

The Effect of Inert Salts on Explosive Emulsion Thermal Degradation

Pengcheng Yu,^[a] Nicholas N. A. Ling,^[a] Einar O. Fridjonsson,^[a] and Michael L. Johns^{*[a]}

Abstract: Ammonium nitrate fuel oil (ANFO) explosive emulsions are comparatively safe, effective and low-cost products for mining operations. They consist of a supersaturated ammonium nitrate solution dispersed as droplets in a continuous fuel phase. Here we apply a previously developed bench-top Nuclear Magnetic Resonance (NMR) Pulsed Field Gradient (PFG) technique to monitor the emulsion droplet size distribution in ANFO explosive emulsions as a function of time stored at an elevated temperature of 50 °C; we thus investigate the subtle effect of adverse storage conditions on emulsion stability. Storage at 50 °C for 12

weeks lead to a ~60% increase in mean droplet size, whereas a sample stored at 21 °C experienced no change in mean droplet size. The addition of inert salts (calcium nitrate or sodium nitrate) to the ammonium nitrate solution was also considered in terms of their ability to enable stable storage of the emulsions at 50 °C. An addition of 5 wt% calcium nitrate to the aqueous phase was required to suppress any thermal degradation of the explosive emulsions whilst a much lower dosage of only 1 wt% sodium nitrate was required to realise the same stabilizing effect.

Keywords: Explosive emulsions • Thermal degradation • PFG NMR • Droplet size distributions

1 Introduction and Background

Explosives are substances that undergo a rapid chemical reaction under the right conditions, in the process releasing potential energy in a short period of time (on the micro-second time scale) [1]. In addition to their military application, they are also used in a range of industrial applications, of which mining activities are the most prominent [2–4]. Using Australia as an example, the mining industry contributed \$279 billion in 2018/2019 to export revenue [5], annual consumption of explosives in the state of Queensland alone amounts to approximately 500 000 tonnes per year [6]. These explosives are used to both displace rock masses during both surface and underground mining and to reduce the resultant ‘fragment’ size to allow for easier subsequent mineral extraction. A low cost explosive with good storage and transport stability as well as sufficient explosiveness is clearly highly desirable [7, 8].

Ammonium nitrate fuel oil (ANFO) is one of the common commercial explosives used in the mining industry. It is a physical blend of ammonium nitrate pellets and diesel fuel and is comparatively cheap. There are however limitations on its application (e.g. [9–11]) as detonation can be difficult to control. Spontaneous detonation of ANFO can also occur either due to reactive grounds, where the ammonium nitrate reacts with sulphides, or hot ground, where local hot spots from geothermal sources can detonate the explosion [11–13]. In addition, ANFO has poor water resistance and consequently sub-optimal detonation can occur during the use of ANFO in regions with elevated moisture contents. Sub-optimal ANFO detonation can lead

to significant safety and environmental concerns mainly in terms of the generation of nitrous oxides (NO_x) [14–17].

To mitigate the spontaneous detonation and low water resistance issues associated with the use of ANFO, additional chemicals are introduced into the blend formulation to produce gelatinous suspensions, slurries, or emulsions [10]. These can be tailored to specific geologic conditions and customer needs (e.g. the range of explosive products supplied by Dyno Nobel [9]). Here we focus on explosive emulsions, which are water-in-oil explosive emulsions that are formulated from a supersaturated ammonium nitrate aqueous solution dispersed in a continuous fuel phase (typically diesel). This ANFO-based explosive emulsion is particularly inert to sulphides and insensitive to local hotspots in the ground, thereby making it more resistant to spontaneous detonation. Its effectively waterproof characteristic is also critical in avoiding sub-optimal detonation. In the form of such emulsions, the use of ANFO explosive has been extended to a wider range of applications (e.g. [18, 19]). However, a significant limitation with respect to ANFO emulsions is their stability. These explosive emulsions are highly concentrated macro-emulsions (droplet sizes are greater than 1 μm in diameter) that are consequently inherently thermodynamically unstable and thus practically feature a shorter expiration date relative to alternatives.

