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Structure/property comparisons of chemistries based on renewable 1,3-propanediol and petroleum-derived alkylene oxides

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Summary

Structure/property comparisons were made of chemistries based on renewable 1,3-propanediol (PDO)- versus petroleum-based alkylene oxides as well as comparisons of the respective polyethers, emulsifiers, and cosmetic formulations based on these feedstocks. Green Chemistry Principles were applied in the manufacture of polyethylene glycol (PEG)-free renewable PDO-based oligomers and PDO-based fatty acid ester emulsifiers. Sustainable cosmetic products formulated with renewable PDO-based emulsifiers gave equivalent performance in sensory and moisturization evaluations compared to those formulated with the petroleum-derived PEG-based emulsifiers.

INTRODUCTION

Petroleum-based alkylene oxides, i.e., ethylene oxide (EO) (1) and propylene oxide (PO) monomers are widely used feedstocks for the production of polyethylene glycol (PEG) and polypropylene glycol (PPG) polyethers that find application in a variety of industries. PEG and PPG are useful raw materials for the production of alkoxylated fatty acid and alkoxylated fatty alcohol surfactants/emulsifiers used in the personal care industry. Some of the drawbacks of the ethoxylated nonionic surfactants include that they are petroleum based and contain residual levels of hazardous unreacted EO monomers and 1,4-dioxane by-products (2). For these reasons, there have been efforts to develop PEG-free alternatives. Examples of some of the commercially available PEG-free fatty acid esters include the polyglycerol esters, sorbitol esters, and sucrose esters (3–5). The later surfactants have found success as nonionic PEG-free alternatives in the personal care markets, although the ethoxylate-based chemistry still holds a large share of the nonionic surfactant market in personal care. There remains a need for more sustainable PEG-free nonionic surfactant

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options that perform as well as the alkylene oxide–based nonionic surfactants in cosmetic applications. In this presentation, structure/property comparisons were made of chemistries based on renewable 1,3-propanediol (PDO)- and alkylene oxide–based feedstocks as well as the respective polyethers, emulsifiers, and cosmetic formulations based on these feedstocks. Green Chemistry Principles were applied in the manufacture of sustainable PEG-free emulsifiers that were evaluated in cosmetic applications.

BIO-BASED PDO VERSUS PETROLEUM-DERIVED PEG-BASED CHEMISTRIES, STRUCTURE/PROPERTY COMPARISONS

Bio-based PDO monomer is produced from the fermentation of renewable vegetable sources in accordance with the 12 principles of Green Chemistry (6). A life cycle assessment comparison found that from cradle to gate, the production of bio-PDO consumes 40% less energy and reduces greenhouse gas emissions by more than 40% versus petroleum-based PDO or propylene glycol (7). The structure/property differences of the feedstocks used to produce the bio-based PDO monomer versus the EO and PO monomers have an impact on their safe handling and manufacturing processes (Figure 1). The PDO diol chemical structure has a greater degree of hydrogen bonding than the EO or PO and as a result has a higher boiling point (418°F)/low volatility. The bio-based PDO is made by the process of fermentation of sustainable plant-derived sugars at ambient temperatures and pressures. In contrast, the low boiling point/volatile (EO) (51°F) and PO are made under high pressures (150 psi or more) from their low-boiling ethylene and propylene petroleum-derived feedstocks, respectively. The resulting EO and PO monomers are highly reactive due to the three-membered epoxy ring structures with strained carbon–oxygen–carbon bond angles of ~60° versus the less strained PDO carbon–oxygen–hydrogen bond angles of ~110°. Engineering safety controls, including EO and PO sensors, are necessary to ensure that accidental releases of the highly flammable, toxic, and potentially explosive EO and PO are detected early and resolved. Acid-catalyzed condensation of the bio-based PDO monomer produced poly-PDO (PPDO) polyether oligomers (8,9) (Figure 1).

