Solvent-Free Extrusion Emulsification
Inside a Twin-Screw Extruder

Solvent-Free Extrusion Emulsification Inside a Twin-Screw Extruder

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LAY ABSTRACT

The creation of nanoparticles has been a growing area of research in recent years, with numerous different means of generation being developed. Extruders have seldom been used for the generation of nanoparticles due to issues related to controlling generated particle characteristics. Previous work has shown that twin-screw extruders are capable of generating 100–200 nm particles, but the process has shown minimal robustness to variations in operating conditions. The aim of this study has been to continue the work of nanoparticle generation within a twin-screw extruder, with a specific focus on the impacts that special soap-like particles (surfactants) have on the process. Surfactants are special particles consisting of both a hydrophilic ("water-loving") and hydrophobic ("water-hating") end group that allows multiple substances to combine on a chemical level. Variations in the molecular structure and electronic charge of these surfactants, along with blends of different types of surfactants have been tested to gain a better understanding of their role in the process, and hopefully increase the overall robustness of the process. Overall, it was determined that surfactants with a negative charge were more successful in creating polyester latex particles than ones with a neutral molecular structure. The blending of a charged and neutral surfactant has been shown in this study to not only be successful in generating particles of desired size, but have also shown the ability to reduce the overall charge of the final latex particles.

ABSTRACT

Solvent-free extrusion emulsification (SFEE) is a novel emulsification technology that operates without solvent to produce sub-micron sized particles (100–200 nm) using a twin-screw extruder (TSE) with high viscosity polymers (up to 600 Pa.s has been tested to date) and only water as the liquid medium. Surfactants have always been known to play a key role in the success of the SFEE process, however very little work has been done to investigate the mechanisms by which they operate, along with isolating the region of the process to which they play the most vital role.

The first part of this thesis focused on an investigation into how different surface-active properties impacted the mechanism of SFEE. Three ionic (SDBS, Unicid 350, Calfax DB-45) and three non-ionic surfactants (Igepal CO-890, Brij 58, Synperonic F-108), each with differing surface-active properties were tested in solvent emulsification (SE) prior to their evaluation in SFEE. Synperonic F-108 was the only surfactant found unsuccessful in the SE process, and was therefore disregarded prior to SFEE testing. Of the three ionic surfactants, SDBS and Calfax were the only ones found to successfully create a stable emulsion in SFEE; the latter species doing so with 50% reduced molar loading. Igepal and Brij were found to produce very low amounts of emulsified material (5-25% of the total solids mass), requiring molar loadings that greatly exceed those of SDBS and Calfax to do so. Particles generated by both SE and SFEE were tested at extreme operating conditions to compare their relative stabilities, and were found to experience similar stability behaviours. This result reinforces previous findings that the dispersion stage controls the SFEE technique.

The second part of this thesis continued the investigation on the use of non-ionics in SFEE, with a focus on the impact of their molecular structure on the overall process. Non-ionic surfactants with varying hydrophilic end group chain lengths were tested in SFEE, and it was determined that the optimal hydrophilic chain length was between 10–12 ethoxy units, where shorter chains resulted in coarse particle generation. The structure of the hydrophobic end group was tested as well, and through experimentation it was determined that a branched end group structure was slightly more beneficial than a linear end group to emulsion stabilization. As seen in the first part of this thesis, none of the new selection of non-ionic surfactants were capable of inducing sufficient phase inversion to result in a high percentage of emulsion leaving the extruder. The most promising ionic surfactant, Calfax DB-45, was combined with various promising non-ionic surfactants to create binary surfactant mixtures, and were tested in SFEE. Initial results yielded the most promising blend as Calfax/Igepal CA-630. After manipulation of both molar ratio and total surfactant loading, it was determined that a minimum Calfax loading of 0.06 mmol/g resin was required in the blend to achieve a stable 100 – 200 nm emulsion in both SE and SFEE processes, regardless of non-ionic concentration. The benefits of adding a non-ionic surfactant in the blend were seen with the substantial reduction of Calfax entrapped in the final latex particles, apparent by the distinct decrease in overall particle charge. A mini-study examining the impacts of increasing the viscosity of the water phase by hydrocolloid addition for the dilution stage has shown that positive changes to emulsion properties can be seen by this approach, but further experimentation is required before concrete conclusions can be made.

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LIST OF ABBREVIATIONS AND SYMBOLS

Brij: Polyoxyethylene Acyl Ether

Calfax DB-45: Branched alkylbenzene diphenoloxide disulfonate

CMC: Critical Micelle Concentration

$C_{12}E_6$: hexa(ethylene glycol) mono n-dodecylether

$D_{10}/D_{50}/D_{90}$: Mean Volume Diameter

DPC: Dodecyl pyridinium chloride

FIPI: Flow-induced Phase Inversion

HMWSP: Hydrophobically Modified Water-soluble Polymers

Igepal/Triton: Alkyl Phenol Ethoxylates

KOH: Potassium Hydroxide

LDPE: Low Density Polyethylene

M_N: Number Average Molecular Weight

M_W: Weight Average Molecular Weight

MECSM: Multiple Expansion-Contraction Static Mixers

NaOH: Sodium Hydroxide

NPE: Nonylphenol Ether

O/W: Oil-in-water Emulsion

PIE: Phase Inversion Emulsification

SDBS: Sodium dodecylbenzenesulfonate

SDS: Sodium dodecyl sulfate

SEM: Scanning Electron Microscopy

SE: Solvent-Emulsification

SFEE: Solvent-free Extrusion Emulsification

SML: Sorbitan Monolaurate

Synperonic: Triblock Co-polymer

T_g: Glass Transition Temperature

TSE: Twin-screw Extruder

Unicid 350: Long Chain Carboxylic Acid

W/O: Water-in-oil Emulsion

CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW

1.1 Overview

Nano-sized polymer dispersions have gained major attention in recent years, and numerous industrial applications for them exist, such as: coatings, adhesives, printing technologies, construction materials, and pharmaceuticals. The main issue involved in creating these dispersions is the immiscibility of most polymers in water. Initial technologies used to create polymer-water dispersions involved the use of extreme mechanical agitation to bring the two phases together [1]. These types of top-down agitation-based approaches were only successful at achieving micron-sized particle dispersions and will not be discussed in this thesis. A more popular alternative to these methods is phase inversion emulsification (PIE), a top-down chemical approach where the polymer is first dissolved in an organic solvent before water is added [2]. The PIE approach to creating polymer-water dispersions has been shown to be a robust process and exhibit greater control over particle size and achieve smaller particle sizes than mechanical agitation techniques. However, these emulsification methods are slowly losing popularity due to their reliance on solvents, which brings with it high raw material costs, substantial energy costs for their recovery, as well as strict regulatory handling requirements due to their hazardous nature. These issues have prompted research into PIE technologies that remove the need for organic solvents.

Solvent-free extrusion emulsification (SFEE) is an emulsification technology that operates without solvent, emulsifying high viscosity polymers (up to 600 Pa.s has been tested to date) solely with water to generate particles on the nano-scale. [3-5]. SFEE is conducted within a twin-screw extruder (TSE), applying extremely high shear rates to thoroughly mix the two immiscible phases and generate stable sub-micron emulsions. The absence of solvents brings with it a need for surface-active agents to help overcome the challenge of generating sufficient surface area between a highly viscous polymer phase and water. Surfactants are of key importance to the SFEE process, and have two major roles in the process; to aid in the reduction of overall system interfacial tension between polymer and water phases, and act as a particle stabilizer to prevent particle growth after phase inversion. In addition to the removal of solvents, SFEE also has the added benefit of being a continuous process, operating on the time-scale of minutes as opposed to batch-like PIE processes that require several hours for completion.

1.2 Phase Inversion Emulsification (PIE)

Phase inversion emulsification is one of the most industrially popular forms of nano-particle generation. These processes operate on the principle of inverting the structure of the emulsion, from either oil-in-water (O/W) to water-in-oil (W/O), or vice-versa. This transition can be induced by altering various environmental conditions such as: temperature, shear, pressure, and proportion of oil or water in solution [6]. PIE provides two major advantages over the traditional mechanical agitation technologies. The first advantage is that it allows for emulsions to be produced at increased solid concentrations. The second is that it is capable of processing extremely high viscosity ratios, where top down agitation-based emulsification methods cannot. In a study involving the dispersion phenomena of highly viscous fluids using static mixers, Grace showed that droplet breakup was not possible with simple rotational shear if the viscosity ratio exceeded 3.5 [7], whereas PIE processes have been shown to successfully emulsify materials with drastically higher phase viscosity ratios (discussed in later sections).

Phase inversion can be classified into two main categories: catastrophic phase inversion (CPI) and transitional phase inversion (TPI). A schematic representation of the two phase inversion techniques is shown in Figure 1-1. Both of these inversion techniques operate by changing the spontaneous curvature of the surfactant molecules in the solution. For CPI, this is done by changing the water volume fraction in the emulsion (shown by the horizontal arrow in Figure 1-1). For TPI, the change in surfactant assembly curvature is induced based on the type of surfactant being used. For ionic surfactants, TPI is induced by changing the salinity of the solution, either with ionic concentration or overall emulsion pH [8]. For non-ionic surfactants, TPI is induced with a change in environmental conditions (i.e. system hydrophilic-lipophilic balance [HLB] and temperature) [8]. Both of these inversion methods are illustrated with the vertical arrow in Figure 1-1. The region where the net curvature at the oil/water interface is zero, and the interfacial tension is at a minimum is defined by an inversion locus based on the overall water fraction and surfactant hydrophilic/lipophilic affinity present. This inversion locus is defined by the solid black line in Figure 1-1, where the dotted lines represent the hysteresis zone.

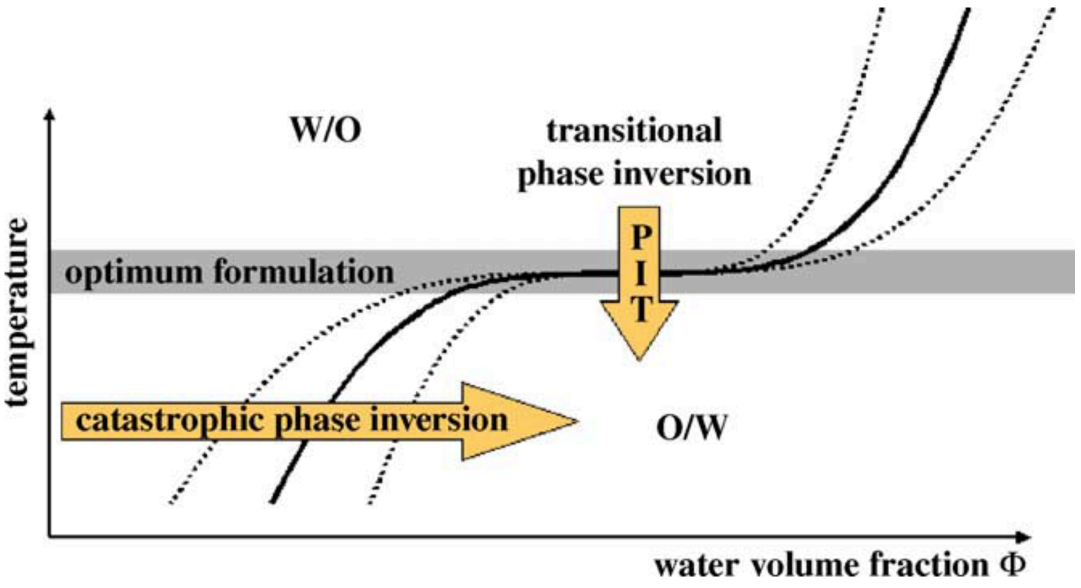


Figure 1-1. Schematic representation of the two phase inversion techniques: transitional phase inversion, and catastrophic phase inversion. Adopted from Fernandez et al [8].

1.2.1 Transitional Phase Inversion

Inducing a change in the spontaneous curvature of the surfactant molecules at the polymer/water interface by manipulating the environmental conditions of an emulsion is known as transitional phase inversion. The surfactant layer curvature at the interface is dependent on the surfactant's relative solubility in either the oil or water phase. Bancroft's rule states that the continuous phase of an emulsion should be the phase in which the emulsifier (i.e. surfactant) is more soluble [9]. For ionic surfactants, changing the surfactant affinity difference by manipulating ionic concentration or system pH will induce transitional phase inversion, as described by Salager [10]. Silva et al. performed TPI by changing the ionic concentration of an emulsion stabilized with sodium dodecyl sulfate (SDS) using NaCl, while keeping the water/oil ratio constant [11]. However, to achieve TPI using a non-ionic surfactant, environmental conditions such as system temperature or

HLB need to be manipulated. Shinoda et al. found that with non-ionic surfactants, the curvature of the surfactant monolayer changes at the oil-water interphase changes with variations in system temperature [12]. At lower temperatures, non-ionic surfactants will preferentially create O/W emulsions, and increasing temperature through their respective phase inversion temperatures results in a W/O emulsion, and vice-versa. An illustration of this change in surfactant layer at the oil/water interface can be seen in Figure 1-2.

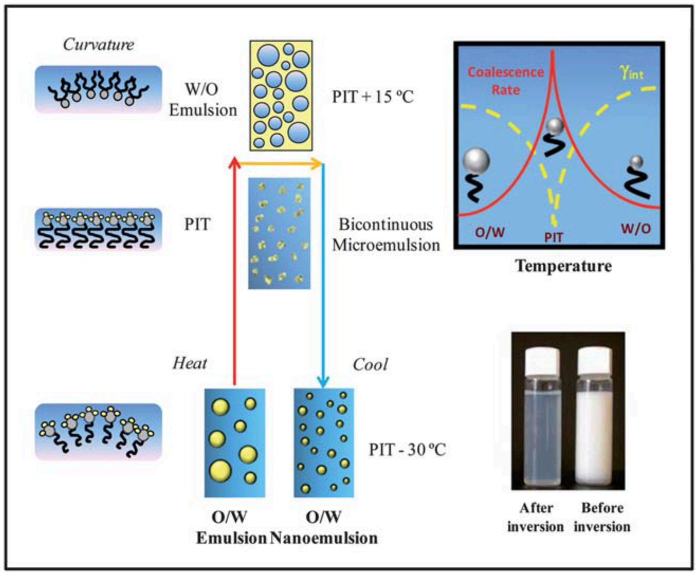


Figure 1-2. Illustration of the change in curvature at the surfactant layer interface with changing temperature for a non-ionic surfactant. Adopted from McClement [13].

1.2.2 Catastrophic Phase Inversion

Catastrophic phase inversion is induced on an emulsion by gradually changing the water volume fraction in the system. McClement's describes this form of phase inversion, where first a W/O emulsion with a high oil phase concentration is created with a particular surfactant, and then water is gradually added to the system under continuous agitation [13]. The gradual addition of water leads to the eventual creation of a bi-continuous system with lamella like morphology, where further addition of water results in total inversion, creating an O/W emulsion. A schematic representation of this process is shown in Figure 1-3. The emulsifiers used in this inversion method are limited to surfactants that are able to stabilize both W/O emulsions (in the initial short-term stages), and O/W emulsions (over the long-term). The final size of the oil droplets depends on variables such as viscosity ratio between phases, mechanical agitation, and water addition rate. The most impactful variable on final particle size is phase viscosity ratio, and will be discussed further in future sections.

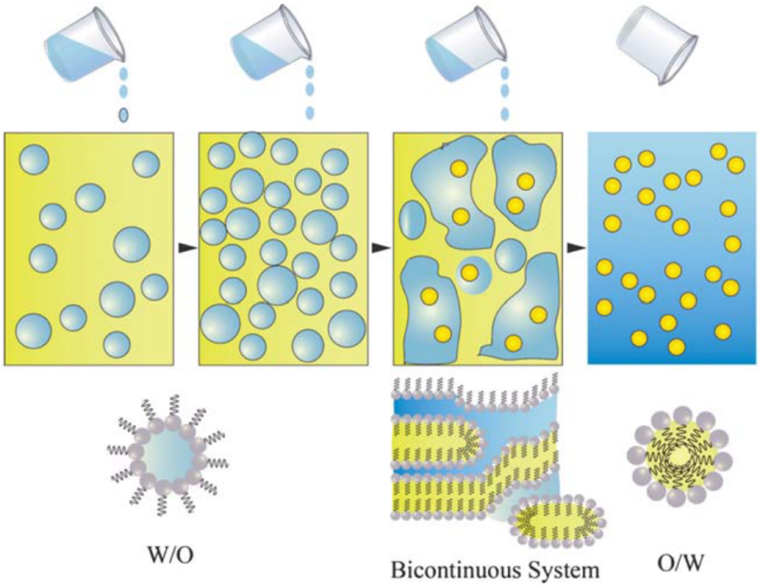


Figure 1-3. Illustration of the catastrophic inversion process from a W/O emulsion to an O/W emulsion. Adopted from McClement [13].

1.3 Solvent-Free Emulsification

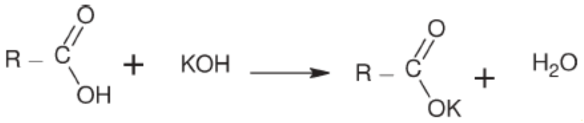
As mentioned previously, one of the most influential variables on both emulsion stability, and final emulsion particle size is the viscosity ratio between the initially dispersed oil phase and initially continuous water phase. Galindo-Alvarez et al. studied the impact of the oil/water viscosity ratio on emulsion formation for viscosity ratios ranging from 1-12.5 Pa.s using linear polydimethylsiloxane, operated in a batch reactor at varied stirrer speed settings [14]. They concluded that the influence of stirring speed was impacted by the phase viscosity ratio, stressing the fact that the viscosity ratio in the moments prior to inversion is the most impactful variable to stable emulsion formation [14]. They also found that lowering the phase viscosity ratio ultimately enhanced emulsion formation [14]. Rondon-Gonzalez et al. conducted a similar study where they investigated the impact of viscosity on phase inversion by continuous stirring. The oil for this study was low viscosity (0.001 Pa.s) Kerosene, and its viscosity was increased using a commercialized lubricating oil. They found that as they increased the viscosity of the oil phase under a constant shear rate, the efficiency of both the deformation and droplet breakup of this phase was reduced [15]. This reduction in oil phase deformation consequently hindered the water droplet inclusion process, meaning that the inclusion of water droplets in a continuous oil phase becomes increasingly difficult as oil phase viscosities increase [15].

A study conducted by Zerfa et al. looked at TPI behaviour of low molecular weight polyisobutylene (PIB) [2]. The emulsifiers used in their study consisted of mixtures of two types of non-ionic surfactants: polyoxyethylene nonylphenyl ether (NPE) surfactants (Igepal 520 and 720) and polyoxyethylene sorbitan monolaurate (SML) surfactants (Tween 20 and Span 20) [2]. TPI was induced by changing the overall HLB of the system, done so by differing the amount of each surfactant used. The total HLB of the binary surfactant mixture can be calculated using Equation 1:

$$HLB_{Mix} = f_A * HLB_A + (1 - f_A) * HLB_B \qquad [1]$$

where $HLB_{A/B}$ is the hydrophilic-lipophilic balance value for each respective surfactant, and f_A is the weight fraction of surfactant A. All of their experiments were conducted in a 1 litre jacketed glass vessel, operated at a constant RPM of 500, and a constant jacket temperature of 60 ± 0.2°C. Zerfa et al. found that no obvious reduction in droplet size was observed when using SML surfactants, regardless of the overall HLB or respective surfactant concentrations, leading them to believe that no TPI was observed [2]. Using NPE surfactants, Zerfa et al. determined that a stable emulsion was created via TPI at an HLB value of 10.47 [2]. When operated at a total surfactant loading of 5 wt%, the droplet size was reduced to between 200 nm – 2 μm, where prior to inversion the droplet size varied between 4 – 30 μm [2]. Furthermore, they found that increasing the total surfactant loading had a negligible impact on both the transitional boundary and final droplet size. It was also discovered that decreasing the rate of component addition had a positive impact on overall droplet size reduction after inversion [2].

A study conducted by Song et al. looked at the emulsification of a rosin ester via catastrophic inversion. They reacted rosin acid with an aqueous solution of 45 wt% potassium hydroxide (KOH) to form an ionic surfactant, for which the reaction is represented as:



[2]

All experimentation in this study was conducted inside a 4 litre jacketed mixing tank. Parameters such as agitation speed, jacket temperature, and water addition rate were all tested to determine what impact they would have on final emulsion size and viscosity [16]. Through experimentation they determined that the jacket temperature did not have a major impact on final emulsion size as long as it was below a critical level. At a constant water addition rate and impeller speed, the mean particle diameter ranged between 0.6 – 0.7 μm for jacket temperatures between 43.3 – 51.7°C, but was seen to increase to ~ 1.1 μm at 54.4°C [16]. Catastrophic inversion was found to occur at approximately 20 wt% water for all tested jacket temperatures [16]. Their results for changes in agitation speed and water addition rate showed a coupled behaviour, where good emulsions (D_{50} ~ 0.5 μm) were obtained with higher water addition rates, and correspondingly higher agitation speeds [16]. The phase inversion point was seen to be unaffected by a change in agitation rate, while it was determined that as water addition rate decreased, phase inversion occurred at gradually lower water volume fractions [16].

A different form of phase inversion, known as flow-induced phase inversion (FIPI) was applied in a study by Akay to create concentrated colloidal dispersions of highly viscous polymer resins. The difference in this form of phase inversion is that the inversion is not completely reliant on the manipulation of thermodynamic state variables, but relies also on deformation state variables (i.e. flow) [17]. Akay described the mechanism of FIPI as water extending into cylindrical threads and being compressed into discs, later to trigger oil phase encapsulation at critical phase inversion conditions [17]. In this study, Akay utilized 3-6 multiple expansion-contraction static mixers (MECSM) to induce FIPI on Epikote, an epoxide polymer [17]. A schematic illustration of the internal structure of the MECSM used in this study can be seen in Figure 1-4. Akay utilized a binary mixture of two surfactants consisting of an anionic surfactant (Aerosol OT) and a non-ionic surfactant (Dobanol 91-2.5) at varied total molar concentrations and relative blend ratios [17]. Akay tested two epoxy resins with distinctly different viscosities (42 and 2.1 Pa.s respectively) and found that similar final emulsion particle sizes were obtained using his flow inversion setup (0.64 and 0.68 μm respectively) [17]. Akay also found that as you increase the anionic surfactant concentration, both the water volume fraction and critical flow rate through the MECSM required for phase inversion decreased [17]. The findings in this study show that flow conditions have a large impact on phase inversion behaviour, but are still dependent on the thermodynamic state variables. This means that by using FIPI, thermodynamic state variables can be minimized while still being able to successfully emulsify polymer/water mixtures with high viscosity ratios.

