Journal of Oil Palm Research Vol. 26 (4) December 2014 p. 366-374

OIL-IN-WATER EMULSION (EW) OF MIXED GLYPHOSATE ISOPROPYLAMINE (IPA) AND TRICLOPYR BUTOXYETHYLESTER (BEE) STABILISED BY PALM-BASED EMULSIFIERS FOR WEED CONTROL

ISMAIL, A R*; NOR FARHANA, N*; MAHIRAN, B; DZOLKHIFLI, O[‡] and HAZIMAH, A H***

ABSTRACT

Conventionally, an emulsifiable concentrate (EC)-triclopyr butoxyethylester (BEE) is tank-mixed with glyphosate isopropylamine (IPA) prior to spray application for the effective control of mixed weeds in plantation areas, such as oil palm and rubber plantations. However, the EC-triclopyr BEE is a petroleum-based formulation that can cause hazards to both the spray operators' health and the environment. Thus, incorporation of two herbicide actives in the oil-in-water emulsion (EW) system is a new approach to maximise the coverage of weed control and also being safe to the spray operators and the environment. The EW herbicide formulations containing two herbicide actives, i.e., *28% glyphosate IPA and 4.5% triclopyr BEE, were prepared by mixing non-ionic surfactants: DISPONIL OC 25 (or DISPONIL) and Dehydol LS 2EO (or DLS 2) with varying hydrophyl lipophyl balance (HLB) values (10, 11, 12, 13, 14 and 16.5). The oil phase used was C_{12-18} palm methyl esters (PME). The accelerated thermal stability studies at 45°C for two weeks showed that the EW formulation prepared at HLB 12±1 was the optimum formulation with particles sizes in a range of 13 -15 µm. The EW formulation showed lower surface tensions than the commercially available herbicides, such as Roundup®, Comet, and a mixture of Roundup® and Comet. In biological efficacy studies, the EW-herbicides formulation and the conventional herbicides were applied to* Paspalum conjugatum *(grassy-weed),* Asystasia gangetica *(broad leaved-weed) and* Clidemia hirta *(woody-weed) at the same dose of glyphosate IPA (615 g ai ha^{-1}) and triclopyr BEE (99 g ai ha^{-1}). The EW formulation showed comparable and/or better performance as the commercial herbicide formulations in controlling grassy, broad leaved and woody weeds.*

Keywords: emulsion in water (EW), palm-based materials, 2-in-1 herbicides, weed control.

Date received: 16 October 2013; **Sent for revision:** 31 October 2013; **Received in final form:** 7 August 2014; **Accepted:** 27 August 2014.

* Malaysian Palm Oil Board,
6 Persiaran Institusi, Bandar Baru Bangi,
43000 Kajang, Selangor, Malaysia.
E-mail: ismail@mpob.gov.my

** Chemistry Department,
Faculty of Science, Universiti Putra Malaysia,
43400 UPM Serdang, Selangor, Malaysia.

‡ Plant Protection Department,
Faculty of Agriculture, Universiti Putra Malaysia,
43400 UPM Serdang, Selangor, Malaysia.

INTRODUCTION

Triclopyr [3,5,6-trichloro-2-pyridyloxyacetic acid] is a systemic, post-emergence and selective foliar-applied herbicide used to control dicotyledonous woody and herbaceous broadleaf weeds (McMullin *et al.*, 2012). Triclopyr controls selective weeds by mimicking the plant hormone auxin that acts like indole acetic acid (Tse-Seng *et al.*, 2009). Conventionally, triclopyr is tank-mixed with glyphosate herbicide prior to spray application for the effective control of mixed weeds in plantation areas such as oil palm and rubber plantations. Glyphosate [N-(phosphonomethyl) glycine] is a systemic and non-selective foliar-applied herbicide for post-emergence control of monocotyledonous and dicotyledonous weed species (Santos *et al.*, 2007). It inhibits the biosynthesis of aromatic amino acids such as phenylalanine, tryptophan and tyrosine via the shikimate pathway by deactivation of 5-enolpyruvyl shikimate-3-phosphate synthase (EPSPS) to inhibit weed growth (Steinrucken and Amrhein, 1980; Franz *et al.*, 1997). Harrington and Miller (2005) reported that glyphosate and triclopyr possess no soil activity at the recommended dose and represent little risk when applied to non-native shrubs of *Ligustrum sinense*.