[a] P. Yu, N. N. A. Ling, E. O. Fridjonsson, M. L. Johns
Dept. of Chemical Engineering, School of Engineering, The University of Western Australia, 35 Stirling Highway, CRAWLEY WA 6009, Australia
*e-mail: michael.johns@uwa.edu.au

The use of Nuclear Magnetic Resonance (NMR) Pulsed Field Gradient (PFG) techniques for the determination of emulsion droplet size distributions has been widely validated (e.g. [20–22]) across a range of emulsion systems [20] including concentrated emulsion (e.g. [23–25]). In previous work [26], such NMR PFG techniques were employed to conduct a series of parametric studies to investigate the influence of various formulation characteristics of ANFO explosive emulsions on both initial mean emulsion droplet size and how the droplet size distribution evolved over 12 weeks storage at room temperature ($\sim 21^\circ\text{C}$). Droplet size measurements were successfully validated against optical droplet size determination on diluted samples. Whilst variations in the wt % of fuel phase, ammonium nitrate and the addition of inert salts were all observed to affect the initial mean droplet size, all emulsions remained stable (i.e. no significant variation in the mean aqueous phase droplet size was observed) over a period of 12 weeks. In the current work, we consider the effect of storage temperature on explosive emulsion stability as determined via monitoring of the mean emulsion droplet size. Again with reference to Australia, atmospheric temperatures consistently in excess of 40°C are common in many mine sites [27] with emulsion storage temperatures either in the ground or in warehouses likely to exceed 50°C . It is well known that heat is a reasonably effective emulsion destabilisation mechanism (e.g. [28,29]). Here we consider the effect of storage at 50°C on the stability of ANFO explosive emulsions over a 12-week period using NMR PFG techniques to periodically monitor the emulsion droplet size distributions of these explosive emulsions. We proceed to consider the effect of the addition of various inert salts on this emulsion stability.

2 Methodology

2.1 Material and Sample Composition Range

The standard explosive emulsion formulation was retained from that used in previous work [26]. This consists of a 7 wt% fuel phase and a 93 wt% oxidiser (aqueous) phase. The fuel phase is formulated using 83 wt% paraffin oil (featuring a viscosity of 140 MPa at 20°C , supplied by Sigma Aldrich) and 17 wt% XP1820 (a derivative of polyisobutenyl succinic anhydride (PIBSA) and which is an emulsifier supplied by Clariant). The oxidiser phase contains 83 wt% ammonium nitrate (an industrial grade ammonium nitrate supplied by CSBP Ltd) and 17 wt% de-ionised water. In the cases where inert salts-sodium nitrate or calcium nitrate (both sourced from Sigma Aldrich) were added, the wt% concentration of ammonium nitrate was reduced accordingly. A summary of the range of explosive emulsion samples formulated (in terms of deviations away from the standard emulsion) is contained in Table 1.

2.2 Emulsion Preparation

The explosive emulsion is a blend of oxidiser and fuel phase, where the oxidiser phase is a supersaturated ammonium nitrate solution and the fuel phase comprises of the oil and emulsifier [10]. The formulation of explosive emulsions on a laboratory scale replicates the industrial process (e.g. [30]) and the procedure remains consistent with our previous work [26] as follows:

- The oxidiser phase is prepared by gradually adding the ammonium nitrate and the inert salts (if required) into preheated water whilst being stirred continuously at 80°C . The oxidiser phase preparation is deemed complete when all salts have dissolved completely at 80°C . Note: This process is time consuming (e.g. [31,32]) due to

Table 1. Formulation Range.

Composition		Standard		E1		E2		E3		E4	
Fuel phase						7 %					
Fuels	Paraffin oil					83 %					
Emulsifiers	XP1820 (PIBSA derivative)					17 %					
Oxidiser phase						93 %					
Oxidizing agent salt	Ammonium Nitrate	83 %		82 %		78 %		82 %		78 %	
Stabilizing salt	Calcium Nitrate	0		1 %		5 %		0		0	
	Sodium Nitrate	0		0		0		1 %		5 %	
Solvent	DI water					17 %					
Storage Temperature ($^\circ\text{C}$)		21	50	21	50	21	50	21	50	21	50

Explosive emulsion samples were stored at both a room temperature of $21 \pm 2^\circ\text{C}$ and an elevated temperature of $50 \pm 0.5^\circ\text{C}$ in a laboratory oven with the droplet size distribution being monitored periodically over a 12-week period.

the fact that the dissolution of ammonium nitrate is endothermic and generally takes 20 to 30 minutes.