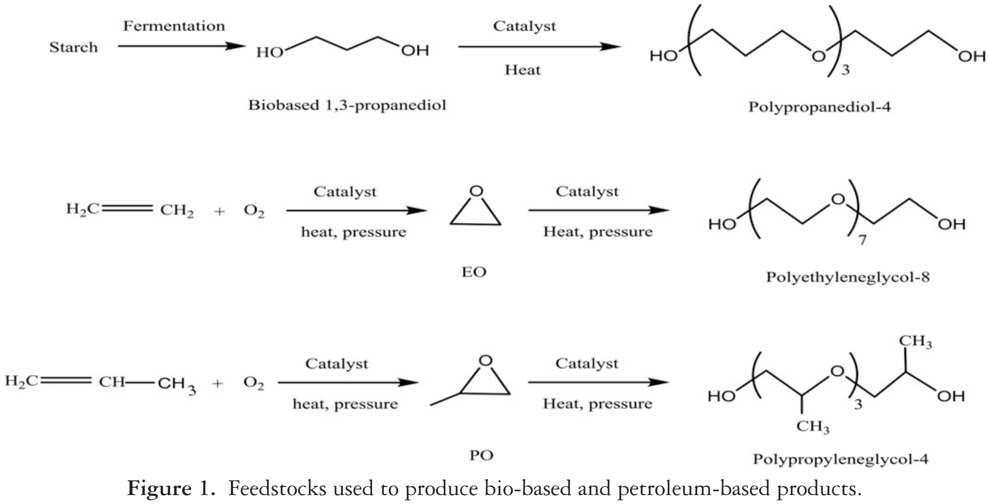


Figure 1. Feedstocks used to produce bio-based and petroleum-based products.

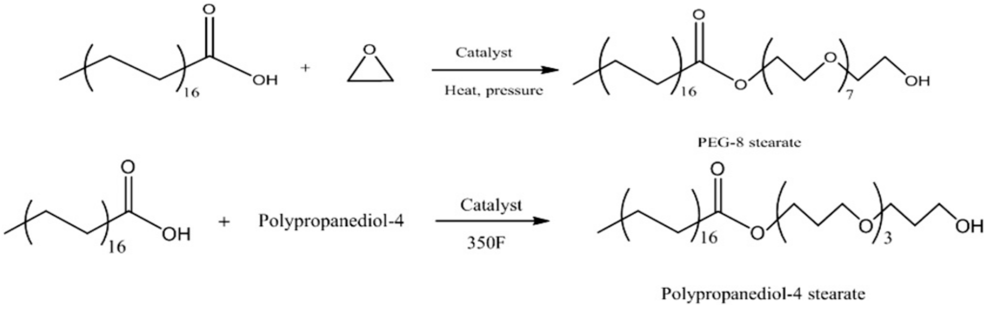


Figure 2. Fatty acid esters made from bio-based or petroleum based oligomers.

The GPC (Figure 2) analysis indicated a distribution of low-molecular-weight PDO oligomers ($M_n = 250$) with polydispersity of 1.2. The ^{13}C NMR DEPT analysis was useful in structural eluicidation by confirming methine, methylene, or methyl carbons in the spectra. The PDO oligomer structures are composed solely of methylene carbons. The PPDO oligomers were made in standard lab or plant batch reactors (heating, cooling, condenser, and agitation) at ambient pressures with no special modifications/engineering controls needed to monitor the nonhazardous PDO monomers. Accidental releases or spills of the nonhazardous bio-based PDO can also be handled safely. The polymerization of EO to the PEG polyethers results in residual amounts of EO and hazardous 1,4-dioxane by-product (dimerization to favorable six-membered ring structure). In comparison, GC analysis of the PDO oligomer product shows no 1,4-dioxane by-product since there is no synthetic route to 1,4-dioxane from the PDO monomer.

