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 petroleumbased 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 carbonoxygen-carbon bond angles of ~60° versus the less strained PDO carbon-oxygen-hydrogen bond angles of $\sim 110^{\circ}$. 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.

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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 ¹³C 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.

| | Green Chemistry Principles of P | Table I PDO-4 (Compared to PEG-8 and PPG-4) | |
|---|--|--|--|
| Principles of Green Chemistry | Polypropanediol-4 | PEG-8 Ho O OH | PPG-4 Ho |
| 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 messure) |
| 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 Design for energy efficiency | BP = 418°F FP = 244°F Vapor pressure at 20 = 0.08 mmHg PDO nonvolatile, combustible Reaction of PDO at ambient pressures | BP = 51°F FP = -20°F Vapor pressure at 20 = 1095 mmHg EO extremely flammable, explosive, toxic Reaction of EO under pressure | BP = 93°F FP = -35°F Vapor pressure at 20 = 445 mmHg PO extremely flammable, explosive Reaction of PO under pressure |

| | Sustainability of PPDO-4 Stearate on Life Cycle (Compared to PE | G-8 Stearate) |
|---------------------------|---|---|
| Sustainability life cycle | Polypropanediol-4 stearate | PEG-8 stearate o |
| | A Mile A Martin and | HO LO |
| 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 |
| | | |

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Table II

| 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 |

Formulation 1. Personal Care Emulsion Formulation (oils)

acid ester emulsifiers were synthesized by reacting PPDO-4 oligomers with plantderived 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

| Emulsifier 1 | Emulsifier 2 Vi | iscosity after 1 week (cP) | Stability, 1 month at 50°C |
|----------------|---|--|--|
| DO-4 stearate | Polypropanediol-4/polyglycerin-3 copolymer sesquistearate | 182,000 | Passed |
| G-8 distearate | PEG-8 stearate | 9,400 | Failed (after 1 week) |
| eareth-2 | Steareth-20 | 81,000 | Passed |
| MS | POE 100 MS | 83,000 | Passed |
| DO-4 stearate | Polypropanediol-4/polyglycerin-3 copolymer sesquistearate | 138,000 | Passed |
| G-8 distearate | PEG-8 stearate | 18,000 | Failed (after 1 week) |
| eareth-2 | Steareth-20 | 83,000 | Passed |
| MS | POE 100 MS | 61,000 | Passed |
| DO-4 stearate | Polypropanediol-4/polyglycerin-3 copolymer sesquistearate | 224,000 | Passed |
| MS | POE 100 MS | 16,000 | Failed |
| | ämulsifier 1 DO-4 stearate G-8 distearate areth-2 MS DO-4 stearate areth-2 AS MO-4 stearate | Emulsifier 1Emulsifier 2VDO-4 stearatePolypropanediol-4/polyglycerin-3volueG-8 distearatePEG-8 stearatestearateG-8 distearatePEG-8 stearatesteareth-20ASPOE 100 MSPOI ypropanediol-4/polyglycerin-3steareth-20ASPOE 100 MSPOE 100 MSstearateG-8 distearatePolypropanediol-4/polyglycerin-3stearateG-8 distearatePOE 100 MSstearateASPOE 100 MSstearate | Imulsifier 1Emulsifier 2Viscosity after 1 week (cP)DO-4 stearatePolypropanediol-4/Polyglycerin-3182,000Copolymer sesquistearate9,400G-8 distearatePEG-8 stearate9,400areth-2Steareth-2081,000ASPOE 100 MS83,000MSPOE 100 MS83,000MSPOE 100 MS83,000ASPOE stearate138,000ASPOE stearate138,000ASPOE stearate138,000ASPOE stearate18,000ASPOE stearate18,000ASPOOlymer sesquistearate18,000ASPOE stearate18,000ASPOE stearate10,000ASPOE 100 MS61,000ASPOE 100 MS224,000ASPOE 100 MS16,000ASPOE 100 MS16,000 |

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Table III

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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.

| i offituation 5. Moista | 112411011 | |
|---|-------------------|-------------------|
| 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 |

Formulation 3. Moisturization



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 petroleumbased 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),