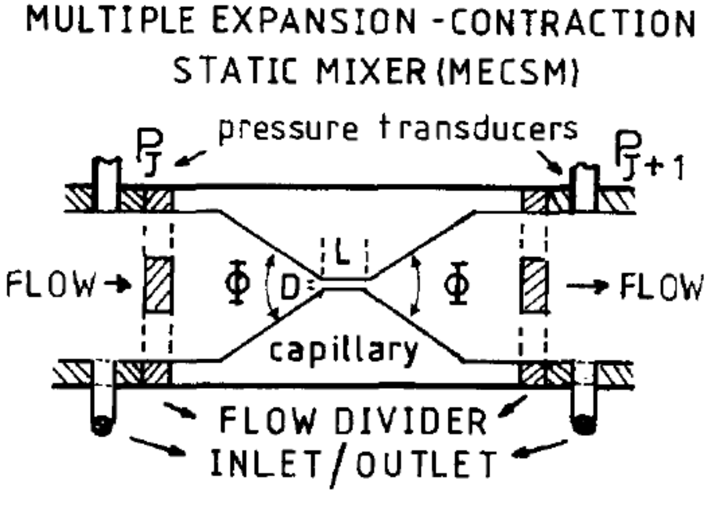


Figure 1-4. Schematic representation of the internal structure of the multiple expansion-contraction static mixer utilized in a study by Akay for flow-induced phase inversion on highly viscous polymer resin [17].

A second study conducted by Akay and Tong involved the emulsification of low-density polyethylene (LDPE) latexes using FIPI [18]. The emulsifiers used consisted of two types of hydrophobically modified water-soluble polymers (HMWSP): acrylic acid/lauryl methacrylate sodium salt (mole ratio 25:1 and 8:1), acrylic acid/stearyl methacrylate (mole ratio 8:1), as well as sodium polyacrylates, and both non-ionic and anionic surfactants. The emulsification process was conducted in a HAAKE high torque rheometer, where the LDPE would be mixed with the chosen aqueous emulsifier, and charged into the reactor at 120°C, with the aqueous phase being given time to evaporate under constant agitation (60 RPM). When the torque on the reactor reached the desired value, water was added into the mixer at 1.5 g/min creating a W/O emulsion, and was continually added until the inversion took place, creating an O/W emulsion. Akay and Tong discovered that emulsification of LDPE was not possible with any of the surface-active agents, except with the HMWSP's, which yielded particle sizes in the range of 0.91 – 4.19 μm [18]. The lower ratio of acrylic acid to lauryl methacrylate was deemed to be beneficial in creating smaller emulsion droplets. Phase inversion using HMWSP's as emulsifiers was found to occur at a water volume fraction of approximately 20 wt%. Akay and Tong also discovered that the time at which the water addition is started has an impact on final particle size, as a prolonged timeframe for the mixing of the polymer melt and emulsifier phases resulted in a larger measured final particle size [18].

1.4 Solvent-Free Extrusion Emulsification (SFEE)

The previous section discussed different studies related to solvent-free emulsification processes. Very few of these studies involved the use of a continuous process, nor did they deal with emulsification of highly viscous polymers (> 100 Pa.s). Solvent-free extrusion emulsification is a novel technology that utilizes a twin-screw extruder to continuously emulsify highly viscous polymers (up to 600 Pa.s has been tested so far), generating 100 – 200 nm particles. In general, a TSE is used to apply high shear to highly viscous immiscible polymer(s) for melting and mixing. The extruder barrel itself can be modified to allow for injectors and side-feeders to be attached, providing the opportunity for the addition of various additives, regardless of their physical state. Prior to SFEE, very little work had been done regarding the emulsification of polymers using a TSE. Recently, many companies have begun commercializing variants of this process, which are seen in the following patents [19-23].

SFEE is a green manufacturing technology that utilizes a TSE to produce aqueous dispersions of polyester resin without the need for any organic solvent. The SFEE process operates continuously, turning solid polyester resin into stable polyester latex emulsions on the time-scale of minutes. For this process, the TSE is split into three distinct zones: *melting, dispersion, and dilution zones.* A schematic representation of the SFEE process along the TSE barrel is shown in Figure 1-5. The *melting zone* is attributed to the initial portion of the extruder (zones Z0 – Z2) where the solid polyester resin, along with any solid additives are melt-mixed into a polymer melt. The *dispersion zone* (zones Z3 – Z6) is where a small weight fraction of water, along with any required liquid additives are injected into the extruder and mixed together with the molten polymer, creating a W/O emulsion. The *dilution zone* (zones Z7 – Z9) is the final portion of the extruder, and is where the large portion of water is injected in, initiating the phase inversion, and creating an O/W emulsion. These zones will be denoted in the subsequent chapters as stages to generalize the mechanisms between the process taking place in the extruder and the process taking place in a beaker. The emulsion is then extruded out of the die and quenched in water at a specific dilution ratio, signifying an end to the process.

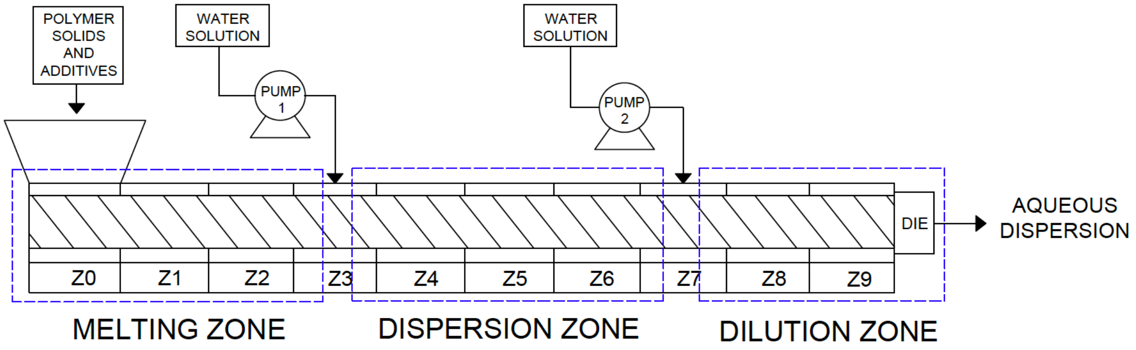


Figure 1-5. Schematic representation of the SFEE process within a twin-screw extruder.

Previous SFEE studies conducted by Goger et al. have shown that stable, nano-sized particles (100 – 200 nm) can be created using SFEE [3-5]. Goger et al. measured the transient viscosity behaviour in the process using an in-line rheometer that was able to detect changes in the overall viscosity of the system throughout the duration of the process. What they found was that large drops in apparent viscosity (~ 100 Pa.s) were measured within 1 – 2 minutes after initial water addition [4]. The explanation to this phenomenon was described as the morphological development of a polymer-water matrix, where the water droplets penetrating the polymer melt formed striated lamella like structures, eventually leading to the phase inversion of the emulsion. This phenomenon can be seen in Figure 1-6.

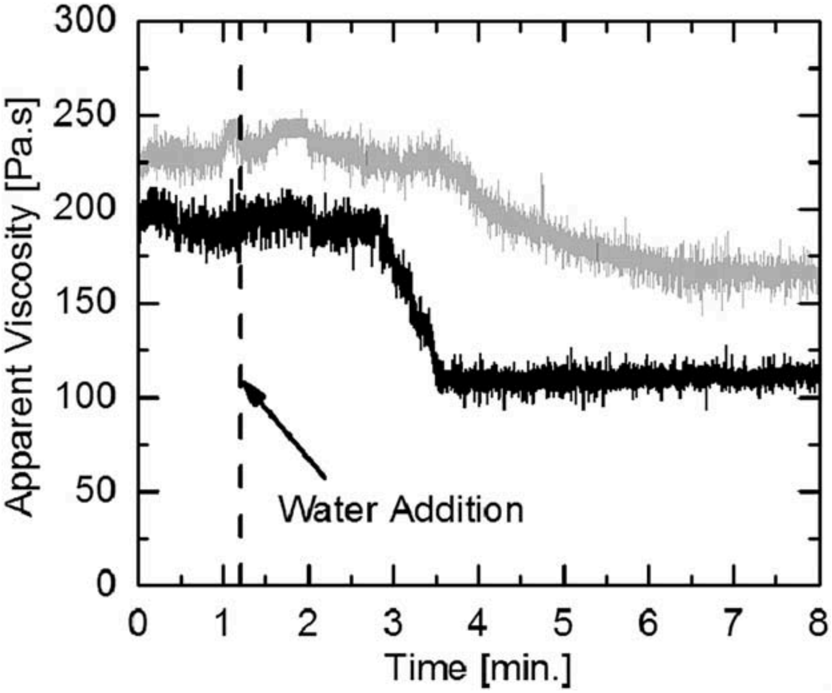


Figure 1-6. Measured change in viscosity over time of a polyester resin melt after water addition takes place in a TSE during SFEE. Viscosity measurements made using an inline rheometer. Image adopted from Goger et al. [4].

Further studies by Goger et al. focused on the W/O emulsion being created in the dispersion zone, with a specific focus on how both end group conversion of polyester via sodium hydroxide (NaOH) addition, as well as surfactant content (sodium dodecylbenzenesulfonate [SDBS] in their case) impacted the interfacial tension between the polymer and water phases [3]. What they found was that functionalizing the polyester chain end groups with NaOH alone was unable to sufficiently promote water incorporation into the polymer phase, resulting in poor downstream phase inversion due to inadequate W/O emulsion formation [3]. However, with the addition of 7 wt% SDBS to the already present 1 wt% NaOH in the process, the concentration of surface active functional groups per kilogram resin were measured to increase from 0.08 mol/kg to 0.3 mol/kg, which was found to promote sufficient water incorporation into the polymer phase prior to inversion, yielding a stable latex emulsion [3]. What was not focused on in these previous SFEE studies was the type of surfactant being used in the process, and what impact surfactants have on the mechanism of SFEE.

1.5 Role of Surfactants in the Emulsification Process

Surfactants are amphiphilic molecules consisting of two distinct ends, one being hydrophilic, and one hydrophobic [24]. The hydrophilic end is attracted to polar regions (i.e. water molecules) and the hydrophobic end is attracted to non-polar regions (i.e. oil phase). As mentioned previously, surfactants play two major roles in the emulsification process. The first is to aid in the reduction of overall system surface tension, promoting contact between the immiscible polymer and water phases. The second key role that surfactants play in the emulsification process is preventing particle aggregation after phase inversion, acting as a shield, surrounding the newly formed polymer droplets. Surfactants are able to prevent particle aggregation by two mechanisms: electrostatic, and steric stabilization [24]. Electrostatic stabilization is the subsequent repulsion of charged surfactant hydrophilic end groups, and is only noticeably present with ionic surfactants. Steric stabilization is a result of the bulky surfactant hydrophilic end groups preventing the particles from aggregating with each other.

In SFEE, the need for surfactants is greatly increased due to the nature of the process itself. With SFEE being a continuous process, the timescale for the W/O emulsion preparation in the dispersion zone is extremely short. Combined with the extremely high viscosities present in the system due to the absence of any solvents, the effectiveness of the surfactants in promoting water penetration into the polymer melt must be extremely high in order to achieve stable emulsion inversion. The harsh conditions inside of the TSE (i.e. high temperatures) result in high surfactant loadings being required to sufficiently prevent any particle aggregation from taking place after phase inversion. In the following sections, the different types of surfactants currently being used in emulsification processes are discussed.

1.5.1 Ionic Surfactants

Ionic surfactants can be sub-categorized as either anionic or cationic. These types of surfactants have a charged moiety on their hydrophilic end; negatively charged for anionic surfactants, and positively charged for cationic surfactants. For anionic surfactants, this charged end group very often consists of either a phosphate or sulfonate group, whereas for cationic surfactants it is very often a nitrogen-based group [24]. In this thesis, three different anionic surfactants are reported: sodium dodecylbenzenesulfonate (SDBS), Unicid 350 (a long chain carboxylic acid), and alkyldiphenoloxide disulfonate (Calfax DB-45). In terms of SFEE, the charged hydrophilic end group of these types of surfactants increases their affinity towards the water phase, impacting their performance in the dispersion zone. The charged end group on ionic surfactants also improves their electrostatic stabilization effects, positively impacting their particle stabilization abilities post-inversion.

Ionic surfactants are vastly popular in a great deal of emulsification processes conducted to date. Sole et al. studied the impact ionic surfactants have on the nano-particle formation of a low-energy emulsification process. The ionic surfactant used in their study (potassium oleate) was created along the emulsification path, where potassium hydroxide was added to a mixture of hexadecane-oleic acid-$C_{12}E_{10}$ [25]. Sole et al. created their O/W emulsions by varying the degree of ionization of the surfactant at a constant system temperature of 25°C [25]. Their resulting O/W emulsions had a minimum measured droplet size of 17 nm. Silva et al. studied the hysteresis zones of dynamic inversion for a Kerosene oil/water system using two types of anionic surfactants: SDS, and a petroleum sulfonate sodium salt [11]. They tested both forms of phase inversion: transitional and catastrophic, induced by either changing the ionic concentration of the emulsion and changing the overall water content respectively [11]. These changes were done in small increments and were continued until inversion was detected via a change in electrolytic conductivity. In the end, Silva et al. determined that the hysteresis zone for the point of inversion for both catastrophic and transitional phase inversion was impacted similarly by both surfactants and was shown to depend on both the overall emulsion formulation and the surfactant concentrations. Goger et al. showed the effectiveness of the anionic surfactant SDBS in their previous work with SFEE, as discussed previously [3,5].

1.5.2 Non-ionic Surfactants

In contrast to ionic surfactants, the hydrophilic end group of non-ionic surfactants carries no charge. There exist many commercially available types of non-ionic surfactants, but the ones discussed in later chapters of this thesis consist of variants of the following: alkyl phenol ethoxylates, polyoxyethylene acyl ethers, and triblock co-polymers made up of polyethylene oxide and polypropylene oxide units. The lack of a charged end group results in their reduced affinity towards water molecules and negligible electrostatic stabilization abilities. However, their bulky molecular structures allow for these types of surfactants to exhibit greatly improved steric stabilization effects.

Just like ionic surfactants, non-ionic surfactants have shown their effectiveness in various emulsification processes. Uson et al. used non-ionic surfactants in their low-energy emulsification of a W/O emulsion containing polyethylene glycol (7) hydrogenated castor oil, and polyethylene glycol (35) castor oil [26]. Phase inversion of this system was induced by the gradual step wise addition of oil to a mixture of water and surfactant at a constant temperature of 30°C, and constant homogenization. Their results show that particles ranging in size from 60 – 160 nm were created, and their size was found to be a function of the surfactant/water ratio [26]. A second example of emulsification with non-ionic surfactants was shown in the work of Akay et al., where ethylene vinyl acetate (EVA) copolymer latex particles were created using flow-induced phase inversion in the presence of a non-ionic surfactant. The FIPI process used in this study was described in earlier sections of this thesis. Two different HMWSP's with varying hydrophobicity were used as surface-active agents in this study. The non-ionic surfactants used in their study were ethoxylated alcohol and ester molecules. Akay et al. found that EVA could not be emulsified using low-molecular weight surfactants [27]. Successful emulsions were achieved using the more hydrophobic HMWSP, yielding particle D_{50} values ranging from 1.52 – 2.08 μm [27]. The minimum surfactant concentration to achieve stable emulsification was found to be 15 wt%.

1.5.3 Ionic/Non-ionic Surfactant Blends

The use of surfactant mixtures in emulsification has become a growing area of interest in the field of nano-particle emulsification. Using a mixture of ionic and non-ionic surfactants allows for the emulsifier mixture to exhibit the positive aspects of both types of surfactants, those being the strong electrostatic repulsion and affinity to water of the ionic surfactant, and the strong steric stabilization of the non-ionic surfactant. Previous exploration of the idea of mixed surfactants has determined that anionic surfactants have a stronger interaction with non-ionic surfactants than cationic surfactants. This is believed to be due to a low concentration of oxonium ions (resonant structures) forming within micelles of polyoxyethylene micelles (resulting in a weak positive charge), which leads to an interaction with the negatively charged anionic end group [28]. An example of surfactant blends in emulsification was shown by Chern et al., where they looked at the emulsification of polystyrene latex particles using an emulsifier mixture of SDS with a nonylphenol ethylene oxide non-ionic surfactant. Their emulsification was conducted in a 250 mL jacketed vessel, at a constant temperature of 80°C under constant agitation. It should be noted that this process did not involve phase inversion. They tested the impact of pure nonylphenol ethylene oxide, and found that the resulting latex was very unstable, and they concluded that the steric stabilization effect provided by the non-ionic surfactant was not enough to prevent particle flocculation [29]. However, they found that when including SDS in the surfactant mixture, the blend of surfactants together was successful in creating a stable emulsion [29]. The optimal ratio of surfactants was found to be 20/80% SDS/non-ionic, which resulted in particles with D_{50} values of 49 nm, and yielded the greatest polymerization rate [29]. A second study conducted by Goloud and Pugh looked at the impact of surfactant head groups in the emulsification process using a binary ionic/non-ionic surfactant mixture. Goloud and Pugh looked at the emulsification of dodecane with two different surfactant mixtures: anionic SDS with non-ionic hexa(ethyleneglycol) mono n-dodecylether ($C_{12}E_6$), and cationic dodecyl pyridinium chloride (DPC) with the same $C_{12}E_6$ [30]. Emulsions of dodecane and water were prepared under constant flow rate conditions. They found that uniformly increasing surfactant amounts of each mixture resulted in a decrease in particle size up to a certain loading, which was found to correspond to the critical micelle concentration (CMC) of the mixture [30]. They measured an increase in droplet size at CMC when the loading of the ionic surfactant was increased, which was concluded to be a result of increased head group repulsion, subsequently increasing interfacial tension [30]. When comparing the anionic/non-ionic and cationic/non-ionic blends, they found that smaller particle sizes were achieved with the anionic/non-ionic blend, which was attributed to the increased interactions between sulfate head groups and the non-ionic molecular chain [30].

1.6 Objectives

A study on the solvent-free extrusion emulsification process is conducted in this thesis, with a specific focus on surfactant impact on the process. Previous work with SFEE lacked a true investigation into the impact of surfactants with different surface-active properties on the SFEE process. Gaining a better overall understanding of how surfactants behave in each zone of the SFEE process will allow for a more robust system, as well as allow for their overall optimization, leading to a more environmentally friendly process. The specific objectives of this thesis are:

1. To gain a better understanding of how surfactants with differing surface-active properties impact the SFEE process.
2. To examine the behaviour of SFEE particles at extreme operating conditions after phase inversion, and compare their behaviour to that of particles made with a traditional solvent based process.
3. Attempt to reduce the overall surface charge of the final SFEE latex particles by minimizing the amount of surfactant molecules embedded in the latex particles.
4. To gain a better understanding of how surfactants of differing molecular structures impact the SFEE process.
5. Compare the impact of ionic/non-ionic surfactants being used both as sole emulsifiers, and together in binary emulsifier mixtures on the SFEE process.
6. Investigate the impact of increasing water viscosity entering the dilution zone on final emulsion characteristics generated with SFEE.

1.7 Thesis Outline

Chapter 1. Introduction and Literature Review: This chapter introduces solvent-free extrusion emulsification technology, along with background information related to the process, including: phase inversion emulsification, solvent-free emulsification, and the impact of different types of surfactants (ionic and non-ionic) on the emulsification process. This chapter also summarizes relevant studies on each of the relevant research areas related to SFEE. A research objective and general thesis outline are provided as well.

Chapter 2. Examining Surfactant Behaviour on Solvent-Free Extrusion Emulsification: This chapter, written as a paper, looks to examine how surfactants with differing surface-active properties impact the overall SFEE process and how viscosity influences their effectiveness. This was done by testing surfactants with differing surface-active agents (both ionic and non-ionic) in both a traditional solvent emulsification (SE) process as well as SFEE to determine their respective impacts on each process. A particle coalescence study was also conducted to evaluate both SE and SFEE latex particle behaviour at extreme operating conditions and create a comparison between their relative stabilities. This manuscript is in preparation for publication.

Chapter 3. Investigating the Impact of Surfactant Structure and Anionic/Non-ionic Surfactant Blends on Solvent-Free Extrusion Emulsification: This chapter, written as a paper, looks at the impact that various features of a non-ionic surfactant molecular structure have on emulsification. This was done by testing numerous non-ionic surfactant variants with differing molecular structures, as well as end group geometries (linear vs branched) in an SE process to determine their overall effectiveness as an emulsifier, and then comparing those results to ones conducted using SFEE. This chapter also evaluates the behaviour of the SFEE process stabilized by a blend of anionic/non-ionic surfactants. Blends of a singular anionic surfactant with numerous non-ionic surfactants were tested using both SE and SFEE processes. An ion-exchange analysis was conducted on the SFEE blend samples to determine if blending anionic/non-ionic surfactants helped to reduce the amount of embedded surfactant in the final latex particles, consequently lowering their overall surface charge. A final mini-study in SFEE was conducted to determine if increasing the viscosity of the large portion of water entering the SFEE process in the dilution zone would have any positive impacts on the resultant emulsions. This manuscript is in preparation for publication.

Chapter 4. Conclusion: This chapter acts as a summary of conclusions made throughout the work presented in this thesis with a focus on the key findings, and presents possible future work for the project.

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CHAPTER 2: EXAMINING SURFACTANT BEHAVIOUR ON SOLVENT-FREE EXTRUSION EMULSIFICATION

In chapter 2, all experiments and data analysis were conducted by the thesis author. J. Pawlak and D. Lawton provided technical guidance during the project. The manuscript version of this chapter is being prepared for publication in 2019.

