



## Does power ultrasound affect Nafion® dispersions?

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### ABSTRACT

The effect of low frequency power ultrasound on Nafion® ionomer used for fabricating proton exchange membrane fuel cell (PEMFC) and water electrolyzer (PEMWE) catalyst inks was investigated. In this study, a series of Nafion® dispersions having three concentrations (10, 5, and 2.5% w/v) were studied under various irradiation durations ( $t_{\text{us}}$ ), at fixed ultrasonic frequency ( $f = 42$  kHz) and ultrasonic power ( $P > 2$  W), under either controlled or unregulated bulk solution temperature conditions using a laboratory ultrasonic cleaning bath. Viscosity ( $\eta$ ), thermal degradation, and glass transition temperature ( $T_g$ ) for all Nafion® dispersion samples was measured and compared to untreated Nafion® samples. In our conditions, it was found that power ultrasound lowered the viscosity of all tested Nafion® dispersion samples; whilst thermogravimetric and differential scanning calorimetry analyses showed that for all ultrasonically irradiated samples, a negligible overall polymer degradation and no obvious change in  $T_g$  was observed under controlled and unregulated bulk temperature conditions. It was found that it is possible that acoustic cavitation causes depolymerisation followed by a polymerisation initiation step during ultrasonication. By comparing the ultrasonically treated and high-shear mixed samples, it was also observed that acoustic and hydrodynamic cavitation played an important role in the reduction of dispersion viscosity.

### 1. Introduction

Literature searches indicate that in the case of proton exchange membrane fuel cell (PEMFC) and water electrolyzer (PEMWE) catalyst ink formulation (Platinum Group Metal (PGM)/Carbon Black (CB) + Nafion® ionomer + solvent + water) preparations, ultrasonication (in the form of a laboratory ultrasonic cleaning bath) is commonly used for efficient homogenisation and dispersion of the inks prior to fuel cell and electrolyser electrode fabrication (as either GDE – Gas Diffusion Electrode or CCM – Catalyst Coated Membrane). However, in many studies in the hydrogen fuel cell community, researchers often do not report on the following important experimental set up and parameters, such as (i) the ultrasonic source type and make, ultrasonic frequency ( $f$ ), power ( $P$ ), intensity ( $\Psi$ ) and irradiation time ( $t_{\text{us}}$ ); and, (ii) the bulk solution temperature ( $T$ , which is often not controlled nor regulated during the ultrasonic experiment) [1]. In the area of *sonochemistry* (the use of ultrasound in chemistry), it is well-known that low frequency high power ultrasound yields rapid temperature increases with  $\Delta T$ 's of up to  $\sim +50$  °C in short exposure times ( $> 1$  min) starting from room temperature and causes cavitation within the

solution [2–4]. In some cases where ultrasonic irradiation time is stated, experiments can vary from a few minutes to a few hours (and even days) [1–4]. In 2014, Pollet demonstrated that a careful and systematic approach should be adopted when ultrasonically fuel cell and electrolyser catalyst inks, due to the fact that low frequency high intensity ultrasound is known to affect solution properties due to cavitation [1,2]. Recently, the National Renewable Energy Laboratory (NREL) and the Argonne National Laboratory (ANL) in the US confirmed, in a detailed and systematic joined study [5], the early findings from Pollet [1,2] i.e. that extended ultrasonication affects the catalyst ink activity and care should be taken when using ultrasound as a dispersing method.

Cavitation phenomenon is well known to cause erosion, emulsification, molecular degradation, sonoluminescence and sonochemical enhancements of reactivity solely attributed to the collapse of cavitation bubbles and efficient and vigorous stirring [3,4]. It is also well accepted in the field that power ultrasound can be employed to polymerize monomers depending upon the experimental conditions used, such as in free radical-based polymerizations [3,4,6]. This is likely due to the well documented formation of radicals induced by sonolysis

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[3,6–9]. For instance, it was reported that organic initiators were unnecessary in the emulsion polymerisation of systems such as styrene in the presence of power ultrasound [3,4,6].

