CHARACTERIZING THE RHEOLOGICAL PROPERTIES OF WAX EMULSIONS USED AS CARRIERS FOR BIOPESTICIDES IN AGRICULTURAL PEST MANAGEMENT

A thesis presented to the faculty of the Graduate School of Western Carolina University in partial fulfillment of the requirements for the degree of Masters of Science in Chemistry.

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ABSTRACT

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The purpose of this research was to characterize the rheological properties of various wax emulsions developed as carriers for biopesticides used for agricultural pest management. Wax emulsions have been developed as carriers for the controlled release of non-toxic materials such as insect pheromones and essential oils used in crop protection as part of Integrated Pest Management (IPM) programs. However, the rheological properties of these wax emulsion carriers had not been evaluated and reported in the literature. Therefore, to obtain a more thorough evaluation of these wax emulsions, the rheological properties were characterized. The data collected can be used to determine the best rheological properties for different field application methods. In this research, wax emulsions were prepared using different formulations, such as different waxes, emulsifiers, and biopesticides, and different concentrations of each. These emulsions were tested using an Anton Paar® Physica MCR 101 rheometer. The goal was to characterize the rheological properties to understand how the various components affect the overall behavior and application of these emulsions. The biopesiticides explored were insect pheromones used for mating disruption in IPM and essential oils that are used as deer feeding deterrents for crops and landscaping plants. Geranyl propionate was used as a substitute for insect pheromones because it is structurally similar to many insect sex pheromones and is less expensive. The insect pheromone emulsions had a high viscosity allowing the emulsions to be applied in thick masses with a low surface area to achieve long term release of the volatile pheromones. Wax emulsions were also prepared with a small concentration of spearmint oil, which has been shown to be an effective feeding deterrent for white-tailed deer. The emulsions containing spearmint oil were prepared with a lower viscosity compared to the insect pheromone emulsions. This was done so that the emulsions could be effectively sprayed onto plant surfaces. It was found that both paraffin wax and soy wax were effective for the insect pheromone emulsions. However, when investigating the deer feeding deterrent emulsions, the soy wax emulsions displayed rheological properties more suited for spraying.

CHAPTER 1: INTRODUCTION

1.1 Wax Emulsion Biopesticides

Many hazards are associated with the use of agricultural pesticides, including harm to the human population, the surrounding environment, and wildlife. Pesticides not only kill insects or weeds, but they can also kill birds, fish, non-target plants, and beneficial insects. Some of the higher risk human populations affected by hazardous pesticides include formulators, sprayers, production workers, mixers, agricultural farm workers, and loaders. Other ways the human population can be affected by harmful pesticides is through consumption of food containing residual pesticides. For example, it was found that 5.2% of apples, lettuce, tomatoes, strawberries, and grapes contained pesticide residues.[1] Due to the increasing concern for the environment and human and animal contamination, there is a desire for organic and less toxic pesticide alternatives for use in agricultural pest management.

Previous research has been conducted on developing a carrier for the controlled release of biopesticides made from various wax emulsions that slowly release insect sex pheromones.[2] These wax emulsions release volatile pheromones that can be used in integrated pest management (IPM) programs to manage insect pests that damage crops.[2] Multiple wax emulsion formulations were developed for this purpose. Further research was conducted by Ballew[3] and McCracken[4] to characterize the rheological properties and optimize the wax emulsion formulation. McCracken compared different waxes for the insect pheromone emulsions and expanded on Atterholt's formula by using microcrystalline wax and then comparing it to the previously used paraffin wax.[4] However, there was a lack of rheological data.[3] Ballew based his thesis research on measuring the rheological properties of basic wax emulsions consisting of wax and emulsifier.[3] Ballew did not collect rheological data on the emulsion with the biopesticide components. This research evaluated the rheological properties of the wax emulsion with the biopesticide component, which is important for determining the best method for applying the material to agricultural crops and landscaping plants.

Researchers have also investigated the use of essential oils as a feeding deterrent for deer, since deer cause considerable damage to agricultural crops and landscaping plants.[5,6] Land owners and farmers have used homeopathic deer repellents or commercially available repellents to deter deer feeding. Noell and Rogers used the previously developed wax emulsion formula for insect pest management and adapted it as a formulation to incorporate essential oils used as feeding deterrents for deer.[7] During the research conducted by Rogers and Noell, spearmint oil was determined to be the best feeding deterrent after field testing different essential oils in areas that had a high population of white-tailed deer.[7] The emulsions developed to repel deer were created to be less viscous (using less wax) than the earlier emulsions used in insect pest management. Though these emulsions were created to be less viscous, the viscosity still proved to be too high to allow for the emulsions to be easily sprayable. More research was needed to develop emulsions that were more sprayable.

1.2 Rheology

Rheology is the science of deformation and flow, derived from the branch of physics and physical chemistry that studies force, deflection, and velocity variables.[8] The term "rheology" coins from the Greek word "rhein", which means "to flow."[8] Rheological measurements give information about the flow behavior of liquids as well as the deformation of solids, making it an essential tool to understanding and characterizing the behavior of viscoelastic materials.[8]

The ideal viscous liquid flow can be defined by Newton's Law of Viscosity; Newtonian fluid visocisities are independent of shear rate.[9] Shear rate is a force that is applied by varying the speed in which the measurement system is rotated. Shear rate is mathematically defined as:

$$\dot{\gamma} = \frac{v}{h} \tag{1}$$

where v is defined as the change in x over time (t):[8]

$$v = \frac{dx}{dt} \tag{2}$$

Shear rate is presented in units of reciprocal seconds (s^{-1}). The ideal elastic solid deformation can be defined by Hooke's Law; the stress imposed on a solid is directly proportional to the strain produced.[10] Stress, or shear stress, is a force that is applied by pressing down varying amounts of force over the surface area of the material. Shear stress is mathematically defined as:[8]

$$\tau = \frac{F}{A} \tag{3}$$

where F is the force and A is the area of the upper surface of the measurement system. Shear stress is presented in units of Pascals (Pa). Strain is the displacement of the material along to x and y-axis. Strain (γ) is mathematically defined as:[8]

$$\gamma = \frac{x}{h} \tag{4}$$

where x is defined as the displacement along the x-axis and h is defined as the height between the top and bottom plates in the measurement system. Strain is either unit-less or presented in terms of percent (%). Viscoelastic materials are materials that deform almost instantaneously, then reform over time after the deformation force is removed.[11] These materials do not fit the ideal viscous liquid flow nor the ideal elastic solid deformation.[8,11] The wax emulsions display such viscoelastic characteristics and are thus not considered a Newtonian fluid nor a Hooke's solid. Rheometry is used to characterize and understand these complex flow behaviors.

In order to study the rheology of these viscoelastic materials, an instrument called the rheometer was developed. A rheometer is an instrument that applies a certain deformation to a material and measures the subsequent mechanical response.[12] In other words, a rheometer measures the flow of a material as forces are applied.[12] These forces may be classified as either shear rate, shear stress, or strain.

Since the rheometer is able to apply a multitude of forces, the experimental tests it can perform are categorized as either a rotational or oscillatory measurement. Rotational tests are used to investigate the non-Newtonian behaviors of liquids, solutions, melts, and emulsions.[8] One of the more commonly used rotational tests is the flow curve and viscosity function. This test is performed by observing a change in viscosity, or flow behavior, measured in pascal-seconds (Pa·s) as a function of shear rate or shear stress.[8] These tests work by applying a shear force via rotating the top plate of the measurement system while the temperature is held constant using a Peltier temperature control system. The resulting deformation is measured by observing the flow resistance of the material.[8] The data collected are presented in terms of τ vs. $\dot{\gamma}$ (a flow curve) or η vs. $\dot{\gamma}$ (a viscosity curve). The viscosity (η) is defined as:

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{5}$$

Viscosity and flow curves can be fit with mathematical functions for curve fitting using a small number of curve parameters.[8] The Herschel-Bulkley viscosity curve fit is defined by the following mathematical equation:[8]

$$\tau = \tau_{\text{HB}} + c \cdot \dot{\gamma}^{p} \tag{6}$$

The parameter c is defined as the flow coefficient, or Herschel/Bulkley viscosity, in pascal-seconds (Pa·s). The parameter p can be defined as the Herschel/Bulkley index.[8] If $p < 1$, then the material is experiencing shear-thinning. If $p > 1$, then the material is experiencing shear-thickening. If $p = 1$, then the material is experiencing ideally viscous flow behavior.[8]

Oscillatory measurements are used to investigate the viscoelastic properties of low-viscosity liquids, melts, emulsions, and gels.[8] These types of measurements are performed by having a top plate oscillate using a drive wheel while the bottom plate is kept stationary. The motion of the top plate causes the shearing of the sample that is placed between the two plates. The subsequent mechanical response is measured via the displacement of the sample held between the plates and its relative resistance to the movement of the top plate.[8] The resulting data are shown as the loss modulus (G'') in pascals (Pa) and the storage modulus (G') in pascals (Pa). The loss modulus describes viscous (liquid-like) behavior, whereas the storage modulus describes elastic (solid-like) behavior.[8] The two most common oscillatory measurements that use this representation of data are the amplitude and frequency sweeps.

The amplitude sweep is an oscillatory measurement that changes the amplitude (γ_A) of oscillation while keeping the angular frequency (ω) and temperature constant.[8] This particular test is used to determine the limiting value of the linear viscoelastic (LVE) range (γ_L) in percent (%), the yield point (τ_y) in pascals (Pa), the flow point (τ_f) in pascals (Pa), and the damping factor ($\tan\delta$) of a material. The limiting value of the LVE range is the last point in which G' and G'' display constant plateau values.[8] The sample shows stability up to this point. At higher strains than the γ_L value, the structure of the sample will break down and the material will begin to flow. The τ_y is the limiting value of the LVE range in terms of shear stress (τ).[8] The τ_f is where G' and G'' values are equal. After the flow point, the material begins to favor viscous behavior and will flow. The $\tan\delta$, also called the loss factor, is the ratio of the viscous to the elastic behavior.[13] The damping factor can be defined as:[13]

$$\tan\delta = \frac{G''}{G'} \tag{7}$$

If $\tan\delta > 1$ when the curve plateaus, then the material is more likely to separate over time. If $\tan\delta < 1$, then the material holds a stable solid state that is not likely to separate over time. If $\tan\delta = 1$, then the viscous and elastic behavior is equally balanced.[13]

The frequency sweep, also known as the angular frequency sweep, is another oscillatory measurement performed by the rheometer that changes the angular frequency (ω) in radians per second (rad/s) while keeping the amplitude (γ_A) and temperature constant in the frequency sweep.[8] This test is used to investigate time-dependent deformation behavior of a sample.[8] The LVE range (γ_L), found through the amplitude sweep, is the amplitude value that is held constant. The data collected produce a curve that displays the loss and storage moduli, as well as the complex viscosity ($|\eta^*|$), in relation to the increase in angular frequencies. If $G' > G''$ at high angular frequencies, the sample experiences elastic-solid behavior. Elastic-solid behavior is when a material reforms immediately after deformation force is removed.[8]

CHAPTER 2: OBJECTIVE

The objective of this research was to characterize the rheological properties of wax emulsions used as carriers for various biopesticides used to manage agricultural pests. The biopesticide varied, depending on the pest being targeted. The deer feeding deterrent emulsion contained spearmint oil. For the insect pheromone biopesticide, geranyl propionate was used as a model compound due to its structural similarities to the Oriental fruit moth (OFM) insect sex pheromone.[14] Rheological tests were used to compare the properties of the emulsions. The rheological properties determined through these tests could aid in the determination of the optimal formulations and how to apply these wax emulsions.

CHAPTER 3: MATERIALS AND METHODS

3.1 Paraffin Wax and Soy Wax

Paraffin and soy waxes were used to make the wax emulsion carriers to compare and contrast their relative stabilities and structural strength in emulsions. Paraffin wax is a byproduct of the petroleum industry that is made up of a saturated hydrocarbon chain length ranging from 20-40 carbons. The paraffin wax used for this research was the Gulf Wax Household Paraffin Wax. At room temperature, paraffin wax is a hard waxy solid with a melting point between approximately 47 °C and 64 °C and a density of approximately 0.9 g/cm^3.[15]

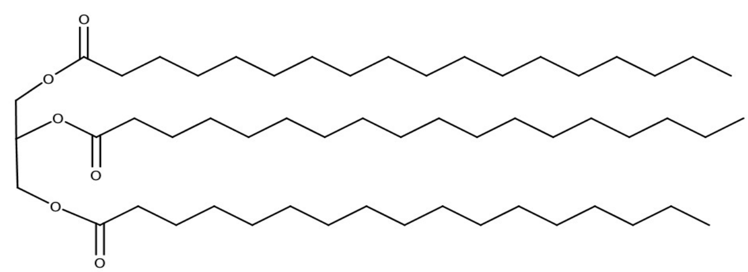


Figure 1. Soy wax structure. CAS number: 8016-70-4.

Soy wax is a partially hydrogenated soybean oil with the structure as seen in Figure 1. The soy wax used for this research was Golden Brands, LLC 415 Soy Wax. At room temperature, soy wax looks similar to paraffin wax with a melting point between approximately 48 °C and 52 °C and the same density as paraffin wax.[16]

3.2 Emulsifiers

Two emulsifiers were used in this research, sorbitan monostearate (Span60®) and triethanolamine stearate (TEA stearate), and they were paired with paraffin and soy wax, respectively. Previous studies had shown that the Span60® and paraffin wax produced a stable emulsion, as well as soy wax and TEA stearate.[3]

The Span60®used in this research was reagent grade from Alfa Aesar®. Span60® has a molecular weight of 430.62 g/mol and a molecular formula of $C_{24}H_{46}O_6$.[17] The chemical structure of Span60® is shown in Figure 2.

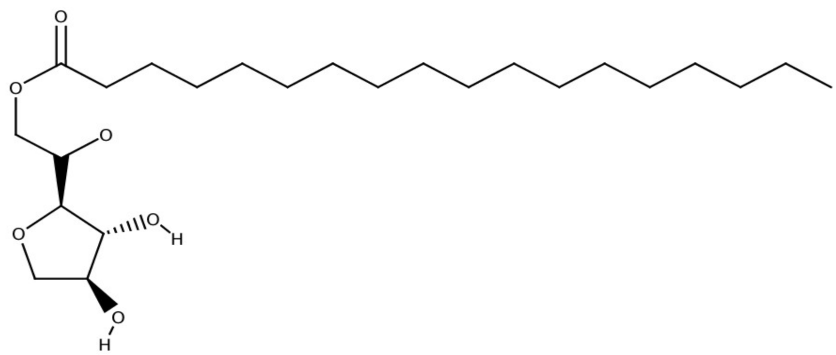


Figure 2. Span60® structure. CAS number: 1338-41-6.

The TEA stearate used in this research was synthesized using the preparation method adapted from Goddard.[18] It required a 1:1 mole ratio of stearic acid and triethanolamine. The stearic acid and triethanolamine were lab grade chemicals purchased from Fisher Scientific.

The required amount of stearic acid was weighed using a tared beaker then heated to approximately 80°C and allowed to melt. The appropriate amount of triethanolamine was weighed using a tared weigh boat. Once the stearic acid was fully melted, the triethanolamine was slowly added while stirring using a glass stirring rod. After all the triethanolamine was added, the temperature of the solution was raised to 95°C in order to obtain an isotropic solution. After the solution became isotropic, it was transferred to an aluminum foil boat and allowed to cool to room temperature and harden. It was then ground to a fine powder using a mortar and pestle and transferred to a glass jar for storage.

TEA stearate has a molecular weight of 433.67 g/mol and the molecular formula of $C_{24}H_{51}NO_5$.[18] The chemical structure of TEA stearate is shown in Figure 3.

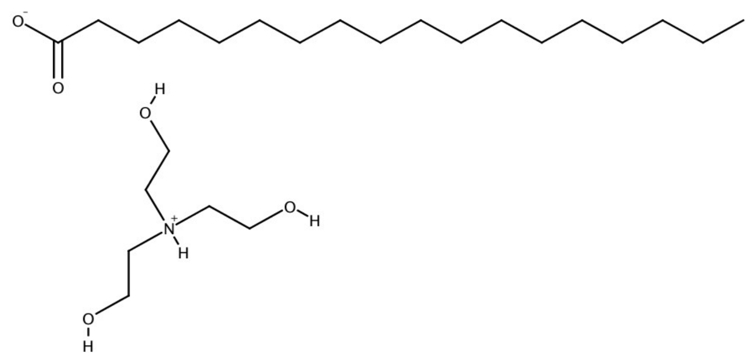


Figure 3. TEA stearate structure. CAS number: 4568-28-9.

3.3 Vegetable Oil

Vegetable oil was used to make all wax emulsions in order to prevent the emulsion from becoming friable once the water evaporated after being applied to a surface. The vegetable oil used was Great Value™ brand, found in local stores.

3.4 Biopesticides

Biopesticides are natural compounds that can be used for pesticidal applications. Two compounds were used to make the wax emulsions. Geranyl propionate was used to simulate the OFM pheromone, due to its availability, lower cost, and structural similarity.[14] The second compound was spearmint oil, used to prepare the deer feeding deterrent emulsions.

Geranyl propionate was purchased from Sigma-Aldrich. It has a molecular weight of 210.13 g/mol and a molecular formula of $C_{13}H_{22}O_2$.[19] The chemical structure of geranyl propionate is shown in Figure 4.

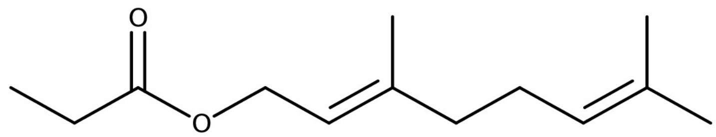


Figure 4. Geranyl propionate structure. CAS number: 105-90-8.

The 100% pure spearmint oil was purchased from aromappeal™. It has a molecular weight of 182.17 g/mol and a molecular formula of $C_6H_{14}O_6$.[20] The chemical structure of spearmint oil is shown in Figure 5.

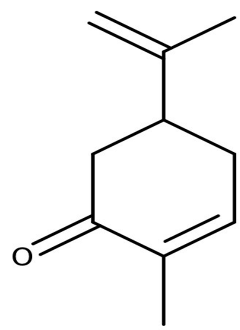


Figure 5. Spearmint oil structure. CAS number: 8008-79-5.

3.5 Emulsion Preparation

3.5.1 Insect Pheromone Emulsion Preparation

The emulsions used for pheromone applications were prepared with 30% (w/w) wax, 4% (w/w) emulsifier, 5% (w/w) vegetable oil, 3.8% (w/w) geranyl propionate, and 57.2% (w/w) water.[4] In previous research, this was shown to work well for the pheromone applications.[2,14] The composition of each emulsion prepared is listed in Table 1. Each emulsion was made in triplicate to verify reproduciblility.

Table 1. Insect pheromone wax emulsion compositions.

Emulsion	Soy wax	Paraffin wax	TEA stearate	Span 60®	Vegetable oil	Geranyl propionate	Water
1	-	30%	-	4%	5%	3.8%	57.2%
2	30%	-	4%	-	5%	3.8%	57.2%

The wax, emulsifier, and vegetable oil were weighed using a tared beaker with a magnetic stir bar on an analytical balance and then placed on an electronic hot/stir plate. The wax was stirred and heated until melted. A measured amount of hot water ($\sim$ 80 °C) was added to the molten wax. A measured amount of geranyl propionate was added to the mixture using a transfer pipette. The contents of the beaker were then emulsified for one minute using a CAT X520D homogenizer with a T10 dispersing tool on setting one, which is 11,000 rpm. The emulsion was mixed using the homogenizer every 10 minutes until it cooled to approximately 35 °C. The emulsions were transferred to a wide-mouthed jar and stored over night. All emulsions were measured using the rheometer within three days of preparation in order to avoid aging effects.