Many agrochemical industries are currently interested in formulating green environmental-friendly herbicide formulations, which offer less phytotoxicity to plants, are safer to the operator, and cost less to produce (Ismail *et al.*, 2004). The novel emulsion formulation described here containing two herbicide actives (28% glyphosate IPA and 4.5% triclopyr BEE) is a new approach to maximise the coverage of weed control and to minimise any problems to the spray operators. This oil-in-water emulsion (EW)-formulation was stabilised by mixed surfactants and palm-based solvent, which are 'green' adjuvant in the formulation. The conventional emulsifiable concentrate (EC) herbicide formulation is a solvent-based formulation comprising the mineral oil and surfactants derived from petroleum. Due to the interest in green formulations, plant-based oil such as palm fatty acid methyl esters (PFAME) is suitable to replace any petroleum-based adjuvant to improve the quality and performance of agricultural products. The oil phase in emulsion system could enhance the deposition, penetration, and translocation of the herbicides active through the waxy and cuticle layers of the leaves to reach target site of metabolic reaction (Leaper and Holloway, 2000).

Many researchers have studied and discussed the tank-mixing of two herbicide components prior to spray application. The application of quizalofop pre-mixed with broadleaf weed herbicides resulted in better weed control in sorghum (Abit *et al.*, 2011). A study conducted by Tse-Seng *et al.* (2009) found that tank-mixing of 160 g ai ha^{-1} triclopyr and 0.2 g ai ha^{-1} metsulfuron combined with 0.25% surfactant were effective for the control of *H. verticillata.* The antagonistic effects by this mixed herbicides in spray tank are rare. However, synergistic reactions were more apparent resulting in better performance for controlling weeds when herbicide mixtures were applied as spray application (Baghestani *et al.*, 2008). Therefore, the development and physico-chemical properties of EW-herbicide formulations containing glyphosate IPA and triclopyr BEE are discussed. Their biological efficacy are also evaluated on grassy-weed *P. conjugatum,* broadleaved-weed *A. gangetica* and woody-weed *C. hirta*. The performance and efficacy of the palm-based EW-herbicide formulation is compared with the commercially available herbicides towards target weeds.

MATERIALS AND METHODS

Materials

Technical grade of glyphosate IPA 62% and triclopyr BEE 98% were gifts from Hextar Chemicals (M) Sdn Bhd. Non-ionic surfactants of fatty alcohol ethoxylates, DISPONIL (HLB 16.5) and DLS2 (HLB 7.3) and PFAME were supplied by Emery Oleochemicals (M) Sdn Bhd and Carotech (M) Sdn Bhd. Xanthan gum from *Xanthomonas campestris* was supplied by Sigma-Aldrich. Distilled water was prepared using water distiller (FAVORIT W4L) in the laboratory.

Methods

Preparation of emulsion formulation. Emulsion formulations were prepared using high-energy emulsification method. The oil-phase of emulsion system contained the mixtures of palm fatty acid methyl esters (C_{6-8} and C_{12-18} PFAME), fatty alcohol ethoxylates (DISPONIL and DLS2) and triclopyr BEE (4.5%). The water-phase consisted of xanthan gum and distilled water as the final consumption of all the materials used in the emulsion system. Mixed non-ionic surfactants of DISPONIL and DLS2 were prepared according to the calculation of HLB_{mix} as expressed by the Equation (1) proposed by Griffin (1949) (*Table 1*).

$$HLB_{mix} = W_A HLB_A + W_B HLB_B; \quad W_A + W_B = 1g \qquad (1)$$

HLB_{mix}, HLB_A, HLB_B, W_A and W_B are defined as hydropyl-lipopyl balance value of mixed surfactants, surfactant A, surfactant B, and weight of surfactant A and surfactant B, respectively.

Equation (1) is strictly applicable to a combination of non-ionic surfactants used in an emulsion system. All the materials were weighed by using analytical balance (Model: HM-300, Japan). The water-phase was then added slowly to the oil-phase under high shear homogeniser (Model: Polytron PT 3100, Kinematica) at 6000 – 7000 rpm. Then, herbicide active glyphosate IPA (28%) was added slowly to the emulsion system with increasing speed up to 9000 rpm at 52°C as control temperature for 30 min.

TABLE 1. PERCENTAGE (W/W) COMPOSITIONS OF (A) 3% (W/W) AND (B) 5% (W/W) SURFACTANT(S) CONCENTRATION, OIL, SOLVENT, THICKENER AND HERBICIDE ACTIVES CONTAINED IN EMULSION FORMULATIONS PREPARED AT DIFFERENT HLB VALUE

(a)

Sample	DISPONIL	DLS2	HLB_{mix}	PFAME (SPFAME + LPFAME)	Water (solvent)	Xanthan gum (thickener)	Glyphosate IPA (active)	Triclopyr BEE (active)
EW1	-	3	7.3	10.5	53.65	0.35	28	4.5
EW2	0.88	2.12	10	10.5	53.65	0.35	28	4.5
EW3	1.21	1.79	11	10.5	53.65	0.35	28	4.5
EW4	1.53	1.47	12	10.5	53.65	0.35	28	4.5
EW5	1.86	1.14	13	10.5	53.65	0.35	28	4.5
EW6	2.18	0.82	14	10.5	53.65	0.35	28	4.5
EW7	3	-	16.5	10.5	53.65	0.35	28	4.5

