

Investigating the Synergistic Anionic/Non-Ionic Surfactant Interaction on Nanoparticle Synthesis with 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 in resulting nano-sized polyester particles. Five similar non-ionic surfactants with only minor structural differences from one another, 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 more hindered branched alkyl structure was more desirable in preparing particles in the desired size range of 100-200 nm for this polymer. The preferred blend of Calfax/Igepal CA-630 found in preliminary study, was shown to exhibit a synergistic interaction in SFEE in subsequent trials. The synergistic interaction was considered to arise from the high viscosity of the system, keeping the two surfactants partitioned across the interface of the emulsifying phases, which allowed a lower total surfactant concentration to be used than possible in a comparable solvent-based emulsification method. This partitioning across the interface decreased the non-extractable amount of Calfax left in the polyester latex. This approach of blending anionic and non-ionic species shows an important step in preparing nanosized particles with controlled charge.

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

1. Introduction

Solvent-free extrusion emulsification (SFEE) utilizes only water to produce an oil-in-water (O/W) emulsion with relatively high viscosity polymers (up to 600 Pa.s has been tested to date) via catastrophic phase inversion. The particles often sought by this method lie between 100-500 nm in diameter.¹⁻⁴ Commercial variants of this process are reported in the patent literature by several major chemical companies.⁵⁻⁹ The mechanical energy input by the extruder is important to bringing water and polymer phases together, but alone mixing is not enough to generate a stable emulsion. Surface-active agents are necessary to develop a lamellae dispersion over the first two-thirds of the machine length,¹⁰ and aid in both water incorporation into the bulk polymer melt as well as stabilization of the final emulsion. In order to reach an interfacial state beneficial for phase inversion, sufficient lamellae thinning of the first developed water-in-oil (W/O) emulsion must occur within the short residence time of the extrusion process, adding to the importance of choosing an effective surfactant. When incorrectly chosen surfactants are used, the extent of phase inversion decreases substantially, resulting in exiting material that has the appearance of 'wet plastic' corresponding to the W/O emulsion.

The performance of surfactants depends on their hydrophilic/hydrophobic end group molecular structure. The hydrophilic end can either contain a charged moiety or be charge neutral. The charged moieties of ionic surfactants increase their affinity towards water molecules and prevent particle aggregation by electrostatic repulsion. Non-ionic surfactants have a lower affinity for water (especially at the high temperatures of SFEE), being drawn to the aqueous interface by hydrogen bonding associations and relying largely upon the steric stabilization provided by their bulky molecular structures to prevent domain aggregation of an emulsified system.¹¹ Non-ionic species properties are notably influenced by temperature, which makes them suitable to both

catastrophic and transitional phase inversion methods. Both forms of surfactants have been successfully used in phase inversion emulsification processes.¹²⁻¹⁵

Studies in solution have shown that there can be benefits associated with using a combination of ionic and non-ionic surfactants.¹⁶⁻¹⁹ Non-ionic surfactants blended with anionic surfactants can result in a synergistic effect beneficial in producing smaller particles by emulsion polymerization,¹⁸ and when used in their proper blend ratio, have shown performance insensitive to temperature changes.¹⁷ The combined electrostatic and steric stabilization mechanism of these blended surfactants yields a notable enhancement in emulsion stability but it is unclear how their individual position at the interface is important to witnessing this synergistic effect and whether a viscosity difference between the phases will be influential.

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 pharmaceuticals). It was hypothesized that if anionic surfactants could be partially replaced with non-ionic species, charge tuning would be possible in the final nanoparticles. 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 due to their low affinity with water at standard processing temperatures for molten polymers.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.

2. Experimental

2.1. Material

A polyester was supplied by Xerox corporation (Webster, NY, USA) that had a measured T_g of 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. Calfax DB-45 (alkyldiphenyloxide disulfonate; $M_w \cong 542$ g/mol, HLB = 16.7) was the only anionic surfactant in the study, purchased from the Pilot Chemical Company (Cincinnati, OH, USA) as a 47 wt% aqueous solution. The molecular properties and effectiveness of this surfactant for the SFEE process have been discussed in a previous study.²⁰ Five different non-ionic surfactants were covered in this study, all 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 (octylphenyl-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 a 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 the driving force 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 Leistritz 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). 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 discharge capacity) and a high-pressure syringe pump (51 MPa discharge capacity), respectively. An illustrated layout of the process can be seen in Figure 1.