Examining Surfactant Behaviour on Solvent-Free Extrusion Emulsification

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ABSTRACT

This study examines the impact that surfactants have on the mechanism of a new solvent-free extrusion emulsification (SFEE) technique. Two sets of surfactants were used in this work. Three anionic surfactants were tested (SDBS, Unicid 350, Calfax DB-45) and three non-ionic surfactants were tested (Igepal CO-890, Brij 58, Synperonic F-108). From the anionic surfactant group, only SDBS and Calfax were found to create stable O/W emulsions with a polyester in the desired 100–200 nm size range; the latter requiring a lower molar concentration to achieve this goal. Use of Igepal CO-890 and Brij 58 resulted in only partial emulsification despite requiring much higher molar loadings than their anionic counterparts to accomplish this outcome, with majority of the polymer leaving the extruder without phase inverting. The study reinforced previous findings that the dispersion stage (zone) controls the SFEE technique, and highlighted the importance of water affinity displayed by a surfactant species to compensate for high retarding viscous force for mixing water into the polymer melt.

KEYWORDS: twin screw extruder; surfactants; emulsion; coalescence

INTRODUCTION

Nanoparticles have been gaining major attention over the past decade, and are being utilized in various applications such as adhesives, printing technologies, construction materials, and pharmaceuticals. There exist numerous methods for preparing nanoparticles, but the preferred top-down approach is production by phase inversion emulsification (PIE). Industrially, particles are formed in a solvent-based PIE process (solvent emulsification, SE) where the polymer, dissolved in an organic solution, is dispersed in an excess of water. Many variables such as temperature, mixing speed, and pH impact the size and particle distribution of a resulting emulsion, but overall SE is robust and easily scalable [1-4]. However, the organic media in this process has lost popularity due to the high material cost, substantial energy requirements for removal, and restricted handling due to strict environmental regulations. The batch-like nature of SE is another aspect where improvements would be desirable since yields will be lower than continuous processes. Greener alternatives are currently being sought to directly disperse the polymer phase within water, but they bring many challenges. This paper focuses on a new continuous manufacturing process conducted in a twin-screw extruder (TSE) that avoids the need for solvents to create stable emulsions with high viscosity polymers.

Solvent-free extrusion emulsification (SFEE) operates without solvent, solely utilizing water as the liquid medium to create particles as small as 100–200 nm with high viscosity polymers (up to 600 Pa.s has been tested to date) [5-7]. Variants of this emulsification technique have been proposed by several companies for commercialization, seen in the following patent literature [8-13]. Processes in the TSE are separated into three distinct zones or stages, namely melting, dispersion, and dilution. The dispersion stage seems to hold the critical role of gradually incorporating water into the bulk polymer phase with the aid of surface active agents, whereas the dilution stage controls the subsequent phase inversion creating the desired emulsion; the rate of lamellae thinning for the melt/water system in the dispersion stage directly impacts final particle size [14], which must be relatively fast to fit within the available length of the extruder (approximately 50% of the overall machine length). The technique has notable needs for higher concentrations of surfactant compared to solvent-based PIE due to the rate of lamellae thinning required and high viscosity medium, which impacts production costs as well as applications for the final particles. A better understanding of the role of surfactants in SFEE would give processors more control over features of the final particles generated by the technique. This paper analyzes surfactant use based on a comparison of emulsification between SE and SFEE.

Use of a solvent in SE is responsible for lowering the overall system viscosity prior to inversion by dissolving the polymer into solution. This effectively lowers the time to intimately mix the water (W) and oil-like polymer (O) phases, forming a W/O emulsion prior to phase inversion [14]. The dispersion stage in SFEE generating a W/O emulsion is strongly dependent on the mechanical energy imparted by the extruder to bring the two phases together intimately in the absence of solvent [7]. The timescale for maximizing interfacial area between the water and polymer phases is strongly influenced in both SE and SFEE by surface-active agents such as surfactants, and so the dispersion stage of SFEE can be better understood by perturbing the system with varying surfactants in comparison to SE were viscous effects are less prominent. It is believed that the highly viscous environment in the dispersion zone of SFEE retards surfactant migration to the W/O interface being generated. To properly perturb the system, surfactants of both charged (ionic) and neutral (non-ionic) character should be investigated. Ionic surfactants have a charged hydrophilic head group and rely on head group repulsion to prevent unfavourable self-assembly, whereas non-ionic surfactants rely on the steric hindrance of their hydrophilic head groups [15-16]. There are advantages and disadvantages to using each type of surfactant. For example, non-ionic surfactants are less affected by electrolyte concentration in dilute aqueous solutions compared to their ionic counterparts whereas ionic surfactants are more effective particle stabilizers at lower molar concentrations and are far less sensitive to temperature [17]. In cases of both SE and SFEE, the sudden introduction of a large quantity of water destabilizes the W/O emulsion generated with surfactant(s), and due to the low osmotic pressure, the emulsion inverts into an O/W emulsion to generate the desired nanoparticles.

In this regard, the paper is seen as an examination of how surfactants with differing surface-active properties contribute to the mechanism of SFEE and how viscosity influences their effectiveness. Differences in particle size between solvent emulsification and solvent-free emulsification extrusion were used to study this mechanism whereas, a particle coalescence study was used to confirm that both processes produced particles with similar stability as a result.

EXPERIMENTAL

Material

A polyester synthesized from dipropoxylated bisphenol A and fumaric acid was supplied by Xerox Corporation (Webster, NY). The resin had a T_g of approximately 60°C, M_W of 17080 g/mol (M_W/M_N=4.2), and acid number of 17.7 ± 1.7 mg/g KOH (mass of KOH required to neutralize one gram of resin). The anionic surfactant, 4-dodecylbenzenesulfonic acid (SDBS) (M_W=348.5 g/mol), along with three non-ionic surfactants: Igepal CO-890 (polyoxyethylene nonylphenyl ether; M_W=1982), Brij 58 (polyethylene glycol hexadecyl ether; M_W=1124), Synperonic F-108 (polyethylene glycol-polypropylene glycol-polyethylene glycol triblock copolymer; M_W~14600 g/mol) were all purchased from Sigma-Aldrich. The anionic surfactant, Unicid 350 (long chain carboxylic acid; M_W=340 g/mol) was donated by Baker Hughes (Houston, TX) and Calfax DB-45 (alkyldiphenyloxide disulfonate; M_W=542 g/mol) was purchased from the Pilot Chemical Company (Cincinnati, OH); Calfax was the only surfactant in liquid form for the study, being supplied as a 47 wt% aqueous solution. Sodium hydroxide (NaOH) was purchased from Caledon Laboratories Ltd (Georgetown, ON, CA). Deionized Milli-Q water was used in the preparation of all samples.

Apparatus

All extrusion experiments were done using a 27 mm 40 L/D Leistritz ZSE-HP co-rotating twin-screw extruder (American Leistritz Extruder Corporation; Somerville, NJ). The extruder barrel was comprised of a feed port (zone Z0) and nine heated zones (Z1-Z9), with a 15 mm bore diameter die at the outlet. The polyester granules were fed into the extruder at Z0 using a Brabender Technologie KT20 twin-screw gravimetric feeder (Mississauga, ON). Liquid injection sites were located at Z3 and Z7, connecting to a high-pressure Optos piston pump (41 MPa capacity) and a high-pressure syringe pump (51 MPa capacity) respectively. A layout of the process is shown in Figure 2-1.

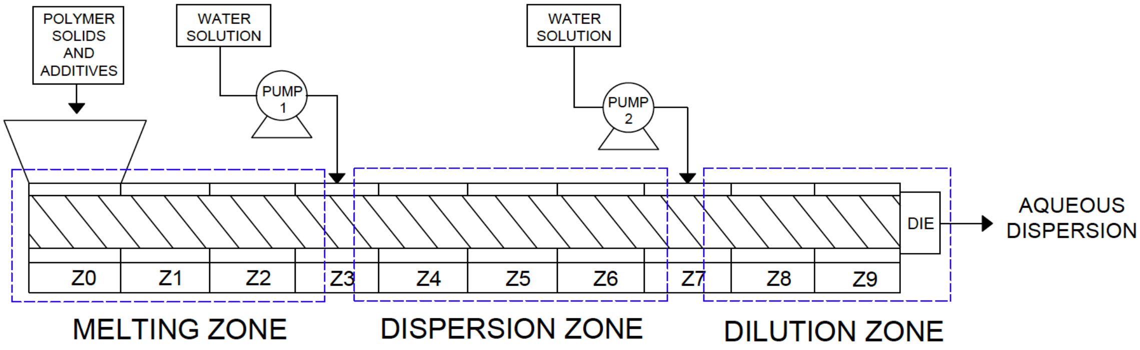


Figure 2-1. Schematic representation of the SFEE process inside a twin-screw extruder.

The bench scale coalescence trials were conducted using a custom-made 100 mL stainless steel vessel (D = 5.08 cm, h = 50 cm). A schematic representation of this vessel can be seen in Figure 2-2, showing a cooling system and sampling port whereas heat and mixing were provided from a hot plate below the unit. Heat was provided by immersing the vessel up to its lid in silicone oil (rated for service up to 140°C). Constant pressure (270 kPa) was applied to prevent boiling but also assisted in sampling particles during trials without opening the unit. The apparatus was set up to collect samples reflecting the state of agglomeration inside with minimal chance to coalesce during their removal.

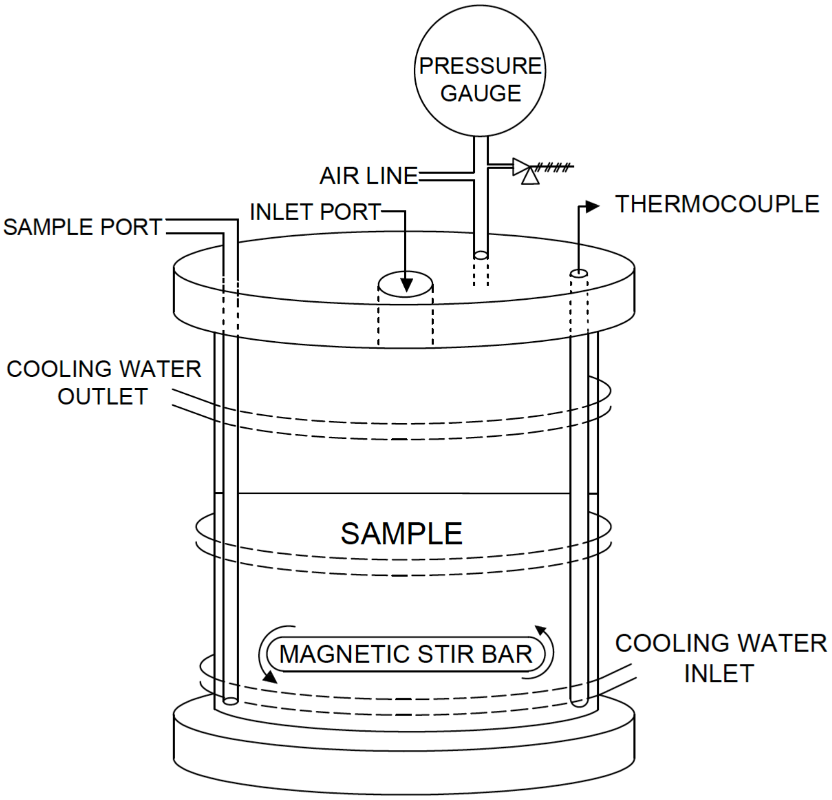


Figure 2-2. Schematic drawing of aggregation testing vessel.

Solvent Emulsification (SE)

Polyester was dissolved in ethyl acetate in a glass vessel at a 1:1.5 weight ratio at 60°C under agitation at 550 RPM with a stirrer. Methods for surfactant addition (at varied molecular loadings) were chosen based on their physical state; SDBS and Unicid 350 were dissolved directly in the polyester, with the remainder of surfactants (Calfax, Igepal CO-890, Brij 58, Synperonic F-108) added as aqueous solutions during the dispersion stage. The dispersion stage involved the addition of an aqueous surfactant solution (if applicable), along with an alkaline solution containing 1% (w/w polymer) NaOH into the polymer solution, producing a W/O emulsion with resultant resin/water (R/W) ratio of 3.5. The mixture was stirred for 5 minutes. For the dilution stage, phase inversion occurred by adjusting the R/W ratio to 1.3, followed by continually stirring the emulsion for an additional hour without heat. This emulsion was subsequently heated to 88°C for three hours to evaporate the ethyl acetate, aided by a low flow of blanketing nitrogen into the vessel. The complete procedure was based on Example 4 of US Patent 8,466,254 [18].

Solvent-Free Extrusion Emulsification (SFEE)

Extrusion trials were conducted at a uniform barrel temperature of 95°C and screw speed of 300 RPM. A constant feed rate for the resin was set at 8 kg/hr for all experiments. The first injection site at zone Z3 represented the start of the dispersion stage, where the R/W ratio was adjusted to 3.5 using a 1% (w/w resin) aqueous solution of NaOH; NaOH aided the function of the surfactants and converted over 50% of the end groups of the polyester into carboxylates to help water incorporation [7]. The second injection site at zone Z7 corresponded to the start of the dilution stage, where the system was further adjusted to a R/W ratio of 1.3.

The surfactants being tested in these experiments were fed into the process by various methods. SDBS and Unicid 350 had to be fed into the process as dry blends with the polyester resin. Calfax was fed as a solution together with aqueous NaOH at zone Z3. The feeding of Igepal CO-890 or Brij 58 was done using two different approaches (for reasons explained in a later section); both as a dry blend with the polyester or combination of dry blend and as a solution together with aqueous NaOH. When fed as a solid, the surfactants were ground using a coffee grinder to break up lumps before being blended with the polyester by tumble mixing. When both Igepal CO-890 and Brij 58 were fed as solutions, they required dissolution in Milli-Q water at a raised temperature (40°C) and constant agitation for 30 minutes prior to injection at zone Z3 along with NaOH. Synperonic F-108 was never used in the SFEE process due to reasons discussed in a later section. A complete list of surfactant molar loadings used in both SE and SFEE processes can be seen in Table 2-1.

Table 2-1. Range of surfactant molar loadings used in both SE and SFEE experimentation.

Surfactant	Solvent Emulsification				Solvent-Free Extrusion Emulsification			
	Range of Surfactant Weight Fractions (pph)		Range of Molar Loadings (mmol/g Resin)		Range of Surfactant Weight Fractions (pph)		Range of Molar Loadings (mmol/g Resin)	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
SDBS	3.6	7.5	0.10	0.22	4	7.5	0.11	0.22
Unicid 350	7.5	16	0.10	0.44	8.1	17.7	0.22	0.52
Calfax	7.1	24	0.06	0.22	2.4	12	0.04	0.22
Igepal CO-890	7.5	86	0.04	0.44	20.3	41.7	0.11	0.22
Brij 58	7.5	48	0.07	0.44	24.2	35.2	0.22	0.32
Synperonic F-108	7.5	313	0.01	0.22	*N/A*			

Coalescence Study

Emulsions prepared by both SE and SFEE were tested for their tendency to aggregate depending on temperature, agitation speed and pH, examining conditions that might arise in the dilution stage of the twin screw extruder, using the previously described vessel immersed in an oil bath (Figure 2-2). A constant emulsion volume of 30 mL was used for each experiment with ~8% solids. The varied conditions included three temperatures (60, 90, and 120°C), two stirrer speeds (100 and 400 RPM), and two pH values (pH 7 and 10); the emulsion pH was raised using 0.5M aqueous NaOH. Each trial began once the temperature of the emulsion inside the vessel was ±5°C of the setpoint temperature. The entire vessel was removed from the oil bath and quenched in an ice bath after 5 minutes ± 10 seconds from the start of the trial. When the temperature inside the vessel reached ~30°C, the vessel was removed from the ice bath and a single sample of ~15 ml was collected at the sampling port.

Characterization

Prior to any characterization mentioned below, samples were triple filtered using a 35 μm sieve to minimize any coarse particles present. Emulsified samples prepared by SE and SFEE were compared based on their particle size distributions, using two instruments. A NANOTRAC NPA250 dynamic light scattering particle size measurement system was capable of measuring particle sizes between 0.8 and 6500 nm. A Mastersizer 2000 particle size measurement system was used for measuring particle sizes between 0.2 and 2000 μm. The combined results were reported based on three replicated measurements. To compare conditions in the coalescence tests where samples prepared by the different surfactants had significantly differing particle sizes, the span of the particle size distribution was the preferred measure to observe change. Span is a unitless value and is calculated from the difference in the mean volume diameter distribution moments, D_{10} and D_{90}, and normalized by D_{50}.

Zeta potential results were obtained using the previously described NANOTRAC NPA 250, calculated from four replicates. Images of selected samples by scanning electron microscopy (SEM) used a JEOL JSM-7000F electron microscope equipped with a Schottky Field emission gun.

Critical micelle concentration (CMC) for each surfactant was determined using a digital goniometer (First Ten Ångstroms) to analyze sessile drop contact angles. The method resembles the approach described by Chen [19]. At an ambient temperature of 25°C, the contact angle was measured for a 10 µL droplet of water with a varied surfactant concentration placed on a compression molded sheet of the polyester. The droplet surfactant concentration was plotted versus contact angle, and the concentration value corresponding to the sharp change in the slope of the curve was taken as the CMC value for a surfactant. The statistical uncertainty for each respective characterization value described above has been summarized in Table 2-2.

Table 2-2. Relative standard error values for the different characterization parameters presented.

Parameter	Average Relative Standard Errors
D_{50}	± 0.02 µm
Span	± 0.05 µm
Zeta Potential	± 3.00 mV
CMC	± 0.01 mM

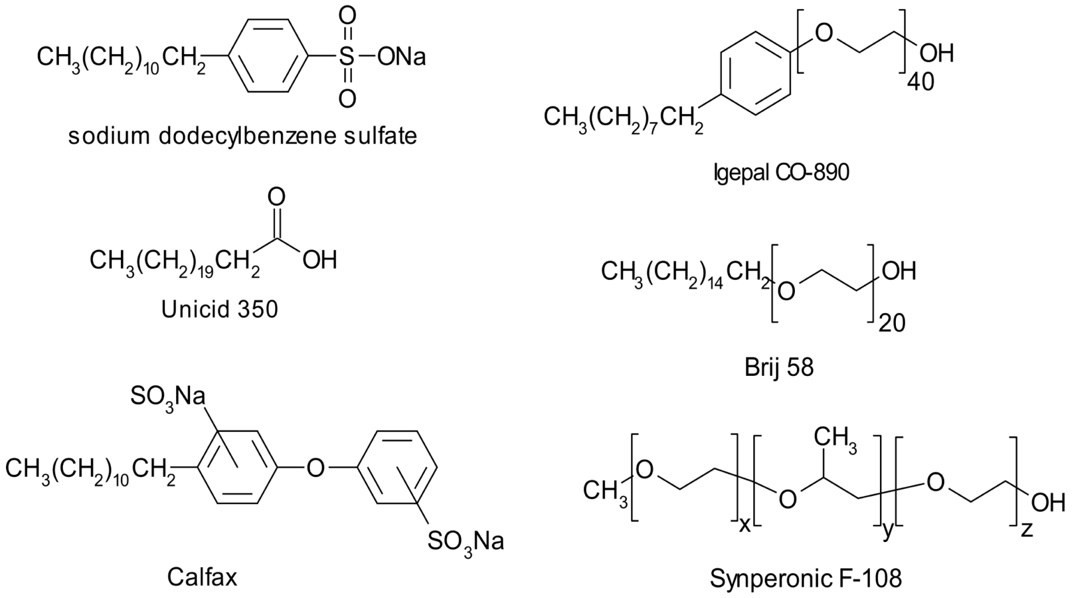
RESULTS

Surfactant Properties

The anionic surfactants (SDBS, Unicid 350, and Calfax) and non-ionic surfactants (Igepal CO-890, Brij 58, Synperonic F-108) were all chosen based on their differing molecular structures and similar estimated HLB values. Each of the six surfactants had an estimated HLB value larger than 8, which is related to the stabilization of O/W emulsions [20]. As chosen anionic surfactants, SDBS and Calfax had similar C_{12} alkyl chains but different structures around their ionic functionality to affect their positioning at the interface and interaction with water. Unicid was a simpler, less hydrophilic anionic species with a longer nominal C_{21} alkyl chain and carboxylate head after saponification. The chosen non-ionics had alkyl chains varying in length but close to C_{12} (with the exception of Synperonic) as well as varying oxyethylene chains. In the case of non-ionics, they were felt to lay across the polyester boundary rather than protrude into the water phase due to their higher solubility in the oleic phase at elevated temperatures, making their ethoxy-based chain length important to their overall surface activity (Traube's Rule) [21]. A list of surfactant properties supplied by the vendors and the measured CMC values are given in Table 2-3. The molecular structures of the surfactants are shown in Figure 2-3. Since very little work has been done in SFEE with these surfactants (with the exception of SDBS), the dissimilarities in these tested species allowed for a more intensive analysis on which types of molecules were more or less effective emulsifiers.

Table 2-3. Selected surfactant physical and chemical properties.

Name	Surfactant Type	Physical State	Molecular Weight (g/mol)	HLB	CMC (mM)
SDBS	Anionic	Solid	348.5	10.6	1.2
Unicid 350	Anionic	Solid	340	8.9	*N/A*
Calfax DB-45	Anionic	Liquid	542	17	1.04
Igepal CO-890	Non-Ionic	Solid	1982.5	18	0.27
Brij 58	Non-Ionic	Solid	1122	15.7	0.06
Synperonic F-108	Non-Ionic	Solid	~14600	> 20	1.89



sodium dodecylbenzene sulfate

Igepal CO-890

Unicid 350

Brij 58

Calfax

Synperonic F-108

Figure 2-3. Molecular structures for the six surfactants tested in this study.

From the CMC values measured, it is seen that each tested surfactant, in both SE and SFEE trials, had the capacity to form micelles in the study; Unicid 350 was immiscible in water and so no CMC measurement was possible. There was a minor concern these chemical species might interfere with the particle size measurement. It was beyond the scope of this project to identify micelles in the systems studied but it was assumed they did not interfere in the results, accepting the analysis of others for both ionic and non-ionic surfactants where micelle diameters have been approximated to fall in the range of 2–20 nm [22-24]. Synperonic F-108 may have presented larger micelles in the range of 50–100 nm, but it was not extensively studied in this work due to difficulties with its handling. [25].