3.5.2 Deer Feeding Deterrent Emulsion Preparation

Emulsions were prepared with a range of wax and vegetable oil concentrations to determine which visocsities were sprayable. Previous research has shown that 0.5% (w/w) of spearmint oil, 2.5% (w/w) vegetable oil and 3% (w/w) emulsifier worked well for the deer feeding deterrent applications. The composition of each emulsion prepared in order to investigate the range of spray-ability is listed in Table 2. The composition of each emulsion prepared to explore the rheological properties is displayed in Table 3.

Table 2. Deer feeding deterrent wax emulsion compositions produced to explore the range of sprayability.

Emulsion	Soy wax	Paraffin wax	TEA stearate	Span 60®	Vegetable oil	Spearmint oil	Water
7	-	20%	-	3%	2.5%	0.5%	74%
8	-	10%	-	3%	2.5%	0.5%	84%
9	-	5%	-	3%	2.5%	0.5%	89%
10	20%	-	3%	-	2.5%	0.5%	74%
11	10%	-	3%	-	2.5%	0.5%	84%
12	5%	-	3%	-	2.5%	0.5%	89%

Table 3. Deer feeding deterrent wax emulsion compositions produced to characterize the rheological properties.

Emulsion	Soy wax	Paraffin wax	TEA stearate	Span 60®	Vegetable oil	Spearmint oil	Water
3	-	10%	-	3%	2.5%	0.5%	84%
4	-	5%	-	3%	2.5%	0.5%	89%
5	10%	-	3%	-	2.5%	0.5%	84%
6	5%	-	3%	-	2.5%	0.5%	89%

The procedure used to prepare the deer feeding deterrent emulsions was similar to the preparation method for the insect pheromone emulsions. Through previous research conducted by Noell, the method was altered to increase the reproduciblility of these emulsions.[7] During the emulsification step, the emulsions were homogenized every 10 °C until they cooled to approximately 30 °C.

3.6 Rheometer

The rheometer used in this research was an Anton Paar® Physica Modular Compact Rheometer (MCR) 101. The MCR 101 rheometer is an air bearing system that can perform measurements in both rotational and oscillatory modes that is equipped with a Peltier temperature control unit that provides temperature control from -40 °C to 200 °C.[21] For this research, the parallel plate measurement system was equipped with a 50 mm diameter top plate. The rheometer was controlled using a Windows® XP personal computer running the Rheoplus/32 software version 3.4.

3.7 Rheological Measurements

When using the parallel plate measurement system, a gap between the two plates was chosen to accommodate the sample held between the plates. The optimal gap for this type of emulsion was 1.0 mm.[8] By having the Peltier temperature control system, the bottom plate was set to keep a constant temperature of 25 °C during all measurements.

In order to ensure accurate measurements, the sample loading technique was kept constant for each wax emulsion. The sampling technique for the insect pheromone wax emulsion, due to its high viscosity, involved removing an aliquot from the jar using the oblong end of a double sided spatula in one stroke then placing it on the bottom plate of the measurement system, as outline by previous research.[3] The sampling technique for the deer feeding deterrent wax emulsion was slightly different due to its lower viscosity. The sample was extracted from the jar using a disposable plastic 1 mL pipette that was placed halfway into the jar to ensure foam was not extracted. The sample was then released onto the bottom plate of the measurement system. This technique was chosen in order to minimize the effects of work softening.[22,23] Also called shear breakdown, work softening occurs when shear is applied to a rested sample, thus resulting in a decrease in viscosity before measurement is taken.[22,23]

After the sample was loaded, the top plate was lowered until it reached the trim position. This position was at 1.05 mm and allowed excess sample to be removed from the edges of the measurement system by using either the flat end of the spatula or the plastic pipette, depending on the wax emulsion biopesticide. Once trimmed, the plate was lowered to the measurement gap of 1.0 mm.

Due to the effects of work softening, a rest time was set before each measurement was taken using Rheoplus/32 software. From previous research performed on the insect pheromone biopesticides, a 10 minute rest time was selected in order to ensure the sample reached relaxation and temperature equilibrium.[3] The rest time chosen for the deer feeding deterrent emulsion was 5 minutes due to a higher rate of evaporation for a lower viscosity sample, as previously described.[7]

The amplitude sweep, frequency sweep, and flow curve measurements were chosen to characterize the rheological characteristics of these wax emulsions. The amplitude sweep was chosen to investigate the τ_y, τ_f, γ_L, and the $\tan\delta$ values of each emulsion. The amplitude sweep measurement was taken for each wax emulsion using controlled shear deformation (CSD) from $\gamma = 0.01\%$ to 100% and an angular frequency (ω) of 10 s^{-1}.[3] The recommended optimal amplitude that was set for the frequency sweep was determined by the amplitude sweep γ_L value. Reproducible data of the deer feeding deterrent emulsions could not be obtained from the frequency sweep measurements.

The frequency sweep tests using controlled shear deformation (CSD) from $\omega = 500$ s^{-1} to 0.05 s^{-1} were performed on the geranyl propionate emulsions. The constant amplitude was set at $\gamma_A = 0.05\%$ strain for both the soy wax and paraffin wax emulsions. This measurement was used to investigate the structural strength, or consistency, of the emulsions over time.[3,8]

The flow curve measurement was taken using the controlled shear rate (CSR) with 30 measuring points and a logarithmic ramp from $\dot{\gamma} = 1\,s^{-1}$ to 100 s^{-1}. The measuring point duration profile of "no times setting" was chosen, which allows the instrument to determine when to take each data point. The CSR method was chosen because the test simulates the change in viscosity the material will experience as it is being sprayed through a nozzle or if the material was stirred before application.[8] Due to the use of the CSR flow curve measurement, the data collected was fit with the Herschel-Bulkley mathematical model, as seen in Eqn.6. By using the Herschel-Bulkley fit, the viscosity (η) in Pa·s at a shear rate of 1 s^{-1}, the Herschel/Bulkley index (p), and the correlation ratio (r^2) was determined. The correlation ratio describes how well the mathematical model fits the actual data collected.[8] The closer the r^2 value is to 1, the more accurate the Herschel-Bulkley fit is to the actual data.

3.8 Software and Calculations

All resulting data were extracted from the Rheolplus/32 software and transferred to Microsoft Excel files. The triplicate emulsion measurements were averaged and plotted in Excel with x and y-axis standard deviation error bars (x-axis error bars were only used if the measurement points varied between triplicates) for the amplitude sweep and frequency sweep measurements. The flow curve measurements were fitted with the Hershel-Bulkley mathematical model for each triplicate then averaged and plotted in Excel with y-axis error bars. The individual data sets collected for all averaged and fitted measurements can be found in the Appendices B-E.

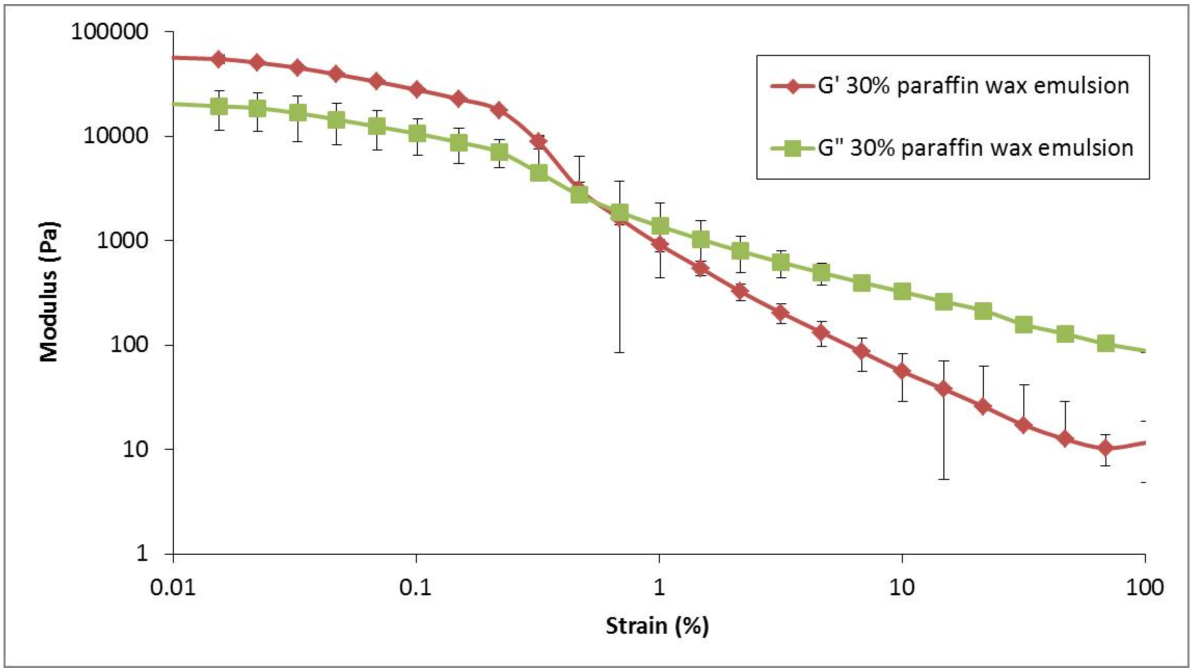
The Rheoplus/32 software version 3.4 has multiple built-in data anaylses and evaluation methods. Using this software, the LVE range was determined using the "LVE Range" analysis on the amplitude sweep measurement. This produced the γ_L value which was the optimal amplitude setting for using frequency sweeps. The software calculates this by observing the measuring curve and determining at what γ value the G' curve begins to deviate from the LVE plateau by more than 5%.[8] The last point in the LVE range before the points deviate is the γ_L value. The analysis method called "Cross-Over" is used to calculate the yield point from the CSS amplitude sweep graph. This is performed by observing the stress (τ) value at which the curve begins to deviate from the LVE plateau.[8] The flow point, also called the cross-over point, is also calculated using the "Cross-Over" analysis on the CSS and CSR amplitude sweep graph. The damping factor is measured during the amplitude sweep and was therefore plotted as $\tan\delta$ vs. strain. The points in which the curve plateaus were then averaged for comparison.

The data collected from the CSR flow curve measurement were plotted in Excel as a viscosity curve, η vs. $\dot{\gamma}$. The Rheoplus/32 software fitted the data with the Herschel-Bulkley fit (Eqn.6) using the "Herschel-Bulkley" analysis. For the triplicate emulsion measurements, the parameters generated by the Herschel-Bulkley analysis for each triplicate were averaged and plotted in Excel.

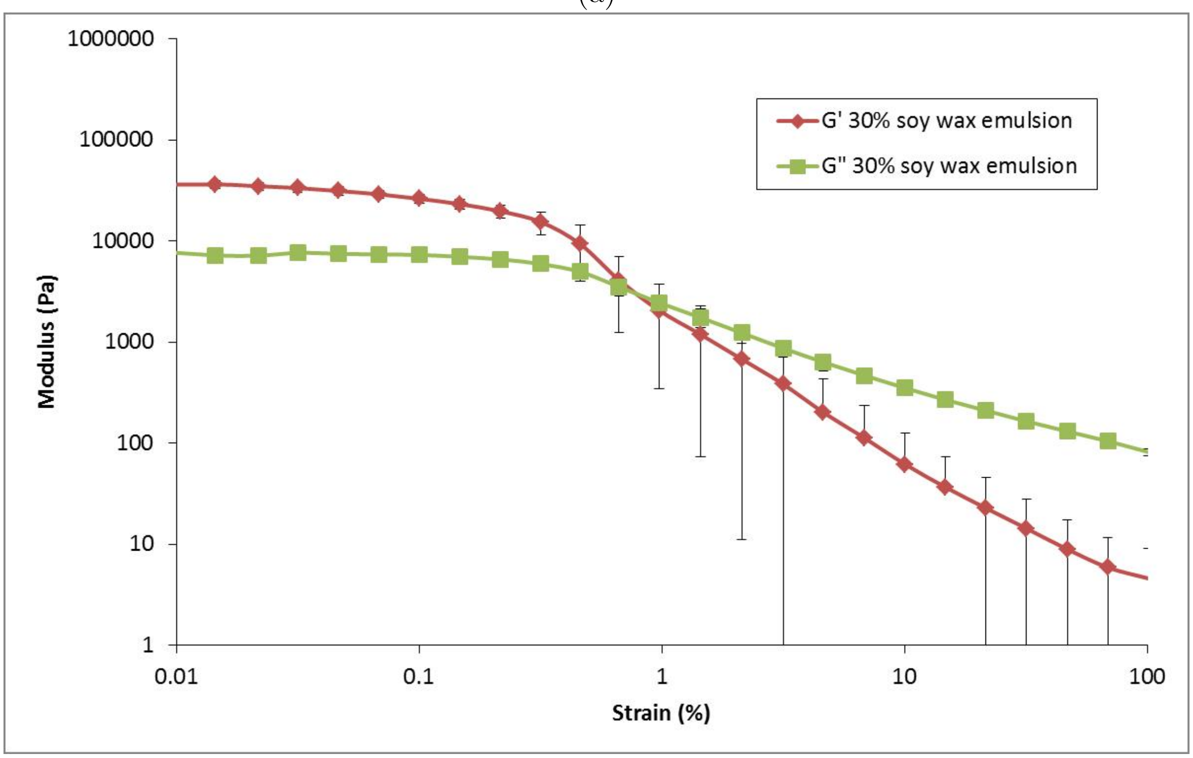
CHAPTER 4: RESULTS AND DISCUSSION FOR INSECT PHEROMONE WAX EMULSIONS

4.1 Amplitude Sweep

The oscillatory amplitude sweep diagrams for the paraffin wax emulsions and soy wax emulsions were averaged and plotted, shown in Figure 6. The averaged τ_y, γ_L, and τ_f values found through amplitude sweep measurement are listed in Table 4 for the paraffin and soy wax emulsions.



(a)



(b)

Figure 6. Amplitude sweep for (a) 30% paraffin wax emulsion and (b) 30% soy wax emulsion taken at 25 °C.

Table 4. Amplitude sweep parameters for 30% paraffin wax and soy wax geranyl propionate emulsions at 25 °C.

Wax type	Yield point τ_y (Pa)	Limiting value of LVE range γ_L (%)	Flow point τ_f (Pa)
Paraffin	27 ± 6	0.044 ± 0.001	$3.0 \pm 2.0 \times 10^3$
Soy	35 ± 8	0.055 ± 0.001	$3.0 \pm 2.0 \times 10^3$

In the amplitude sweep of each wax emulsion, the storage modulus (G') is greater than the loss modulus (G'') in the LVE range. A greater value in G' indicates that the emulsion favors solid state behavior when at stable conditions with low strain values. This characteristic is commonly found in gel-like structures.[8] These structures posses shelf stability and the resistance to flow when at rest.

The γ_L value indicates the amount of strain the material can be subjected to and still maintain its original structure.[8] The γ_L for the paraffin wax and soy wax emulsions have similar values, as seen in Table 4, meaning they have similar gel-like structures that easily break down under applied strain. Both γ_L values are less than 1%, which is typical for materials possessing a network of physical-chemical superstructures predominantly found in dispersion materials (i.e. emulsions).[8] The superstructures formed by these emulsions resemble a network of spheres suspended in water. The hydrophobic tails of the emulsifier, wax, and vegetable oil surround the inner sphere with the insect pheromone dispersed throughout. The hydrophilic ends interact with the water and the other spheres creating a network of frictional forces that hinder the relative flow of the emulsion.[24]

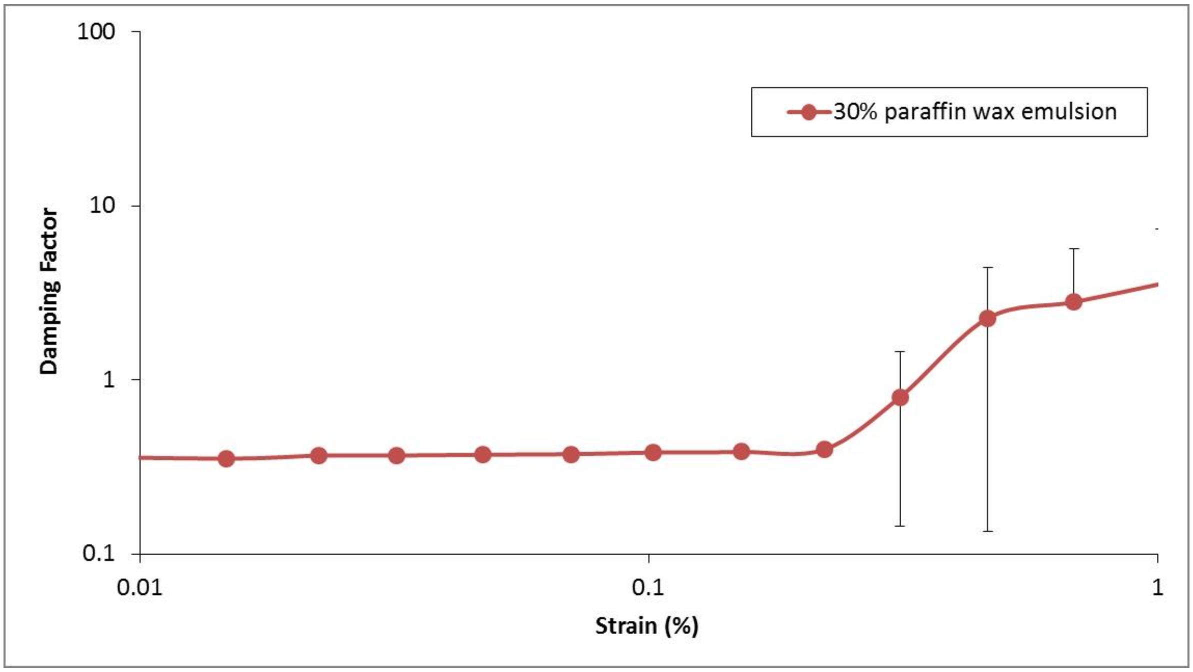
The τ_y value is the maximum amount of shear stress that can be applied before the internal structure of the material begins to break down. These values are seen in the controlled shear stress (CSS) amplitude sweep diagrams shown in Appendix A: Figure 20.[8] Before reaching the yield point, the material shows reversible viscoelastic behavior. After the yield point, the internal structure can be damaged and unable to return to its original structure.

Even though the average τ_y value for the soy wax emulsions is higher than the τ_y value for the paraffin wax emulsions, there is no significant difference between the two when the standard deviation is taken into consideration.