(b)

Sample	DISPONIL	DLS2	HLB_{mix}	PFAME (SPFAME + LPFAME)	Water (solvent)	Xanthan gum (thickener)	Glyphosate IPA (active)	Triclopyr BEE (active)
EW8	-	5	7.3	10.5	51.65	0.35	28	4.5
EW9	1.47	3.53	10	10.5	51.65	0.35	28	4.5
EW10	2.01	2.99	11	10.5	51.65	0.35	28	4.5
EW11	2.55	2.45	12	10.5	51.65	0.35	28	4.5
EW12	3.10	1.90	13	10.5	51.65	0.35	28	4.5
EW13	3.64	1.36	14	10.5	51.65	0.35	28	4.5
EW14	5	-	16.5	10.5	51.65	0.35	28	4.5

Characterisation and determination of stable emulsion formulation.

a. Thermal stability test

Emulsion samples were put into a white screw-cap bottle and stored in the oven at temperature 45ºC±1 for two weeks, which represent a standard evaluation for physical stability of agrochemical products for more than a year at ambient temperature (~25ºC). The samples were visually observed for unstable physical appearance such as creaming, sedimentation, oil separation and colour change.

b. Particle size distribution

The particle size distributions were measured using laser diffractometer Mastesizer 2000 equipped with a Hydrosizer 2000 module (Malvern Instruments, UK). The emulsion sample was dispersed in water at 1645 rpm until an obscuration rate reached around 17% to 19%. Then, the dispersed sample was subjected to ultrasound with 80% vibration rate for 15 s before measuring the particle size distribution of the sample. Each sample was measured for 15 s in triplicate.

c. Surface tension measurement

Surface tension of samples was measured using surface tensiometer, model KSV Sigma 70 (KSV Instrument Ltd, Finland) with the de Nuoy ring method. This method utilises the interaction of a platinum ring with the surface of the sample being tested. Prior to using, the ring was flamed to red-orange colour with a gas burner to ensure no contamination of the ring. Then, calibration was conducted using distilled water, which showed surface tension in a range of 72-73 mN m^{-1}. The measurements were conducted after the samples reached the equilibrium state. The average of three times reading were taken for each measurement of the samples.

Biological efficacy study. The biological efficacy of emulsion formulation and the conventional herbicide formulations of Roundup®, Comet and tank-mixing of Roundup® and Comet prior to spray application were carried out on grassy-weed *P. conjugatum,* broadleaved-weed *A. gangetica* and woody-weed *C. hirta* in a glasshouse at Universiti Putra Malaysia (UPM). The seeds of *P. conjugatum, A. gangetica* and *C. hirta* were sown in small pots containing a mixture of top soil, sand and peat at a ratio of 3:2:1 by weight and were watered twice per day. Weeds of seven- to eight-week old were used in the bioefficacy study of the herbicide formulations. Five replications of weeds *P. conjugatum*, *A. gangetica* and *C. hirta* for each herbicide treatments were arranged in a completely randomised design (CRD). The spray equipment used was lever-operated knapsack sprayer (Registered No. 2025702, UK) fitted with a brass fan nozzle (MB/48F) and a sprayer swath with 2 m width. The spray volume was calibrated at 450 litres ha^{-1} with spray pressure maintained at 3 bars and the flow rate measured was 2.08 litres min^{-1}. The dose of herbicide active glyphosate IPA (615 g ai ha^{-1}) and triclopyr BEE (99 g ai ha^{-1}) carried by each herbicide treatments was applied the same for all weed species. Non-treated weeds spraying with water only was used as a control treatment in this study.

a. Visual mortality evaluation

Analysis on weed control rating was expressed on a scale ranging from 0% (no visible injury) to 100% (completely dead plant) based on percent necrosis, chlorosis, wilting, browning and stunting of the weeds as compared to the control treatment (*Table 2*). The assessment on visual mortality rate for weeds *P. conjugatum, A. gangetica,* and *C. hirta* were made at 3, 7, 10 and 14 days after application (DAA) for each herbicide treatment application on the weed species.

TABLE 2. VISUAL WEED CONTROL RATING THROUGH THE CLASSIFICATION EVALUATION ON WEED SYMPTOMS APPEARANCE

Weed control ratings (%)	Symptoms
0	No symptoms
10-30	Insignificant to poor weed control; little or no defoliation
40-60	Inadequate weed control; moderately severe symptoms; less than 70% defoliated
70	Adequate weed control; severe symptoms; all leaves chlorotic or more than 70% defoliated
80	Good weed control; very severe symptoms; 80% defoliated
90	Excellent weed control; very severe symptoms; 90% defoliated
100	Complete control; no sign of life

Source: Motooka (1999).

b. Statistical analysis

All collected data for visual mortality evaluation were analysed by using the analysis of variance (ANOVA) followed by Duncan's Multiple Range Test (DMRT) to identify the statistical significant differences among treatments. The homogenous group within the means was identified using Statistical Analysis System (SAS) at 5% probability level ($P \leq 0.05$).