However, it has also been demonstrated in numerous studies that power ultrasound can greatly enhance the decomposition and degradation of some polymers [10–15]. Power ultrasound is now regarded as a powerful method for the depolymerisation of macromolecules, usually observed in the reduction of the polymers' molecular weights (MW), mainly caused by acoustic cavitation [12]. This effect depends upon the solvent employed, as various mixtures are known to cavitate with different solvents used [16]. It has also been observed that in the presence of power ultrasound, the degradation of polymers (i) increases with decreasing ultrasonic frequency ( $f$ ), due to the lower frequency providing a longer time for bubble growth and then collapse; (ii) decreases in the presence of a volatile solvent, attributed to a lower cavitation pressure due to an increase in vapour pressure; and (iii) increases in de-aerated solutions, caused by stronger cavitation due to a higher acoustic amplitude in liquids containing fewer air bubbles. In all these investigations, long-time ultrasonic irradiation of the polymer yielded a permanent reduction in solution viscosity, which was in most cases irreversible [10–15].

Viscosity measurements are often used in characterizing changes in polymeric solutions following power ultrasound irradiation [10–13]. In the case of Nafion<sup>®</sup>, it was shown (preliminary studies only) that its ultrasonication over various irradiation durations revealed a decrease in dispersion viscosity [1,2,14]. However, it was observed that at a minimum ultrasonic irradiation time ( $t_{us}$ ) and at a fixed ultrasonic frequency ( $f$ ), an increase in Nafion<sup>®</sup> polymer viscosity was also observed [14]. This observation was mainly attributed to the fact that depolymerisation caused by ultrasound supplies new chain carriers for polymerisation. In other words, under carefully chosen conditions, power ultrasound may initiate polymerisation as previously observed in other studies using various polymers [3,4,6–9].

In this study, the effects of power ultrasound of varied  $t_{us}$  but fixed  $f$  and  $P$  on Nafion<sup>®</sup> dispersions were investigated. Three different concentrations of Nafion<sup>®</sup> dispersion were prepared and treated under power ultrasonic irradiation, at either controlled or unregulated bulk solution temperatures. Shear viscosities, thermal degradation profiles, and glass transition temperatures ( $T_g$ ) of each polymer dispersion, or corresponding dry powders, were then assessed and compared to untreated reference samples. Nafion<sup>®</sup> dispersions were also subjected to high shear mixing at varied rotation speeds ( $\omega$ ), and the resulting effects were compared to those observed from power ultrasound treatments.

## 2. Experimental methods

A Nafion<sup>®</sup> D2020 dispersion (alcohol based 1000 equivalent weight dispersion at 20 wt%, purchased from Ion Power, Inc., LOT# LGE-13-02CS) was used to prepare various concentrations (10, 5, and 2.5% w/v) of Nafion<sup>®</sup> in 3:1 H<sub>2</sub>O:isopropyl alcohol (IPA) stock dispersions. They were labelled as D1020, D520, and D320, respectively. This nomenclature was used all throughout the experiments conducted. Each stock dispersion was partitioned into  $27.0 \pm 0.5$  mL samples held in 30 mL, 9 cm tall VWR<sup>®</sup> glass vials (short form style with phenolic cap), which were then subjected to individual ultrasonic, high shear stirring, and thermal treatments, or set aside as reference samples, as per Table 1. All measurements were performed a minimum of 3 times, and errors are reported as the standard deviation (SD) of minimum 3 data points. An independent  $t$ -test was used to assess the measured viscosity values relative to corresponding reference samples, from which were determined  $p$  values [17], as per the Supporting Information. Herein, a  $p$  value of  $< 0.05$  signifies a statistically significant difference, to a 95% confidence interval.