- The fuel phase is prepared by dissolving the emulsifier, XP1820, in paraffin oil and blending the mixture continuously at 150 RPM for 5 minutes whilst the mixture temperature is maintained at 50 °C.
- The oxidiser phase is added to the fuel phase and the mixture is blended at 850 RPM for 5 minutes to form explosive emulsions.
- The mixer speed is then increased to 1200 RPM for 2 minutes to further refine the emulsions formed.

All mixing processes were carried out in an 80 mm diameter mixing vessel using an IKA RW 20 digital overhead stirrer that drives a 50 mm diameter 4-blade turbine. 2 ml of the resultant emulsion is sub-sampled and placed in a 5 mm outer diameter NMR test tube for NMR PFG droplet sizing that was carried out every week over a 12-week period.

2.3 Nuclear Magnetic Resonance

A bench top NMR system, featuring a Halbach array permanent magnet with a field strength of 1T and a 5 mm r.f. coil tuned to the ^1H resonance of 43 MHz (as shown in Figure 1) was used to conduct the study. The field homogeneity (Water LW50: ~ 4 Hz) is sufficient to provide unambiguous chemical shift resolution of the water and oil NMR ^1H signal, and thereby the droplet sizing analysis can be performed on the water signal. The critical feature that this system has (without which the droplet sizing measurement via the stimulated echo pulsed field gradient (STE PFG) [33,34] is not possible) is a gradient coil capable of generating pulsed magnetic field gradients up to 1 T/m. In addition to this magnet and gradient assembly, the system also consists of a spectrometer (Kea2), a gradient amplifier and a temperature controller to control the coil assembly and magnet temperature. The entire system was purchased from Magritek, New Zealand. The magnet is stored within a chamber (supplied by Espec) to ensure optimum stability for measurements.

The stimulated echo pulsed field gradient (STE PFG) shown in Figure 2 is a common PFG technique used for self-diffusion measurements. Self-diffusion can occur in all

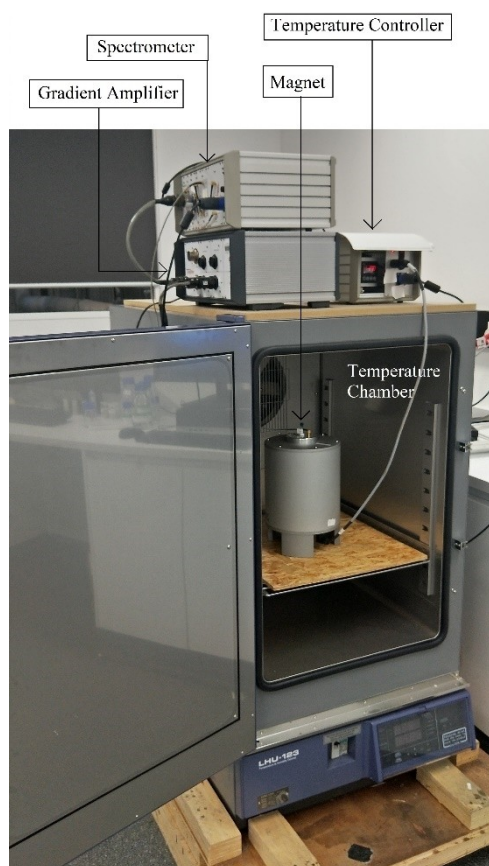


Figure 1. Magritek NMR system.

fluids, resulting in the positional change of individual molecules over time. As a result of the positional change that occurs within the observation window, Δ (the time interval between the two pulsed field gradient as shown in Figure 2) there is a loss in net magnetisation and thus a NMR signal loss. By increasing the duration or intensity of the pulsed field gradients, the NMR signal loss is increased. This can be described using the Stejskal and Tanner [35] equation:

$$\frac{S}{S_0} = \exp \left[-D(\gamma g \delta)^2 \left(\Delta - \frac{\delta}{3} \right) \right], \quad (1)$$