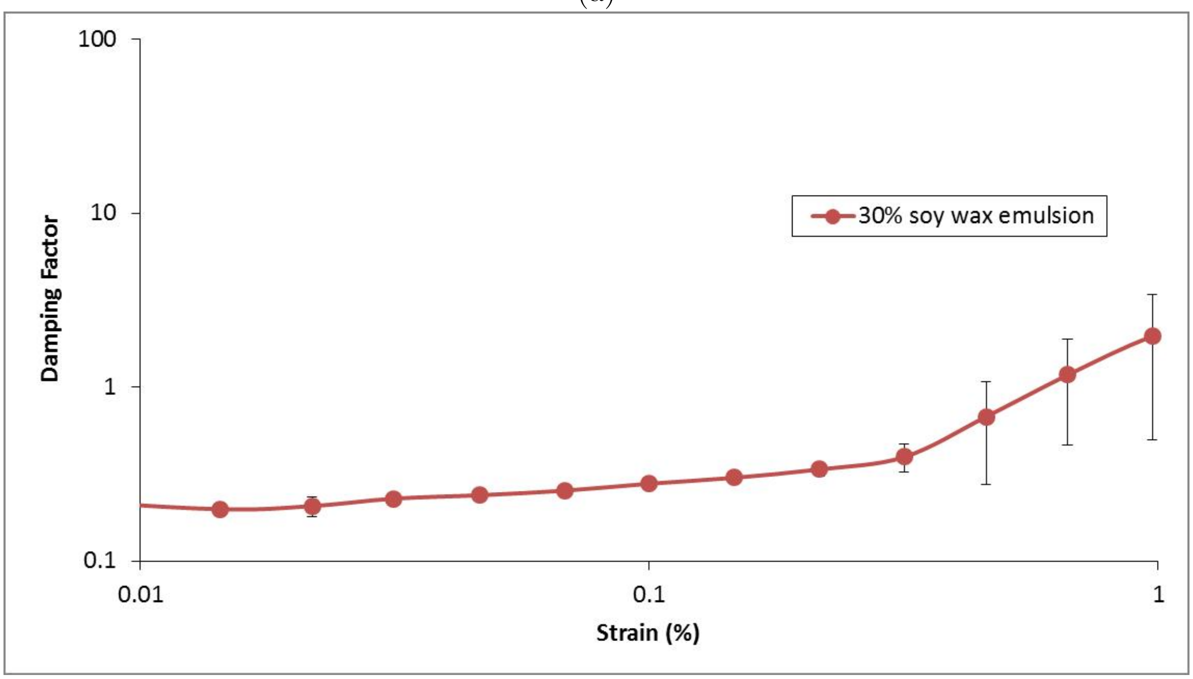
The τ_f value is the point in which the sample, if exhibiting gel-like structure ($G'>G''$), changes to favor the liquid state ($G'<G''$). This is also referred to as the crossover point, when $G' = G''$.[8] The τ_f value, in a scientific sense, is considered a relative value and not an absolute value due to its occurrence in the non-linear deformation range.[8] The flow point exhibited by both wax emulsions is very similar, as shown in Table 4, meaning that the amount of strain applied before the emulsion begins to favor the liquid state is approximately the same. Therefore, similar forces would be required to expel these emulsions from a spray nozzle.

4.2 Damping Factor

The damping factor diagrams, derived from the oscillatory amplitude sweep measurement for the averaged paraffin wax and soy wax emulsion replicates are displayed in Figure 7. The range before the damping factor diagram deviates from the plateau is between the strains 0.1% to 0.22%. This range in the diagram denotes the strain in which the material exhibits stable behavior before beginning to flow with higher strain.[13] The averaged $\tan\delta$ values from 0.1% to 0.22% strain for the paraffin and soy wax emulsions are displayed in Table 5.



(a)



(b)

Figure 7. Damping factor for (a) 30% paraffin wax emulsion and (b) 30% soy wax emulsion taken at 25 °C.

Table 5. Average damping factor from 0.1% to 0.22% strain for 30% paraffin wax and soy wax geranyl propionate emulsions at 25 °C.

Wax type	Paraffin wax	Soy wax
$\tan\delta$	0.39 ± 0.02	0.244 ± 0.006

Both emulsions exhibit $\tan\delta<1$, which indicates stable solid state behavior. When comparing the waxes, the soy wax emulsion has a lower $\tan\delta$ value than the paraffin wax emulsion as shown in Table 5. This indicates greater shelf and structural stability.

4.3 Frequency Sweep

The frequency sweep diagrams for the averaged paraffin and soy wax emulsions are displayed in Figure 8. The frequency sweeps for the paraffin and soy wax emulsions have $G'>G''$ indicating gel-like character over a range of frequencies.[8] Due to both emulsions exhibiting $G'>G''$ at higher frequencies, they exhibit elastic-solid behavior.[8] This behavior indicates stability under high shear, much like being sprayed. For most dispersions and gels, the slope of G' indicates the long-term stability of the material at rest and low frequencies.[8] The soy wax emulsion has a smaller slope displaying an almost parallel trend with the x-axis indicating long-term stability at resting conditions. In contrast, the paraffin wax emulsion displays an intersection between G' and G'' at low frequencies indicating less shelf stability.

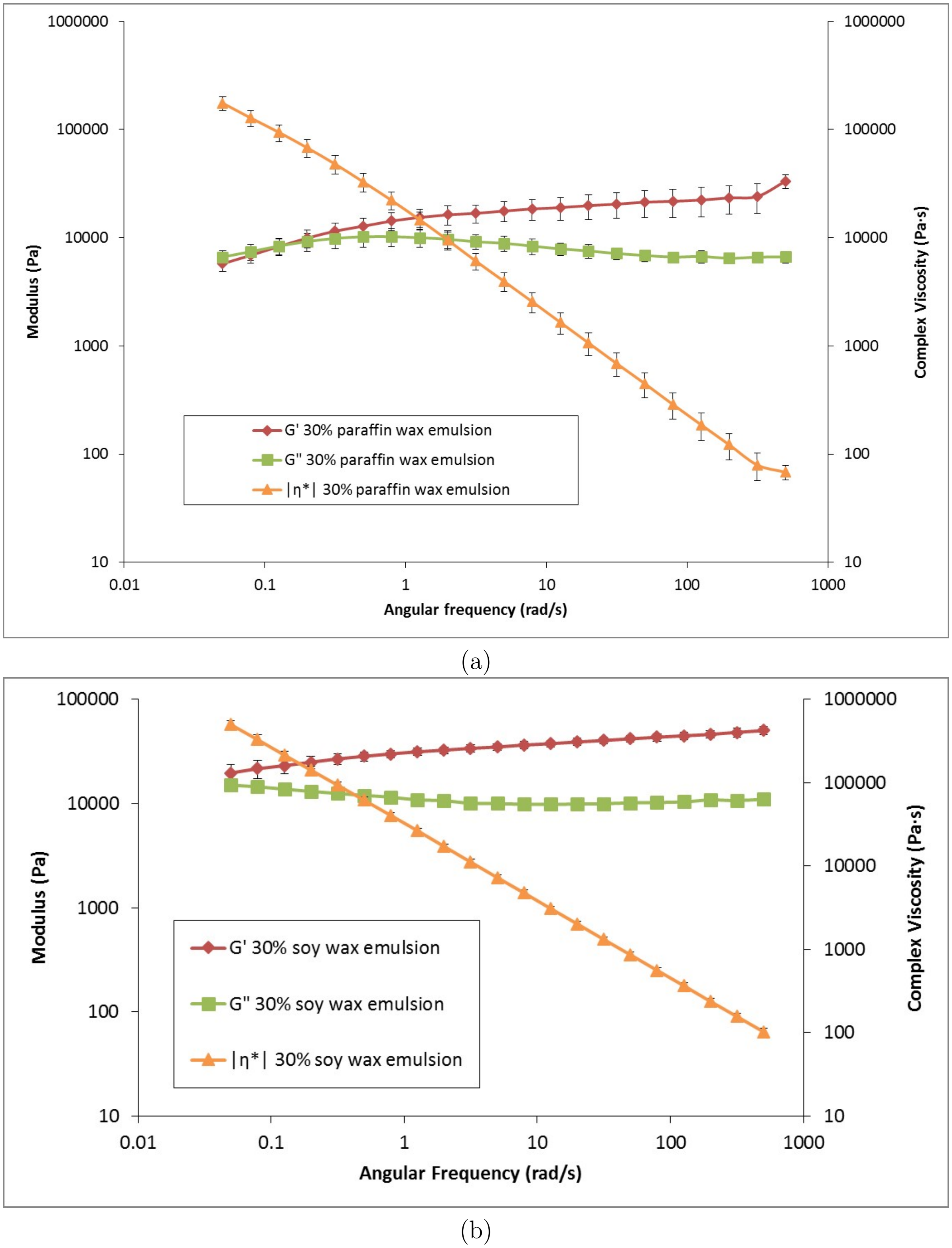


Figure 8. Frequency sweep for (a) 30% paraffin wax emulsion and (b) 30% soy wax emulsion taken at 25 °C.

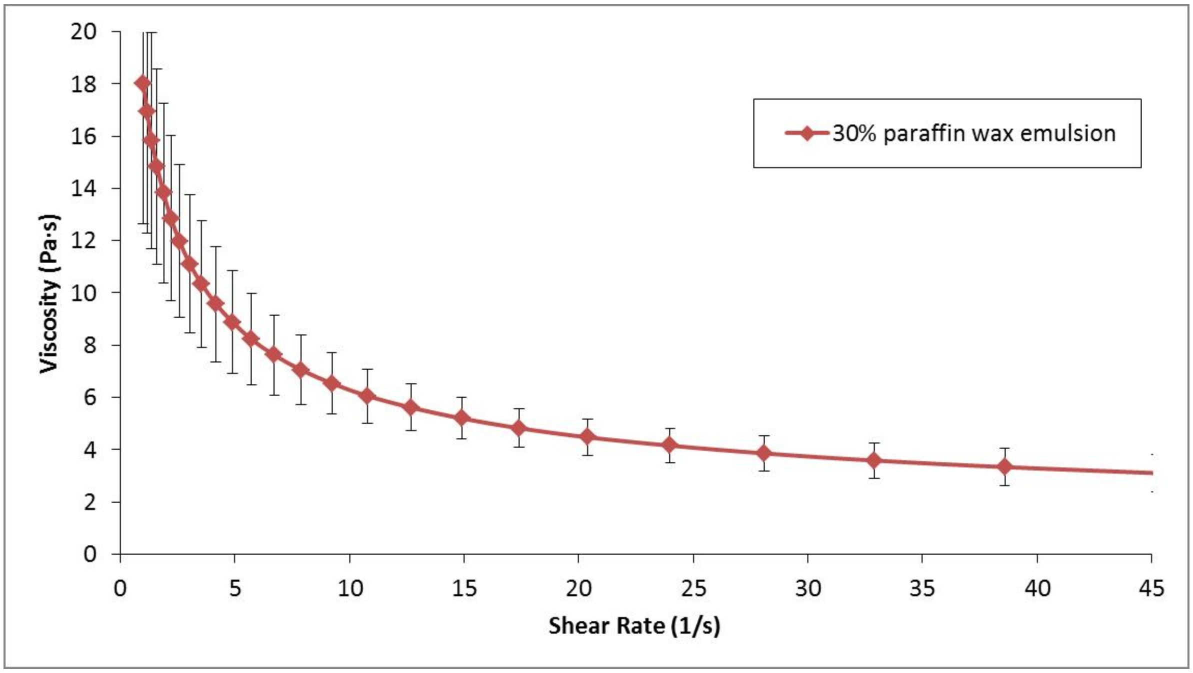
The G' curve derived from the frequency sweep is used to describe the structural strength or consistency of the material.[13] In order to characterize the structural strength/consistency, the magnitude of G' is determined at lower frequencies ($\omega = 0.05\ s^{-1}$). The average magnitude of G' values for paraffin and soy wax emulsions are listed in Table 6. Both emulsions exhibit values equal to or greater than 10^3, indicating high structural stability.[8]

Table 6. Average magnitude of G' at the lowest frequency ($\omega = 0.05\ s^{-1}$) for 30% paraffin wax and soy wax geranyl propionate emulsions at 25 °C.

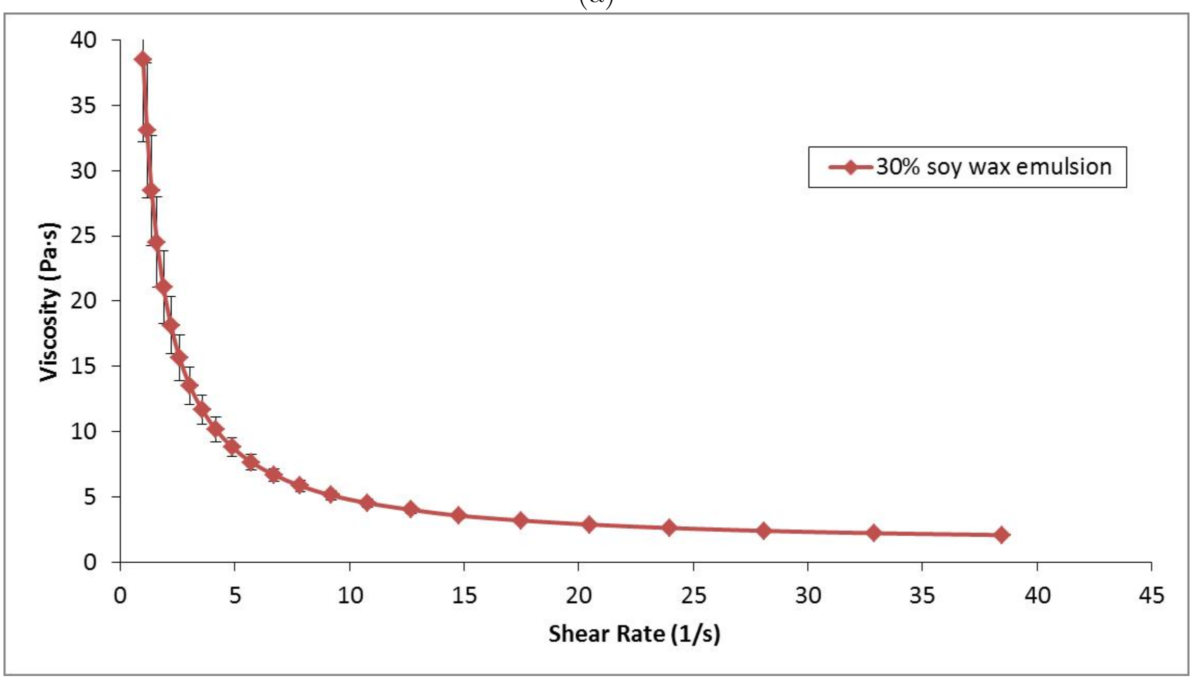
Wax type	Paraffin wax	Soy wax
Magnitude (Pa)	$6.6 \pm 0.1 \times 10^3$	$1.51 \pm 0.02 \times 10^4$

4.4 Flow Curve

The averaged Herschel-Bulkley fitted viscosity curves were plotted and displayed in Figure 9 for the paraffin and soy wax emulsions. The data collected from the flow curve measurement (without the fit) for the paraffin and soy wax emulsions are displayed in Appendix D: Figure 30. The viscosity curves plotted with the averaged Herschel-Bulkley fit display the effects of shear-thinning.[8] The shear-thinning observed by the emulsion is likely due to droplet deformation. The droplets that form a dispersion deform into ellipsoids in order to move in the direction of flow.[8] This decrease in equatorial radii decreases the reoccurring collisions between droplets, thus increasing flow.[8] Both emulsions show a rapid drop in viscosity (η), or increase in flow, as shear rate ($\dot{\gamma}$) is increased, gradually approaching Newtonian behavior.[13] This point is observed when the shear viscosity approaches η_∞, the limit of the viscosity function as it approaches an infinite shear rate.



(a)



(b)

Figure 9. Herschel-Bulkley fitted viscosity curve for (a) 30% paraffin wax emulsion and (b) 30% soy wax emulsion taken at 25 °C.

The averaged flow parameters from the Herschel-Bulkley regression analysis for the paraffin and soy wax emulsions are listed in Table 7. The viscosities (η) at a shear rate of 1 s^{-1} for soy wax emulsions are higher than the paraffin wax emulsions. Both emulsions display a Herschel/Bulkley index (p) less than one with the standard deviation, indicating shear-thinning behavior.[8] The correlation ratio is the value that indicates how well the Herschel-Bulkley regression fits the actual data. The closer the value is to one, the more accurate the regression fit. The high correlation ratio for both wax emulsions indicate that the CSR flow curve measurement using the Herschel-Bulkley fit is a good description of these emulsions.

Table 7. Average Herschel-Bulkley viscosity curve parameters for 30% paraffin wax and soy wax geranyl propionate emulsions at 25 °C.

Wax type	Viscosity η (Pa $\cdot$ s)	Herschel/Bulkley index p	Correlation ratio r^2
Paraffin	18 ± 5	0.5 ± 0.3	0.8 ± 0.1
Soy	38 ± 6	1.1 ± 0.6	0.88 ± 0.03

CHAPTER 5: RESULTS AND DISCUSSION FOR DEER FEEDING DETERRENT WAX EMULSIONS

The sprayability of the deer feeding deterrent emulsions was investigated. For emulsions that were found to be sprayable, the rheological properties were explored.

5.1 Range of Sprayability

Understanding the range of forces and viscosities in which the deer feeding deterrent wax emulsions are sprayable is imperative in designing the emulsion formulation. The paraffin wax emulsions used as carriers for the deer feeding deterrent biopesticide were made with 20%, 10% or 5% wax. The range of wax concentrations was used to determine which of these emulsions would be considered sprayable. Similarly, the soy wax emulsions used as carriers for the deer feeding deterrent biopesticide were produced with 20%, 10%, or 5% wax. In order to determine which emulsions were sprayable, all emulsions were sprayed using a standard bottle sprayer onto plants and a wall. Listed in Table 8 are the paraffin and soy wax emulsions that were determined to be sprayable.

Table 8. Sprayablility of deer feeding deterrent paraffin and soy wax emulsions.

Wax (%) (w/w)	Paraffin wax sprayablility	Soy wax sprayability
20	No	No
10	Yes	Yes
5	Yes	Yes

The spray test of the paraffin wax determined that the 20% wax concentration was not sprayable, as seen in Figure 10(a). The emulsion exited the spray nozzle in a thick stream that immediately clumped onto the surface. This emulsion was determined to be too viscous to be sprayed. The 10% and 5% were considered sprayable but clumped onto the surface when sprayed.

The 20% soy wax emulsion clumped onto the surface when sprayed, thus it was considered not sprayable. The 5% soy wax emulsion was sprayable but ran off the surface when sprayed. An optimal spray pattern, as seen in Figure 10(b), was performed by the 10% soy wax emulsion. The emulsion gave an even coverage on the plant surface and a large radius on the wall with little clumping occurring.

(a)

(b)

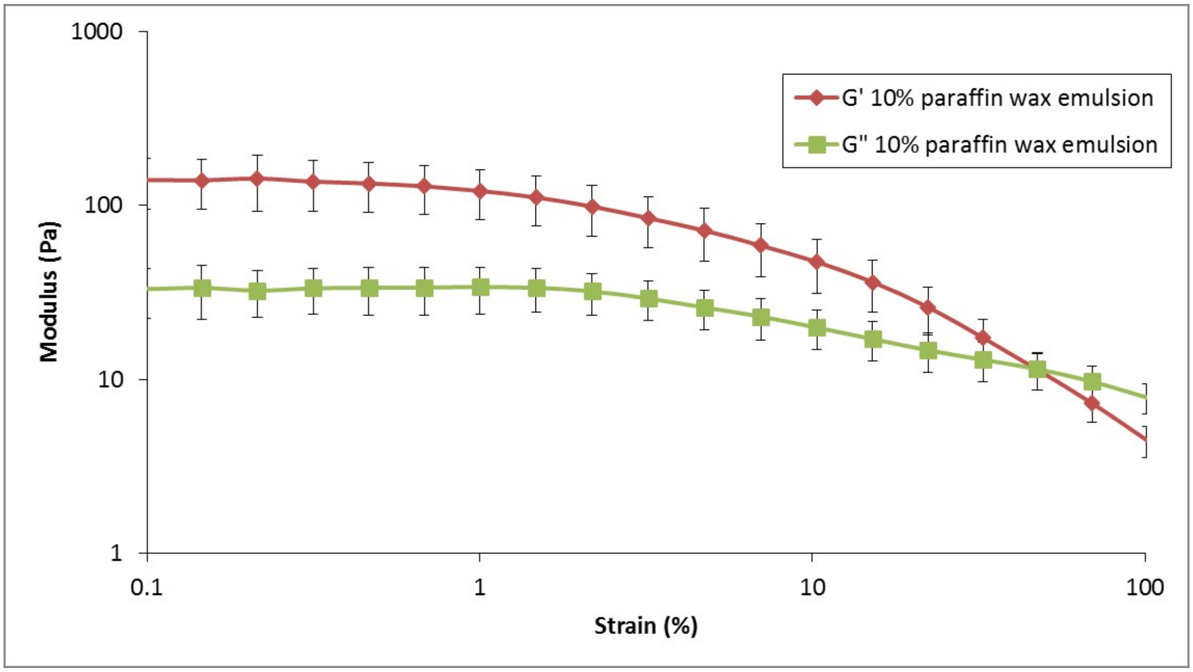
Figure 10. Spray test of (a) 20% paraffin wax deer feeding deterrent emulsion and (b) 10% soy wax deer feeding deterrent emulsion.