Samples (in the glass vials) were subjected to ultrasonication via immersion in a 42 kHz, 70 W output power Bransonic B1510R-MT

**Table 1**  
Ultrasonic and stirring treatments performed for Nafion<sup>®</sup> dispersions.

Treatment	Duration (t)	Temperature (T)	Stirring ( $\omega$ )
None (Control)	N/A	20 $\pm$ 1 °C	200 RPM <sup>a</sup>
None (Control)	N/A	25 $\pm$ 2 °C	200 RPM <sup>a</sup>
Ultrasound (US)	5 min	25 $\pm$ 2 °C	200 RPM <sup>a</sup>
	10 min		
	20 min		
	30 min		
	60 min		
Ultrasound Without Temperature Control (USWTC)	5 min	18–20 °C	200 RPM <sup>a</sup>
	10 min	18–21 °C	
	20 min	18–22 °C	
	30 min	18–24 °C	
	60 min	18–28 °C	
Rapid Stirring	24 h	20 $\pm$ 1 °C	1,000 RPM
High Shear Mixing <sup>b</sup>	0 min	20 $\pm$ 1 °C	5,000 & 10,000 RPM
	5 min	20 $\pm$ 1 °C	5,000 & 10,000 RPM
	10 min	20 $\pm$ 1 °C	5,000 & 10,000 RPM
	30 min	20 $\pm$ 1 °C	5,000 & 10,000 RPM
	60 min	20 $\pm$ 1 °C	5,000 & 10,000 RPM

<sup>a</sup> Stirring was during initial sample preparation.

<sup>b</sup> Only performed with Nafion D520 dispersions.

Ultrasonic Cleaner sonicating bath, immersed approximately 7 cm deep, for 0, 5, 10, 20, 30, or 60-minute durations. The ultrasonic bath was either held at a constant temperature (25  $\pm$  2 °C) or left unmoderated – starting from 18 °C and allowed to heat up as result of input ultrasonic energy. Sample solution rheologies were then assessed. Inherent viscosities were calculated from the rheology data according to the methodology outlined in the Supporting Information, using Eqs. S1 and S2. The dispersions were then evaporated to extract pure Nafion<sup>®</sup> powders, as described in the Supporting Information. The polymer samples were characterized for their glass transition temperatures ( $T_g$ ) via differential scanning calorimetry (DSC), and thermal degradation profiles via thermogravimetric analyses (TGA), as detailed in the Supporting Information. The ultrasonic power was determined calorimetrically and was found to be  $2.1 \pm 0.2$  W [2,15,18].

Rapid stirring treatments and high shear mixing treatments were performed using Nafion<sup>®</sup> D520 samples, after which solution rheologies were immediately assessed. Rapid stirring was achieved using an IKA RCT Basic magnetic stirring plate and Teflon-coated stirring bar set to 1,000 RPM. High shear mixing was achieved using a Silverson L4RT High Shear Mixer set to 5,000 or 10,000 RPM for 0, 5, 10, 30 or 60-minute durations.

## 3. Results and discussion

Cavitation phenomenon in the ultrasonic bath was initially qualitatively assessed by the ‘aluminum foil method’ [19]. Two 30 mL VWR<sup>®</sup> glass vials were filled with approximately 27 mL of pure 3:1 H<sub>2</sub>O:IPA, or Nafion<sup>®</sup> D2020 dispersion, and into each was placed a 1 cm  $\times$  8 cm strip of aluminum foil and covered with a phenolic cap. Both samples were immersed into the ultrasonication bath and subjected to 30 s of sonication at 42 kHz (Fig. 1a&b). While the former exhibited noticeable surface damages (e.g. pinholes, Fig. 1c) as a result of acoustic cavitation [9,20,21], the latter sample showed significantly reduced effects of this nature (Fig. 1d), suggesting that the Nafion<sup>®</sup> dispersion dampened, or even absorbed, the input energy from the ultrasonic bath. It is worth noting that IPA yields lower cavitation events than water (approx. 38%) [16]. Hence, the addition of IPA to a water-based polymeric dispersion may reduce the effects of ultrasonic cavitation.

