A Simple Derivation of the Critical Condition for the Ultrasonic Atomization of Polymer Solutions

Hyungsu Kim* and Jaegeun Lee

Department of Chemical Engineering, Dankook University, Yongin-si, Gyunggi-do, 448-701, Korea

You-Yeon Won

School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907, USA

Keywords: Ultrasonic atomization; Micro droplets; Polymer solution; Acoustic pressure; Surface tension

* Corresponding author. Tel +82 31 8005 3537

E-mail addresses: hkim@dku.edu (H. Kim), jkleee8813@naver.com (J. Lee), yywon@ecn.purdue.edu (Y.Y. Won)

ABSTRACT: A simple model is proposed for the ultrasonic atomization of polymer solutions. In this model, the atomization process is approximated as an equilibrium process. It is shown that the minimum attainable droplet size is determined by two parameters, the (Rayleigh) acoustic pressure acting on the surface of the liquid, and the surface tension of the liquid. Increasing the viscosity of the liquid suppresses the formation of small-sized droplets because of increased attenuation of the sound wave and thus decreased acoustic pressure. Lowering the surface

tension of the liquid (e.g., by spreading a surfactant film on the liquid surface) has the opposite effect of enhancing the formation of smaller droplets. Also, there exists a maximum limit for the droplet size, because when the produced droplet is too large, the aspiration flow is unable to carry the droplet against sedimentation. These predictions are supported by experimental observations.

1. Introduction

Ultrasonic atomization (or spray) is a versatile technique for producing liquid micro droplets for various uses, particularly for particulate drug formulations [1,2]. The ultrasonic spray method is also recognized as a powerful tool to prepare nanostructured materials [3]. The problem of estimating acoustic radiation pressures at free liquid surfaces has been a subject of theoretical study for some 50 years [4-8]. Many empirical studies have been reported on how process conditions (such as excitation frequency and amplitude, and liquid flow rate and geometry) and liquid properties (e.g., viscosity, surface tension) impact the numbers and sizes of droplets produced for processes involving continuous flows of liquids [9-14]. Recently, our laboratory has demonstrated a very simple batch-type ultrasonic atomization process in which liquid droplets produced are collected using a bench-top aspirator [15,16]. Using this procedure, we were able to produce micron-scale particles of a variety of polymeric materials (such as poly(vinyl alcohol), poly(ethylene oxide), poly(vinyl pyrrolidone), and their composites with carbon nanotubes). In these previous studies, we showed that the number and size of ultrasonically generated drops are governed by two dimensionless parameters: the so-called Ohnesorge number, $Oh (\equiv \eta_o / (\rho R \gamma)^{1/2})$ where η_o is the zero-shear-rate viscosity of the liquid, ρ

is the density of the liquid, γ is the surface tension of the liquid, and R is the radius of the capillary formed by extension), and the Deborah number, De ($\equiv \lambda/t_R$ where λ is the relaxation time of the liquid, and t_R is the Rayleigh time ($\equiv \rho R^3/\gamma$)^{1/2}). When $De > 1$ (i.e., when capillary wave breakup is delayed by a long relaxation time relative to the Rayleigh time scale), larger droplets were observed; the elongated stream of liquid breaks up into droplets due to the surface tension-driven Rayleigh instability. The droplet number drops rapidly with increasing Oh (i.e., as the viscous effect becomes dominant), and eventually the process fails to produce any droplets when Oh exceeds a certain value. These observations confirm the current understanding of the ultrasonic atomization mechanism. In this paper, we propose an alternative (and much more simplistic) way of understanding the key aspects of the process. We are not aware of any similar previous attempts in the literature.

2. Theoretical Models

We propose a simple theoretical model that can be used to rationalize the sizes of ultrasonically atomized liquid droplets. A detailed analysis of this problem would require the use of interfacial fluid mechanical approaches and simulations [5-7]. However, in the present work, we will only use a simple thermodynamic argument. Referring to the situation described in Fig. 1, let us specifically consider a droplet of radius R formed from a liquid under acoustic pressure. We define the liquid in the droplet as the control volume. The Gibbs free energy change associated with transferring the liquid in the control volume from the bulk state to the droplet form (ΔG_{drop}) can be expressed as

$$\begin{aligned}\Delta G_{drop} &= G_{drop}^l(T, P) - G_{bulk}^l(T, P_{aco}) \\ &= [G_{bulk}^l(T, P) + 4\pi R^2\gamma] - G_{bulk}^l(T, P_{aco})\end{aligned}\quad (1)$$

