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"Leveraging Naturally Derived Polymeric Film Formers to Achieve Enhanced Sensory and Water Resistance in Clean Makeup Formulations"

1. Introduction

The limitation of fossil fuels has for decades spurred the development of alternatives produced from sustainable feedstock[1]. Petroleum alternatives have been steadily accumulating, not only in the form of direct replacements but in the introduction of novel chemical manifolds which were not previously explored. The availability of new materials has fostered rapid growth in the exploration of biobased alternatives, as well as previously unrealized novelties, with many commercially viable materials emerging[2].

The manufacture of the polyol 1,3-propanediol (PD) has been refined to provide a high purity raw material used extensively as a cosmetic ingredient as well as a monomer in polyester and other polymer synthesis. Poly(1,3-propanediol) (PPD) has been available on high-volume industrial scale for years, with application in poly urethanes[3], [4]. This material has found use in poly urethane synthesis and represents an important leap in production of sustainable textiles. One of the principle industrial uses of PPD has been as a biobased alternative to polytetrahydrofuran (PTHF), owing to its polyether backbone which is both flexible like PTHF and more hydrophobic than polyethylene glycol.

So far, examples of polyesters utilizing PPD remain limited and only very recently has incorporation into polyester fibers been explored[5]. Applications in personal care have seen no commercial examples and research remains nearly absent. Film formers, which require flexibility and can dominate the sensory of cosmetic[6] after dry-down, would be a suitable choice for application of PPD-based materials. In addition, they can have a significant role in sensory during and after application. Research into quantitative sensory analysis has been well covered in food science but remains more rare in cosmetic science[7], [8], [9].

In this paper, we present a 100% bio-sourced polymer film former synthesized from dimer acid and poly(1,3-propanediol), dimer acid/polypropanediol copolymer (DAPPD). The use of this unusual macromonomer incorporates polyether blocks into the backbone, resulting in performance and sensory less common in natural based cosmetic ingredients. The application in liquid lipstick is investigated in the context of water and wear resistance and DAPPD is compared to common examples of natural, silicone and petroleum derived film formers. Sensory properties are also explored through in-vitro analysis by a tribology approach utilizing artificial skin, as well as traditional tack testing and sensory panels.

2. Materials and Methods

In-vitro Water Resistance Analysis

20 mm by 75 mm strips of VitroSkin™ were cut and hydrated in a 55% humidity chamber for 16-20 hours. To each strip, approximately 40 mg of analyte product was dispensed to a tared strip fixed to a slide. The material is immediately applied and evenly distributed using a finger. Material was quickly distributed using a swirling motion, followed by several horizontal and vertical strokes over 35 seconds. Control images of all strips are taken in a lightbox capable of providing even lighting. Samples were clipped to a stand and immersed 3 cm into a 25°C 5-liter water bath stirred at 700 RPMs. After 80 minutes, samples were removed and placed onto a tray and allowed to dry in a 32% relative humidity chamber with air flow.

$$\text{\% Apparent Transfer} = \left[\frac{I_{ctrl}-I_t}{I_{ctrl}}\right] * 100\%$$

I_{ctrl} = blank background

I_t = amount of lipstick transferred using tape after water immersion

Equation 1.

To each dried strip, transparent adhesive tape was applied and held for 30 seconds with a 0.5 kg weight. The tape was removed using a quick, even stroke and placed against a piece of white paper. To control for variations in lighting, a blank portion of the tape (I_{ctrl}) was compared to the portion which contacted the formulation applied to the substrate (I_t). The transfer percentage is calculated using Equation 1. Quantitative digital analysis was performed using ImageJ. For each trial, every formulation was tested in triplicate. For trials using three challenges, these were performed immediately after the first tape pull. Cumulative results were used since each tape pull was performed on the same surface which had been fundamentally altered by the prior challenge.

Formulation of Liquid Lipstick

According to Formulation 1, ingredients 1 through 9 were mixed using a high sheer dispersion blade for 30 minutes at 80°C. Ingredients 10, 11 and 12 are then added and mixed for 10 minutes. Temperature is reduced to 50°C and ingredients 13 and 14 are added and mixed for 10 minutes. The batch is then cooled and discharged.

