Physicochemical Characterization of Nonionic Surfactants in oil-in-water (O/W) Nano-emulsions for New Pesticide Formulations

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Abstract

Physicochemical characteristics of pre-formulation concentrates of an emulsion system of LFAMEs/APG:organosilicone/water were determined. The surfactants used were octyl/decyl polyglucosides (short-chain APG; SAPG) and dodecyl/tetradecyl/hexadecyl polyglucosides (long-chain APG; LAPG). Alkyl chain length of the APG was found to dominate the different flow behaviours of emulsions. The SAPG-emulsions exhibited Newtonian behaviour with constant viscosity, while LAPG-emulsions showed non-Newtonian behaviour with reduced viscosity. The morphology study showed larger size assembly of irregular aggregates for LAPG-emulsions as compared to SAPG-emulsions. The presence of glyphosate IPA in SAPG/LAPG emulsions formed polymerized multi-connected network structure, with the network being more densely packed in the LAPG-emulsions than SAPG-emulsions. Glyphosate IPA was found to reduce shear thinning on LAPG-emulsions while no effect was observed on SAPG-emulsions. Upon dilution of the pre-formulation concentrates, nano-formulations were formed. In SAPG-emulsion system, particles size was smaller, more uniformly dispersed and surface tension was lower than in LAPG-emulsion system.

Keywords: Rheology, shear thinning, alkylpolyglucosides, glyphosate IPA, nano-emulsions

1. Introduction

In agrochemical industry, pesticides are formulated with inert ingredients called adjuvants to improve biological performance of the pesticides by modifying the physicochemical characteristics of formulation mixtures [1].

The pesticide adjuvants comprise repellents, adherents, foam/anti-foam agents, stickers, stabilizers, controlled release agents, deposition/drift control agents and dispersants. They enhance solubility, spreading, absorption, penetration and translocation of pesticides into target for optimizing killing capacity on weeds, pests and diseases and alternatively, to reduce the lost of pesticide active via spray drift, off-target deposition, run-off, rainfastness and leaching [2]. These formulation adjuvants have demonstrated great impact on the stability and bioavailability of the products thus newer and more efficient formulations could be developed in the worldwide market.

Recently, emulsion-based adjuvants of pesticide formulations have triggered vast interests due to their green characteristics. The use of renewable resources of plant oils and esterified derivatives in oil-in-water (O/W) emulsions for biocide formulation [3] and water-in-oil-in-water (W/O/W) multiple emulsions for antifungal formulations [4], and also the use of biodegradable carbohydrate-derived surfactants are becoming increasingly important to replace non-renewable resources of petrochemical adjuvants in the pesticide products [5,6]. Emulsion comprised of two immiscible liquids of oil and water which one dispersed as droplets throughout the other one as continuous phase [7]. Emulsions are stabilized by surfactants to form macroemulsion, microemulsion and nano-emulsion [8]. These emulsion types create many disparate characteristic structure in the microscale insights that determine macroscopic properties of the product concentrate including consistency, rheology and shelf-life stability [9,10].

Rheology pertains to the science of flow and deformation of matter which is very important in deciding the patterns of colloidal dispersion of crop protection products. For emulsion, rheology is strongly influenced by the physicochemical characteristics of dispersed phase of oils and surfactants, in aspects of concentration, elasticity and droplet size dependencies [11]. In previous studies, alkyl chain length of surfactants has been shown to affect the average droplet size and viscosity of the dispersed phase. As such the rheological properties of O/W emulsion for formulations of cosmetic, pharmaceutical and home care products could be designed by the chain length of the surfactant [12,13]. In addition, knowing the emulsion anisotropic structure aids to ensure the product concentrates disperse well in water when applied onto crops after dilution. The emulsion-based products commonly contain rheology modifiers such as bentonite clay and xanthan gum [14] to increase the viscosity and reduce the flowability of products from the applied surface run-off owing to its Newtonian behaviour with constant shear viscosity [15]. Without rheology modifier, the viscoelasticity of the emulsions can be ameliorated by the nature and peculiarities of surfactants and oils.

In this work, the physicochemical behaviour of emulsions with different alkyl chain length of mixed surfactants was studied. These emulsions were then incorporated with herbicide active, glyphosate isopropylamine (IPA) to produce new pre-formulation concentrates. Upon dilution of the pre-formulation, nano-formulations were formed and the samples were investigated.

2. Materials and methods

2.1 Materials

Alkylpolyglucosides (APG) surfactants: octyl/decyl (45/55 (w/w)) polyglucosides (short-chain APG; SAPG) and dodecyl/tetradecyl/hexadecyl (68/26/6 (w/w)) polyglucosides (long-chain APG; LAPG), with a degree of polymerization (DP) 1.6 were gifts from Cognis (Malaysia). Organosilicone surfactant: ethoxylated 3-(3-hydroxypropyl)-heptamethyltrisiloxane (90% wt) was provided by Dow Corning (Singapore). Fatty acid methyl esters (FAMEs): methyl octanoate/decanoate/laurate/ myristate/palmitate/stearate/oleate/linoleate/linolenate/arachidate (0.1/0.1/52.1/17.7/ 8.9/2.2/15.8/2.8/0.2/0.1 (w/w)) (long-chain FAMEs; LFAMEs) was supplied by Cognis (Malaysia). Pesticide active, aqueous glyphosate IPA (62% (w/w)) was provided by Crop Protection (Malaysia). Deionized water was prepared using Mili-Q water system (USA). All materials were of analytical grade unless otherwise specified.

2.2 Methods

2.2.1 Determination of stable pre-formulation concentrates region

Mixtures of SAPG with LFAMEs and LAPG with LFAMEs were prepared in surfactant-oil ratios (SOR) of (w/w) 10:0, 9:1, 8:2, 7:3, 6:4 and 5:5, respectively. Water was added at 5% (w/w) incrementally into the mixtures. Glyphosate IPA was added at 41% (w/w) after each increment of water. The pre-formulations were weighed using analytical balance, Mettler Toledo Model Dragon 204 (Spain), sealed, vibro-mixed with vortex mixer, Model VTX-3000L (Japan) and centrifuged utilizing Hermle Model Ettek centrifuge (Germany) at 4000 rpm, room temperature (25 °C) for 15 min.

