Effect of Viscosity on Solvent-Free Extrusion Emulsification: Varying System Temperature

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ABSTRACT

Solvent-free extrusion emulsification (SFEE) is a new continuous approach for producing nanoparticles from high viscosity molten polymers using a twin-screw extruder. In a previous study, the influence of melt viscosity on lamellae development in the phase inversion mechanism was investigated for an otherwise fixed system of variables including temperature, mixing intensity and surfactant content. Varying system temperature in the current study to produce the same melt viscosities as those previously examined, did not produce the same linear effect on particle size. The investigation to understand the influence of system temperature on the SFEE mechanism was done by using an inline rheometer and different screw/barrel configurations to simulate different zones of SFEE. Characterizations of the emulsified polyester included colorimetric titrations, particle size analysis, parallel plate rheometry, and gel permeation chromatography (GPC). Raising system temperature has a negative effect on the mechanism for producing smaller particles, countering the positively affected parameters, namely lower melt viscosity and a higher content of surface active species based on a contributing neutralization reaction. The findings show good fit to published studies of an osmotic pressure driven emulsification mechanism, which is beneficial in clarifying the role of surfactants in the process. Overall, the results show system temperature to be a complex variable in SFEE, deeming it undesirable in optimizing the process.

KEYWORDS: Mixing, temperature, matrix viscosity, emulsification, twin screw extruder, solid-liquid dispersion

INTRODUCTION

In order to produce solid-liquid dispersions with particles as small as 100-200 nm with polymers of high viscosity (in the range of 1000 Pa.s), solvent-free extrusion emulsification (SFEE) was recently introduced as a novel top-down approach without use of solvents.[1-3] The process divides a twin-screw extruder (TSE) into three major zones, which include the: i) *melting zone* where bulk polymer and potentially other solids are melt-mixed, ii) *dispersion zone* where interfacial area growth between injected water and the continuous polymer phase progresses in the presence of surfactant species, and iii) *dilution zone* where the final addition of water initiates phase inversion and subsequently minimizes the coalescence of produced particles. SFEE has been a challenging process to implement in industry to date due to its sensitivity to an unusually large number of material and system variables complicating its stability and scale-up. A better understanding of the phenomena taking place is important to controlling and optimizing the operational and formulation variables involved.

The formation of nanoparticles via SFEE is attributed to self-emulsification by a combination of mechanisms which seem best described by 'interfacial turbulence'[4] and the osmotic pressure driven mechanism of Greiner and Evans.[5] Mechanical energy is involved in developing interfacial area between the bulk phases of the initial W/O emulsion in the dispersion zone but the process is ultimately incapable of generating sufficient work to produce nano-sized molten droplets as additional water is added in the dilution zone. To create the microemulsion conditions responsible for producing the desired nanoparticles, surfactant is introduced and aided by partial conversion of the polymer acid endgroups into carboxylates. For high viscosity systems, the related interfacial area generation for the microemulsion occurs by folding not droplet generation,[4,7-13] which has been observed in SFEE as striated lamellae of polymer

sampled at the end of the dispersion zone.[2,6] Formation of nano-sized melt droplets occurs by immediately exposing the microemulsion to a high volume of additional water at the start of the dilution zone; the importance of this rapid addition is similarly noted in the batch prepared rosin microemulsion of Greiner and Evans.[5] The spontaneous phase inversion generating the small droplets seems likely to be driven by a lower osmotic pressure present in the W/O microemulsion, drawing the added water into the high viscosity medium to cause the water phase to swell and eventually invert.[5] With the heterogeneity of surfactant species in the high viscosity melt phase during dispersion, there is likely contributions of interfacial turbulence to the melt droplet generation.[4]

An interesting observation of systems reportedly exhibiting the osmotic driven mechanism for spontaneous inversion is particle coarsening with increasing temperature.[5] Recognizing that this mechanism may be descriptive of SFEE has offered possible reasons why controlling particle size with temperature is problematic, since the effects on melt viscosity do not give predictive outcomes. To probe the influence of temperature in SFEE, a previous study[1] by the authors was first conducted to observe the influence of viscosity on the SFEE process alone without variation of the system temperature. In that study particles were produced in the range of 100 nm for polymer viscosities up to 620 Pa.s, though as viscosity increases so did the nominal size of the final particles. Varied matrix viscosity was accomplished by molecular means (i.e. crosslinking) in that study and its results serve as a reference point for the current study.

The purpose of this paper is to evaluate the influence of system temperature on particle size generation by SFEE, and attempt to relate its effects to the resin or surfactants in the process. This continuous process is unique in the field of dispersions due to its targeted handling

of very high viscosities for producing nano-sized polymer particles within a short, confined processing time. As usual in this series of studies on SFEE, the target for the work is to produce particles in the 100-300 nm range. To make definitive conclusion on the effects of temperature, other variables were probe for comparison with previous data[1] including the length of the dispersion zone, surfactant content, and method of sodium hydroxide addition for endgroup conversion.