5.2 Rheological Properties

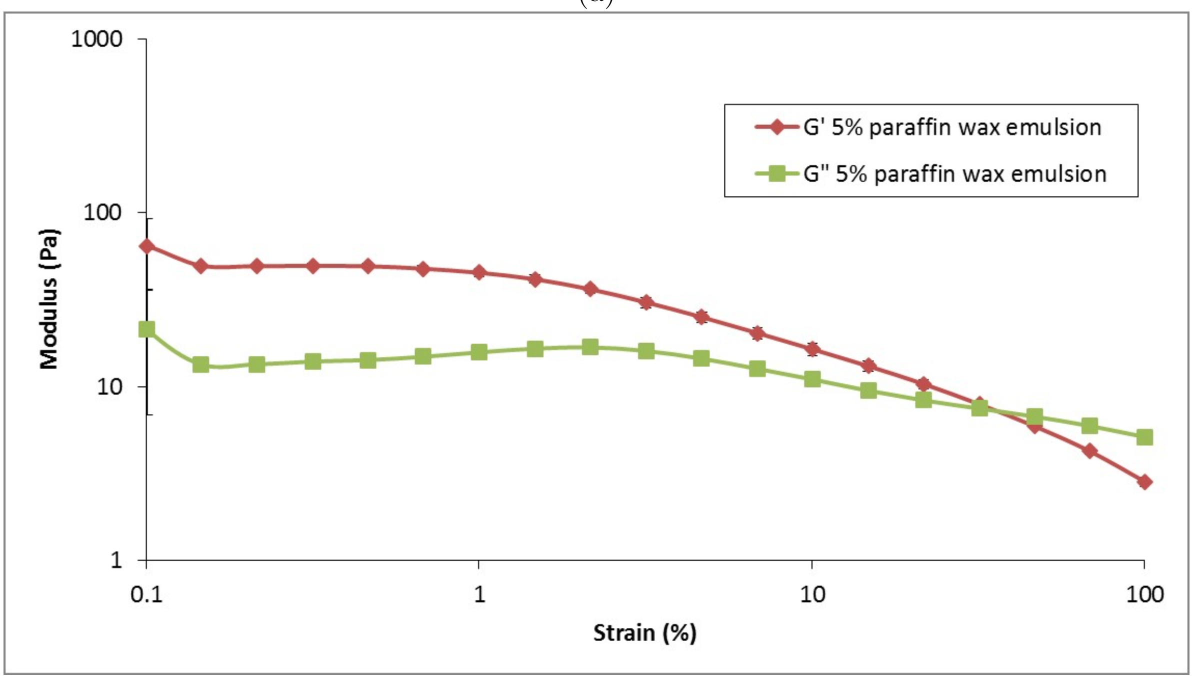
In order to characterize the rheological properties of the sprayable deer feeding deterrent emulsions, the paraffin wax concentrations of 10% and 5% were produced in triplicate and measured using the amplitude sweep and flow curve. The soy wax concentrations of 10% and 5% were produced in triplicate and measured using the amplitude sweep and flow curve.

5.2.1 Amplitude Sweep

The averaged amplitude sweep diagrams for the 10% and 5% paraffin wax emulsions are displayed in Figure 11. The averaged τ_y, γ_L, and τ_f values, found through the oscillatory amplitude sweep, for the 10% and 5% paraffin wax emulsions used as carriers for the deer feeding deterrent biopesticide are listed in Table 9.



(a)



(b)

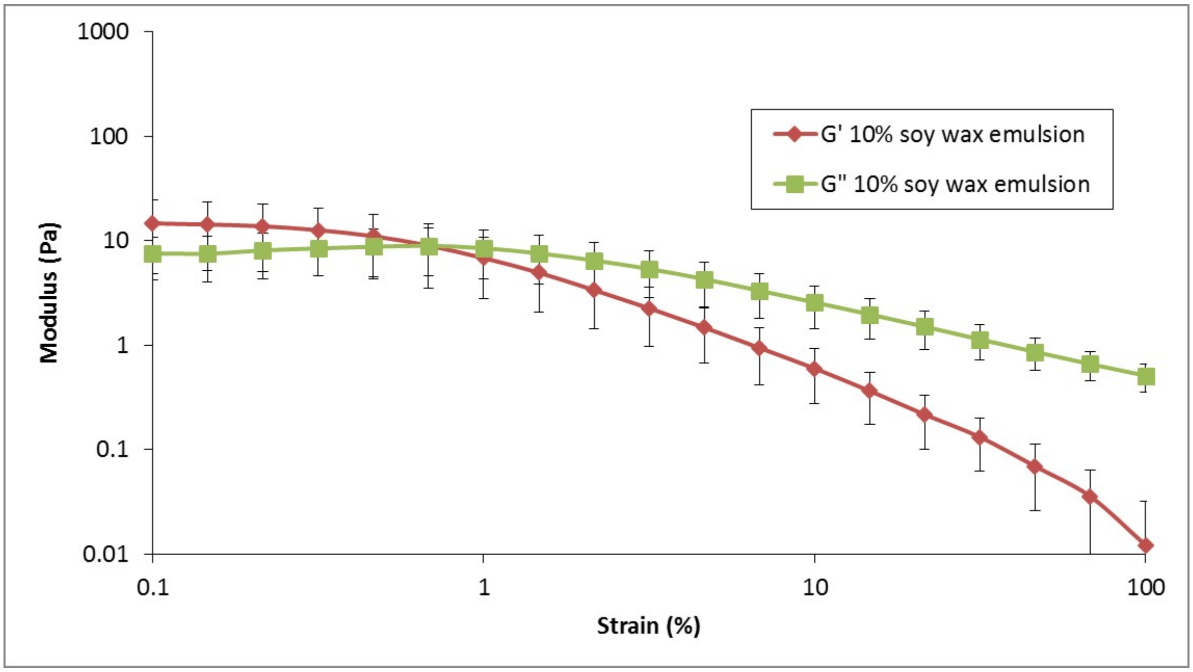
Figure 11. Amplitude sweep for (a) 10% paraffin wax emulsion and (b) 5% paraffin wax emulsion taken at 25 °C.

Table 9. Averaged amplitude sweep parameters for 10% and 5% paraffin wax deer feeding deterrent emulsions at 25 °C.

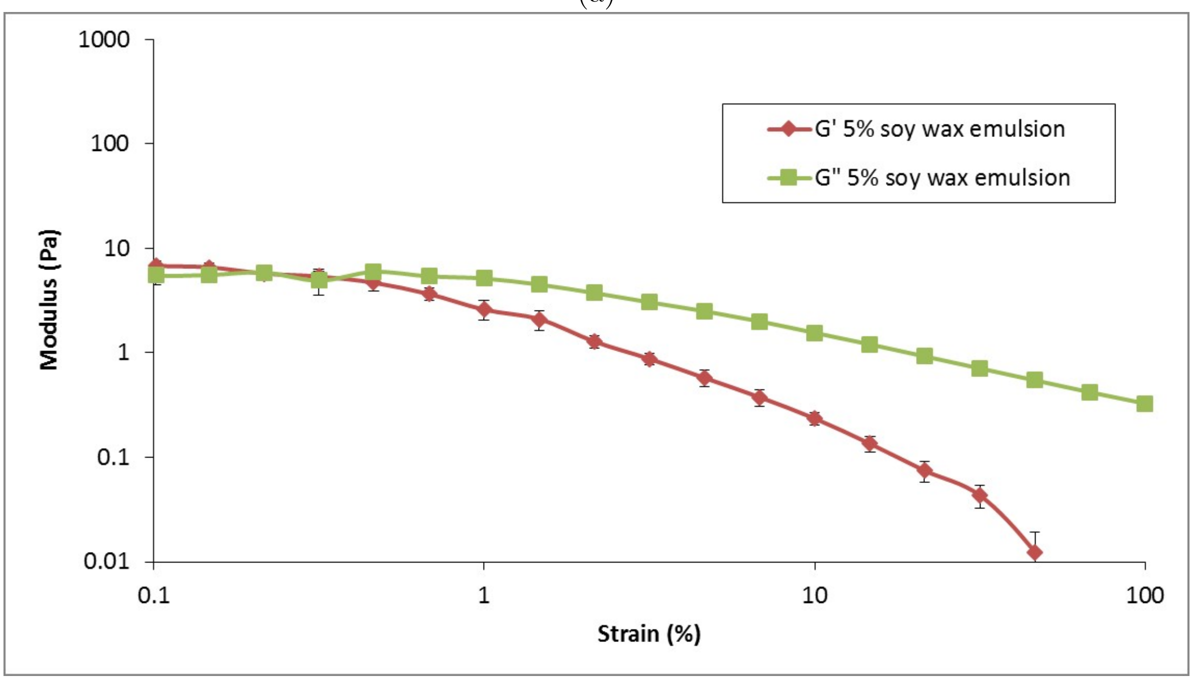
Paraffin wax	Yield point τ_y (Pa)	Limiting value of LVE range γ_L (%)	Flow point τ_f (Pa)
10	8 ± 2	0.3 ± 0.3	12 ± 2
5	3.62 ± 0.02	0.8 ± 0.3	7.3 ± 0.3

Both concentrations of the paraffin wax show gel-like character due to the $G'>G''$ in the LVE range. The γ_L values display no significant difference when the standard deviation is taken into consideration. The γ_L is less than 1% for both paraffin wax emulsions, as expected for materials that posses a network of physical-chemical superstructures typically observed in emulsions.[8] The emulsions' ability to hold a superstructure did not change significantly between the 10% and 5% paraffin wax emulsions. As seen in Table 9, the τ_y and τ_f values decreased as the wax concentration decreased. This indicates a loss in structural strength as the wax concentration decreases, indicating that the strength is dependent upon the amount of wax present in the emulsion.

The averaged amplitude sweep diagrams for the 10% and 5% soy wax emulsions are displayed in Figure 12. Both concentrations of wax used display $G'>G''$ at low strains. The 10% and 5% soy wax emulsions exhibit gel-like behavior at low strains, though they begin to favor liquid behavior as the strain is increased.



(a)



(b)

Figure 12. Amplitude Sweep for (a) 10% soy wax emulsion and (b) 5% soy wax emulsion taken at 25 °C.

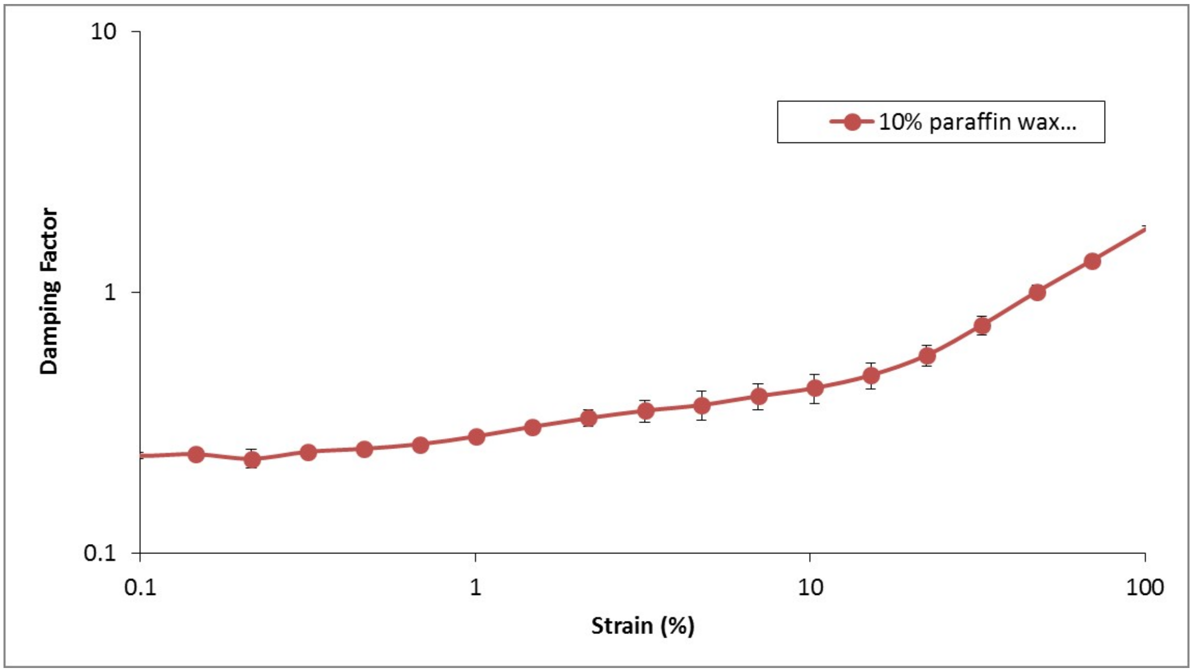
The averaged parameters determined using the oscillatory amplitude sweep for the 10% and 5% soy wax emulsions are listed in Table 10. The γ_L values for the soy wax concentrations are the same within the standard deviation. The γ_L is less than 1% for both soy wax emulsions, as expected for materials that posses a network of physical-chemical superstructures typically observed in emulsions.[8] The τ_y and τ_f values found through the amplitude sweep decreased as the wax concentration decreased, but it did not affect the overall sprayability of these emulsions. The loss in structural strength as the wax concentration decreases indicates that the strength is dependent upon the amount of wax present in the emulsion.

Table 10. Averaged amplitude sweep parameters for 10% and 5% soy wax deer feeding deterrent emulsions at 25 °C.

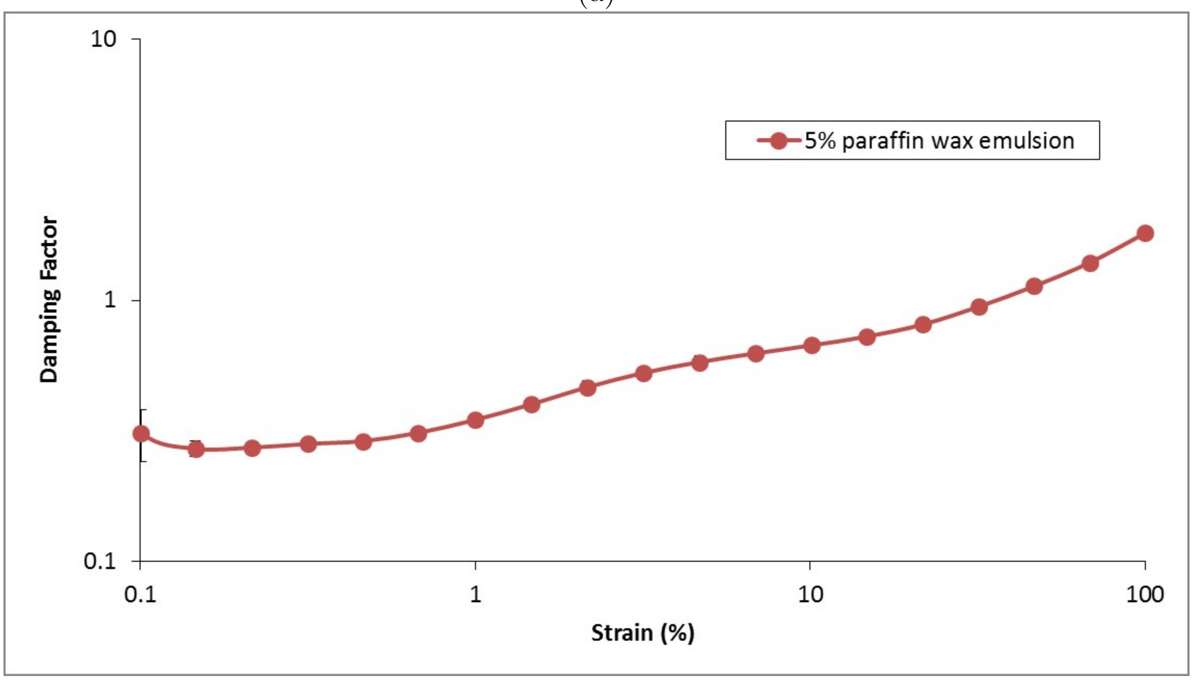
Soy wax	Yield point τ_y (Pa)	Limiting value of LVE range γ_L (%)	Flow point τ_f (Pa)
10	0.13 ± 0.02	0.09 ± 0.06	11 ± 2
5	0.021 ± 0.009	0.14 ± 0.08	5.6 ± 0.4

5.2.2 Damping Factor

The damping factors for the 10% and 5% paraffin wax emulsions were averaged and plotted with error bars to verify the reproducibility of each in Figure 13. In these diagrams, $\tan\delta$ is less than one until high strains are applied. This behavior indicates stable solid state behavior over a large range of strains.



(a)



(b)

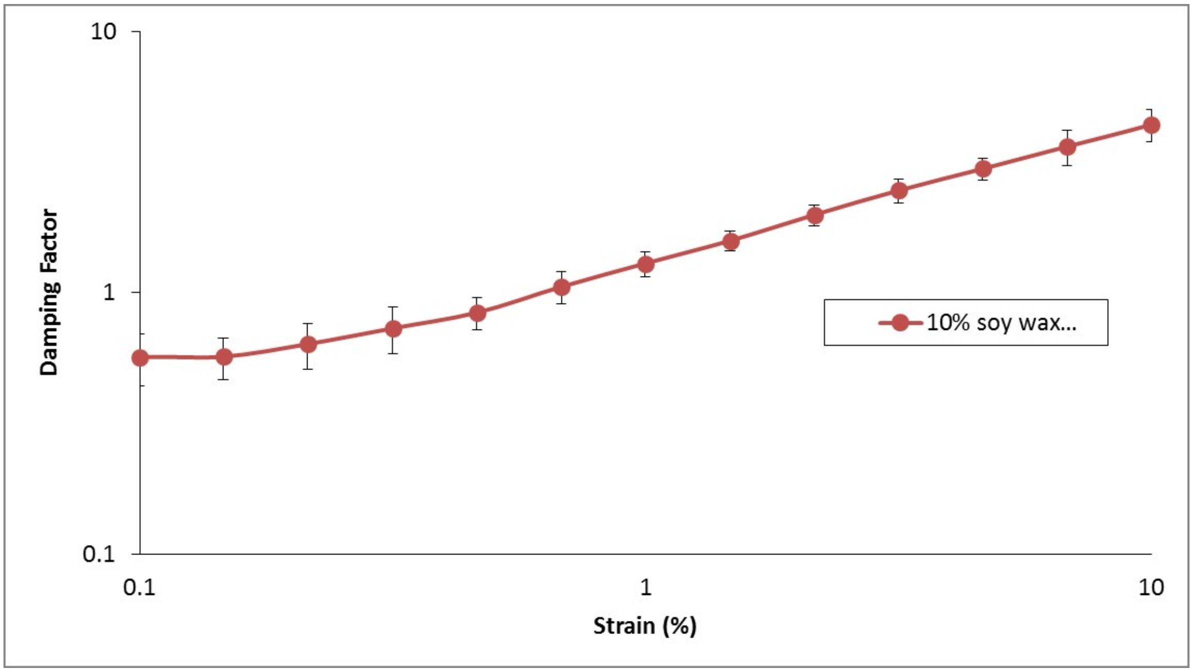
Figure 13. Damping factor for (a) 10% paraffin wax emulsion and (b) 5% paraffin wax emulsion taken at 25°C.