The centrifuged pre-formulations were visualized through crossed polarized plates which was equipped with light for recognition of the samples stability via physical phase appearance. The previous steps were repeated using mixed surfactants SAPG:organosilicone and LAPG:organosilicone instead of single surfactant. Ratios of the mixed surfactants were started at 9:1, 8:2, 7:3 and ended at 6:4 whereby no stable pre-formulation was observed.

2.2.2 Preparation of pre-formulations and emulsions

Four pre-formulation concentrates namely F1, F2, F3 and F4 were selected from the stable pre-formulations region and the compositions were listed in Table 1. The emulsion of the pre-formulations (without glyphosate IPA) namely E1, E2, E3 and E4, respectively were prepared (Table 1). The emulsions and the pre-formulations were stirred with IKA RW20 digital overhead stirrer (Germany) with 200 rpm for 2 h using four “elephant ear” blades impeller with diameter of 4.5 cm.

2.2.3 Rheology

Rheology of emulsions and pre-formulation concentrates was characterized using Modular Compact Rheometer (MCR) 300 (Paar Physica GmbH, Austria-Europe) for interfacial shear measurements. A cone and plate geometry with a cone angle of 1^o and a cone diameter of 17 mm with 0.05 mm gap was used. The apparent viscosity of the samples was determined by rotation tests of controlled shear rate in a range of 0 – 500 s^{-1} at 25 ^oC. The apparent viscosity (η_{app}) (Pa.s) of the emulsions and the pre-formulations were determined using power law equation (1), where k is the consistency coefficient (Pa.s^n) related to viscosity, γ is the shear rate (1/s) and n is the flow behaviour index (dimensionless) related to the indicator of viscous nature of system. For Newtonian fluid, n=1 and non-Newtonian of pseudoplastic fluid, n<1 and dilatant, n>1 [16].

$$\eta_{app} = k\,\gamma^{(n-1)} \qquad (1)$$

2.2.4 Morphology

High resolution transmission electron microscopy (TEM) (Hitachi H-7100, Japan) was used to characterize the microstructure of the samples. The samples were dropped on copper grid coated with Formvar films, then negatively stained with 2% uranyl acetate solution. Filter paper was used to gently wipe off the exudate uranyl acetate on the copper grid and dried in an open air, at ambient temperature 25 ^oC, overnight. The samples were then examined in the TEM operating system at 200kV.

2.2.5 Formation of nano-formulations

Nano-formulations were generated from the dispersion of pre-formulation concentrates. The pre-formulations were diluted in a ratio 1 to 200 in distilled water, under mild stirring at 200 rpm for 2 min. TEM, particle size and surface tension of the nano-formulations were characterized.

2.2.6 Particle size

The particle size of nano-formulations was measured using Nanophox particle analyzer model SympaTec GmbH, Clausthal-Zellerfeld (Germany), equipped with photon cross correlation spectrometer (PCCS) using laser light scattering which was monitored at an angle of 90^o. The samples were loaded into 1 cm^2 cuvettes in a thermostated chamber, at 25 ^oC for the measurement.

2.2.7 Surface tension

Surface tension of the nano-formulations was measured using Kruss K6 tensiometer (Kruss, UK) with the de Nouy ring method. Before measurement, calibration was conducted with deionized water to show surface tension at 72.0 mN/m. Readings of the surface tension were recorded after the samples attained equilibrium state.

3. Results and Discussion

3.1 Pre-formulation concentrates determination study

The resulting phase characteristics of pre-formulation concentrates using surfactants SAPG and LAPG are shown in Table 2 and Table 3, respectively. For the pre-formulations utilizing single surfactants of SAPG and LAPG, the incorporation of LFAMEs was very limited and optimized at surfactant-oil ratio (SOR) 10:0 (Table 2(a)) and 9:1 (Table 3(a)), respectively. However, the mixed surfactants SAPG:organosilicone and LAPG:organosilicone loaded pre-formulations showed effectively high oil content of LFAMEs at SOR 7:3 and 5:5, at mixed surfactant ratio (MSR) 6:4 (Table 2(e)) and 8:2 (Table 3(c)), respectively. Binary surfactants tend to exhibit synergism which was caused by mutual electrostatic attraction of hydrophilic group or Van der Waals attraction of hydrophobic group, thus the effectively reduction of interfacial tension at oil-water interface [17].

The longer alkyl chain LAPG surfactant gave relatively higher oil solubilization than SAPG, due to formation of larger micelles [18] and the existence of cubic phase microemulsion [19]. Oil incorporation into pre-formulations is important for delivering hydrophilic pesticide of glyphosate IPA onto hydrophobic cuticle and waxy layer of leaves.

3.2 Preparation of pre-formulations and emulsions

Fig.1 shows the pre-formulation concentrates (with glyphosate IPA) and emulsions (without glyphosate IPA) were stable without phase separation in liquid state. The appearance for the pre-formulation concentrates F1, F2 and F3 was transparent and F4 was translucent, while for the emulsions E1 and E2 was transparent, E3 was translucent and E4 was milky white. The prepared emulsions were used to observe the effect of surfactant alkyl chain length and the role of emulsion in the formation of the pre-formulations.

3.3 Rheology analysis

The rheology plots of apparent viscosity versus shear rate of emulsions and pre-formulation concentrates are shown in Figs. 2(a) and 2(b), respectively. Emulsions E1 and E2 exhibited constant viscosity, indicating $n=1$ and behaved as Newtonian fluid. This could be due to the surfactant showing globular and rod-like micelles which have weak effect on rheology [20]. Emulsions E3 and E4 exhibited reduced viscosity indicating $n<1$ and behaved as non-Newtonian fluid. As shear rate was increased, the three dimensional droplet structure of emulsion aggregates were disrupted and led to formation of ordered layer structure, leading to a decrease in flow resistance, thus exhibited pseudoplastic flow [21,22]. The increase in alkyl chain length from SAPG (C_{8-10}) to LAPG (C_{12-16}) in the emulsions increased the emulsion viscosity and transformed the mixture to have shear thinning property which was caused by the characteristics of worm-like micelles due to enhanced hydrophobic interaction [18,23,24,25].