Anionic Surfactant with SE and SFEE Processes

While comparing samples between SE and SFEE was ultimately intended in this study to gain new insights on viscous effects on emulsification in the extruder, the solvent method was also being tested as a screening tool for useful surfactants before use in the larger-scaled method of SFEE. Due to this latter consideration, the tests began at the bench scale using SE with the three chosen anionic surfactants. In this trial, SDBS was considered the baseline case due to earlier reported success with the species in SFEE [5-7]. Similarly, a surfactant loading of 0.22 mmol/g resin was considered the benchmark concentration since it was the concentration found in those same earlier SFEE studies to yield robust emulsification performance when other processing conditions were being varied. A summary of the representative moments for the mean (D_{50}) and range of particle sizes (D_{10}, D_{90}) in these samples with the three anionic surfactants is seen in Table 2-4, while the full particle size distributions at their best condition are shown in Figure 2-4 (a).

A monodisperse emulsion with particles predominantly in the 70–150 nm size range was produced with SDBS at the benchmark condition. The same surfactant loading with Unicid 350 yielded an emulsion with a slightly higher D_{50}, along with some observable coarse generation in the 5–100 μm size range. Raising the surfactant loading of Unicid 350 did little to improve the resultant emulsion, therefore 0.22 mmol/g resin was considered to be its preferred loading in the SE process. Lowering the surfactant content of Unicid to 0.11 mmol/g resin proved disastrous with no emulsion evident (data not shown), whereas with SDBS the distribution only showed some broadening at this lower concentration but still the highest frequency of particles matched the desired particle size.

Replacing SDBS with Calfax at the benchmark condition of 0.22 mmol/g resin was seen to yield a nearly identical emulsion to the other two species. When the surfactant loading of Calfax was reduced to 0.11 mmol/g resin, no major changes in the final emulsion were seen. A further reduction in Calfax loading was seen to yield coarser particles though at 0.06 mmol/g resin, many of the produced particles were still acceptable. In summary, it was found that the benchmark concentration was suitable for SE with all tested anionic surfactants, and the order of these surfactants as emulsifiers for the system was Calfax>SDBS>Unicid 350.

The SFEE results are summarized in Table 2-5 giving the representative distribution moments again, whereas the full particle size distributions for the best condition of each surfactant are presented in Figure 2-4 (b). At the benchmark condition of 0.22 mmol/g resin, SDBS was seen to result in a monodisperse emulsion having a D_{50} of 130 nm, reproducing the results observed by SE as well as those SFEE findings published to date [5-7]. The direct translation of results at the benchmark condition between processes illustrates the robustness of SDBS in emulsifying polyester into nanometre sized latex particles but the higher viscosity of the medium in SFEE does appear to require a critical concentration of the surfactant to diffuse to the interface at an appropriate rate corresponding to the residence time of the dispersion stage. For example, SDBS did not yield a satisfactorily emulsified product at the lower concentration of 0.11 mmol/g resin, unlike the findings by SE. Unicid 350 was far less successful in the SFEE process despite being added as a solid, like SDBS, along with the polyester at the start of the melting zone. Unicid produced some coarse particles but the majority of resin exited as a W/O emulsion (euphemistically referred to as 'wet plastic') at the benchmark condition, needing to be increased to 0.52 mmol/g resin before emulsification was moderately successful; wet plastic looks like a shiny rod or rope of molten polymer exiting the extruder but shows no visibly separated water phase. At this higher Unicid concentration, the fraction of wet plastic decreased to 50% while the emulsified fraction had a higher than desirable particle size ($D_{50} \cong 400$ nm) and contained a significant portion of coarse particles in the 10–500 μm range. No further increases in surfactant loading were tested for Unicid 350, with the feeling that the concentration was getting unrealistically high for commercial use. At the benchmark condition, use of Calfax DB-45 produced very similar results to SE ($D_{50} \cong 160$ nm), with all of the polymer being emulsified successfully like SDBS. Decreasing surfactant loading to 0.13 mmol/g resin still achieved a successful emulsification, with a resulting D_{50} of 190 nm. At the lowest concentration of 0.06 mmol/g resin, Calfax showed poor emulsification behaviour like SE, illustrated by the increase in measured coarse particles ($D_{90} = 3.90$ μm, Span = 12.3). In summary, the order of effective surfactants was the same between SFEE and SE, but a higher minimum concentration of anionic surfactant was required for SFEE.

Table 2-4. Particle size summary for anionic surfactant based emulsions created using SE.

Surfactant	Surfactant Amount (pph)	Surfactant Loading (mmol/g resin)	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	Span
SDBS	7.5	0.22	0.07	0.10	0.15	1.36
SDBS	3.6	0.11	0.07	0.12	0.23	1.35
Unicid 350	15	0.44	0.08	0.20	0.59	2.55
Unicid 350	11.3	0.33	0.08	0.18	0.54	2.56
Unicid 350	7.5	0.22	0.09	0.19	0.87	4.11
Calfax	12.4	0.22	0.07	0.12	0.21	1.17
Calfax	6.1	0.11	0.07	0.11	0.20	1.18
Calfax	3.5	0.06	0.07	0.16	10.1	62.9

Table 2-5. Particle size summary for anionic surfactant based emulsions created using SFEE.

Surfactant	Surfactant Amount (pph)	Surfactant Loading (mmol/g resin)	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	Span	Percent Emulsified Material (%)
SDBS	7.5	0.22	0.07	0.11	0.19	1.09	100
SDBS	4.0	0.11	2.55	30.3	552	18.1	10
Unicid 350	17.7	0.52	0.12	0.39	68.9	176	50
Unicid 350	12.4	0.36	0.21	0.89	319	358	50
Unicid 350	8.1	0.24	0.24	9.67	131	13.6	10
Calfax	19	0.22	0.08	0.16	0.39	2.29	100
Calfax	11.3	0.13	0.08	0.19	0.52	2.32	100
Calfax	5.1	0.06	0.20	0.30	3.90	12.3	100

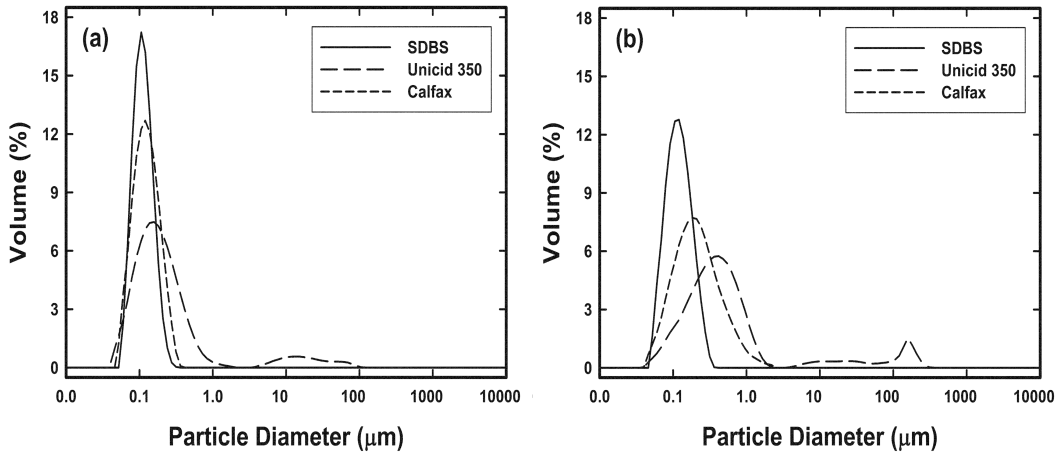


Figure 2-4. a) Particle size distribution results for SE latex emulsions with surfactant loadings of: SDBS and Unicid 350 at 0.22 mmol/g resin, and Calfax at 0.11 mmol/g resin. b) Particle size distribution results for SFEE latex emulsions with surfactant loadings of: SDBS at 0.22 mmol/g resin, Unicid 350 at 0.52 mmol/g resin, and Calfax at 0.13 mmol/g resin.

Non-ionic Surfactant with SE and SFEE Processes

Following the same approach used with the anionic group, SE testing was conducted first using the selected non-ionic surfactants to determine a benchmark molar concentration for SFEE and determine their respective feasibility to aid emulsification of the polyester in water. A summary of the representative distribution moments for samples produced with the non-ionic surfactants by SE is given in Table 2-6. The resulting particle size distributions for each non-ionic surfactant at its respectively preferred loading can be seen in Figure 2-5 (a). The first surfactant tested in the SE process was Igepal CO-890 and after some variation in concentration, it was determined that a minimal loading of 0.11 mmol/g resin was necessary to achieve the desired goal. This concentration produced a monodisperse latex emulsion with a D_{50} of 120 nm and minimal coarse generated. A loading of 0.22 mmol/g resin performed equally well in achieving the desired nanoparticles, whereas a concentration of 0.04 mmol/g produced an unsatisfactory yield with too many coarse particles. This was an extremely positive finding since the effectiveness of non-ionics for SE compared to anionic species was not clear originally, but this outcome shows close equivalence in performance. A surfactant loading of 0.22 mmol/g resin was then tested with Brij 58, producing an almost identical monodisperse emulsion to Igepal, and similarly, reducing the loading of Brij 58 below 0.11 mmol/g resin resulted in an increase in D_{50} and coarse particle generation. Synperonic F-108 was the last tested surfactant with SE and at 0.11 mmol/g resin, it was unsuccessful in creating a monodisperse emulsion. The lowest possible surfactant loading that resulted in nanoparticles with Synperonic F-108 was 0.22 mmol/g resin, which is an excessively large mass due to its high molecular weight. However, even at this concentration the resulting emulsion did not meet the desired particle size; the sample shows a tri-modal distribution with distinct peaks centered at approximately 250 nm, 2 μm, and 100 μm. As a result, Synperonic F-108 was rejected from further consideration beyond the SE trials. In summary, two non-ionic surfactants (Igepal CO-890 and Brij 58) were considered as possible candidates for SFEE with near-equal suitability, and apparently similar performance to anionic species by SE. It was decided to keep the benchmark condition the same for the non-ionic group (0.22 mmol/g resin) even though 0.11 mmol/g resin was consistently the minimum concentration for SE since experience with extrusion in the anionic case had already shown that more surfactant is generally needed for SFEE.

The resulting particle size distributions for the two non-ionic surfactants in SFEE are seen in Figure 2-5 (b) and their distribution moments are listed in Table 2-7. At the benchmark condition, Igepal CO-890 exhibited challenges related to feeding into the extruder. Igepal CO-890 is a waxy solid material, and feeding it in excess amounts through the hopper together with polyester resin resulted in bridging at the extruder inlet. Due to this blockage, it was not possible to introduce the full amount of Igepal CO-890 at 0.22 mmol/g resin by the feeder. To resolve this issue, approximately 12% of the total amount of Igepal was dissolved into the alkaline water and pumped into the extruder at zone Z3 (any larger increase in dissolved Igepal resulted in solution viscosities that exceeded our pumping capabilities), with the remainder of the surfactant being fed as a solid using the feeder. Looking at Figure 2-5 (b), one can see that although the bulk of the particles are present in the 100–200 nm range, coarse particles in the range of 1–100 μm were present. It is also important to note that approximately only 25% of the extrudate was emulsified material, with the rest being wet plastic. An attempt to increase surfactant loading was done to try and reduce coarse particle generation, but increasing surfactant loading resulted in an unresolvable pumping issue related to the now higher viscosity of the aqueous solution at zone Z3. Looking at Brij 58, similar bridging issues were encountered that had to be resolved by dissolving 20% of the total surfactant into the injected alkaline solution at zone Z3. At 0.22 mmol Brij 58/g resin, only about 5% of the solids were emulsified, having a D_{50} of 10 μm. Increasing the surfactant loading resulted in similar pumping issues of high solution viscosity seen with Igepal but at least in this case, a concentration of 0.32 mmol/g Brij 58 was possible. At this higher concentration, the 5% emulsified fraction exhibited a D_{50} decrease to 0.4 μm but coarse particles as well (D_{90} = 734 μm), as seen by the distribution shown in Figure 2-5 (b). The majority of the solids for both Igepal CO-890 and

Brij 58 cases did not experience phase inversion, remaining as wet plastic. In summary, both non-ionic surfactants did poorly at testable conditions, even when fully introduced, though Igepal CO-890 emulsified more of the polyester compared to Brij 58 at the same concentration. Their performance in SFEE was not reflective of the SE results, which is markedly different from the anionic group.

Table 2-6. Particle size summary for non-ionic surfactant based emulsions created using SE.

Surfactant	Surfactant Amount (pph)	Surfactant Loading (mmol/g polyester)	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	Span
Igepal CO-890	43	0.22	0.07	0.11	0.17	0.91
Igepal CO-890	22	0.11	0.06	0.12	0.22	1.32
Igepal CO-890	7.5	0.04	0.09	0.31	277	898
Brij 58	24	0.22	0.07	0.11	0.18	1.03
Brij 58	12	0.11	0.06	0.12	0.24	1.45
Brij 58	7.5	0.07	0.10	0.40	244	617
Synperonic F-108	310	0.22	0.10	0.30	1.28	3.99

Table 2-7. Particle size summary for non-ionic surfactant based emulsions created using SFEE.

Surfactant	Surfactant Amount (pph)	Surfactant Loading (mmol/g polyester)	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	Span	Approx. Percent Emulsion (%)
Igepal CO-890	42	0.22	0.09	0.3	1.7	5.4	25
Igepal CO-890	32	0.16	0.10	0.2	62.5	312	25
Igepal CO-890	22	0.11	0.10	0.2	74.6	373	25
Brij 58	24	0.22	0.13	9.7	354	36.5	5
Brij 58	35	0.32	0.10	0.4	734	1830	5

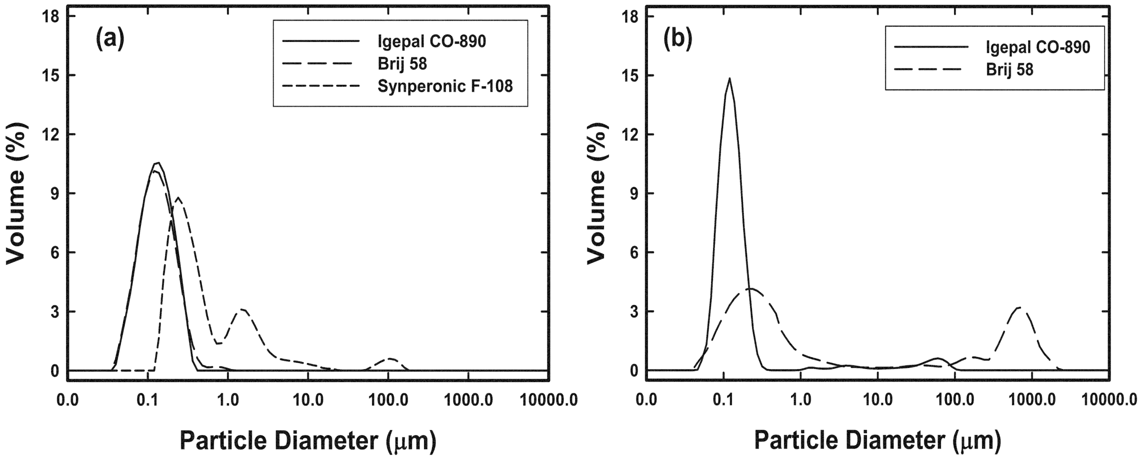


Figure 2-5. a) Particle size distribution results for SE latex emulsions with surfactant loadings of: Igepal CO-890 and Brij 58 at 0.11 mmol/g resin, and Synperonic F-108 at 0.22 mmol/g resin. b) Particle size distribution results for SFEE latex emulsions with surfactant loadings of: Igepal CO-890 at 0.22 mmol/g resin and Brij 58 at 0.32 mmol/g resin.

Particle Stability Examined by Zeta Potential and Coalescence Testing

To ideally relate the differences seen by the surfactants between SE and SFEE to only the dispersion stage of the extruder, it was felt necessary to establish that the emulsion created by either method produced particles of similar stability; if the coarse particles seen are related to how the emulsions were generated rather than agglomeration after formation then the study could focus on just one stage of the SFEE process to explain the function of the surfactants. To examine particle stability, SE and SFEE O/W emulsions created with each of the previously described surfactants were tested at extreme conditions (for the dilution stage) to determine which conditions (if any) would lead to particle de-stabilization. The complete set of aggregation results for each of the six surfactants can be seen in Figure 2-6 (a-f). These figures illustrate destabilization by a change in the span of the particle size distribution since even the slightest increase in the volume percentage of coarse particles will impact this value and as a normalized value, it was better as a comparator between SE and SFEE.

The overall stability of emulsions at 60 or 90°C and at pH 7 or 10, were considered excellent based on their negligible change in span, whether prepared by SE or SFEE. This observation was seen with all surfactants except Synperonic F-108 which was only made in the SE process. Looking at Figure 2-6 (f), it can be seen that any emulsions produced with Synperonic F-108 showed an increasing span and were deemed unstable. For the other surfactants, significant particle agglomeration was only detected for the samples at 120°C and pH 10, seen for both SE and SFEE. Emulsions with any of the anionic and non-ionic surfactants showed no aggregation for any tested temperatures whenever the pH of the system was 7. Emulsions with Brij 58 were the only samples to never agglomerate at any condition in the tests.

The agglomeration observed at high pH is related to the increased overall ionic strength of the solution compressing the electrostatic double layer, which in turn reduced repulsive forces between particles [26-27]. Combined with temperatures far above the glass transition of the polyester (60°C), it is not surprising that particles could approach close enough to aggregate at 120°C and pH 10. SEM images of samples at the high pH and temperature conditions are presented in Figure 2-7, showing particles sintered together. This instability in agglomerated samples was also quantitatively observed in their measured zeta potential values. The closer the measured zeta potential was to zero, the less stable the suspension. The zeta potential values for both the SE and SFEE samples can be seen in Tables 2-8 and 2-9, respectively. The samples with anionic surfactants ranged in zeta potential from -30 mV to -50 mV at neutral pH and 60°C, while those with non-ionic surfactants ranged from -15 mV to -25 mV; the non-zero zeta potential for non-ionic species is not uncommon in studies [20] and often relates to contaminants, which in this case should be the sodium carboxylate polyester end groups. The tables illustrate changes in zeta potentials for emulsions that had been coalesced at 60 or 120°C for both pH conditions. Looking at these results, one can see similar trends in sample instability to those observed in Figure 2-6. No large drops in zeta potential were observed for any of the surfactants at pH 7 (with the exception of Igepal CO-890) regardless of preparation technique. When looking at the values measured at pH 10, almost all of the tested surfactants were seen to experience a significant drop in zeta potential as conditions changed from 60 to 120°C, reflecting the overall emulsion instability seen with particle size measurement. Overall, the emulsions prepared with both SE and SFEE exhibited similar trends in measured zeta potential over the tested conditions.

Table 2-8. Zeta potential data for SE samples tested at various pH values, and temperatures for six different surfactants at their respective molar loadings: SDBS [0.22 mmol/g resin], Unicid 350 [0.22mmol/g resin], Calfax [0.11 mmol/g resin], Igepal CO-890 [0.22 mmol/g resin], Brij 58 [0.22 mmol/g resin], Synperonic F-108 [0.22 mmol/g resin].

Name	Tested Emulsion Zeta Potentials (mV)			
	pH 7		pH 10	
	60°C	120°C	60°C	120°C
SDBS	-40.1	-29.8	-46.7	-10.7
Unicid 350	-48.9	-22.6	-46.5	-22.6
Calfax	-29.2	-30.5	-26.9	-17.7
Igepal CO-890	-25.5	-9.6	-26.5	-13.9
Brij 58	-22.6	-20.3	-26.7	-21.8
Synperonic F-108	-16.5	-12.2	-12.2	-4.6

Table 2-9. Zeta potential data for SFEE samples tested at various pH values, and temperatures for five different surfactants at their respective molar loadings: SDBS [0.22 mmol/g resin], Unicid 350 [0.52mmol/g resin], Calfax [0.13 mmol/g resin], Igepal CO-890 [0.22 mmol/g resin], Brij 58 [0.22 mmol/g resin].