Each Nafion<sup>®</sup> dispersion was subjected to a series of ultrasonic

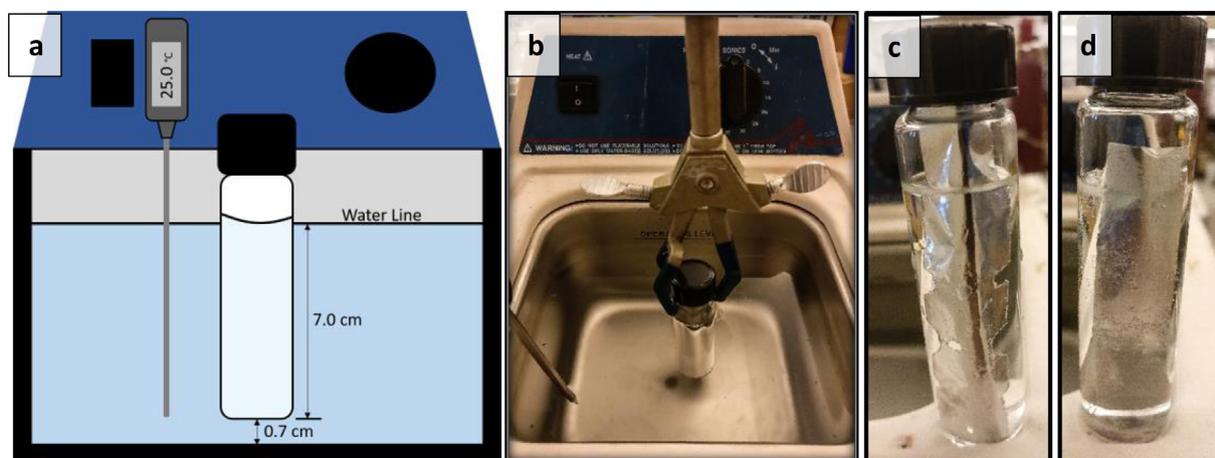


Fig. 1. (a) Ultrasonicating bath experimental setup diagram; (b) Image of the ultrasonicating bath, and damage to the aluminum foil strips immersed in (c) 3:1 H<sub>2</sub>O:IPA and (d) Nafion® D2020 dispersion caused by acoustic cavitation following 30 s of sonication.