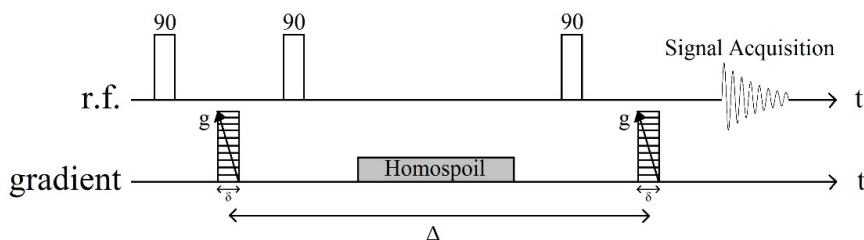


Figure 2. Stimulated spin echo pulsed field gradient Process (STE-PFG) [36].

where S is the NMR signal, S_0 is the signal measured when $g=0$, g is the magnetic field gradient strength (T/m), δ is the duration of the magnetic field gradients applied, γ is the gyromagnetic ratio of the nucleus ($^1\text{H}=2.68\times 10^8\text{ T}^{-1}\text{s}^{-1}$) and Δ is the time interval between the two magnetic gradient pulses. This method and equation is applied to measure the self-diffusion coefficient, D of the relevant fluid.

In the case of emulsions, the self-diffusion of the dispersed phase molecules is restricted by the droplets' boundaries. In the explosive emulsions the dispersed phase providing the NMR signal is the water content of the oxidizer phase. The degree of restriction on self-diffusion experienced by the dispersed phase molecules is related to the droplet size; this phenomenon is exploited to determine the emulsion droplet size. The successful implementation of the pulsed field gradient technique for emulsion droplet sizing has been detailed in our previous explosive emulsion study [26] as well a number of previous publications concerning emulsions (e.g. [23–25, 34, 37–39]).

The relationship between NMR signal and droplet size is significantly more complicated than Equation 1. In the implementation used here, this is achieved via the Block Gradient Pulse (BGP) method [40] which effectively eliminates previous assumptions of a Gaussian phase accumulation in the NMR signal [39] or an infinitely short value for δ [41]. Due to the fact that emulsions consist of a range of droplet sizes, the computation of a droplet size distribution, $P(a)$, is required. This is an ill-conditioned problem that requires the use of Tikonov regularisation techniques. As demonstrated in the work of Hollingsworth and Johns [22], a generalized cross validation (GCV) is a suitable method to determine the required regularisation parameters. This regularisation approach to determine $P(a)$ has been extensively used and validated in several previous studies (e.g. [23, 37, 40, 42, 43]).

3 Results and Discussions

3.1 The Effect of Storage Temperature

Figure 3 shows example droplet size distributions (DSDs) of standard explosive emulsion samples stored at room temperature ($\sim 21^\circ\text{C}$) and in an oven at 50°C respectively. The sample stored at room temperature had minimal change in DSD over the 12-week period (Figure 3(a)) with droplet sizing remaining persistently below $10\text{ }\mu\text{m}$ in diameter. However, the sample stored in the oven at 50°C experienced growth of a finite amount of much larger droplets (Figure 3(b)) which hence serves as evidence of the early onset of emulsion degradation (the two emulsions were visually indistinguishable from one another and over time).

To better summarise the acquired data, the mean droplet size is computed for each DSD (measurements were performed weekly) and is shown in Figure 4 for both samples.