Name	Tested Emulsion Zeta Potentials (mV)			
	pH 7		pH 10	
	60°C	120°C	60°C	120°C
SDBS	-50.9	-44.6	-37.6	-18.5
Unicid 350	-26.3	-22.5	-37.3	-16.2
Calfax	-60.1	-49.5	-58.1	-41.6
Igepal CO-890	-24.5	-19.9	-22.1	-14.2
Brij 58	-36	-33.5	-29.4	-20.0
Synperonic F-108	*N/A*	*N/A*	*N/A*	*N/A*

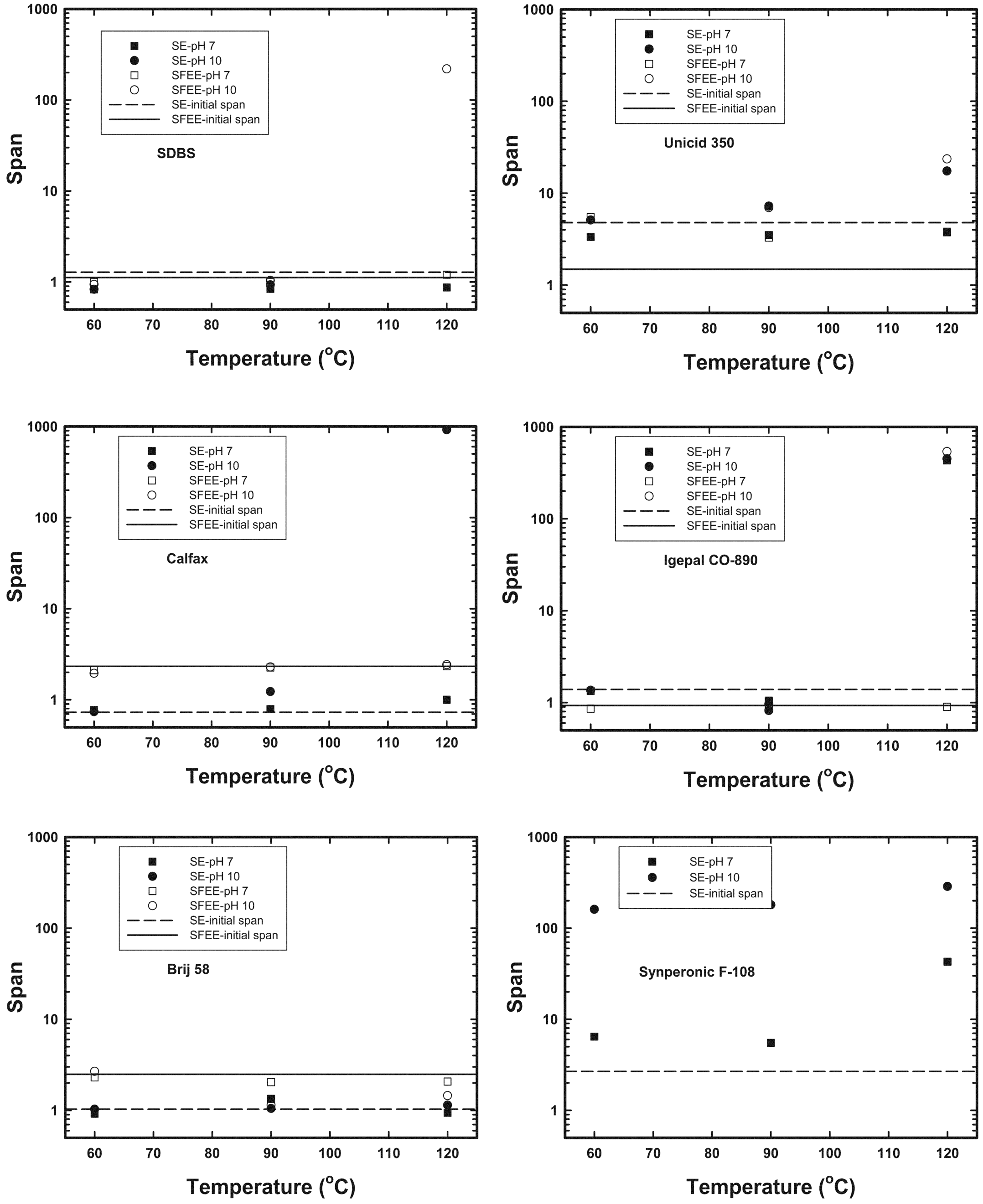


Figure 2-6. Aggregation data for both SE and SFEE samples tested at various pH values, and temperatures for six different surfactants at their respective molar loadings: a) SDBS [SE & SFEE: 0.22 mmol/g resin], b) Unicid 350 [SE: 0.22mmol/g resin, SFEE: 0.52mmol/g resin], c) Calfax [SE: 0.11 mmol/g resin, SFEE: 0.13 mmol/g resin], d) Igepal CO-890 [SE & SFEE: 0.22 mmol/g resin], e) Brij 58 [SE & SFEE: 0.22 mmol/g resin], f) Synperonic F-108 [SE: 0.22 mmol/g resin].

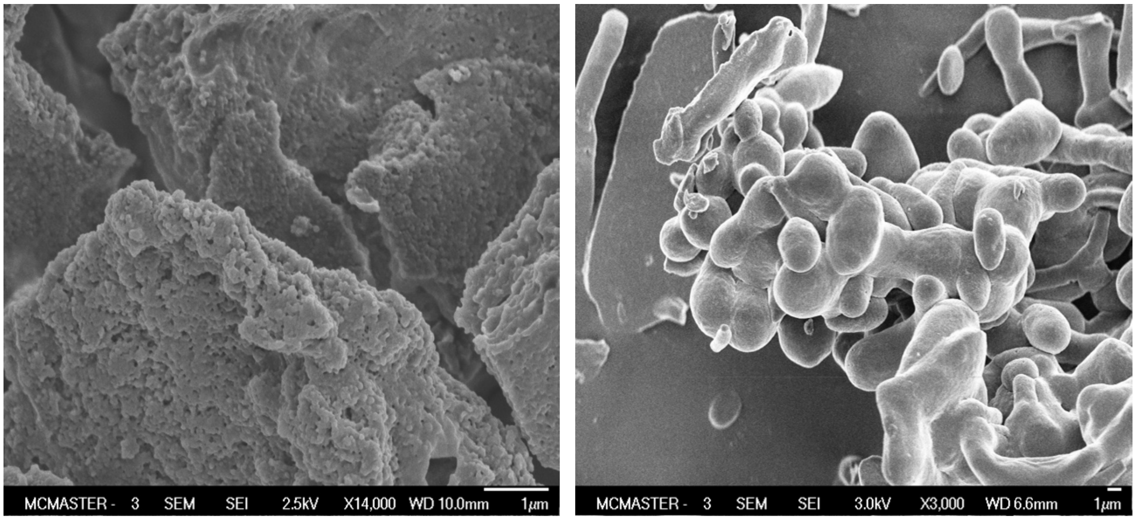


Figure 2-7. Images of aggregates formed from SE emulsions tested at 120°C and pH 10 emulsified with SDBS (left) and Calfax (right).

DISCUSSION

Prior to discussing the contribution of surfactants in SFEE, it is important to recognize that the important function of the added NaOH was to functionalize the end groups of polyester, lower interfacial tension of the system and promote water incorporation. In the absence of surfactant, the anionic carboxylate groups of polyester have only been effective in producing particles as small as 1.3 μm [5-7,13] but never have sub-micron sizes been achieved. The rate of this reaction is notably improved by the presence of a surfactant [7]; the influential contributions of surface-active species to chemical reactions have been studied elsewhere [29]. With the lower interfacial tension created by the addition of surfactants, a more evolved, thinner lamellae phase morphology is possible prior to phase inversion. Previous studies have related the thickness of striated lamella in the shear field of the extruder prior to phase inversion, to the final particle size for SFEE [13]. Without the successful generation of the W/O lamellae morphology, the creation of nano-sized latex particles is improbable, making the function of surfactants in the dispersion stage critical for this process.

Anionic Surfactant Performance

The anionic and non-ionic surface active species chosen had HLB values intended to drive the system to produce stable O/W emulsions by the dilution stage, though both W/O and O/W emulsions were produced in this study based on surfactant performance. Their performance for the limited residence time of the process was dependent on their chemical functionality but also affected by the manner of their introduction into the system; surfactant migration to the interface from the oleic phase was assumed to be more significantly impeded, at least initially, in SFEE due to restricted mobility, with an oil-phase measured viscosity of 230 Pa-s versus 0.66 Pa-s for SE (at process temperature). As discussed below, this appeared to be a reasonable assumption, though complicated to definitively prove, since chemical functionality and molar mass of a species are inter-related just as droplet dispersion is related to both convective mixing and interfacial forces. The physical properties of each surfactant determined the manner by which it was added, in the oil phase or aqueous phase, while SFEE imposed additional constraints compared to SE. Since coalescence testing was helpful in showing the particles were all similarly stabilized once formed irrespective of the surfactant used, we assume the different particle size distributions observed reflected the migration of the active species from one phase to the interface which had been retarded or aided by the difference in oleic phase viscosity.

The anionic species covered the range of HLB values relevant to producing an O/W emulsion but also, unintentionally, covered the three main methods of incorporating emulsifying agents [30]. Unicid 350 was added by the *nascent soap method* (fatty acid added to the oleic phase while the alkaline reactant is present in the water phase). The poor performance of Unicid 350 as an anionic surfactant compared to the other two species can be partially attributed to this method of addition as well as its HLB value. Using the nascent soap method creates a mixing constraint on water incorporation by the fact that forming the W/O emulsion is kinetically controlled by the neutralization reaction which will be rate-limited by interfacial area growth for Unicid and NaOH to access one another. The fact that this surfactant's effectiveness is strongly affected by the oleic phase viscosity (comparing SE versus SFEE results) points to this rate-limitation being a significant factor; at least 140% more Unicid was needed to get reasonable sized particles in SFEE compared to SE whereas only 100% more SDBS or Calfax accomplished the same goal. The limited effectiveness of the carboxylated end groups of the polyester in interfacial growth has been similarly attributed to their slow neutralization reaction in the bulk phase of SFEE [7]. The second issue for Unicid 350 was its low HLB value (a cause of its longer lipophilic group), meaning it will exhibit a lower tendency to drive inversion of a W/O emulsion formed in the dispersion stage upon the second addition of water. The lack of a phenyl group also likely hindered the effectiveness of Unicid in SFEE, where the phenyl rings present in both SDBS and Calfax contribute significantly to their steric stabilization abilities. To overcome these issues, much higher molar loadings of Unicid 350 were required (0.52 mmol/g resin) to achieve the same stabilization in SFEE compared to Calfax (0.11 mmol/g resin) or SDBS (0.22 mmol/g resin).

Neither Calfax nor SDBS were dependent on neutralization in the process and so, both were immediately effective for water incorporation into the oleic phase. Consistent between SE and SFEE, Calfax performed equivalent to SDBS but at a 50% lower molar loading. The fact that both SDBS and Calfax needed 100% more content in SFEE versus SE suggests that the different methods of addition employed did not introduce any time-dependency based on surfactant location in terms of their functionality when no reaction was required; SDBS was added by the *agent-in-oil method* and Calfax was added by the *agent-in-water method* [30]. Surfactant mobility appeared to have a negligible rate-limiting effect on interfacial growth of the W/O system with these anionic species based on their manner of addition. However, the rate-limitations imposed by phase viscosity on lamellae formation and thinning was considered the primary cause for needing 100% more surfactant content in SFEE versus SE. The high HLB value of Calfax was felt to explain its improved performance compared to SDBS by needing a lower concentration for phase inversion; possessing disulfonated groups increased the affinity of Calfax to draw water into the oil phase. Adding SDBS into the process as a dry blend with polyester resin did present concerns initially over its homogeneity in the melt but comparing its performance in both processes versus Calfax (which would not be expected to have dispersion concerns in the water phase), the results do not support this factor as a reason for the difference in particle size between SE and SFEE.

Overall, the results with the anionic species show the importance of the surfactant to provide immediate performance in the short residence time of the dispersion stage. However, phase viscosity only appeared to affect the neutralization reaction, not a species' capacity to participate in interfacial growth. This is perhaps related to their relatively small molar mass and strong driving tendency to incorporate water that brings them to the interface so readily. Oleic phase viscosity will certainly affect mixing of the two phases in the dispersion stage, being seen when comparing SE versus SFEE as well as in previous results of SFEE where the melt viscosity was purposefully altered [5].

Non-Ionic Surfactant Performance

Used alone, non-ionic surfactants can impart steric stabilization and decrease interfacial tension, though they are primarily considered as auxiliary surfactants with ionic surfactants required to achieve sufficiently small particle diameters [31,32]. The effectiveness of the non-ionic surfactants was more strongly dependent on the PIE method used in this study than seen with the anionic species, and that could be in part due to their temperature sensitivity though we primarily are focused on viscous effects in this paper. In SE, surfactant concentrations for Igepal and Brij were comparable to SDBS in order to achieve similar particle sizes in the emulsified O/W system due in part to their HLB values being similar; Synperonic was never effective and this can be ascribed to its poorer affinity with the oleic phase compared to the others since it lacks an alkyl chain end. This meant that both Igepal and Brij had the chemical affinity to drive the system to an O/W emulsion when there was no kinetic barrier related to mixing to impede their positioning at the interface. In SFEE, the non-ionic surfactants were incapable of inducing complete phase inversion, with more than 75% of solids remaining as a W/O emulsion by the exit of the extruder. The higher molecular weight of both non-ionic species compared to the anionic species will certainly impact their migration in the high viscous melt and the higher system temperature of SFEE will increase their affinity for the oleic phase rather than water phase [33]. However, these species are not that much larger than the anionic species (3-5 times larger) and the temperature difference (35°C) is not so great between SE and SFEE to be seen as a completely encompassing explanation for the differences in emulsification performance. Especially when we reflect on the fact that Igepal with its higher HLB and CMC value emulsified more of the polyester than Brij, as well as the previous anionic results, it seems more appropriate to state the selection of an effective surfactant in SFEE relies on it possessing a higher affinity for water to overcome retarding viscous forces affecting its migration to the interface. Both of the non-ionic species we tested lacked a high enough affinity for water in compensation for the melt viscosity as well as their larger molecular sizes to be effective with this polyester/water system. It is pointed out that this finding is specific to the kinetics of mixing and generation of interfacial area, not necessarily to migration within a specific phase. Migration in a specific phase could not be studied in this work since the two non-ionics (Igepal and Brij) needed to be employed by both *agent-in-water* and *agent-in-oil* addition methods simultaneously.

Our results showed a slight improvement in emulsification characteristics with Igepal compared to Brij. The slightly larger HLB value and higher CMC value of Igepal was felt to indicate its higher affinity for water over Brij explained this result. Surfactants with shorter, bulky end groups like Igepal exhibit greater extension into the two phases than species like Brij. The increased hydrodynamic radius of Igepal cause it to orient more-or-less perpendicularly at the interface due to steric reasons while species like Brij are more likely to lay across the interface [34].

Overall, the results of the non-ionic species have shown their ineffectiveness as sole emulsifiers in the SFEE process. The positive results obtained in SE did not translate to SFEE, a clear indication to the inability of these non-ionic surfactants to overcome the high phase viscosity ratio present in SFEE within the short residence time in the dispersion stage. This is believed to be a combination of their weak affinity to water, and their increased adsorption to the oleic phase with the high temperatures present in SFEE. Increasing molar concentration would likely improve the overall performance of the non-ionic surfactants but the physical limitations associated with their loading into the extruder makes this difficult to determine as true.

CONCLUSIONS

The higher phase viscosity of the oleic phase typical of SFEE presents a major challenge for the considered surfactants. The findings of this study indicate that the chemical affinity of the surfactant must increase in compensation for the retarding viscous forces opposing interfacial generations during mixing in the dispersion stage of a PIE process. In this study, only Calfax exhibited sufficient water affinity to not require an increase in its molar concentration for stable SFEE operation. SDBS required a 100% increase in molar concentration from SE, while Unicid 350 was found to be ineffective in SFEE at practical surfactant loadings. Neither of the two non-ionics were capable of completely inducing phase inversion in the SFEE process, with over 75% of solids made with either surfactant being made up of a W/O emulsion. Igepal was seen to slightly outperform Brij in SFEE; the slightly higher HLB value and higher CMC value related to its bulky hydrophobic end group are believed to be the reason. Future studies with more highly water soluble non-ionic species will avoid the issues seen in the present study regarding their addition, allowing for a better assessment on the relevance of surfactant location on their ultimate performance. The success achieved with Calfax in SFEE is promising, and future work will look at its incorporation into SFEE at lower molar concentrations, blended together with a non-ionic surfactant.

ACKNOWLEDGEMENTS

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CHAPTER 3: INVESTIGATING THE IMPACT OF SURFACTANT STRUCTURE AND ANIONIC/NON-IONIC SURFACTANT BLENDS ON SOLVENT-FREE EXTRUSION EMULSIFICATION

In chapter 3, all experiments and data analysis were conducted by the thesis author. Particle surface charge measurement and ion-exchange testing was conducted by Robin Sheppard at Xerox in Webster, NY. J. Pawlak and D. Lawton provided technical guidance during the project. The manuscript version of this chapter is being prepared for publication in 2019.

Investigating the Impact of Surfactant Structure and Anionic/Non-Ionic Surfactant Blends on Solvent-Free Extrusion Emulsification

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ABSTRACT

This paper examines different binary mixtures of anionic/non-ionic surfactants in a new technique known as solvent-free extrusion emulsification (SFEE) in order to control the surface charge of the resulting nano-sized polyester particles. Five non-ionic surfactants (Igepal CO-890, Igepal CA-630, Igepal CO-630, Triton X-114, Triton X-45) along with an anionic surfactant (Calfax DB-45) were considered. The optimal hydrophilic end for the non-ionic species was found to be 10–12 ethoxy units, whereas in respect to their hydrophobic end group, a branched alkyl structure was desirable. Although suited for producing O/W emulsions, none of the tested non-ionic surfactants were capable of fully emulsifying the high viscosity polymer alone by SFEE. The preferred blend of Calfax/Igepal CA-630 showed a synergistic effect in SFEE, due to the high viscosity of the system keeping the two components partitioned across the interface of the emulsifying phases, allowing a lower surfactant concentration to be used than possible in a comparable solvent-based emulsification method. This partitioning across the interface resulted in a decrease in the non-extractable Calfax left in the polyester latex after washing through an ion-exchange resin. This approach of blending anionic and non-ionic species shows an

important step in developing SFEE to prepare nanosized particles with controlled charge for sensitive applications like toners or pharmaceutical dispersions.

KEYWORDS: twin-screw extruder; surfactant blends; anionic; non-ionic; emulsions

INTRODUCTION

Solvent-free extrusion emulsification (SFEE) refers to a fairly new emulsification technology that operates continuously using a twin-screw extruder (TSE). SFEE operates in the absence of organic solvents, utilizing only water to produce an oil-in-water (O/W) emulsion from relatively high viscosity polymers (up to 600 Pa.s has been tested to date). The resulting particles range from 100-500 nm in diameter [1-4]. Commercial variants of this process are reported in the patent literature by various major chemical companies [5-9]. The nano-sized particles are produced by phase inversion of an initial water-in-oil (W/O) emulsion with notable lamellae morphology developed over the first 2/3 of the machine length. The mechanical energy input by the extruder is important to bringing these two main phases together, but alone it is not enough to generate a stable emulsion. Surface-active agents are added to develop the lamellae dispersion [10], believed to aid water incorporation into the bulk polymer melt as well as stabilize the final emulsion. Useful agents ultimately drive the formation of the O/W emulsion once a sufficient amount of water is added for catastrophic phase inversion. To reach an interfacial state required for phase inversion, sufficient lamellae thinning of the W/O emulsion must occur within the shortened time-scale of the extrusion process, adding to the importance of choosing an effective surfactant. When incorrectly chosen surfactants are used, the majority of exiting material consists of the W/O emulsion and has the appearance of ‘wet plastic’.

Based on the description of the SFEE process above, surfactants serve two major purposes in the SFEE process: promotion of intimate contact between the polymer and water phases by lowering interfacial tension; and prevention of particle aggregation after phase inversion by electrostatic and steric repulsion between the newly generated oleic particles. The performance of surfactants depends on their molecular structure. Surfactants are amphiphilic molecules consisting of two distinct ends, a hydrophilic and a hydrophobic chain [11]. The hydrophilic end can either contain a charged moiety (classified as ionic surfactants) or be charge neutral (classified as non-ionic surfactants). The charged groups of ionic surfactants increase their affinity towards water molecules, as well as electrostatically stabilize particles to prevent their aggregation. Non-ionic surfactants have a lower affinity for water (especially at the high temperatures of SFEE), being drawn to an aqueous interface by hydrogen bonding and rely upon steric stabilization provided by their bulky molecular structures to prevent domain aggregation of an emulsified system [11]. Non-ionic species are notably influenced by temperature but largely at lower temperatures than that used in SFEE, which makes them suitable to both catastrophic and transitional phase inversion methods. Both of these forms of surfactants have been used in solvent-free emulsification processes [12-15], but recent studies have shown that there are benefits associated with using a combination of ionic and non-ionic surfactants [16-19] making them attractive to consider for SFEE.

Blending together different types of surfactants has become a very popular alternative to sole reliance on a single surfactant in polymer emulsification. Using both ionic and non-ionic surfactants creates a mixed micelle system in which the benefits of both individual surfactants are present; the ionic surfactant allows for increased water affinity as well as electrostatic repulsion between particles, while the non-ionic further prevents particle aggregation with its bulky molecular structure (steric stabilization). Research into blends of ionic/non-ionic surfactants has shown that anionic surfactants have a stronger interaction with non-ionics than seen with cationic surfactants, which is believed to be due to their negatively charged end group being attracted to the slight positive charge of the oxygen atoms found in non-ionic molecules [19]. Used alone, non-ionic surfactant species can be insufficient in preventing particle interactions, however when blended with an anionic surfactant, particle stability experiences a synergistic effect of the combined electrostatic and steric stabilization mechanisms [18], and when used in their proper ratio, a blend has shown performance insensitive to temperature changes [17]. The positive impacts on emulsification properties seen when using these emulsifier mixtures is the reason their incorporation into SFEE is currently of great interest.

The motivation behind the present study was to control the surface charge of particles produced by SFEE for applications where a high anionic charge might affect usefulness (such as toner and pharmaceutics). It was hypothesized that if ionic surfactants could be partially replaced with non-ionic species, charge tuning would be possible in the final nanoparticle product. Previous SFEE studies with non-ionic surfactants have shown the possibility of charge tuning but also found this class of surfactants to be ineffective as primary emulsifiers in SFEE due to their low affinity with water at standard processing temperatures [20]. The present paper aims to explore two specific areas of interest: to further study non-ionic surfactants with a focus on their molecular features; and to explore the idea of using a binary mixture of ionic and non-ionic surfactants in SFEE, utilizing the improved understanding of non-ionic surfactants to be able to create a blend with maximized emulsifier abilities.

EXPERIMENTAL

Material

A polyester synthesized using fumaric acid and dipropoxylated bisphenol A having an approximate T_g of 60°C, M_W of 17081 g/mol ($M_W/M_N = 4.2$), and acid number of 17.7 ± 1.7 mg/g KOH (mass of KOH required to neutralize one gram of resin) was supplied by Xerox corporation (Webster, NY, USA). Calfax DB-45 (MW ≅ 542 g/mol, HLB = 16.7) was the only anionic surfactant in the study, purchased from the Pilot Chemical Company (Cincinnati, OH, USA), supplied as a 47 wt% aqueous solution. Five different non-ionic surfactants were covered in this study, all having been purchased from Sigma-Aldrich at 99% purity: Igepal CO-890 (polyoxyethylene (40) nonylphenol ether; $M_W \cong 1982$ g/mol, HLB = 17), Igepal CO-630 (polyoxyethylene (9) nonylphenol ether; $M_W \cong 617$ g/mol, HLB = 13), Igepal CA-630 (octylyphenyl-polyethylene glycol, $M_W \cong 603$ g/mol, HLB = 13), Triton X-45 (polyethylene glycol 4-tert-octylphenyl ether, $M_W \cong 427$ g/mol, HLB = 9.8), Triton X-114 (polyethylene glycol tert-octylphenyl ether, $M_W \cong 537$ g/mol, HLB = 12.4). The hydrophilic-lipophilic balance (HLB) values listed for each surfactant give a means of relative comparison between the species; admittedly these values are not strong indicators of whether any surfactant will yield an O/W emulsion by the end of the process. Deionized Milli-Q water was used for all samples discussed in this paper. NaOH (Caledon

Laboratories Ltd) was added to improve driving forces for bringing the water and polymer phases together by converting over 50% of the polyester end groups into carboxylates [3].