Pre-formulation concentrates were the emulsions loaded with 41%(w/w) glyphosate IPA. Pre-formulation concentrates F1 and F2 showed constant viscosity indicating glyphosate IPA had no effect on emulsions E1 and E2 that behaved as Newtonian fluid. Conversely, glyphosate IPA showed strong influence on non-Newtonian emulsions of E3 and E4. Pre-formulation concentrate F4 showed constant viscosity after addition of glyphosate IPA into emulsion E4. Glyphosate IPA behaved as an agent making the viscosity constant whereby the presence of excess salt broke the micelle network junctions and reduced the micelle length [26]. The viscosity of F3 and F4 was reduced as compared to E3 and E4. Glyphosate IPA reduced the aggregation of emulsions, thus reducing the viscoelasticity characteristic of worm-like network.

3.4 Morphology

The microstructure of emulsions E1, E2, E3 and E4 are shown in Figs. 3(a), 3(b), 3(c) and 3(d), respectively. The emulsions exhibited disordered aggregates. The formation was due to the intermolecular forces attraction of hydrophilic-hydrophilic and hydrophobic-hydrophobic parts of the surfactant molecules. In contrast, the emulsion aggregate sizes were larger for E3 and E4 than E1 and E2. The increase in alkyl chain length of surfactant, the hydrophobicity effect induced a progressive growth to larger micellar size [27], thus causing the larger size of the emulsion aggregates. Lin and Lin (2003) [28] suggested that when the surfactant hydrophobic affinity was increased, the solubility in water was decreased, thus promoting higher self-association into aggregates. The microstructure of pre-formulation concentrates F1, F2, F3 and F4 are shown in Figs. 4(a), 4(b), 4(c) and 4(d), respectively. They were formed as polymerized multi-connected network. The presence of 41% (w/w) glyphosate IPA reduced the aggregation size of emulsions. In fact, salt affected the hydrogen bonding of water to the surfactant head group [29]. The solubilization of glyphosate IPA in water reduced the hydration of surfactants head groups, thereby decreasing their swelling, thus reduced the emulsions assembly size. The polymerized network of F3 and F4 was shown to be densely packed than F1 and F2. This could be caused by the larger emulsions aggregate of E3 and E4 occupied the multi-connected network of glyphosate IPA (Fig. 4(e)) to form higher compact system.

3.5 Formation of nano-formulations

Nano-formulations were produced from the pre-formulations by low emulsification method of dilution with gentle stirring. The microstructure of nano-formulations NF1, NF2, NF3 and NF4 is shown in Figs. 5(a), 5(b), 5(c) and 5(d), respectively. The dilution of the pre-formulation concentrates with water led to destruction of the polymerized network structure and formed dispersed nano-particles. The nano-formulations NF3 and NF4 showed average larger particle size than NF1 and NF2. This could be due to the longer alkyl chain of surfactant LAPG contributed to the larger molecular size, hence, the larger nano-particles size.

3.6 Particle size analysis

The particle sizes of nano-formulations NF1, NF2, NF3 and NF4 are shown in Table 4. The mean particle sizes of NF3 and NF4 showed significantly larger than NF1 and NF2. The increase of alkyl chain length in LAPGs increased the particle diameter of nano-droplets. The increase in particle size reduced molecular movements of Brownian motion and the flow of particles wass dependant on the action of dynamic forces [11]. Surfactants SAPG, LAPG and organosilicone have hydrophilic lipophilic balance (HLB) numbers at 13.6, 12.1 and 11.5, respectively. From the Bancroft rule, these surfactants were water-soluble surfactants adsorb at droplet surface to form oil-in-water (O/W) nano-emulsion.

3.7 Surface tension

The surface tension of nano-formulations is shown in Table 5. The nano-formulations NF1 and NF2 showed lower surface tension than NF3 and NF4. Shorter alkyl chain length of SAPG imparted the lower surface tension. In fact, the smaller size SAPG molecules imparted higher packed adsorbed layer with organosilicone with dilution concentration lower than critical micelle concentration (CMC) level, therefore, achieving greater reduction in surface tension [18]. The presence of nano-emulsions system in the nano-formulation effectively reduced the surface tension about 2-3 folds whereby the glyphosate IPA showed high surface tension without the aid of adjuvants. Nevertheless, the nano-droplets was believed to improve the delivery system into the target organisms as the nano-droplets possessed larger surface area, reduced surface tension, increased spreading and thus improvement on the pesticides performance [30].

4. *Conclusion*

The physicochemical characteristics of emulsion-based pre-formulations were strongly dependant on hydrophobicity of the surfactants. The different hydrocarbon chain decided the aggregation behaviour of emulsions, thus the Newtonian or non-Newtonian flow. Glyphosate IPA, a zwitterionic molecule reduced the shear thinning property of emulsions whereby the compact aggregate of emulsions was reduced. Upon dilution and formation of nano-formulations, surfactant alkyl chains imparted the substantial effect on droplet size, surface tension and determined the dispersion pattern. Ultimately, this hydrophobic character is crucial to influence the dynamic movement of droplets in flow, and essential for pesticide delivery system processes into the target organisms.

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References

[1] Green, J.M., and Beestman, G.B. (2007). Recently patented and commercialized formulation and adjuvant technology. *Crop Protection*, 25, 320-327.

[2] Wang, C.J., and Liu, Z.Q. (2007). Foliar uptake of pesticides – present status and future challenge. *Pesticide Biochemistry and Physiology*, 87, 1-8.

[3] Varona, S., Martin, A., and Cocero, M.J. (2009). Formulation of a natural biocide based on lavandin essential oil by emulsification using modified starches. *Chemical Engineering and Processing: Process Intensification*, 48, 1121-1128.