RESULTS AND DISCUSSION

Stability Study and Physico-chemical Characterisations

Stability study and physico-chemical characterisations of emulsion formulations were carried out through thermal stability study, particle size analysis and surface tension measurement. The selected emulsion formulation showed optimum results from the characterisation studies.

Thermal stability study. The physical stability study of emulsion formulations stored at ambient temperature (~25ºC) and 45ºC for three months and two weeks, respectively is shown in *Table 3*. At 3% (w/w) concentration of single or mixed surfactants system for formulations EW1, EW2, EW3, EW4, EW5, EW6 and EW7, the phase separation of emulsions was visually observed at ambient temperature (RT) and 45ºC storage condition. This indicated as unstable emulsion formulations due to insufficient amount of surfactants adsorbed at oil in water interface of the emulsion system. The increase in surfactant concentration to 5% (w/w) showed formulations EW9, EW10 and EW11 promoted stable single phase emulsions with milky white appearance at RT (*Figure 1*) and even at higher temperature (45ºC) storage. DISPONIL and DLS2 surfactants bearing the ethoxylate group might affect the stability of the emulsion system at higher temperature due to the ethoxylates group of the surfactants which demonstrated distinct temperature dependence (Rybinski *et al.*, 1998). At higher temperature, dehydration process occurred on the ethoxylated molecules of the surfactants. Thus, the surfactants became less polar and therefore might reduce the stability of the incorporated glyphosate IPA with the less hydrophilic emulsion system (Jiang *et al.*, 2012). In addition, Chen and Tao (2005) reported that higher temperature might increase the kinetic energy of the molecules, thus resulted in destabilisation phenomenon. Formulations EW9, EW10 and EW11 were selected for further characterisation studies on particle size analysis.

TABLE 3. THE PHYSICAL APPEARANCE AND STABILITY OF EMULSION FORMULATIONS PREPARED AT (a) 3% (w/w) AND (b) 5% (w/w) SURFACTANT(S) CONCENTRATION STORED AT 25°C (ambiant temperature) AND 45°C FOR THREE MONTHS AND TWO WEEKS, RESPECTIVELY

(a)

Formulation	HLB_{mix}	Appearance at	
		25°C	45°C
EW1	7.3	x	x
EW2	10	x	x
EW3	11	x	x
EW4	12	x	x
EW5	13	x	x
EW6	14	x	x
EW7	16.5	x	x

Note: ✔ = One-phase stable formulation; x = Formulation with phase separation.

(b)

Formulation	HLB_{mix}	Appearance at	
		25°C	45°C
EW8	7.3	x	x
EW9	10	✔	✔
EW10	11	✔	✔
EW11	12	✔	✔
EW12	13	x	x
EW13	14	x	x
EW14	16.5	x	x

Note: ✔ = One-phase stable formulation; x = Formulation with phase separation.

Particle size analysis. The particle size ageing for formulations EW9, EW10 and EW11 stored at ambient temperature (25°C) is shown in *Figure 2*. Based on the results, formulations EW9, EW10 and EW11 exhibited significant pattern in particle sizes within three months period but with different particles growth rate due to different degree of coalescence and flocculation. Upon storage, the emulsion particles tend to flocculate, then the particles coalescence could occur when the particle flocs merge together to form a larger particles (Hayati *et al*., 2007). Moreover, EW11 showed the least increase in particle size as compared to EW9 and EW10 due to the balance ratio of Disponil/ DLS2 of 1:1 (2.55% w/w: 2.45% w/w) with the assistance of xanthan gum as a polymer additive in the formulation. This condition could provide sufficient and optimum condition for stable particle sizes aging process. Due to the balance composition of Disponil and DLS2 molecules in emulsion system, equivalent strength of van der Waals forces between hydrocarbon molecules and steric repulsion forces between polyoxyethylene (POE) with water molecules occurred within formulation system (Kunieda *et al*., 2001). This phenomenon contributed to enhance stability by slowing down the degree of migration, flocculation and coalescence processes among dispersed particles (Dickinson, 2009; Jafari *et al*., 2012). Formulation EW11 was selected for surface tension measurement to compare the result with the selected conventional herbicide formulations.

Surface tension measurement. The surface tension measurement for formulation EW11 (T4) and conventional herbicide formulations of Roundup® (T1), Comet (T2) and a mixture of Roundup® and

EW8 EW9 EW10 EW11 EW12 EW13 EW14

Figure 1. Visual appearance of emulsion formulations EW8, EW9, EW10, EW11, EW12, EW13 and EW14 prepared at 5% (w/w) mixed DISPONIL and DLS2 with different HLB value for a month of storage at 25°C.