Apparatus

Extrusion experiments were conducted using a 27 mm 40 L/D Leistritiz ZSE-HP co-rotating twin-screw extruder (American Leistritz Extruder Corporation; Somerville, NJ, USA). The extruder barrel consisted of a water-cooled feed port (zone Z0), followed by nine heated zones (Z1-Z9). The same extruder die at the outlet of the barrel was used for all experiments discussed in this paper, having a bore diameter of 15 mm. A Brabender Technologie KT20 twin screw gravimetric feeder (Mississauga, ON, CAN) was used to feed granules into the extruder through zone Z0. Liquid injection needed for the process occurred at zones Z3 and Z7 along the extruder barrel, utilizing a high-pressure Optos piston pump (41 MPa capacity) and a high-pressure syringe pump (51 MPa capacity), respectively. An illustrated layout of the process and extruder setup can be seen in Figure 3-1.

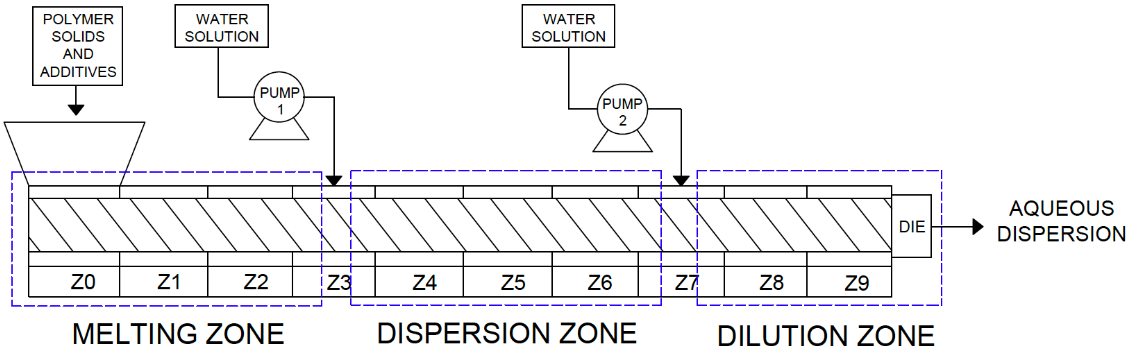

Figure 3-1. Schematic illustration of the twin-screw extruder layout used for SFEE experiments.

Solvent Emulsification

Bench-top screening for suitable concentrations of the surfactant blends was done using solvent emulsification (SE). Ethyl acetate was used to dissolve the polyester granules in a glass vessel at a respective weight ratio of 1.5:1 and temperature of 60°C, all while under the constant agitation of a magnetic stir bar at 550 RPM. In order to mimic the dispersion zone of SFEE as closely as possible with the SE process, an alkaline solution containing 1% (w/w polymer) NaOH, along with the chosen surface-active species at varied molar loadings were added into the dissolved polymer, resulting in a resin/water (R/W) ratio of 3.5, followed by a 5 minute period of agitation. At the end of this 'dispersion stage', the system was diluted by adjusting the R/W ratio to 1.3 with 25°C water to cause phase inversion. The resulting emulsion was left under continued agitation for an additional hour without any additional heat being applied. The emulsion was then heated to 88°C and left for approximately 3 hours to evaporate the ethyl acetate, with water being added into the emulsion as the ethyl acetate evaporated, such that the emulsion volume remained relatively constant. The evaporation process was aided by a steady stream of inert nitrogen flowing into the vessel. This procedure was adapted from Example 4 of US Patent 8,466,254 [21].

Solvent-Free Extrusion Emulsification

A uniform barrel temperature of 95°C and screw speed of 300 RPM was used for all extrusion trials discussed in this paper. Polymer granules were fed into the extruder at a constant feed rate of 8 kg/hr for all experiments. The first injection site (located at zone Z3) represented the beginning of the dispersion stage, where an aqueous solution of water, surfactant, and NaOH were added to adjust the R/W ratio to 3.5. All of the surfactants presented in this study were injected in solution through zone Z3 using the *agent-in-water* method of addition. The range of concentrations for each respective surfactant used in the study, as well as surfactant blends for both SE and SFEE processes can be seen in Table 3-1. The second injection site was located at zone Z7, signifying the beginning of the dilution stage, where the overall R/W ratio was adjusted to 1.3 using 25°C pure water.

Table 3-1. Range of surfactant molar loadings and weight fractions used in both SE and SFEE processes.

Surfactant	Solvent Emulsification				Solvent-Free Extrusion Emulsification			
	Range of Total Surfactant Weight Fractions Tested (pph)		Range of Total Molar Loadings Tested (mmol/g)		Range of Total Surfactant Weight Fractions Tested (pph)		Range of Total Molar Loadings Tested (mmol/g)	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Igepal CO-890	7.5	86	0.04	0.44	20.3	41.7	0.11	0.22
Igepal CA-630	6.77	13.5	0.11	0.22	6.40	12.4	0.11	0.22
Igepal CO-630	6.88	20.6	0.11	0.33	6.50	12.6	0.11	0.22
Triton X-114	11.9	17.9	0.22	0.33	*N/A*			
Triton X-45	9.46	28.5	0.22	0.67	*N/A*			
Calfax/Igepal CO-890	34.4		0.21		8.80		0.10	
Calfax/Igepal CO-630	12.7		0.21		8.00		0.12	
Calfax/Igepal CA-630	3.44	12.6	0.06	0.21	2.40	8.00	0.04	0.12

Characterization

All emulsions were triple filtered using a 75 μm sieve to remove any excessively coarse particles prior to any characterization measurements. Particle size measurements taken for a sample emulsion were conducted using two instruments. A Mastersizer 2000 particle size measurement system was used for determining sizes ranging between 0.2 and

2000 μm. A NANOTRAC NPA250 dynamic light scattering particle size measurement system was capable of measuring sizes ranging between 0.8 – 6500 nm. The combined results were reported based on the average taken from three replicated measurements. Span values have also been reported in an attempt to better encompass a samples complete particle size distribution. Span is a unit less value and is defined using Equation 1.

$$Span = \frac{D_{90} - D_{10}}{D_{50}} \quad [1]$$

where the values for D_{10}, D_{50}, and D_{90} represent the mean volume diameters for which 10, 50 and 90% of particles are equal to or less than respectively.

Zeta potential measurements were obtained using the previously described NANOTRAC NPA250, with average values from four repeat measurements reported. Select samples were imaged using a JEOL JSM-7000F scanning electron microscope (SEM) equipped with a Schottky Field emission gun. A VWR symphony pH meter was used to measure final emulsion pH values, whereas conductivity was measured using a Mettler Toledo Seven Compact conductivity meter.

Particle surface charge was measured at the Xerox Corporation (Webster, NY) using a Kinetex XB-C18 column on an Accela High Speed LC system interfaced to the Q-Exchange Mass Spectrometer. Prior to surface charge measurement, surfactants were removed by two methods; ionic surfactants were removed with an ion-exchange resin (Dowex Marathon MR-3), and non-ionic surfactants were removed using a Carbograph Extract-Clean cartridge (graphitized carbon, from Alltech). Statistical uncertainty values for each respective instrument described above have been summarized in Table 3-2.

Table 3-2. Relative standard error values for the different characterization parameters presented.

Parameter	Average Relative Standard Errors
D_{50}	± 0.02 μm
Span	± 0.05 μm
Zeta Potential	± 3.00 mV
pH	± 0.05
Conductivity	± 0.04 mS/cm

RESULTS AND DISCUSSION

Impact of Non-Ionic Surfactant Molecular Structure on Emulsifier Performance

A previous study had identified an effective anionic surfactant, Calfax DB-45, capable of producing particles in the desired range of 100-200 nm at low concentration but the non-ionic species presented feeding issues and poor emulsification performance when used alone in SFEE [20]. The initial studies in the present work sought to find a preferred non-ionic species, exploring different structural parameters, to ultimately work with the previously identified anionic surfactant in a detailed blend study. The first trial tested variations in the hydrophilic polyethoxy chain length. Four non-ionic surfactants were tested, and their molecular structures can be seen in Figure 3-2, where 'n' refers to the number of ethoxy repeat units. The order of increasing hydrophilic chain length is as follows: Triton X-45 → Triton X-114 → Igepal CA-630 → Igepal CO-890. Admittedly, SE was conducted at a lower temperature and so, translating the finding to SFEE assumes surfactant solubility in the oleic phase changed for all tested species to the same degree.

However, our previous study [20] illustrated the similarities between particles generated between SE and SFEE, albeit needing a higher surfactant concentration for the latter, acknowledging some influence of temperature but most likely a result of diffusion constraints ascribed to the viscosity difference between the two processes. Ideally, a surfactant with a minimized chain length is desired for SFEE in order to minimize the quantity of surfactant for sufficient molar loadings to achieve stable emulsification.

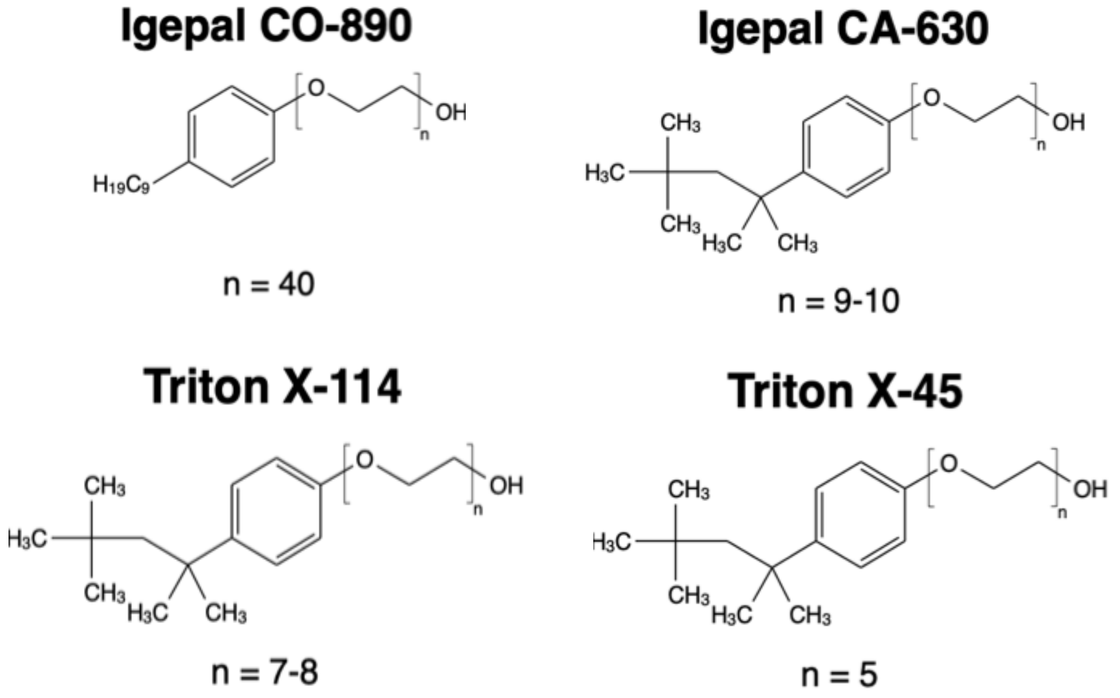

Figure 3-2. Molecular structures for the four non-ionic surfactants tested with varying hydrophile alkyl chain length.

Table 3-3. SE characterization results for Igepal CO-890, Igepal CA-630, Triton X-114, and Triton X-45 at their lowest loading to meet the desired particle size.

Surfactant	Surfactant Loading		Results				
	pph	mmol/g resin	D_{50} (µm)	Span	Zeta Potential (mV)	pH	Conductivity (mS/cm)
Igepal CO-890	21.5	0.11	0.12	1.32	-27.7 ± 9	6.0	1.71
Igepal CA-630	6.77	0.11	0.15	1.25	-49.5 ± 15	6.9	1.88
Triton X-114	11.9	0.22	0.21	1.92	-51.8 ± 13	6.6	1.99
Triton X-45	28.5	0.67	0.17	0.67	*N/A*	6.6	1.61

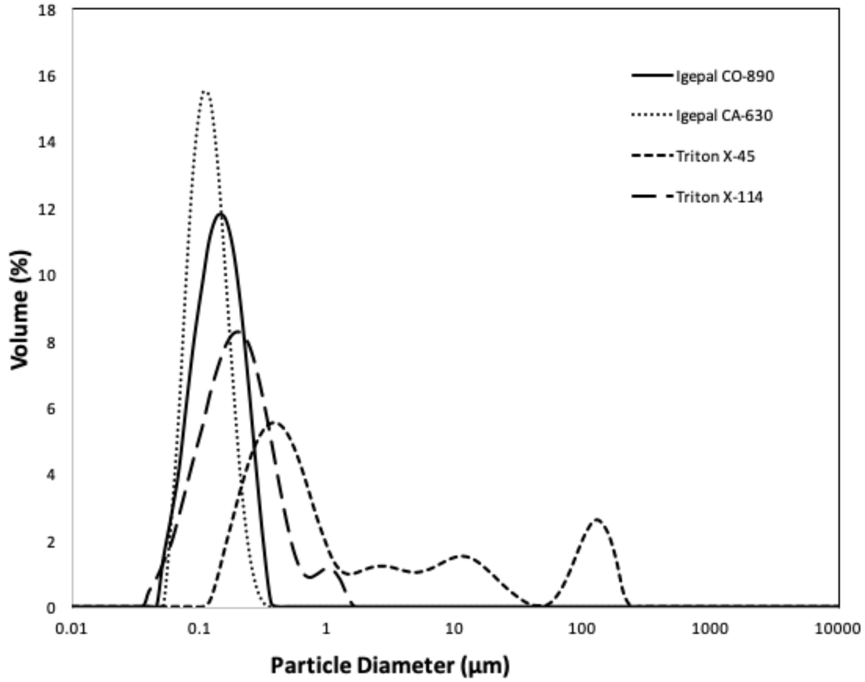

Figure 3-3. Particle size distributions for four different SE samples created using four different non-ionic surfactants: Igepal CO-890 (0.22 mmol/g resin loading), Igepal CA-630 (0.22 mmol/g resin loading), Triton X-45 (0.22 mmol/g resin loading), Triton X-114 (0.22 mmol/g resin loading).

The results obtained by SE at the lowest surfactant loading for each non-ionic species to achieve the desired particle size of 100-200 nm are seen in Table 3-3, whereas comparative particle size distributions at a fixed molar loading of 0.22 mmol/g resin are shown in Figure 3-3. Looking at Table 3-3, the emulsified system was not strongly sensitive to hydrophilic chain length. Considering the desired final particle size range, both Igepal CO-890 (n = 40) and Igepal CA-630 (n = 9-10) performed similarly at the same molar loading. The average zeta potential was slightly higher for the Igepal CA-630 sample, indicating better dispersion stability compared to Igepal CO-890 and making it preferable for subsequent consideration in the SFEE trials. A molar loading below 0.11 mmol/g resin was found to result in particle destabilization with both Igepal CA-630 and Igepal CO-890. A minimum chain length of n = 9 appeared to be significant for this process, with deteriorating performance as 'n' decreased below this threshold length. The difference in chain length between Igepal CA-630 and Triton X-114 was only one ethoxy group, but sufficient enough to result in increased coarse generation noted by the increase of span to 1.92 for Triton X-114 even at a molar loading almost 100% greater. The increased span is illustrated in Figure 3-3 with a minor peak present around 1 μm for the samples with Triton X-114. Further decreasing the alkyl chain length by two additional ethoxy units with Triton X-45 was seen to result in very poor O/W emulsion stability at a molar loading of 0.22 mmol/g. Looking at Figure 3-3, the particle aggregation and general emulsion instability observed with Triton X-45 is demonstrated in the resulting tri-modal distribution. In fact, a molar loading of 0.67 mmol/g resin was required to achieve a suitable O/W emulsion using Triton X-45.

Previous studies considering O/W emulsion stability as a function of hydrophilic chain length in polyoxyethylene non-ionic surfactants have shown that chain lengths below n=10 units are prone to destabilization, with major particle destabilization being measured at n=7.5 [22]. The negative impact of shortening the hydrophilic end group chain length is related to the resultant HLB value of the surfactant, which increased with chain length of the hydrophile group (assuming the lipophilic chain end remained constant) [23]. Triton X-45 had a quoted HLB value of 9.8, and realistically, the effective HLB value at elevated temperatures was lower since it would have become more significantly partitioned into the oleic phase, making it poorly suited as an O/W emulsifier for our process. Due to the poor results of both Triton X-45 and Triton X-114 in SE, they were both abandoned from further testing in SFEE.

The second set of trials to identify a suitable non-ionic by SE screening considered the alkylphenol end group structure. In this evaluation, two surfactants with similar ethoxylate end groups but either a branched or linear alkylphenol lipophile end group structure were tested. From the previous results above, either Igepal CA-630 and Igepal CO-890 could have been examined in this secondary evaluation but CA-630 was selected because it had a higher water solubility making it ultimately easier to feed into the subsequent SFEE process. An illustration of the respective molecular structures for Igepal CA-630 and CO-630 can be seen in Figure 3-4.

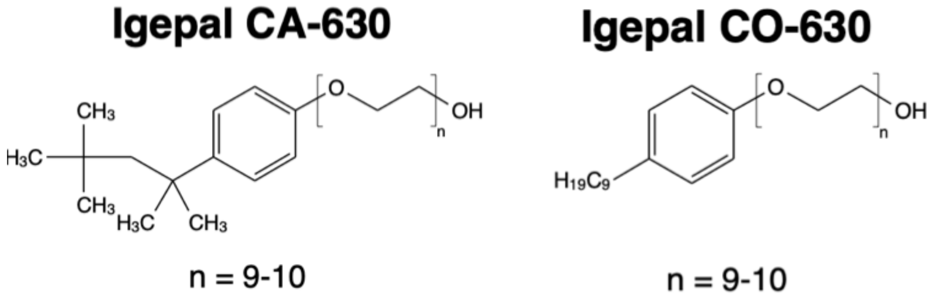

Figure 3-4. Molecular structures for the two surfactants tested with differing lipophile chain structures.

Table 3-4. SE characterization results for emulsions made with Igepal CA-630 and Igepal CO-630 at their lowest tested loading.

Surfactant	Surfactant Loading		Results				
	pph	mmol/g resin	D_{50} (μm)	Span	Zeta Potential (mV)	pH	Conductivity (mS/cm)
Igepal CA-630	6.77	0.11	0.15	1.25	-49.5 ± 15	6.9	1.88
Igepal CO-630	6.88	0.11	0.19	1.53	-30.4 ± 13	6.6	1.63

A comparison of the resulting emulsions created using the two surfactants by SE is presented in Table 3-4. The emulsions stabilized with Igepal CO-630 were fairly similar to those with Igepal CA-630. Considering triplicate samples prepared with each surfactant, the slight increase in nominal D_{50} and span to 0.19 μm and 1.53 respectively, as well as the decrease in zeta potential (absolute value) to -30.4 mV suggested less than optimal performance would arise with the linear nonylphenol group for our polyester/water system. This result is consistent with a study conducted by Rekvig et al., who determined that for surfactants with less hydrophilic head groups (typically non-ionic surfactants), branched hydrophobic tails more effectively reduced interfacial tension compared to linear tails [24]. They explained that the branched alkyl tail sterically occupied more space in the oil phase, producing a stronger volume interaction between the tails buried in the oil phase. Certainly, there is little difference between these two surfactants in producing the desired O/W emulsion but for the purpose of selecting an optimal non-ionic candidate for SFEE, Igepal CA-630 was preferred from these trials.

Emulsification by SFEE with only a non-ionic surfactant generally yields a poor outcome, but before considering the performance of anionic/non-ionic blends, benchmarking trials with Igepal CA-630, and Igepal CO-630 were conducted to ensure their differences were replicated in the more viscous environment compared to SE. Particle properties and particle size distributions of samples prepared with these surfactants compared to the anionic surfactant Calfax are given in Table 3-5 and Figure 3-5 respectively.

Table 3-5. SFEE characterization results for emulsions made with Igepal CA-630, Igepal CO-630, and Calfax at their respective minimum loadings.

Surfactant	Surfactant Loading		Results			
	pph	mmol/g resin	D_{50} (μm)	Span	Zeta Potential (mV)	Approximate % Emulsion in Extrudate
Calfax	7.2	0.11	0.19	2.32	-48.4 ± 3	100
Igepal CA-630	6.4	0.11	15.7	8.44	-41.3 ± 17	5
Igepal CO-630	6.5	0.11	74.7	2.36	*N/A*	5

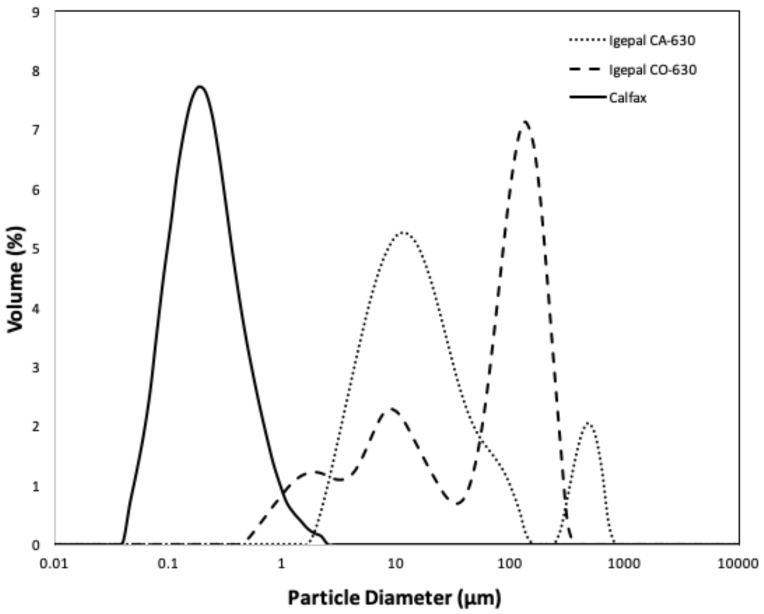

Figure 3-5. Particle size distributions for three different SFEE samples created using two different non-ionic surfactants: Igepal CA-630 (0.11 mmol/g resin loading), Igepal CO-630 (0.11 mmol/g resin loading), as well as an anionic surfactant: Calfax (0.11 mmol/g resin loading).