MATERIALS AND METHODS

Material

A high flow grade polyester resin (M_W=17,081 g/mol; M_W/M_N=4.2) was supplied by the Xerox Corporation (Webster, NY) having an acid number of 17.7±1.7 mg KOH/g. The polyester consisted of a 1:1 molar ratio of propoxylated bisphenol A (pBPA) and fumaric acid (FA). Sodium hydroxide pellets (NaOH) purchased from Caledon Laboratories Ltd. (Georgetown, Ontario) were dried, ground and sieved to 850 µm-1180 µm for faster dissolution in the process. Sodium dodecylbenzenesulfonate (SDBS) was purchased from Sigma-Aldrich (Toronto, Ontario). Deionized water (>0.1 $\mu S/cm^2$) was used in all trials.

General Process Set-up

Trials were performed on a 40 L/D, 27 mm Leistritz ZSE-HP co-rotating twin-screw extruder (TSE) from the American Leistritz Extruder Corporation (Somerville, NJ); L/D refers to the axial length versus screw diameter as a standard measure of length for extrusion machinery. Flat barrel temperature profiles were used for simplicity, with barrel zones 1-9 held at either 90 ºC, 100 ºC or 110ºC while barrel zone 0 was supplied with only chilled water. A dry blend consisting of polyester resin, SDBS and for some conditions, ground solid NaOH particles, which was fed to

the extruder by a DDSR20 twin-screw gravimetric feeder (Brabender Technology, Mississauga, Ontario) at 8 kg/h. The extruder screw speed was kept at 300 rpm. An intensive mixing screw design consisting of many kneading elements was used, similar to the one described by Neubauer and Dunchus.[14] A conceptual drawing of the screw design is included in Figure 1.

The SFEE process uses two sites for liquids injection, where the first injection location adds a small quantity of water into the process (either pure or as an aqueous NaOH solution depending on trial conditions) yielding a resin-to-water weight ratio of R/W = 3.5, and the second injection location adds a larger amount of only deionized water to decrease the resin-to-water ratio to R/W = 1.3; the chosen R/W ratios provided robust operations in order to probe the effects of viscosity and formulation on the process but the sensitivity of this parameter on emulsification has yet to be studied. Figure 1 illustrates the extruder layout, showing the two water injection locations for the three configurations covered in the study. The water or aqueous NaOH solution was fed by a pair of ISCO 260D high pressure syringe pumps (Teledyne ISCO; Lincoln, NE). The injected water temperature was controlled with an Isotemp™ circulating bath (ThermoFisher Scientific Inc.; Waltham, MA) connected to two pump jackets. The injected water temperature was kept 90ºC below the melt temperature at the first injection location, consistent with previous studies,[1,2] to minimize heat transfer influences between the three barrel temperatures; melt temperature at the first injection location (without water added) was measured with a K-type thermocouple, with average values shown in Table 1 for the different barrel temperatures.

Extruder Barrel Configurations

Two different extruder barrel configurations are seen in Figure 1. By altering the dispersion zone length and its proximity to the inline rheometer, the different configurations examine the

mixing in the zone as well as gaining preliminary understanding of particle solidification in the dilution zone; future on-going studies will examine phenomena in the dilution zone in greater detail. ***Set-up 1***: In this configuration, the feeding port was placed at Zone 3 (14 L/D forwards from the back of the barrel) and screw elements were shifted so that the polymer experience identical shear conditions between Zone 3 to the end of the machine as found between Zone 0 to Zone 7 in the *standard layout*. First and second injectors were positioned at Zone 5 and the last zone of the extruder (i.e. Zone 9), as shown in Figure 1. Set-up 1 is referred to as the '*short screw*' configuration and possess the same process lengths for the melting and dispersion zones as found in the standard layout[13] but minimized the dilution zone length (2 L/D rather than 10 L/D) after the second water injection location. ***Set-up 2***: This configuration represents the standard layout for SFEE used for normal manufacturing, with the feeding port placed at Zone 0 and water addition at Zone 3 and Zone 7, as shown in Figure 1. It is denoted as the '*long screw*' configuration, featuring a 14 L/D melting zone, 16 L/D dispersion zone and 10 L/D dilution zone. It is the design by which the other two set-ups are compared. The terminology of short and long screw is therefore in reference to the length of the dispersion zone in each screw design and used consistently in this work as it was established in our previous paper.[1]

