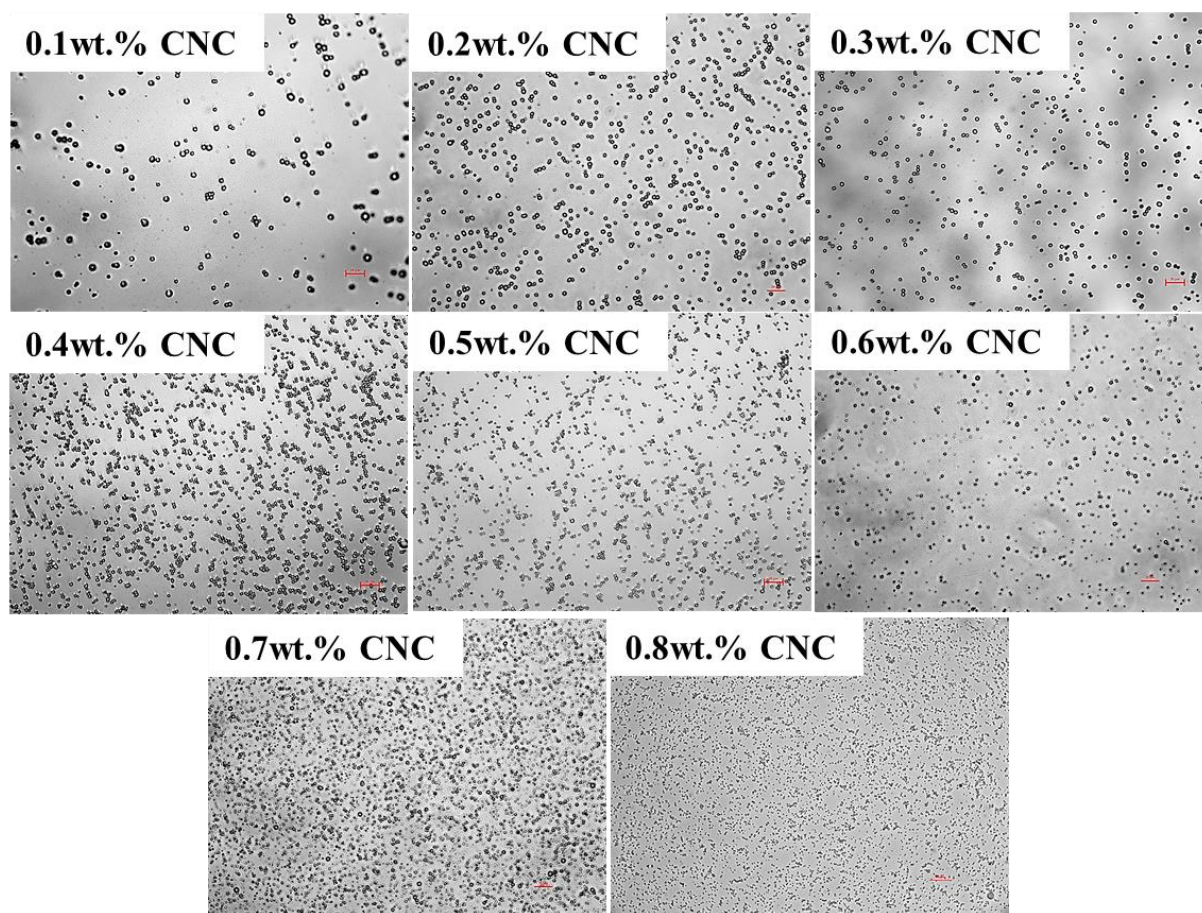


Figure 6.2. Microscopic images of paraffin wax emulsions stabilized by different CNC concentrations in the range of 0.1 to 0.8 wt.% in the aqueous phase.

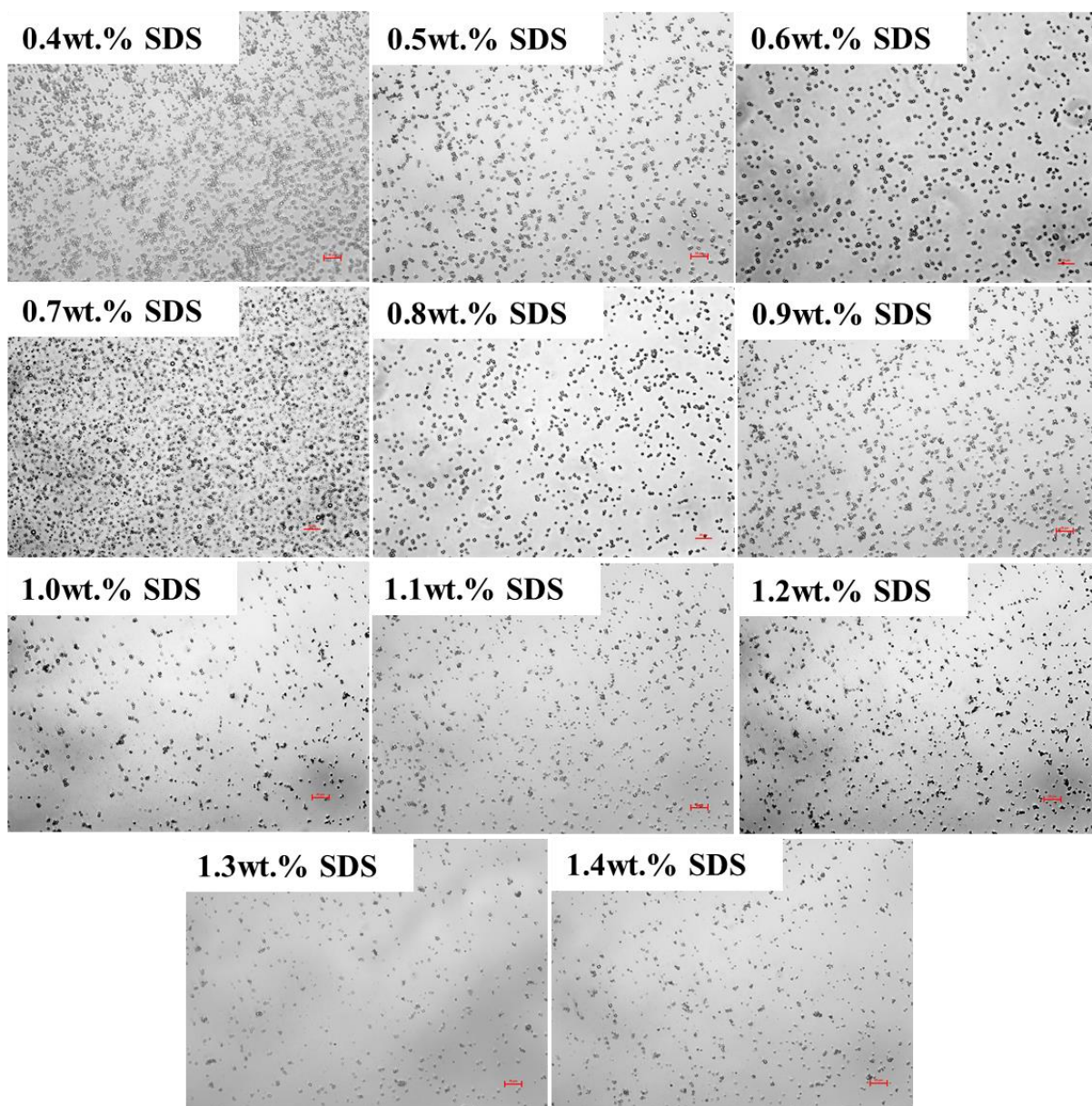


Figure 6.3. Microscopic images of paraffin wax emulsions stabilized by different SDS concentrations in the range of 0.4 to 1.4wt.% in the aqueous phase.

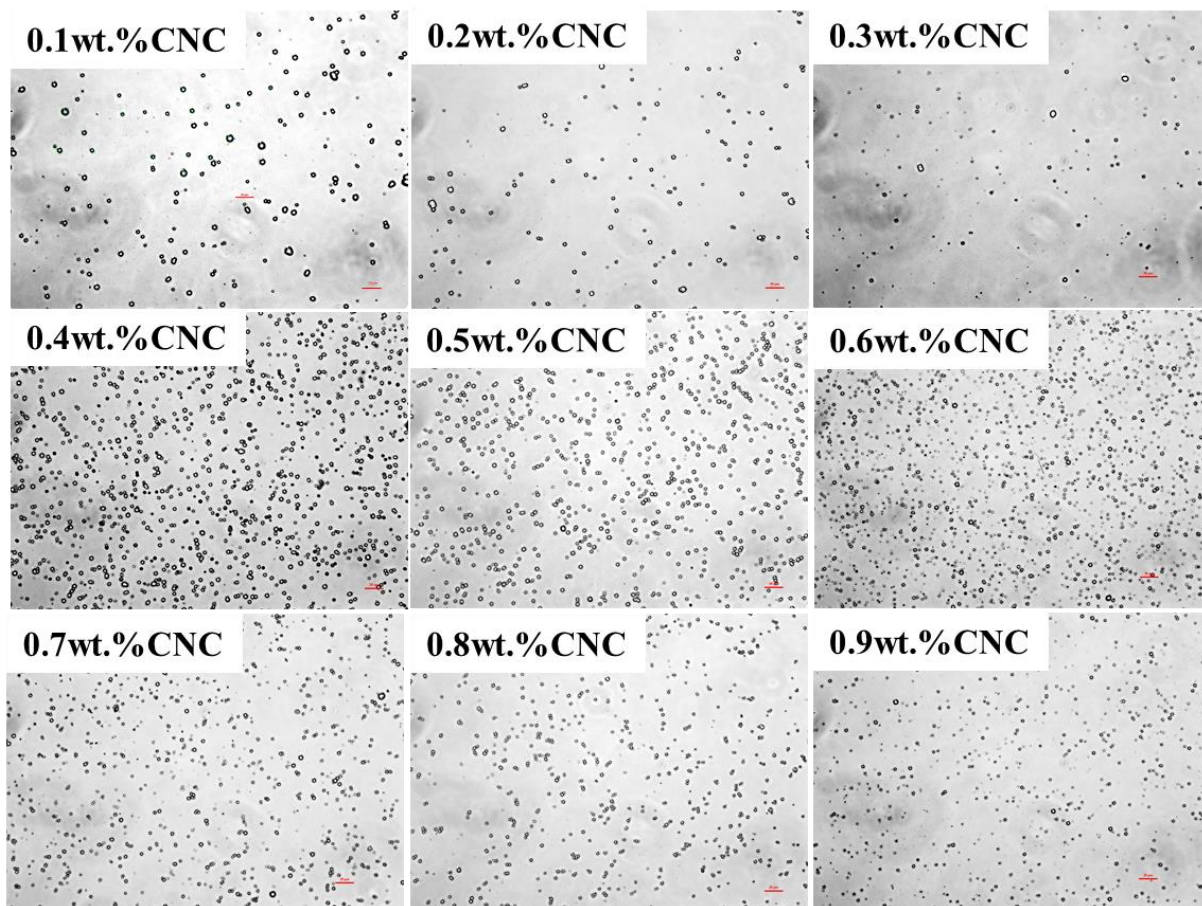


Figure 6.4. Microscopic images of paraffin wax emulsions stabilized by different CNC concentrations in the range of 0.1 to 0.9 wt.% in the aqueous phase after 1 hr. storage.

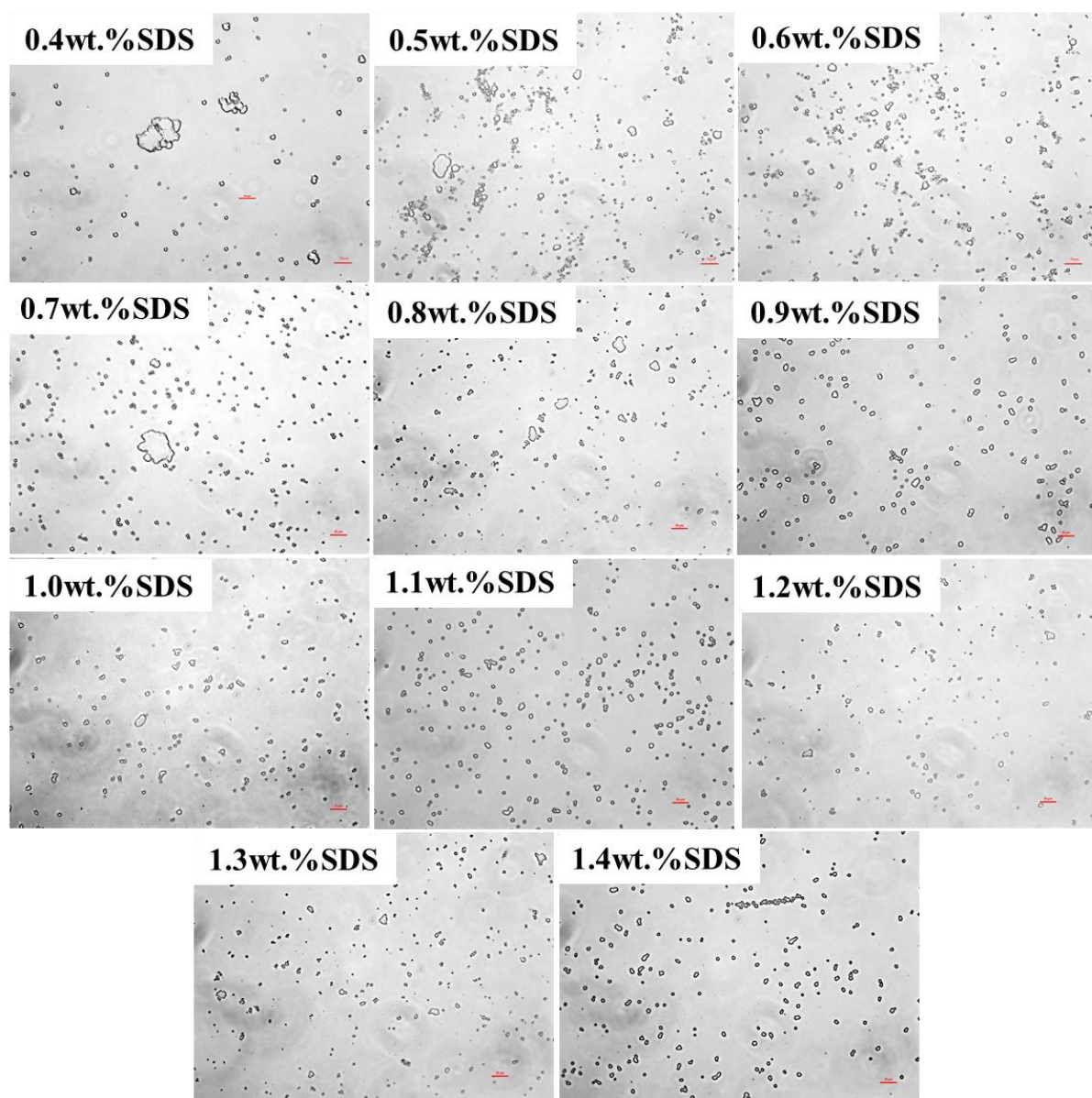


Figure 6.5. Microscopic images of paraffin wax emulsions stabilized by different SDS concentrations in the range of 0.4 to 1.4wt.% in the aqueous phase after 1 hr. storage.

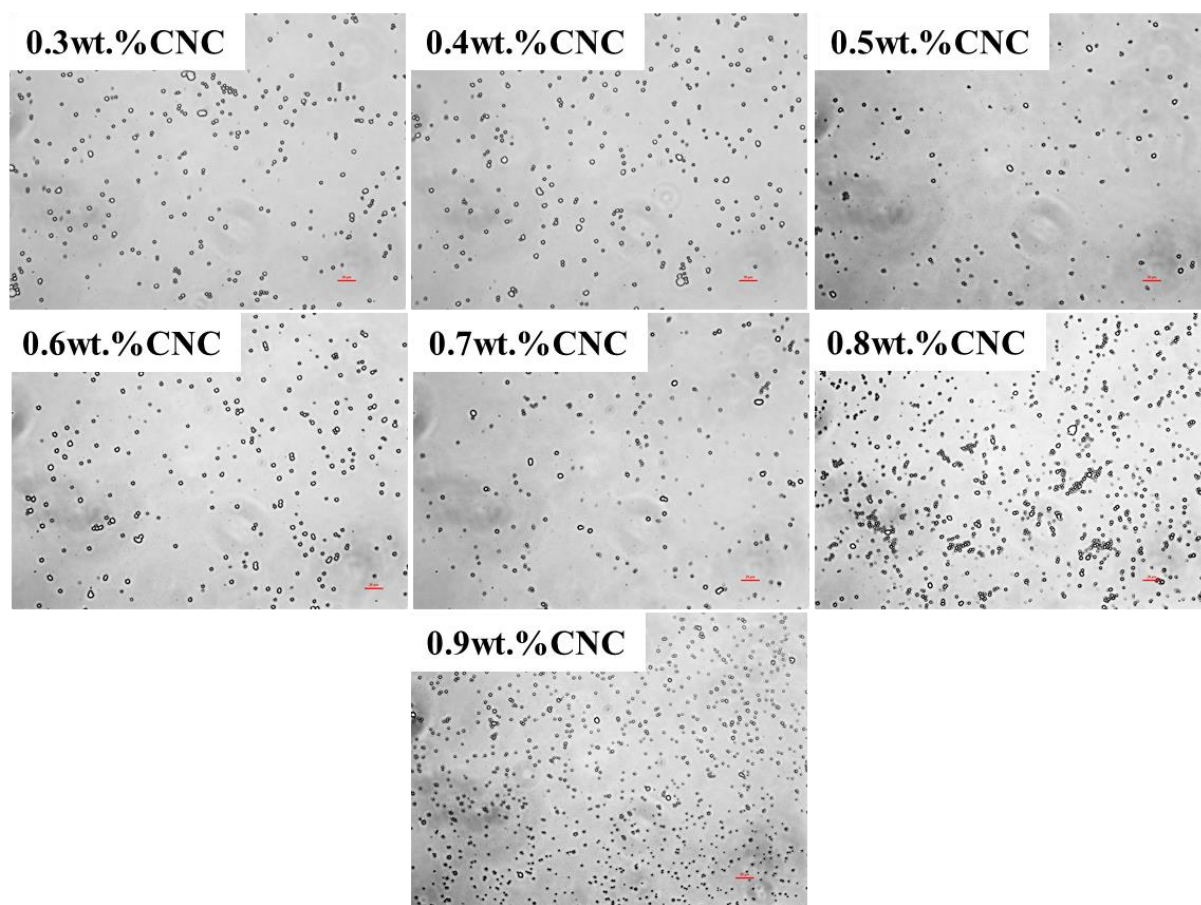


Figure 6.6. Microscopic images of paraffin wax emulsions stabilized by different CNC concentrations in the range of 0.3 to 0.9 wt.% in the aqueous phase after 24 hr. storage.