Mechanical Analysis on Artificial Skin

Two-sided silicone tape was cut to fit and applied to a flat plate geometry of a Netzsh rheometer. A layer of VitroSkin was applied to the other side of the tape such that the surface of the geometry was modified to represent a skin surface. A patch of VitroSkin was fixed to the lower plate to simulate skin-to-skin contact. The rheometer geometry rotation rate was increased from 0.01 s^{-1} to 100 s^{-1}, under a constant normal force of 3 newtons. Force measurements were converted to coefficients of dynamic friction according to $\mu=(3/2)F/(N*r)$, where F was the measured force over the area of the upper parallel plate, N was the fixed normal force and r was the radius of the plate. Friction measurements were found to reach an equilibrium where the response plateaued and a rate of 10 s^{-1} was used as a point of comparison.

Tack Testing

Using a texture analyzer, foundation makeup formulations were applied to a substrate and then compressed up to 40 N with a robotic arm equipped with an artificial skin modified plate geometry. The force response was measured as the arm was lifted, and the total area of the negative peak was taken as the tack response, which was used to calculate the work of adhesion.

Polymer Film Formers

Polybutene (PB), polyisobutene (PiB), hydrogenated polyisobutene (HPiB), dimer linoleyl dimer dilinoleate (DADD), methyl rosinate (ROS) and trimethylsiloxysilicate resin (TMS) were obtained from commercially available sources. Dilinoleic acid/polypropanediol copolymers were synthesized in laboratory using well established esterification techniques and discharge at various conversions based on reaction time.

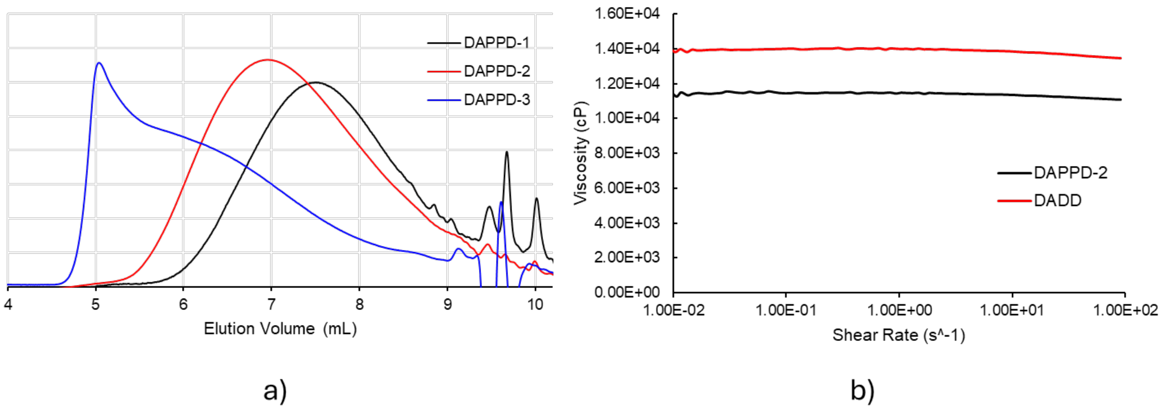


Figure 1. a) GPC traces for three different molecular weights of DAPPD polymer and b) viscometry comparison for DAPPD-2 and DADD.

3. Results

A series of polymers were synthesized from dimer acid and poly(1,3-propanediol) with different molecular weight targets. Molecular weights were achieved ranging from a few thousand daltons, up to approximately one hundred thousand daltons. A representative set was selected for evaluation in this study, DAPPD-1, DAPPD-2 and DAPPD-3 (Figure 1). For Sample DAPPD-3, the molecular weight distribution's leading tail fell above the maximum size range of the column. The high molecular weight was supported by titration of chain end functionality.