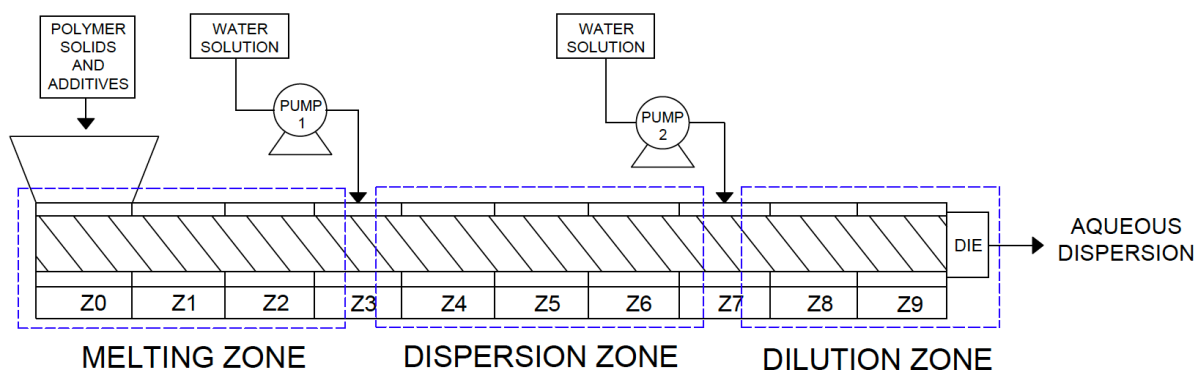


Figure 1. Schematic illustration of the twin-screw extruder layout used for SFEE experiments.

2.2. Solvent Emulsification

Bench-top screening for suitable concentrations and ratios of surfactants 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. 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 5 minutes of agitation using an IKA RW 20 benchtop mixer operated at low speeds of 100-200 RPM sufficient to provide a well-mixed solution. 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. This procedure was adapted from Example 4 of US Patent 8,466,254.²¹

2.3. 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 as solutions at 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 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 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

2.4. Characterization

All emulsions were triple filtered using a 75 μm sieve to remove any excessively large particles prior to the characterization measurements; the weight fraction of screened particles was used in the calculation of percent emulsified polymer. Particle size measurements taken for a sample emulsion were conducted using two instruments. A Mastersizer 2000 particle size measurement system capable of accurately measuring sizes ranging between 0.2 and 2000 μm was primarily used to report particle size measurements. All samples were diluted to a ratio of 1:50 in deionized Milli-Q water prior to testing. Samples were circulated through the instrument at a flow rate sufficient to prevent both bubble formation and particle settling during testing. A NANOTRAC NPA250 dynamic light scattering system, capable of measuring sizes ranging between 0.8 and 6500 nm was used to verify particle size measurements, especially those that fell slightly outside the accuracy limits of the Mastersizer, while recognizing the differences in the techniques for size determination.²² All samples were diluted to a ratio of 1:100 in deionized Milli-Q water prior to testing. The results were reported based on the average taken from three replicated measurements. Span values were also reported to represent the breadth of the particle size distribution. Span is a unitless value and is defined by 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.

The amount of retained surfactant was measured at the Xerox Corporation (Webster, NY) using electrospray ESI mass spectrometry in both positive and negative modes after separation 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, free surfactant were removed by one of two methods (or both for mixtures of ionic and non-ionic surfactants); 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).

Average relative standard error for each respective measurement described above was D_{50} ($\pm 0.02 \mu\text{m}$), Span ($\pm 0.05 \mu\text{m}$), zeta potential ($\pm 3.00 \text{ mV}$), pH (± 0.05), and conductivity ($\pm 0.04 \text{ mS/cm}$).

3. Results and Discussion

3.1 Impact of Non-Ionic Surfactant Molecular Structure on Emulsifier Performance

A previous study had identified Calfax DB-45 as a highly effective anionic surfactant, capable of producing particles in the desired range of 100-200 nm at low concentration but the non-ionic species examined in that work presented feeding issues and poor emulsification performance when used alone in SFEE.²⁰ The non-ionic species used in the current study were selected to avoid those feeding issues. The initial studies described below sought to find a preferred non-ionic species among this new group of surfactants, exploring different structural parameters

to ultimately work with Calfax in a detailed blend study. Much of these exploratory trials relied upon SE to screen for surfactant effectiveness without excessive use of materials.

The first SE trials tested variations in the hydrophilic polyethoxy chain length. Four non-ionic surfactants were tested, and their preferred molecular structures can be seen in Figure 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 findings over to SFEE assumes surfactant solubility in the oleic phase changed for all tested species to the same degree. However, our previous study illustrated the similarities between particles generated between SE and SFEE, albeit needing a higher surfactant concentration for the latter due to temperature and viscosity difference between the two processes.²⁰

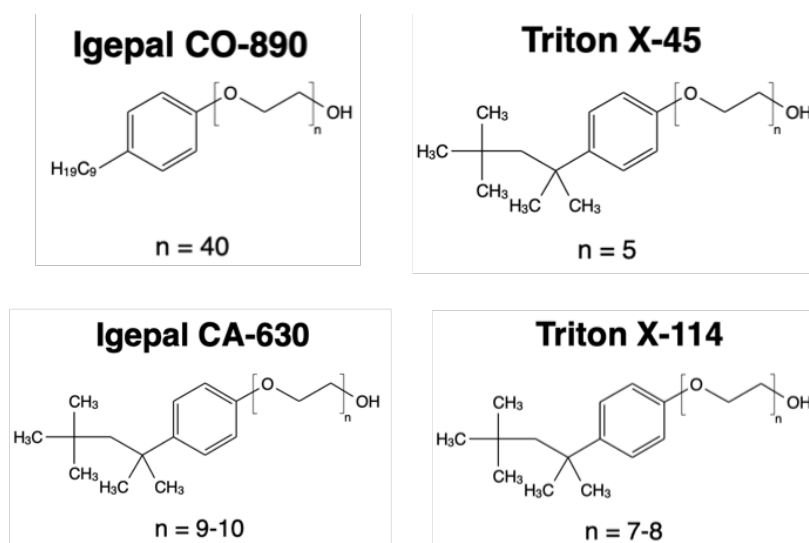


Figure 2. Molecular structures for the four non-ionic surfactants tested with varying hydrophile alkyl chain length.