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| | | | Formulation 4. | | |
|---|---|-------------|--|-------------|--|
| | A. Body lotion ^a | | B. Moisturizing cream ^b | | C. Body butter ^c |
| % | Ingredient | % | Ingredient | % | Ingredient |
| 82.9 0.1 | Water Disodium EDTA | 72.0 0.1 | Water Disodium EDTA | 70.5 0.1 | Water Disodium EDTA |
| 0.25 2.5 | Xanthan gum Glycerin | 0.25 2.0 | Xanthan gum Glycerin | 0.25 3.5 | Xanthan gum Glycerin |
| 2.45 | Propanediol stearate | 3.5 | PPDO-4 stearate | 3.5 | PPDO-4 stearate |
| 1.05 3.0 | PPDO-4/PGLY-3 copolymer sesquistearate Persea Gratissima (Avocado) oil | 1.5 2.5 | PPDO-4/PGLY-3 copolymer sesquistearate Cetvl esters | 1.5 3.0 | PPDO-4/PGLY-3 copolymer sesquistearate Cetvl 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 |
| ds | Preservative | 3.0 | Cetearyl alcohol | 3.0 | Cetearyl alcohol |
| | | 0.1 | Tocopherol | 0.1 | Tocopherol |
| | | ds | Preservative | Qs | Preservative |
| ^a 45,000 ^b 160,00 '360,00 |) cps/stable 1 month at 50°C. 30 cps/stable 1 month at 50°C. 30 cps/stable 1 month at 50°C. | | | | |

Purchased for the exclusive use of nofirst nolast (unknown) From: SCC Media Library & Resource Center (library.scconline.org) and readily biodegradable. Oil in water cosmetic emulsions formulated with the PDObased 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.

REFERENCES

- (1) Ethylene Oxide, 3rd Ed. (American Chemistries Council's Ethylene Oxide/Ethylene Glycols Panel, Copyright May 2007).
- (2) Agency for Toxic Substances and Disease Registry, *Toxicological Profile for 1,4-Dioxane*. (U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA, 2012).) www.atsdr.cdc
- (3) M. Kawaguchi, M. Yamamoto, T. Nakamura, M. Yamashita, T. Kato, and T. Kato, Surface Properties of mono, di- and triglycerol monstearate monolayers spread at the air-water interface. *Langmuir*, 17, 4677– 4680 (2001).
- (4) M. Biermann, F. Lange, R. Piorr, U. Ploog, H. Rutzen, J. Schindler, and R. Schmid, "Synthesis of Surfactants," in Surfactants In Consumer Products: Theory, Technology and Application, Chapter 3 (Springer-Verlag, Berlin, Germany, 1987).
- (5) C. Le Hen-Ferrenbach, M. Beuche, and M. Roussel 054432, Cognis (2005).
- (6) P. T. Anastas and J. C. Warner, Green Chemistry Theory and Practice. (Oxford University Press, New York, 1998).
- (7) Life cycle analysis approach on Bio-PDO. Data based on DuPont Tate and Lyle Bioproducts Loudon, TN Plant.
- (8) R. A. Morris and A. V. Snider, Polymers of trimethylene glycol, US2520733 (1950).
- (9) M. A. Harmer, C. Hoffman, S. C. Jackson, E. R. Murphy, and R. Spence, Preparation of polytrimethylene ether glycol or copolymers thereof, US 8143371, B2 (March 27, 2012).
- (10) H. B. Sunkara and H. C-H. Ng, Polytrimethylene ether glycol and polytrimethylene ether ester with excellent quality, US 7323539 (January 29, 2008).
- (11) H. B. Sunkara and H. P. R. Poladi, Deodorant compositions, US 8114423 B2 (2012).
- (12) E. J. Lind, P. A. Mayer, J. A. Chase, and C. S. Fouts, Derivatives of 1,3-propanediol, WO 2016040956 A1 (2016).
- (13) T. F. Tadros, "Colloid Aspects of Cosmetic Formulations with Particular Reference to Polymeric Surfactants." Colloids and Interface science Series, in *Colloid Stability*, Vol. 4.