[4] El-Shafei, G.M.S., El-Said, M.M., Attia, H.A.E., and Mohammed, T.G.M. (2010). Environmentally friendly pesticides: Essential oil-based W/O/W multiple emulsions for anti-fungal formulations. *Industrial Crops and Products*, 31, 99-106.

[5] Graf, A., Ablinger, E., Peters, S., Zimmer, A., Hook, S., and Rades, T. (2008). Microemulsions containing lecithin and sugar-based surfactants: Nanoparticle templates for delivery of proteins and peptides. *International Journal of Pharmaceutics*, 350, 351-360.

[6] Baseeth, S.S., and Sebree, B.R. (2010). Renewable surfactants in spray adjuvants. *Lipid Technology*, 22, 79-82.

[7] McClements, D.J. (2005). Food emulsions: Principles, practices, and techniques (2nd ed.), CRC Press, Boca Raton, FL, pp. 609.

[8] Jafari, S.M., Assadpoor, E., He, Y., and Bhandari, B. (2008). Re-coalescence of emulsion droplets during high-energy emuldification. *Food Hydrocolloids*, 22, 1191-1202.

[9] Schubert, H., Ax, K., and Behrend, O. (2003). Product engineering of dispersed systems. *Trends in Food Science and Technology*, 14, 9–16.

[10] Stang, M., Schuchmann, H., and Schubert, H. (2001). Emulsification in high-pressure homogenizers. *Engineering in Life Sciences*, 1, 151–157.

[11] Derkach, S.R. (2009). Rheology of emulsions. *Advances in Colloid and Interface Science*, 151, 1-23.

[12] Niraula, B., King, T.C., Chun, T.K., and Misran, M., (2004). Rheology properties of glycopyranoside stabilized oil-water emulsions: effect of alkyl chain length and bulk concentration of the surfactant. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 251, 117-132.

[13] Pflaumbaum, M., Muller, F., Peggau, J., Goertz, W., and Gruning, B. (2001). Rheological properties of acid gel cleansers. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 183-185, 777-784.

[14] Faers, M.A., Choudhury, T.H., Lau, B., McAllister, K., and Luckham, P.F. (2006). Syneresis and rheology of weak colloidal particle gels. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 288, 170-179.

[15] Faers, M.A. (2003). “Cahiers de Formulation”, eds. Foissy A and Bachiri SA, Dispersabilit´e, EDP Sciences, ISBN 2-86883-638-0, pp. 207.

[16] Pestana, K.C., Formariz, T.P., Franzini, C.M., Sarmento, V.H.V., Chiavacci, L.A., Scarpa, M.V., Egito, E.S.T., and Oliveira, A.G. (2008). Oil-in-water lecithin-based microemulsions as a potential delivery system for amphotericin B. *Colloids and Surfaces B: Biointerfaces*, 66, 253-259.

[17] El-Batanoney, M., Abdel-Moghny, Th., and Ramzi, M., (1999). The effect of mixed surfactants on enhancing oil recovery. *Journal of Surfactants and Detergents*, 2, 201-205.

[18] Jiang, L.C., Basri, M., Omar, D., Abdul Rahman, M.B., Salleh, A.B., and Rahman, R.N.Z.R.A. (2011). Self assembly behaviour of alkylpolyglucosides in mixed surfactant-stabilized emulsions system. *Journal of Molecular Liquids*, 158, 175-181.

[19] Alam, M.M., Sugiyama, Y., Watanabe, K., and Aramaki, K. (2010). Phase behavior and rheology of oil-swollen micellar cubic phase and gel emulsions in nonionic surfactant systems. *Journal of Colloid and Interface Science*, 341, 267-272.

[20] Raghavan, S.R., Fritz, G., and Kaler, E.W. (2002). Wormlike micelles formed by synergistic self-assembly in mixtures of anionic and cationic surfactants. *Langmuir*, 18, 3797–3803.

[21] Logaraj, T.V., Bhattacharya, S., Sankar, K.U., and Venkateswaran, G. (2008). Rheological behaviour of emulsions of avocado and watermelon oils during storage. *Food Chemistry*, 106, 937-943.

[22] Szelag, H., and Paudzer, B. (2003). Rheological properties of emulsion stabilized by acylglycerol emulsifiers modified with sodium carboxylates. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 219, 87-95.

[23] Schubert, B.A., Kaler, E.W., and Wagner, N.J. (2003). The microstructure and rheology of mixed cationic/anionic wormlike micelles. *Langmuir*, 19, 4079.

[24] Yin, H., Lin, Y., and Huang, J. (2009). Microstructures and rheological dynamics of viscoelastic solutions in a catanionic surfactant system. *Journal of Colloid and Interface Science*, 328, 177-183.

[25] You, Y.L., Hao, L.S., and Nan, Y.Q. (2009). Phase behavior and viscous properties of cethyltrimethylammonium bromide and sodium dodecyl sulfonate aqueous mixtures. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 335, 154-167.

[26] Khatory, A., Lequeux, F., Kern, F., and Candau, S.J. (1993). Linear and nonlinear viscoelasticity of semidilute solutions of wormlike micelles at high salt content. *Langmuir*, 9, 1456-1464.

[27] Patel, T., Ghosh, G., Aswal, V., and Bahadur, P. (2009). Structural characteristics of the aqueous mixed nonionic-cationic surfactants: Effect of chain length, head group and temperature. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 333, 145.

[28] Lin, J.J. and Lin, S.F. (2003). Phase inversion of self-aggregating Mannich amines with poly(oxyethylene) segments. *Journal of Colloid and Interface Science*, 258, 159.

[29] Michaels, M.A., Sherwood, S., Kidwell, M., Allsbrook, M.J., Morrison, S.A., Rutan, S.C., and Carpenter, E.E. (2007). Quantitative model for prediction of hydrodynamic size of nonionic reverse micelles. *Journal of Colloid and Interface Science*, 311, 70-76.

[30] Tadros, ThF., Izquierdo, P., Esquena, J., and Solans, C. (2004). Formation and stability of nano-emulsions. *Advances in Colloid Interface Science*, 108, 303-318.