6.3.3. Droplet Size Distribution (PSD)

6.3.3.1. Role of Salt Concentration

The optimum value of required NaCl to stabilize the CNC-based paraffin wax emulsion was determined by measuring droplet size. Paraffin wax emulsion stabilized by 0.5wt% CNC at a 4/6 volume ratio of paraffin wax to water was prepared based on different amounts of NaCl. The result indicated that paraffin wax emulsions were stable after adding 0.1wt% NaCl (17mM). However, the addition of NaCl exceeding 0.5wt% NaCl (85 mM) did not reduce the droplet size (Figure 6.7). Therefore, 0.5wt.% of NaCl was determined to be the optimum NaCl content to provide the highest surface coverage of paraffin wax droplets.

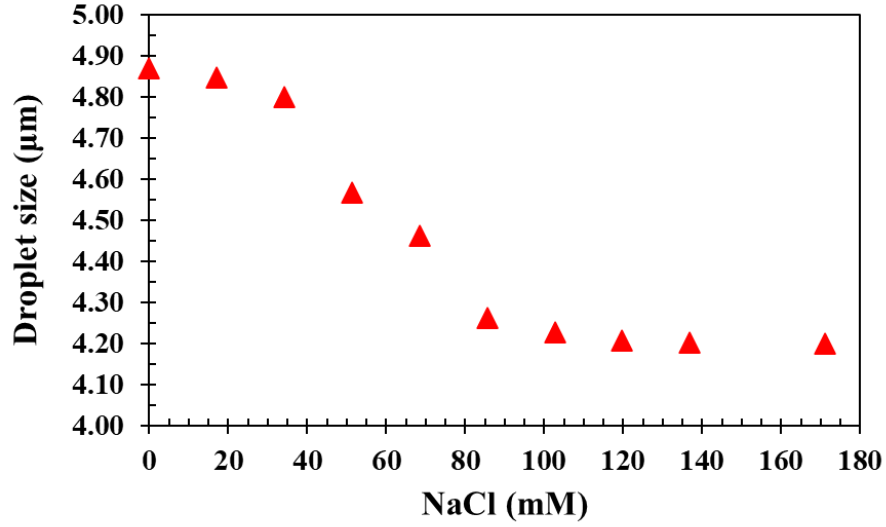


Figure 6.7. Droplet size of paraffin wax emulsions stabilized by CNC (0.5wt.%) at different NaCl concentrations.

6.3.3.2. Role of Emulsifier's Concentration

Theoretically, the emulsion droplet size is a function of the minimum effective surface density of the emulsifier (σ_{em}), the emulsifier mass concentration to oil portion ($\rho_{em/oil}$) as defined by Eq. ((6.2));^{129,339}

$$D = \frac{6\sigma_{em}}{\rho_{em/oil}} \quad (6.2)$$

In developing Eq. (6.2), it was assumed that all the emulsifiers in the aqueous phase would be absorbed onto the oil-water interface. Moreover, it can be concluded from Eq. (6.2) that reducing the droplet size can be achieved by introducing more emulsifiers to the system. Eq. (6.2) can be rewritten as Eq. ((6.3) to include these practical limitations.

$$D = \frac{C_1}{\rho_{em/oil}} + C_2 \quad (6.3)$$

where C_1 and C_2 are constant and are unique for each emulsifier and oil combination.

Figure 6.8 (A) and (B) show the mean droplet size of CNC stabilized Pickering emulsions and the SDS-stabilized conventional emulsions, respectively. The red dashed line represents the prediction using the theoretical droplet size model (Eq. (6.3)). The root-mean-square error represents the fitting of the models within the interquartile range (RMSE-IQR) of the logarithmic scale (Eq. (6.4)).

$$RMSE - IQR = \sqrt{\frac{\sum_{i=1}^n \{[\log_{10} D_{lab} - \log_{10} D_{model}]^2\}}{n}} \quad (6.4)$$

where D_{lab} is the mean droplet size measured in the lab, D_{model} is the mean droplet size predicted by the model, and CDF^{-1} is the quantile function.

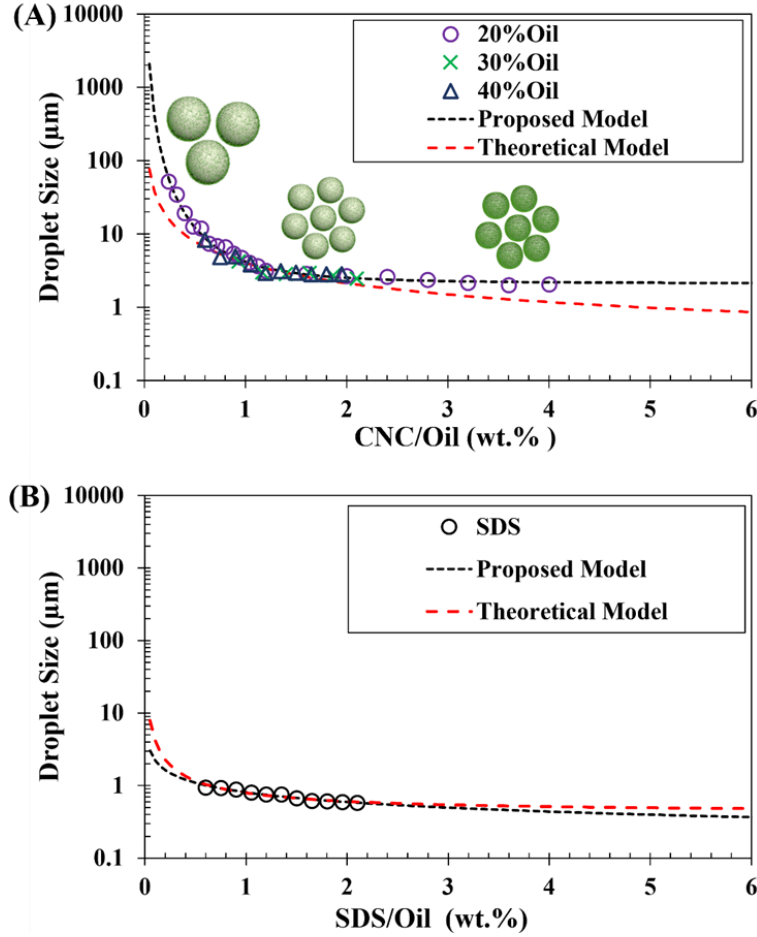


Figure 6.8. Droplet size over emulsifier/oil ratio for (a) CNC Pickering emulsions and (b) SDS conventional emulsion systems.

Although the model fitting for the SDS stabilized emulsion was fairly good (RMSE-IQR = 0.29%), the predictions for the CNC Pickering emulsion were not satisfactory (RMSE-IQR = 4.56%). The model's failure for the CNC Pickering emulsions could be attributed to several factors. For instance, in developing Eq. 6.3, we assumed that all the CNCs added were partitioned to the oil-water interface. This assumption is valid for the high polarity of surfactants, and the fitting curve results confirmed it. However, it might not be the case for Pickering emulsions, and part of solid particles might disperse in the aqueous phase and not be partitioned to the interface. The

shape and physical properties of CNCs could cause the dependency of $\sigma_{em,min}$ on the interface curvature. The high modulus fibres of CNCs can provide lower coverage for smaller particles due to their high modulus and low bending flexibility.^{9,129} As a result, by reducing droplet size, the efficiency of CNC to cover the surface would be reduced, and more CNCs would be required to provide the physical barrier at the interface.

A new empirical model for the relationship between droplet size and emulsifier concentration is described by Eq. (6.5)). The black dashed line in Figure 6.8 represents the prediction of this model for both emulsion systems. The goodness of the fitting of the proposed model is significantly higher for the CNC Pickering emulsions (RMSE-IQR=0.46%) and slightly better for the SDS-based conventional emulsion system (RMSE-IQR=0.16%). Model parameters and RMSE-IQR values are summarized in Table 6.2.

$$D = K \times \left[\frac{1}{(\rho_{em/oil})^P} \right] + C \quad (6.5)$$

where K, P, and C are empirical model constants representing minimum droplet size.

A noticeable difference in the mean droplet size was observed for the two systems. While the minimum droplet size in the CNC Pickering emulsion system was about 2.1 μm , the SDS system exhibited a minimum value of 0.6 μm . As expected, by increasing the emulsifier concentration, the droplet size would decrease to minimum droplet size, after which the addition of an additional emulsifier would not change the droplet size. The minimum required CNC concentration (CNC/oil: 1.2) to stabilize emulsion was found to be lower than SDS (CNC/oil: 1.8) due to the large surface area of CNC particles.

Table 6.1. Fitted parameters for the theoretical and proposed model for the mean droplet size of two emulsion systems.

Sample	Theoretical Model			Proposed Model			
	C ₁	C ₂	RMSE-IQR	K	P	C	RMSE-IQR
Pickering Emulsion with CNC	3.82	0.22	4.56%	2.06	2.31	2.11	0.46%
Conventional Emulsion with SDS	0.29	0.42	0.29%	0.81	0.44	0.001	0.16%

An emulsion's stability under dynamic loading is an important criterion that describes the reliability of the emulsion during pumping and transport. Droplet size analyses were performed on both systems after the frequency sweep (0.1 to 100 Hz at 0.1% shear strain) at 35 and 75°C to evaluate the stability of systems subjected to dynamic conditions and temperatures. **Table 6.3** summarizes the sheared and unsheared emulsions at 35 and 75°C. Figure 6.9(A) presents the mean droplet size for both CNC and SDS systems. As shown in the Figure 6.9, the surface coverage of CNC particles prevented the crystallized paraffin wax from protruding out of the oil interface, and the droplet size of CNC-based emulsions was not significantly affected. However, the size of SDS-based droplets at emulsifier concentrations below 1.1 wt.% increased significantly. Figure 6.9(B) compares the droplet size of the emulsions before and after dynamic loading at high and low temperatures. In this figure, both axes show the mean droplet size of fresh emulsions and sheared emulsions at 35 and 75°C. The 45° line represents no change in the droplet size, indicating that the system was stable. The CNC-based samples displayed excellent stability regardless of the droplet size and emulsifier content, and their data were close to the 45° line. For SDS base emulsions, the system was stable after the dynamic loading at 35°C (SDS-Fresh/35); however, a significant deviation from the 45° line was observed after the dynamic loading at 75°C (SDS-Fresh/75) and a larger deviation was observed for the larger initial droplet size. Figure 6.10 shows the effect of dynamic loading at 35 and 75°C on the percentage increase of the droplet size of CNC and SDS-based paraffin wax emulsions. The morphology of paraffin wax emulsion stabilized with CNC and SDS after applying frequency sweep at 35°C is presented in Figure 6.11.

Table 6.2. Naming of paraffin wax emulsions before and after frequency sweep loading at 35 and 75°C.

Name of Sample	Unsheared	Sheared at	
		35°C	75°C
CNC, Fresh	✓	-	-
CNC, FS-35	-	✓	-
CNC, FS-75	-	-	✓
SDS, Fresh	✓	-	-
SDS, FS-35	-	✓	-
SDS, FS-75	-	-	✓

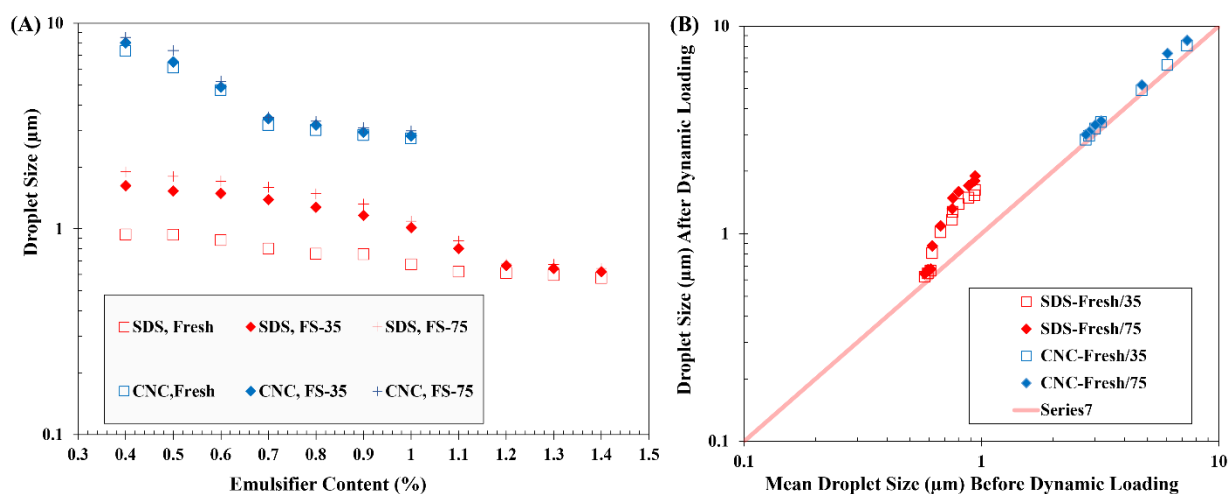


Figure 6.9. (A) Effect of dynamic loading on droplet size before and after frequency sweep test at 35 and 75°C for CNC- and SDS-based systems, (B) Correlation between droplet sizes at fresh and sheared under dynamic loading at 35 and 75°C.

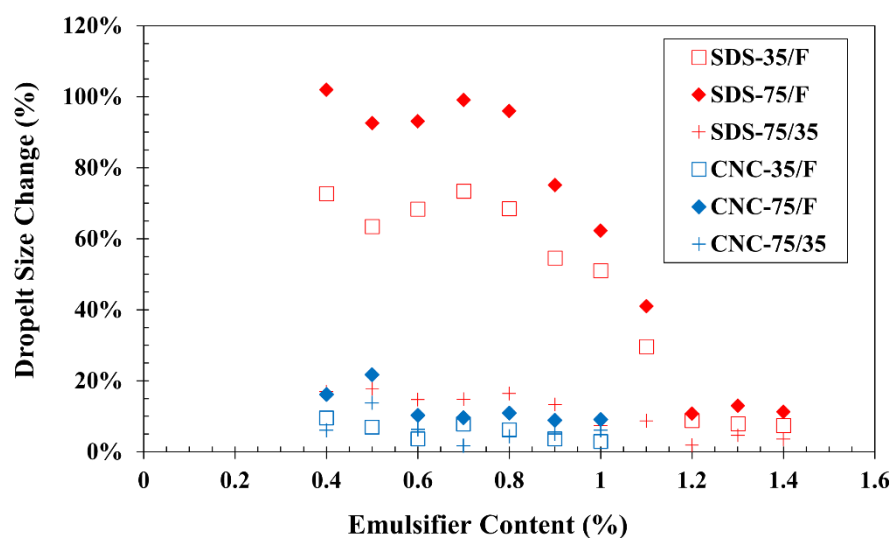


Figure 6.10. Percentage increase of droplet size stabilized via CNC and SDS before and after applying frequency sweep at 35 and 75°C.