Inline Rheometer

To best characterize the rheology of the process as polyester and water were mixed under appropriate temperature, pressure and shear conditions, a custom designed extruder die was used in the studies, validated in an earlier paper.[3] The inline rheometer has a 15 mm bore diameter and includes an orifice plate with 2 mm diameter opening located mid-way along the length of the die; the orifice plate design minimizes water draining from the extruder unless under pressure. Pressure drop across the orifice plate was monitored with two Dynisco PT467E pressure

transducers while melt temperature was determined with a K-type thermocouple near the die exit. The exit temperature of the polyester-water mixture was used to adjust the apparent viscosities calculated by the rheometer to a comparable set temperature of 110ºC, 100 ºC or 90ºC depending on the barrel temperature, using an Arrhenius shift factor of 42.9 kJ/mol.

Two transient rheological parameters are used to characterize the state of emulsification, which occur within the span of 3-4 minutes once water begins to be injected into the dispersion zone at Zone 3. These parameters are the slope of the viscosity transition with time ($\Delta\eta/\Delta t$, being negative in value if the viscosity drops during the transition) where η is the system viscosity measured by the rheometer, and relative viscosity ($\lambda=\eta/\eta_m$) corresponding to the steady state viscosity after the transition relative to the matrix viscosity (η_m) before water was added. Both are described in detail in earlier work.[2-3]

Trial Procedure

Barrel temperature of extruder was the primary variable of study in this work, considering three conditions (90ºC, 100ºC or 110ºC) to vary the matrix viscosity; the viscosities of the matrices at these temperatures were nearly identical to those produced by addition of a crosslinked polymer in an earlier study.[1] Consistent with earlier papers on SFEE,[1,2] other variables considered to probe the mechanism of dispersion included: method of 1 wt.% NaOH addition (ground solids added by the gravimetric feeder versus an aqueous solution added at the first injector location), SDBS content (0 wt.% or 7.5 wt.%), and extruder configuration (set-up 1, set-up 2 or set-up 3); all weight fractions are relative to the mass flow rate of resin.

Normal operation of the extruder started by running without water for five minutes to establish a steady baseline condition. Next, water (or an aqueous NaOH solution) began at the

first injection location to reach a resin-to-water of $R/W_1 = 3.5$ while the second injector was not used. In this mode (commonly called Mode 1 in all papers on SFEE), inline rheometer data was collected, with both transient information and final steady state results being important to analyzing phenomena related to the dispersion zone. It should be mentioned that R/W_1 is equals to total resin-to-water ratio (R/W_T) exiting the process in Mode 1. The material exiting the extruder under Mode 1 appeared as a molten polymer extrudate with no phase separated water visible. Finally, under Mode 2 operations, water was added at the second injector in addition to the first injector to decrease the total resin-to-water ratio to $R/W_T=1.3$ (i.e. Mode 2) before the dilution zone, producing a milky-looking emulsified product after the die that was collected for particle analysis.

The inline rheometer was not used for analysis of the dispersion mechanism when operating in Mode 2 since viscosity values show little variation to the variables of study with so much water present; variation in the emulsion viscosity under Mode 2 by the rheometer was used to evaluate process stability in its own section of the discussion.

Characterizations

A Brookhaven 900Plus with 35 mW laser source at 600 nm wavelength was used to determine the particle size distribution of emulsion samples, for particles less than 1 μm. The characterization was repeated 5 times per sample. On the other hand, a Malvern MasterSizer 2000™ (Malvern, United Kingdom) with detection range of 0.1 to 2000 μm was used to quantify particle sizes larger than 1μm. Mean diameter (D_{50}) of particles was calculated on a volume basis. Three repeats were made in water for each sample.

Molecular weight of the extruded samples was determined by Gel Permeation Chromatograph (GPC). A dried sample (5 mg) was dissolved in spectral grade $CHCl_3$ with 10% v/v triethylamine (99% purity). After filtering the dissolved samples with 0.2 µm syringe filter (Whatman PTFE), it was pour into 2 mL sample vials. Analysis used a Polymer Labs GPC-50 system using two 5 µm PL Mixed Bed C GPC columns (300 x 7.5 mm) with a guard column and a Wyatt triple detection system (light scattering, viscometry and refractive index) for measurements. A polystyrene linear 10-point calibration was used to calculate the standard molecular weights using the triple detection data. The characterization was done at the Xerox Corporation (Webster, NY). The determined number-average molecular weight (M_N) was used to correct the neutralization ratio mentioned below.

