The blossoming of glossy new raw materials for cosmetic use: a new family of Bio-based polyurethanes for anhydrous formulations

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Abstract

Background: Anhydrous products play a primary role in make-up, especially for the decoration of lips and eyes, where they can deliver special effects and textures able to create peculiar sensory responses. Combining and balancing the ingredients to obtain all the various forms and consistencies is a complex task; in addition, the need to achieve extreme and sophisticated performances together with high naturality uncompromisingly, in innovative cosmetic products, needs high level research, starting from the creation of unique ingredients.

Methods: The new polymers were synthesized by means of polyaddition reactions between biobased (macro)-dialcools and diisocyanates. Characterizations involved ATR-FTIR, DSC and SEC-GPC to determine their structure, thermal behavior and molecular weight, water contact angles and gloss of films, viscosity measurements and refractive index on the bulk. The compatibility with common cosmetic ingredients was studied.

Results: The versatility of polyurethane chemistry was adopted to develop unique raw materials, tuned to the need of giving improved cosmetic performances to new and sophisticated anhydrous formulations. The polyurethanes were successfully synthesized starting from agricultural by-products containing precious building blocks otherwise wasted.

In this regard, the introduction of derivates of Succinic Acid or Azelaic Acid as a macro-diols in the polymer structure was modulated together with an alkyl diol (Hydrogenated Dilinoleyl Alcohol). The new materials were used as the staple components in a challenging make-up formulation: a comfortable super-glossy lip fluid.

Conclusion: The present research represents a step towards the synthesis of biobased cosmetic ingredients with the desirable properties of adhesion and film-forming capabilities.

Keywords: bio-based polyurethanes, film-formers, high gloss fluids, chemical platforms

Introduction

The cosmetic industry is moving at a fast pace towards various sustainability goals, pushed not only by regulations (e.g. microplastics [1], D4 and D5 [2]), but also societal concerns about the ultimate fate of chemicals composing each formulation (e.g. silicones), about which compounds are used during manufacturing (e.g. ethylene oxide used for PEG derivatives), on the ethical origin (palm oil and palm oil derivatives, mica, talc), on the natural origin (renewability) of the ingredients [3], the energy consumption for manufacturing ingredients and products *et cetera*. To keep the pace, cosmetic manufacturers must follow suit by adopting a fast formulation turnover involving, mainly, the dismission of undesired ingredients and their replacement with ethical, biobased, and biodegradable counterparts, possibly with the very same performance. Reformulations are an everyday task for the cosmetic formulators, but the continuous removal of INCIs from their “artist’s palette”, put them under sustained strain.

To balance these continuous restrictions, the adoption of before-neglected ingredients and their re-evaluation as alternatives is of great value, however the process is lengthy and hardly rationalizable given that the relationship between structure and physical properties as physical properties and cosmetic properties are difficult to draw easily and the choice of alternative ingredients is often a lengthy trial and error process. Moreover, competitors can benefit from the findings since INCI lists are transparently shown on product labels and the "rediscovery" of any known compound for a new application can be readily adopted by everyone.

On the other hand, the synthesis of new ingredients has many drawbacks such as the necessity to perform all the due diligence involving the characterization, stability study, safety assessment, and ingredient registrations. However, from a point of view of advantages-disadvantages balance, the hedge over competitors is overwhelming when successful formulations are designed starting from exclusive ingredients.

In the past years, various platforms have been investigated by the Intercos laboratory to provide an exclusive set of "green" cosmetic ingredients: one of these platforms involves the creation of a whole PLGA-based "ecosystem" addressing the issues of microplastic replacement and new composite pigments [4] and the preparation of high Natural Origin Index fluids, pastes and waxes [5][6].

As the function of these new ingredients are sometimes chosen *a posteriori* depending on the outcome of an unknown synthesis, the ability of synthetic cosmetic chemists is twofold: first, to make reasonable assumptions for the design of a new ingredient starting from the experience that has been distilled over years of research; and second, developing the "taste" to recognize and properly select those products that are encountered and deemed promising over the course of a systematic set of syntheses.

In the PLGA-ecosystem, the "film former" function was lacking at the time of development of the present work and efforts were made to fill the gap accordingly. The favorite platform for research on materials with tailored film-forming and structuring properties is the one of polyurethanes since it allows the creation of chemical structures by choosing the co-monomers: diisocyanates with rigid or flexible structures (Isophorone Diisocyanate, IPDI, or Hexamethylene Diisocyanate, HDI), diols or macro-diols and their relative amount, and of course overall stoichiometry dictating final molecular weight. [7]. Also, the solvent chosen as a synthesis medium plays a role: it must be a cosmetically accepted ingredient, compatible with both starting monomers and the end-product to ensure a stable mixture. The present work is thus related to the research on new polyurethane polymers starting from commercially available bio-based diols and/or macro-diols to obtain linear structures.

From previous research experience [7][8][9], structures containing Di-C12-13 Alkyl Tartrate and Hydrogenated Dilinoleyl Alcohol (Figure 1) and HDI and/or IPDI display convenient properties of film-forming, hydrophobicity, adhesion to skin and water-proof. However, C12-13-Alkyl Tartrate as the main monomeric diol has the drawback of a fully synthetic origin, and biobased counterparts are not yet commercially available. Moreover, Isododecane used as a solvent has a petrochemical origin, likewise HDI and IPDI diisocyanates.