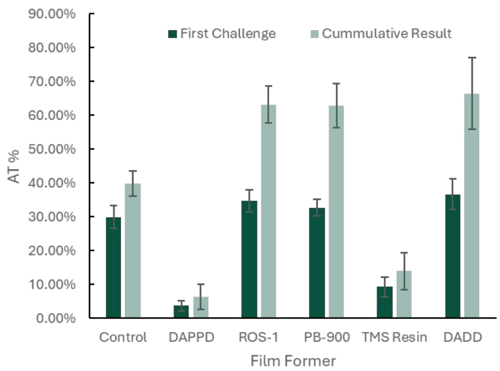
Using a spin coater and a 20 wt% solution in THF, a 25 mm x 25 mm borosilicate glass substrate was coated with DAPPD-2. The slide was evenly and completely coated with a layer of the film former, allowing contact angle to be measured by drop analysis using Image J. The contact angle was measured to be approximately 38.91 degrees, indicating a relatively hydrophilic character.

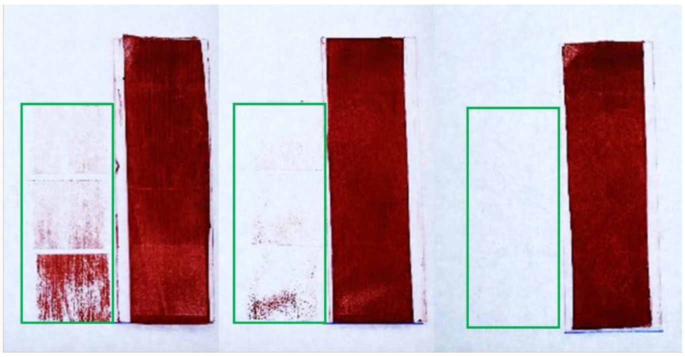
In-vitro Water and Wear Resistance

Formulations were prepared using an anhydrous liquid lip base containing 25% of a film forming ingredient. For each formulation, a different film former was selected, keeping all other parameters constant. Film formers ROS and DADD represent common 100% naturally sourced alternatives to traditional petroleum or silicone products. Selections PB-900, PB-1300, PiB and TMS Resin represent common petroleum or silicone-based ingredients with proven track records for high performance. The water resistance and transfer tests results are summarized in table 1.

Table 1. Water and transfer resistance results for film forms in a liquid lipstick formulation

Film Former	Single-pull Transfer	Cumulative Transfer	Monomers	INCI
No film former (Control)	29.80%	39.75%	-	-
DAPPD-1	4.69%	-	Polypropanediol, Dimer Acid	Dilinoleic acid/polypropanediol copolymer
DAPPD-2	3.66%	6.92%	Polypropanediol, Dimer Acid	Dilinoleic acid/polypropanediol copolymer
DAPPD-3	5.11%	-	Polypropanediol, Dimer Acid	Dilinoleic acid/polypropanediol copolymer
DADD	36.54%	66.37%	Dimer Acid, Dimer Diol	Dimer linoleyl dimer dilinoleate
PGDA	7.25%	-	Isostearic acid, Polyglycerol-3, Dimer Acid	Diisostearoyl Polyglyceryl-3 Dimer Dilinoleate (and) Caprylic/Capric Triglyceride
PB-900	32.62%	62.84%	Butene	Polybutene
PB-1300	19.41%	-	Butene	Polybutene
PiB	28.78%	-	Isobutene	Polyisobutene
HPiB	26.64%	-	Isobutene	Hydrogenated polyisobutene
TMS Resin	9.24%	13.83%	Trialkyl silane, silica, propyltrichlorosilane	Trimethylsiloxysilicate (and) Polypropylsilsesquioxane
ROS	34.7%	63.12%	-	Methyl rosinate





a) b) c) d)

Figure 2. a) Apparent percentage transfer of liquid lip formulations from artificial skin substrates after one and after 3 cumulative challenges. Images displayer the artificial skin substrates beside the transfer test tape for samples b) control, c) TMS Resin and d) DAPPD.

Comparison of apparent transfer of liquid lip formulations prepared according to Formula 1 (Table 2) are presented in Figure 2. The control formulation replaces the entire film former content with 25% CCTG. A typical high performance TMS resin had a %AT of 9.24% after the first challenge and up to 13.82% after combining the %AT of three successive tape pulls. This material is well established in the color cosmetic industry and was selected as a positive control. In comparison, the blank control formulation showed a much higher transfer at 29.80% for the first challenge and up to 39.75% total. Positive and blank results were repeated extensively to establish confidence in the method and results supported repeatability.