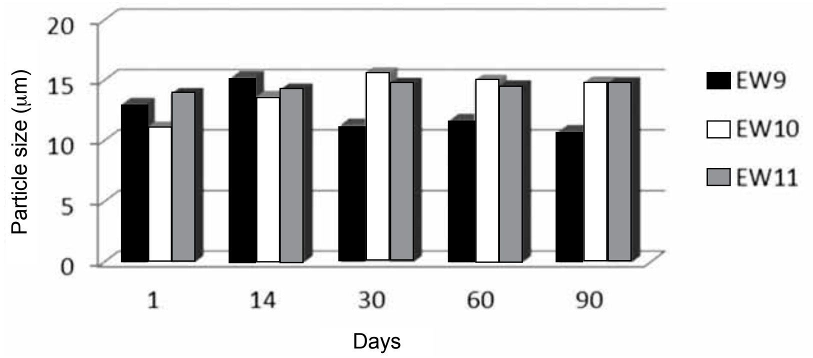


Figure 2. Particle size ageing for emulsion formulations (EW9, EW10 and EW11) over three months of storage at ambient temperature (25°C).

Comet (T3) are shown in *Table 4*. Formulation EW11 exhibited lower surface tension (33.58 mN m^{-1}) than the conventional formulations. Roundup® and Comet formulations showed similar surface tension (46.31 – 46.64 mN m^{-1}), but a mixture of Roundup® and Comet with the respective dilution rate resulted to a decrease in surface tension to 36.96 mN m^{-1}. These results indicated that combined adjuvant systems of tallow amine surfactant from Roundup® and petroleum-based adjuvants from Comet formulations contributed to the surface tension reduction. However, the performance of palm oil-based adjuvants used in formulation EW11 (with regard to surface tension) was better than a mixture of conventional adjuvants from Roundup® and Comet. Lower surface tension indicated good spreading and wetting characteristics of the emulsion droplets to be deposited on the leaf surface, thus could enhance the uptake of the herbicide actives at the intended target sites.

Visual Mortality Evaluation

The effectiveness of emulsion formulation EW11 (T4) on targeted weed species was evaluated with the conventional herbicide formulations, which included Roundup® (T1), Comet (T2) and tank-mixed of Roundup® and Comet (T3). By comparing the application of herbicide treatments with the control treatment (T5), the statistical results of weed mortality could be obtained as shown in *Figures 3a, 3b* and *3c*. The results significantly showed the pattern of increasing mortality rates for *P. conjugatum*, *A. gangetica* and *C. hirta* evaluated at 3, 7, 10 and 14 DAA. These were due to the systemic and translocation action exhibited by the glyphosate IPA and/or triclopyr BEE incorporated in herbicide formulations.

TABLE 4. SURFACE TENSION OF EMULSION FORMULATION (EW11) AND COMMERCIAL ROUNDUP®, COMET AND A MIXTURE OF ROUNDUP® AND COMET FORMULATION

Treatment	Surface Tension (mNm^{-1})
T1 (Roundup®)*	46.64 ± (0.04)
T2 (Comet)*	46.31 ± (0.59)
T3 (Roundup®+ Comet)*	36.96 ± (0.05)
T4 (EW11)	33.58 ± (0.12)

Note: * Indicate commercial herbicide formulations.

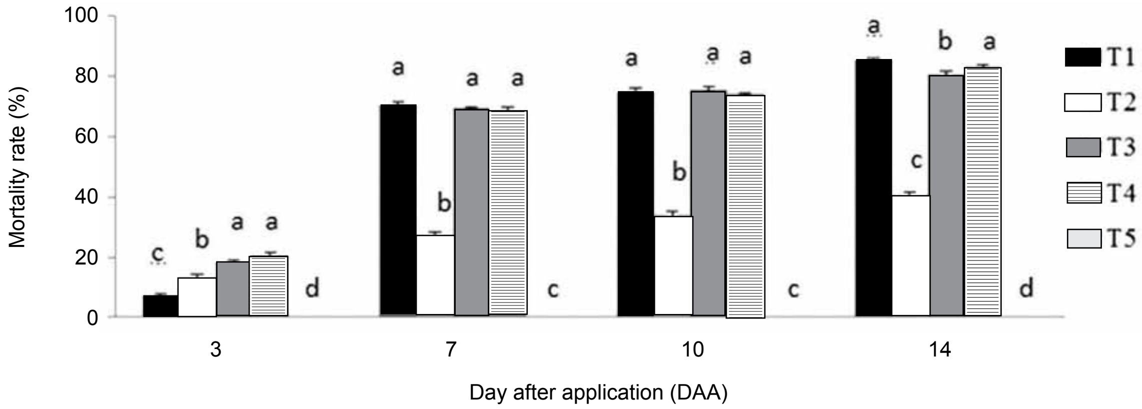
In addition, statistical analysis of weeds mortality apparently observed the role of herbicide active carried by the commercial Roundup® (glyphosate IPA) and Comet (triclopyr BEE), where glyphosate IPA was effective to control grassy-weed *P. conjugatum,* while triclopyr BEE was more prone to control those broadleaved-weed *A. gangetica* and woody-weed *C. hirta.* The emulsion formulation and tank-mixed formulation incorporated with two herbicide actives, glyphosate IPA and triclopyr BEE showed broader coverage to control various weed species.