Here we assume that the atomization process occurs at a constant temperature (T), and the acoustic stress at the air-water interface (P_{aco}) that causes the droplet to form immediately relaxes to a value, P ($< P_{aco}$), for the liquid inside the atomized droplet. Under the isothermal condition, the fundamental free energy equation becomes $dG (= VdP - SdT) = VdP$ (where V is the volume, and S is the entropy), and since a liquid is typically effectively incompressible, $\Delta G = V\Delta P$. Therefore, Eq. (1) can be rewritten as

$$\Delta G_{drop} = V_{drop}(P - P_{aco}) + 4\pi R^2\gamma = \frac{4}{3}\pi R^3(P - P_{aco}) + 4\pi R^2\gamma \quad (2)$$

where V_{drop} is the volume of the droplet. It is obvious that the first term on the right-hand side of the equation (i.e., the bulk term) favors the formation of the droplet, whereas the second term (the surface term) suppresses it. Also, the bulk term varies as R^3 , whereas the surface term varies as R^2 ; this means that at small R the surface term dominates, while for large R the opposite is true. Therefore, the acoustic stress would not be able to break up the liquid at the air-water interface into too small-sized droplets – smaller than a certain critical size; the surface tension imposes a minimum attainable droplet size. We would like to point out that Eq. (2) is analogous to the expression of the classical homogeneous nucleation theory for the free energy change of forming a liquid drop in surrounding vapor; the difference is that Eq. (2) concerns the detachment of a droplet from a body of liquid, whereas the classical nucleation theory describes the nucleation of a liquid phase from a supersaturated vapor; for this reason, the first terms of the

two free energy equations are different [17]. Similarly to the derivation of the Kelvin equation for homogeneous droplet nucleation [17], this critical minimum droplet radius (designated as R_{min}) can be calculated by differentiating Eq. (2) and equating to zero (i.e., $d\Delta G_{drop}/dR = 0$ at $R = R_{min}$). This procedure gives

$$R_{min} = \frac{2\gamma}{P_{aco} - P} \quad (3)$$

The equilibrium pressure of the liquid inside the droplet (P) is unknown. To an approximation, one can assume that the pressure inside the droplet is not much different from the vapor pressure of the liquid at the given temperature; that is, $P \cong P_{sat}(T)$. In reality, P is expected to be greater than $P_{sat}(T)$. Therefore, this assumption likely provides a minimum likelihood estimate for R_{min} .

We would like to note that in form Eq. (3) is identical to the Young-Laplace equation that relates pressure differences to curvature across a surface, $\Delta P = 2\gamma/R$ [17]. This analogy allows us to explain how ultrasonic surface disturbances give rise to atomization. When the acoustic wave reaches the liquid's surface, the acoustic pressure produces capillary waves [4,9]. If the sizes of the wave protrusions ($\sim R$) are large that the Laplace pressure ($2\gamma/R$) is less than the acoustic radiation pressure ($\Delta P \cong P_{aco} - P_{sat}(T)$), the wave peaks break off into droplets. Therefore, P_{aco} and γ primarily determine the sizes of the resulting droplets. Eq. (3) specifically explains how the parameters P_{aco} and γ affect the sizes of the droplets formed by ultrasonic atomization of a liquid; if one wants to reduce the sizes of the droplets, one would need to increase the acoustic stress transmitted to the surface of the liquid (e.g., by decreasing the viscosity of the liquid) or decrease the surface tension of the liquid (e.g., by coating the surface of the liquid with

surfactants). We performed experimental tests to qualitatively confirm these trends (discussed in 4. Comparison with Experiment).

We note that Eq. (3) predicts that R_{min} scales linearly to γ (given that P_{aco} is independent of γ). This prediction is different from the previously proposed relation, $R = 0.17(8\pi\gamma/\rho f^2)^{1/3}$ where ρ is the liquid density, and f is the frequency of the capillary waves on the liquid surface [9]. The exact scaling relationship between R and γ remains to be tested experimentally. It is also interesting to note that Eq. (3) shows how R depends on P_{aco} (the “amplitude” of the ultrasonic waves) and thus to the energy intensity (“loudness”) of the ultrasonic waves ($I \sim P_{aco}^2$), whereas the Robert Lang’s equation above defines R as a function of the frequency (“pitch”) of the waves.