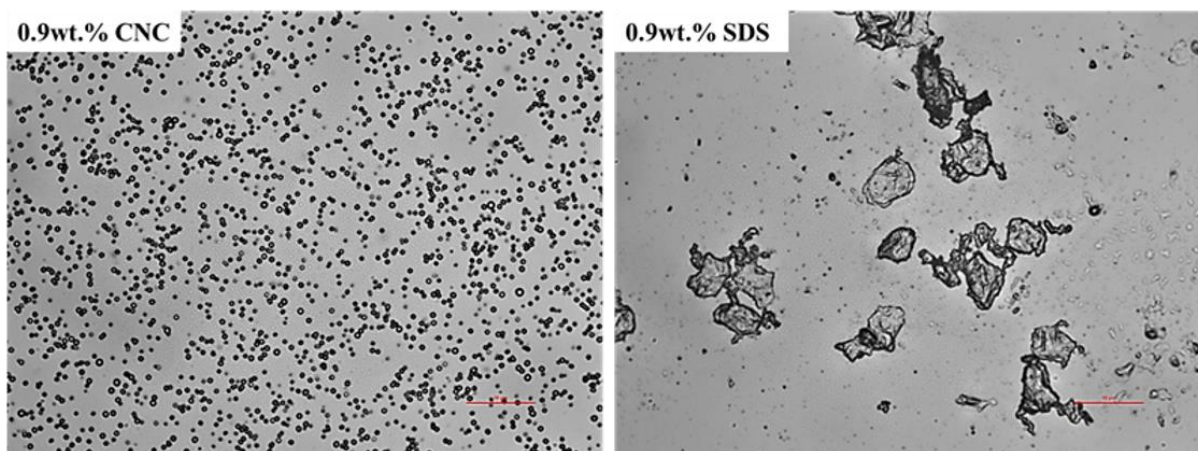


Figure 6.11. Optical microscopy images of paraffin wax emulsions stabilized with CNC and SDS after frequency sweep loading at 35°C

6.3.4. Differential Scanning Calorimetry (DSC)

The impact of the droplet coverage by the CNC on the thermodynamics of the oil phase during phase transition was investigated during the heating and cooling processes between 20 to 80°C. Two observed peaks represented the solid-solid and solid-liquid transitions, with endothermic peaks at slightly higher temperatures than the exothermic (cooling) peaks (Figure 6.12(A)). The solid-liquid transition at 58°C for endothermic and 56°C for exothermic were more significant than the solid-solid transition occurring at 39°C for endothermic and 37°C for exothermic. Figure 6.12(B) shows the difference between the melting and crystallization temperature for liquid-solid phase transition with increasing CNC concentrations. Forming a more robust solid-like CNC network around particles provided more resistance to deformation necessary for the phase transition.

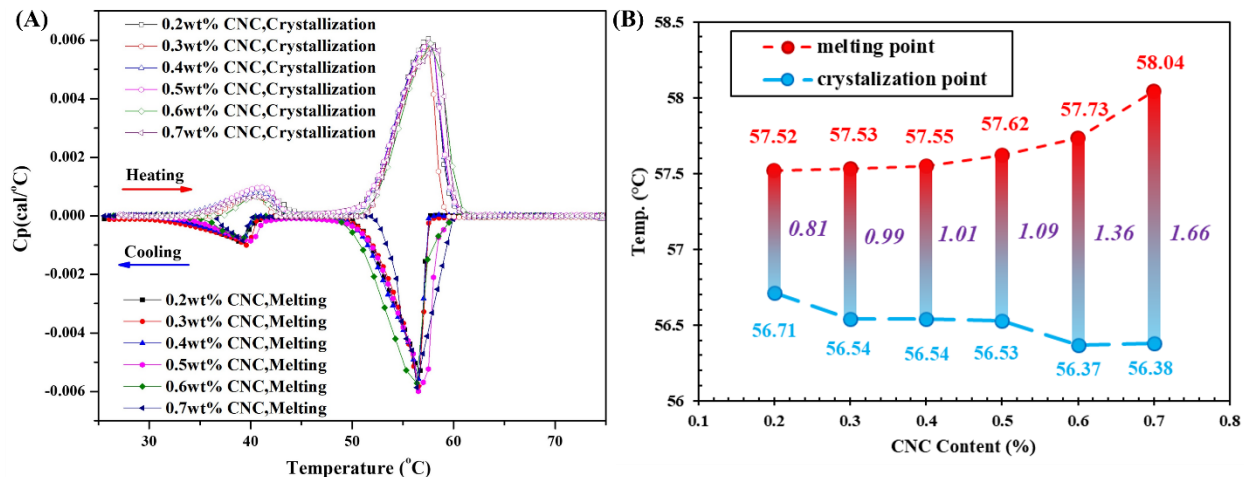


Figure 6.12. (A) Representative DSC thermograms of paraffin wax emulsion prepared with different CNC concentrations, (B) The changes on melting points and crystallization points of paraffin wax droplets of emulsions based on CNC concentrations.

6.3.5. Rheological Analysis

6.3.5.1. Shear Strain Amplitude Sweep

The linear viscoelastic region (LVE) of emulsion stabilized by CNC (0.8wt.%) containing NaCl (85mM) was calculated from the rheological data fitted to the sigmoidal model described by Eq. ((6.6)). The linear behavior was analyzed according to the strain level representing 5% drop in complex modulus (Table 6.4).

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + a\gamma^P} \quad (6.6)$$

where η is the viscosity (can be η^* , η' , or η''), η_0 and η_{∞} are maximum and minimum values, γ is shear strain amplitude, and a and P are shape parameters.

Complex viscosity (η^*) and its components (η' and η'') results (Figure 6.13) revealed that the emulsion at 70°C possessed viscosities (complex, storage, and loss) that were less sensitive to changes in the strain level. The viscous viscosity curves (η'') (Figure 6.13(C)) exhibited a more profound difference in the rheological behavior of the emulsions at various temperatures.

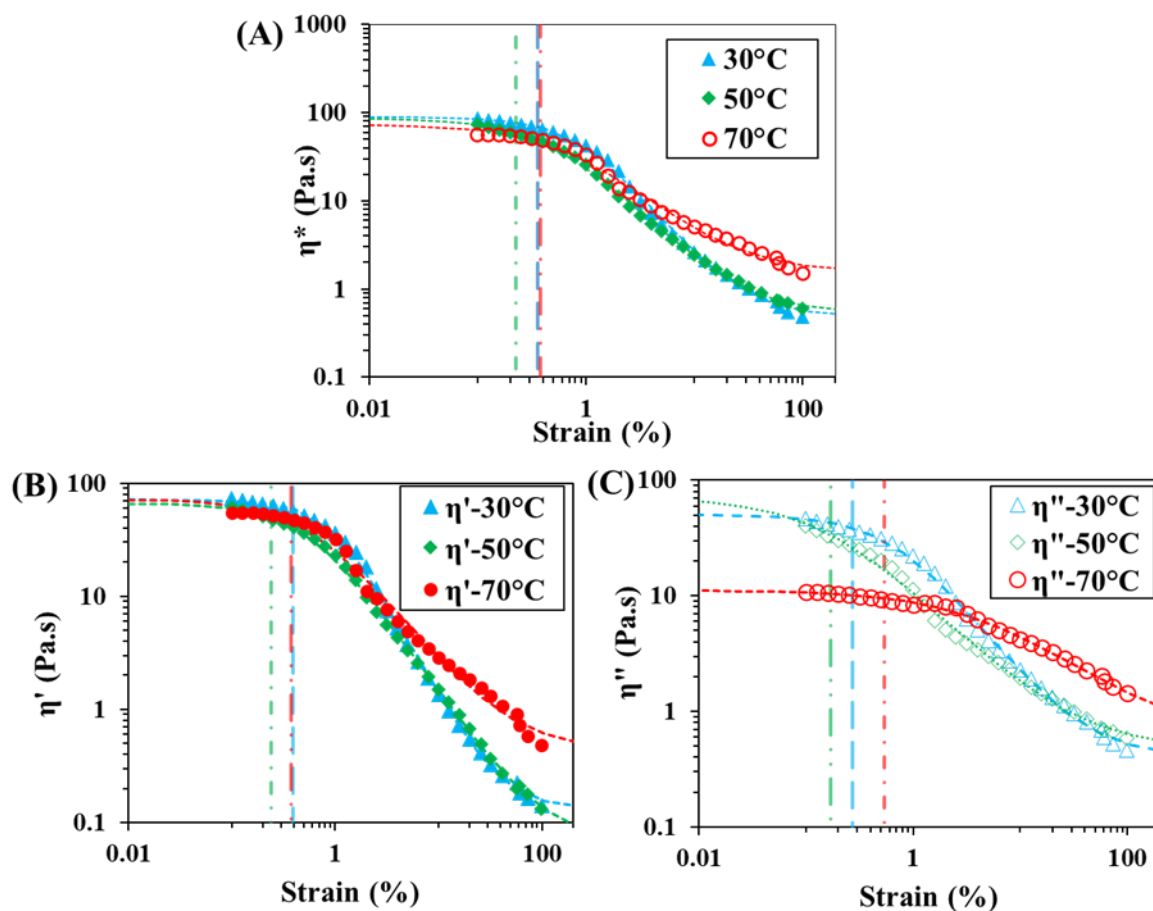


Figure 6.13. Linear viscoelastic region of CNC-based paraffin wax emulsion based on (A) Complex viscosity (η^*), (B) Elastic component of complex viscosity (η'), and (C) Viscous component of complex viscosity (η'') in the shear strain amplitude sweep test at 1Hz cyclic loading at 30, 50, and 70°C.

Table 6.3. Calculated rheological LVE limit of CNC (0.8wt.%) stabilized paraffin wax emulsion at three different temperatures.

Temperature (°C)	LVE Range (% Strain)		
	η^*	η'	η''
30	0.36	0.39	0.27
50	0.22	0.24	0.17
70	0.38	0.37	0.54

6.3.5.2. Temperature Sweep Test

Temperature sweep profiles of CNC-based and SDS-based emulsions are presented in Figure 6.14. The vertical lines are the phase transition temperatures of the paraffin wax (red line for the liquid-solid and blue for the solid-solid transition). For both systems, irregular viscosity versus temperature profiles were observed at both transition temperatures, where three temperature zones were identified: low (L), medium (M), and high (H) temperature zones. At the liquid-solid transition temperature (when the temperature was reduced), the CNC-based emulsions experienced a slight reduction in the viscosity (Figure 6.14(A)). In contrast, the viscosity of SDS-based emulsions experienced a significant increase (Figure 6.14(B)), and this magnitude decreased with increasing emulsifier content. This drastic increase in the viscosity suggested that the dispersed phase in SDS systems had coalesced, where the viscosity profile corresponded to a heterogeneous system.

Figure 6.14(C) compares the temperature sweep profiles of CNC- and SDS-based paraffin wax (as phase changing oil) emulsion with a CNC-based emulsion of a non-phase changing oil (vegetable oil). Paraffin wax emulsions experienced an abrupt change at the transition temperature. While the viscosity of the CNC-based emulsion recovered after the liquid-solid transition, the SDS system became heterogeneous due to aggregation resulting in a significant increase in the viscosity.

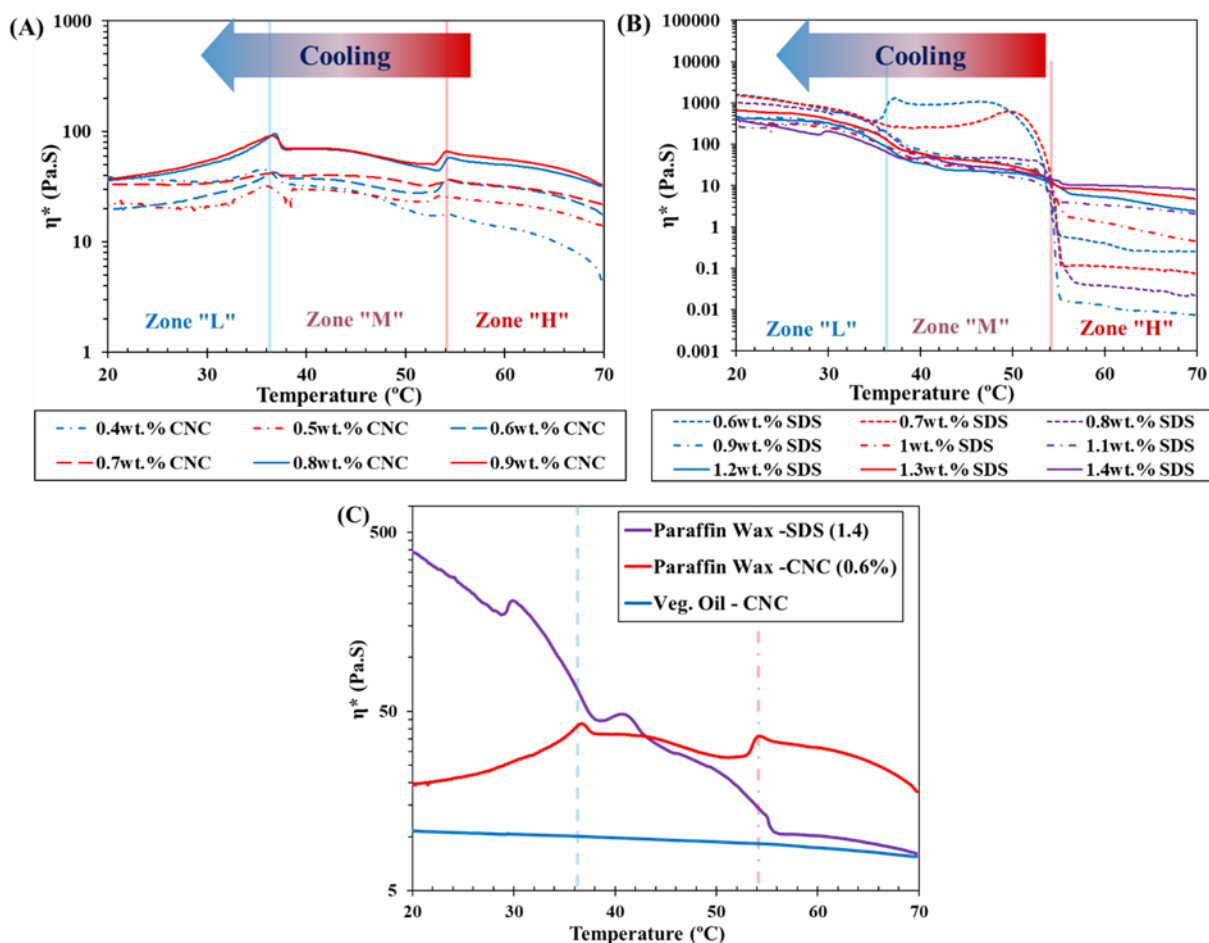


Figure 6.14. Temperature sweep of paraffin wax emulsions stabilized in different concentrations of (A) CNC, (B) SDS, (C) Temperature sweep comparison of CNC-based vegetable oil emulsion stabilized with CNC- and SDS-based paraffin wax emulsions.

6.3.5.3. Frequency Sweep Test

The complex viscosity of the CNC-stabilized system at low temperature (Figure 6.15(A)) changed significantly with CNC concentration (Figure 6.15(B)). While at high testing temperature (Figure 6.15(B)), the change in the CNC concentration mainly influenced the complex viscosity at low loading frequencies (below 2 Hz), where the free CNC in the aqueous phase strengthened the partial network, thereby increasing the complex viscosity. However, the CNC networks were disrupted at higher frequencies, and the viscosity decreased due to the loss of the network. In SDS-stabilized systems, the complex viscosity was significantly affected by the emulsifier content at both temperatures (Figure 6.15(C) and (D)). The emulsifiers' smaller droplet size and thickening effect were the main contributors to the observed rheological profiles. The comparison between the complex viscosity of paraffin wax prepared with CNC (0.9wt.%) and SDS (0.9wt.%) under

frequency sweep at 35°C is shown in Figure 6.16. In general, all the complex viscosity curves (Figure 6.15) decreased with increasing frequency, reaching a minimum value, after which the data were scattered and showed an increase due to aggregation resulting in a heterogeneous system. The loading frequency corresponding to the minimum viscosity of the complex viscosity curve indicated the emulsion stability against dynamic loading. Using a sigmoidal model for the relationship of the complex viscosity and loading frequency, the frequency at failure was calculated and plotted in Figure 6.17.

The emulsion samples subjected to dynamic loading were examined to reveal different instabilities for the CNC and SDS systems. The loss of stability in the CNC-based systems was recoverable (creaming) due to emulsion coated with particles which lowered the frequency to restore the emulsion system effectively. In contrast, the failure in SDS-based systems was non-recoverable due to irreversible phase separation. Figure 6.18 shows both systems after dynamic loading at 35 and 75°C.