Table 2. Solvent emulsification 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	-28 ± 9	6.0	1.71
Igepal CA-630	6.8	0.11	0.15	1.25	-49 ± 15	6.9	1.88
Triton X-114	11.9	0.22	0.21	1.92	-52 ± 13	6.6	1.99
Triton X-45	28.5	0.67	0.17	0.67	N/A	6.6	1.61

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 2, whereas comparative particle size distributions at a fixed molar loading of 0.22 mmol/g resin are shown in Figure 3. Looking at Table 2, 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 more negative in value for the Igepal CA-630 sample, suggesting better stability compared to Igepal CO-890. A molar loading below 0.11 mmol/g resin was found to result in particle destabilization with either Igepal CA-630 or Igepal CO-890. A chain length of n = 9 appeared to be the minimum 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 nominally one ethoxy group, but sufficient enough to result in increased coarse generation noted by the increase in span to 1.92 for Triton X-114 even at a molar loading almost 100% greater (0.22 mmol/g resin). The increased span is illustrated in Figure 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. Other 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 matching our results closely, with major particle destabilization being measured at $n=7.5$.^{23,24} Looking at Figure 3, the particle aggregation and general emulsion instability observed with Triton X-45 resulted in a tri-modal distribution. In fact, a molar loading of 0.67 mmol/g resin was required for SE to achieve a suitable O/W emulsion using Triton X-45. Triton X-45 has a quoted HLB value of 9.8, though realistically, its effective HLB value at elevated temperatures will be lowered by becoming 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 disregarded from further testing.

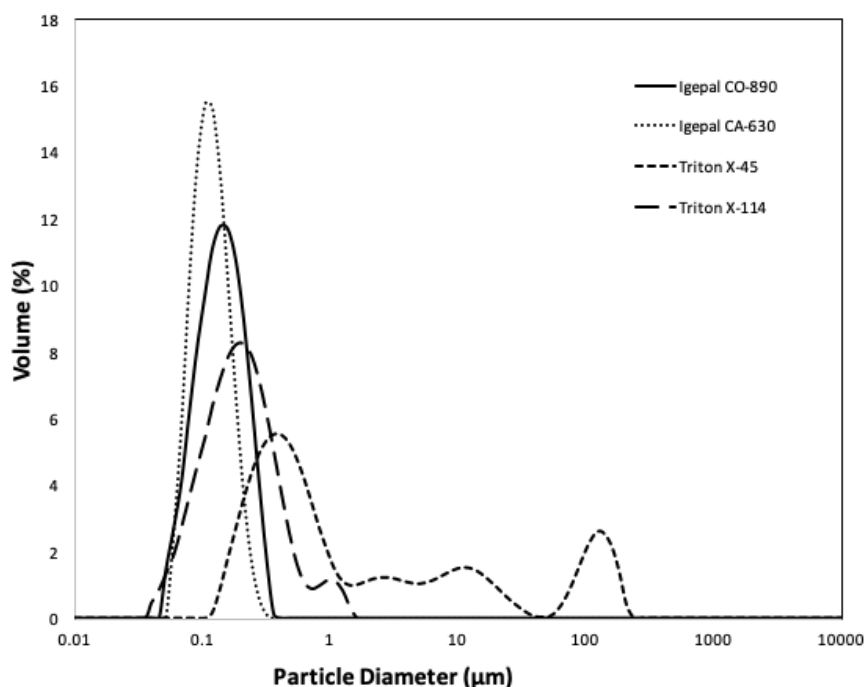


Figure 3. Particle size distributions for four different SE samples created using four different non-ionic surfactants: Igepal CO-890 (0.22 mmol/g resin loading), Igepal CA-630 (0.22 mmol/g resin loading), Triton X-45 (0.22 mmol/g resin loading), Triton X-114 (0.22 mmol/g resin loading).