We expect that there also exists a maximum limit for the size of the droplet (R_{max}). This upper limit is imposed by the fact that if the droplet is too large, the aspiration force applied to the droplet may not be sufficient to overcome the sedimentation force and pull the droplet towards the filter where the dried polymer particle will be collected. This R_{max} quantity can be evaluated by comparison of the downward sedimentation versus upward aspiration forces. The magnitude of the sedimentation force can be calculated as

$$F_{sed} = \frac{4\pi R^3}{3}(\rho_{drop} - \rho_{air})g \cong \frac{4\pi R^3}{3} \rho_{drop}g \quad (4)$$

where ρ_{drop} is the density of the liquid inside the droplet ($= 1,000 \text{ kg/m}^3$), ρ_{air} is the density of the surrounding air ($\approx 1 \text{ kg/m}^3$), and g is the gravitational acceleration ($= 9.8 \text{ m/s}^2$). The magnitude of the aspiration force can be calculated as

$$F_{asp} = f v_{vap} = (6\pi\eta_{air}R) \left(\frac{\dot{M}_{vap} v_{sat}^v}{A} \right) \quad (5)$$

where f is the viscous drag coefficient ($= 6\pi\eta_{air}R$ for a spherical droplet in air according to Stokes' law), v_{vap} is the water vapor flow velocity, η_{air} is the viscosity of the air ($= 1.827 \times 10^{-5}$ Pa·s), $\dot{M}_{vap}$ is the molar evaporation rate of water (experimentally estimated to be about 0.18 mol/s under a typical setting of aspiration environment), v_{sat}^v is the molar volume of saturated water vapor at the given temperature ($= 1.8 \times 10^{-5}$ m³/mol at room temperature), and A is the surface area of the liquid being aspirated ($= 3.14 \times 10^{-4}$ m²). For the aspiration process to work, F_{asp} should be greater than F_{sed} ; this condition is not met when the size of the droplet is too large. Therefore, the maximum aspiratable droplet radius (R_{max}) can be calculated by equating these two forces:

$$R_{max} = \left(\frac{9\eta_{air}\dot{M}_{vap}v_{sat}^v}{2\rho_{drop}gA} \right)^{1/2} \quad (6)$$

The actual value of R_{max} is estimated to be about 9.3 μm.

In experiment, the liquid droplets are dried during the aspiration process, and the polymer component is collected in the form of dried particles. Therefore, the size of a final polymer particle (R_p) is related to the initial size of its liquid droplet precursor (R) by

$$R_p = R \cdot \phi_p^{1/3} \quad (7)$$

where ϕ_p is the volume fraction of the polymer in the liquid solution phase; therefore, the

minimum and maximum attainable polymer particle sizes can be calculated, respectively, as

$R_{p,min} = R_{min} \cdot \phi_p^{1/3}$ and $R_{p,max} = R_{max} \cdot \phi_p^{1/3}$. Here we assume that dried polymer particles are non-

porous; PVA microspheres dried from water are known to be non-porous with densities close to their bulk values (≈ 0.5 g/cc) [18].

3. Experimental

3.1 Materials

The poly(vinyl alcohol) (PVA) was purchased from Sigma-Aldrich. This polymer has a weight-average molecular weight of 31,000 g/mol, and a hydrolysis content in the range of 87 – 89 % by mole. The PVA granules were dissolved in 1 dl of deionized water at 60°C for 4 hours.

The polyoxyethylene (20) oleyl ether (POE) surfactant was purchased from Sigma-Aldrich. 9 μ l of a 1 wt.% POE solution in chloroform was spread onto the surface of the liquid (i.e., the PVA/water solution), and the spreading solvent (chloroform) was allowed to evaporate for 5 minutes. A setup of the ultrasonic atomization has been reported elsewhere [15]. The frequency of the ultrasonic waves was set at 1.6 MHz, and the ultrasonic energy intensity (I) was 1.47 W/cm² at the transducer plate. Each atomization experiment was run for 5 minutes. The

temperature of the atomization system was controlled using a circulating water bath. Dried polymer particles were collected on a Teflon filter, and were further dried in a vacuum desiccator before analysis.

3.2 Measurements

Surface tension measurements were performed using the Wilhelmy plate method with a Nima 612D Langmuir trough. Measurements typically reached stable values within less than ± 0.1 mN/m fluctuations within about 20 minutes. Shear viscosities were measured using an Ostwald viscometer immersed in a constant-temperature (± 0.1 °C) water bath. Scanning electron microscopy (SEM) measurements were performed on gold-coated samples using a COXEM CX-200 system at an accelerating voltage of 20 kV.