Fatty acid esters made from the bio-based PPDO oligomers (10,11) or petroleum-based PEG oligomers and plant-derived stearic acid were compared (Figure 2). The PEG-8 stearate is produced by reacting the stearic acid with EO under pressure and using engineering controls as described earlier. The PPDO-4 stearate was produced in standard lab or plant batch reactors (heating, cooling, condenser, and agitation) at ambient pressures and with no special modifications /engineering controls needed. The polyether chains, ethyl versus propyl groups in the latter PEG-8 stearate, and PPDO stearate emulsifiers resulted in HLBs of ~11.5 versus ~3 (calc), respectively. Higher HLB PDO–based fatty

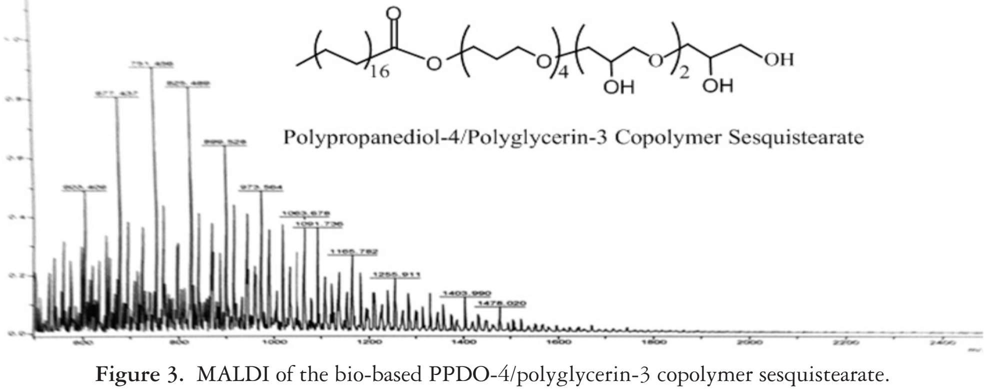


Figure 3. MALDI of the bio-based PPDO-4/polyglycerin-3 copolymer sesquistearate.

Table I
Green Chemistry Principles of PPDO-4 (Compared to PEG-8 and PPG-4)

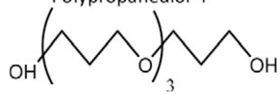
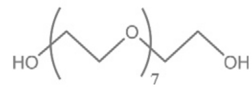
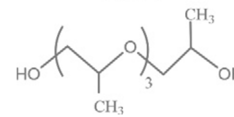
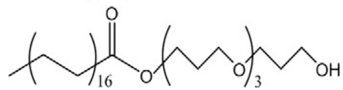
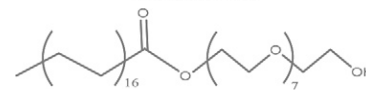
Principles of Green Chemistry	Polypropanediol-4 	PEG-8 	PPG-4 
Use of renewable feedstocks	Made from bio-based PDO (bio-based PDO made by fermentation of plant-based sugars)	Made from petroleum based EO monomer (Petroleum based EO made from oxidation of ethylene BP = -155°F, under pressure)	Made from petroleum based PO monomer (Petroleum based PO made from oxidation of propylene, BP = -54°F under pressure)
Less hazardous chemical syntheses	Nonhazardous PDO monomer feedstock PPDO EO and 1,4-dioxane free	Hazardous EO monomer PEL (8 h TWA) = 1 ppm, exposure limit PEG—Residual 1,4-dioxane, EO	Hazardous PO monomer PEL (8 h TWA) = 100 ppm, exposure limit
Inherently safer chemistry for accident prevention	BP = 418°F FP = 244°F Vapor pressure at 20 = 0.08 mmHg PDO nonvolatile, combustible	BP = 51°F FP = -20°F Vapor pressure at 20 = 1095 mmHg EO extremely flammable, explosive, toxic	BP = 93°F FP = -35°F Vapor pressure at 20 = 445 mmHg PO extremely flammable, explosive
Design for energy efficiency	Reaction of PDO at ambient pressures	Reaction of EO under pressure	Reaction of PO under pressure

Table II
Sustainability of PPDO-4 Stearate on Life Cycle (Compared to PEG-8 Stearate)