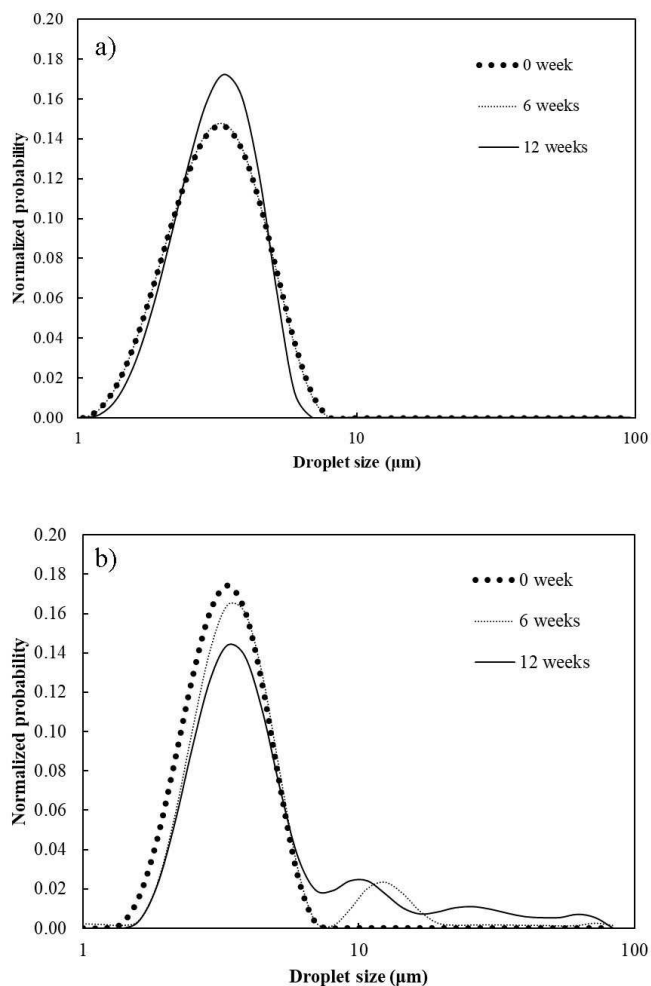


Figure 3. Droplet size distributions (over 12 weeks) of a standard explosive emulsion stored at (a) a room temperature of $\sim 21^\circ\text{C}$ and (b) a, oven temperature of 50°C .

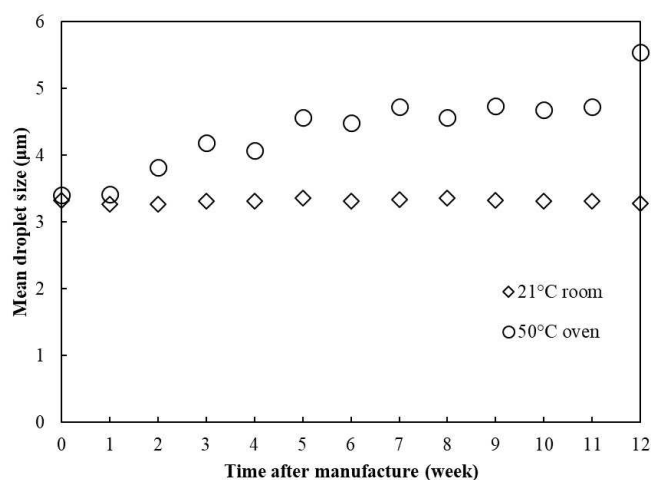


Figure 4. Mean droplet size evolution over 12 weeks for the standard explosive emulsions at different storage temperatures.

Clearly, the standard explosive emulsion stored at 50 °C experienced a persistent increase in mean droplet size over this time period (this increased from 3.40 μm (at 0 week) to 4.49 μm (at 6 weeks) to 5.54 μm (at 12 weeks)) whereas the sample stored at room temperature was comparatively very stable and experienced no change in mean droplet size.