3.3 Numerical simulation

The acoustic module of COMSOL Multiphysics (Version 4.3) was used to model the acoustic radiation pressure in the liquid exerted by a plane ultrasonic wave. Computations were performed with the actual dimensions of the setup using the “Viscous Fluid Model” option. The pressure boundary condition at the transducer surface was $P_{aco}(z = 0) = 1.80 \times 10^5$ Pa, which was calculated based on the equation, $I = P_{aco}^2 / (2\rho c)$ where I is the ultrasonic energy intensity, ρ is the density of the liquid ($= 1,000$ kg/m³), and c is the velocity of the sound in water ($= 1,480$ m/s) [19,20]. As demonstrated in Figure 3, there is negligible attenuation of the wave amplitude

over the length scale of the system. Therefore, during the atomization process, even though the liquid volume is continually decreasing, P_{aco} should be invariant over time, and so is R .

4. Comparison with Experiment

Previously, we have reported the ultrasonic atomization behavior of poly(vinyl alcohol) (PVA) solutions in water under varying concentrations of PVA [15,16]. Atomized PVA droplets are typically easily produced at low PVA concentrations (up to about 2 wt.%); for example, see Fig. 2 of Reference (15). At slightly higher PVA loadings, e.g., at 2.25 wt.% PVA, the droplet number sharply decreases, as demonstrated in Fig. 2(a). When the PVA concentration is further increased to 2.5 wt.%, no droplet is formed (Fig. 2(c)). As listed in Table 1, the viscosity of the PVA/water solution was measured to increase from 2.14 to 2.42 mPa·s, as the PVA concentration was increased from 2.25 to 2.5 wt.%. It is known that in polymer solutions, the sound wave becomes increasingly attenuated with increase of polymer concentration because of increased viscosity of the solution [21-23]. Therefore, it appears that at 2.5 wt.% PVA, the acoustic pressure at the surface of the liquid becomes insufficient to overcome the surface tension, and thus ultrasonic atomization does not work.

The situation becomes drastically changed when a surfactant, polyoxyethylene (20) oleyl ether (POE), is added to the liquid to a concentration of 1.5×10^{-4} wt.% (to reduce the surface tension of the liquid). In the presence of added POE, the number of polymer particles produced is increased by a factor of greater than 2 in the case of 2.25 wt.% PVA (Fig. 2(b)). The addition of POE even enables the production of polymer particles at the 2.5 wt.% PVA condition (Fig. 2(d)).

As summarized in Table 1, POE surfactant decreases the surface tension of the 2.25 wt.% PVA solution from 55.5 mN/m to 50.4 mN/m, and the surface tension of the 2.5 wt.% PVA solution from 54.2 mN/m to 50.0 mN/m, while it does not alter the viscosity of the solution. The experiment with the 2.25 wt.% PVA solution (with no added POE) was also repeated at two other temperatures, i.e., at 5 and 35 °C. The viscosity values of this solution were measured to be 2.91 and 1.41 mPa·s at 5 and 35 °C, respectively. The surface tension values were measured to be 56.4 and 54.7 mN/m at 5 and 35 °C, respectively. As shown in Fig. 2(e), when the atomization temperature is lowered from 18 to 5 °C, atomization is significantly inhibited due to the increase in both viscosity and surface tension. At the increased temperature of 35 °C, the lower viscosity and surface tension significantly enables the formation of droplets (Fig. 2(f)). Therefore, as discussed in relation to Eq. (2), the results presented in Fig. 2 clearly support that reducing the surface tension and the viscosity (through its influence on the acoustic pressure) facilitates droplet formation.

We attempted to estimate the values of the acoustic pressure at the surface of the liquid (P_{aco}) by numerical simulation as described above. Fig. 3 displays a sample result demonstrating an acoustic pressure distribution pattern in a 2.25 wt.% PVA solution in water. For convenience, we define P_{aco} as an average pressure over the region between the top surface and a depth of 3 mm below the surface. The resulting P_{aco} values are listed in Table 1. From this information and using Eqs. (3) and (7) (discussed in Theoretical Models), the smallest attainable polymer particle radii are estimated to be in the range of 0.17 - 0.21 μm for the atomization temperature and PVA concentration conditions examined; see Table 1 for values of other parameters used. For comparison with these predictions, the images presented in Figs. 2(a), 2(b), 2(d) and 2(f) were analyzed to obtain particle size histograms; the histogram results are presented in Fig. 4. The

theoretical values of the minimum and maximum attainable particle radii ($R_{p,min}$ and $R_{p,max}$, respectively) are also marked in the plots; the procedures for these calculations are described in 2. Theoretical Models. As can be seen from the figure, all measured size values fall within the predicted bounds. This agreement with experiment is quite encouraging, especially considering the approximate nature of the models, and thus suggests that the models correctly capture essential features of the ultrasonic atomization process.