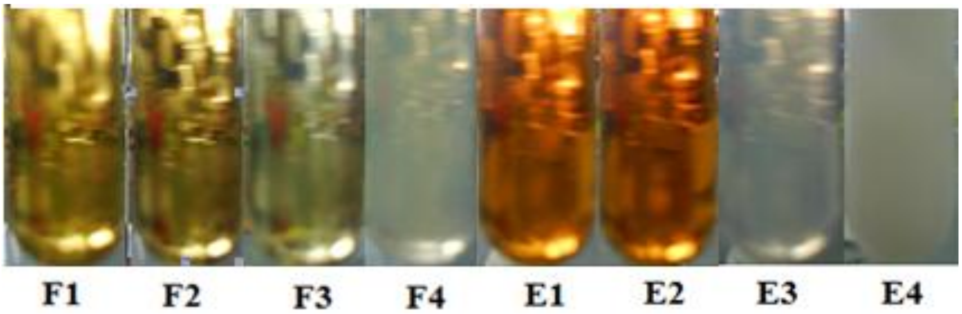
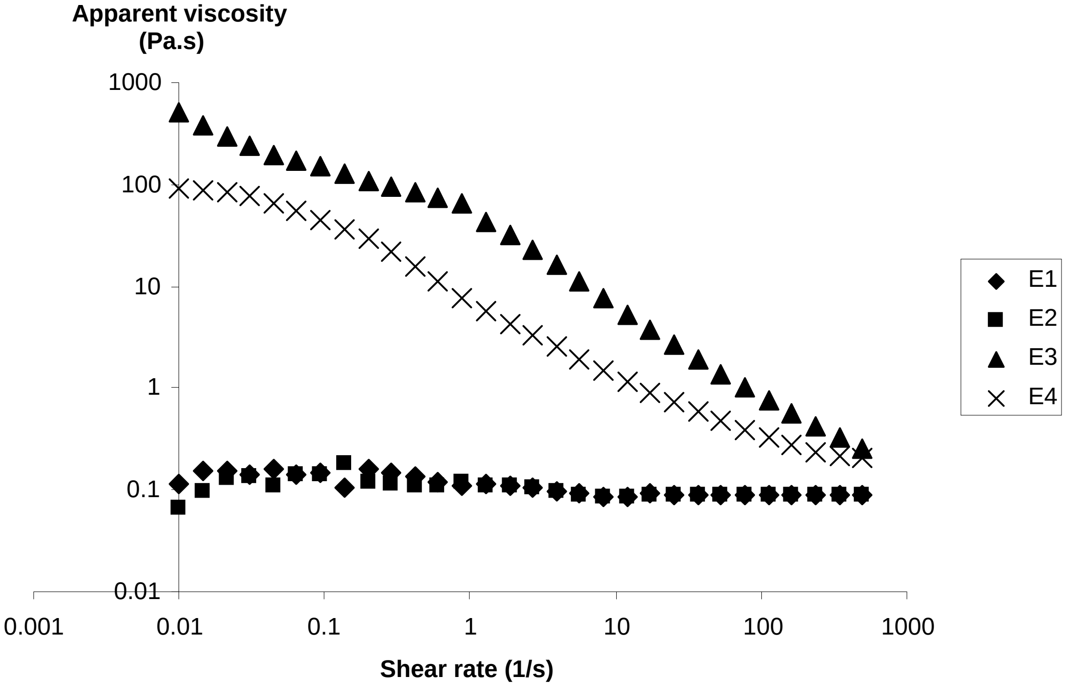


Fig.1: Phase behaviour and visual appearance of pre-formulation concentrates F1, F2, F3 and F4, and emulsions E1, E2, E3 and E4.

(a)



(b)

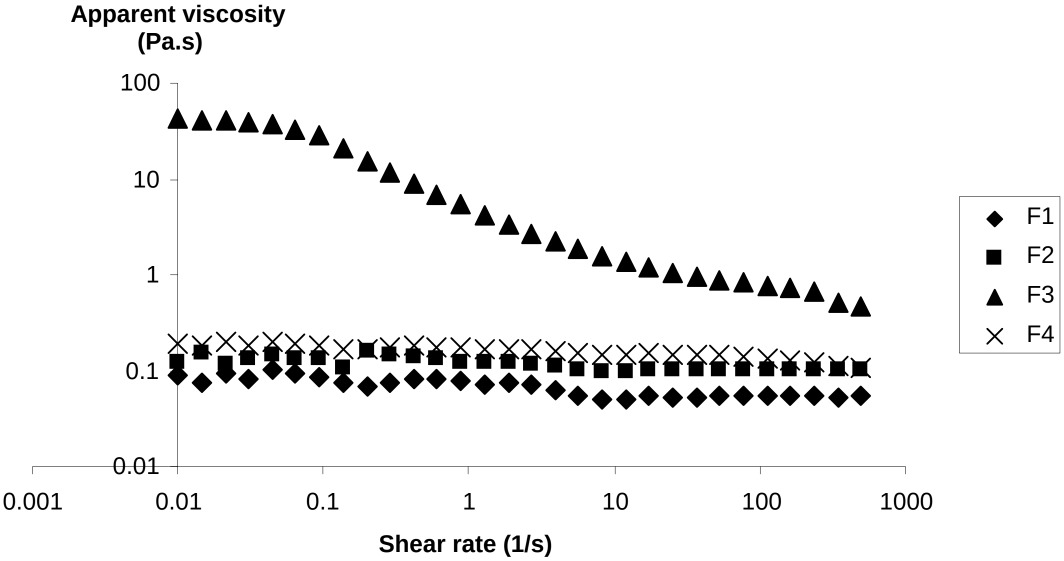


Fig.2: Rheology plots of apparent viscosity (Pa.s) versus shear rate (1/s) for (a) emulsions and (b) pre-formulation concentrates.