3.2 The Stabilising Effect of Inert Salts

It has been observed in the past that the addition of salts can stabilise water-in-oil emulsions (e.g. [24]) with a number of physical mechanisms being proposed: changes in density, interfacial tension or dielectric permittivity or an enhanced surface accumulation of surface-active species. In this study, we explore the use of inert salts to mitigate against explosive emulsion degradation (commencing with an increase in dispersed phase droplet size) as a result of an elevated storage temperature of 50 °C. Two salts—calcium nitrate (CN) and sodium nitrate (SN) – which are commonly used in the industry as stabilisers [44,45], were used in this study. Figure 5(a) and (b) show the droplet size distributions of explosive emulsions E1 (1% CN) and E2 (5% CN) stored in an oven at 50 °C, over the 12-week period. It is obvious that explosive emulsion E1 degrades with the formation of a small population of significantly larger droplets over time. With the addition of 5% calcium nitrate however, the DSDs for emulsion E2 remain very consistent over the equivalent time. The mean droplet size is shown in Figure 6 for both samples E1 and E2 over the 12-week period both stored at 21 °C and 50 °C respectively. Comparing Figure 4 and Figure 6, it is evident that emulsion E1 degrades at a comparable rate to the standard emulsion (with no inert salt addition) when stored at 50 °C. This degradation is completely eliminated when the inert CN concentration is elevated to 5% despite the initial emulsion featuring a mean droplet size which is 29% larger than the standard emulsion (4.4 μm versus 3.4 μm respectively).

Figure 7(a) and (b) show the droplet size distributions of explosive emulsion, E3 (1% SN) and E4 (5% SN) which were also stored in an oven at 50 °C for a 12-week period. For emulsion E3, there was slight droplet growth evident in the DSD measured at both week 6 and week 12 – this was significantly less than what observed in the standard emulsion and emulsion E1 (which similarly featured a 1% inert addition). In Figure 7(b), it is evident that for emulsion E4, the addition of 5% sodium nitrate completely suppresses any emulsion droplet growth. The weekly measured mean droplet sizes for emulsion E3 and E4 are summarised in Figure 8. Interestingly the addition of 1% SN has increased the initial mean droplet size by 38% relative to the standard emulsion, nonetheless differences in mean droplet size over the 12-week period for the samples stored at 21 °C and 50 °C are minimal. For emulsion E4 any differences are essentially completely eliminated. Thus we can conclude that

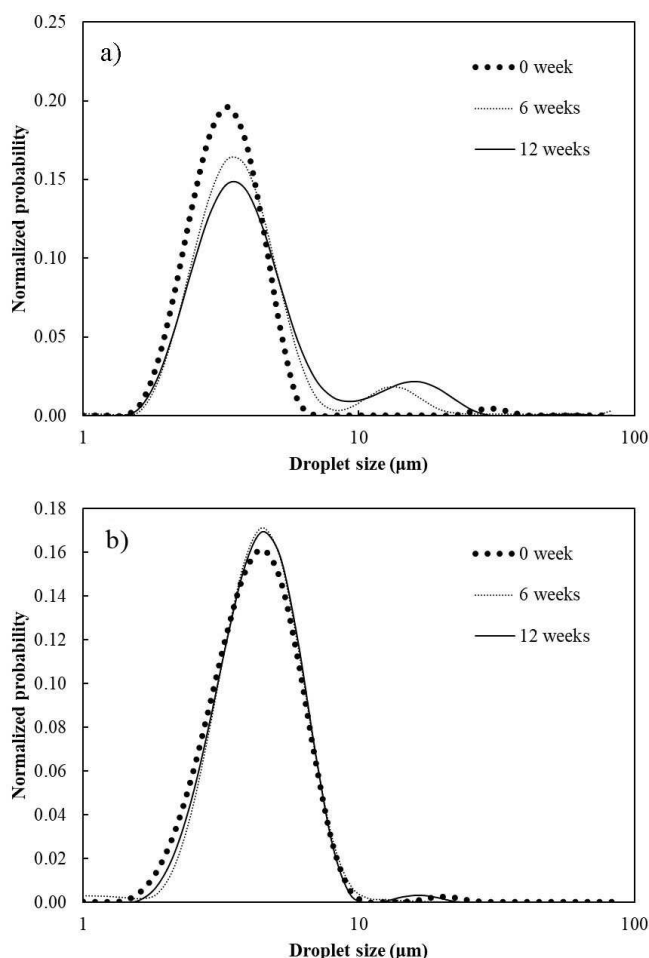


Figure 5. Droplet size distributions (over 12 weeks) of explosive emulsion (a) E1 (1% CN) and (b) E2 (5% CN) stored at an oven temperature of 50 °C.

in comparison to calcium nitrate, sodium nitrate has a better stabilising effect on these explosive emulsions.