Polybutenes and polyisobutenes are common petroleum-based film formers which can impart flexible film forming properties due to their sticky and fluid physical characteristics. Between two different molecular weight polybutenes, PB-900 and PB-1300 at 900 Da and 1300 Da respectively, the higher molecular weight species exhibited moderately improved transfer resistance with 19.41% transfer compared to 32.62%. Commercial samples of polyisobutene and hydrogenated polyisobutene were found to exhibit similar performance at 28.78% and 26.64%.

DADD was selected for analysis since the backbone is built on dimerized linoleic acid derivatives, making it a suitable comparison to elucidate the property changes resulting from the incorporation of PPD into DAPPD. Apparent transfer was observed to be higher than that of the control on the first challenge at 36.54%. Subsequent challenges continued to extract more material from the surface, with a total cumulative apparent transfer of 66.37%. A modified rosin-based film former, ROS, was selected since it presents an example of the commonly accepted and naturally sourced small molecule materials within the industry. ROS was found to have similar performance issues to DADD in the same formulation, exhibiting 34.7% transfer for the first pull and 63.12% for the cumulative.

Evaluation of liquid lip formulations containing DAPPD materials showed similar performance between DAPPD-1, DAPPD-2 and DAPPD-3 at 4.69%, 3.66%, and 5.11% apparent transfer, respectively. DAPPD-2 appeared to have a slight edge and was therefore selected for additional trials using 3 successive challenges. Compared to the other materials, even after three pulls, the total cumulative transfer was the lowest at 6.92%.

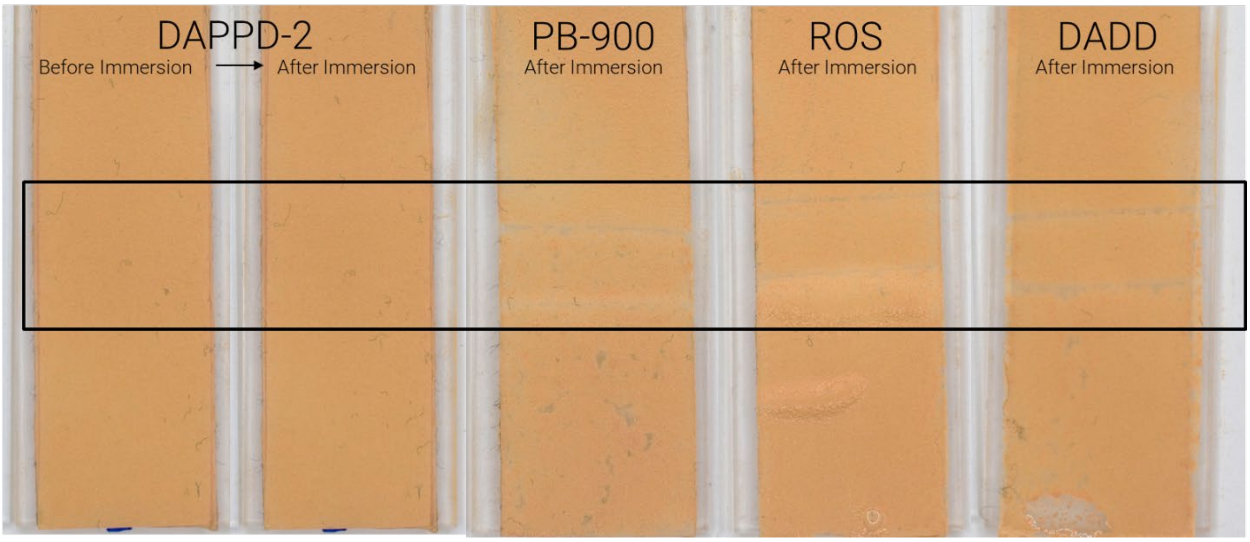


Figure 3. Artificial skin strips coated with foundation makeup containing either DAPPD-2, PB-900, ROS or DADD. For DAPPD-2 an example slide pre-water immersion is shown.