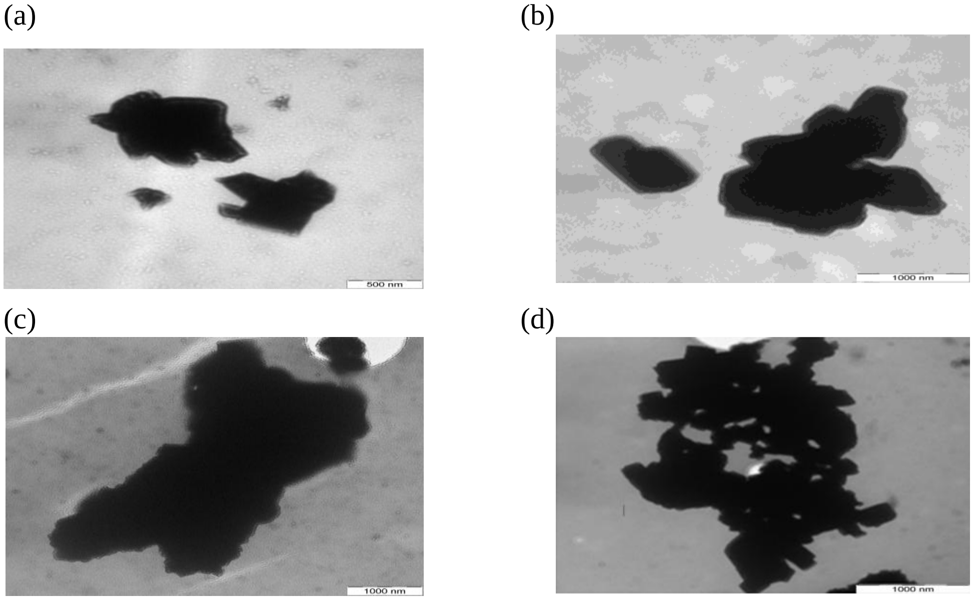


Fig.3: TEM microstructure of emulsions (a) E1, LFAMEs/SAPG:organosilicone/water (3.27/17.73:4.42/74.58); (b) E2, LFAMEs/SAPG:organosilicone/water (5.10/14.22:6.10/ 74.58); (c) E3, LFAMEs/LAPG:organosilicone/water (3.27/17.73:4.42/74.58); (d) E4, LFAMEs/LAPG:organosilicone/water (12.71/10.17:2.54/74.58).

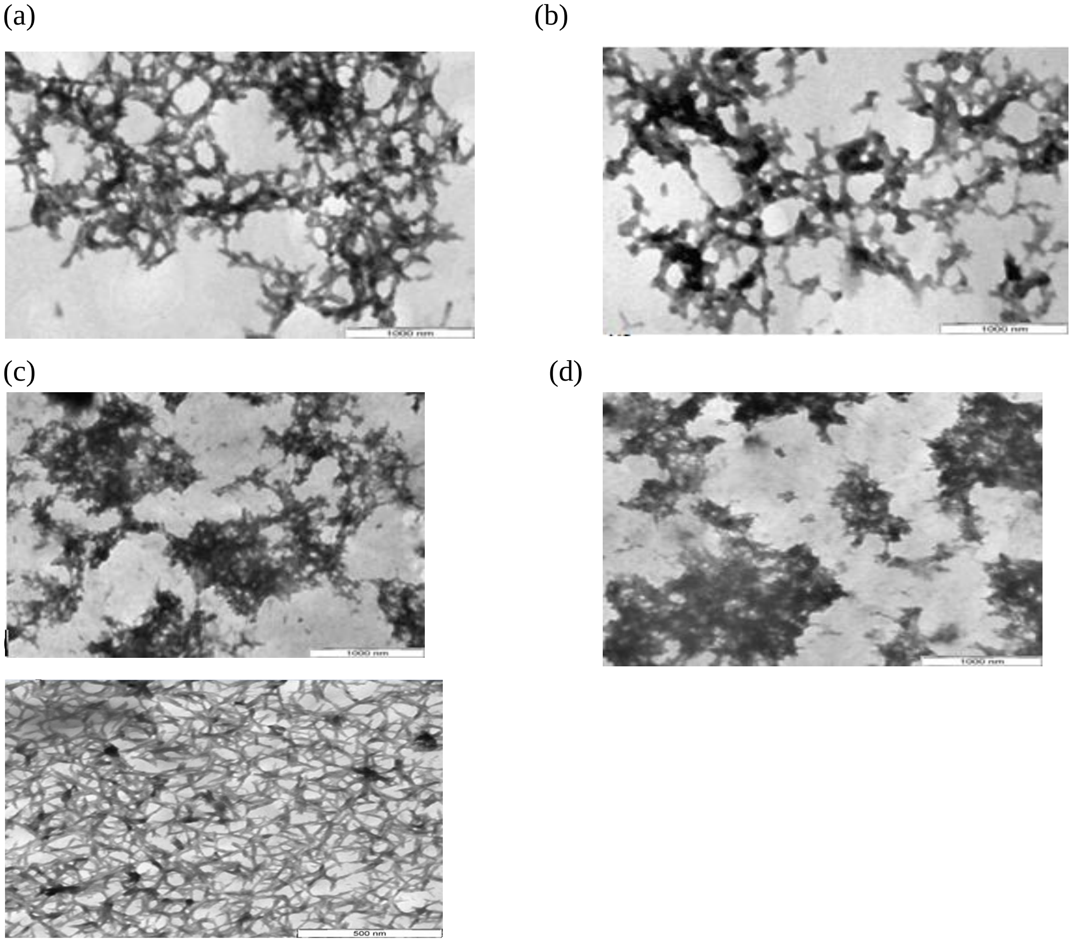


Fig.4: TEM microstructure of pre-formulation concentrates with 41% (w/w) glyphosate IPA in the emulsions (a) F1, LFAMEs/SAPG:organosilicone/water (3.27/17.73:4.42/74.58); (b) F2, LFAMEs/SAPG:organosilicone/water (5.10/14.22:6.10/74.58); (c) F3, LFAMEs/LAPG:organosilicone/water (3.27/17.73:4.42/74.58); (d) F4, LFAMEs/LAPG:organosilicone/water (12.71/10.17:2.54/74.58); (e) 41%(w/w) glyphosate IPA.