Throughout 14 DAA, the order of mortality rates for the targeted weeds was *A. gangetica* (100%) > *P. conjugatum* (80.6% – 85.4%) > *C. hira* (73.2% – 78.4%). The differential in herbicide absorption rates was influenced by foliar structure and cuticle permeability of each weed species (Santos *et al*., 2007). The amount of epicuticular waxes for *A. gangetica* (23.03 μg cm^{-2}), *P. conjugatum* (19.59 μg cm^{-2}) and *C. hirta* (24.03 μg cm^{-2}) (Ngah *et al*., 2011) would be the initial barrier for herbicide uptake. However, the main barrier was due to the plant cuticle composing of cutin and polymer matrix (Santos *et al*., 2007) where each plant contained different cuticle composition as well as cuticular waxes (Heredia and Dominguez, 2009).

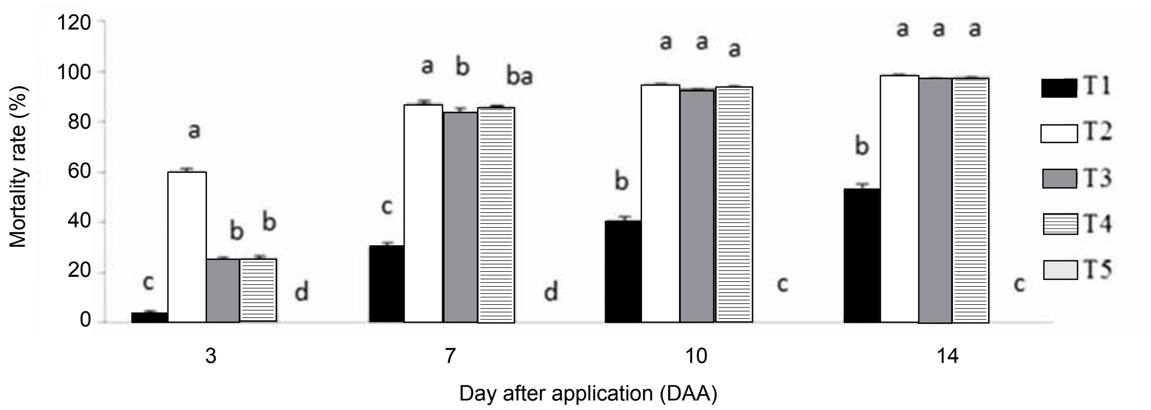
CONCLUSION

The study reported here showed that both the glyphosate IPA and triclopyr BEE could be incorporated into EW system as the novel finding in agrochemical formulation industry. Results of thermal stability study, particle size analysis

(a)



(b)



(c)