The range from 0.1% to 0.22% strain is the range before the plateau begins to deviate. The averaged damping factors ($\tan\delta$) in this range for the 10% and 5% paraffin wax emulsions are displayed in Table 11. There is little difference in the averaged $\tan\delta$ values. These emulsions exhibit $\tan\delta<1$, indicating stable solid state behavior at low or resting conditions.

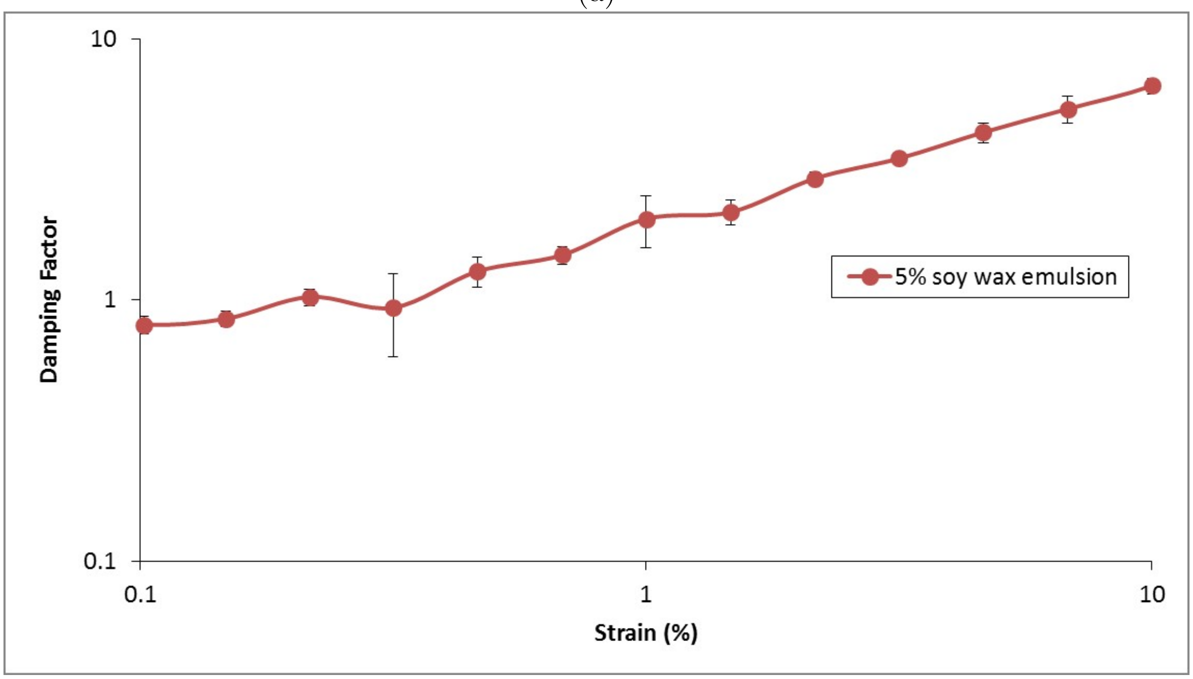
Table 11. Averaged damping factor from 0.1% to 0.22% strain for 10% and 5% paraffin wax deer feeding deterrent emulsions at 25 °C.

Paraffin wax (%) (w/w)	$\tan\delta$
10	0.236 ± 0.004
5	0.28 ± 0.02

The damping factor values for the 10% and 5% soy wax emulsions were averaged and plotted with error bars to display the reproducibility of each in Figure 14.



(a)



(b)

Figure 14. Damping factor for (a) 10% soy wax emulsion and (b) 5% soy wax emulsion taken at 25 °C.

The averaged damping factors ($\tan\delta$) from 0.1% to 0.22% strain for the 10% and 5% soy wax emulsions are displayed in Table 12. The $\tan\delta$ values show that both emulsions are stable, with $\tan\delta<1$.

Table 12. Averaged damping factor from 0.1% to 0.22% strain for 10% and 5% soy wax deer feeding deterrent emulsions at 25 °C.

Soy wax (%) (w/w)	$\tan\delta$
10	0.6 ± 0.1
5	0.90 ± 0.04

5.2.3 Flow Curve

The viscosity curve diagrams of the 10% and 5% paraffin wax emulsions produced from the flow curve measurement were fit with the averaged Herschel-Bulkley regression parameters and displayed in Figure 15. The data collected from the flow curve measurement (without the fit) for the 10% and 5% paraffin wax emulsions are shown in Appendix D: Figures 31 and 32. As seen in these diagrams, viscosity decreases sharply and plateaus at approximately 20 s^{-1} shear rate. This behavior is seen as shear-thinning, likely caused by droplet deformation.[8] The forces applied cause the droplets to deform, resulting in an increase in flow as the material approaches Newtonian behavior.[13]

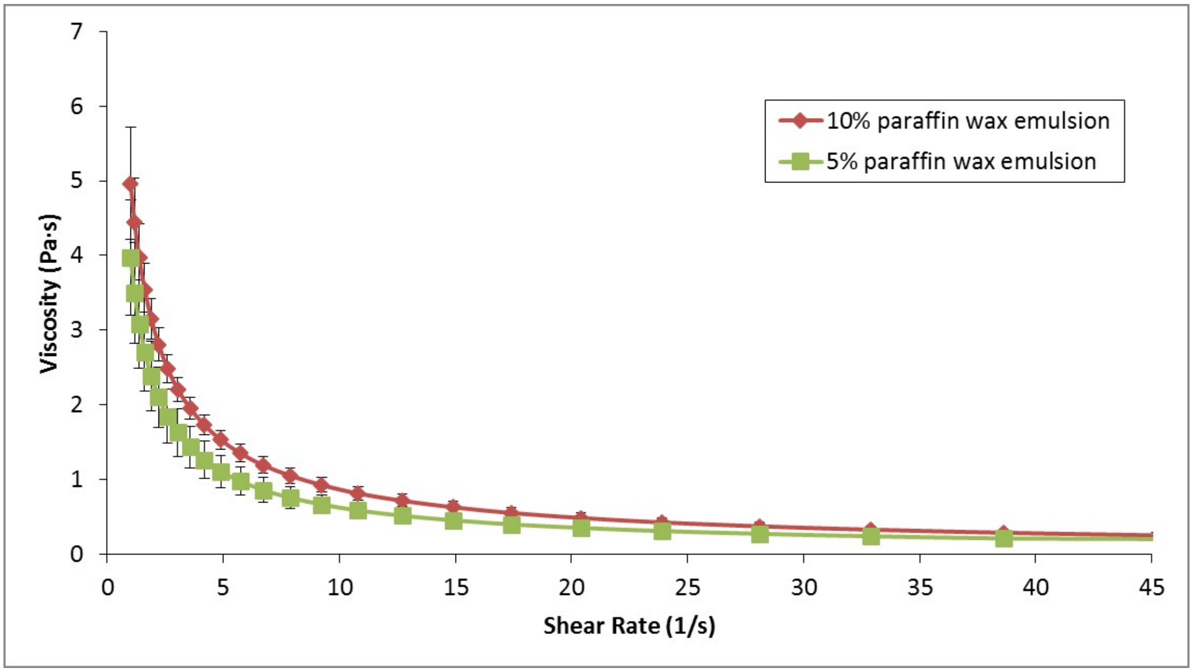


Figure 15. Herschel-Bulkley fitted viscosity curve for 10% and 5% paraffin wax emulsions taken at 25 °C.

The averaged Herschel-Bulkley regression parameters for the 10% and 5% paraffin wax emulsions are displayed in Table 13. The viscosity at a shear rate of 1 s^{-1} decreases as the wax concentration decreases, indicating less viscous behavior for emulsions with less wax concentrations. The Herschel/Bulkley index indicates the emulsions exhibit shear-thinning behavior ($p<1$). The correlation ratio is a value that represents how well the Herschel-Bulkley regression fits the actual plot. The 10% and 5% paraffin wax emulsions correlation ratio values are very close to one, indicating an accurate Herschel-Bulkley regression fit.

Table 13. Average Herschel-Bulkley viscosity curve parameters for 10% and 5% of paraffin wax deer feeding deterrent emulsions at 25 °C.

Paraffin wax	Viscosity η (Pa $\cdot$ s)	Herschel/Bulkley index p	Correlation ratio r^2
10	5.0 ± 0.8	0.04 ± 0.05	0.96 ± 0.03
5	4.0 ± 0.8	0.19 ± 0.04	0.9993 ± 0.0002

The data collected through the flow curve measurement was plotted as a viscosity curve and fitted with the Herschel-Bulkley, or Herschel/Bulkley, regression fit. These diagrams are displayed in Figure 16 for the 10% and 5% soy wax emulsions. The viscosity curve without the fit for the 10% and 5% soy wax emulsions are shown in Appendix D: Figures 31 and 32.

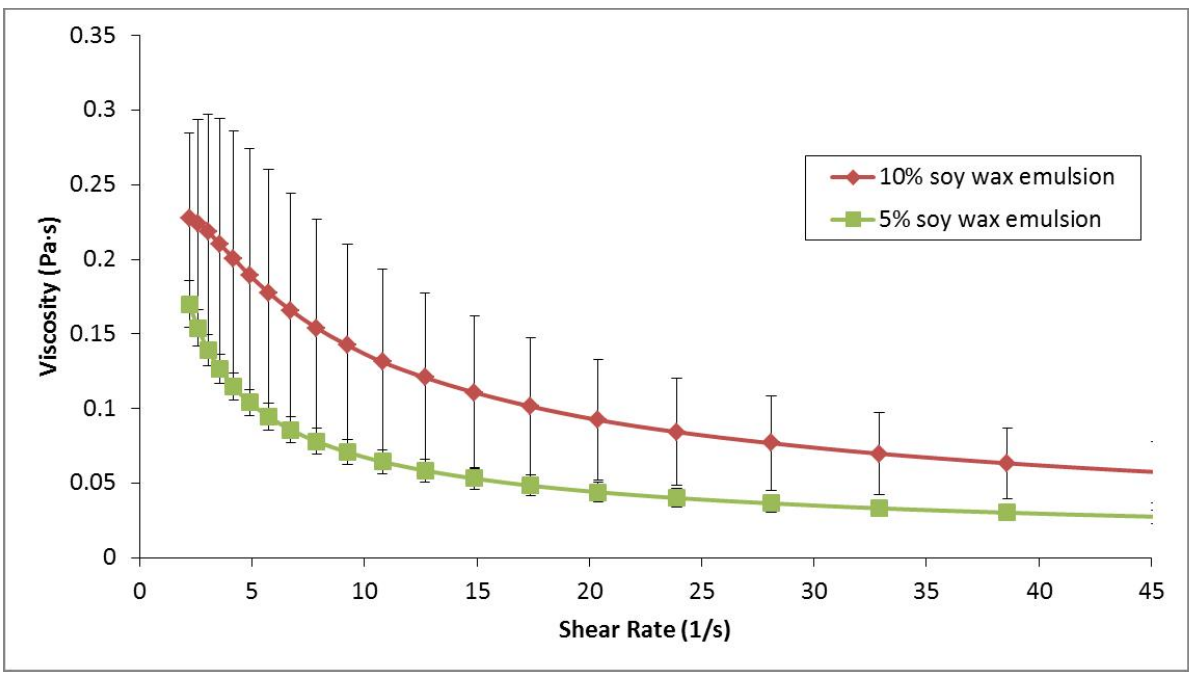


Figure 16. Herschel-Bulkley fitted viscosity curve for 10% and 5% soy wax emulsions taken at 25 °C.

The averaged Herschel-Bulkley regression parameters for the 10% and 5% soy wax emulsions are displayed in Table 14. The average viscosity at a shear rate of 1 s^{-1} decreases as the wax concentration decreases, but the values are not significantly different. The Herschel/Bulkley index values for these wax emulsions are less than one, indicating shear-thinning behavior. The average correlation ratio for each emulsion displays a value approximately one, indicating an accurate Herschel-Bulkley fit of the data.

Table 14. Average Herschel-Bulkley viscosity curve parameters for 10% and 5% soy wax deer feeding deterrent emulsions at 25 °C.

Soy wax	Viscosity η (Pa $\cdot$ s)	Herschel/Bulkley index p	Correlation ratio r^2
10	0.23 ± 0.06	0.3 ± 0.3	0.998 ± 0.002
5	0.17 ± 0.02	0.44 ± 0.06	0.996 ± 0.001

CHAPTER 6: CONCLUSIONS

6.1 Insect Pheromone Wax Emulsions

The rheology of 30% paraffin and soy wax emulsions with Span60® and TEA stearate, respectively, for the controlled release of geranyl propionate was evaluated using the amplitude sweep, damping factor, frequency sweep, and flow curve tests performed using a Physica MCR 101 rheometer. Both waxes proved to be suitable for use and exhibit gel-like structures as well as ideal dispersion behavior, as determined by the amplitude sweep measurement.

In the oscillatory amplitude sweep, both emulsions display a gel-like network of physical-chemical superstructures that easily breaks down under strain. The paraffin and soy wax emulsions display $G' > G''$ at low strain values, indicating gel-like behavior. The $\tan\delta$ of these emulsions also indicates stable solid state behavior. The yield and flow points show no significant difference between paraffin and soy wax emulsions.

In the frequency sweep, the paraffin and soy wax emulsions exhibit elastic-solid behavior. The soy wax emulsion displays a relatively linear plot of G' and G'' without intersecting as the frequency is increased, indicating a longer shelf-stability and stability under high shear. The paraffin wax emulsion exhibited an intersection of G' and G'', indicating shorter shelf-stability.

The viscosity curve derived from the rotational flow curve measurement displayed shear-thinning behavior for both wax emulsions. The shear-thinning behavior is common for emulsions due to waxes displaying solid-like behavior at resting conditions at room temperature. The soy wax emulsions displayed higher viscosities at a shear rate of 1 s^{-1} when compared to the paraffin wax emulsions.

When comparing the emulsions made with soy wax or paraffin wax, there were no significant advantages or disadvantages to either (with exception of the slightly higher shelf stability and viscosity observed in the soy wax emulsion).

6.2 Deer Feeding Deterrent Wax Emulsions

After preparing emulsions that contain various concentrations of soy or paraffin wax, each was tested for sprayability. It was determined that the 20% paraffin and soy wax emulsions were not sprayable using a standard spray nozzle. However, the 10% soy wax emulsion exhibited the optimal spray behavior.

Through the oscillatory amplitude sweep measurement, it was determined that both the paraffin and soy wax emulsions exhibit $G' > G''$, indicating gel-like behavior. The paraffin and soy wax emulsions exhibit flow points at approximately the same applied strain. Based on the yield and flow points, it was determined that as the wax concentration was decreased, the internal structural strength decreased. However, both types of wax emulsions posses a network of physical-chemical superstructures found in dispersion materials despite the change in wax concentration.[8] In these superstructures, the wax component plays an important role in the frictional interactions that determines the overall strength of the emulsion. The soy wax emulsions exhibit overall lower yield points than the paraffin wax emulsions, meaning that the soy wax emulsion can withstand less strain while maintaining its original structure. The damping factor for both wax emulsions indicated stable solid state behavior, thus indicating that the emulsions are unlikely to separate.

Using the flow curve measurement, the viscosity curve was found and fitted with the Herschel-Bulkley regression parameters to compare the viscosities of the different waxes used to make these emulsions. From the regression fit, the viscosity at a shear rate of 1 s^{-1} was determined. The paraffin and soy wax emulsions exhibited a decrease in viscosity as the wax concentration was decreased. Though, the soy wax emulsion displayed a lower overall viscosity when compared to the paraffin wax emulsion. By observing the Herschel/Bulkley index from the Herschel-Bulkley regression, both emulsions experienced shear-thinning behavior.

The soy wax emulsions exhibit optimal spray behavior when compared to the paraffin wax emulsions. The soy wax emulsions exhibit lower yield points and lower viscosities than than the paraffin wax, making it easier to spray. The rheological properties indicate that the soy wax emulsions can be used with a variety of spray applicators.

CHAPTER 7: FUTURE STUDIES

A future study could be conducted on the insect pheromone wax emulsions by using a controlled shear stress (CSS) flow curve measurement in order to determine the yield point of the emulsions during rotational measurements.

Additionally, a controlled release rate study on the wax emulsions containing spearmint oil could be used to determine how the formulation variables affect the release of the biopesticide.