Sustainability life cycle	Polypropanediol-4 stearate 	PEG-8 stearate 
Materials acquisition	Bio-based PDO and sustainable palm derived stearic acid	Petroleum based EO monomer and stearic acid
Transportation	Shipping nonhazardous PDO	Shipping hazardous (flammable, explosive, and toxic) EO over rails and by truck through cities
Manufacturing	Safe PDO chemistry and process, reactions at ambient pressures	Hazardous EO stored under pressure, sensors required for toxic, flammable EO releases, volatile EO reacted at >50 psi pressure.
Cosmetic product	No residual EO or 1,4-dioxane	Residual EO and 1,4-dioxane
Design for degradation	Readily biodegradable (OECD-301 test) RIPT tests = did not demonstrate potential for eliciting dermal irritation or sensitization Skin irritation = nonirritant Skin corrosion = noncorrosive Ocular irritancy = nonirritant	Low biodegradability

Formulation 1. *Personal Care Emulsion Formulation (oils)*

Ingredients	%
DI water	81.45
Disodium EDTA	0.05
Glycerin	3.00
Xanthan Gum	0.25
Oil (specified in Table 3)	8.00
Lipocol SC (cetearyl alcohol)	1.50
Emulsifier 1	3.50
Emulsifier 2	1.50
Preservative	0.75
	100.00

acid ester emulsifiers were synthesized by reacting PPDO-4 oligomers with plant-derived triglycerol (base catalyzed) to give the more hydrophilic PPDO-4/GLY-3 copolymer (12). Reaction of this hydrophilic chain with stearic acid gave the higher ~10 HLB bio-based PPDO-4/polyglycerin-3 copolymer sesquistearate (Figure 3). The latter emulsifier was analyzed by mass spectrometry (MALDI), and the mass/charge data centered ~800 m/z.

SUSTAINABILITY

Bio-based PDO cosmetic ingredients led to improvements in the sustainability life cycle when compared to the petroleum-based PEG cosmetic ingredients. Table II illustrates how the initial choice of the bio-based PDO–sustainable raw material influences many steps in the sustainable life cycle.

RENEWABLE/SUSTAINABLE PDO–BASED EMULSIFIER USED IN COSMETIC PRODUCTS

Personal care oil in water emulsions using renewable PDO-based emulsifiers versus petroleum-based PEG-based emulsifiers were investigated based on their structure/properties. The petroleum-derived PEG-based emulsifier combinations were chosen based on the following. PEG-8 stearate/PEG-8 distearate were made from low-molecular-weight oligomers as were the PDO-based stearates. The steareth-20/steareth-2 combination covered a higher HLB range between the two emulsifiers than the PDO-based stearates. The POE100 monostearate/GMS combination is composed of the highest level (100 moles) of EO and is a widely used commercial emulsifier blend.

Basic personal care formulations, using 5 wt% PDO or PEG-based emulsifiers and three different oils (natural avocado, ester, and silicone), were evaluated. Emulsions with bio-based PDO emulsifiers produced higher viscosity creams compared to emulsions made with the petroleum-based PEG emulsifiers (12) (Formulation 1, Table III).

Emulsions made with the bio-based PDO emulsifiers also had better stability compared to the emulsions made with petroleum-based PEG-8 stearate/PEG-8 distearate (avocado and ester oils) and POE100 MS/GMS emulsifiers (silicone oil). Emulsions made with the