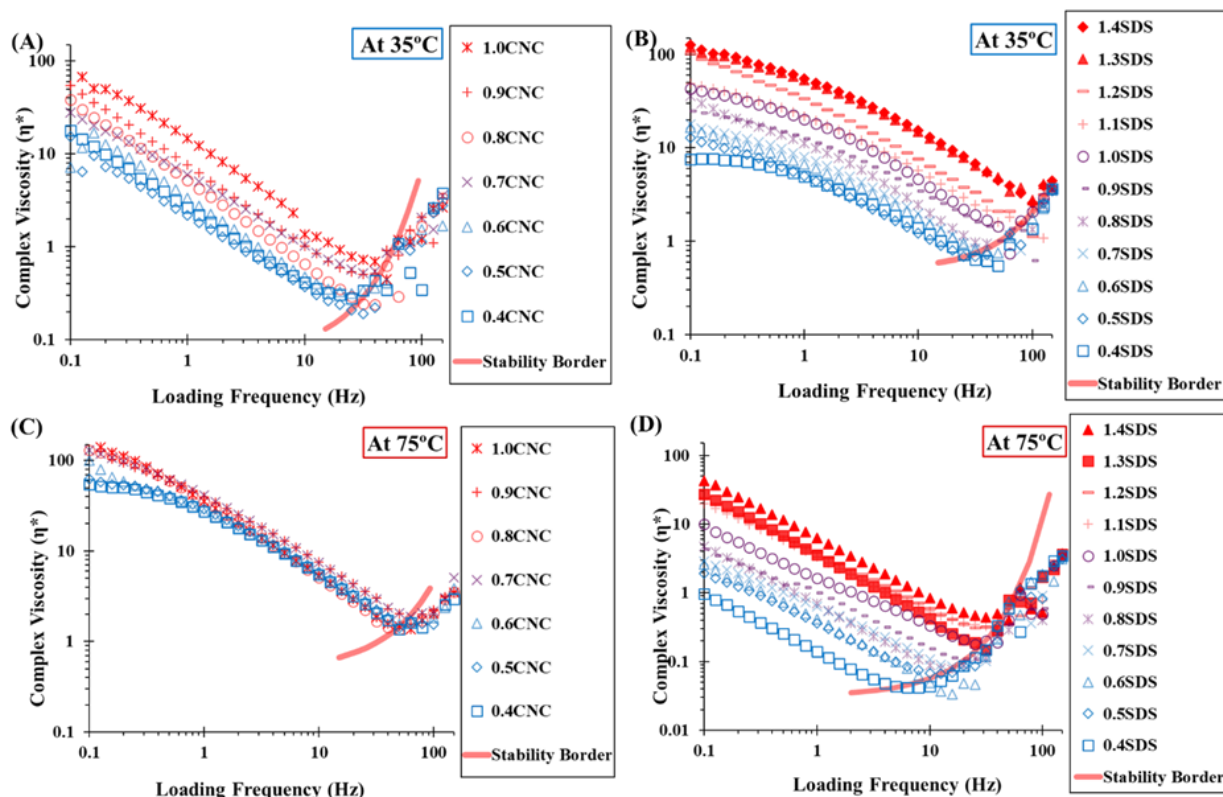


Figure 6.15. Complex viscosity under frequency sweep test for (a) CNC-based system at 35°C, (b) CNC-based system at 75°C, (c) SDS-based system at 35°C, and (d) SDS-based system at 75°C.

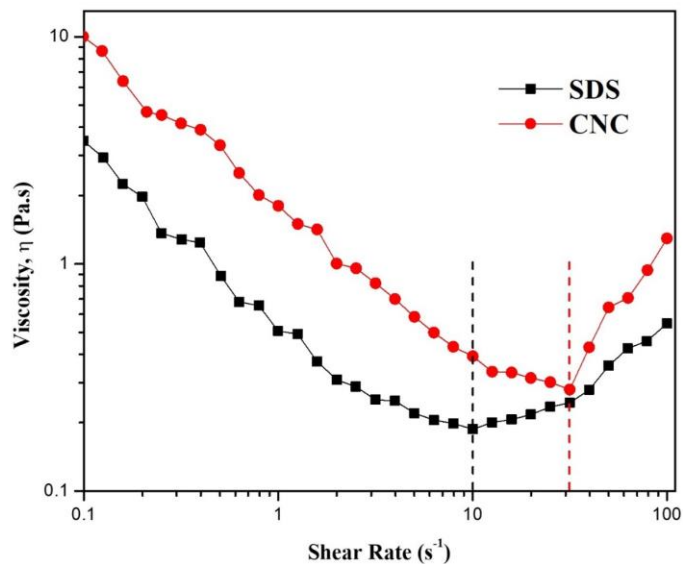


Figure 6.16. Complex viscosity of paraffin wax emulsions prepared with CNC(0.9wt.%) and SDS (0.9wt.%) under frequency sweep at 35°C.

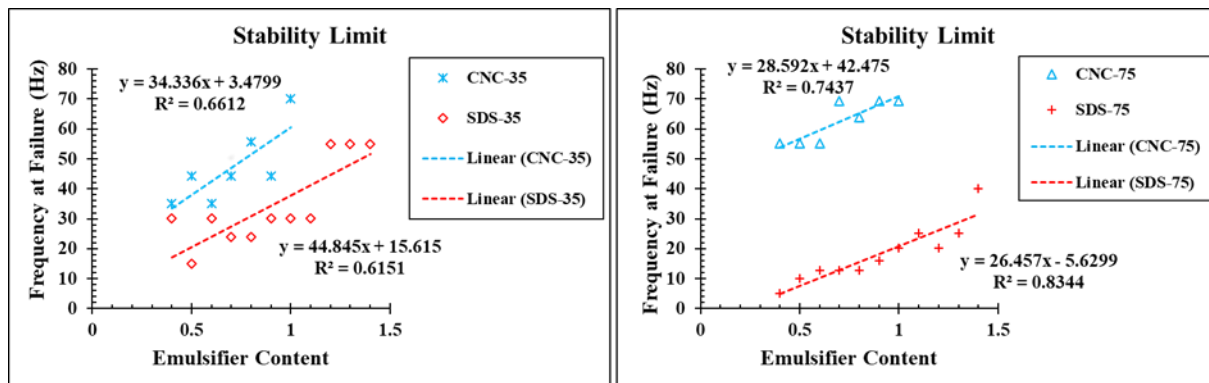


Figure 6.17. Stability limit based on failure frequency for (a) CNC- and (b) SDS-based systems at 35 and 75°C.

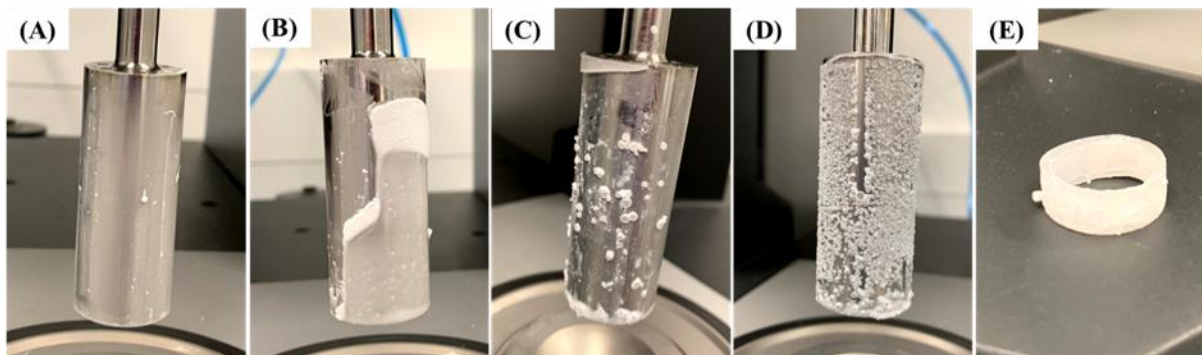


Figure 6.18. Separated paraffin wax from emulsions after frequency sweep tests (A) CNC-based at 0.8wt.% at 35°C, (B) CNC-based at 0.4wt.% at 75°C, (C) SDS-based at 1.4wt.% at 35°C, (D) SDS-based at 0.8wt.% at 35°C, (E) SDS-based at 0.8wt.% at 75°C.

7.4. Conclusions

Cellulose nanocrystals were used to emulsify a phase-change oil (paraffin wax) in water. The effect of CNC to oil ratio on the droplet size distribution was evaluated and compared with the SDS-stabilized system. Optical microscopic images of the paraffin wax emulsions indicated that CNC particles on the droplets enhanced the deformation resistance of crystallized droplets, resulting in spherical crystalized paraffin wax droplets at room temperature. In contrast, SDS-stabilized droplets displayed irregular shapes leading to droplet aggregation. The theoretical model for the relationship of emulsifier concentration and droplet size was modified for Pickering emulsions and used to investigate the impact of dynamic loading on the stability of each system before and after phase transition of the dispersed phase. Comparison of the change in droplet size of the samples showed far better stability under dynamic loading for the CNC stabilized systems. Moreover, unlike the SDS system, the stability of the CNC-based system was not compromised by the phase transition of the dispersed phase.

The differential scanning calorimetry results showed that the difference between phase transition during heating and cooling scans increased with increasing CNC content attributed to the deformation resistance of the CNC network. The effect of the cooling process on the stability of both systems was evaluated using the temperature sweep complex viscosity measurements. Interaction between CNC particles at the droplets' interface resulted in a higher viscosity than SDS stabilized emulsions. During the phase transition, droplets stabilized by CNC reduced the rupture of the oil-water interface, which enhanced the emulsion stability. On the other hand, the SDS-based emulsions aggregated forming an interconnected network that resulted in a higher viscosity.

The SDS-based systems experienced a permanent change in the viscosity over the phase transition, which resulted in severe instability at lower SDS contents.

The complex viscosity measurements under the frequency sweep mode were used to determine the stability of each system against dynamic loading. The frequency at failure (maximum bearing frequency) was determined and correlated with the emulsifier content using a modified cross-regression model. CNC-based emulsions were more resistant to dynamic loading. Moreover, the failure mechanisms in the two systems were different. In CNC-based systems, the heterogeneity was recoverable by mechanical mixing (heterogeneity due to creaming). While in the SDS system, the heterogeneity was non-recoverable, resulting in severe aggregation.

Acknowledgments

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CHAPTER 7: APPLICATION OF CELLULOSE NANOCRYSTAL (CNC) AS AN EMULSIFICATION AGENT IN THE ASPHALT INDUSTRY

Abstract

Traditional surfactant-based emulsifiers dominate the asphalt emulsion market, despite their limitations, such as low stability, compatibility and rheological properties. The use of cellulose nanocrystals having remarkable physical properties and sustainable resources has shown potential candidates for stable asphalt emulsification with tailored properties. This study aims to utilize CNCs to improve the asphalt emulsion storage, handling stability and desirable rheological profiles. The effect of CNC concentration and surface modification on the emulsion properties was evaluated and compared with a paving grade commercial surfactant-base emulsion. Particle size morphological analyses were used to optimize the formulation. The rheological profiles of the emulsion revealed remarkably higher stability and new trend in the CNC-based emulsions compared to the traditional asphalt emulsion. The linear viscoelastic behavior was examined from the moduli versus frequency sweep coupled with the time-temperature superposition principle. Elastic behavior of composite through the formation of CNC network was observed by comparing the complex modulus master curves and black-space diagrams. In the non-linear viscoelastic domain, improvement in the rutting resistance of the CNC-containing residues was achieved. This study demonstrates that CNC-based emulsions provide better stability, adjustable rheology, and improved performance-related properties of the asphalt residues.

7.1. Introduction

Transportation infrastructure, such as road networks, is critical to Canada's economic growth. An average of six percent of direct general expenditure (Federal, Provincial, and local) is allocated for the construction and maintenance of road networks. With the increasing environmental awareness and implementation of new legislation to control carbon emissions, the pavement industry faces new challenges. The necessity of using innovative materials and processes is essential for the construction and maintenance of road networks.

Maintaining a sustainable road network requires a tremendous amount of construction activity to develop the road network, maintenance and rehabilitation of existing roads. Such a construction program is responsible for the consumption of large amounts of raw materials and energy. These road networks ensure the health and sustainable growth of the economy. In Canada, thousands of kilometres of roads are constructed annually, and tens of thousands of kilometres are being maintained and rehabilitated. Considering the size of the road network, it is no surprise that the pavement industry consumes a significant amount of raw materials (aggregates, asphalt cement, portland cement, polymers, and many other types of chemicals and modifiers). The pavement industry is also responsible for significant greenhouse gas emissions and is considered a high energy consumption industry. Various innovations and technologies are being implemented to reduce the environmental impacts of pavement activities by utilizing renewal raw materials and lower energy processes in their construction activities.

The industry has adopted asphalt emulsions since the early 20th century. However, due to the lack of experience and proper technologies, asphalt emulsions did not receive appropriate attention until the oil crisis in the 1970s'. Since then, asphalt emulsification and processing have gained significant attention to reduce energy consumption. Increasing research activities were dedicated to tailoring the chemistry of asphalt emulsion to reduce costs and improve their performance^{206,229,235,346}. Regardless of type, composition, and application, the predominant technology to prepare asphalt emulsion for the pavement industry is surfactant-based technology. Surfactants are amphiphilic organic compounds containing both lipophilic and hydrophilic segments. The lipophilic segments (the tail) are miscible with the oil phase, and the electrostatic charge on the hydrophilic segments (the head) extends to the water phase, preventing oil droplets' coalescence and imparting stability to the emulsion⁶⁹.

In contrast to the classical surfactant-based technology, a conceptually different approach can be used to prepare oil-in-water emulsions by using solid particles partitioned to the surface of oil droplets that offer excellent stability to the oil droplets²⁷⁶. Such particle-stabilized emulsion is widely referred to as Pickering emulsion (named after Spencer Pickering, who proposed this concept in 1907)^{74,75,79,127}. Different organic or inorganic particles have been used to stabilize Pickering emulsions based on their specific application^{84,90–92}. Recently, renewable biomass-derived particles have attracted increasing attention to preparing environmental-friendly Pickering emulsion^{15,84,97}. While developing renewable materials as an emulsifier, polysaccharides nanoparticles, such as cellulose, chitin, and chitosan nanoparticles with biocompatibility and biodegradability, have been used in several industrial applications^{8,15,84}. Compared to other cellulose-based particles, such as cellulose nanofibers, cellulose nanocrystals (CNCs) with more controllable morphology, dimensions, and surface chemistry, are proven to be more efficient to stabilize Pickering emulsions^{83,129,161–163}.

Cellulose nanocrystals (CNCs) are nano-scale crystals extracted from biomass, such as wood, algae, and tunicates. This renewable material offers attractive mechanical properties and stabilization capability due to its large surface area and high modulus. Some of the attractive properties of CNCs are low density, large surface area, and abundant hydroxyl groups for functionalization. Since it is also sustainable, many industries explore its use in various applications^{11,44,57}. Pickering emulsions prepared using CNCs exhibit higher stability, easier processing, and improved residue properties^{9,87,115,165}.

Mechanical and rheological properties of asphalt cement considerably affect the performance of asphalt pavement. In recent years, heavy vehicle loading and varying temperatures have influenced the properties and durability of asphalt residue on pavement structures. Recently, it has been reported that asphalt failure can be minimized through asphalt modification. Depending on the required application, various materials and procedures were introduced to prepare the modified asphalt cement. In between different materials, nanomaterials have attracted greater attention, where a more significant impact on the performance of asphalt was demonstrated. However, nano-modified asphalt preparation requires high temperature and energy to prevent agglomeration during mixing and subsequent processing^{226,255,256,260,274}.

Various researchers have reported on the impact of CNCs on the properties and performance of asphalt cement. Impressive improvements were reported, especially at high and medium

temperatures^{347–349}. The addition of rod-like CNCs improves the asphalt pavement's mechanical properties (tensile strength and stiffness)^{273,350}. However, excessive agglomeration of CNC particles poses a significant challenge. These shortcomings are mainly due to the fibre-like shape of CNC particles, resulting in the formation of a network in the absence of proper mixing conditions and the application of the hot mix asphalt (HMA) at high temperatures. Asphalt emulsions do not normally encounter such elevated temperatures (as application and production temperature of asphalt emulsions are much lower than with asphalt cement during the hot mixing process (may reach 165°C). Thus, the advantage of using CNC particles as Pickering emulsification agent is the homogeneous distribution of these particles in the asphalt, and it can also be processed at room temperature.

In this study, the state-of-the-art knowledge of CNC-based asphalt emulsions was evaluated. Asphalt emulsions were prepared according to various factors, such as CNC content, asphalt/water ratio. Additionally, modifications were performed on CNCs, such as Tempo-oxidized-CNC, Desulfated-CNC, to explore the effect of such modification on the characteristics of the asphalt emulsions. The prepared asphalt emulsions were evaluated using rheological and morphological characterization techniques. The performance of asphalt residue modified with CNCs particles was evaluated based on the rutting resistance and fatigue cracking.

7.2. Experimental Section

7.2.1. Materials

Cellulforce Inc. supplied cellulose nanocrystals (CNCs) and used with and without chemical modification. Coco Paving Inc. supplied the asphalt cement (PG58-28), and an analytical grade sodium chloride (NaCl) (Sigma Aldrich) was used. A commercial-grade surfactant was used to produce the control asphalt emulsion sample.

Two chemical modifications were performed in the laboratory to reduce the surface charge of the CNC, i.e. Carboxyl oxidized (TEMPO-CNC) and Desulfated-CNC^{299,313–315,351}.

7.2.2. Sample preparation

In the pavement industry, asphalt emulsions are produced and applied at various asphalt cement concentrations. This concentration is generally between 35 to 65 percent (by weight of total emulsion). However, in this study, lower concentration was used due to the practical limitations of laboratory production capabilities. Asphalt cement emulsified with prepared aqueous phase at 40% concentration (40% asphalt cement of total weight of emulsion) using the

laboratory-scale colloid mill. To prepare the asphalt emulsions, various aqueous phases were produced separately by adding the required amounts of emulsifier (modified and unmodified CNCs and commercial grade surfactant for the control sample) and salt into the water to achieve the desired concentration of each sample (Table 7.1). To evaluate the effect of oil phase viscosity on rheological behavior and properties of resulting asphalt emulsions, one emulsion containing 5% bio-oil as a replacement for asphalt cement was prepared and examined. The composition of the samples is tabulated in Table 7.1.

Table 7.1. Sample Formulations.