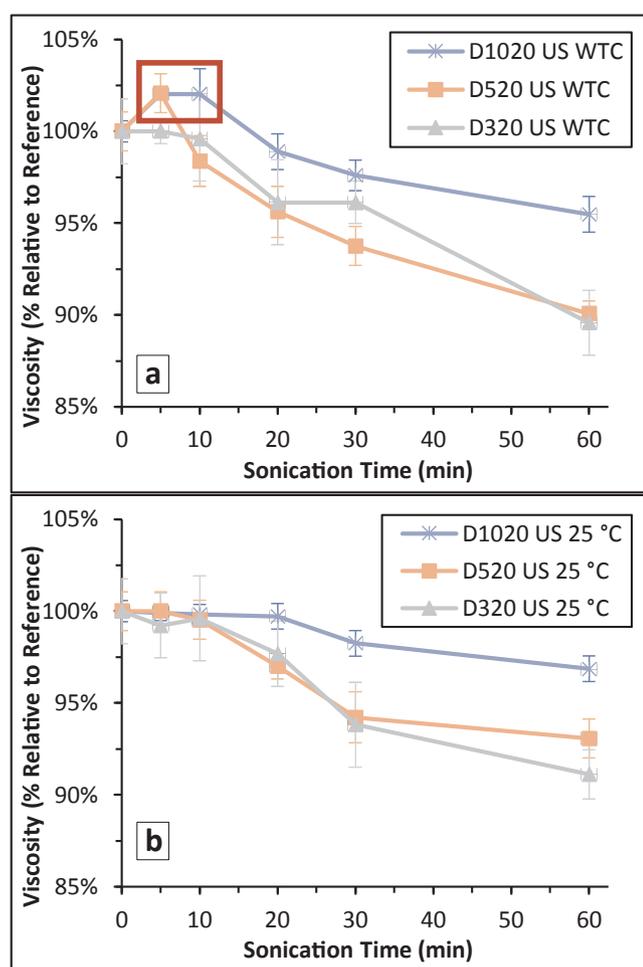


Fig. 2. Average solution shear viscosities normalized to respective reference shear viscosities for Nafion® dispersions following US experiments (a) without temperature control, and (b) at a fixed temperature (25 °C).

treatments in which the ultrasonicating bath temperature was thermally regulated to  $25 \pm 2$  °C, after which sample rheologies were assessed. All the characterized dispersions showed similar trends in their rheological profiles (see Tables S1–S6). Ultrasonication for as little as 20 min caused slight decreases in solution shear viscosity (e.g.,  $3.0 \pm 0.4\%$  for D520 dispersions ( $p = 0.007$ ), see Fig. 2b). Increasing ultrasonication time resulted in further decreased solution shear

viscosities, as high as  $8.9\% \pm 0.6\%$  after 60 min ( $p = 0.001$ ). The highest concentration samples, D1020, showed the smallest decreases in solution shear viscosity with additional time under insonation, possibly suggesting that higher concentrations of Nafion® may be less affected by power ultrasound at an ultrasonic frequency of 42 kHz and ultrasonic power of  $\sim 2$  W.

A second series of ultrasonic experiments were then performed in the absence of thermal regulation (as per Table 1). In this way, the combined effects of ultrasonication and slowly ramping bulk solution temperatures could be assessed (Fig. 2a – see also Tables S7–S12 and Figs. S3 and S4) and compared to temperature-controlled ultrasonication (Fig. 2b). Moreover, the catalyst ink dispersions performed in laboratory ultrasonic bath in which, in most cases, temperature is unregulated. The data generated for both Nafion® D520 and D320 dispersions showed similar trends to those described above, although more drastic decreases in solution shear viscosity were observed in the case of dispersions subject to ultrasound without temperature control (USWTC).

After 60 min of ultrasonication at 25 °C, the D520 solution shear viscosities fell  $6.9\% \pm 0.1\%$  ( $p = 0.001$ ), whereas under the same treatment duration without thermal regulation resulted in a  $\sim 44\%$  greater decrease ( $9.9 \pm 0.3\%$ ,  $p < 0.001$ ). The most drastic changes were observed in the lower concentration samples D520 and D320. These effects may be partially due to the lower initial temperature (18 °C) of the unregulated US experiments, because cavitation events in colder liquids is greater due to reduced saturated vapour pressures [22]. When subjected to 5 and 10 min USWTC treatments, the highest concentration D1020 samples, however, yielded polymer dispersions with statistically significant increases in shear viscosities –  $2.0\% \pm 0.3\%$  ( $p = 0.003$ ) and  $2.0\% \pm 0.8\%$  ( $p = 0.039$ ), respectively – after which they decreased stepwise with increasing ultrasonication time as observed in the case for all other samples. A similar increase was also observed in the case of D520 following 5 min of USWTC treatment:  $2.1\% \pm 0.0\%$  ( $p = 0.037$ ). The observed increases could be due to free radical formation induced by water sonolysis ( $\text{OH}\cdot$ ,  $\text{H}\cdot$ , etc) [20,21,23] leading to the formation of reactive polymer fragment radicals [9]. If sufficiently concentrated (e.g. D1020), these reactive species could cause radical coupling between polymer strands in solution [9,24,25], causing re-polymerization or cross-linking events to occur [24,25], consequently impacting (e.g. raising) polymer solution shear viscosities. The inherent viscosities ( $\eta_{\text{inherent}}$ ) of each aforementioned sample relative to their respective reference samples showed similar trends (Fig. S4). Individual shear viscosity plots of each dispersion following respective treatments can be found in the Supporting Information (Fig. S5a–f).