Table III
Oils in cosmetic formulations

Oil	Emulsifier 1	Emulsifier 2	Viscosity after 1 week (cP)	Stability, 1 month at 50°C
Avocado	PPDO-4 stearate	Polypropanediol-4/polyglycerin-3 copolymer sesquistearate	182,000	Passed
Avocado	PEG-8 distearate	PEG-8 stearate	9,400	Failed (after 1 week)
Avocado	Steareth-2	Steareth-20	81,000	Passed
Avocado	GMS	POE 100 MS	83,000	Passed
Caprylic/capric triglyceride	PPDO-4 stearate	Polypropanediol-4/polyglycerin-3 copolymer sesquistearate	138,000	Passed
Caprylic/capric triglyceride	PEG-8 distearate	PEG-8 stearate	18,000	Failed (after 1 week)
Caprylic/capric triglyceride	Steareth-2	Steareth-20	83,000	Passed
Caprylic/capric triglyceride	GMS	POE 100 MS	61,000	Passed
D5/ dimethicone	PPDO-4 stearate	Polypropanediol-4/polyglycerin-3 copolymer sesquistearate	224,000	Passed
D5/ dimethicone	GMS	POE 100 MS	16,000	Failed

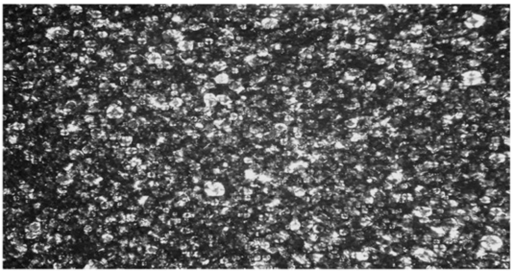


Figure 4. Liquid crystals—emulsion made with PPDO-4/ PGly-3 copolymer sesquistearate and PPDO-4 stearate emulsifiers. Under optical microscope with polarized light at 400× magnification.

bio-based PDO and petroleum-based steareth-20/steareth-2 emulsifiers passed 1-month stabilities at 50°C for all the oils tested.

The bio-based PDO emulsifiers are versatile and emulsify different types of oils including natural plant-derived oils, esters, and silicones. The emulsifying properties of the renewable PDO-based emulsifiers are enhanced by the presence of liquid crystals (Figure 4). The liquid crystals are seen as Maltese crosses (anisotropic) under the polarized light of the optical microscope. The liquid crystals typically form around the oil droplets to help further stabilize the emulsions by forming a barrier against coalescence (13).

Sensory evaluations were performed on 10 panelists using the cosmetic emulsions formulated with the renewable PDO-based and petroleum PEG–based emulsifiers (Formulation 2, Figure 5). Emulsifiers have a significant sensory influence on initial feel and spreading attributes of the product. The panelists evaluated each of the four lotions, from the initial feel on their skin (firmness and cohesiveness) to feel as the lotion was spread around on the skin (smooth, lubricious, aqueous, absorbency, tacky) and then the final feel (waxy, silky, luxurious). The sensory profile shows that the panelists gave higher ratings to the lotion formulated with renewable PDO-based emulsifiers than lotions with the petroleum PEG–based emulsifiers.

MOISTURIZATION

Skin moisturization evaluations were performed on 10 panelists (mixed male and female) using the cosmetic emulsions formulated with the renewable PDO-based and petroleum

Formulation 2. *Sensory*

Ingredients	%
DI water	84.90
Disodium EDTA	0.05
Xanthan Gum	0.25
Lipovol MOS-70	8.00
Lipocol SC (cetearyl alcohol)	1.50
Emulsifiers A,B,C, or D below	5.00
Preservative	0.30
	100.00