Acid number measurement was done by colorimetric titration following ASTM-D974. A 1 g dried sample was dissolved in 50 ml methylene ethylene ketone (MEK) and 0.5 mg p-naphthol benzein was added as an indicator. The solution was continually agitated while titrated with a standardized potassium hydroxide (KOH) solution in isopropanol (Sigma-Aldrich, 0.1 N certified standard). Acid number (AN) was quoted in units of mg KOH/g sample. The neutralization ratio (NR) mentioned in the Discussion section refers to the percentage of converted end groups based on the measured AN as stated in Equation 1 but corrected for new chain ends produced during degradation determined by GPC measurement of the extrudate sample.

$$NR = \left(1 - \frac{AN_{Extrudate}}{AN_{Virgin}} \right) * 100 \qquad (1)$$

Viscosity curves for the polyester and extruded samples without water for different temperatures (i.e. 90ºC, 100ºC and 110ºC) were measured offline with an ARES parallel plate

rheometer (TA Instrument New Castle, DE). Plates of 25 mm diameter were used at a fixed 1.5 mm gap distance. Operating in oscillating mode, complex viscosity was evaluated over a frequency range of 1 to 100 rad/s at a constant strain rate of 4% (selected based on an initial strain sweep test).

Statistical Analysis

For discussions of different factors affecting SFEE, a general factorial statistical analysis was included to consider their significance. The significance level based on P-values was determined using Design Expert 7.1 (State-Ease Inc., Minneapolis, MN). Furthermore, a simple empirical model relating the rheological responses of the process to produced particles was determined using the regression tools in Design Expert 7.1; using the same model as in the viscosity study[1] allows as comparison of dispersion behaviour based on the two approaches to adjust matrix viscosity. The coefficients of C_1 and C_2 were obtained by regression for each matrix viscosity studied in order to gauge the relative impact of the variable on these two rheological responses. The empirical model is shown as,

$$d_{50} = C_1 \left(\frac{\Delta \eta}{\Delta t} \right) + C_2 (\lambda) \tag{2}$$

where d_{50} is normalized mean particle diameter calculated as follows:

$$d_{50} = \frac{D_{50} - \bar{X}_{D_{50}}}{\sigma_{D_{50}}} \tag{3}$$

where $\bar{X}_{D_{50}}$ is the arithmetic mean of D_{50} and $\sigma_{D_{50}}$ is the standard deviation.

RESULTS AND DISCUSSION

Viscosity of the neat polyester with respect to temperature

The results in this section are specifically to characterize the neat polyester at different temperatures prior to considering results from the extruder. Complex viscosity curves measured in the parallel plate rheometer are shown in Figure 2 for the temperatures of 110ºC, 100ºC and 90ºC. The neat polyester exhibited Newtonian-like behaviour with a power law index of 0.98. The Arrhenius activation energy of the neat polyester was calculated to be 42.9 kJ/mol. The nominal viscosity (found by parallel plate rheometer) for the range of shear rates tested were 640 Pa.s at 90ºC, 380 Pa.s at 100ºC and 251 Pa.s at 110 ºC; the online rheometer matched these measurements, making them the denominator values for the quoted *relative viscosity* data. These three values closely resembled those studied in the previous study using a viscosity modifier, which were 251 Pa.s (0% modifier), 374 Pa.s (9% modifier) and 624 Pa.s (27% modifier).[1] Obviously, differences in shear thinning behavior prevented the two approaches from matching exactly; however, being near Newtonian in nature suggested that the matrix viscosity was varying comparably in the dispersion zone for both studies.

Other properties of the polyester have been reported in previous studies[3] with the most significant thermal property relevant to this study being its glass transition temperature, which has been reported to be 59.6ºC.

Influence of temperature on the neutralization reaction

In SFEE, added NaOH is beneficial to the function of all surface active species as well as to the conversion of carboxylic acid end groups *in situ* into carboxylates to reduce the necessary content of surfactant in the process; the reaction occurs over a short distance in the process, ~12 L/D.[2] Figures 3(a) and (b) illustrate NR values of samples collected under Mode 2 operations corresponding to the three different barrel temperatures, measured for both methods of NaOH

addition (solids versus solution) and varied amounts of SDBS in the *short screw* configuration (i.e. minimized dilution zone).   The plots include NR values from the first study on the influence of matrix viscosity, i.e. Part I for comparison.[1]

The NR results are comparable to previous studies where NR lies in the 40-70% range (meaning that about half of all acid groups were converted to carboxylates).[1,2] Since the reaction is restricted to carboxylic acid sites that are in contact with water, the extent of conversion is generally limited for SFEE. However, the range of NR was sufficient to achieve the desired particle sizes sought in this work, as evident in later figures.