Comparing the SFEE performance of each non-ionic surfactant to that of Calfax, it is apparent that the lack of a charged end group severely hindered their ability to generate useful O/W emulsions. Major coarse particle generation was observed with both non-ionic surfactants at 0.11 mmol/g resin and an extremely low quantity of O/W emulsion was found in the extrudate, indicating that the majority of polymer did not phase invert. The lower affinity to water of non-ionics (compared to that of anionic surfactants) results in poor mixing between the oleic and water phases, coupled with the limiting factors of a very high viscosity oleic phase and short residence time in the dispersion stage of the process. Increased loadings with both Igepal CA-630 and CO-630 were attempted, but above 0.11 mmol/g resin the viscosity of the solution was too high to pump into the extruder. These results reaffirmed the belief that non-ionic surfactants alone are incapable of being used in the SFEE process.

Emulsification Performance of a Binary Mixture of Anionic and Non-ionic Surfactants in SE and SFEE

Initially, the three most promising non-ionic surfactants mentioned above were considered for blends with Calfax DB-45, namely Igepal CO-890, Igepal CA-630, and Igepal CO-630. Each formulation was tested with a total surfactant loading of 0.11 mmol/g resin; this molar loading was deemed sufficient for each individual surfactant, and was chosen as our baseline for initial blend trials in both SE and SFEE. The limited solubility of Igepal CO-890 in water was a constraint by which the surfactant ratio was determined; at the chosen molar loading, the maximum molar ratio possible for a Calfax/Igepal CO-890 blend was 80/20 respectively. The remaining two non-ionics did not experience this same solubility constraint, therefore their baseline ratios were chosen to be 66/33

Calfax/non-ionic to immediately experiment with a larger reduction in Calfax given that the ultimate goal of using blends was to reduce anionic surfactant in the SFEE process. Particle properties of the final aqueous polyester dispersions by SE and SFEE are given in Table 3-6 and Table 3-7, respectively. By SE, all three formulations exhibited emulsified products with narrow monomodal particle size distributions (Figure 3-6) and nominal particle diameters meeting the targeted specifications. The blend with Igepal CA-630 had a slightly higher D_{50} (0.18 µm) compared to the other two surfactant blends, but no coarse particle generation was observed. All three of the blends tested in SE generated very similar average zeta potential values, all of which indicating stable emulsions. Based on these successful trials, all three blended formulations were subsequently tested in the SFEE process.

Table 3-6. SE results for binary blends of Calfax and three non-ionic surfactants made at varied molar ratios, all with a total molar concentration of 0.11 mmol/g resin.

Surfactants	Blend Characteristics		Results				
	Molar Ratio	mmol/g resin	D_{50} (µm)	Span	Zeta Potential (mV)	pH	Conductivity (mS/cm)
Calfax/Igepal CO-890	80/20	0.11	0.11	0.94	-47.0 ± 11	7.0	1.83
Calfax/Igepal CA-630	66/33	0.11	0.18	0.95	-48.7 ± 18	7.3	1.79
Calfax/Igepal CO-630	66/33	0.11	0.13	1.04	-44.2 ± 17	7.1	1.91

Table 3-7. SFEE results for pure Calfax, as well as binary mixture of Calfax and three non-ionic surfactants at varied molar ratios and total molar concentrations.

Surfactant	Blend Characteristics		Results					
	Molar Ratio	mmol/ g resin	D_{50} (μm)	Span	Zeta Potential (mV)	pH	Conductivity (mS/cm)	State of Extrudate
Calfax	-	0.11	0.19	2.32	-48.4 ± 3	*N/A*	*N/A*	100% Emulsion
Calfax/Igepal CO-890	80/20	0.11	0.24	286	-27.3 ± 15	7.5	0.89	90% Emulsion
Calfax/Igepal CA-630	66/33	0.12	0.14	1.62	-53.7 ± 11	6.8	0.71	100% Emulsion
Calfax/Igepal CO-630	66/33	0.12	0.12	8.58	-37.5 ± 8	6.7	0.59	100% Emulsion

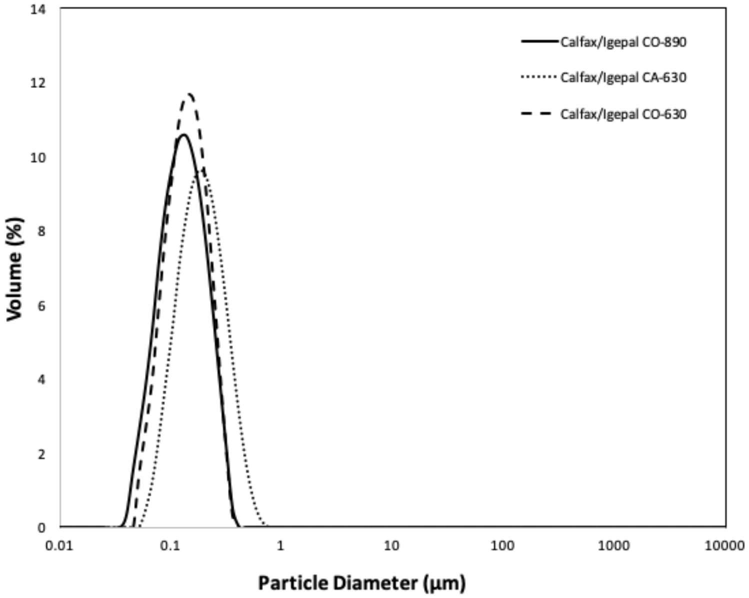

Figure 3-6. Particle size distributions for SE samples containing binary surfactant mixtures: Calfax/Igepal CO-890 (80/20 molar ratio, 0.11 mmol/g resin total), Calfax/Igepal CA-630 (66/33 molar ratio, 0.11 mmol/g resin total), Calfax/Igepal CO-630 (66/33 molar ratio, 0.11 mmol/g resin total).

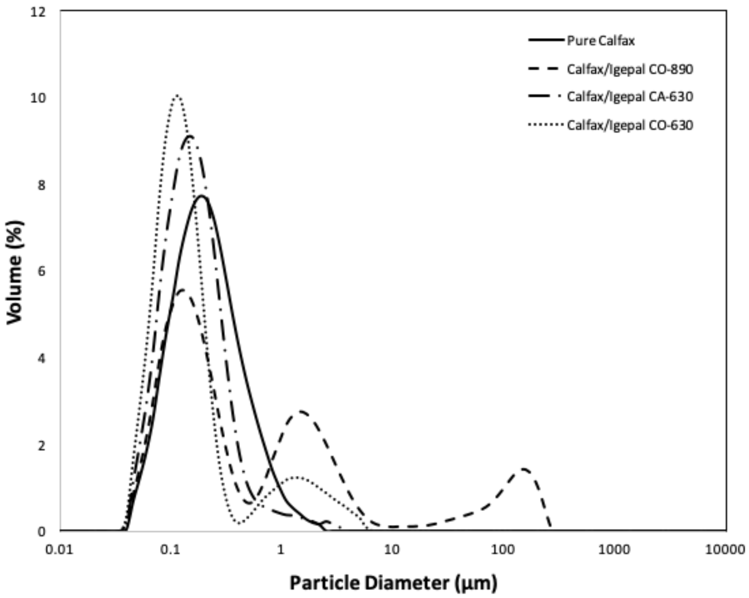

Figure 3-7. Particle size distributions for SFEE samples containing pure Calfax (0.11 mmol/g resin), along with three binary surfactant mixtures: Calfax/Igepal CO-890 (80/20 molar ratio, 0.11 mmol/g resin total), Calfax/Igepal CA-630 (66/33 molar ratio, 0.12 mmol/g resin total), Calfax/Igepal CO-630 (66/33 molar ratio, 0.12 mmol/g resin total).

In comparison with the SE results, a larger overall extent of coarse particle generation was seen in SFEE, but the solids were nearly completely emulsified which is substantially better than cases with the pure non-ionic species (only 5-25% solids emulsified). Where all three blends were seen to result in very similar emulsions in SE, the blend with Igepal CO-890 was found to be the least effective of the three blends in SFEE, shown by its large span and trimodal size distribution shown in Figure 3-7. The poor performance of Igepal CO-890 in the trial is believed to stem from it being a solid of relatively poor water solubility and its high molar mass, resulting in its lower affinity for water and rendering it difficult to prepare for addition into the process. Based on its processing constraints and poor SFEE results, both as a sole emulsifier and in a blend with Calfax, Igepal CO-890 was deemed an ineffective and undesirable surfactant for the SFEE process with our polyester. The sample prepared with the blend of Calfax/Igepal CO-630 had a span of 8.58, signifying moderate coarse particles generation, which is seen in Figure 3-7 by the small peak in the 1 μm range. The blend of Calfax/Igepal CA-630 was found to be the most promising formulation in SFEE, producing results very similar to those obtained with SE, with a slight D_{50} decrease of 0.04 μm, and an average zeta potential magnitude increase of 22.1 mV; the better results with Igepal CA-630 reinforce the previously described benefits of the branched hydrophobic end group as opposed to a linear one.

Comparing the SFEE results of each blend to that of pure Calfax, only the blend with Igepal CA-630 was seen to result in improved D_{50} and span values. The remaining two non-ionic surfactants were seen to negatively impact the effectiveness of Calfax in the SFEE process. It has been shown that when an anionic/non-ionic emulsifier blend is used for oil/water emulsification, the non-ionic surfactant preferentially adsorbs to the oleic phase, while the anionic predominantly interacts with the water phase [16]. The slight benefits of a branched hydrophobic end group to that of a linear one observed previously could explain the better results with Calfax/Igepal CA-630 blends in SFEE to that of pure Calfax, since Calfax has a linear hydrophobic end group. This could also explain the slight increase in coarse particle generation with Igepal CO-630, where its presence reduces the amount of anionic surfactant present, and its nearly identical hydrophobic end group provides no added benefits to Calfax.

In a less viscous, solvent based environment, the weak affinity of non-ionic surfactants to water was sufficient enough for bringing the polymer and water phases together, but in the highly viscous SFEE environment, the need for an anionic surfactant to drive water into the oleic phase is very apparent in these studies. The positive results in SFEE with the Calfax/Igepal CA-630 blend indicate that replacing molar amounts of anionic surfactant with a suitable non-ionic is possible without inducing any increases in overall particle size. This was important because in order to reduce particle surface charge, anionic surfactant concentrations need to be minimized, and using emulsifier blends in SFEE was seen as the simplest possibility to implement without negatively impacting the emulsion particle characteristics.

Effect of Binary Mixtures of Calfax/Igepal CA-630 on Particle Properties

The primary objective of this paper was to evaluate the extent a surfactant blend of anionic and non-ionic species could control particle charge while successfully emulsifying our polymer system by SFEE. The studies so far have established the suitability of a Calfax/Igepal CA-630 blend for more detailed tests. Concerned with viscous effects on the emulsification mechanics, both SE and SFEE continued to be used in this section as particle properties were determined based on different molar ratios of surfactant and total surfactant concentration in the formulation.

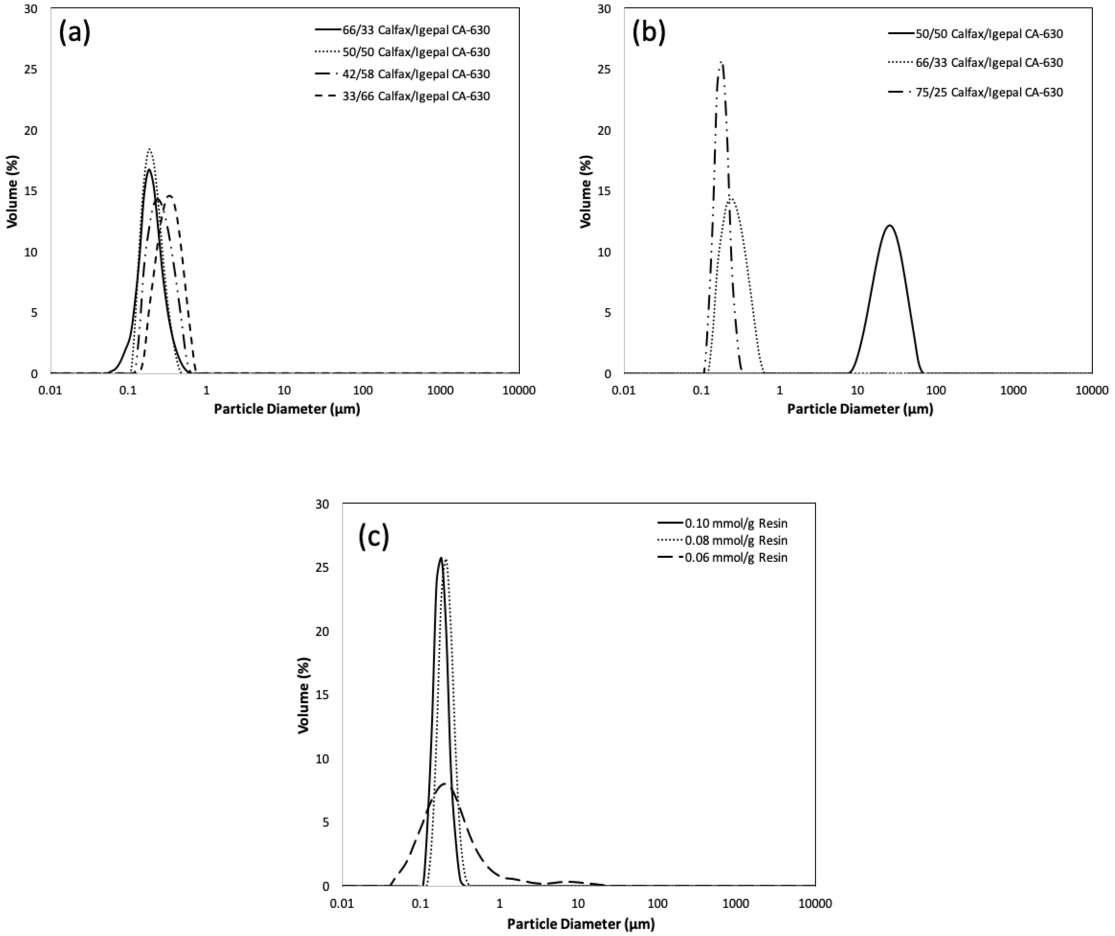

Figure 3-8. Particle size distributions for SE samples made with a binary mixture of surfactants consisting of Calfax/Igepal CA-630. (a) SE samples made using a Calfax/Igepal CA-630 blend at varied ratios of surfactant and a constant total molar concentration of 0.12 mmol/g resin. (b) SE samples made using a Calfax/Igepal CA-630 blend at varied ratios of surfactant and a constant total molar concentration of 0.1 mmol/g resin. (c) SE samples made using a Calfax/Igepal CA-630 blend at varied total molar loadings and constant blend ratio containing 75 wt% Calfax.

Table 3-8. SE Calfax/Igepal CA-630 blend study formulation conditions and resulting final emulsion characterization data.

Molar Ratio	mmol/g resin	Results				
		D_{50} (μm)	Span	Zeta Potential (mV)	pH	Conductivity (mS/cm)
25/75	0.16	0.24	1.23	-31.5 ± 8	6.91	1.68
66/33	0.12	0.18	0.95	-59.1 ± 21	7.25	1.11
50/50	0.12	0.18	0.79	-42.0 ± 19	7.12	2.06
42/58	0.12	0.24	0.97	-26.9 ± 8	7.10	1.09
33/66	0.12	0.31	0.92	-41.7 ± 17	7.05	1.63
50/50	0.10	23.2	1.13	-12.7 ± 9	7.41	0.17
66/33	0.10	0.23	0.95	-29.9 ± 16	7.15	1.24
75/25	0.10	0.17	0.52	-27.9 ± 1	7.23	1.94
75/25	0.08	0.17	0.53	-38.4 ± 15	7.25	1.96
75/25	0.06	0.20	2.76	-25.6 ± 5	7.21	0.25

Particle size distributions for SE prepared dispersions with differing molar blend ratios and total surfactant concentrations are seen in Figure 3-8. All distributions were monomodal by SE though the span could vary significantly based on the amount of each surfactant species present. A summary of the characterization results for these emulsion samples is given in Table 3-8. Nominal particle size (D_{50}) of these emulsions increased linearly with a decrease in the molar percentage of Calfax present. For example, at a molar loading of 0.12 mmol/g resin, particle size increased from 180 nm at 66% to 310 nm at 33% Calfax. With declining total surfactant loading, a higher molar percentage of Calfax was required to maintain the particle distribution in the size range sought, as shown in Figure 3-8 (c) but probably more significantly witnessed by the coarse generation seen at the 50/50 ratio by dropping from 0.12 mmol/g resin to 0.10 mmol/g resin; Figure 3-8 (c) shows the distributions broadening with decreasing surfactant loading at a 75/25% ratio for

Calfax/Igepal CA-630, which was the only ratio where a stable emulsion could be prepared at 0.08 mmol/g resin. The destabilization of the 50/50 sample at 0.10 mmol/g resin was quantitatively described by the low magnitude average zeta potential measured (-12.7 mV), whereas all others had zeta potentials having higher magnitude average values than -25 mV. The conductivity between samples was not as constant as other characteristics (possibly due to impurities such as sodium ions), but large drops in emulsion conductivity were consistently seen with samples having measurable coarse particle generation (i.e. 50/50 at 0.1 mmol/g resin and 75/25 at 0.06 mmol/g resin). Alone, the lower limit of Calfax in blends before significant coarse particle generation by SE has been determined previously [20] to be approximately 0.06 mmol/g resin, which is equivalent in content to a 50/50% Calfax/Igepal CA-630 ratio at 0.12 mmol/g resin, or 75/25% Calfax/Igepal CA-630 ratio at 0.08 mmol/g resin. As long as at least 0.06 mmol/g resin of Calfax was present in the blend ratio, a stable emulsion will be achieved. No synergistic benefit was seen in SE by the addition of a non-ionic surfactant to the anionic performance as an emulsifier. Conversely, a sample containing 25/75% ratio of Calfax/Igepal CA-630 at 0.16 mmol/g resin was tested to determine whether the molar loading of Calfax could decline below 0.06 mmol/g resin without destabilizing the emulsion if Igepal loading exceeded its lower limit threshold of 0.11mmol/g resin (determined in a previous study [20]). The result shows a resulting D_{50} of 0.24 μm and span of 1.23 indicating a stable emulsion could be achieved if either surfactant exceeded its lower threshold concentration. These findings point to the two surfactants acting exclusive to one another in the SE process, making the results found with SFEE (presented in the following section) all the more interesting.

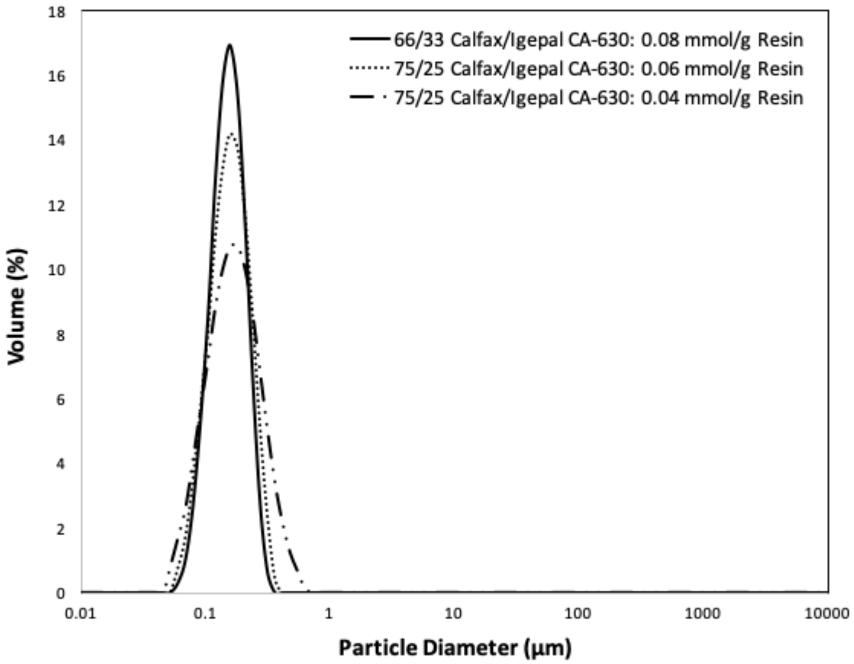

Figure 3-9. Particle size distributions for select SFEE samples made with binary blends of Calfax/Igepal CA-630 at varied total molar loadings and blend ratios.

Table 3-9. SFEE Calfax/Igepal CA-630 blend study formulation conditions and resulting emulsion characterization data.