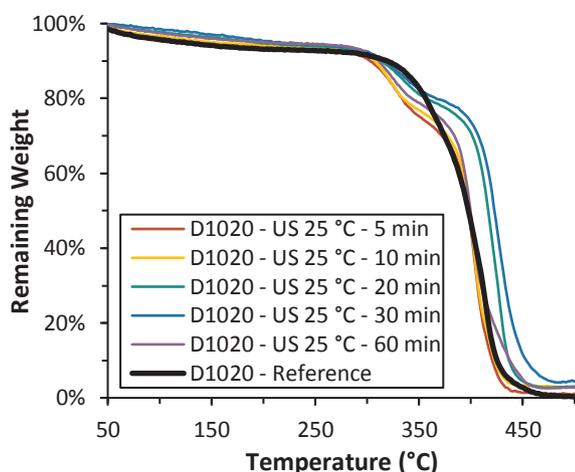


Fig. 3. Thermal degradation profiles for Nafion D1020 dispersions following temperature-controlled ultrasound experiments.

Thermogravimetric analyses of all samples treated with ultrasound at 25 °C showed similar thermal degradation profiles (Figs. 3 and S9a,b). In the case of each reference sample, two thermally-induced mass loss events were observed: a loss of ~6% between 50 and 200 °C, which is typically attributed to dehydration of adsorbed water within the acid-bearing polymers [26–28], and loss of the entirety of the remaining sample mass at  $\geq 300$  °C, corresponding to gradual total sample decomposition [26,28]. Treated samples showed negligible differences in overall degradation temperature ranges, and there appeared to be no general trends in the data. In the case of the highest concentration dispersion, D1020, ultrasonication may have increased the onset temperature of backbone degradation in some of the samples assessed, by up to 80 °C (e.g., Fig. 3, 20 and 30 min). However, one distinct difference between the reference and treated samples was observed throughout: following ultrasonication, a third mass loss event of  $19.6 \pm 0.3\%$  between 300 and 400 °C was observed (outlined in Fig. S8). This mass loss is indicative of an event unique to treated samples, and may correspond to more defined cleavage of acidic side chains about the chemically-labile ether linkage [26,28] (Fig. 4), which may be caused by reorganization of the polymer strands within the dispersions due to ultrasound. Perfluorosulfonic acid polymers of this EW range, such as Nafion® 117 membranes (1100 EW), have been shown to retain approximately 3-H<sub>2</sub>O molecules per sulfonic acid group at 31% relative humidity (RH) [29], which reflects the ambient conditions under which polymer samples were evaluated ( $30 \pm 0.5\%$  RH).

The theoretical mass loss of 3 molecules of H<sub>2</sub>O per repeat unit, and cleavage of the acidic side chain at the aforementioned ether linkage, respectively, are 5.2 and 19.8%. These values are in good agreement with the data collected, as well as those previously published [28].

Similarly to the case of samples treated at 25 °C, all USWTC samples displayed formation of a third, distinct mass loss event between 300 and 400 °C of  $19.6 \pm 0.3\%$  (Fig. 5 and S10a,b). One key difference, however, was a notable upward shift in the decomposition temperature

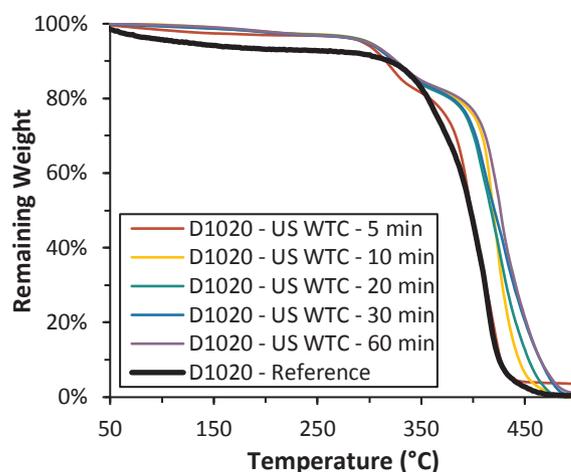


Fig. 5. Thermal degradation profiles for Nafion® D1020 dispersions following ultrasonic experiments without temperature control.