Without SDBS surfactant, the NR results show that the extent of endgroup conversion increased with increasing barrel temperature (i.e. decreasing matrix viscosity) by ~5% per 10 $^\circ$C increment for solution addition and by ~2% per 10 $^\circ$C increment for solid NaOH addition. In comparison, the results from the previous study[1] using the viscosity modifier (data included in Figure 3) did not find any change in the extent of endgroup conversion with changing matrix viscosity. This was an interesting finding since a reaction in the bulk phase would normally be considered to be rate-limited by diffusion but in these results, the reaction kinetics are showing a stronger dependency on temperature than the related changes in diffusion rate accompanying varied system viscosity. As has been typical of this SFEE system, NR was lower with solid NaOH addition compared to solution addition, due to the rate limiting step of NaOH dissolution for the former case.

With SDBS added, a similar increase in NR with temperature was observed in plot (b) though now NR values were significantly lower by NaOH solution addition than without the surfactant present in plot (a). The lower NR values in the solution case was related to increased chain degradation[15,16] generating more endgroups on account of greater water incorporation in

the presence of surfactant.[2] NR values for the case with NaOH solids still remained lower than the comparative solution case.

The reaction trend with temperature means that NR values in this study were always lower for the base case at 110°C and 251 Pa.s matching conditions in the viscosity study.[1] The lower concentration of surface active species at 90°C and 100°C for equivalent viscosities will be expected to increase particle size, especially for the case without SDBS added.

Influence of temperature on the transient rheological properties of the system

In the study of Greiner and Evans,[5] the authors observed a more rapid increase in solution conductivity with water addition occurred with more stable O/W emulsions comprised of smaller particles. Seemingly similar, inline rheological monitoring of SFEE has found a more rapid decline (i.e. more negative value for $\Delta\eta/\Delta t$) after the dispersion zone gives a O/W emulsion with greater stability and smaller particles.[2,3] As a result, this transient rheological response to water addition, along with the relative viscosity, has become an invaluable analysis tool for predicting emulsification performance in SFEE.

The trends for $\Delta\eta/\Delta t$ and λ with the variables of surfactant content and NaOH addition method appeared similar to those in the viscosity study[1] where the matrix viscosity was controlled with a viscosity modifier. The regression coefficients of Equation (3) are listed in Table 2 for the three matrix viscosities examined, varied based on system temperature or by concentration of a viscosity modifier; the model fit was sufficient in all cases with $R^2 > 0.90$. A higher fitted coefficient value for C_1 or C_2 in the table indicates that SFEE experienced greater difficulties in dispersing water into the polyester and subsequently producing smaller particles, at a given matrix viscosity. The model results for the viscosity modifier, where NR was unaffected

as viscosity changed, show that producing smaller particles was only difficult at 624 Pa.s; the coefficients indicate the resistance to produce small particles was approximately four times larger at the highest viscosity condition. This behaviour was inferred to be reflecting the impeded kinetics of incorporating water into the polyester melt with higher matrix viscosity for SFEE. Conversely, the model reflects significant differences were present within the dispersion zone when system temperature was adjusted instead. The coefficients were lowest (C_1= 0.002 and C_2=1.8) at 110 °C (matrix viscosity of 251 Pa.s) and matched those found using the viscosity modifier; the match in coefficients was expected since the trial conditions are identical for the two approaches to control matrix viscosity (i.e. 0% modifier, 110 °C barrel temperature). SFEE exhibits the least rheological resistance to producing small particles at this viscosity and temperature. Unlike the results with the viscosity modifier, the resistance to disperse water into the polyester melt increased very little with viscosity by changing system temperature and even appeared slightly more resistant at 100 °C compared to the lowest temperature. The appearance of a maxima suggests two competing phenomena are affecting particle size as system temperature increases, one of which was not witnessed by adding the viscosity modifier to control matrix viscosity.

Influence of temperature on the nominal size of polymer particles

Figure 4 illustrates the influence that viscosity had on emulsified particle size without and with SDBS for the long (standard) screw configuration, comparing the influence of system temperature versus viscosity modifier. Consistent with previous work,[1] particles were in the targeted size range with the use of SDBS while only micron-sized particles were collected when

the process was solely reliant upon the generated polymer carboxylate endgroups for improved interfacial association between the polyester and water.

Without SDBS added, Plot (a) shows particle size increased with viscosity regardless of NaOH addition method used; the trend was linear with the use of viscosity modifier yet it plateaued above 360 Pa.s as system temperature was varied. For the trend generated by viscosity modifier where NR was the same for all conditions, particle size was responding to the varying resin viscosity but in the case of system temperature, NR decreased as resin viscosity increased, meaning that a larger particle was expected at 624 Pa.s not one similar to the 360 Pa.s condition.