The second set of SE trials to identify a suitable non-ionic for SFEE considered the alkylphenol end group structure. In this evaluation, two surfactants with similar ethoxylate end groups but either a branched alkyl (1,1,3,3-tetramethylbutyl substituted) (Igepal CA-630) or branched nonylphenol (from a mixture of branched C9 olefins) (Igepal CO-630) lipophilic end group structure were tested. An illustration of the respective molecular structures for Igepal CA-630 and CO-630 can be seen in Figure 4. Schematically, the Igepal CO-630 substituent is a complex mixture of 9-carbon alkyl units that presents a less sterically hindered lipophilic endgroup of the two species. From the previous results above, either Igepal CA-630 or 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. A comparison of the resulting emulsions created using the two surfactants by SE is presented in Supporting Information Table S1. The emulsion stabilized with Igepal CO-630 was fairly similar to the sample with Igepal CA-630. Given a choice between the two species for the subsequent blends trials, the sample with Igepal CA-630 showed slightly better performance in terms of D_{50} and span, though zeta potential showed no difference in stability. The study by Rekvig et al. reinforced our preference for CA-630 as they found it more effective in reducing interfacial tension.²⁵ They explained that lipophilic end groups sterically occupying more space in the oil phase, producing a stronger volumetric interaction.

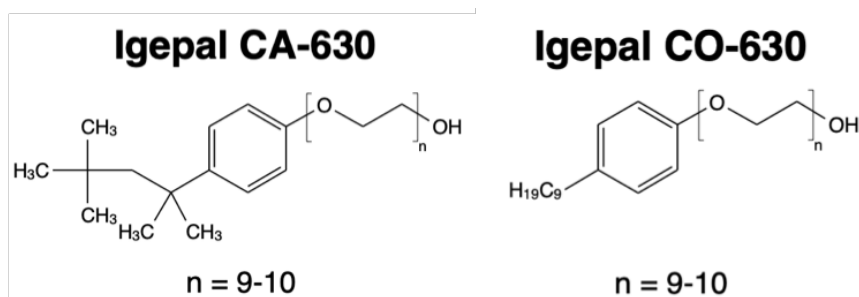


Figure 4. Molecular structures for the two surfactants tested with differing lipophile chain structures

Emulsification of polyester by SFEE with only a non-ionic surfactant will generally yield an emulsion with poor stability based on prior experiences,²⁰ but before considering the performance of anionic/non-ionic blends, benchmarking trials with Igepal CA-630, and Igepal CO-630 were conducted to ascertain whether their differences were replicated or amplified in the more viscous environment compared to SE. Emulsion properties and particle size distributions of samples prepared with these surfactants compared to Calfax are given in Supporting Information Table S2 and Figure 5, respectively.

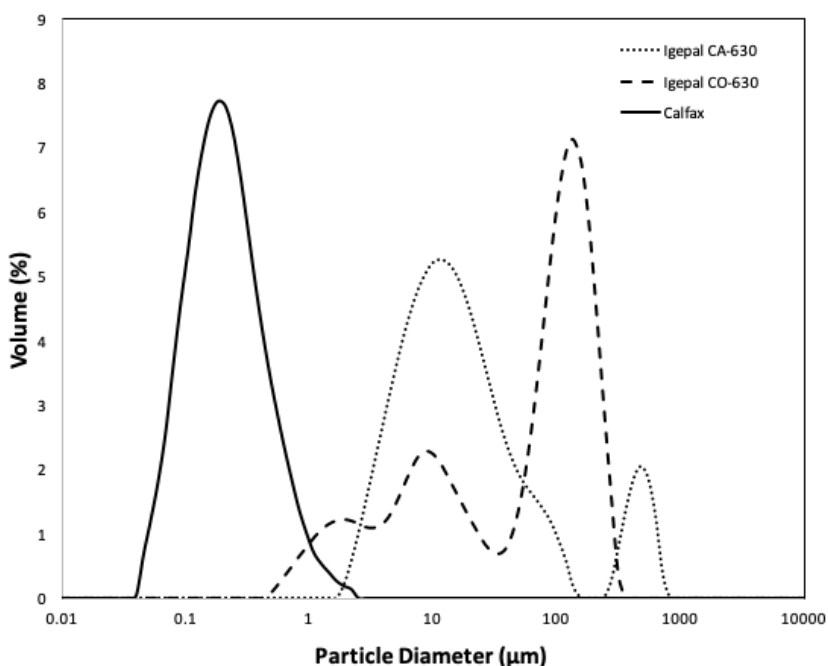


Figure 5. Particle size distributions for three different SFEE samples created using two different non-ionic surfactants: Igepal CA-630 (0.11 mmol/g resin loading), Igepal CO-630 (0.11 mmol/g resin loading), as well as an anionic surfactant: Calfax (0.11 mmol/g resin loading).

Comparing SFEE performance of the two non-ionic surfactants to that of Calfax, it is seen that the lack of a charged end group hindered a surfactant's ability to generate useful O/W emulsions in this highly viscous environment. Major coarse particle generation was observed with both non-ionic surfactants at 0.11 mmol/g resin, while an extremely low quantity of O/W emulsion

was found in the exiting mass from the extruder. The lower affinity for water by the non-ionics (compared to Calfax) resulted in poor interfacial growth between the oleic and water phases, being inadequate to compensate for the already retarding aspects of the process, namely mixing phases with an extremely high viscosity ratio ($10^6:1$) and carrying out that mixing in short duration in the dispersion zone (approximately 2 minutes of residence time). However, the high viscosity process showed better discrimination between the two non-ionic surfactants than found by SE, with the more hindered branching of Igepal CA-630 producing much smaller particles than CO-630. Since this observation is based on the limited amount of material emulsified (i.e. only 5% of the mass actually emulsified with either non-ionic species), it cannot be considered conclusive, but it was seen to reinforce the decision to use Igepal CA-630 in the blend study. The result also gives further support to our earlier claims that non-ionic species should not be used as primary surfactants for this process, at least with polyester.