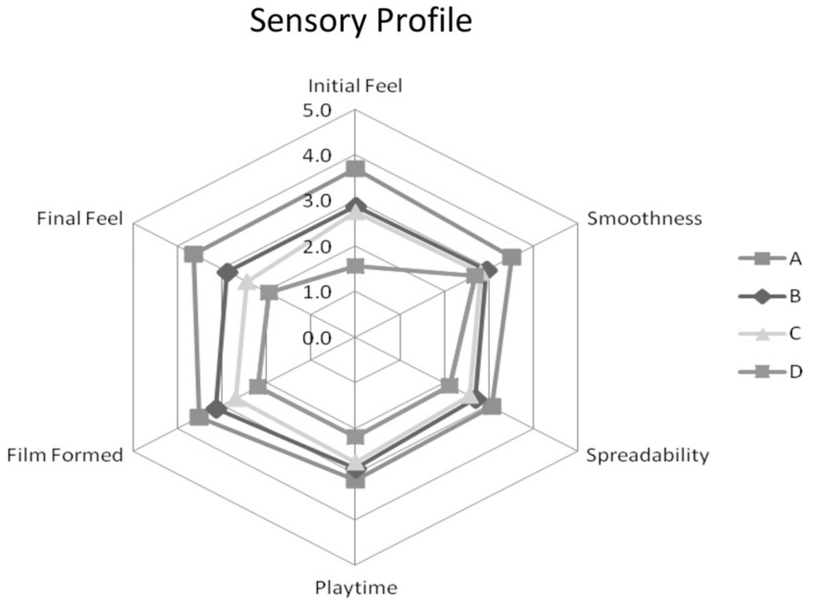


Figure 5. Sensory profile for emulsions with PPDO- or PEG-based emulsifiers. {A = polypropanediol-4/polyglycerine-3 copolymer sesquistearate (1.5 wt%) and propanediol stearate (3.5 wt%). B = PEG-100 stearate and glycerin monostearate blend (5 wt%). C = Steareth-20 (1.5 wt%) and steareth-2 (3.5 wt%). D = PEG-8 stearate (1.5 wt%) and PEG-8 distearate(3.5 wt%).}

PEG–based emulsifiers (Formulation 3, Figure 6). A Dermalab Cortex instrument was used to measure the baseline conductance of each panelist's skin initially before any lotion was applied. Then each lotion was applied to the inner forearm of the panelists only once and conductance readings were taken after 30 min, 1 h, 2 h, 3 h and 4 h. The lotion containing PDO-based emulsifiers showed immediate moisturization that was 47% higher than baseline after 30 min and 57% higher than baseline after 1 h. The lotion containing the PDO-based emulsifiers showed higher moisturization (statistically significant), at each conductance reading over the 4-h period, than the lotion formulated with the PEG-based emulsifier.

Formulation 3. *Moisturization*

Ingredients	Formulation A (%)	Formulation B (%)
DI water	81.45	81.45
Disodium EDTA	0.05	0.05
Xanthan Gum	0.25	0.25
Lipovol MOS-70	8.00	8.00
Lipocol SC (cetearyl alcohol)	1.50	1.50
Polypropanediol-4/polyglycerin-3 copolymer sesquistearate	3.50	
PPDO-4 stearate	1.50	
Lipomulse 165 emulsifier		5.00
Preservative	0.75	0.75
	100.00	100.00

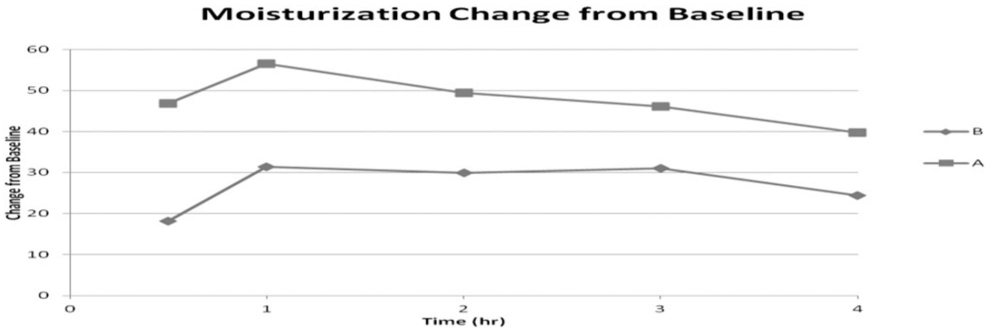


Figure 6. Moisturization change from baseline (in percent).

Longer term moisturization evaluations were performed using a total of 12 female subjects selected to participate in the evaluation of two moisturizing creams containing both the PDO-based and petroleum PEG-based emulsifier. Test material was applied twice a day for 3 days. Moisturization and subject self-assessment of product performance was evaluated 8 and 24 h after last application. Equal moisturization performance was seen between emulsions made with PDO- and petroleum PEG-based emulsifiers. There was a preference for emulsions with PDO-based emulsifiers in the subject's self-assessment evaluation. (Clinical moisturization and self-assessment studies done at Clinical Research Laboratories, LLC/Piscataway, NJ.) (Figure 7).