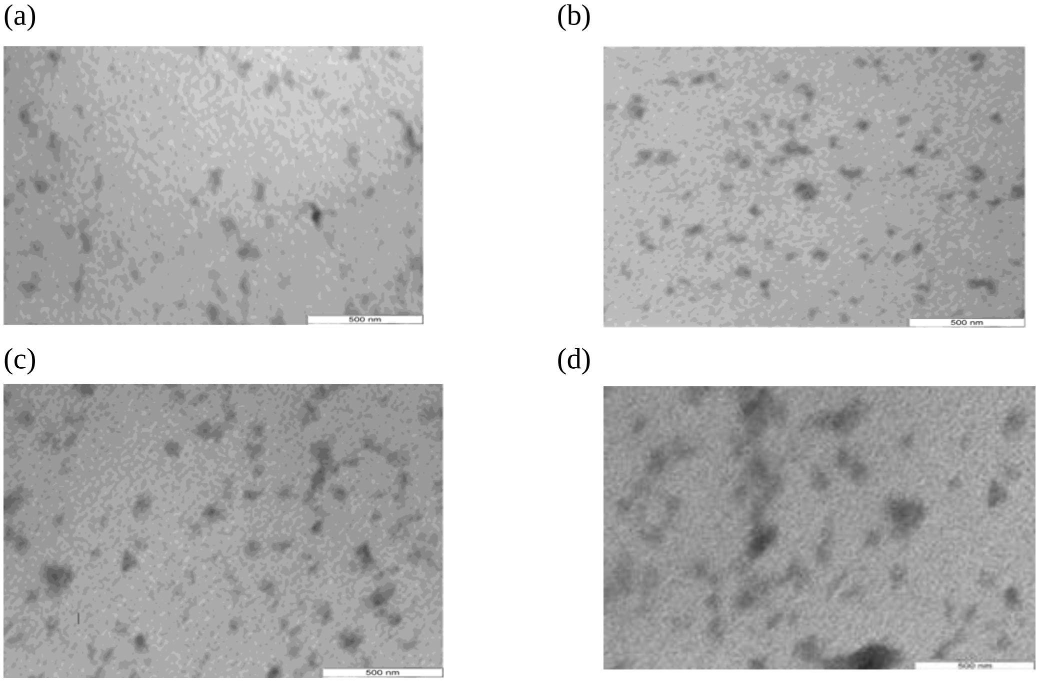


Fig.5: TEM microstructure depicting the nano pre-formulations (a) NF1, (b) NF2, (c) NF3 and (d) NF4 which were produced from dilution of F1, F2, F3 and F4, respectively with gentle stirring.

Table 1: Percentage (w/w) compositions of surfactants, oil, solvent and active ingredient in pre-formulation concentrates and emulsions

Sample (w/w)	SAPGs (surfactant)	LAPGs (surfactant)	Organosilicone (surfactant)	LFAMEs (oil)	Water (solvent)	Glyphosate IPA (active)
F1	10.46	-	2.61	1.93	44.00	41.00
F2	8.39	-	3.60	3.01	44.00	41.00
F3	-	10.46	2.61	1.93	44.00	41.00
F4	-	6.00	1.50	7.50	44.00	41.00
E1	17.73	-	4.42	3.27	74.58	-
E2	14.22	-	6.10	5.10	74.58	-
E3	-	17.73	4.42	3.27	74.58	-
E4	-	10.17	2.54	12.71	74.58	-

Table 2: The physical appearance and stability of pre-formulation concentrates in different compositions with surfactant(s) (a) SAPG; (b) SAPG:organosilicone (MSR 9:1); (c) SAPG:organosilicone (MSR 8:2); (d) SAPG:organosilicone (MSR 7:3); (e) SAPG:organosilicone (MSR 6:4)

(a)

Water	SAPG + LFAMEs	Surfactant-oil ratio (SOR)					
(w/w)	(w/w)	10:0	9:1	8:2	7:3	6:4	5:5
10	90	✓	✗	✗	✗	✗	✗
20	80	✓	✗	✗	✗	✗	✗
30	70	✓	✗	✗	✗	✗	✗
40	60	✓	✗	✗	✗	✗	✗
50	50	✓	✗	✗	✗	✗	✗
60	40	✓	✗	✗	✗	✗	✗
70	30	✓	✗	✗	✗	✗	✗
80	20	✓	✗	✗	✗	✗	✗
90	10	✓	✗	✗	✗	✗	✗
99	1	✓	✗	✗	✗	✗	✗

✓ = Stable pre-formulation; ✗ = Pre-formulation with phase separation. *All pre-formulations consisted of 41% (w/w) glyphosate IPA.

(b)

Water	SAPG:O (9:1) + LFAMEs	Surfactant-oil ratio (SOR)					
(w/w)	(w/w)	10:0	9:1	8:2	7:3	6:4	5:5
10	90	✓	✗	✗	✗	✗	✗
20	80	✓	✗	✗	✗	✗	✗
30	70	✓	✗	✗	✗	✗	✗
40	60	✓	✗	✗	✗	✗	✗
50	50	✓	✗	✗	✗	✗	✗
60	40	✓	✗	✗	✗	✗	✗
70	30	✓	✗	✗	✗	✗	✗
80	20	✓	✗	✗	✗	✗	✗
90	10	✓	✗	✗	✗	✗	✗
99	1	✓	✗	✗	✗	✗	✗

✓ = Stable pre-formulation; ✗ = Pre-formulation with phase separation. *All pre-formulations consisted of 41% (w/w) glyphosate IPA.

(c)

Water	SAPG:O (8:2) + LFAMEs	Surfactant-oil ratio (SOR)					
(w/w)	(w/w)	10:0	9:1	8:2	7:3	6:4	5:5
10	90	✓	✓	✗	✗	✗	✗
20	80	✓	✓	✗	✗	✗	✗
30	70	✓	✓	✗	✗	✗	✗
40	60	✓	✓	✗	✗	✗	✗
50	50	✓	✓	✗	✗	✗	✗
60	40	✓	✓	✗	✗	✗	✗
70	30	✓	✓	✗	✗	✗	✗
80	20	✓	✓	✗	✗	✗	✗
90	10	✓	✓	✗	✗	✗	✗
99	1	✓	✓	✗	✗	✗	✗

✓ = Stable pre-formulation; ✗ = Pre-formulation with phase separation. *All pre-formulations consisted of 41% (w/w) glyphosate IPA.