4 Conclusions

NMR PFG has been utilised in this study to investigate the effect of storage temperature on the stability of ANFO based explosive emulsions via the measurement of droplet size distributions in these inherently opaque samples. It was clearly shown that these explosive emulsions degrade at a greater rate when stored in an elevated temperature environment (50 °C) compared to room temperature. Degradation proceeded via the formation of a small population of significantly larger droplets, the amount of which as well as their respective mean droplet size both consistently increased with storage time. Mitigation methods were explored in this study via the inclusion of inert salts in the explosive emulsion formulation. This showed that the use of sodium nitrate was most effective in stabilising these ex-

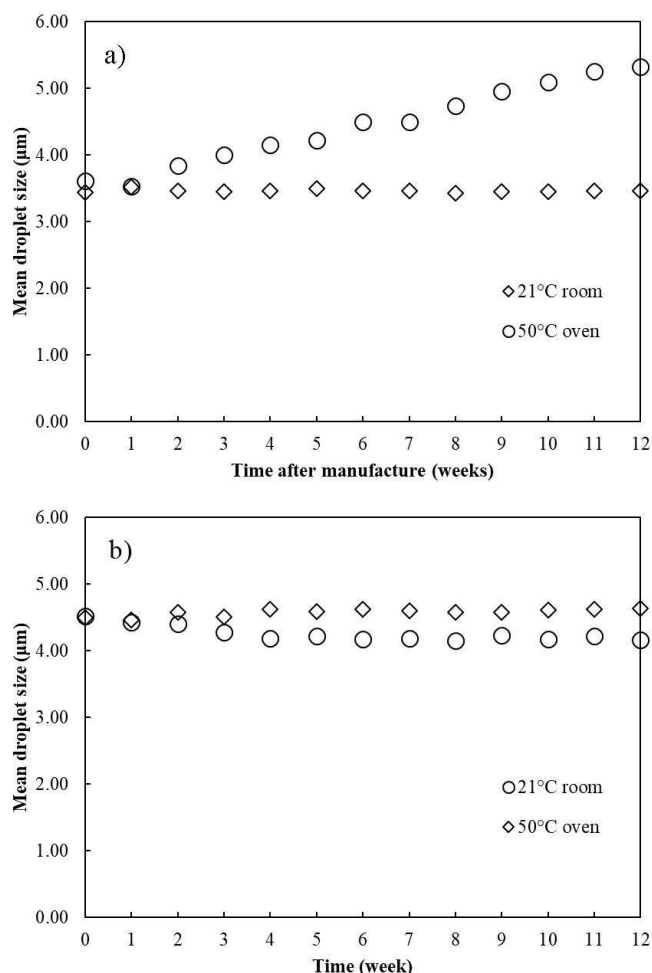


Figure 6. Mean droplet size evolution of explosive emulsion (a) E1 (1% CN) and (b) E2 (5% CN) at different storage temperatures.

plosive emulsions; the addition of 1 wt% sodium nitrate almost completely suppressed any emulsion degradation. This was not the case for calcium nitrate where the equivalent stabilising effect was only evident at 5 wt% calcium nitrate.

Acknowledgements

The author acknowledges Nitro Sibir Australia (NSA) and Explosives Manufacturing Services (EMS), and associated subcontractors, for key knowledge and information provision. The advice of Nathan Hayward is gratefully acknowledged.

Data Availability Statement

Data available on request from the authors.