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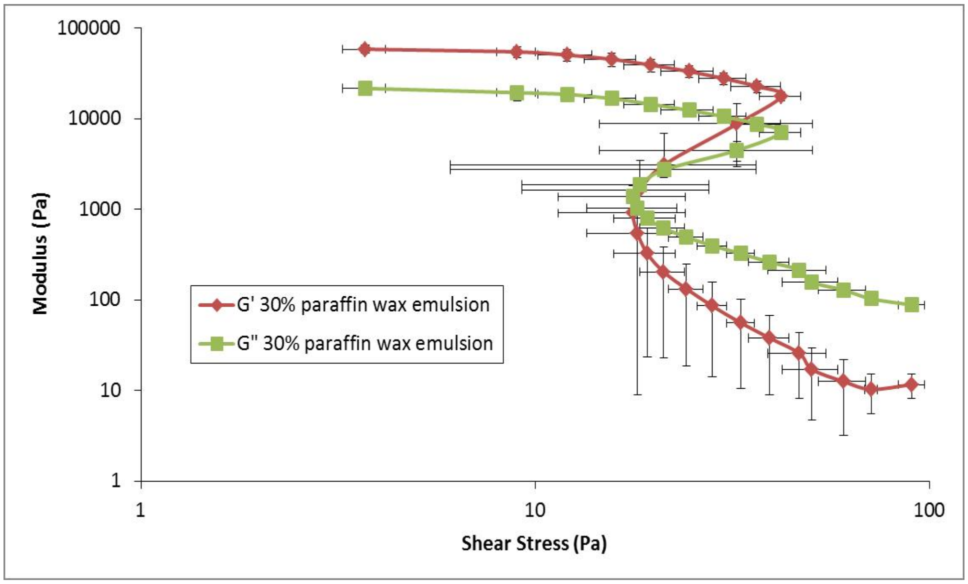
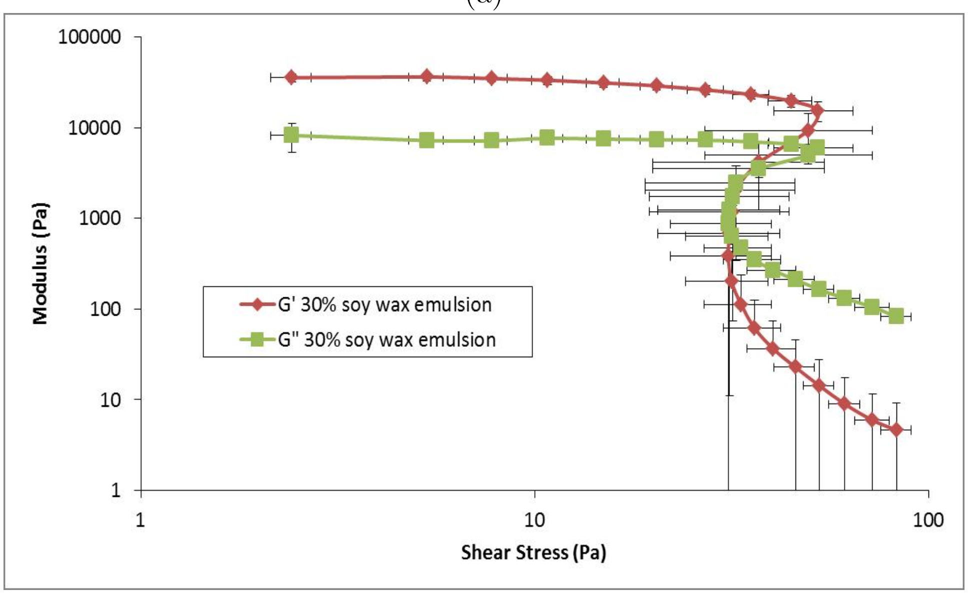
APPENDIX A: AMPLITUDE SWEEP CSS DIAGRAMS

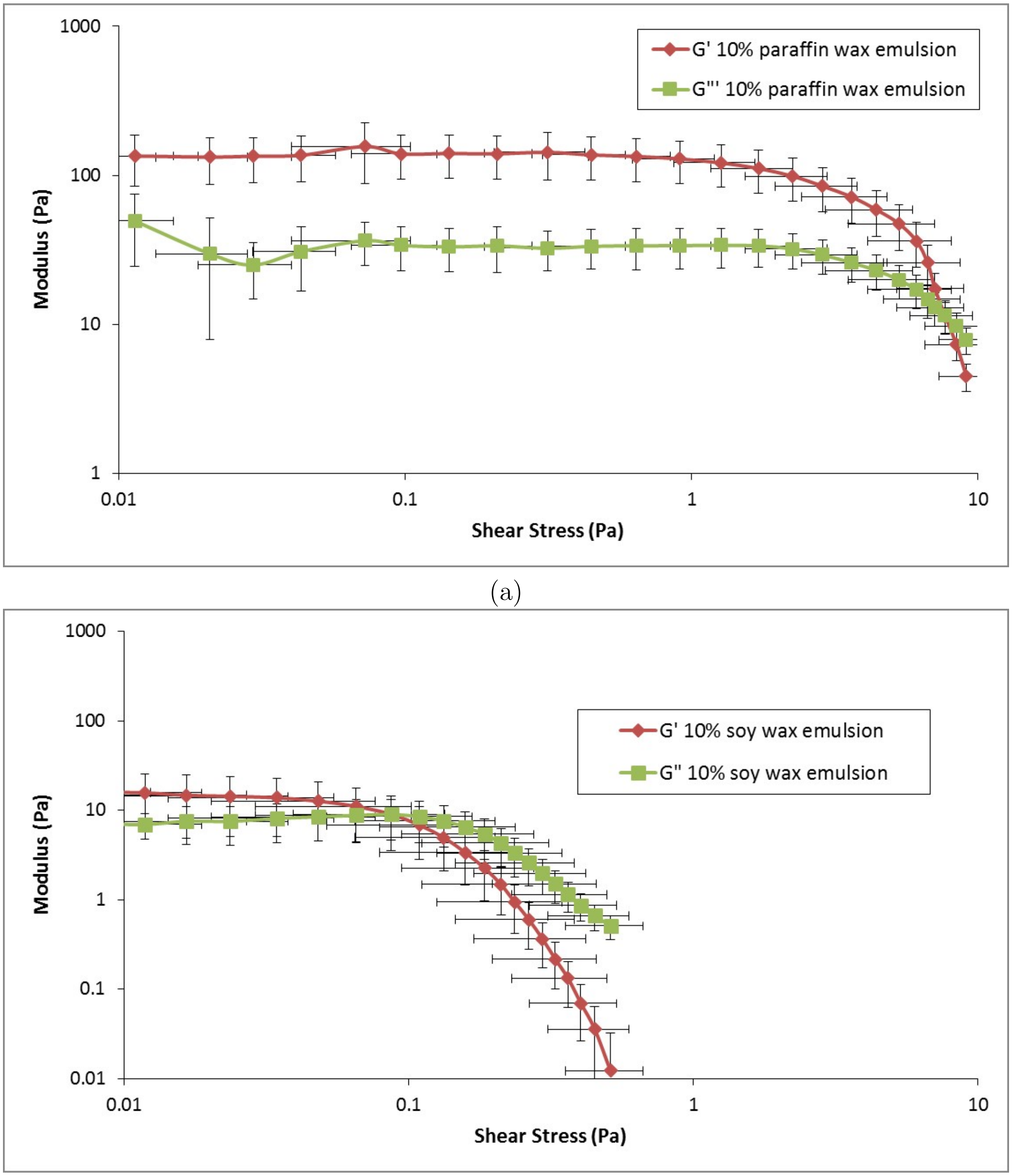


(a)



(b)

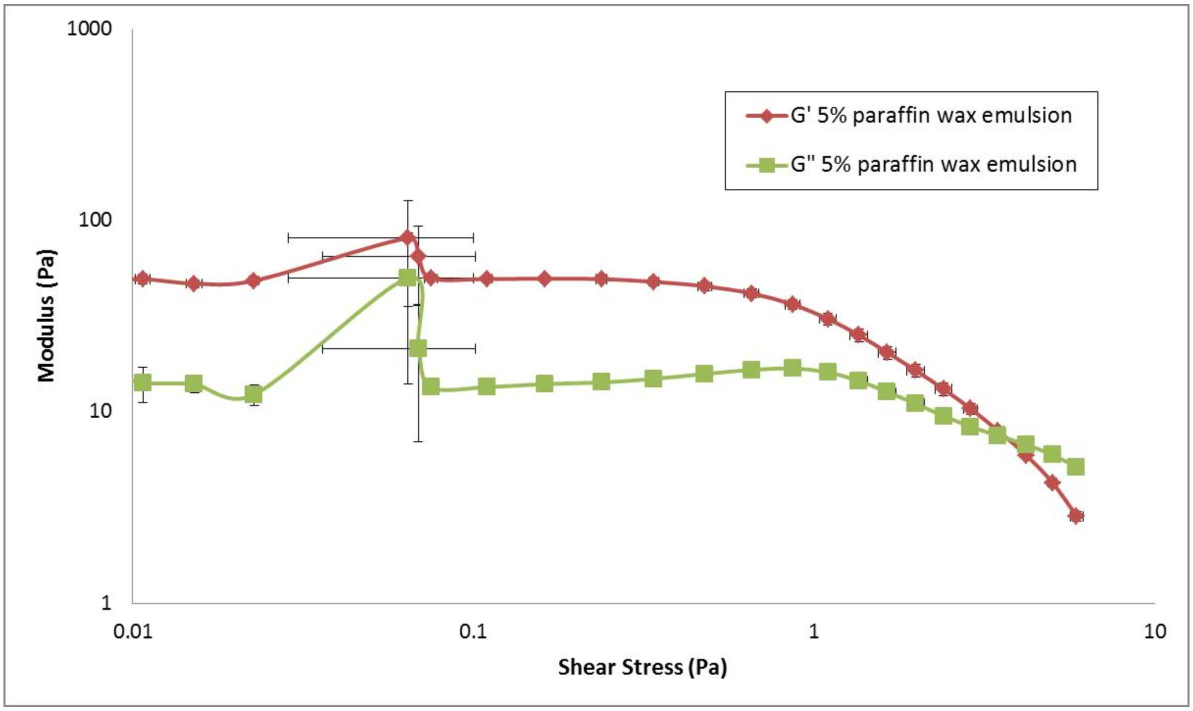
Figure 17. Amplitude sweep (CSS) for (a) 30% paraffin wax insect pheromone emulsion (b) 30% soy wax insect pheromone emulsion taken at 25 °C.



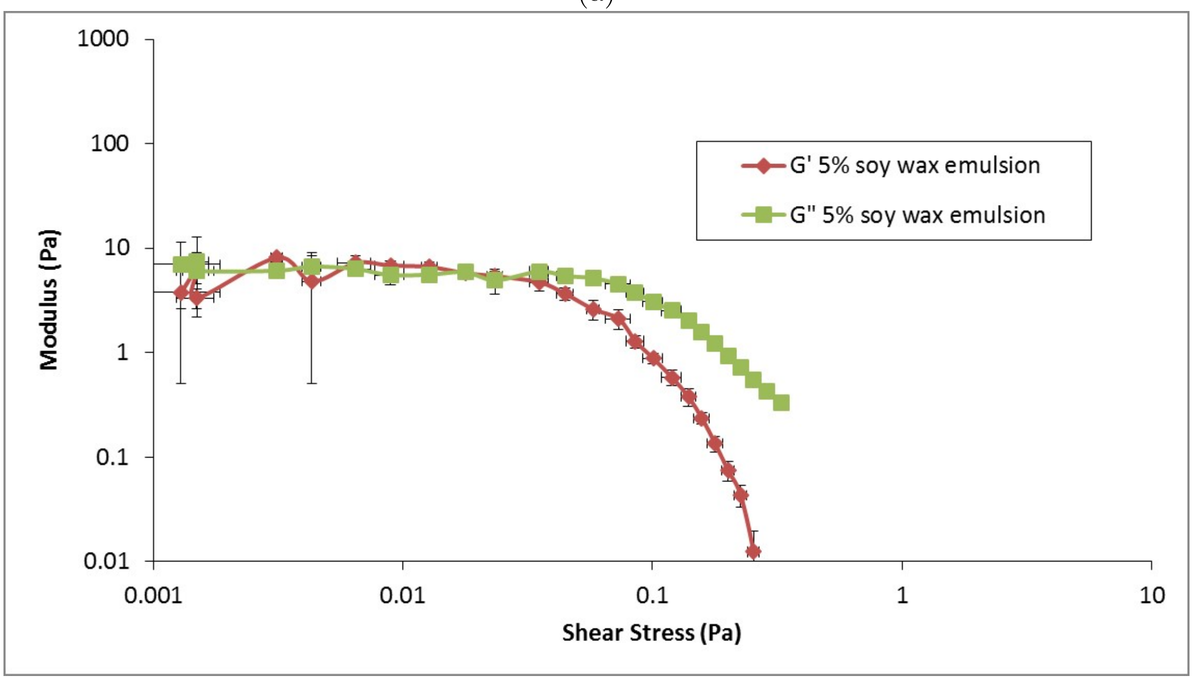
(a)

(b)

Figure 18. Amplitude sweep (CSS) for (a) 10% paraffin wax deer feeding deterrent emulsion and (b) 10% soy wax deer feeding deterrent emulsion taken 25 °C.



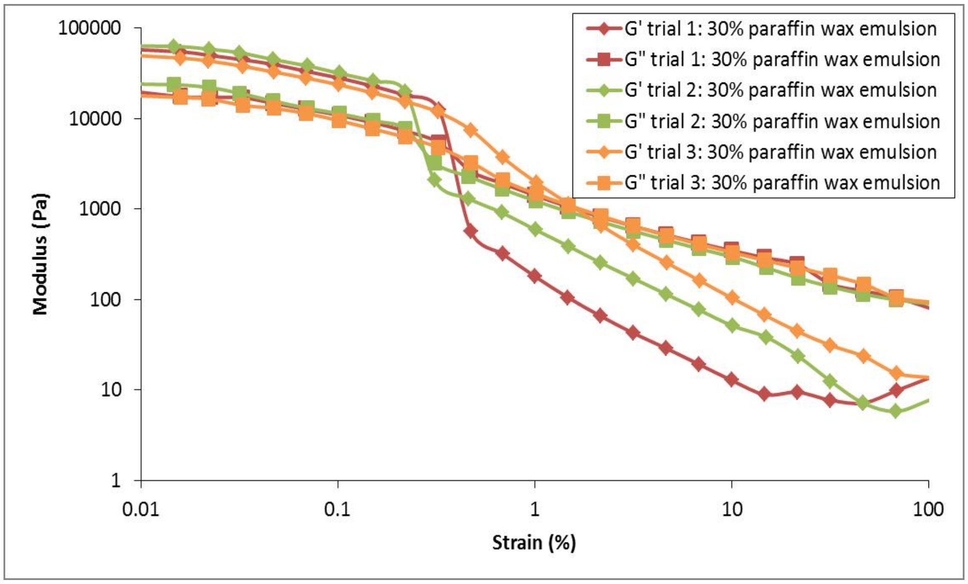
(a)



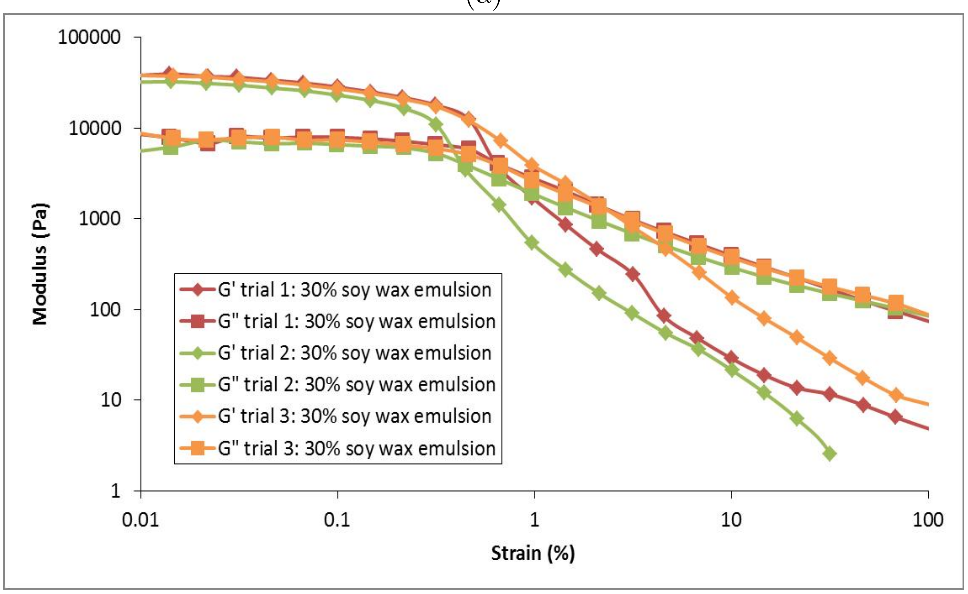
(b)

Figure 19. Amplitude sweep (CSS) for (a) 5% paraffin wax deer feeding deterrent emulsion and (b) 5% soy wax deer feeding deterrent emulsion taken 25 °C

APPENDIX B: INDIVIDUAL AMPLITUDE SWEEP DIAGRAMS

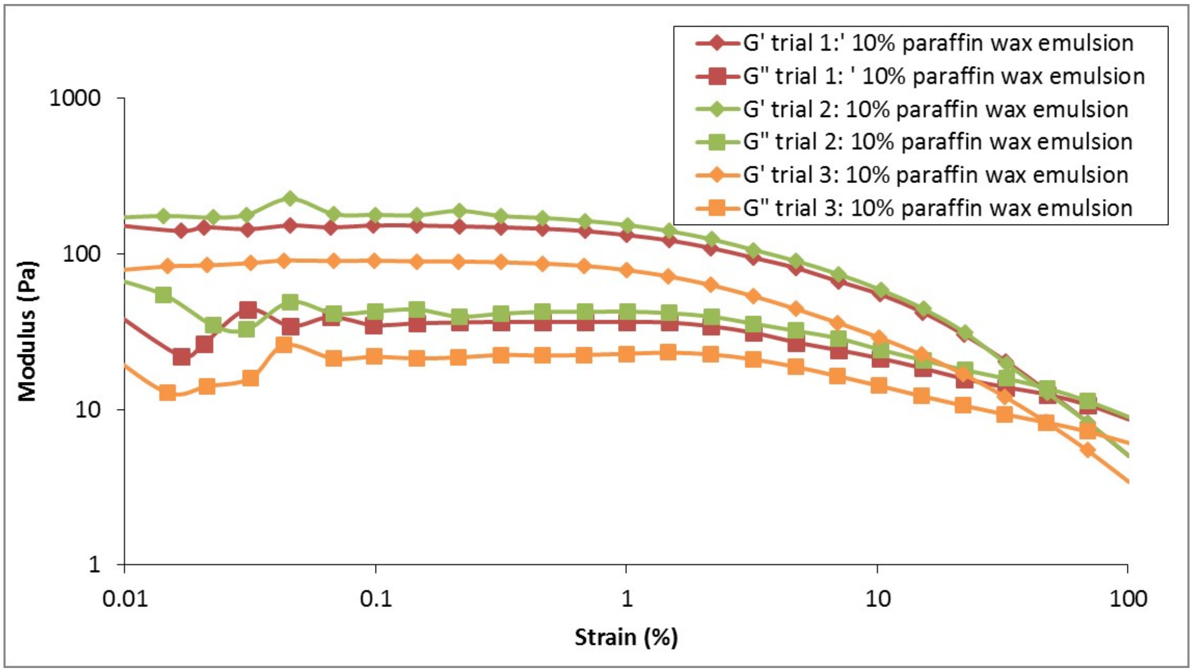


(a)

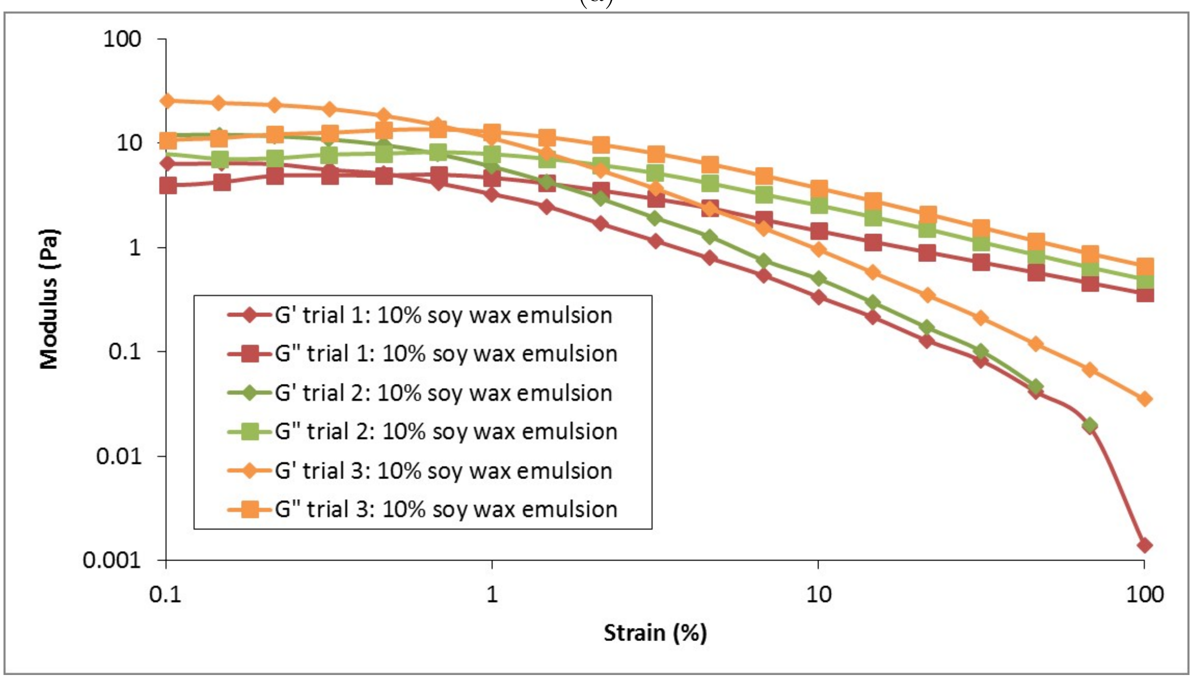


(b)

Figure 20. Individual amplitude sweep for (a) 30% paraffin wax insect pheromone emulsion (b) 30% soy wax insect pheromone emulsion taken at 25 °C.