Four foundations were prepared using the same base formulation while replacing the 10 wt% film former content with one from the selection of DAPPD, DADD, ROS or TMS. Utilizing the water resistance testing method, each artificial skin sample was immersed for 80 minutes under flowing water. The results presented in Figure 3 depict a representative sample from the triplicates for each of the four film former trials. Qualitatively, it was observed that, with the exception of DAPPD, all artificial skin samples displayed obvious desorption of material on the surface. The most severe desorption occurred around the area of the air-water interface. In contrast, the foundation made with DAPPD showed minimal to no observable desorption. This was attributed to water tolerability imparted by the inclusion of PPD, which features a high density of hydrogen bond acceptors.

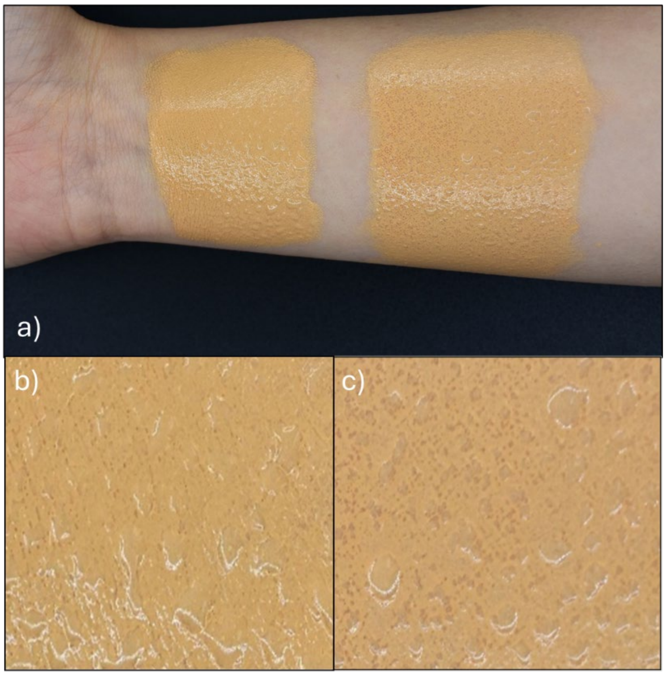


Figure 4. a) Foundations prepared with DAPPD-2 (left) and PB-900 (right) applied to skin and sprayed with water. A close-up image for the foundation with b) DAPPD-2 showing an intact film and c) for PB-900 showing a separation of the formulation on the skin surface.

A simple qualitative assessment was performed by applying a cosmetic to the skin and then spraying water directly on the dried film. The tolerance of water could be visibly assessed based on the impact on the film integrity. Comparing the foundation makeup formulation made with either DAPPD-2 or PB-900, it was observed that the latter began to retreat and leave clearly visible voids which exposed the skin beneath (Figure 4). Upon encountering water, extremely hydrophobic materials can repel the water but are also being similarly repelled. In the case where the deposited film has flowable characteristics, this can result in the loss of film integrity as a formulation gives way to allow water to contact the more suitable skin beneath.