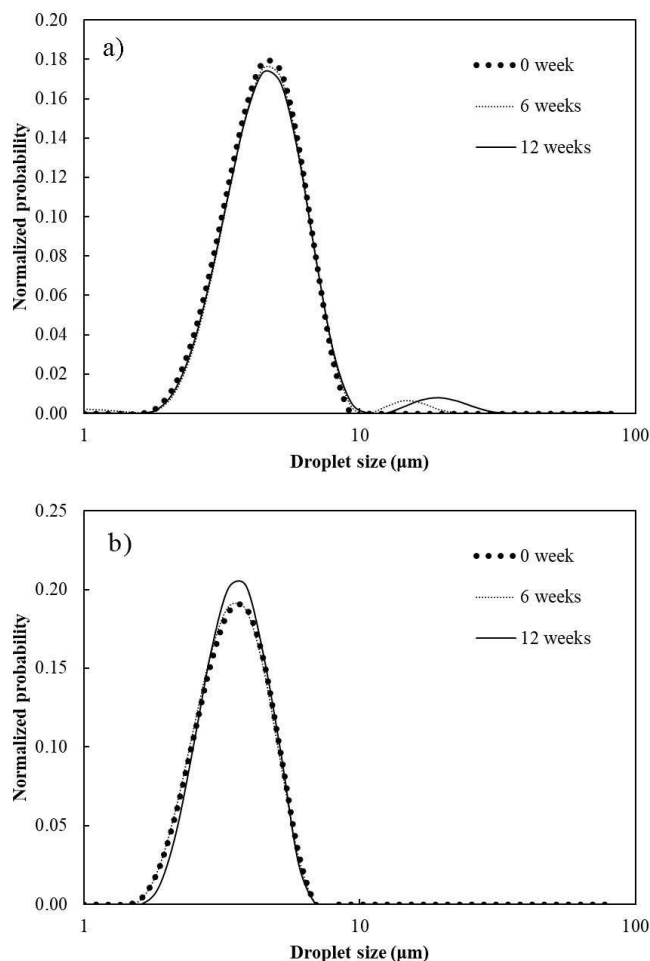


Figure 7. Droplet size distributions (over 12 weeks) for explosive emulsion (a) E3 (1% SN) and (b) E4 (5% SN) stored at an oven temperature of 50°C.

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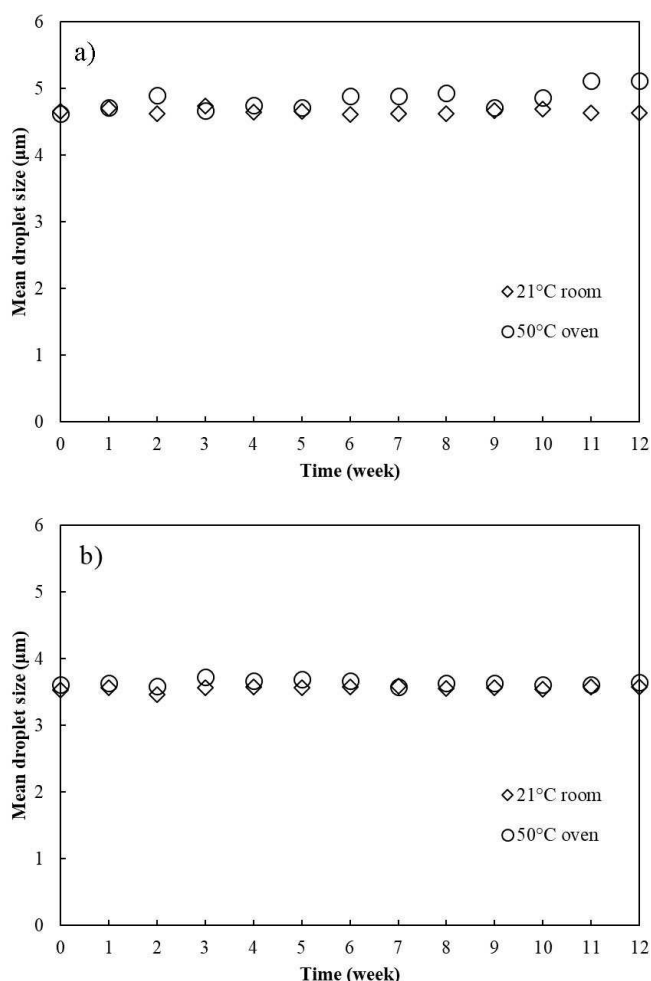


Figure 8. 12-week mean droplet size evolution of explosive emulsion (a) E3 (1% SN) and (b) E4 (5% SN) at different storage temperatures.

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Manuscript received: October 2, 2020

Revised manuscript received: October 15, 2020

Version of record online: February 2, 2021