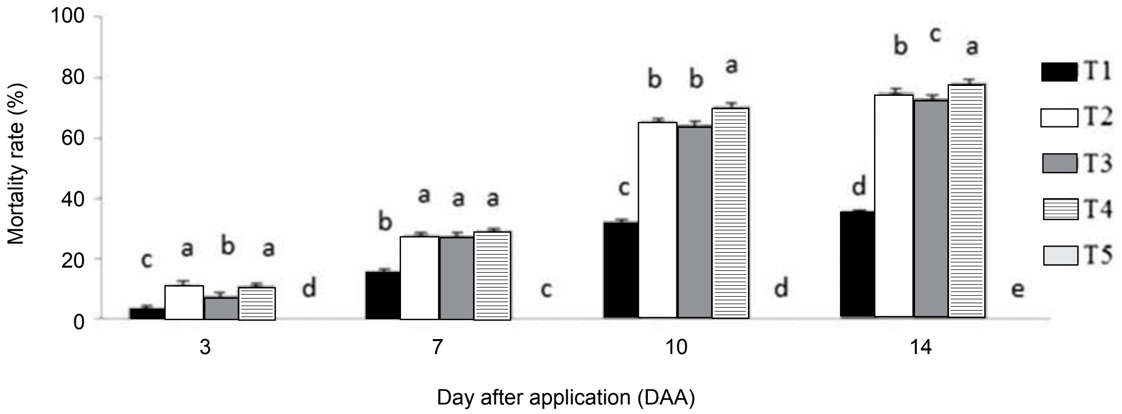
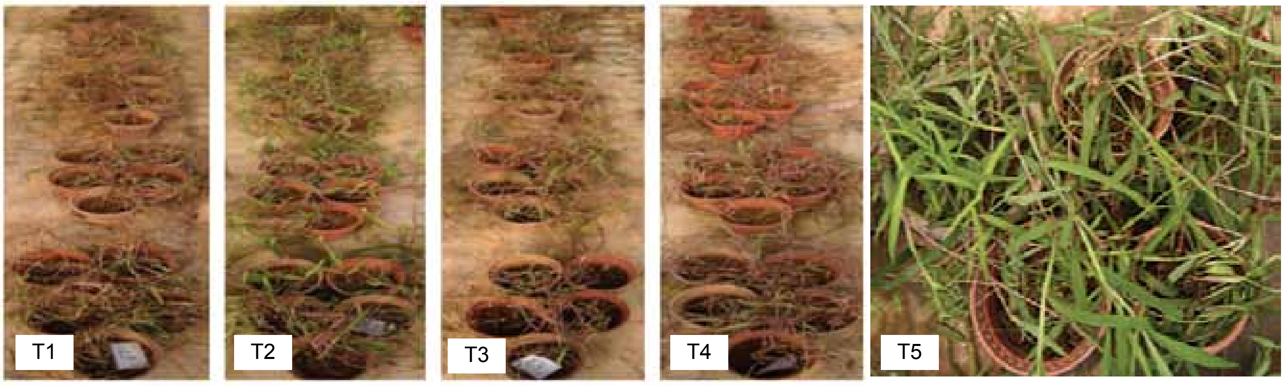
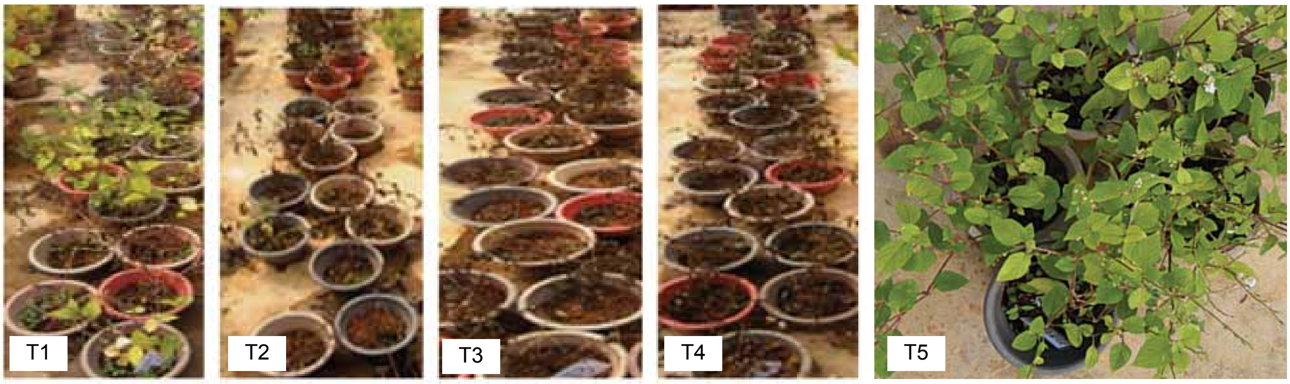


Figure 3. Mortality evaluation (%) of (a) grassy-weed P. conjugatum, *(b) broadleaved-weed* A. gangetica *and (c) woody-weed* C. hirta *at, 3, 7, 10 and 14 day after application (DAA) for each herbicide treatment applications.*



(a) T1: Roundup® T2: Comet (C) T3: R+C T4: EW11 T5: Control
(tank-mixed)



(b) T1: Roundup® T2: Comet (C) T3: R+C T4: EW11 T5: Control
(tank-mixed)

(c) T1: Roundup® T2: Comet (C) T3: R+C T4: EW11 T5: Control
(tank-mixed)

Figure 4. Visual weed mortality observation of (a) P. conjugatum, *(b)* A. gangetica *and (c)* C. hirta *at 14 DAA for each herbicide treatments (T1, T2, T3, T4 and T5).*

and surface tension measurements showed that EW formulation prepared with 5% (w/w) mixed nonionic surfactants of DISPONIL and DLS2, with HLB 12±1 resulted in the most stable emulsion formulation system. This novel emulsion-herbicide formulation exhibited comparable performance to conventional commercial herbicide formulations against grassy-weed *P. conjugatum* and broadleaved-weed *A. gangetica*, but which performed slightly better for woody-weed *C. hirta*. This novel emulsion-herbicides formulation could reduce the time and cost for application as well as helping to preserve the environment since it uses 'green' palm-based materials.

ACKNOWLEDGEMENT

The authors wish to thank MPOB for support and funding this research work. The authors wish to thank the Director-General of MPOB for permission to publish this article.