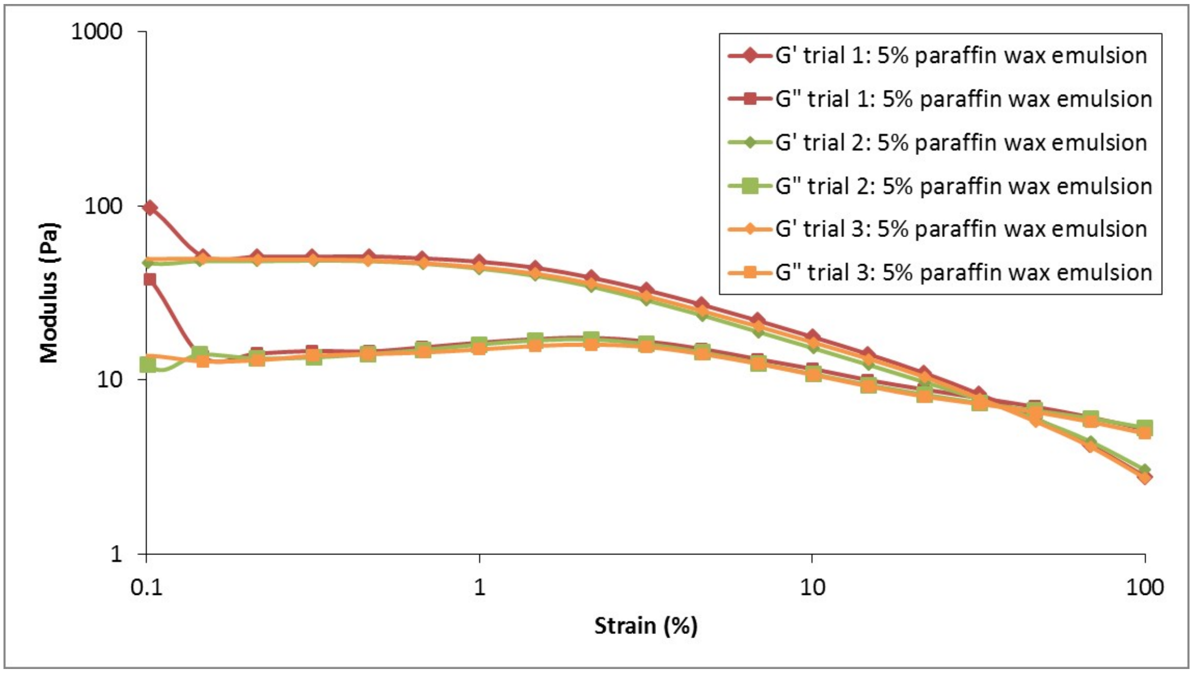


(a)

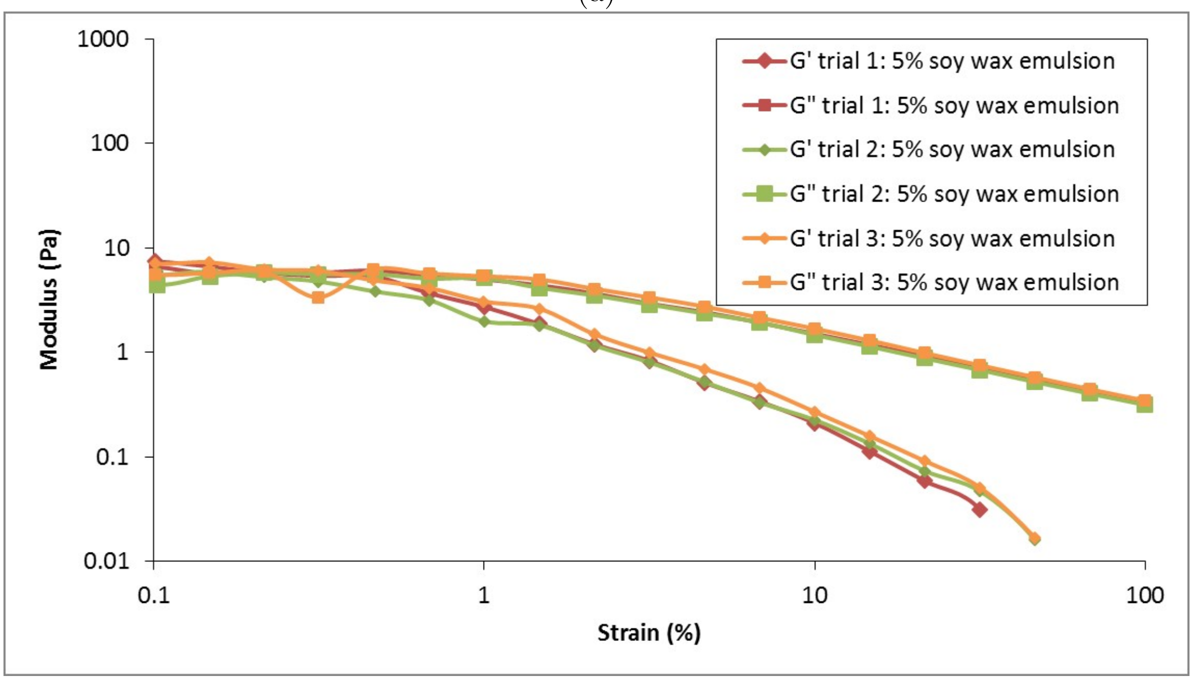


(b)

Figure 21. Individual amplitude sweep for (a) 10% paraffin wax deer feeding deterrent emulsion and (b) 10% soy wax deer feeding deterrent emulsion taken 25 °C.



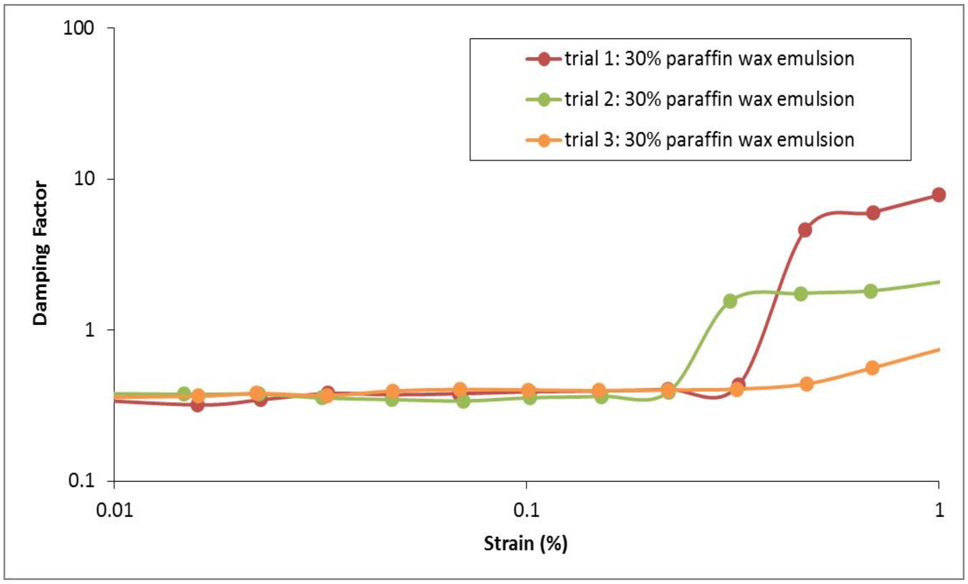
(a)



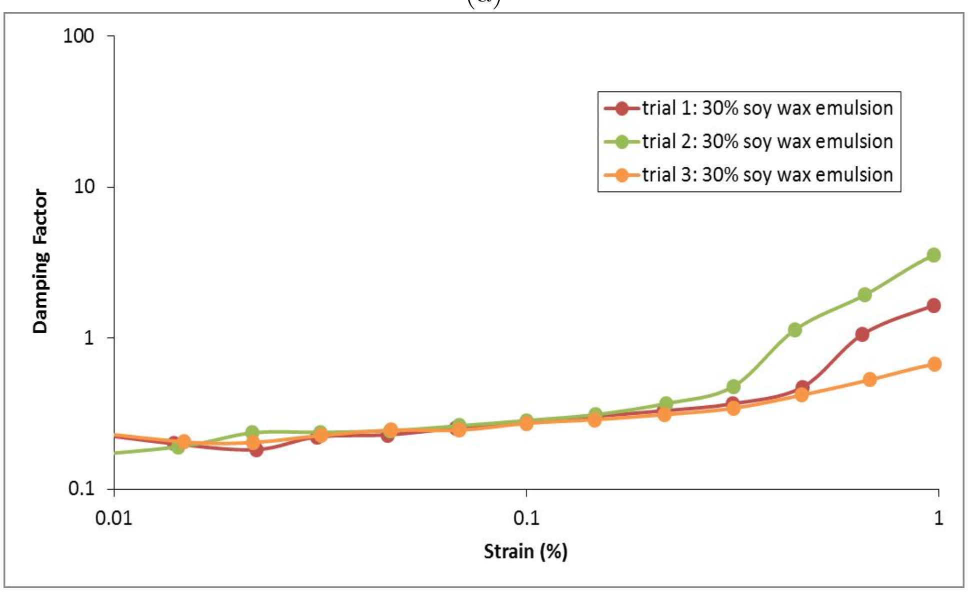
(b)

Figure 22. Individual amplitude sweep for (a) 5% paraffin wax deer feeding deterrent emulsion and (b) 5% soy wax deer feeding deterrent emulsion taken 25 °C.

APPENDIX C: INDIVIDUAL DAMPING FACTOR DIAGRAMS

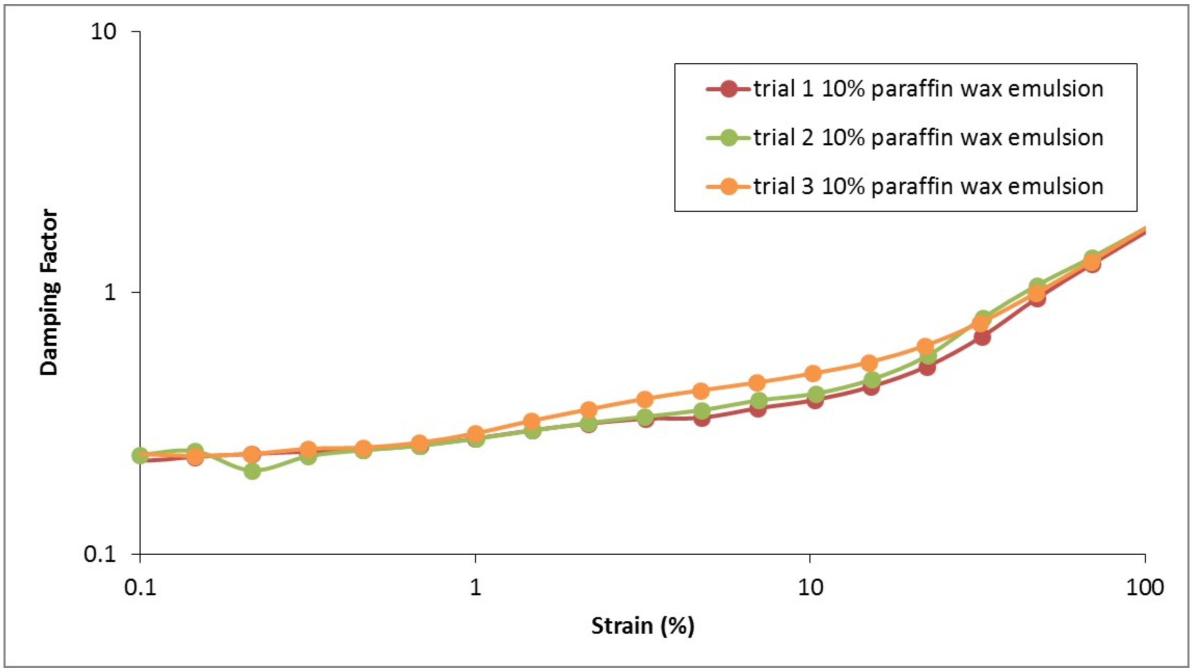


(a)

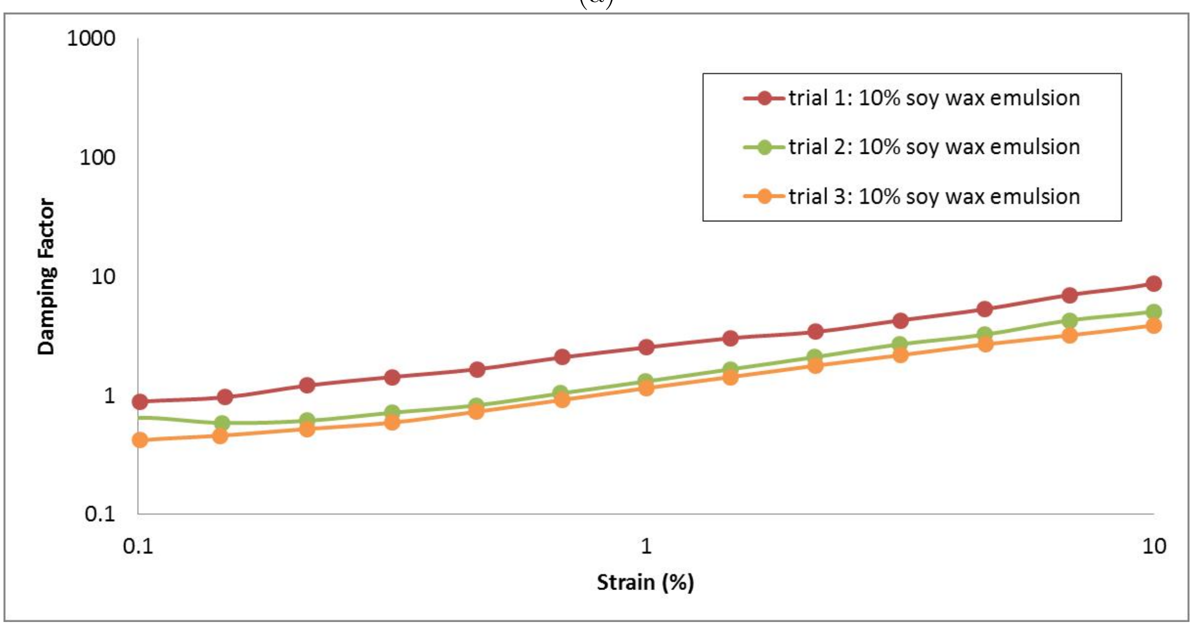


(b)

Figure 23. Individual damping factor for (a) 30% paraffin wax insect pheromone emulsion (b) 30% soy wax insect pheromone emulsion taken at 25 °C.

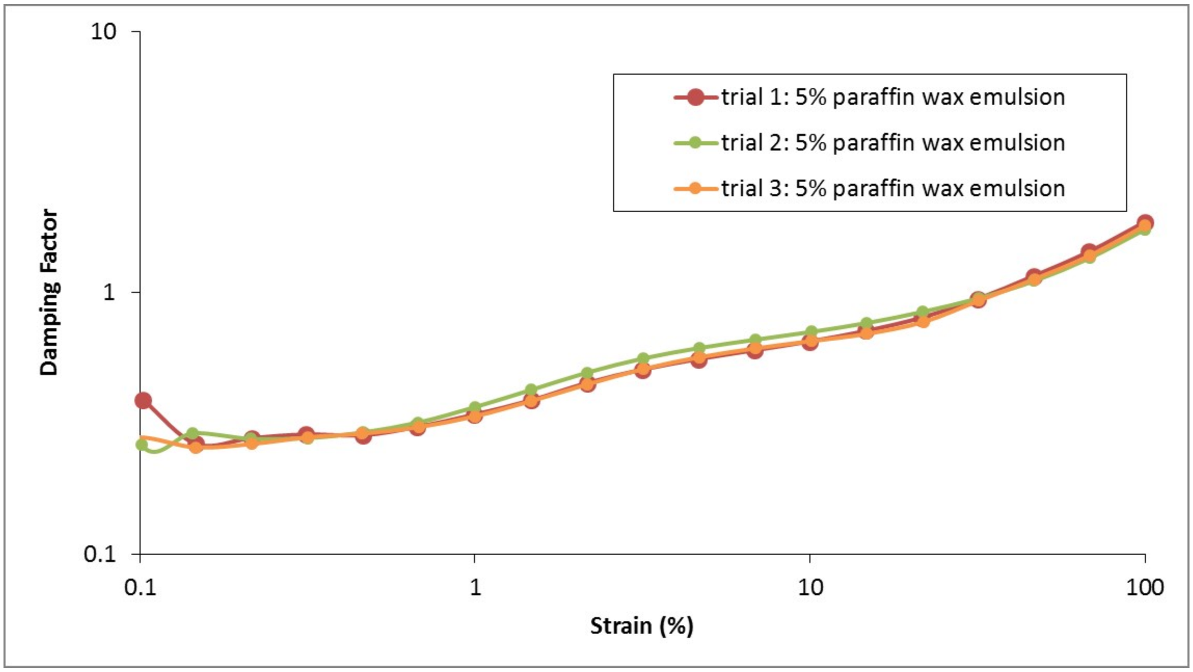


(a)

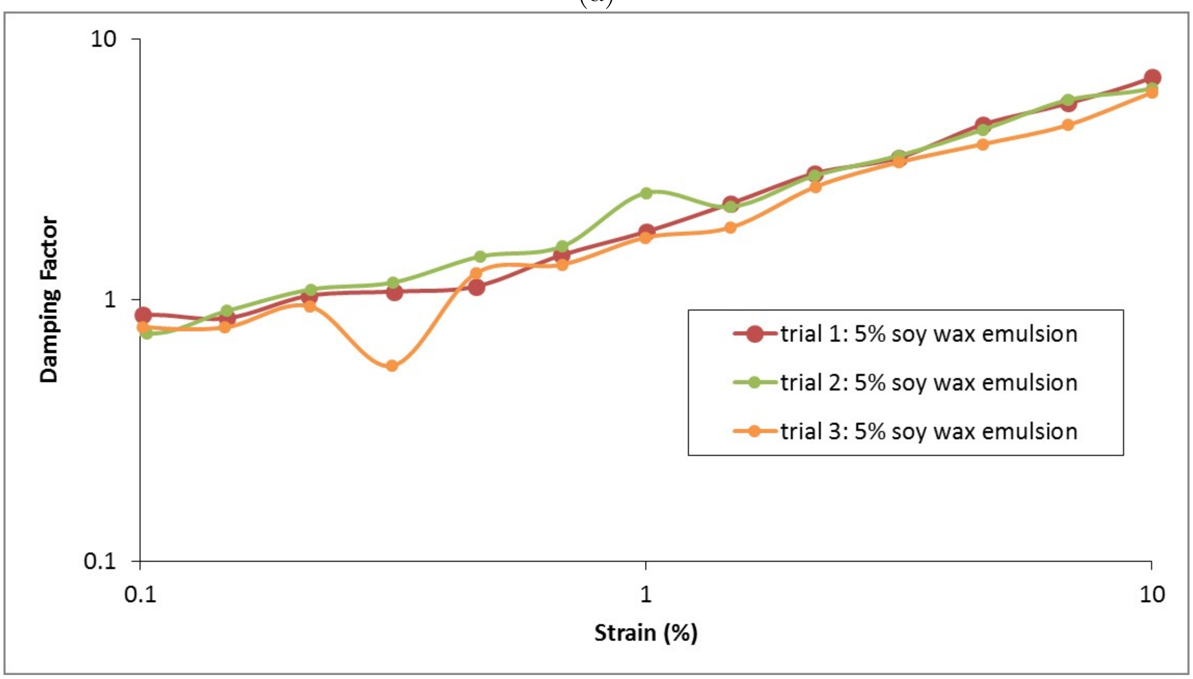


(b)

Figure 24. Individual damping factor for (a) 10% paraffin wax deer feeding deterrent emulsion and (b) 10% soy wax deer feeding deterrent emulsion taken 25 °C.