With SDBS added, Plot (b) shows a linear trend once again was present for increasing particle size with resin viscosity for the case with the viscosity modifier. The trend is consistent with Plot (a) in this case, though the particles were much smaller with the SDBS added.   In comparison, the trend exhibited by varying system temperature shows a maxima in D_{50} centered at 360 Pa.s (for 100ºC). This corresponds to the same maxima noted in the regression analysis. Though the maxima seems genuine, we are not convince the trends between Plot (a) and (b) are different; it seems more likely that the higher surface active content with SDBS was simply exaggerating a trend which was present in both plots for varying system tememprature.

Effect of temperature in the dilution zone

In order to relate the effects of system temperature being seen on particle size to the emulsification mechanism rather than possible downstream coalescence after phase inversion, the dilution zone needed to be perturbed while still held to the chosen system temperatures. The water (at both locations) was always added at a temperature well below the glass transition temperature of polyester (i.e. 59.6ºC by DSC) and at a constant temperature difference relative to

the polymer melt for similar cooling rate in the hopes to consistently solidify the melt droplets and retain their original size. However, the final temperature of the exiting O/W emulsion was always closer to 100ºC, which meant the polymer droplet remained molten and able to coalesce inside the extruder. Varying the dilution zone length by using the short screw versus the long screw under Mode 2 should increase the opportunity for coalescence in the latter case to affect particle size.

Results were exclusively obtained with the inclusion of SDBS and solid NaOH in the process. The plot of D_{50} with respect to dilution zone length in Figure 5 showed that a longer zone produced smaller particles and yet those produced at 100ºC were still larger than at the other two temperature. The temperatures of exiting emulsions were 98±3ºC, 87±2ºC, 83±1ºC for short screw, while 109±1ºC, 98±1 ºC and 91±2ºC for long screw configuration, respectively for system temperatures of 110ºC, 100ºC and 90ºC. The tendency for larger particles in the short screw though being ~10ºC cooler and hence higher in matrix viscosity, suggesting that their size was a function of the dispersion zone.

General discussion

The results above show that system temperature affects the emulsification mechanism in a manner that can not be solely attributed to viscous forces or NR. When resin viscosity increases without change in system temperature or NR, particle size linearly increases due to progressively diminished interfacial area generation for fixed input mechanical energy.[1] When system temperature increases, resin viscosity decreases and NR increases which implies an amplified linear trend should again be expected where smaller particles are created with increasing temperature, but that was not found. A maxima in particle size was seen instead with

varying system temperature and the results suggest that the non-linearity may become stronger with higher surfactant content. The high viscosity system of Greiner and Evans[5] that displayed spontaneous phase inversion, demonstrated larger particles as the system temperature increased. Certainly, the same phenomenon appears to contribute to particle generation in SFEE, explaining how particles can be smaller than expected at lower system temperatures and how a maxima might arise. The opposing effect is related to the dependency of the emulsification mechanism on osmotic pressure in the micelles present. The phenomena is related to increased disruption of structured water around the surfactant head and a decrease in the interfacial adsorption parameter of the system with increasing temperature.[17,18]   Ultimately, the effect did not have a strong impact on the final particle size, but optimization of particle size in SFEE should ideally not depend on system temperature due to conflicting contributions to the emulsification mechanism. However, the study has confirmed that SFEE responses similar to the study of Greiner and Evans,[5] supporting the belief that their osmotic driven emulsification model is an appropriate descriptor of SFEE as well.

CONCLUSION

System temperature was varied as a means to control the matrix viscosity of the process, with the ramifications of this approach examined for impact on the dispersion mechanism. In the previous study, using a viscosity modifier to control matrix viscosity, the results obtained indicate that particle size should decrease when matrix viscosity decreases. However, varying temperature affects other internal phenomena in addition to matrix viscosity, which was noted by maxima in particle sizes at 100ºC, in the middle of the tested temperature range. Viscosity decreased with increasing temperature, aided by increasing degradation and endgroup conversion

but declining adsorption of surfactant at the interface. The negative effect of temperature on particle size is related to the osmotically driven emulsification model for high viscosity systems proposed by Greiner and Evans. Overall, the effects of system temperature are complicated and it should be considered a less desirable parameter for varying to control the matrix viscosity in a SFEE process.

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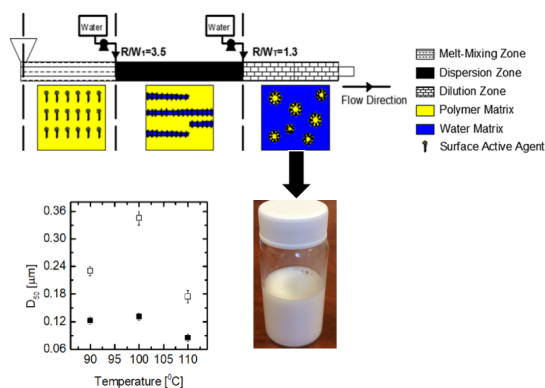
Abstract Graphic

FIGURE CAPTIONS

Figure 1. Conceptual layouts of the different extruder set-ups used in this study. a: Set-Up 1 (Short Screw), b: Set-Up 2 (Long Screw), c: Conceptual drawing of the screw design.