3.2. 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 the polymer system by SFEE. For some commercial products, it is desirable to prepare particles that exhibit little charge so as to not interfere with other interacting features. 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.

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

Blend Characteristics		Results			
Molar Ratio	mmol/g resin	D_{50} (μm)	Span	pH	

				Zeta Potential (mV)		Conductivity (mS/cm)
25/75	0.16	0.24	1.23	-31 ± 8	6.91	1.68
66/33	0.12	0.18	0.95	-59 ± 21	7.25	1.11
50/50	0.12	0.18	0.79	-42 ± 19	7.12	2.06
42/58	0.12	0.24	0.97	-27 ± 8	7.10	1.09
33/66	0.12	0.31	0.92	-42 ± 17	7.05	1.63
50/50	0.10	23.24	1.13	-13 ± 9	7.41	0.17
66/33	0.10	0.23	0.95	-30 ± 16	7.15	1.24
75/25	0.10	0.17	0.52	-28 ± 1	7.23	1.94
75/25	0.08	0.17	0.53	-38 ± 15	7.25	1.96
75/25	0.06	0.20	2.76	-26 ± 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 6. All distributions were mono-modal 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. 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 6(c); this is clearly seen in Figure 6(c) by the distribution broadening with decreasing total surfactant loading at a 75/25% ratio for Calfax/Igepal CA-630, which was the only ratio where a stable emulsion could be prepared for a concentration as low as 0.08 mmol/g resin. The unstable nature of emulsions at low Calfax content was quantitatively denoted by their low magnitude zeta potential, particularly evident for the 50/50 blend sample at a total surfactant loading of 0.10 mmol/g resin that measured at -12.7 mV whereas all others had zeta potentials having more negative values than -25 mV. The conductivity between samples was not as constant

as other characteristics (possibly due to impurities), but large drops in emulsion conductivity were consistently seen with samples having measurable coarse particle generation.