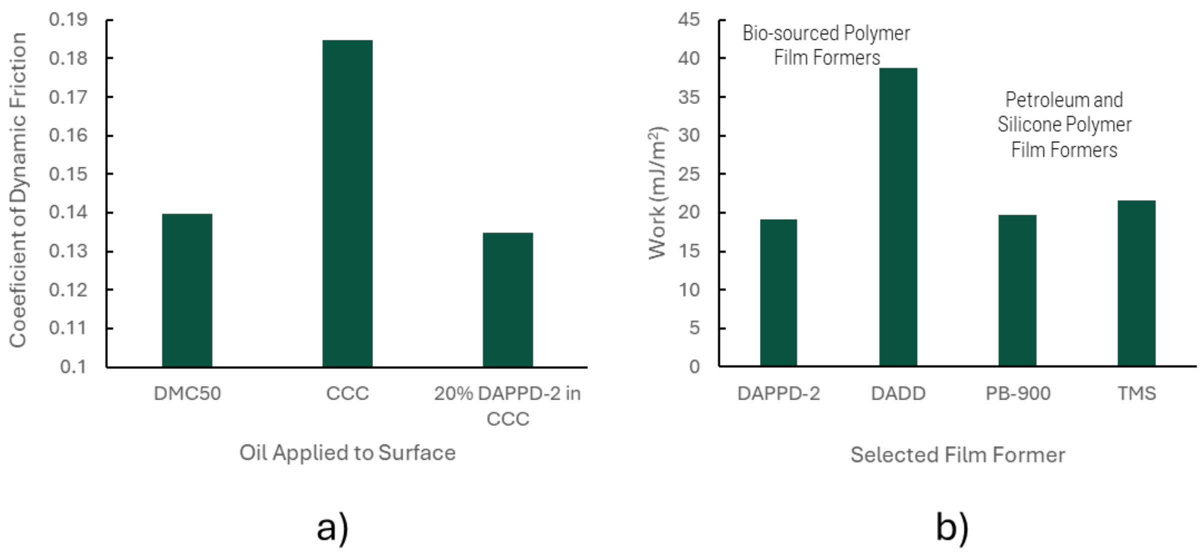


Figure 5. A) Coefficient of dynamic friction at 10 s^{-1} for artificial skin-on-skin lubricated with 50 cst dimethicone oil, coco caprylate/caprate and 20 wt% DAPPD-2 in coco caprylate/caprate. B) Tack response results for foundations with a selection of four different film forming polymers.

Mechanical Analysis

Using a customized tribology approach, a comparison of contact between two artificial skin surfaces measured contrasting friction responses between substrates coated with a 50 centistoke dimethicone oil (DMC50) and a light naturally sourced ester, coco caprylate/caprate (CCC). Silicone oils, with their low surface energy, are expected to have good slip and this was consistent with the results (Figure 5a). The DMC50 had a measured coefficient of dynamic friction of 0.1399 while the CCC coated substate was 0.1847. At 20 wt% DAPPD-2 in CCC, the coefficient dropped to 0.1348, close to the value of the slippery silicone.

A tack test was used to emulate the stickiness aspect of topical formulations by using an artificial skin substrate (Figure 5b). Foundation makeup made with a selection of 4 different film formers: DAPPD-2, DADD, PB-900 and TMS. DADD exhibited higher response at a measured 38.73 mJ/m^2 versus DAPPD-2 at 19.07 mJ/m^2. A higher force response was interpreted as a measure of overall stickiness that may be perceived by human touch. The DAPPD-1 measurement was close to that of the foundations formulated with PB or TMS.

Table 2. Formulation of liquid lip

Ingredient No.	Ingredient INCI	Formulation 1 %
1	Titanium Dioxide (pigment grade)	4.00%
2	Red Iron Oxide	4.00%
3	Russet Iron Oxide	2.00%
4	Polyhydroxystearic Acid (and) Caprylic/Capric Triglyceride (and) Isostearic Acid (and) Lecithin (and) Polyglyceryl-3 Polyricinoleate	0.50%

5	Capric/caprylic triglyceride	6.00%
6	C13-15 Alkane (Sugarcane) (and) Quaternium-90 Bentonite (and) Triethyl Citrate	12.50%
7	PTIS	5.00%
8	Saccharomyces Ferment (and) Lauroyl Lysine	5.00%
9	Mica	5.50%
10	Film Former	N
11	Beeswax	2.00%
12	Microcrystalline Wax	2.50%
13	Capric/caprylic triglyceride	25% - N
14	Isododecane	25.00%
15	Preservative	1.00%
	Total	**100%**

4. Discussion

Designing a film forming material which can interact with polar protic materials was proposed as method of countering water tolerance problems in addition to hydrophobic character. The interaction at the water-film interface could be additionally characterized by a “one-way” hydrogen bonding as the ether acts exclusively as a hydrogen bond acceptor. By enabling interaction with water, the entropic burden could be lessened and therefore prevent the spontaneous separation of semi-flowable film consisting of an oily continuous phase.

When designing cosmetic ingredients, a significant challenge is presented by the lack of well accepted standards for specialized performance properties for many common functions. In order to increase the probability of generating meaningful results, method development is crucial to create a foundation on which structure-property relationships can be formed. Refinement of the in-vitro water and transfer resistance method included the use of multiple tape pulls to remove the random variation from force distribution uniformity in the pressing process. This step gave more consistent results and revealed the susceptibility of a material to repeated instances of wear, as can be expected when consumers use a product. Adhesive tape was selected over cloth as it was found to cause greater transfer and therefore improved data resolution.