Name	Emulsifier Type	Emulsifier (wt.%) *	Salt (wt.%) *	Asphalt/Water
C2.4-S1.1	CNC	2.4	1.1	4/6
C2.4-S1.1-BO5	CNC	2.4	1.1	4(5% Oil)/6
C2.4-S0.8	CNC	2.4	0.8	4/6
C1.8-S0.8	CNC	1.8	0.8	4/6
C2.4-S0.2	CNC	2.4	0.2	4/6
TCNC2.4-S1.1	TEMPO-CNC	2.4	1.1	4/6
DCNC2.4-S1.1	Desulf-CNC	2.4	1.1	4/6
S2-S0.06	Surfactant	2	0.06	4/6

7.2.3. Emulsion Characterization

An Anton Paar PSA 1190 particle size analyzer was used to examine the droplet size distribution of asphalt emulsion samples. For each sample, three consecutive measurements were performed, and an average was reported. To evaluate the morphology of the asphalt emulsions, one droplet of a diluted emulsion (10 times diluted) was examined under the optical microscope using a Nikon Elipse Ti-S (Agilent Cary Eclipse) equipped with a CCD camera (QImaging ReTIGA 2000R).

A Kinexus Ultra+ rheometer was used to investigate the rheology of asphalt emulsion using 20-mm cone and plate geometry and one millimeter gap distance. The solvent trap was employed to prevent evaporation and composition change for rheological testing of asphalt emulsion at

elevated temperatures. Rheological measurements of all prepared asphalt emulsions were performed using temperature, amplitude, and frequency sweeps.

A simple rheological model (Eq. (7.1)) was fitted to the laboratory results to determine the rheological parameters for the emulsions. The linear viscoelastic region (LVE) range for all the asphalt emulsion samples was determined using the shear strain amplitude sweep test (0.1 – 100%) at 25°C and 1 Hz (2π Rad/s) loading frequency. Then, the calibrated model was then used to calculate the LVE limit for each sample based on the shear strain that causes a 5% drop in complex viscosity value (Eq. (7.2)).

$$|\eta^*| = \eta_{\infty} + \left(\frac{\eta_0 - \eta_{\infty}}{1 + a \cdot \gamma^p} \right) \quad (7.1)$$

$$\eta(\gamma_{LVE}) = 0.95 \cdot \eta_0 \quad (7.2)$$

where η^* is the magnitude of complex viscosity, η_0 and η_{∞} are maximum and minimum values for the curve with the same dimension as viscosity, γ is shear strain amplitude, and a and p are the shape parameters.

To understand the effect of temperature on the rheological behavior of emulsions, complex viscosity measurements were performed by conducting a temperature sweep from high to low temperatures. For this purpose, continuous viscosity measurements were performed while the sample was cooled from 80 to 20°C at two °C/min.

The shear rate-dependent viscosity of various asphalt cement emulsion samples was examined from 10^{-2} to 10^3 s^{-1} at 25 and 75°C, representing storage and production temperatures. Eq. ((7.3)) was used to model the shear-rate dependency of the viscosity.

$$\eta(\dot{\gamma}) = \eta_{\infty} + \left(\frac{\eta_0 - \eta_{\infty}}{1 + \alpha(\dot{\gamma})^{\beta}} \right) \quad (7.3)$$

where η is the rotational viscosity, $\dot{\gamma}$ is the shear rate, η_0 and η_{∞} are extreme values of viscosity corresponding to zero-shear and infinity, and α and β are shape parameters.

The effect of emulsifier type and concentration on asphalt emulsions' thixotropic behavior was evaluated using three intervals thixotropy test (3iTT) in a controlled shear rate (CSR) mode. Thixotropy test (3iTT) was conducted on CNC and surfactant stabilized asphalt emulsions, and rebuild time was measured.

7.2.4. Residue Analysis

The asphalt cement residue properties were evaluated after the extraction of residue from the emulsion. For this purpose, a low heating evaporation protocol was used, which consisted of heating thin layers of asphalt emulsion at 60°C in a force draft oven. Multiple layers were sprayed on the previously dried layer to prepare the desired asphalt sample thickness. This mechanism would ensure that the prepared samples would have a similar microstructure under the actual conditions. Control asphalt cement and extracted residue from the prepared emulsions were subject to various types of rheological analyses, including complex shear modulus (G^*) under frequency sweep mode over a wide temperature range, linear amplitude sweep test (LAS), and multiple stress creep recovery test (MSCR). All these rheological evaluations were performed using the Anton Paar SmartPave 102 Dynamic Shear Rheometer (DSR).

To evaluate the effect of emulsifiers on the properties of asphalt cement residue, complex modulus measurements were performed in a wide range of temperatures (0 to 75°C) and loading frequencies (0.1 – 100 Rad/sec). As a viscoelastic material, the physical parameters of asphalt emulsion would be independent of shear strain when the selected shear strain is within the linear viscoelastic region. The strain level was set at 0.1% to assure all measurements were within the linear viscoelastic range (LVE). The modified Arrhenius model for the time-temperature superposition principle was coupled with the 2S2P1D (two springs, two parabolic, and one dashpot) analogical viscoelastic model to map complex modulus (G^*) and phase angle (δ) master curves using Eq. (7.4) and (7.5)^{194,198,202}. Black Space and Cole-Cole diagrams were plotted to investigate the rheology of residues independent of loading frequency and testing temperature. Fractional modulus master curves (loss and storage moduli) were also plotted.

$$\log a_T = 10^{C_1 \left(\frac{1}{T^{C_2}} - \frac{1}{T_r^{C_2}} \right)} \quad (7.4)$$

where a_T is shift factor, T and T_r are test temperature, and reference temperature in Kelvins and C_1 and C_2 are model constants.

$$G^*(i\omega\tau) = G_0 + \frac{G_\infty - G_0}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h} + (i\omega\beta\tau)^{-1}} \quad (7.5)$$

where $G^*(i\omega\tau)$ is the shear complex modulus at the reference temperature as a function of loading frequency, G_0 is the minimum complex number under static load, G_∞ is the maximum value of complex modulus, ω is the loading frequency in rad/s, k , h , and β are model parameters, and δ and τ are shape parameters.

The 2S2P1D rheological model was then used to analyze further and determine several critical performance-related temperatures. These are (1) Cross-Over temperature (the temperature at which loss and storage moduli are equal), (2) Rheologically determining glass transition temperature (the temperature that loss modulus reaches to its maximum value note this is different from T_g determined from calorimetry), and (3) Critical Glover-Rowe temperatures. The cross-over and rheological glass transition temperatures were calculated at ten rad/s loading frequency, defined as the temperature where the loss and storage moduli are equal ($\delta=45^\circ$). It measures the resistance of the asphalt cement to fatigue crack initiation (the resistance to cracking against repeated loading). The rheological glass transition temperature is a low-temperature parameter, and it correlates with low-temperature crack resistance. A lower glass transition temperature would be an indicator of better low-temperature properties for pavement application. The Glover-Rowe parameter (Eq. (7.6)) is a rheological indicator for the low-temperature crack resistance of an asphalt cement for pavement application. Two critical values of 180 and 450 kPa have been used as indicators for the damage onset and the start of significant cracking. Lower G-R temperatures are more favorable for low-temperature performance.

$$\mathbf{G} - \mathbf{R} = \mathbf{G}^* \times \left(\frac{\cos \delta^2}{\sin \delta} \right) @ \mathbf{0.005 \text{ Rad/s}} \quad (7.6)$$

The multiple stress creep recovery (MSCR) tests (AASHTO T350) were performed at high performance temperature of base binder (58°C) to estimate the permanent deformation resistance of asphalt cement (rutting). Non-recoverable creep compliance (J_{nr}) of samples were determined at two different stress levels of 0.1 and 3.2 kPa in a cyclic loading scheme where the samples were subjected to 0.1s loading followed by 0.9 s rest period. Higher permanent deformation-resistant would be expected for samples with lower J_{nr} values.

The Linear Amplitude Sweep (LAS) results were used to estimate samples' fatigue and fracture resistance at medium performance temperature range. Using the fracture index analysis (FIA) and Viscoelastic Continuum Damage (VECD) theory, the Fracture Index (af) and the number of load repetitions to failure at strain levels of 2.5 and 5.0 percent (representing thin and thick asphalt pavement layers) were determined.

7.3. Results and Discussion

7.3.1. Emulsion Properties

7.3.1.1. Particle Size Analysis

The results of particle size measurements are presented in Table 7.2 and Figure 7.1. As shown in Figure 7.1(A), salt concentration had a more significant impact on the droplets size than the CNC concentration at the same dosages. The particle size almost doubled by reducing salt concentration from 1.1 to 0.8 wt.% (changed from 17.5 to 40.8 μm). The effect of the chemical modification of CNC on the resulting droplet size is shown in Figure 7.1(B). The addition of bio-oil to the dispersed phase (asphalt) was performed to evaluate the effect of viscosity on droplet size. As expected, adding 5% wt. of bio-oil extensively affected particle size, which increased from 17.5 μm in the original sample to 92.4 μm . At similar CNC and salt concentrations, the use of unmodified CNC resulted in the smallest particle size, while the desulfated CNC resulted in the highest particle size (31.8 μm). The particle size in the original CNC sample (unmodified CNC with 1.1% salt concentration) and the control sample produced using a commercial surfactant displayed somewhat similar particle sizes. Moreover, the effect of storage time was evaluated by running the particle size analysis on both samples after two weeks of storage, and the CNC-stabilized asphalt emulsion maintained a more constant droplet size after two-week storage.

Table 7.2. Average droplet size of asphalt in different samples.

Sample	Mean Diameter (μm)	
	Fresh samples	Two-week storage
C2.4-S1.1	17.5	17.6
C2.4-S1.1-BO5	92.4	-
C2.4-S0.8	40.8	-
C1.8-S0.8	38.6	-
C2.4-S0.2	116.4	-
TCNC2.4-S1.1	26.5	-
DCNC2.4-S1.1	31.8	-
S2-S0.06	21.6	23.2

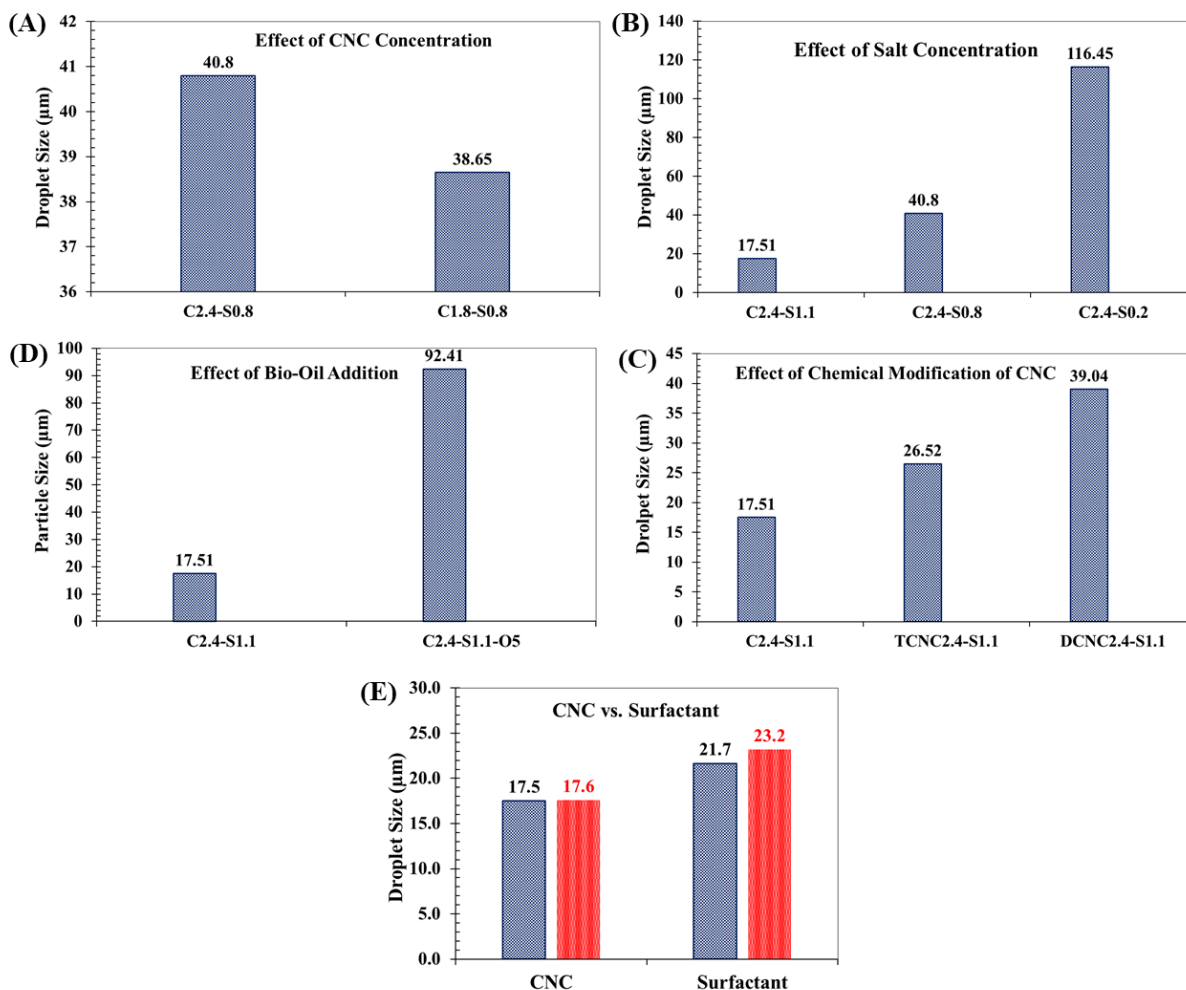


Figure 7.1. The droplet size of asphalt as affected by (A) CNC concentration (B) salt concentration (C) Bio-Oil addition, (D) various CNC chemical modifications (D) storage time of CNC and conventional surfactant based-emulsions.

7.3.1.2. Morphology Analysis

The microscopic images confirmed particle size analysis for all samples (shown in Figure 7.2). The C2.4-S0.2 sample possessed a low salt content (0.2% wt.), leading to the multiple W/O/W emulsion. The large droplet size of the DCNC2.4-S1.1 sample (Figure 7.2(G)) was related to the agglomeration of Desulphated-CNC in water that reduced the available dispersed emulsifier leading to droplet aggregation. The morphology of sample C2.4-S1.1 was similar to the S2-S0.06 (Figure 7.2 (A) and (H)) prepared using a commercial surfactant. The main morphological

difference between these two samples was the presence of a large number of small particles for the CNC-based emulsion (Figure 7.2 (A)).

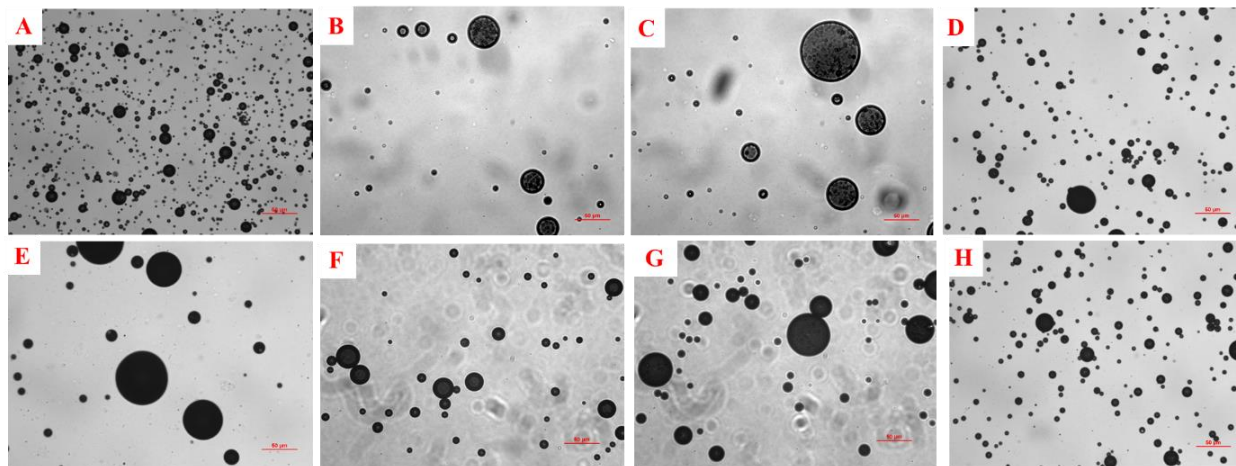


Figure 7.2. Optical microscopy images of (A) C2.4-S1.1, (B) C2.4-S0.8, (C) C2.4-S0.2, (D) C1.8-S0.8, (E) C2.4-S1.1-BO5, (F) TCNC2.4S1.1, (G) DCNC2.4-S1.1, (H) S2-S0.06.