of the polymer backbone in these samples. Whilst the untreated reference samples began a gradual decomposition at  $\geq 300$  °C with a peak mass loss rate at ca. 400 °C, D1020, D520, and D320 samples began their respective gradual decompositions at ca. 400, 385, and 375 °C, with peak mass loss rates between 420 and 430 °C.

Differential scanning calorimetry (DSC) was used to determine sample glass transition temperature ( $T_g$ ) relative to each respective sample reference. Polymer  $T_g$  is often linked to the overall degree of molecular order within a given sample [30,31], and when assessed under identical parameters, comparisons between sample morphologies and microstructures may be drawn [31,32]. Hence, deviations in this metric may be indicative of structural changes occurring as result of sample degradation following ultrasonic treatments. However, under our experimental conditions, there appeared to be no significant differences or distinguishable trends in sample  $T_g$  following ultrasonication treatments at either 25 °C (Fig. S7a) or without temperature control (Fig. S7b); although slight deviations outside the experimental error window were noted. Moreover, it was found that the concentration of Nafion® dispersions when treated with power ultrasound appeared to have no impact on the measured  $T_g$ .

In order to separate the effects of acoustic cavitation and intense mixing induced by ultrasonication, the effects of high shear mixing (under *silent* conditions i.e. in the absence of ultrasound) were briefly explored using the intermediate concentration Nafion® dispersions, D520. It is well documented that high shear stirring (e.g.  $\geq 5,000$  RPM) induces measurable mechanical degradation in polymer solutions mainly due to hydrodynamic cavitation [33,34]. For instance, poly (methacrylic acid) solutions stirred at 12,000 RPM for 2 min exhibited up to 64% decreases in measured solution viscosity [35]. When subjected to 2 min of ultrasonication via quartz crystal oscillator operating at a maximum intensity of 20 W, these same solutions exhibited up to 53% decreases in measured solution viscosity. Both findings were attributed to mechanical degradation associated with the formation and

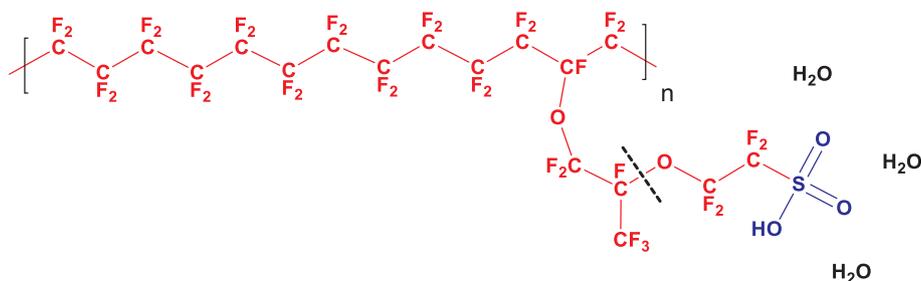


Fig. 4. Representative structure of a 1000 equivalent weight Nafion® polymer.

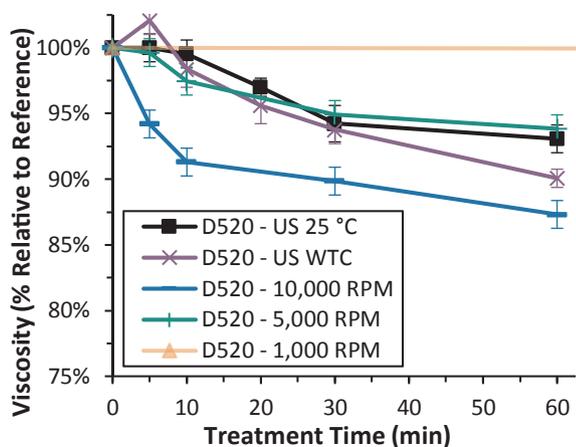


Fig. 6. Average solution shear viscosities for Nafion® dispersions following either ultrasonic or high shear mixing experiments.

collapse of high energy cavitation bubbles [35].