5. Conclusion

A combined theoretical and experimental study supports that the process of ultrasonic atomization of a liquid is controlled by two opposing forces, i.e., the acoustic stress (that forces the liquid at the surface to form droplets) and the surface tension (that suppresses that process). Increasing the concentration of polymer in the liquid solution causes an increased attenuation of the sound wave, and thus suppresses the formation of droplets. Coating the liquid surface with a surfactant lowers the surface tension of the liquid, and thus enhances atomization.

Acknowledgements

This work was supported by the research fund of Dankook University in 2014. YYW acknowledges grants from US NSF (DMR-0906567, and CBET-1264336).

References

1. Y. Yeo, K. Park, A New Microencapsulation method using an ultrasonic atomizer based on interfacial solvent exchange, J. of Controlled Release 100 (2004) 379–388.

2. S. Freitas, H.P. Merkle, B. Gander, Ultrasonic atomisation into reduced pressure atmosphere-envisaging aseptic spray-drying for microencapsulation, *J. of Controlled Release* 95 (2004) 185-195.
3. J.H. Bang, Y.T. Didenko, R.J. Helmich, K.S. Suslick, Nanostructured materials through ultrasonic spray pyrolysis, *Material Matters* 7 (2012) 15-20.
4. R.L. Peskin, R.J. Raco, Ultrasonic atomization of liquids, *J. Acoust. Soc. Am.* 35 (1963) 1378-1381.
5. J.A. Rooney, W.L. Nyborg, Acoustic radiation pressure in a travelling plane-wave, *Am. J. Phys.* 40 (1972) 1825-1830.
6. B.T. Chu, R.E. Apfel, Acoustic radiation pressure produced by a beam of sound, *J. Acoust. Soc. Am.* 72 (1982) 1673-1687.
7. T. Hasegawa, T. Kido, T. Iizuka, C. Matsuoka, A general theory of Rayleigh and Langevin radiation pressures, *Acoustical Science and Technology* 21 (2000) 145-152.
8. D.J. Collins, O. Manor, A. Winkler, H. Schmidt, J.R. Friend, L.Y. Yeo, Atomization of thin water films generated by high-frequency substrate wave vibrations, *Phys. Rev. E.* 86 (2012) 056312.
9. R.J. Lang, Ultrasonic atomization of liquids, *J. Acoust. Soc. Am.* 34 (1962) 6-8.
10. R. Rajan, A.B. Pandit, Correlations to predict droplet size in ultrasonic atomization, *Ultrasonics* 39 (2001) 235-255.

11. B. Avvaru, M.N. Patil, P.R. Gogate, A.B. Pandit, Ultrasonic atomization: Effect of liquid phase properties, *Ultrasonics* 44 (2006) 146–158.
12. A.A. Barba, M. d'Amore, S. Cascone, G. Lamberti, G. Titomanlio, Intensification of biopolymeric microparticles production by ultrasonic assisted atomization, *Chem. Eng. Process* 48 (2009) 1475-1481.
13. A. Dalmoro, A.A. Barba, G. Lamberti, M. d'Amore, Intensifying the microencapsulation process: Ultrasonic atomization as an innovative approach, *Eur. J. Pharm. Biopharm.* 80 (2012) 471-477.
14. A. Dalmoro, A.A. Barba, M. d'Amore, Analysis of size correlations for microdroplets produced by ultrasonic atomization, *The Scientific World Journal* 2013 DOI 10.1155/482910.
15. Y. Kim, H. Kim, Effect of extensional properties of polymer solutions on the droplet formation via ultrasonic atomization, *Polym. Eng. Sci.* 51 (2011) 2446-2452.
16. T. Kim, H. Kim, Microdroplet formation of polyvinylpyrrolidone/carbon nanotube by ultrasonic atomization, *Macromol. Res.* 22 (2014) 990-995.
17. R.J. Stokes, D.F. Evans, *Fundamentals of Interfacial Engineering*, Wiley-VCH, New York, 1997.
18. G. Fundueanu, M. Constantin, P. Ascenzi, Poly(vinyl alcohol) microspheres with pH- and thermosensitive properties as temperature-controlled drug delivery, *Acta Biomaterialia* 6 (2010) 3899-3907.
19. T.J. Mason, J.P. Lorimer, *Applied Sonochemistry*, Wiley-VCH, Weinheim, 2002.