7.3.1.3. Linear Viscoelastic Region (LVE) Analysis

The results of the shear strain amplitude test and calculated LVE limits for the samples are presented in Figure 7.3. The higher LVE limit for C2.4-S0.2 compared to C2.4-S1.1 could be related to free CNC in the continuous phase forming an interparticle network yielding a gelled structure with high viscosity. As shown in Figure 7.3(A), reducing salt concentration within the applied range resulted in a higher LVE limit (0.46% to 0.99%). However, reducing CNC concentration from 2.4 to 1.8 drastically reduced the LVE critical strain from 0.9% in the C2.4-S0.8 sample to 0.16% in the C1.8-S0.8 sample. As for the effect of chemical modification of CNC, it was observed that the Desulf-CNC yielded a small critical LVE strain level, which was related to lower repulsion between droplets increasing the droplet aggregation. At the same time, TEMPO-CNC caused an increase due to a stronger hydrogen bond with lower interparticle repulsions (Figure 7.3(B)). Lowering the viscosity of the dispersed phase using pyrolysis oil did not substantially affect the LVE critical strain. However, as shown in Figure 7.3(C), the sample containing pyrolysis oil (C2.4-S1.1-BO5) possessed a lower viscosity than the sample prepared with the original binder (C2.4-S1.1). As LVE region of surfactant-based emulsions is related to the electrostatic repulsion, while Pickering emulsions depend on the interparticle interaction to form the network of emulsion droplets. By comparing the CNC-based control emulsion (C2.4-S1.1) with that emulsified with commercial surfactant (S2-S0.06), a lower critical LVE strain and

a higher viscosity was observed for the CNC-based emulsion (Figure 7.3(D)). Therefore, CNC modification or the use of sufficient amounts of CNC and salt concentration improved the stress-bearing network of emulsion droplets. The LVE values of all asphalt emulsions are compared in Figure 7.4.

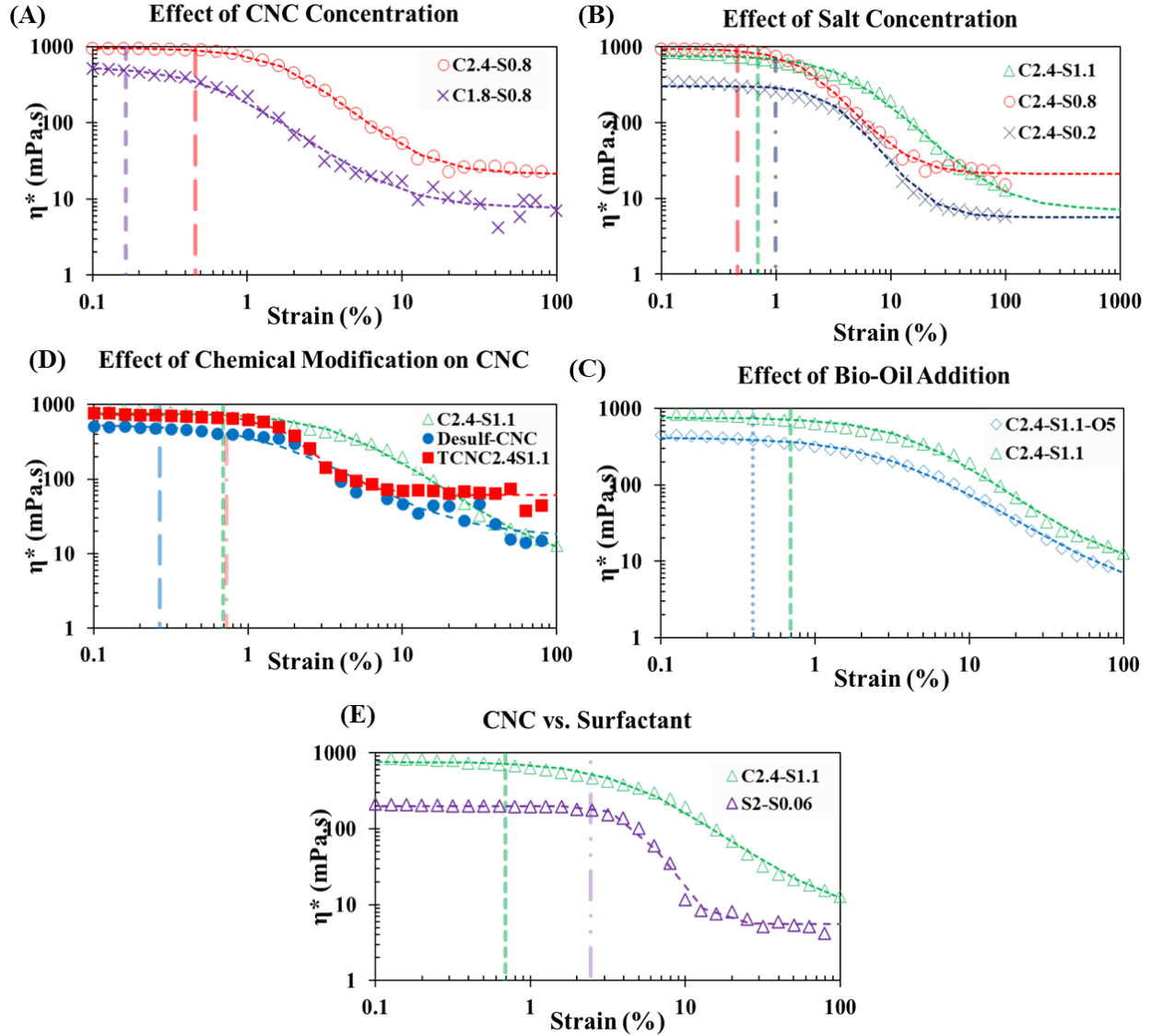


Figure 7.3. Shear strain amplitude sweep test results at 25°C and 1 Hz (2π Rad/s) loading time and corresponding LVE limits.

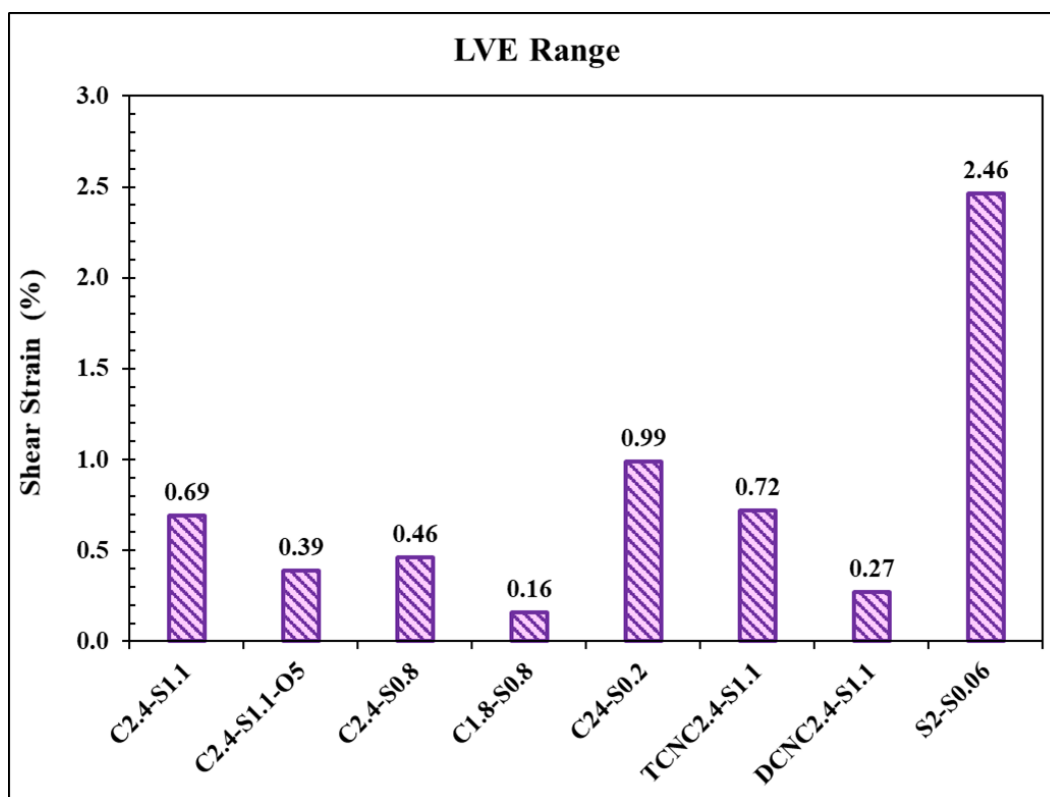


Figure 7.4. LVE limit at 25°C and 1 Hz (2π Rad/s) loading time.

7.3.1.4. Temperature Sweep Analysis

In comparing samples prepared with different concentrations of unmodified CNC and salt (Figure 7.5(A)), similar viscosity behavior versus temperature was observed, where the viscosity increased during cooling except for C2.4-S0.2. The sample with reduced CNC concentration (C1.8-S0.8) displayed lower viscosity over the temperature range, and the sample with the highest CNC and salt concentration (C2.4-S1.1) possessed higher viscosity. Reducing the viscosity of the dispersed phase by the addition of bio-oil (C2.4-S1.1-BO5) resulted in a significant reduction in the tested temperature range (Figure 7.5(B)). The viscosity of the emulsions using chemically modified CNC was less temperature-sensitive than the unmodified CNC sample (Figure 7.5(D)). As expected, the surfactant-based emulsion (S2-S0.06) possessed much lower viscosity than all the other samples (Figure 7.5(D)). The viscosity of surfactant-based emulsion increased sharply during the solidification of the asphalt due to the bridging between oil droplets resulting in droplet aggregation. In contrast, the viscosity of asphalt emulsions stabilized by irreversibly absorbed CNC increased gently.

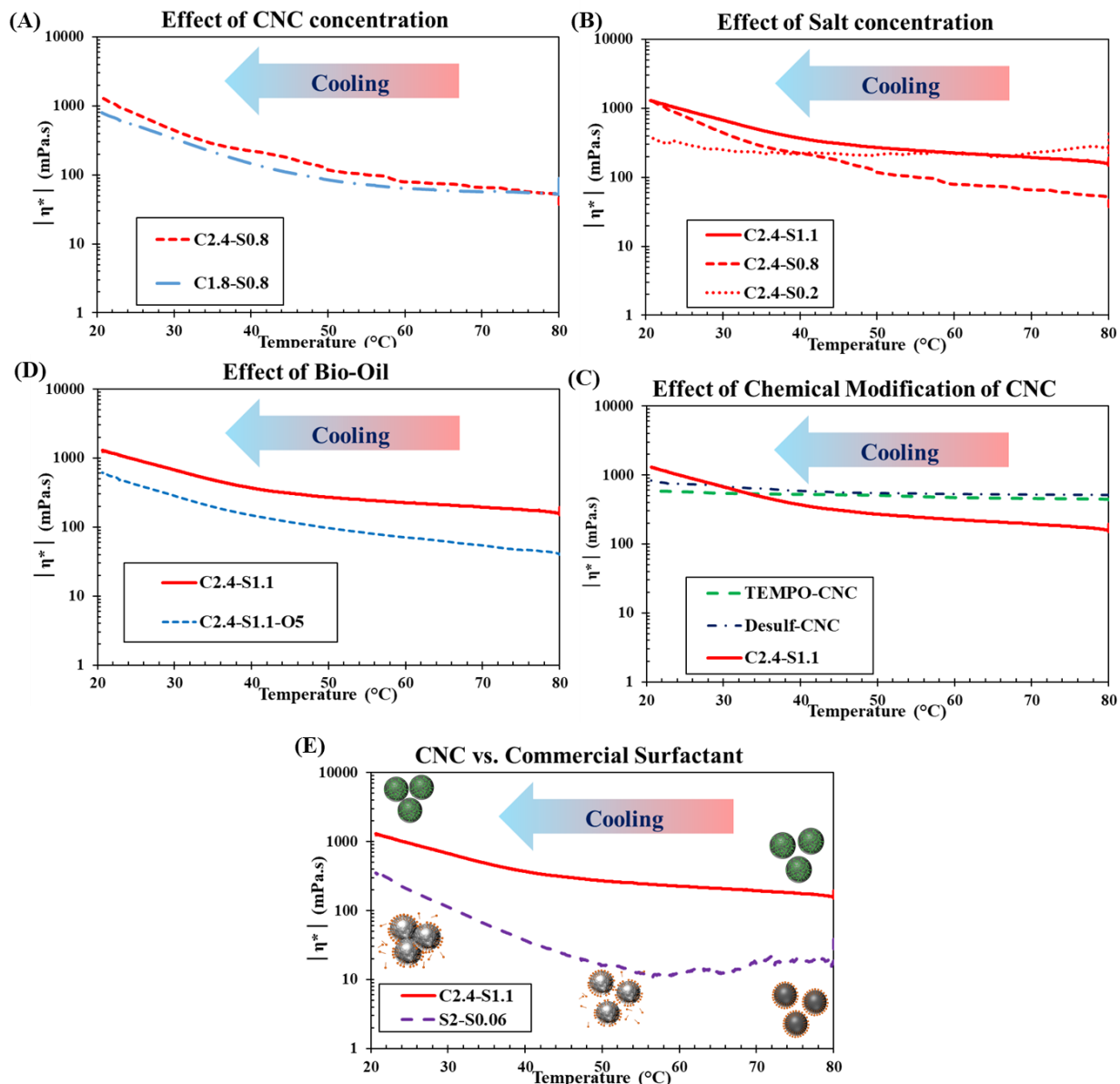


Figure7.5. Complex viscosity of samples under temperature sweep mode.

7.3.1.5. Shear Rate Dependency Analysis

For emulsions prepared using unmodified CNCs in the presence of salt at different concentrations, the viscosity versus shear-rate curves at 25°C are very similar, and more considerable differences were observed at 75°C (Figure 7.6(A) and Figure 7.7(A)). The same behavior was observed in comparing emulsion stabilized via different CNC concentrations and the same salt content. The viscosity reduction of emulsion containing lower CNC concentration (C1.8-S0.8) was more significant than the C2.4-S0.8 sample (Figure 7.6(B) and Figure 7.7(B)). The viscosity's reduction over the shear rate of emulsion prepared using 5% Bio-oil as asphalt

replacement (C2.4-S1.1-BO5) displayed a similar profile to emulsion without bio-oil. As the C2.4-S1.1-BO5 sample forms a significantly larger particle size, there is a higher amount of free CNC in the aqueous phase contributing to entanglement and an increase in the viscosity of the aqueous phase ((Figure 7.6(C) and Figure 7.7(C)).

Emulsions stabilized via unmodified and modified CNCs at 25°C displayed similar trends of viscosity shear-rate dependency. While asphalt droplets stabilized with modified CNCs (TCNC2.4-S1.1 and DCNC2.4-S1.1) at 75°C, they have higher degree of shear rate dependency (Figure 7.6(D) and Figure 7.7(D)). While comparing the viscosity curve of the unmodified CNC sample (CNC2.4-S1.1) with commercial surfactant (S2-S0.06), it can be seen that the shear dependency (the slope of the curve in the middle straight part) of CNC based sample is lower (Figure 7.6(E) and Figure 7.7(E)).

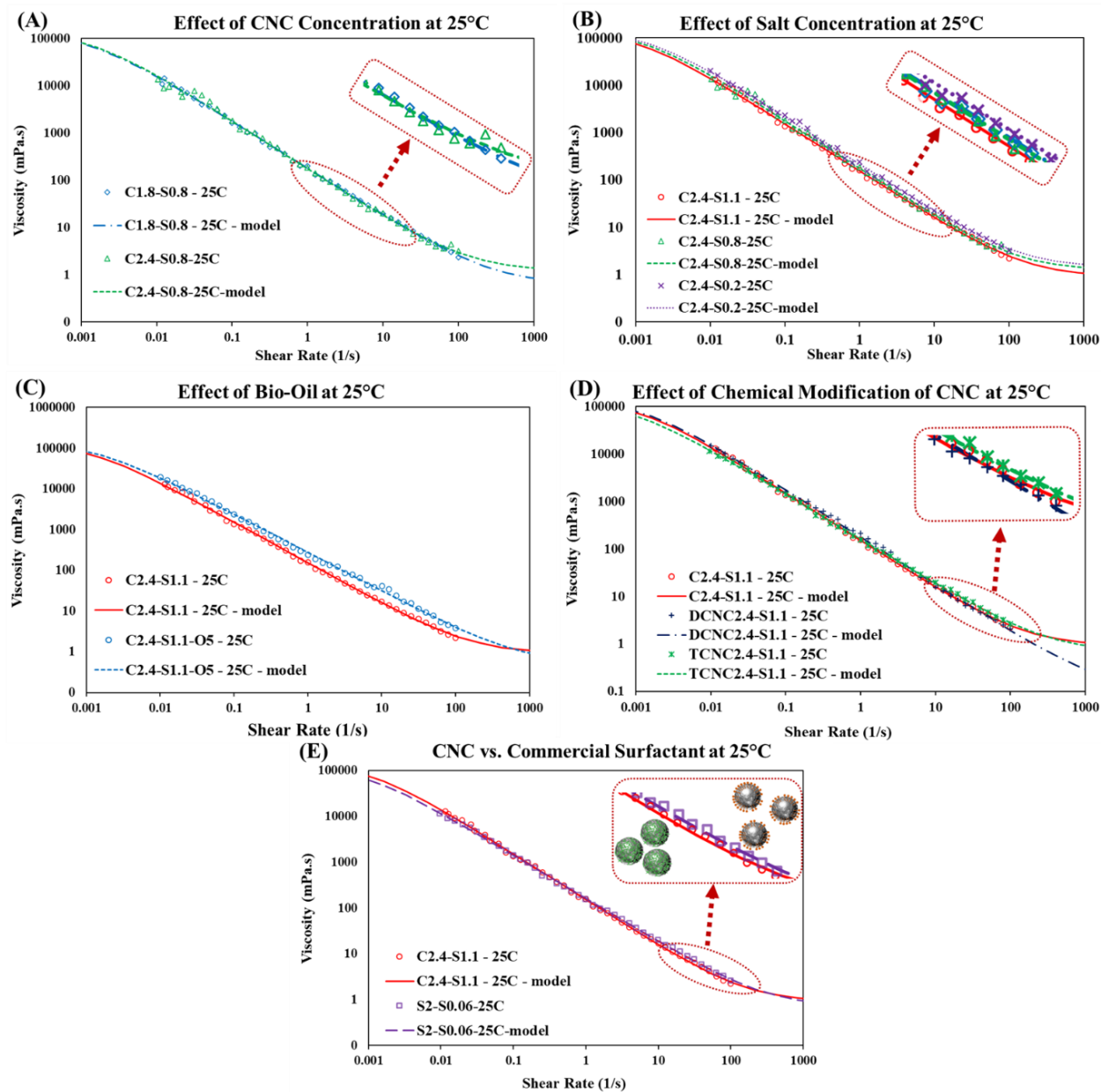


Figure7.6. Shear-Rate Dependency of the Rotational Viscosity of Emulsion at 25°C.