Consequently, the D520 samples were subjected to stirring at either 5,000 or 10,000 RPM for up to 60 min, after which their viscosities were measured and compared to both US and USWTC data (

Fig. 6). Similar decreases in solution viscosity were observed to the power ultrasound-treated samples. After 60 min of treatment, samples stirred at 5,000 or 10,000 RPM showed 6.2 or 12.7% decreases in average solution viscosity, respectively ( $p \leq 0.001$ ). In context, 60 min of ultrasonic treatment at 25 °C or without temperature control resulted in 8.1 or 10.7% decreases, respectively ( $p \leq 0.001$ ), suggesting that power ultrasound indeed may be causing mechanical degradation of the polymer dispersions [9]. Given that Nafion® ionomer-containing catalyst inks for electrochemical device applications are often prepared and homogenized using ultrasonication baths and/or “rapid” stirring with conventional stirring plates for extended periods of time (e.g. overnight) [27,36,37], the Nafion® D520 dispersion was also subjected to rapid stirring (1,000 RPM) for 24 h using a common laboratory magnetic stir plate and stirring bar. Following treatment, samples showed an average decrease of  $1.1\% \pm 0.4\%$  in solution shear viscosity ( $p = 0.063$ , statistically insignificant), a thermal degradation profile *akin* to those observed for samples treated with ultrasound, and no measurable changes in  $T_g$ . Hence, although both power ultrasound and high shear mixing at  $\geq 5,000$  RPM may be inducing mechanical degradation within the Nafion® dispersions studied, the effects of homogenization via magnetic stirring at  $\leq 1,000$  RPM appear to be negligible.

#### 4. Conclusions

A systematic study was performed to investigate the effects of power ultrasound on a series of three Nafion® ionomer dispersion concentrations under various irradiation durations ( $t_{\text{us}}$ ), at fixed ultrasonic frequency (42 kHz) and ultrasonic power ( $> 2$  W), and at either controlled or unregulated bulk solution temperature using a laboratory ultrasonic cleaning bath. Shear viscosity ( $\eta$ ), thermal degradation, and glass transition temperature ( $T_g$ ) for all Nafion® dispersion samples were measured and compared to untreated Nafion® samples. Nafion® dispersion samples were also subjected to high shear mixing at various rotation speeds in order to separate the effects of ultrasonication. It was found that, under controlled bulk solution temperature (25 °C), as the ultrasonication irradiation duration increased to  $t > 20$  min, statistically significant ( $p < 0.05$ ) decreases in viscosity were observed for all Nafion® dispersion samples. However, this effect was more pronounced for all samples treated under unregulated bulk solution temperature, most-so at lower dispersion concentrations. This may be partially due to the lower initial temperature of the unregulated experiments (18 °C).

Thermogravimetric analyses showed that for all ultrasonically irradiated samples, a negligible overall degradation was observed over the temperature range used, and no general trends in the data was observed. However, all samples irradiated under controlled and unregulated bulk solution temperatures showed an additional mass loss event possibly corresponding to a more defined cleavage of acidic side chains about the chemically-labile ether linkage. Differential scanning calorimetry experiments showed that no evident effect of ultrasonic irradiation on polymer  $T_g$ . Finally, by comparing the ultrasonically treated and high-shear mixed samples, it was also found that acoustic cavitation and high shear mixing both played important roles in decreasing solution viscosity. The data obtained suggested that it might be possible to reduce the observed effects when ultrasonically treating Nafion®-based dispersions by carefully regulating the bulk solution temperature at 25 °C.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ultsonch.2019.104758>.

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