Molar Ratio	mmol/ g resin	Results					
		D_{50} (μm)	Span	Zeta Potential (mV)	pH	Conductivity (mS/cm)	State of Extrudate
66/33	0.12	0.14	1.76	-52.0 ± 14	6.57	0.71	100% Emulsion
50/50	0.12	0.14	1.06	-39.8 ± 14	6.72	0.40	100% Emulsion
66/33	0.10	0.14	1.00	-18.5 ± 5	6.70	0.58	100% Emulsion
66/33	0.08	0.14	0.82	-44.3 ± 19	6.62	0.40	100% Emulsion
75/25	0.08	0.15	1.24	-68.2 ± 21	6.74	0.53	100% Emulsion
66/33	0.06	0.16	1.28	-24.1 ± 12	6.63	0.31	Thick Sludge
75/25	0.06	0.16	0.97	-53.5 ± 19	6.73	0.33	Thick Sludge
75/25	0.04	0.20	1.36	-49.8 ± 11	6.65	0.38	Thick Sludge

Particle size distributions for select dispersions prepared with SFEE at varied molar blend ratios and total molar loadings are shown in Figure 3-9. The SE blend trials above showed increasing coarse particle generation for ratios containing less than 50% Calfax, which discouraged testing any blend ratios containing less than 50% Calfax, with the lowest tested ratio being a 50/50% blend at 0.12 mmol/g resin. Therefore, the focus of this set of experiments was centred on testing reduced total molar loadings. Each of the samples prepared resulted in a similar monomodal distribution, but the gradual decrease in volume percentage of 150 nm sized particles, and subsequent broadening of the distributions with decreasing total surfactant molar loading is apparent. Table 3-9 contains a complete summary of the formulation conditions for each of the SFEE trials, along with their corresponding characterization data. Compared to the SE trials, the same formulation conditions resulted in lower D_{50} and span values by SFEE in this study. For a point of comparison, emulsions with only Calfax below a surfactant loading of 0.11 mmol/g resin will exhibit coarse generation in SFEE, a limit almost double the concentration in SE due to slow interfacial growth of the highly viscous oleic phase when solvent is not present [20]. Considering the trend seen with SE, none of these samples should have met the target particle size since the Calfax concentration was always below its threshold loading represented by the pure surfactant case. In contrast to what we expected, no significant coarse fraction was observed in any of the tested formulation conditions for SFEE, even at a Calfax loading of 0.03 mmol/g resin. Unlike in SE, the two surfactants were showing synergistic contributions to emulsification in SFEE.

The conductivity values for the SFEE emulsions were found to be much lower than that of the SE values, ranging between 0.31–0.71 mS/cm. When comparing the zeta potential values with SE, SFEE samples were seen to have slightly higher magnitude average values, with the exception of the low values measured for the 66/33 Calfax/Igepal CA-630 sample at 0.10 mmol/g resin and the 66/33 Calfax/Igepal CA-630 sample at 0.06 mmol/g resin (likely due to poor measured sample quality). Comparing these results to SE further reinforces the findings that the SFEE samples were generally more stable.

The solids were fully emulsified in these trials; however, the resulting extrudates appeared differently for a total surfactant loading of 0.06 mmol/g resin or lower. The extrudate was seen to change from a milky-like emulsion of low apparent viscosity, to a thick sludge-like extrudate of distinctly higher viscosity. Adding the sludge to a beaker of water and gently stirring, a milky-like emulsion was once again obtained. Figure 3-10 (a) and (b) show SEM images of the emulsified polyester sample (66/33 Calfax/Igepal CA-630 at 0.08 mmol/g resin), while (c) and (d) show SEM images of a sludge-like extrudate sample (75/25 Calfax/Igepal CA-630 at 0.04 mmol/g resin). Both samples showed 100–200 nm spherical particles, but there was more frequent bridging between the spheres in the sludge. The agglomerated particles are highlighted with circled sections in the images. Figure 3-10 (e) shows a close up image of one of the agglomerates present in the sludge-like extrudate sample. Since the sludge-like samples dispersed into excess water readily for the measurement of particle size, and no major differences in emulsion D_{50} or span were measured prior to imaging, this bridging was likely occurring during the drying process in preparation of the SEM analysis. The phenomenon of emulsion creaming and subsequent particle coalescence is common [25]. The sludge-like state exiting the extruder is believed to be attributed to the poor repulsive nature of these particles, but in the presence of shear they were without the means to aggregate together. This is an interesting outcome, where if true, it means the surfactant blend sufficiently contributed to the emulsification mechanism in SFEE but the repulsive forces between final particles was insufficient to avoid agglomeration in the absence of shear while drying.

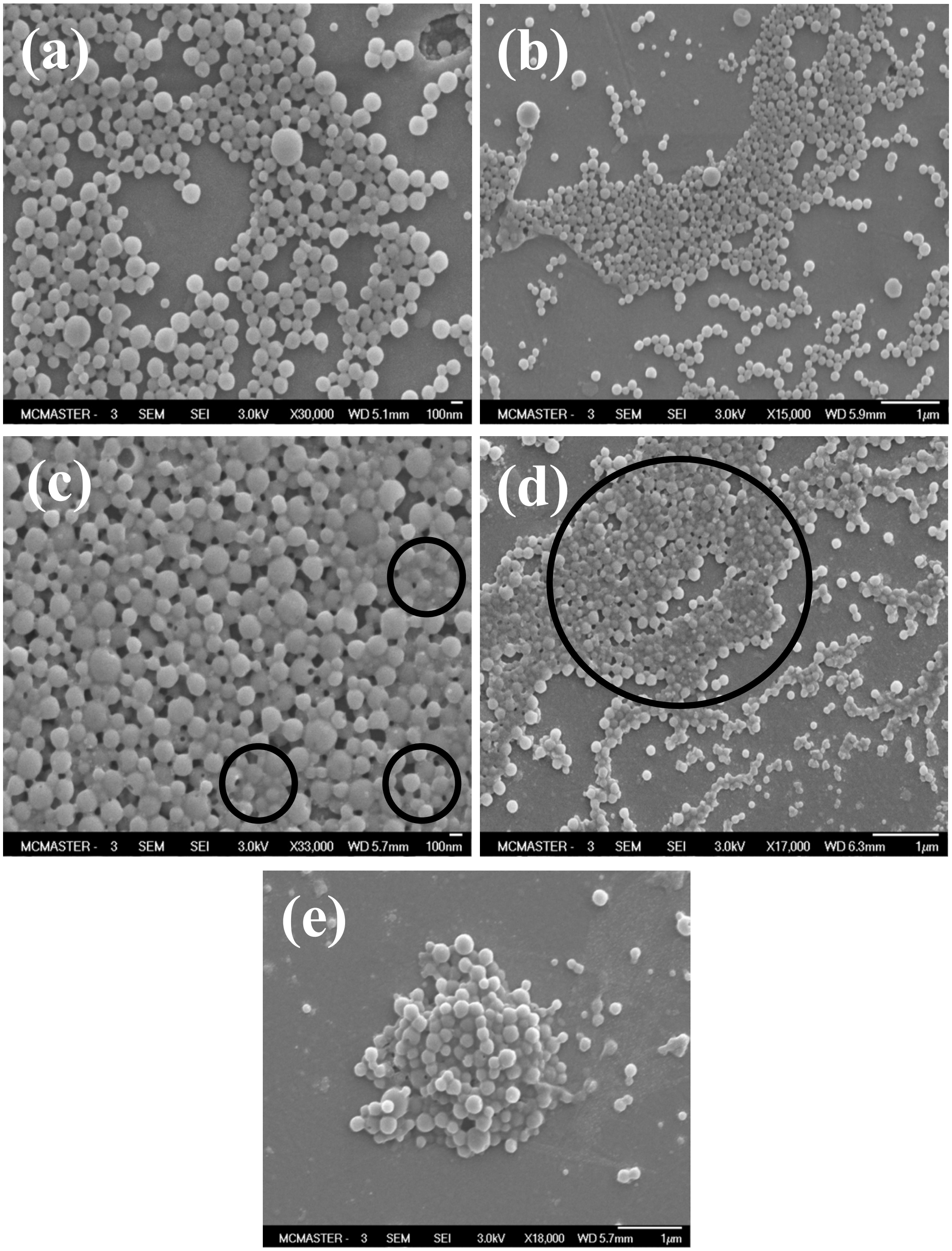

Figure 3-10. SEM images for blends of Calfax and Igepal CA-630 at varied magnifications. (a) and (b): 66/33 molar ratio of Calfax/Igepal CA-630 at 0.08 mmol/g resin loading. (c) – (e): 75/25 molar ratio of Calfax/Igepal CA-630 at 0.04 mmol/g resin loading.

Table 3-10. Surfactant entrapment measurements for emulsions made with Calfax as the sole emulsifier and binary 66/33% emulsifier mixture of Calfax/Igepal CA-630 using solvent emulsification and solvent-free extrusion emulsification.

Surfactant	Process	mmol/ g resin	Results					
			D_{50} (μm)	Span	Initial Calfax in Sample (wt%)	Calfax in Sample After Cleaning (wt%)	Initial Igepal in Sample (wt%)	Igepal in Sample After Cleaning (wt%)
Calfax	SFEE	0.08	0.3	3.94	4.4	0.41	N/A	N/A
Calfax/Igepal CA-630	SE	0.12	0.18	0.95	3.9	< 0.1	1.2	< 0.1
Calfax/Igepal CA-630	SFEE	0.12	0.14	1.62	9	< 0.1	0.63	< 0.1

To assess the impact of the Calfax/Igepal CA-630 mixture on the charge of final latex particles, emulsions were put through different washing techniques to remove any surface bound surfactant, and the level of entrapped surfactant in the final latex particles was measured. The results from these tests are shown in Table 3-10; all three of the samples presented in the table were made with the same concentration of Calfax, 0.08 mmol/g resin. The sample prepared with only Calfax had 0.41 wt% still present in the particles after ion-exchange. Looking at the two tested surfactant blend samples, the measured Calfax after ion-exchange was < 0.1 wt%, regardless of the emulsification process. It seems that the non-ionic surfactant inhibited the anionic surfactant from becoming entrapped within the surface of the latex particles. This was a desirable outcome for this study but could also explain the superior performance of the surfactant blends in SFEE versus SE, and perhaps even the sludge-like state observed at low surfactant loading.

Anionic surfactant entrapment in the latex particles, which contributes a surface charge that cannot be removed upon washing, is a result of polymer phase adsorption during W/O emulsion formation, and after phase inversion to an O/W emulsion these surfactant molecules become trapped (either partially or fully) within the latex particle. The amount of entrapped anionic surfactant was found to significantly drop with the addition of a non-ionic surfactant in the process. The cause of this decline is believed to be related to the arrangement of surfactants at the oil/water interphase. In blends of anionic/non-ionic surfactants, it has been shown that the non-ionic surfactant preferentially adsorbs into the oleic phase surface, leaving the anionic molecules to concentrate in the water phase [16]. With the high operating temperatures of SFEE, the non-ionic surfactant becomes more soluble in the polymer phase, and with the increased adsorption in the presence of an anionic surfactant, it is believed that the Igepal CA-630 molecules are concentrating at the polymer surface and partially dissolving into the polymer. This concentrated layer of Igepal micelles would prevent oleic phase adsorption of Calfax, as the lipophilic Calfax tails are less likely to adsorb onto the Igepal ‘shell’ created than they would be to exposed polymer surface. This interaction leaves the majority of Calfax micelles in the water phase, and prevents them from becoming entrapped in the generated latex particles, subsequently resulting in a lower particle surface charge. The explanation for why less total surfactant is required in SFEE compared to SE is believed to be both a cause of this surfactant interaction and a viscosity effect. The low viscosity of SE allows for increased mobility of the non-ionic micelles on the polymer surface, likely leading to a higher percentage of Calfax adsorbing to the polymer surface and more non-ionic micelles in the water phase.

This results in both surfactants operating independently to reduce interfacial tension. This is not the case with SFEE, where the high viscosity present drastically reduces the mobility of non-ionic surfactants on the polymer surface, resulting in the surfactant interaction described above, subsequently forcing both surfactants to work together and resulting in less overall surfactant required to sufficiently reduce interfacial tension.

Impact of Increasing Water Viscosity Injected in the Dilution Zone of the SFEE Process

It is a well-known fact that the viscosity ratio in a phase inversion emulsification process has a significant impact on stable emulsion formation. In general, solvents are used to dissolve the oleic phase and lower the phase viscosity ratio. However, SFEE operates in the absence of any solvents, meaning that other additive alternatives are required to overcome this extremely high viscosity ratio between the immiscible polymer and water phases. SFEE utilizes surfactants to reduce the interfacial tension of the system and allow for intimate mixing of these two phases, however, quite significant amounts are required to accomplish this. One area of current interest is the possibility of utilizing a hydrocolloid to increase the water phase viscosity, subsequently lowering the phase viscosity ratio in an attempt to minimize the amount of required surfactant without negatively impacting final emulsion characteristics. Since particle washing is common as the final step to making powders by emulsification, an added hydrocolloid could be readily removed and not impact the final product.

Two hydrocolloids were used in this mini-study: corn starch (purchased from Cargill, MN, USA) and MethoCel A15C (methylcellulose thickener; Dow Chemical, MI, USA). Each hydrocolloid was added to adjust the water phase viscosity being injected at zone Z7 (dilution stage of the extruder); the pumps limited the amount of hydrocolloid to be tested. A pure Calfax formulation was tested at a molar loading of 0.06 mmol/g resin, where this concentration was chosen since it gives a stable emulsion with minor coarse particle generation for pure water injection at zone Z7. The test was setup to determine if a hydrocolloid would minimize/eliminate this coarse fraction and reduce the D_{50} to within the desired 100 – 200 nm range for an otherwise unacceptably low concentration of surfactant. The process characteristics and resulting emulsion characterization data, along with particle size distributions can be seen in Table 3-11 and Figure 3-11 respectively.

Table 3-11. Sample characteristics and emulsion characterization results for SFEE samples made with Calfax at 0.06 mmol/g resin with varied water viscosity at zone Z7.

Sample Characteristics			Results			
Hydrocolloid	Hydrocolloid (wt%)	Water Viscosity (cps)	D_{50} (µm)	Span	Zeta Potential (mV)	State of Extrudate
N/A	*N/A*	1.0	0.35	10.7	*N/A*	70% Emulsion
Corn Starch	5.0	2.4	0.19	1.8	-56.8 ± 8	Thick Sludge
MethoCel A15C	0.2	3.1	0.19	2.0	-47.7 ± 10	Thick Sludge

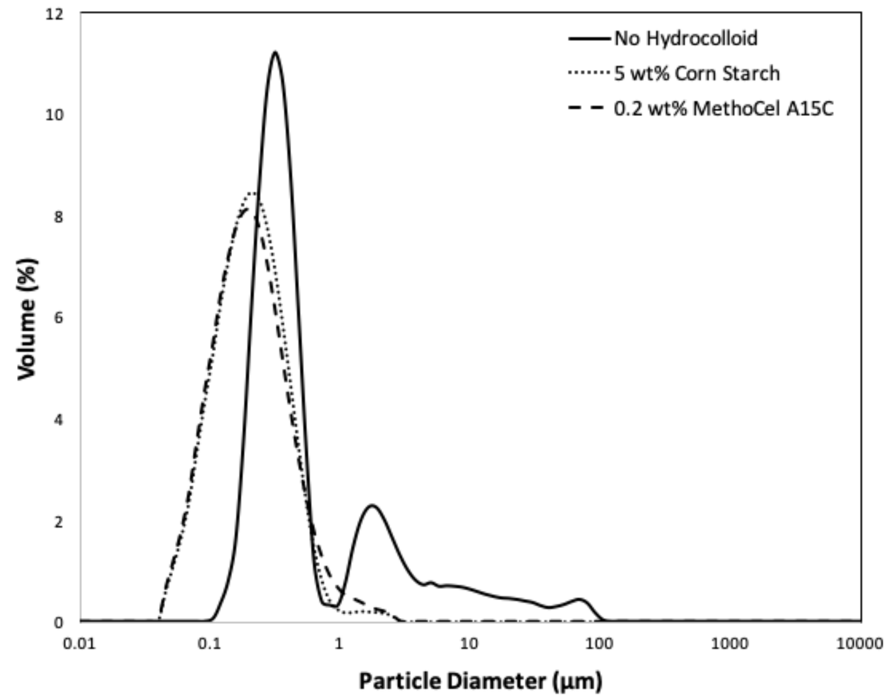

Figure 3-11. Particle size distribution results for SFEE samples made with Calfax at 0.06 mmol/g resin with varied zone Z7 water viscosities.

Looking at Table 3-11, the water phase viscosity increased between 2 – 3 times that of pure water with the hydrocolloids, producing a measurable decrease in D_{50} as well as a significant decrease in coarse particles observed in either sample, illustrated in Figure 3-11. However, as a result of the low Calfax loading, the two emulsions made using hydrocolloids were seen to result in a thick sludge (similar in appearance to what was observed at low Calfax concentrations in the blend experiments). This was interesting because the addition of a hydrocolloid was seen to measurably reduce the amount of material not undergoing phase inversion in the sample extrudate from 30% (with pure water injected in zone Z7) to almost 0%. When comparing the resultant samples from each hydrocolloid, there seems to be no measurable differences between the two species. Higher concentrations of each hydrocolloid were found to not be possible with our current pump setup, as clogging issues were experienced with any increase in either of the tested hydrocolloid concentrations. Although at very low concentrations, the hydrocolloids do seem to positively impact the samples. This further shows that phase viscosity ratio has a major impact on emulsion formation in SFEE, and any reductions in this ratio will result in a positive impact on the final emulsion properties. This idea of increasing water viscosity requires further testing, as no major conclusions can be made with the limited sample size of this mini-study. However, if successful, one may be able to further reduce the amount of Calfax required in the process, potentially even operating below the current minimum threshold of 0.06 mmol/g resin.

CONCLUSIONS

This paper focused on two major areas of investigation; examining the impact that different features of non-ionic molecular structure had on PIE processes with our selected polyester, as well as exploring the use of binary anionic/non-ionic surfactant mixtures to control particle charge. Emulsions created with a non-ionic surfactant containing a hydrophilic chain length shorter than 10 ethoxy units were unsatisfactory, with major destabilization occurring below 7 ethoxy units. It was also determined that a non-ionic surfactant with branched lipophilic end group structures resulted in slightly lower D_{50} values and reduced coarse particle generation when compared to one with a linear structure. After extensive testing, Igepal CA-630 was deemed the preferred non-ionic surfactant based on its molecular structure, and blends of Calfax and Igepal CA-630 were explored in the SFEE process. Blending Calfax/Igepal CA-630 was found to substantially reduce the amount of Calfax surfactant entrapped (either fully or partially) in the generated latex particles. The trials revealed an interesting synergism with the two surfactants that was only seen in SFEE, whereas in SE the two surfactants acted independently to one another. The adsorption and limited mobility of non-ionic surfactant molecules on the surface of the polymer phase in SFEE is believed to have created a 'shell' structure around the polyester, subsequently keeping the majority of the anionic surfactant molecules in the water phase. This interaction forces the surfactants to work together to reduce the overall interfacial tension, and results in less overall surfactant being required to generate stable O/W emulsions. Through variations of blend molar ratio and overall surfactant loadings it was possible to achieve stable emulsification in SFEE with a loading of Calfax in the final emulsion well below what was possible by SE, and that anionic surfactant could be readily washed away in the finished particles.

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CHAPTER 4: CONCLUSION

This thesis investigated the role of surfactants in a new solvent-free extrusion emulsification process. Variations in surfactant molecular structures and surface-active properties were tested to determine their individual impact on the creation of 100–200 nm sized emulsions. Stability of emulsions created with SE and SFEE was compared using offline coalescence testing, operating at extreme environmental conditions (temperature, pH, RPM). Binary blends of ionic and non-ionic surfactants were explored in SFEE as alternatives to using one sole surfactant. Specific findings of this research have been summarized below.

4.1 Key Findings and Contributions

1. Non-ionic surfactants with hydrophilic chain lengths shorter than 10 ethoxy units resulted in coarse particle generation. Shorter chains result in reduced surface activity (Traube's Rule) as well as a lower resultant HLB value, both ultimately reducing the surfactant's ability to drive water into the polymer melt and creating the required W/O emulsion prior to inversion. Non-ionic surfactants with hydrophilic chain lengths of at least 10 ethoxy units were found necessary but longer lengths resulted in no major improvements, and were impractical due to their higher molecular weight.
2. Anionic surfactants were found to greatly outperform non-ionic surfactants as emulsifiers in the SFEE process. The success of anionic surfactants was attributed to the negative charge of their hydrophilic end group increasing their affinity to water, allowing for more effective W/O emulsion formation within the dispersion

stage. The high oleic phase viscosity and short residence time of SFEE proved too extreme for non-ionic surfactants due to their overall neutrality and lower affinity to water.

3. Of the anionic surfactants tested, only SDBS and Calfax were able to successfully generate 100 – 200 nm particles with SFEE, with Calfax performing equivalently to SDBS at a 50% lower molar loading. The poor results of Unicid 350 can be attributed to its relatively low HLB value (reducing its ability to drive inversion of the W/O emulsion formed in the dispersion zone), as well as the nascent soap addition method required for this surfactant. Nascent soap addition created a mixing constraint on water incorporation, as the formation of the W/O emulsion is kinetically controlled by the rate of which NaOH and Unicid 350 reacted with each other within the dispersion stage.
4. Offline coalescence testing determined that the emulsions created with both SE and SFEE had comparable aggregation tendencies at the tested extreme conditions, meaning that the increased coarse particle generation observed in SFEE was likely not a result of aggregation within the dilution stage, but rather related to the development of the W/O emulsion within the dispersion stage.
5. Binary blends of anionic/non-ionic surfactants (Calfax/Igepal CA-630) have been shown to significantly reduce the overall charge on the final latex particles. This reduction in overall charge can be attributed to the adsorption of Igepal onto the oleic phase prior to phase inversion reducing the amount of Calfax being entrapped in the generated latex particles.

6. Initial tests on the effectiveness of increasing the viscosity of the water in the dilution zone were done using hydrocolloids (corn starch and methylcellulose). These results showed a positive impact in reducing coarse particle generation for the generated final emulsion.

4.2 Recommendations for Future Work

Continued experimentation with regards to binary surfactant blends should be conducted to further optimize the blend formulation and minimize the overall surfactant loadings without resulting in emulsion destabilization. A more thorough investigation on the impact of varied water phase viscosity of the mechanism of SFEE with different hydrocolloids at higher viscosity values is recommended. Manipulation of process variables such as screw speed and barrel temperature profile while using a binary emulsifier blend would be interesting as this has yet to be explored. Incorporation of artificial intelligence as a tool to provide predictive insight on how changing different process variables will impact emulsion characteristics would be very beneficial to further improving our understanding of the mechanism of SFEE.