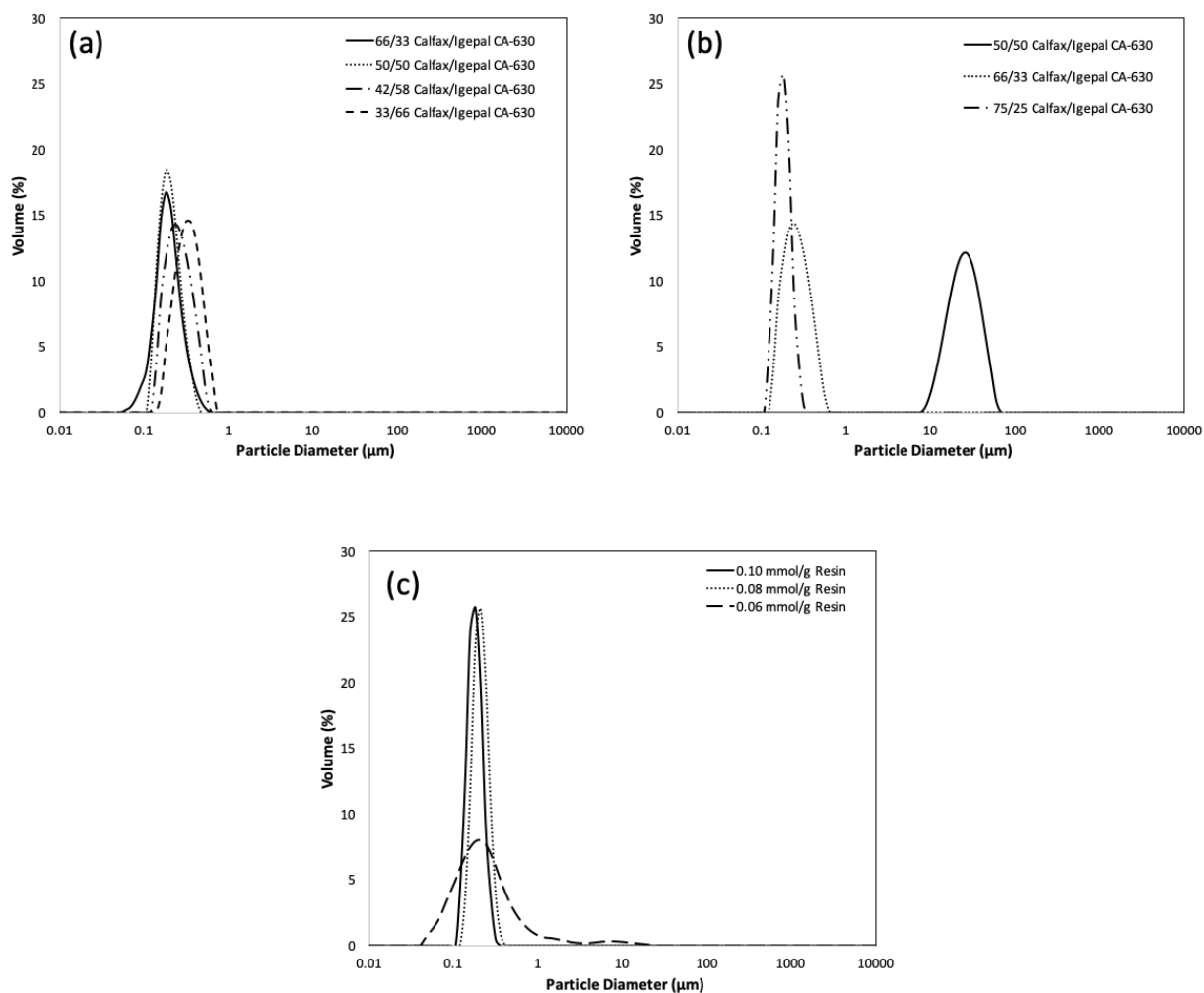


Figure 6. Particle size distributions for SE samples made with a binary mixture of surfactants consisting of Calfax/Igepal CA-630. (a) SE samples made using a Calfax/Igepal CA-630 blend at varied ratios of surfactant and a constant total molar concentration of 0.12 mmol/g resin. (b) SE samples made using 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.

As a primary surfactant, the lowest content of Calfax to adequately emulsify the polyester by SE before significant coarse particle generation was determined previously to be approximately 0.06 mmol/g resin.²⁰ In the blend trials, it can be seen that as long as at least 0.06 mmol/g resin of

Calfax was present in the blend ratio chosen, a stable emulsion was still achieved; samples with 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 showed good results in Table 3. 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 0.11 mmol/g resin (noted in Table 2). The result shows a D_{50} of 0.24 μm and span of 1.23 indicating a stable emulsion could be achieved. We generally found that the two surfactants acted exclusive to one another in the SE process, making the results found with SFEE below all the more interesting.

Table 4. SFEE Calfax/Igepal CA-630 blend study formulation conditions and resulting emulsion characterization data.

Blend Characteristics		Results					
Molar Ratio	mmol/g resin	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 by SFEE at varied molar blend ratios and total molar loadings are shown in Figure 7. The SE blend trials above showed increasing coarse particle generation for ratios containing less than 50% Calfax, which discouraged testing in SFEE of 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 lower total molar loadings. Each of the samples shown in the figure exhibited a similar mono-modal distribution but with decreasing total surfactant loading, there was a gradual decrease in the volume percentage of 150 nm diameter particles in the product and subsequent broadening of the distribution towards larger particle sizes. Table 4 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 above where no synergistic interactions were found between the two surfactants, the same formulation conditions resulted in lower D_{50} and span values by SFEE. Considering the trend seen with SE, none of these SFEE samples should have been produced without significant amounts of coarse particles since the Calfax concentration in the blends was always below its threshold loading as an effective primary surfactant (determined previously to be 0.11 mmol/g for Calfax in SFEE).²⁰ In contrast to what we originally expected, no significant coarse fraction was observed in any of the tested formulation conditions for SFEE, even in surfactant blends where the Calfax loading was as low as 0.03 mmol/g resin. Unlike in SE, the two surfactants were showing a beneficial synergistic contribution in emulsification by SFEE.

The conductivity values for the SFEE emulsions were found to be much lower than those by SE, ranging between 0.31–0.71 mS/cm. When comparing the zeta potential values with SE, SFEE samples were seen to have slightly higher in 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 impurities). Comparing these results to SE further reinforced our findings that the SFEE samples were generally more stable.