20. A.S. Dukhin, P.J. Goetz, Characterization of Liquids, Nano- and Microparticles, and Porous Bodies Using Ultrasound (2nd edition), Elsevier, Oxford, 2010.
21. P.K. Singh, S.C. Bhatt, Investigation of acoustical parameters of polyvinyl acetate, Appl. Phys. Res. 2 (2010) 35-45.
22. T. Norisuye, S. Sasa, K. Takeda, M. Kohyama, Q. Tran-Cong-Miyata, Simultaneous evaluation of ultrasound velocity, attenuation and density of polymer solutions observed by multi-echo ultrasound spectroscopy, Ultrasonics 51 (2011) 215-222.
23. P. Hauptmann, R. Säuberlich, S. Wartewig, Ultrasonic attenuation and mobility in polymer solutions and dispersions. Poly(vinyl alcohol) and poly(vinyl acetate), Polym. Bull. 8 (1982) 269-274.
24. P.K. Sahoo, R. Mohapatra, A. Sahoo, S.K. Swain, Ultrasonic and viscometric investigations of a poly(vinyl alcohol)-dextran mixture in aqueous solution, J. of Appl. Polym. Sci. 88 (2003) 3196-3201.
25. R.H. Perry, C.H. Chilton, Chemical Engineers' Handbook (5th edition), McGraw-Hill Kogakusha, LTD, 1973.

List of Figures

Fig. 1. Schematic illustration of the ultrasonic atomization setup used in this study. The dimensions of the main components are as follows: diameter of the vessel = 6 cm, height of the liquid volume = 2 cm, diameter of the ultrasonic transducer = 2 cm.

Fig. 2. SEM micrographs of dried polymer particles produced by ultrasonic atomization of aqueous solutions containing (a) 2.25 wt.% PVA and no added POE (atomized at 18 °C), (b) 2.25 wt.% POE with added POE (atomized at 18 °C), (c) 2.5 wt.% PVA and no added POE (atomized at 18 °C), (d) 2.5 wt.% with added POE (atomized at 18 °C), (e) 2.25 wt.% PVA and no added POE (atomized at 5 °C), and (f) 2.25 wt.% PVA and no added POE (atomized at 35 °C). Dried particles were collected on a Teflon filter. Images were taken at a magnification of $\times 5,000$. Scale bars indicate 10 μm .

Fig. 3. Acoustic pressure distribution in a 2.25 wt.% PVA/water solution along the centerline with distance from the ultrasound transducer.

Fig. 4. Particle size histograms from the SEM images in (a) Figure 2(a) (for 2.25 wt.% PVA with no added POE atomized at 18 °C), (b) Figure 2(b) (for 2.25 wt.% PVA with added POE atomized at 18 °C), (c) Figure 2(d) (for 2.5 wt.% PVA with added POE atomized at 18 °C), and (d) Figure 2(f) (for 2.25 wt.% PVA with no added POE atomized at 35 °C).

Figure 1

Figure 2ab

Figure 2cd

Figure 2ef

Figure 3

Figure 4ab

Figure 4cd

Table 1. Parameter values used for calculation of minimum attainable polymer particles sizes.

Temperature (°C)	PVA concentration (wt.%)	γ (mN/m)	γ (mN/m)*	η (mPa·s)	η (mPa·s)*	P_{aco} # (10 ⁵ Pa)	$R_{p,min}$ (μ m) [†]
5	2.25	56.4	-	2.91	-	1.53	0.20
18	2.25	55.5	50.4	2.14	2.15	1.68	0.17
35	2.25	54.7	-	1.41	-	1.68	0.19
18	2.50	54.2	50.0	2.42	2.43	1.43	0.21

* In the presence of added 1.5×10^{-4} wt.% POE surfactant.

The sound velocities of 2.25% PVA solutions were assumed to be 1450 m/s at 5 °C, 1500 m/s at 18 °C, and 1550 m/s at 35 °C. The sound velocity of 2.5% PVA solution was assumed to be 1515 m/s [24].

† The P_{sat} values used were 866.6 Pa at 5 °C, 2064.67 Pa at 18 °C, and 5626.2 Pa at 35 °C [25]. For pure water, R_{min} is estimated to be 1.27 μ m; the water surface tension (γ) is 72 mN/m for water at room temperature, and the acoustic pressure at the surface of pure water (P_{aco}) is estimated by simulation to be approximately 1.72×10^5 Pa.