(d)

Water	SAPG:O (7:3) + LFAMEs	Surfactant-oil ratio (SOR)					
(w/w)	(w/w)	10:0	9:1	8:2	7:3	6:4	5:5
10	90	✓	✓	✗	✗	✗	✗
20	80	✓	✓	✗	✗	✗	✗
30	70	✓	✓	✓	✗	✗	✗
40	60	✓	✓	✓	✗	✗	✗
50	50	✓	✓	✓	✗	✗	✗
60	40	✓	✓	✓	✗	✗	✗
70	30	✓	✓	✓	✗	✗	✗
80	20	✓	✓	✓	✗	✗	✗
90	10	✓	✓	✓	✗	✗	✗
99	1	✓	✓	✓	✗	✗	✗

✓ = Stable pre-formulation; ✗ = Pre-formulation with phase separation. *All pre-formulations consisted of 41% (w/w) glyphosate IPA.

(e)

Water	SAPG:O (6:4) + LFAMEs	Surfactant-oil ratio (SOR)					
(w/w)	(w/w)	10:0	9:1	8:2	7:3	6:4	5:5
10	90	✓	×	×	×	×	×
20	80	✓	×	×	×	×	×
30	70	✓	×	×	×	×	×
40	60	✓	×	×	×	×	×
50	50	✓	×	×	✓	×	×
60	40	✓	×	✓	✓	×	×
70	30	✓	×	✓	✓	×	×
80	20	✓	×	×	×	×	×
90	10	✓	×	×	×	×	×
99	1	✓	×	×	×	×	×

✓ = Stable pre-formulation; × = Pre-formulation with phase separation. *All pre-formulations consisted of 41% (w/w) glyphosate IPA.

Table 3: The physical appearance and stability of pre-formulation concentrates in different compositions with surfactant(s) (a) LAPG; (b) LAPG:organosilicone (MSR 9:1); (c) LAPG:organosilicone (MSR 8:2); (d) LAPG:organosilicone (MSR 7:3)

(a)

Water	LAPG + LFAMEs	Surfactant-oil ratio (SOR)					
(w/w)	(w/w)	10:0	9:1	8:2	7:3	6:4	5:5
10	90	✓	✓	×	×	×	×
20	80	✓	✓	×	×	×	×
30	70	✓	✓	×	×	×	×
40	60	✓	✓	×	×	×	×
50	50	✓	✓	×	×	×	×
60	40	✓	✓	×	×	×	×
70	30	✓	✓	×	×	×	×
80	20	✓	✓	×	×	×	×
90	10	✓	✓	×	×	×	×
99	1	✓	✓	×	×	×	×

✓ = Stable pre-formulation; × = Pre-formulation with phase separation. *All pre-formulations consisted of 41% (w/w) glyphosate IPA.

(b)

Water	LAPG:O (9:1) + LFAMEs	Surfactant-oil ratio (SOR)					
(w/w)	(w/w)	10:0	9:1	8:2	7:3	6:4	5:5
10	90	✓	✓	✓	✓	×	×
20	80	✓	✓	✓	✓	×	×
30	70	✓	✓	✓	✓	×	×
40	60	✓	✓	✓	✓	×	×
50	50	✓	✓	✓	✓	×	×
60	40	×	✓	✓	✓	×	×
70	30	×	✓	✓	✓	×	×
80	20	×	✓	✓	✓	×	×
90	10	×	✓	✓	✓	×	×
99	1	×	✓	✓	✓	×	×

✓ = Stable pre-formulation; × = Pre-formulation with phase separation. *All pre-formulations consisted of 41% (w/w) glyphosate IPA.

(c)

Water	LAPG:O (8:2) + LFAMEs	Surfactant-oil ratio (SOR)					
(w/w)	(w/w)	10:0	9:1	8:2	7:3	6:4	5:5
10	90	×	✓	✓	✓	×	×
20	80	×	✓	✓	✓	✓	×
30	70	×	✓	✓	✓	✓	✓
40	60	×	✓	✓	✓	✓	✓
50	50	×	✓	×	✓	✓	✓
60	40	×	✓	×	✓	✓	✓
70	30	×	✓	×	×	✓	✓
80	20	×	✓	×	×	✓	✓
90	10	×	✓	×	×	✓	✓
99	1	×	✓	×	×	✓	✓

✓ = Stable pre-formulation; × = Pre-formulation with phase separation. *All pre-formulations consisted of 41% (w/w) glyphosate IPA.

(d)

Water	LAPG:O (7:3) + LFAMEs	Surfactant-oil ratio (SOR)					
(w/w)	(w/w)	10:0	9:1	8:2	7:3	6:4	5:5
10	90	✓	✓	×	×	×	×
20	80	✓	✓	×	×	×	×
30	70	✓	✓	×	×	×	×
40	60	✓	×	×	×	×	×
50	50	✓	×	×	×	×	×
60	40	✓	×	×	×	×	×
70	30	✓	×	×	×	×	×
80	20	✓	×	×	×	×	×
90	10	✓	×	×	×	×	×
99	1	✓	×	×	×	×	×

✓ = Stable pre-formulation; × = Pre-formulation with phase separation. *All pre-formulations consisted of 41% (w/w) glyphosate IPA.

Table 4: Mean particle size distribution of nano-formulations NF1, NF2, NF3 and NF4

Pre-formulation	Particle size (nm)
NF1	24.86 (±0.17)
NF2	31.94 (±1.95)
NF3	102.19 (±17.33)
NF4	112.29 (±0.56)

Table 5: Surface tension of the nano-formulations and the pesticide active, glyphosate IPA

Pre-formulation	Surface Tension (mN/m)
NF1	25.9 (±0.39)
NF2	25.6 (±0.36)
NF3	29.5 (±0.41)
NF4	28.7 (±0.37)
Glyphosate IPA	62.0 (±0.52)