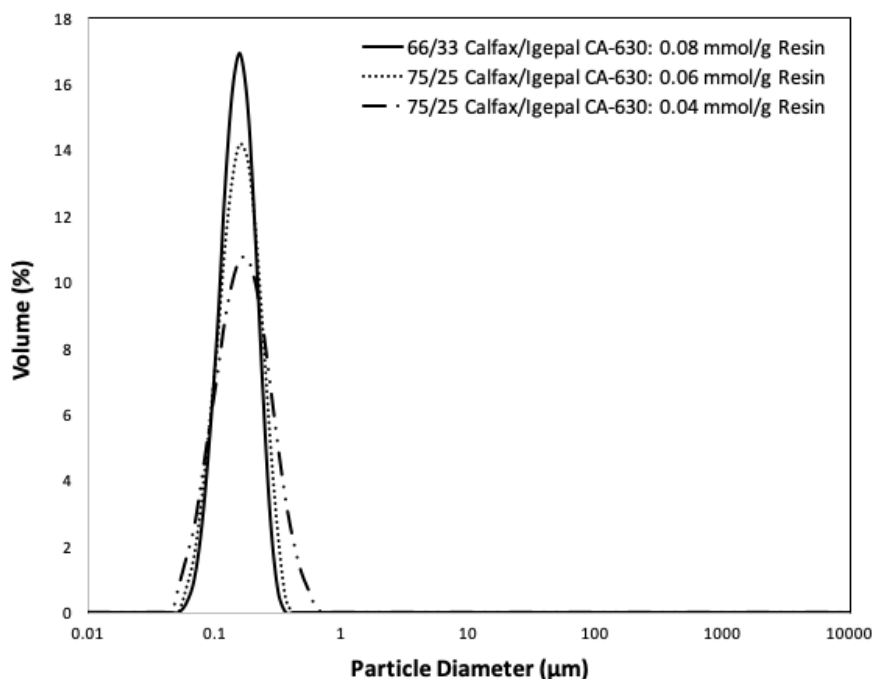


Figure 7 Particle size distributions for select SFEE samples made with binary blends of Calfax/Igepal CA-630 at varied total molar loadings and blend ratios.

The solids were fully emulsified in the SFEE blend trials, as noted in Table 4; however, the appearance of the exiting mass when the total surfactant loading was 0.06 mmol/g resin or lower differed significantly. Normally, at higher surfactant loadings, the extrudate appeared as a milky emulsion of low apparent viscosity, but at 0.06 mmol/g or below it looked like a thick sludge of distinctly higher viscosity. Adding the sludge-like extrudate into a beaker of water and gently stirring, a milk-like emulsion was once again obtained. Figure 8 (a) and (b) show SEM images of the emulsified polyester sample (66/33 Calfax/Igepal CA-630 at 0.08 mmol/g resin), while Figure 8 (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. Examples of the agglomerated particles are highlighted as circled sections in the images. Figure 8 (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 likely occurred during the drying process in preparation of the SEM analysis. The phenomenon of emulsion creaming and subsequent particle coalescence is common.²⁶ The sludge-like state exiting the extruder is 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, which if true, it means the surfactant system in SFEE can sufficiently contribute to the emulsification mechanism yet be inadequate to stabilize the final particles.