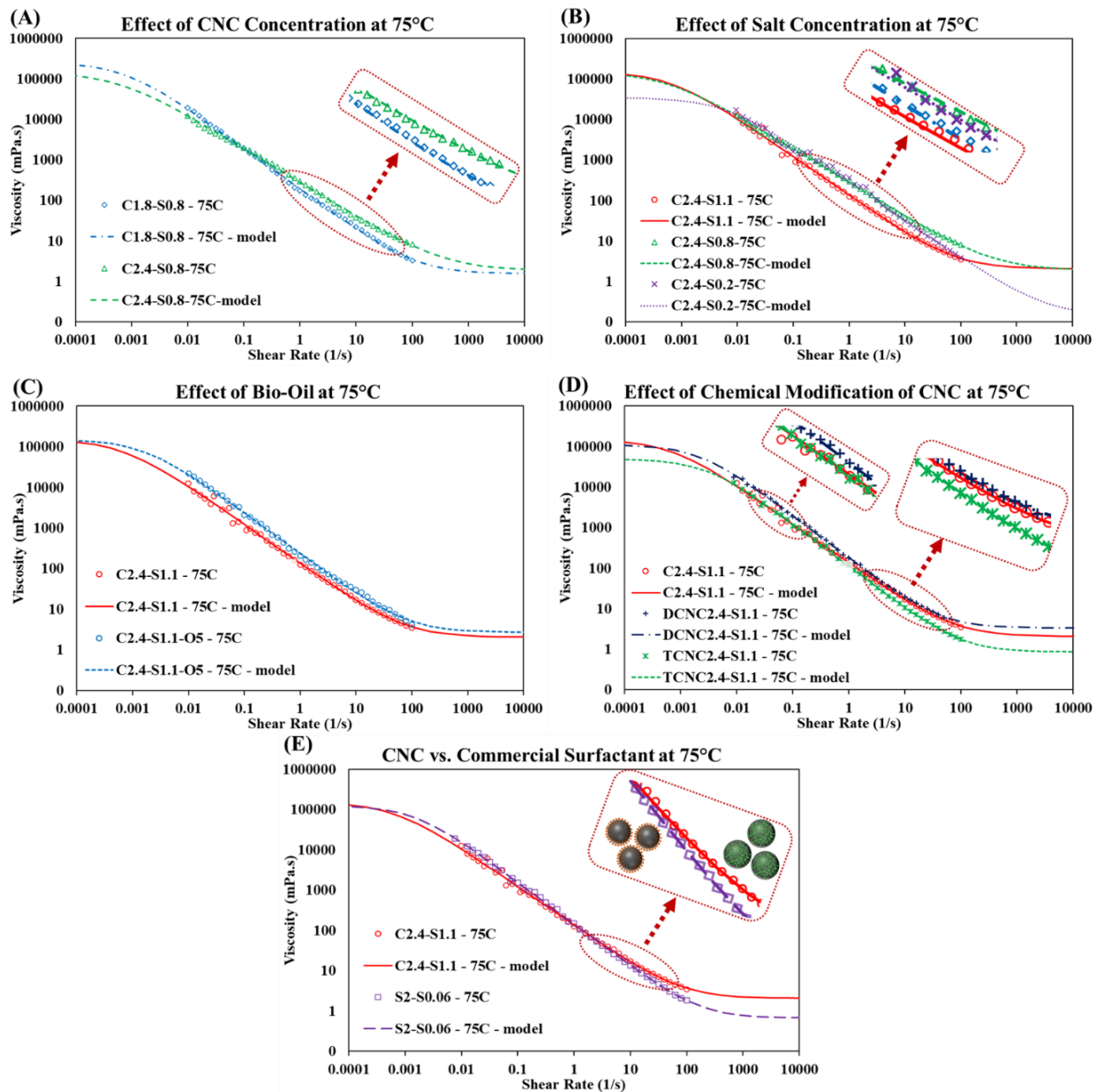


Figure 7.7. Shear-Rate Dependency of the Rotational Viscosity of Emulsion at 75°C.

7.3.1.6. Thixotropy Analysis

The thixotropic behavior of samples was evaluated using the three interval thixotropy test (3iTT), and the calculated rebuild times are presented in Figure 7.8. Comparing the emulsions with different concentrations of salt and CNC (Figure 7.8(A)), an increase in the salt to CNC ratio (S/C) resulted in more thixotropic behavior in terms of rebuild time. The emulsion C2.4-S1.1 (S/C of 0.46) and C1.8-S0.8 (S/C of 0.44) with quite similar S/C values exhibited considerably higher rebuild time. The C2.4-S0.8 with an S/C ratio of 0.3 still possessed significant thixotropic

behavior, while the C2.4-S0.2 with an S/C ratio of 0.08 displayed negligible rebuild time. As salt decreases the repulsion interaction between CNC particles, the thixotropy behavior of CNC-based asphalt depends on the salt concentration. Asphalt emulsion having bio-oil (to C2.4-S1.1 -BO5) shows lower thixotropy behavior compared to C2.4-S1.1 sample (Figure 7.8(B)). Emulsions prepared with chemically modified CNC showed much lower thixotropic behavior (Figure 7.8(C)). Comparing the rebuild time for the emulsions made with CNC and commercial surfactant, negligible thixotropic behavior was observed for the emulsion prepared with commercial surfactants (Figure 7.8(D)).

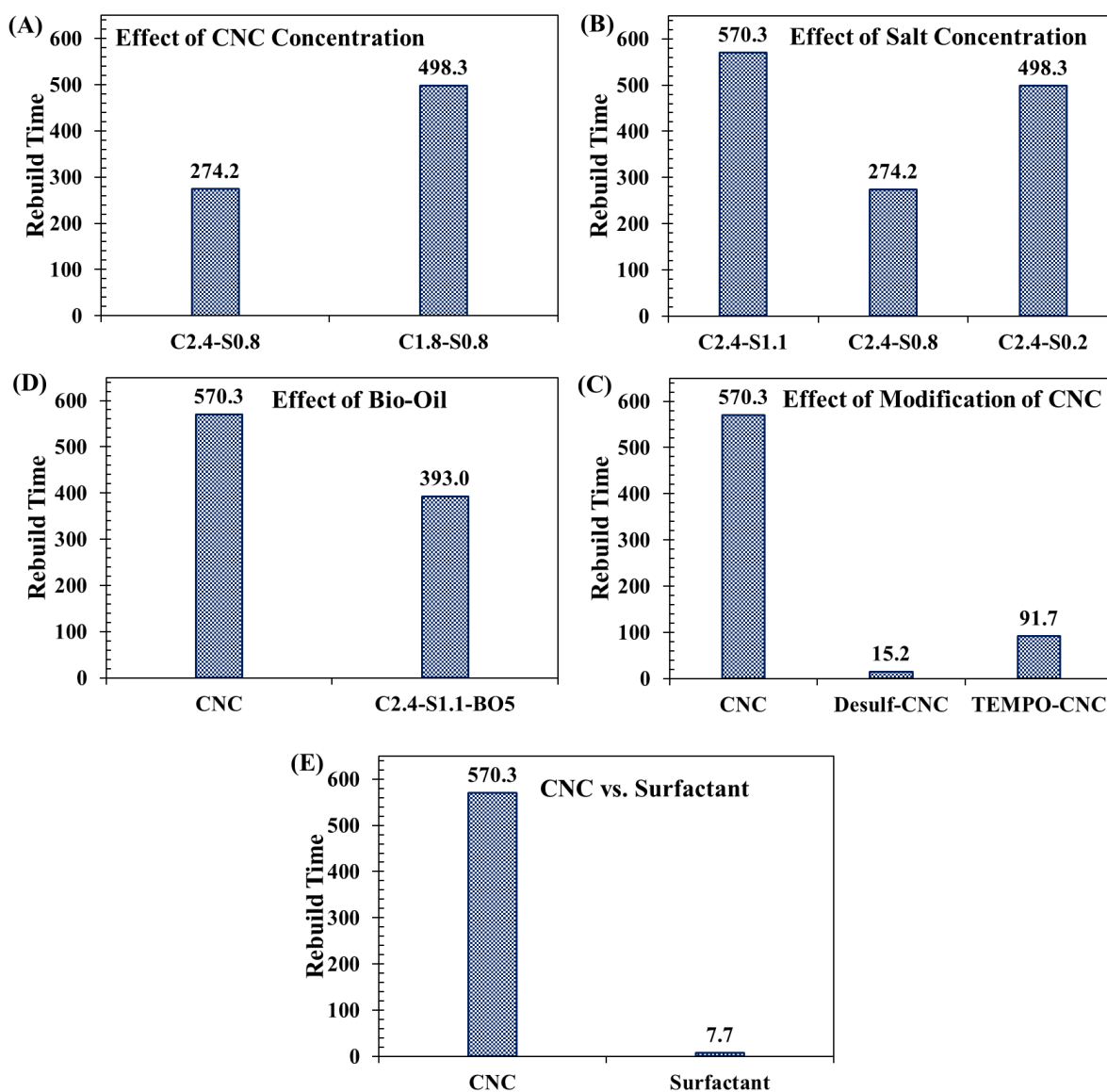


Figure 7.8. Rebuild Time in 3iTT.

7.3.2. Asphalt Residue Properties

7.3.2.1. Frequency Sweep Test Analysis

Comparing the complex modulus master curve of the residues (Figure 7.9(A)), a fundamental difference between CNC-containing samples (whether unmodified or chemically modified) and the residue of the surfactant-based emulsion was observed. This difference was more significant at the lower loading frequency ranges (which represents higher testing temperatures). The residue of surfactant-based emulsion softened considerably at lower frequencies, while CNC-containing samples tended to exhibit comparatively stiffer behavior by their complex modulus master curves standing higher. The sample containing TCNC even shows a plateau at low loading frequency range. The phase angle master curve (Figure 7.9(B)) explained how the CNC-containing samples restored their elastic behavior after reaching a peak point by reducing the loading frequency.

In contrast, the surfactant-based emulsion residue approached the complete viscous behavior ($\delta=90^\circ$) at low frequency (or high testing temperature). The restoration of the elastic behavior of CNC-containing samples was also observed in the black-space diagram, where the representative curves reach their maximum value lower than 90° for medium shear complex modulus values (Figure 7.9(C)). The surfactant-based emulsion (S2-S0.06) displayed a complete rheological behavior transforming from an elastic solid behavior ($\delta=0$) to a viscous liquid ($\delta=90^\circ$), while the CNC containing samples displayed elastic recovery behavior. The sample containing TEMPO CNC (TCNC2.4-S1.1) barely passed the cross-over point, where the loss and storage moduli are identical ($\delta=45^\circ$).

Figure 7.9(D) shows the relationship between loss and storage moduli on a log-log scale. A surfactant-based sample (S2-S0.06) displayed the log scale's linear relationship between the loss and storage moduli. On the other hand, the CNC-containing samples possessed a minimum storage modulus that is associated with the CNC network structure. Comparing the loss and storage moduli diagrams (Figure 7.9(E) and (F)) shows higher loss and storage moduli for CNC-containing samples at low-frequency range (high temperatures). However, just like the control sample, the loss modulus of CNC-containing samples keeps reduction by reduction in loading time, while for storage moduli, CNC-containing samples tend to keep a minimum value.

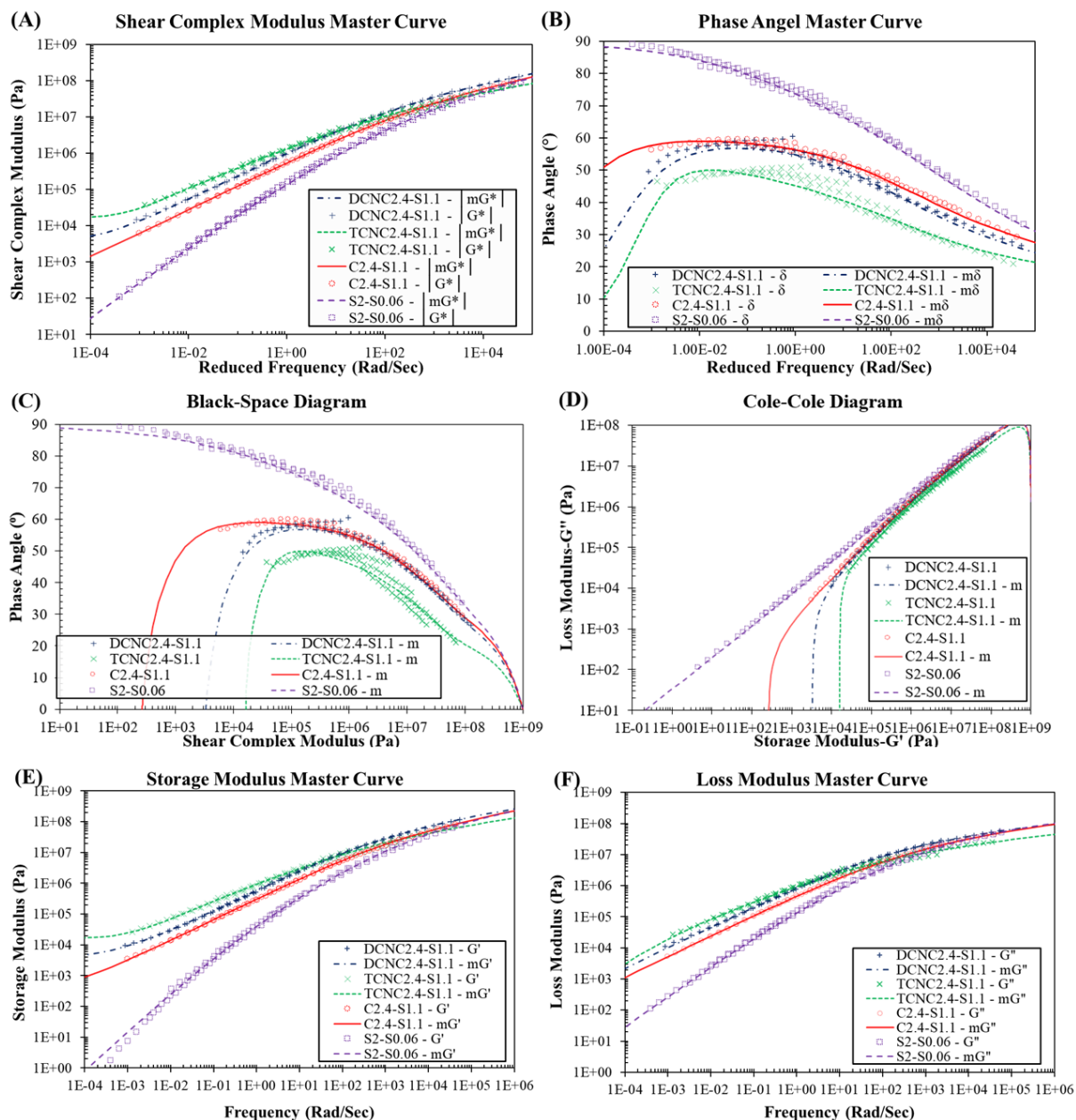


Figure 7.9. Rheological Analysis of The Residue in Frequency Sweep Test (A) Shear Complex Modulus Master Curve, (B) Phase Angle Master Curve (C) Black-Space Diagram (D) Cole-Cole Diagram (E) Storage Modulus Master Curve (F) Loss Modulus Master Curve.

The increase in cross-over temperature for CNC-containing emulsions translated into dominant elastic behavior at the intermediate temperature zone (Figure 7.10). The increase in the cross-over temperature was more significant for the residue prepared using TCNC2.4-S1.1. This increase in the elastic behavior is due to the formation of the CNC network. The CNC network functioned as the reinforcement for asphalt cement. The formation of such elastic structure within

the asphalt cement increased the Glover-Rowe temperatures (damage onset and significant cracking temperatures). Although this increase in crossover and Glover-Rowe temperatures corresponded to the cracking resistance reduction, it should be noted that these indicators were developed for rheologically simple (having homogeneous microstructure) materials. At the same time, the CNC-containing samples exhibited composite behavior due to the formation of the CNC network. However, except for the TEMPO CNC-containing sample (TCNC2.4-S1.1), the rheological glass transition temperature did not change much, which confirmed the composite nature was lower in the samples containing CNC. This glass transition temperature (using extrapolation on the 2S2P1D model) suggested that the existing elastic CNC network did not negatively alter the asphalt cement's desirable low-temperature viscous behavior (Figure 7.10).