FORMULATIONS

Examples of a variety of emulsions made with renewable PDO-based emulsifiers (body lotion with elegant feel, soft moisturizing cream, and rich/smooth body butter) with a range of viscosities and feel on the skin are given in Formulation 4.

CONCLUSION

Structure/property comparisons were made of renewable PDO-based versus petroleum-based alkylene oxide feedstocks along with their respective polyethers, emulsifiers, and cosmetic formulations based on these feedstocks. Based on the structure/property comparisons, the renewable PDO-based chemistry offers advantages over the petroleum-based EO or PO monomers by being renewable, less reactive/can be handled at ambient pressures, nonhazardous/safer chemistry for transporting feedstocks by truck/train and in the manufacturing of cosmetic ingredients, PEG free (no residual EO, no residual 1,4-dioxane),

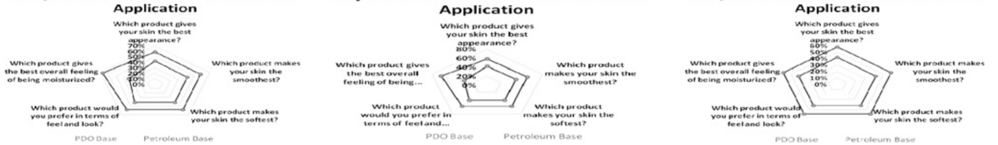


Figure 7. Self-assessment.

Formulation 4.

A. Body lotion[a]		B. Moisturizing cream[b]		C. Body butter[c]	
%	Ingredient	%	Ingredient	%	Ingredient
82.9	Water	72.0	Water	70.5	Water
0.1	Disodium EDTA	0.1	Disodium EDTA	0.1	Disodium EDTA
0.25	Xanthan gum	0.25	Xanthan gum	0.25	Xanthan gum
2.5	Glycerin	2.0	Glycerin	3.5	Glycerin
2.45	Propanediol stearate	3.5	PPDO-4 stearate	3.5	PPDO-4 stearate
1.05	PPDO-4/PGLY-3 copolymer sesquistearate	1.5	PPDO-4/PGLY-3 copolymer sesquistearate	1.5	PPDO-4/PGLY-3 copolymer sesquistearate
3.0	Persea Gratissima (Avocado) oil	2.5	Cetyl esters	3.0	Cetyl esters
4.0	Vitis Vinifera (Grape) seed oil	5.0	Cocos Nucifera (Coconut) oil	5.0	Persea Gratissima (Avocado) oil
2.0	Butyrospermum Parkii (Shea butter)	4.0	Olea Europaea (Olive) oil	4.0	Vitis Vinifera (Grape) seed oil
1.75	Cetearyl alcohol	6.0	Simmondsia Chinensis (Jojoba) oil	6.0	Mangifera Indica (Mango) seed butter
qs	Preservative	3.0	Cetearyl alcohol	3.0	Cetearyl alcohol
		0.1	Tocopherol	0.1	Tocopherol
		qs	Preservative	Qs	Preservative

[a]45,000 cps/stable 1 month at 50°C.
[b]160,000 cps/stable 1 month at 50°C.
[c]360,000 cps/stable 1month at 50°C.

and readily biodegradable. Oil in water cosmetic emulsions formulated with the PDO-based emulsifiers had higher viscosities when compared to the same emulsions that substituted PEG-based emulsifiers. Cosmetic products formulated with renewable PDO-based emulsifiers gave elegant sensory profiles and moisturization performance that were equivalent to those cosmetics formulated with petroleum-based EO emulsifiers. Principles of Green Chemistry were applied in the development and manufacture of these sustainable PDO-based emulsifiers used in cosmetics.

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