Among the liquid film forming materials PB, PiB, ROS and DADD, all showed similar or more apparent transfer than the control in Formulation 1. The accumulation of all three tape pulls revealed that these formulations were more susceptible to repeated wear as well. This may be due to the film thickness compared to the control, which used a medium chain triglyceride oil capable of penetrating further into the substrate and possibly resulting in a thinner exposed film. Meanwhile, the TMS resin was found to be capable of reducing transfer, implying greater wear resistance in line with its broadly accepted capabilities.

Surprisingly, DAPPD was found to greatly improve the transfer resistance of Formulation 1 and outperformed TMS. Among the liquid film formers tested, it was the only one which exhibited high performance on the level of the solid silicate resin. This was partially attributed to the polyether portion of the polymer backbone which is regularly distributed in an alternating pattern with the dimerized linoleic acid monomers. Between the different molecular weight species, no substantial difference in performance was observed between DAPPD-1,2 and 3. This indicated that the molecular weight was sufficient to impart film forming properties in even the lowest MW sample, DAPPD-1, and good performance can be obtained regardless of additional size tuning. This could be useful in applying the same structure to different applications where viscosity building in solution plays a role.

In film former design, a typical strategy is to focus on maximizing hydrophobicity. This can be measured using techniques such as contact angle measurement of membranes formed using the film former or for final formulations containing it. Based on the contact angle of 38.91 degrees, it can be inferred that DAPPD is hydrophilic due to the high weight percent of trimethylene glycol monomers. The strong anti-transfer and water resistance performance observed from DAPPD polymers demonstrates that alternative design strategies have the potential to deliver high performance tailored to narrow ranges of applications, such as skin-deposited cosmetic films. Further research into the mechanism of action and interaction of polyethers with polar materials could aid in creating a more ideal profile desirable for personal care products.

Mechanical analysis using an artificial skin substrate was intended to mimic individual aspects of sensory response and not intended to act as standalone measures of performance. Sensory is a complex problem to properly model and is also highly subjective. In this study, we determined that friction and tack readings indicated similar responses to materials with well accepted sensory benefits in formulation. However, there are other physical and rheological properties that would need to be accounted for if a comprehensive in-vitro evaluation were to be attempted. Previous attempts have shown promise to extract useful data in the prediction of sensory response (ref). Since data is the key ingredient of artificial intelligence (AI, further research into physical characterization methodology for human sensory modeling could be integrated into AI systems tasked with training empirical data against clinical panels.

While the above in-vitro analysis indicates several properties of this novel film former may excel over or mimic silicone or petroleum alternatives, organoleptic evaluation quickly reveals a more unique profile. A sensory panel of cosmetic consumers (n=10) ranked the foundation formulation containing DAPPD-2 as being the least greasy and tacky. Meanwhile, they ranked the body and evenness of application among the highest, close to PB-900. Another panel (n=6) was given lip balm sticks containing 10% film former and again ranked those containing DAPPD-1 as the least greasy and tacky. In contrast to PB or PiB materials, the formulations with DAPPD-1 were ranked as the least shiny as well. The interesting blend of properties in formulation may be a result of the hydrophilic nature combined with the ability to dissolve in the oil phase. The polyether portion, being a non-protic hydrophilic moiety, may be responsible for augmenting the oily phase while still taking on much of the characteristics of the other ingredients. The ability to dissolve such a material into hydrophobic phases indicates the potential to design new sensorial experiences and expand the performance range of naturally sourced cosmetic ingredients.

5. Conclusion

In this work, we present a material carrying some hydrophilic character in the form of a polyether backbone which represents a departure from the accepted practice of targeting high hydrophobicity in oil phase film formers. Despite this, the liquid film former DAPPD was observed to have highly advantageous water and transfer resistance in color cosmetic formulations. The degree of transfer resistance was found to even exceed that of TMS in formulations containing high quantities of ester, hydrocarbon and other naturally derived ingredients. Furthermore, the liquid state of the material did not appear to be a detractor to use at high concentration in formulation, whereas other liquids tended to increase transfer. The exact mechanism for the water tolerance requires further study to elucidate but empirical findings suggest a purely hydrophobic approach may not be universally ideal for topical applications.

6. References

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