Figure 2. Viscosity curves for the different temperatures. Polyester samples measured at ■ 110ºC, ● 100ºC, and ▲90ºC for this study compared to samples containing a crosslinked polyester modifier (PM) as concentrations of ○ 9wt% PM, △ 27 wt% PM measured as 110ºC used in the previous viscosity modifier study)

Figure 3. Neutralization ratios (NR) for different viscosities using the short screw. Plot (a) for samples without SDBS versus plot (b) for samples with SDBS. (■ NR for Solution NaOH based on temperature change, ● NR of Solid NaOH based on temperature change, □ NR of Solution NaOH used in reference 1, ○ NR of Solid NaOH used in reference 1)

Figure 4. Influence of barrel temperature on the mean particle diameter (D_{50}) for the long screw. Plot (a) for samples without surfactant and plot (b) for samples with surfactant. (■ D_{50} for Solution NaOH based on temperature change, ● D_{50} of Solid NaOH based on temperature change, □ D_{50} of Solution NaOH used in reference 1, ○ D_{50} of Solid NaOH used in reference 1)

Figure 5. Effect of dilution zone length in SFEE on the mean particle diameter (D_{50}) exclusively for conditions including surfactant and solid NaOH by comparing short and long screw. (△ 110ºC, ⬤ 100ºC, □ 90ºC)
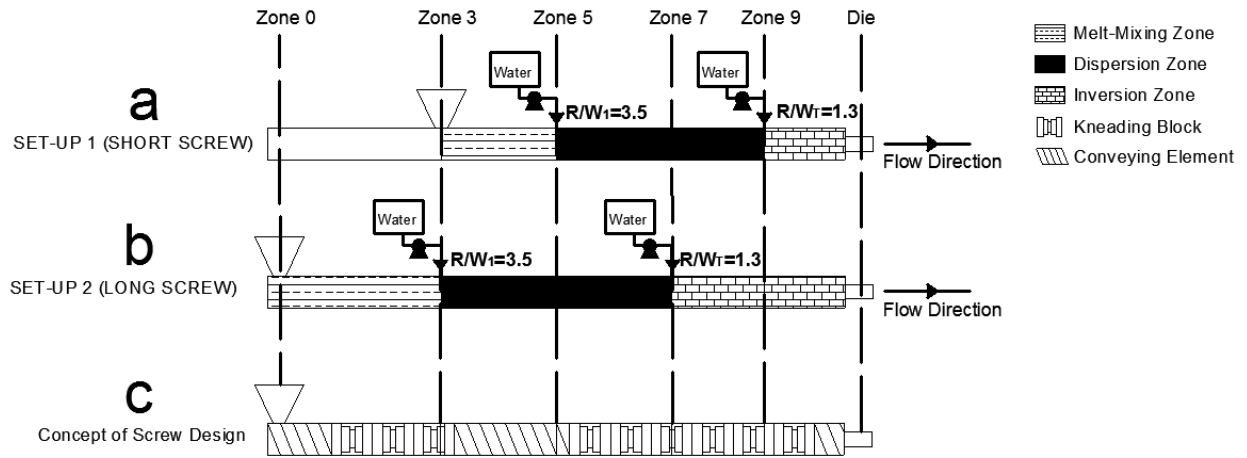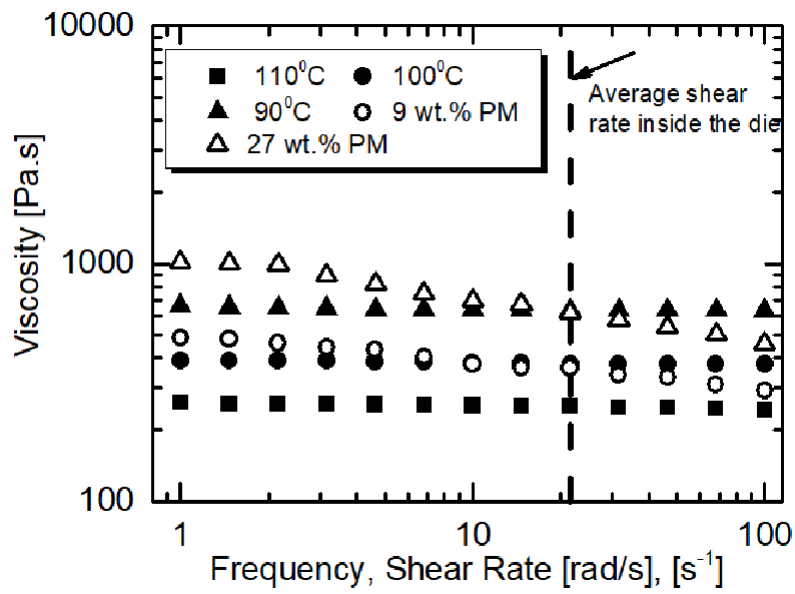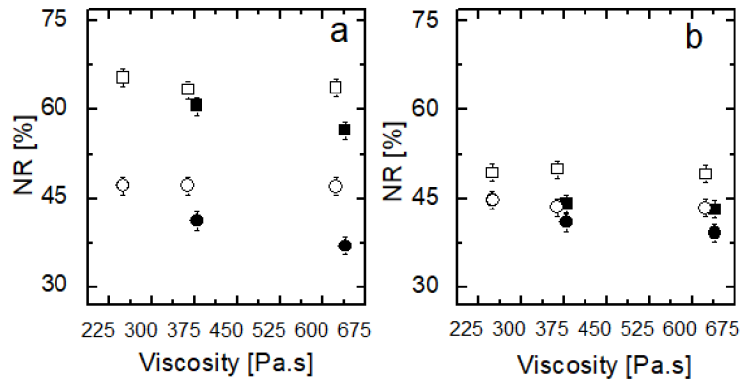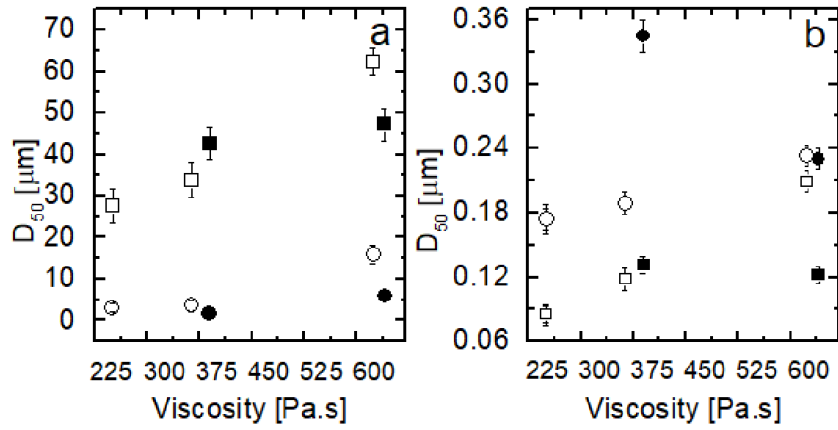
FIGURES