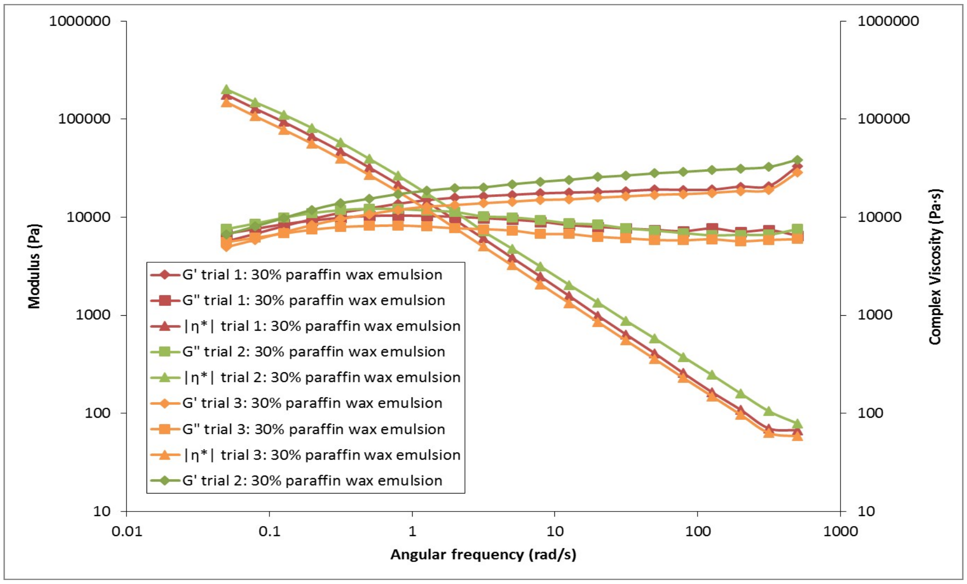
(a)



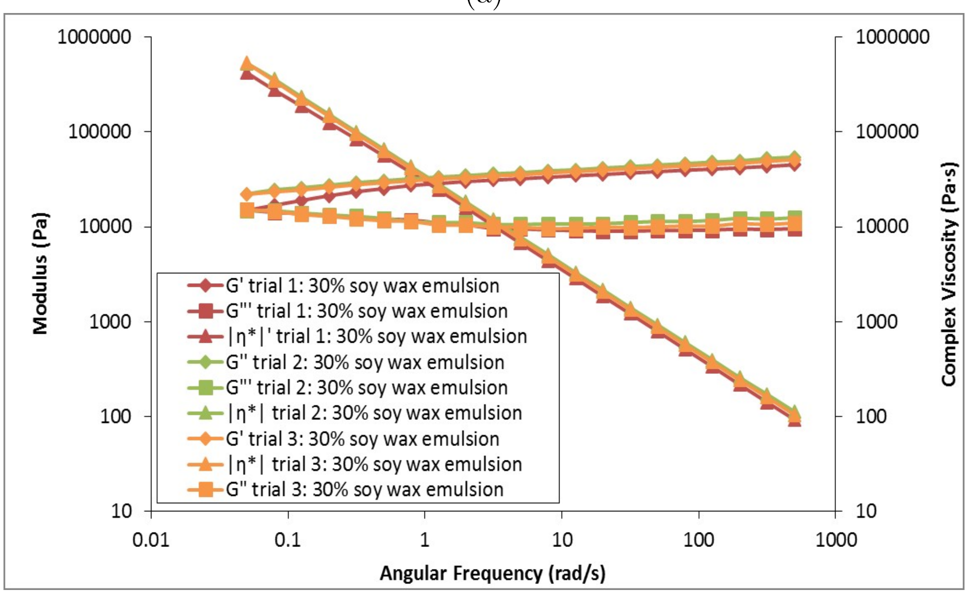
(b)

Figure 25. Individual damping factor for (a) 10% paraffin wax deer feeding deterrent emulsion and (b) 10% soy wax deer feeding deterrent emulsion taken 25 °C.

APPENDIX D: INDIVIDUAL FREQUENCY SWEEP DIAGRAMS



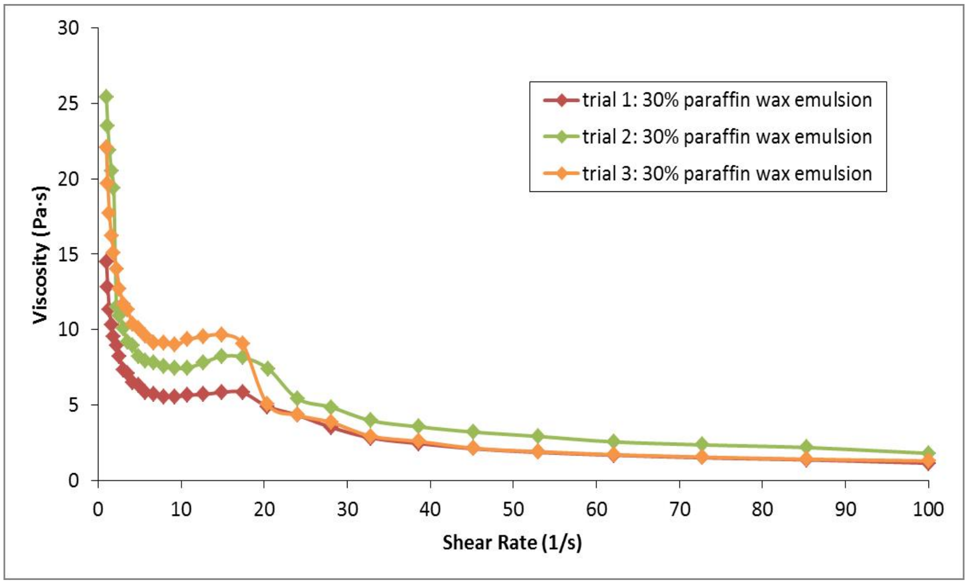
(a)



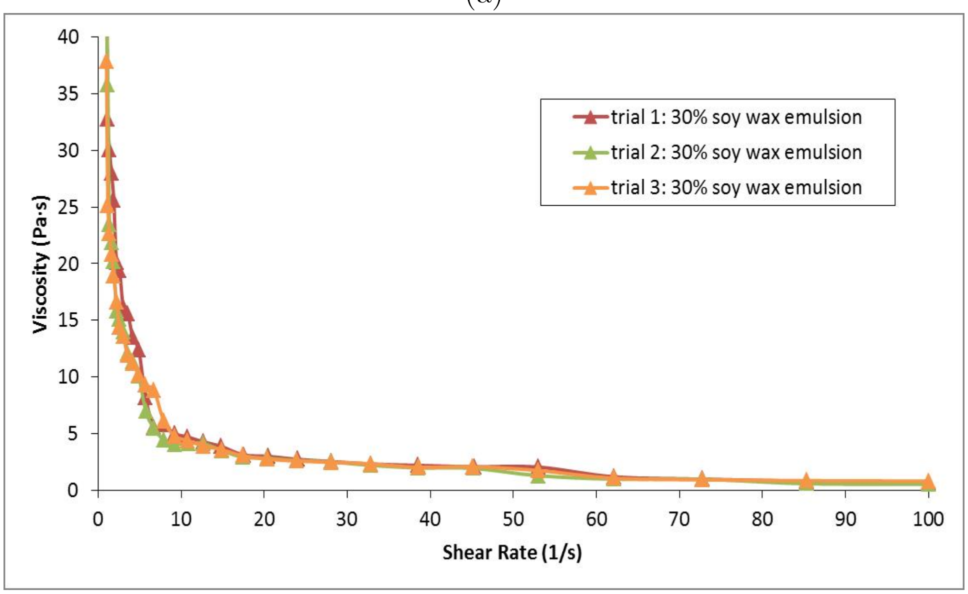
(b)

Figure 26. Individual frequency sweep for (a) 30% paraffin wax insect pheromone emulsion (b) 30% soy wax insect pheromone emulsion taken at 25 °C.

APPENDIX E: INDIVIDUAL VISCOSITY CURVE DIAGRAMS

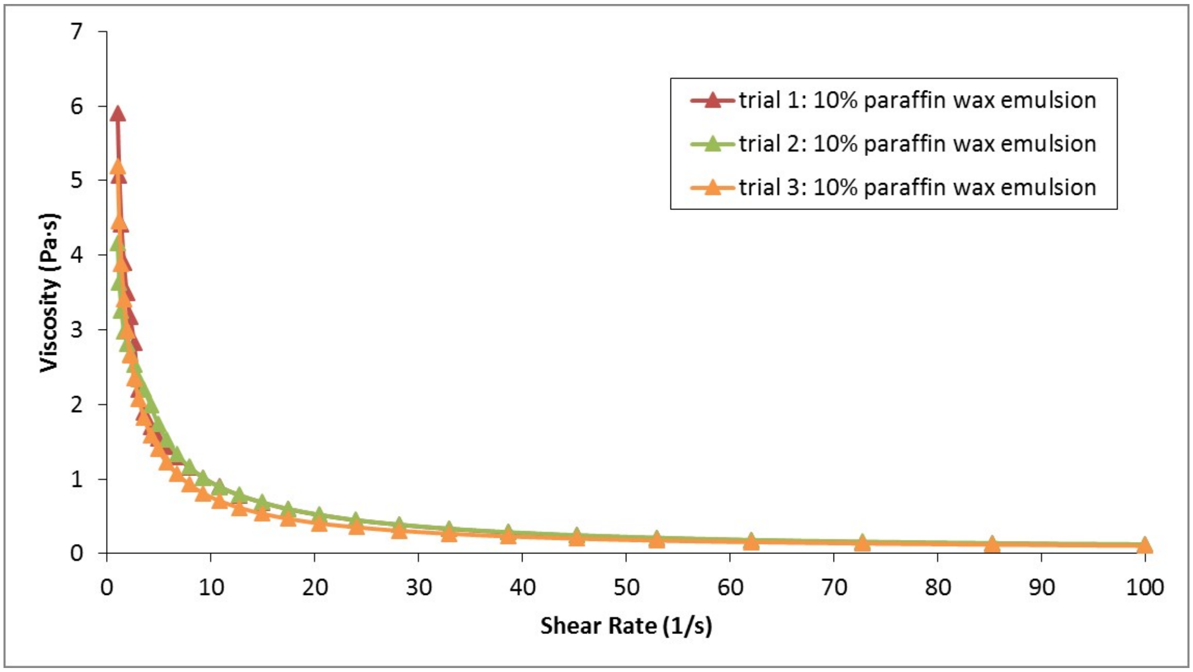


(a)

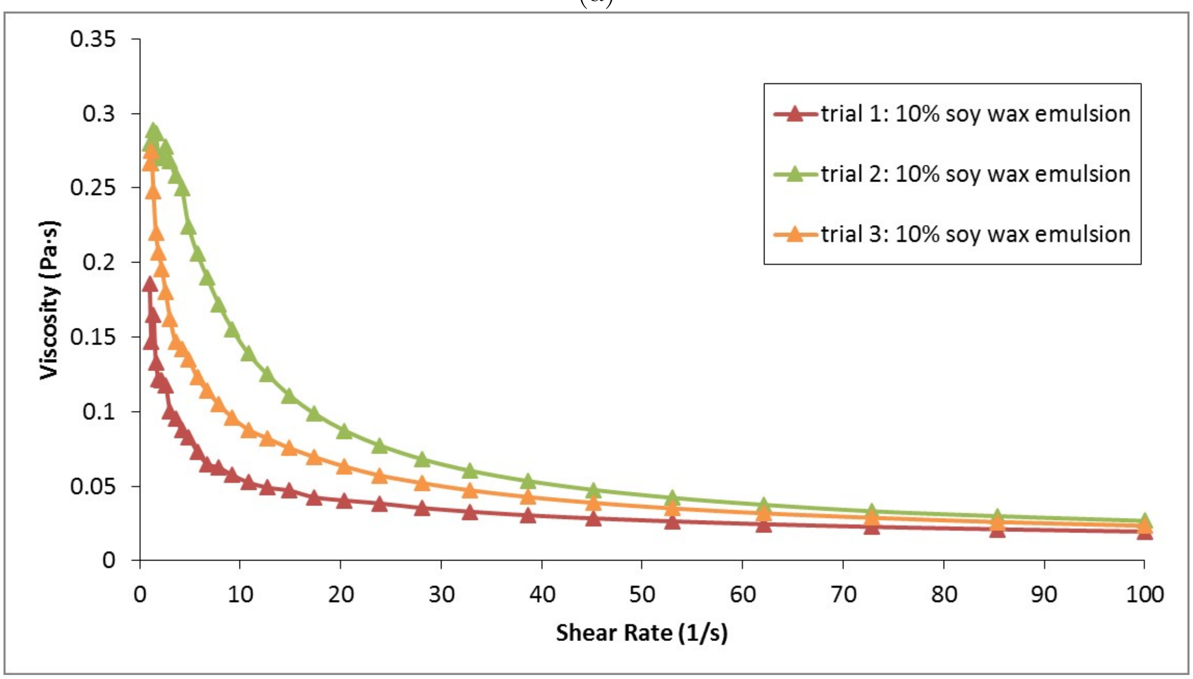


(b)

Figure 27. Individual viscosity curve for (a) 30% paraffin wax insect pheromone emulsion (b) 30% soy wax insect pheromone emulsion taken at 25 °C.

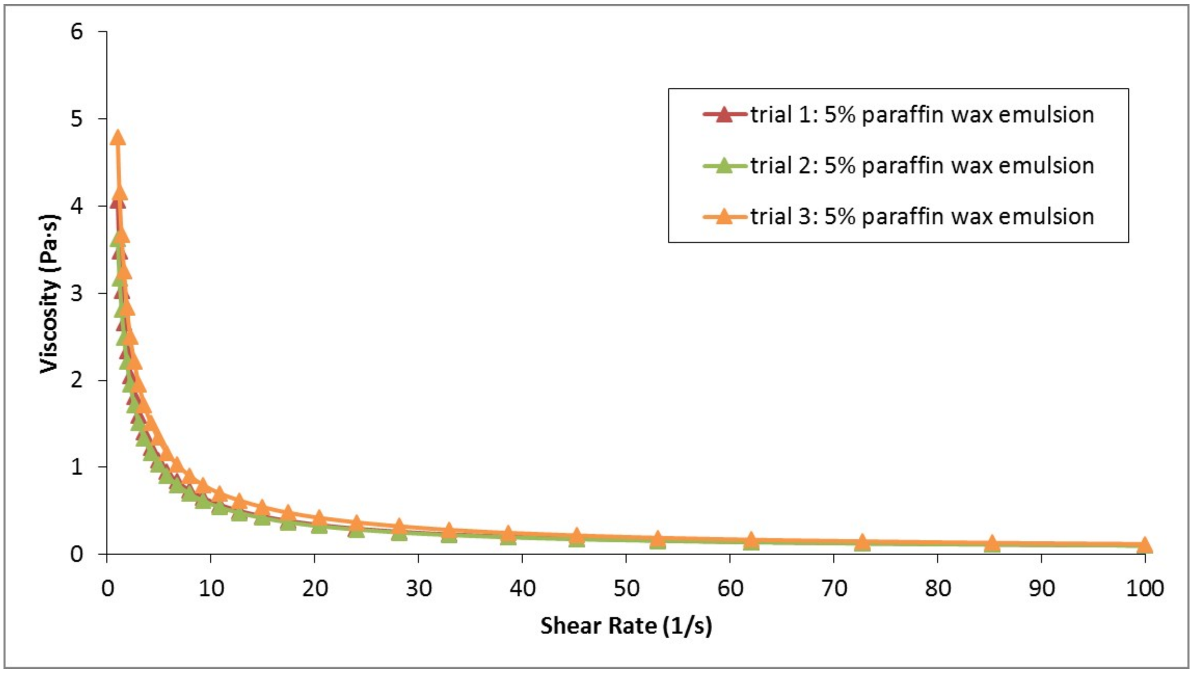


(a)

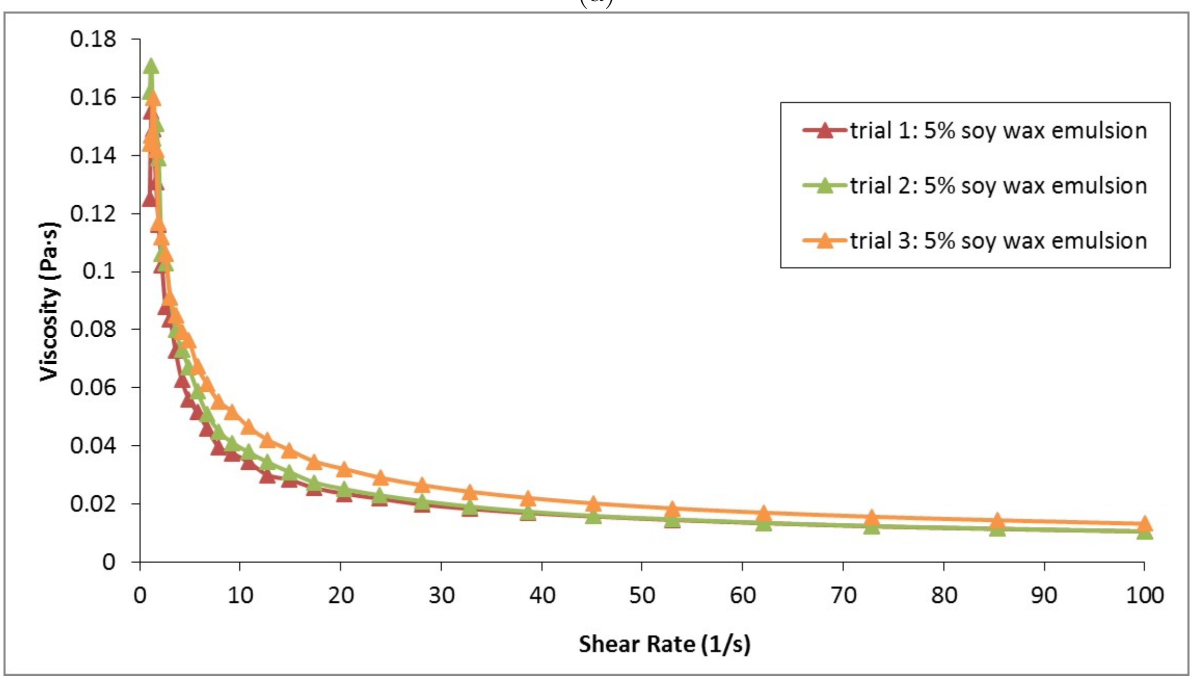


(b)

Figure 28. Individual viscosity curve for (a) 10% paraffin wax deer feeding deterrent emulsion and (b) 10% soy wax deer feeding deterrent emulsion taken 25 °C.



(a)



(b)

Figure 29. Individual viscosity curve for (a) 5% paraffin wax deer feeding deterrent emulsion and (b) 5% soy wax deer feeding deterrent emulsion taken 25 °C.