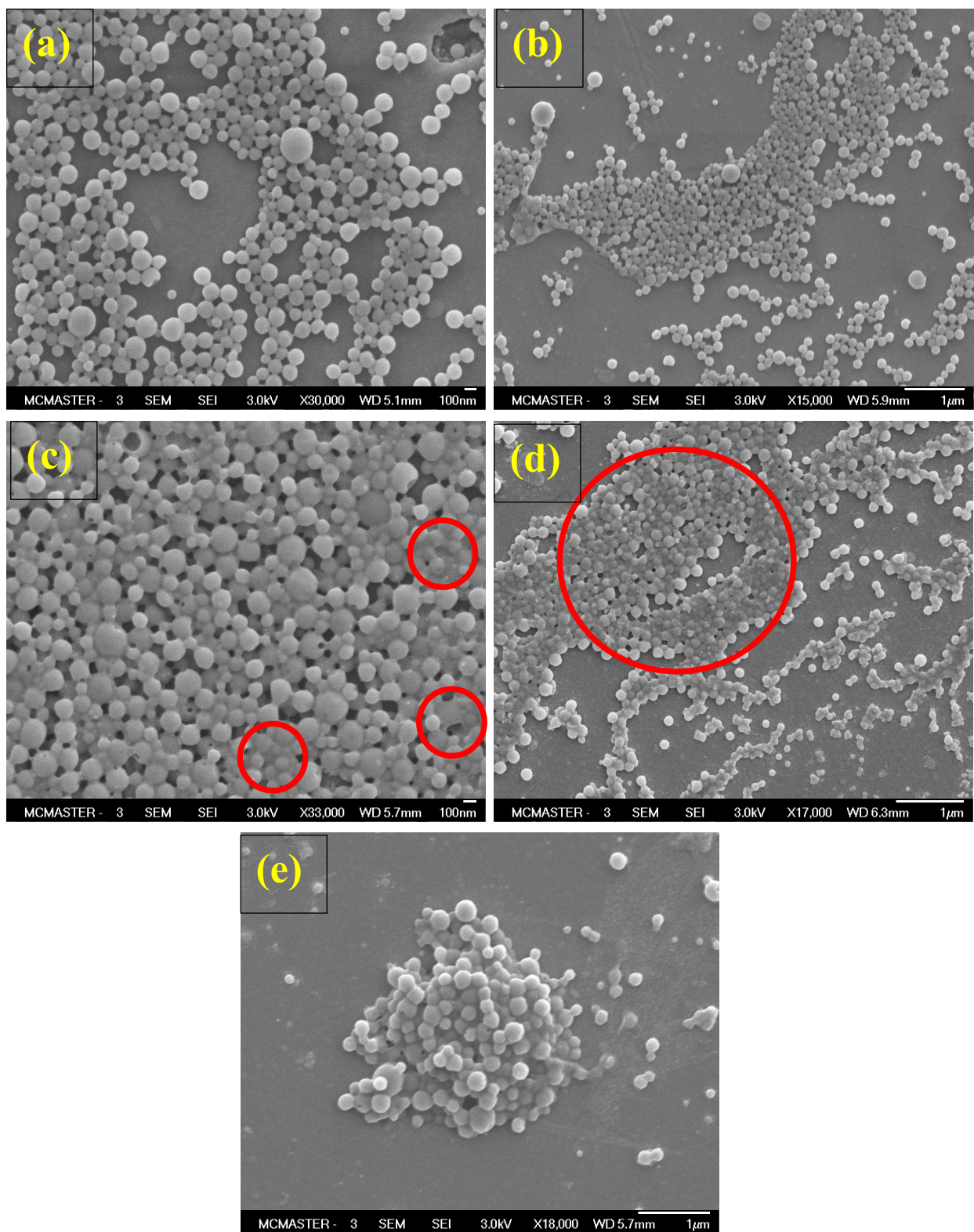


Figure 6. SEM images for blends of Calfax and Igepal CA-630 at varied magnifications. (a) and (b): 66/33 molar ratio of Calfax/Igepal CA-630 at 0.08 mmol/g resin loading. (c) – (e): 75/25 molar ratio of Calfax/Igepal CA-630 at 0.04 mmol/g resin loading.

Table 5. 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% of solids)	Calfax in Sample After Cleaning (wt% of Solids)
Calfax	SFEE	0.08	0.3	3.94	4.4	0.50
Calfax/Igepal CA-630	SE	0.12	0.18	0.95	3.9	< 0.1
Calfax/Igepal CA-630	SFEE	0.12	0.14	1.62	9	< 0.1

To assess the impact of using the blend of Calfax and Igepal CA-630 on the charge of final latex particles, emulsions were put through different washing techniques to remove any surface bound surfactant, and the level of retained surfactant in the final latex particles was measured. Firstly, a comparison between SE and SFEE results with selected samples shown in Table 5; 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 by SFEE had 0.50 wt% of the ionic species still present in the particles after ion-exchange washing. Looking at the two tested surfactant blend samples, the measured Calfax after ion-exchange wash was <0.1 wt% (lower reliable detection limit of the measurement method), regardless of the emulsification process. Viscosity of the emulsified oleic phase seemed to have no impact on the extractable content of Calfax from the final particles. It seems that the non-ionic surfactant at the tested molar loading of 0.04 mmol/g resin, inhibited the anionic surfactant from becoming entrapped within the surface of the latex particles. This notable observation motivated detailed analysis of all samples based on their different surfactant blends.

The testing for entrapped Calfax from the SFEE trials with differing surfactant blends produced the results shown in Figure 9. The reported percent of entrapped Calfax in the figure refers to the measured weight fraction of this surfactant in the washed samples relative to the measured weight fraction in the samples before washing. The figure shows that the emulsified particles retained a higher percentage of their originally present Calfax after washing when lower amounts of the non-ionic surfactant were used. Corroborating the results in Table 5, with an Igepal content above ~ 0.04 mmol/g, the tested samples retained less Calfax than detectable by the measurement method. While it was an obvious outcome that successfully substituting the non-ionic species for the anionic surfactant during emulsification would lower the particle charge, it was unexpected that the remaining anionic surfactant would be more readily dislodged from the particles as that non-ionic concentration was increased.

The cause for this declining entrapment of the anionic species was believed to be related to the arrangement of both surfactants at the oil/water interface. In blends of anionic/non-ionic surfactants, it has been shown that the non-ionic surfactant preferentially adsorbs at the interfaces, leaving the anionic molecules to concentrate in the water phase.¹⁶ This concentrated layer of Igepal CA-630 could be preventing 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 the exposed polymer surface. This interaction leaves the majority of Calfax micelles in the water phase and prevents them from becoming entrapped in the formed latex particles, subsequently resulting a lower particle charge.

The explanation for why less total surfactant was required in SFEE compared to SE in the blend study was believed to be linked to this shell forming phenomenon in conjunction with the influence of the higher viscosity oleic phase. The low viscosity of SE allowed for higher mobility of the non-ionic molecules at the interface during the dispersion stage, 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 was not the case with SFEE, where the high viscosity oleic phase reduced the mobility of non-ionic surfactant, anchoring its hydrophilic chain ends at the polymer surface. The concentration of anionic species more effectively stabilized the interface in this case since far fewer molecules could cross into the oleic phase, and hence less overall surfactant was required to sufficiently reduce interfacial tension.

4. 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; and 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 a more hindered 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 and that effect grew greater as the amount of non-ionic surfactant was present. 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 allowed the two surfactants to work synergistically to reduce the overall interfacial tension and allowed a lower overall surfactant concentration to effectively generate stable O/W emulsions. The additional benefit to this shell-forming phenomenon was that anionic surfactant could be readily washed away in the finished particles, making it possible to lower the particle charge if desired.

5. Supporting Information

The supporting information is available free of charge via the Internet at <http://pubs.acs.org/>. Table S1 provides SE characterization results for emulsions made with Igepal CA-630 and Igepal CO-630 at their lowest tested loading. Table S2 provides SFEE characterization results for emulsions made with Igepal CA-630, Igepal CO-630, and Calfax at their respective minimum loadings.

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