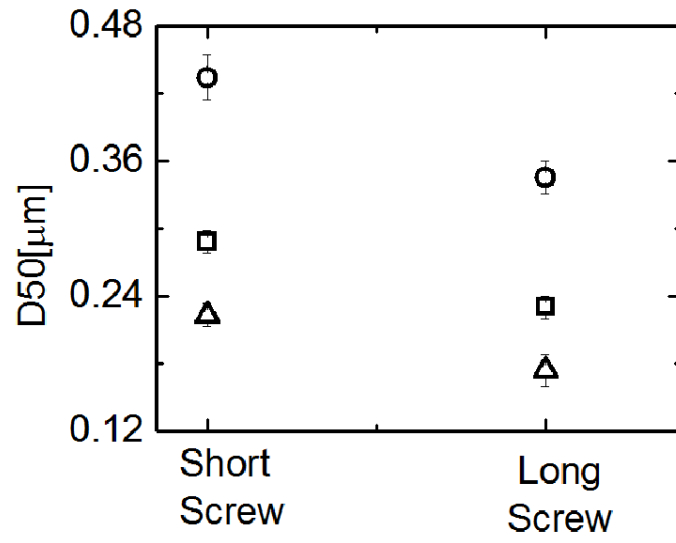
Figure 1

Figure 2

Figure 3.

Figure 4

Figure 5

TABLES

Table 1 Barrel, melt and water temperature for different operating conditions

Barrel Temperature	Melt Temperature	Inlet Water Temperature
[ºC]	[ºC]	[ºC]
110	124±0.4	34
100	117±0.6	27
90	111±0.4	21

Table 2 Coefficients of regression analysis for different matrix viscosities.

Matrix Viscosity (Pa.s)	Viscosity Modifier*		Barrel Temperature	
	C_1 [-]	C_2 [-]	C_1 [-]	C_2 [-]
251	0.002	1.8	0.002	1.8
375	0.002	1.8	0.004	2.7
625	0.012	9.5	0.003	2.2

* data reproduced from Ref [1].