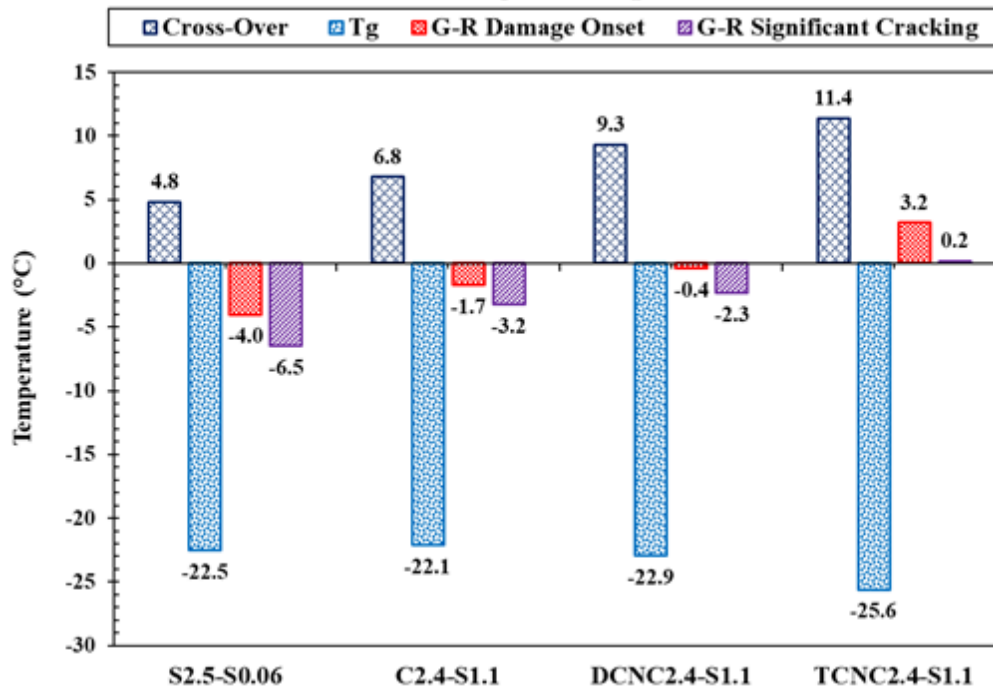


Figure 7.10. Critical Rheological Temperatures Calculated Using the 2S2P1D Model.

7.3.2.2. Non-Linear Viscoelastic range Analysis

Figure 7.11(A) shows the MSCR results at 58°C for all the residue samples. Samples containing CNC possessed drastically lower J_{nr} values which corresponded to a more rutting resistance. However, we observed that the $J_{nr3.2}$ was much higher than $J_{nr0.1}$ for the CNC-containing samples than residue from surfactant-based samples. As the MSCR test was performed in the non-LVE strain levels, the elastic structure formed by the entanglement of CNC particles relaxed when

a higher deformation was applied, resulting in a less stiff network and higher compliance for the system.

Figure 7.11(B) and (C) show the results of VECD and FIA analysis results. Samples containing CNC possessed lower fatigue life in terms of the number of load repetitions (at both 2.5 and 5.0 % strain levels). Crack mouth opening at failure was also reduced. Here, such reduction was expected as the existing CNC particles form an internal structure with less ductile behavior than the asphalt cement. Applying large strains would disintegrate the CNC network resulting in lower resistance to failure. However, traffic loading (as the main cause for fatigue damage in pavements) is stress control, and samples with a higher modulus (like CNC-containing samples) would experience lower strain.

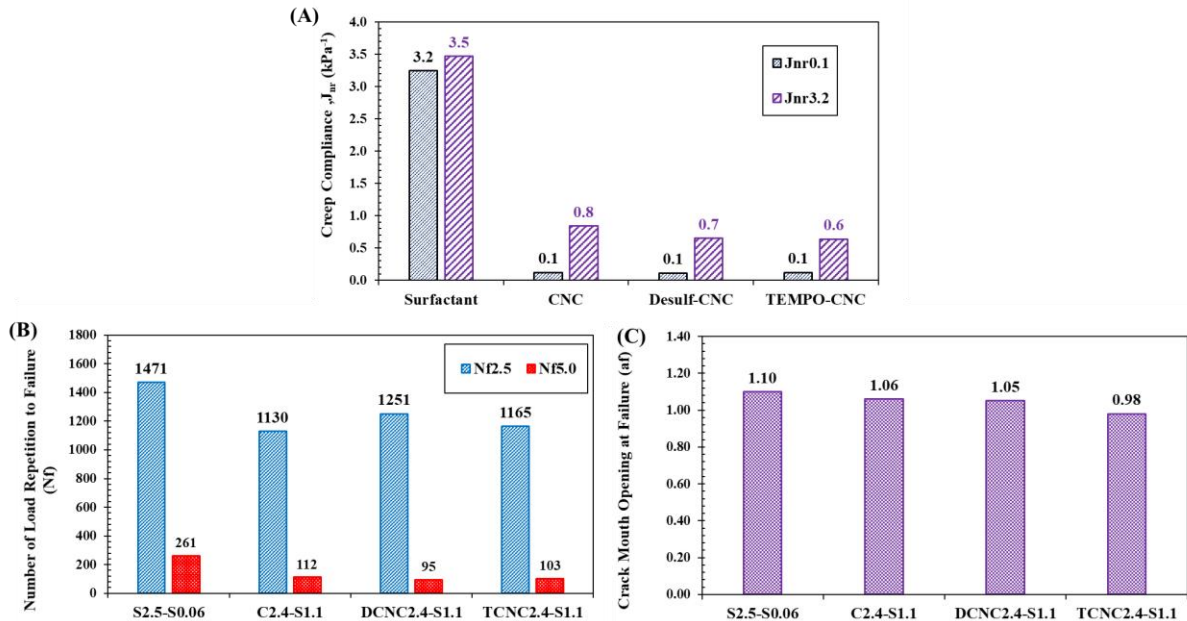


Figure 7.11. (A) MSCR Creep Compliances at 0.1 and 3.2 kPa Shear Stress Levels, (B) Linear Amplitude Sweep Test, (C) Number of Load Repetition to Failure (C) Crack Mouth Opening at Failure.

7.4. Conclusions

The application of cellulose nanocrystals (CNCs) as a Pickering emulsifier for asphalt cement in pavement application was elucidated. The effect of surface energy adjustment either by adding salt or chemical, the modification was evaluated and compared with a sample prepared using a commercial surfactant. The effect of salt to CNC ratio was found to be significant on the emulsion

properties when other factors, such as mixing temperature, milling equipment, and the viscosity of dispersed phase, remained unchanged. Particle size analyses showed similar droplet size distribution for CNC-based Pickering emulsion and surfactant-based emulsion. After two weeks of storage at room temperature, CNC-based emulsion was found to be more stable. Asphalt emulsion's droplet size and morphology containing 5% bio-oil indicated that lowering the dispersed phase's viscosity would result in larger particle size.

The considerably different rheological behavior of CNC base emulsion compared to surfactant-based emulsion was attributed to the irreversible absorption of CNC to the interface and their ability to interact with free CNCs in the aqueous phase. Temperature sweep viscometry showed less temperature sensitivity for CNC-based emulsions compared to the surfactant-based emulsion. This is mainly due to the insensitivity of the CNC partial network to temperature. In contrast to low temperatures, high shear rate dependency was observed for the surfactant-based emulsion at higher temperatures. CNC-based emulsions possessed remarkably higher thixotropic behavior in terms of rebuild time in the three interval thixotropy test (3iTT).

Rheological analyses of residues indicated the formation of a composite structure of CNC network in a medium of asphalt cement with a larger complex modulus, specifically at low loading frequencies (representing high temperatures). The formation of such structure was confirmed by observing an elastic recovery point in the phase angle master curve of CNC-containing samples.

Comparing the pristine CNC and modified CNC, the sample containing TEMPO CNC exhibited higher complex modulus at lower loading frequency rates (representing high performance temperatures) and lower values at high loading rates (representing low temperatures). Black space diagrams showed more elastic behavior for residues containing TEMPO-CNC than pristine CNC. While the residue from surfactant-based emulsion displayed a linear relationship (in log-log scale) for viscous and elastic components of complex modulus (loss and storage moduli), the storage moduli of CNC containing samples exhibited a minimum value in the elastic behavior at low loading frequencies (or high temperatures). Results of the MSCR test at 58°C showed more rutting resistance for CNC-containing samples, which suggested that the reinforcement function of CNC. However, this improvement was less observable at high shear stresses due to the partial destruction of the CNC network. In general, the strong absorption of CNC at the interface of asphalt and water provided a highly stable emulsion with lower sensitivity to temperature and shear loading compared to the surfactant-based emulsion. The property improvement of asphalt cement

residues with CNC indicated CNC as the nanofiller improved the durability of asphalt through higher rutting and fatigue resistance.

Different rheological properties for the various emulsions suggested that the formulation can be tuned to develop the desired system for new applications. High viscosity at rest in conjunction with the thixotropic behavior can widen the application of such emulsion in pavement surface treatments in applications, such as chip sealing by providing a thick layer of asphalt emulsion on a flat surface. Vertical or sloped surface isolation is another application in which the thixotropic behavior could promote the sprayed emulsion to form a thicker coverage. Improved rheological properties of the CNC containing asphalt could promote cold in-place recycling for high traffic roads. Finally, homogeneous distribution of CNC throughout the residue would solve the agglomeration problem observed when CNC is hot mixed with asphalt cement.

Author contribution statement

Parinaz Ataeian: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Software; Validation; Visualization; Writing - original draft; Writing - review & editing

Yashar Azimi Alamdary: Writing - review & editing

Michael Tam: Supervision; Project administration; Funding acquisition; Resources; Writing - review & editing

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

8.1. Contributions to research

The application of asphalt emulsions in pavement structures is increasing remarkably. However, the low shelf-life of conventional surfactant-based asphalt emulsions resulted in material and energy waste loss. Moreover, practical limitations in the properties of current asphalt emulsions and their residue limit their application in the pavement industry.

This research examined the application of cellulose nanocrystals (CNC) as biodegradable material from sustainable resources as a Pickering emulsifier for preparing asphalt emulsions with enhanced residue properties. Various techniques to evaluate the asphalt droplets' coverage in the emulsion system, were utilized and the effect of various chemical modifications on the surface of CNCs on the stability and rheology of the resulting asphalt emulsion system was studied. The rheological properties of CNC-based asphalt Pickering emulsions were investigated. A combination of morphological and rheological analyses was used to evaluate the static and dynamic stability of the resulting systems. A comprehensive rheological and performance comparison was made between the residue of CNC-based emulsion and traditional surfactant-based emulsion.

8.1.1. Development of Fluorescent-labelled CNC as an emulsifier to monitor CNC behavior during crystallization of the dispersed phase

An emulsion of a phase transition oil was prepared using PAMAM dendrimer tagged CNC as the interfacial stabilizer. Fluorescent microscopy was then used to evaluate the partitioning of CNCs at the interface before, during, and after the phase transition of the dispersed phase. A geometrical change of droplets accompanied the phase transition of the dispersed phase. It was confirmed that the CNC present irreversible placement of at the interface, even after phase transition and geometrical change of droplets was confirmed.

8.1.2. Development of CNC-armouring oil droplet during phase transition through the design of the charge density of CNC particles

The denser interface coverage would more effectively prevent droplets' coalescence and result in a more stable system during the phase transition of the dispersed phase. This study investigated

the impact of charge density on CNC particles on providing a denser interface coverage as the emulsion underwent a phase transition. Improvement in CNC adsorption around oil droplets was observed by reducing the repulsion between CNC particles through salt addition and surface modifications of CNCs. The partitioning of CNC at the interface was quantified by measuring surface tension, interface tension, and dynamic interfacial tensions. A sigmoidal model was developed to evaluate the adsorption of CNC at the interface as a function of exposure time, using dynamic interfacial tension measurements. The factors that impacted the final interface density were evaluated, and understanding these factors was critical to achieving the desirable stability for each application. This study suggested that higher CNC concentration and lower interparticle repulsion by adjusting surface charge (through salt addition or surface functionalization) were the most critical factors on adsorption time and surface coverage. The required thresholds of each parameter to provide adequate stability throughout the phase transition of the dispersed phase were determined.

8.1.3. Development of rheological analysis on paraffin wax emulsion stabilized by CNC over SDS

The stability of CNC-based emulsions of a phase-change oil was compared with a surfactant (SDS) stabilized system under dynamic loading and static condition. The change in the particle size was used to measure the system's stability before and after loading (phase transition and dynamic loading). For each system, various emulsifier concentrations were used and examined. In both systems, higher emulsifier content resulted in smaller particle sizes. However, in a surfactant-based system, a significantly high difference between the particle size was observed after the phase transition and dynamic loading. In CNC-based emulsions, dynamic loading before and after the phase transition revealed no significant change in the particle size. The higher stability of CNC-based systems could be attributed to the irreversible adsorption of CNC at the oil-water interface. As part of this research, a systematic method to investigate the stability of emulsions under dynamic loading was established using the complex viscosity measurements under frequency sweep mode. The maximum bearable frequency for each system was determined by fitting a cross-regression model and calculating the deviation of laboratory-measured viscosity from the predicted values.

An empirical model for the relationship between emulsifier concentration and resulting particle size of emulsion was established, which could be fitted to both surfactant-based and Pickering systems. The optimum emulsifier concentration could be determined for various emulsification mechanisms using this model.

8.1.4. Development of novel asphalt emulsified by Cellulose nanocrystal presenting higher stability with proper tailoring properties of asphalt residue

Pristine and surface charge modified cellulose nanocrystals were used to prepare asphalt emulsions and compared with traditional surfactant-based technology. The main observed rheological difference at emulsion state are summarized below;

- Lower linear viscoelastic range and higher thixotropic behavior (in terms of rebuild time) were observed for CNC-based emulsion.
- The viscosity of CNC-based emulsions could be adjusted significantly by CNC concentration to fit requirements for various applications.
- The viscosity of CNC-based emulsion was observed to be less sensitive to the temperature of the system compared to surfactant-based technology.

Asphalt cement residue of the emulsions was prepared using a low-temperature evaporation technique to resemble the natural distribution of remaining CNC in asphalt cement. Complex modulus master curves were constructed on frequency sweep test results at various temperatures compared to the commercial emulsion. Key findings on the rheological analysis of the residue are described below;

- An overall increase in the stiffness of CNC-containing samples was observed in shear complex modulus master curves.
- An elastic return point was observed in the phase angle master curve and black-space diagram of CNC containing the sample. The formed CNC network provided a more elastic behavior at high temperatures (low loading frequency), where the asphalt medium lost its elastic behavior.
- Higher rutting resistance properties were observed for CNC-containing residue samples through multiple stress creep recovery tests (MSCR), implying better high performance properties.

- More brittle crack propagation was observed for CNC containing the sample in the linear amplitude sweep test due to the composite structure of CNC-asphalt composition.
- By calculating glass transition temperature from rheological data, it was confirmed that the added stiffness compromised the low-temperature behavior of CNC-containing samples.

The observed rheological difference of CNC-based asphalt Pickering emulsion with those of commercial surfactant suggested that CNC is a good system for this application. Adjustable viscosity of CNC-based systems in conjunction with thixotropic behavior could be used in applications where a thicker layer of emulsified asphalt is required such as chip seal and surface treatment application in the pavement industry.

The higher stability of the CNC-based system could significantly simplify the use of emulsified asphalt in the pavement industry by reducing the storage and application requirements. Moreover, the extended shelf life of CNC-base asphalt emulsion could prevent material loss due to extended storage time. Also, highly stabilized asphalt emulsions would allow longer transport, that help the application of such material in remote areas.

As for water evaporation, the remaining CNC in the asphalt acted as nanofiber reinforcement, modifying the rheological and performance-related properties of asphalt cement. The CNC asphalt performed as a composite material where the cellulose nanocrystals formed a network in an asphalt cement. The formation of a CNC network increased the system's stiffness and transformed it into a more elastic material suitable for pavement application.

8.2. Recommendations for Future works

As part of this research, cellulose nanocrystals have been used for the first time to prepare paving-grade asphalt cement. The rheological behavior of a resulting system in emulsion state and on residue was thoroughly studied, and factors affecting rheological properties were examined. Adjustment techniques to alter the system's stability under static and dynamic conditions were determined. Modifying the impact of remaining CNC in asphalt cement residue was characterized in detail.

Future related research could focus on the followings;

- various asphalt emulsion applications in the pavement and roofing industry, and to identify and specify rheological requirements for the emulsion and residue and ways to adjust the formulation based on tools developed in current research.
- Investigating the suitability of CNC-based asphalt Pickering emulsion for cold recycling of asphalt pavement. The modified properties of CNC-based emulsion could enhance the durability of the resulting asphalt mix, which requires further study.
- The improved tensile strength and thixotropic behavior of CNC-based asphalt Pickering emulsion could contribute to the final properties of surface treatment techniques such as micro-surfacing and chip-sealing.
- Adjusting the setting time of CNC-based asphalt emulsions using the chemical modification tools presented in this research could be important and would refine and enhance the properties of the emulsion for pavement application.
- Life cycle cost analysis of the application of CNC-based emulsions in various pavement applications should be performed by considering the possible initial added cost and savings due to higher stability, easier application, modified rheological properties of the residue, energy savings and environmental consideration. Such thorough analysis would help pavement industry decision-makers evaluate the application of this technology.

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