REFERENCES

ABIT, M J M; AL-KHATIB, K; OLSON, B L; STAHLMAN, P W; GEIER, P W; THOMPSON, C R; CURRIE, R S; SCHLEGEL, A J; HOLMAN, J D; HUDSON, K A; SHOUP, D E; MOECHNIG, M J; GRICHAR, W J and BEAN, B W (2011). Efficacy of post-emergence herbicides tank-mixed in aryloxyphenoxypropionate-resistant grain sorghum. *Crop Protection, 30*: 1623-1628.

BAGHESTANI, M A; Z E SOUFIZADEH; S BEHESHTIAN; M HAGHIGHI; A BARJASTEH; A BIRGANI, D G and DEIHIMFARD, R (2008). Study on the efficacy of weed control in wheat (*Triticum aestivum* L.) with tank mixtures of grass herbicides with broadleaved herbicides. *Crop Protection, 27*: 104-111.

CHEN, G and TAO, D (2005). An experimental study of stability of oil-water emulsion. *Fuel Processing Technology*, *86*: 499-508.

DICKINSON, E (2009). Hydrocolloids as emulsifiers and emulsion stabilizers. *Food Hydrocolloids, 23*: 1473-1482.

FRANZ, J E; MAO, M K and SIKORSKI, J A (1997). Glyphosate: a unique global herbicide. *ACS Monograph 189.* American Chemical Society, Washington, D C. p. 653.

GRIFFIN, W C (1949). Classification of surface-active agents by HLB. *J. Soc. Cosmet. Chem, 1*: 311-326.

HARRINGTON, T B and MILLER J H (2005). Effects of application rate, timing, and formulation of glyphosate and triclopyr on control of Chinese Privet (*Ligustrum sinense). Weed Technology, 19*: 47-54.

HAYATI, I N; MAN, Y B C; TAN, C P and AINI, I N (2007). Stability and rheology of concentrated O/W emulsions based on soybean oil/palm kernel olein blends. *Food Research International, 40*: 1051-1061.

HEREDIA, A and DOMINGUEZ, E (2009). The plant cuticle: a complex lipid barrier between the plant and the environment. An overview. *Counteraction to Chemical and Biological Terrorism in East European Countries* (C Dishovsky and A Pivovarovi eds.). p. 109-116.

ISMAIL, A R; OOI, T L and SALMIAH, A (2004). Environment friendly palm-based inert ingredient for EW-insecticide formulations. *MPOB Information Series No. 243.*

JAFARI, S M; BEHESHTI, P and ASSADPOOR, E (2012). Rheological behaviour and stability of D-limonene emulsions made by a novel hydrocolloid (Angum gum) compared with Arabic gum. *J. Food Engineering, 109*: 1-8.

JIANG, L C; BASRI, M; OMAR, D; RAHMAN, M B A; SALLEH, A B; RAHMAN, R N Z R A and SELAMAT, A (2012). Green nano-emulsion intervention for water-soluble glyphosate isopropylamine (IPA) formulations in controlling *E. indica. Pesticide Biochemistry and Physiology, 102*: 19-29.

KUNIEDA, H; KABIR, H; ARAMAKI, K and SHIGETA, K (2001). Phase behavior of mixed polyoxyethylene-type non-ionic surfactants in water. *J. Molecular Liquids, 90*: 157-166.

LEAPER, C and HOLLOWAY, P J (2000). Adjuvants and glyphosate activity. *Pest. Manag. Sci., 56*: 313-319.

McMULLIN, R T; BELL, F W and NEWMASTER, S G (2011). The effects of triclopyr and glyphosate on lichens. *Forest Ecology and Management*, *264*: 90-97.

MOTOOKA, P (1999). Summaries of herbicide trials for pasture, range and non-crop land weed control. *Weed Control.* Cooperative Extension Service, University of Hawaii, Manoa.

RYBINSKI, W V; GUCKENBIEHL, B and TESMANN, H (1998). Influence of co-surfactants on microemulsions with alkyl polyglycosides. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 142*: 333-342.

SANTOS, L D T; MEIRA, R M S A; FERREIRA, F A; ANNA-SANTOS, B F S and FERREIRA, L R (2007). Morphological responses of different eucalypt clones submitted to glyphosate drift. *Environmental and Experimental Botany, 59*: 11-20.

STEINRUCKEN, H C and AMRHEIN, N (1980). The herbicide glyphosate is a potent inhibitor of 5-enolpyruvylshikimic acid-3-phosphate synthase. *Biochemical and Biophysical Research Communications, 94*: 1207-1212.

TSE-SENG, C; KABEN, A M and THYE-SAN, C (2009). Proper adjuvant selection to enhance the activity of triclopyr combined with metsulfuron on the control of *Hedyotis verticillata. Weed Biology and Management, 9*: 179-184.