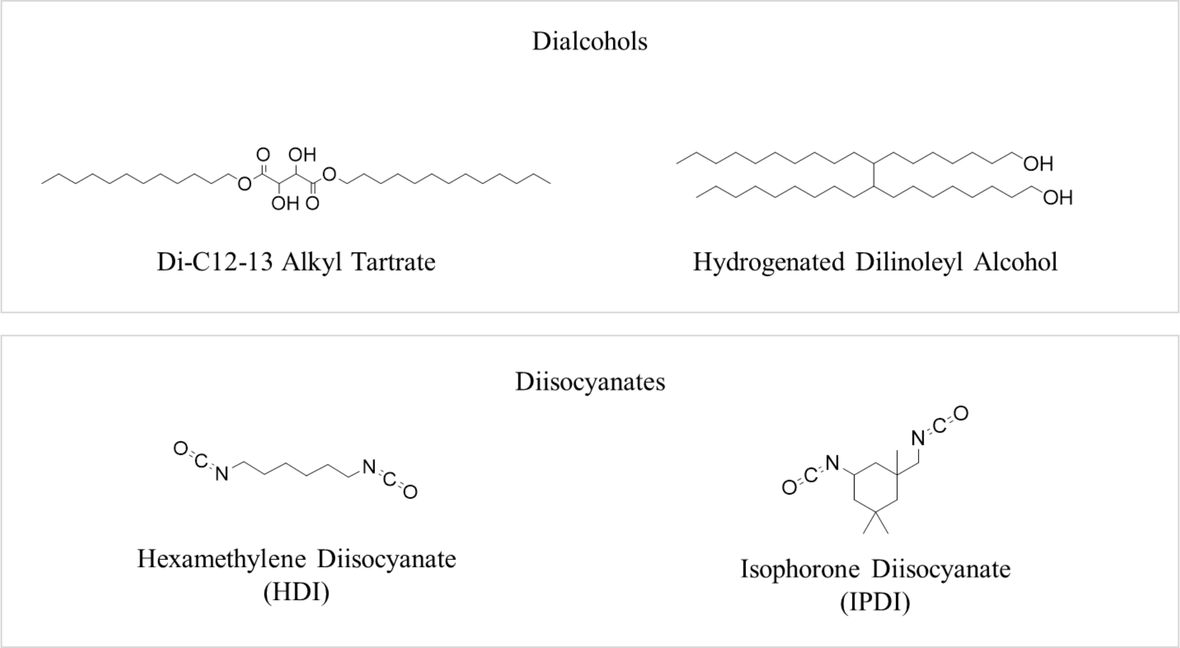


Figure 1 – Main building blocks used for the synthesis of cosmetic film forming polyurethanes [7][8][9]. Only Hydrogenated Dilinoleyl Alcohol is bio-derived

It is necessary then to redesign the synthesis, by selecting a different set of diols to complement Hydrogenated Dilinoleyl Alcohol (which is already derived from linseed oil) and displaying similar functionalities and aliphatic branching, offering an overall “comb-like” structure associated with adhesion and skin affinity. Given that HDI and IPDI monomers are a necessary compromise with respect to their origin, and waiting for other synthetic routes to become industrially viable [10], together with partially bioderived di-isocyanates or tri-isocyanates [11], one of the strategy to reduce the impact of the diisocyanate monomers in the synthesis and this can be achieved by employing macrodiols built on different chemistries, such as polyester structure. Finally, the solvent must be virtually substituted by a bio-derived volatile alkane or a substantive synthetic medium of suitable compatibility with precursors and the end-product.

Among the readily available building blocks that are vegetable-derived we can find glycerin, fatty acids and Succinic Acid (or Azelaic Acid) that, if combined in proper amounts balancing mono-, di-, and tri-functional complementary reactive moieties, can be polymerized into linear polyesters of high molecular weight and residual OH groups, able to undergo diisocyanate addition and chain extension. The introduction of the carbamate group in the backbone will provide additional hydrogen bonding sites that promote the molecular interactions among polymer molecules and with the epidermal substrate.

Materials and Methods

In a typical synthesis of the biobased polyurethanes, Coco-Caprylate/Caprate (BASF, Germany) was used as a vegetable-derived, cosmetically acceptable solvent. Hydrogenated Dilinoleyl Alcohol (Croda Italiana, Italy), Caprylic/Capric/Succinic Triglyceride (Domus Chemicals SPA, Italy) or Caprylic/Capric/Azelaic Triglyceride (proposed INCI, Domus Chemicals SPA, Italy) were dissolved in the medium and Isophorone Diisocyanate (Sigma Aldrich, Italy) was added to the mixture in the presence of a catalytic amount of Zn-Octanoate (OMG Borchers, Germany) at 80-110°C. The mixture is reacted until the complete conversion of the isocyanate groups into carbamate. A small aliquot of Ethanol was used as an end-capping agent to stop the synthesis and quench any unreacted isocyanates and removed under vacuum before cooling and discharge. The product was characterized by means of ATR-FTIR Spectroscopy (PerkinElmer Spectrum 100), Size Exclusion Gel Permeation Chromatography (SEC-GPC) using THF as solvent (Carlo Erba, Italy) and polystyrene columns as stationary phase (Perkin Elmer Series 200 GPC System), Differential Scanning Calorimetry was performed using in aluminum pans, under air in a thermal cycle scanning from 25°C to 140°C to -20°C to 140°C at heating/cooling rates of 5°C/min on mg-sized samples (DSC unity Q2000 with Autosampler TA Instrument). Refractive Index was measured at 25°C using Refractometer RE40 (Mettler Toledo). Water contact angles were measured using Attension Theta optical tensiometer (Biolin Scientific). Gloss measurements were performed using a statistical Glossmeter (Elcometer 407).

Results

The choice of the macro-diol polyester fell on a commercially available product completely derived from renewable resources (Caprylic/Capric/Succinic Triglyceride) with residual hydroxyl functionalities (ca. 170-190 mgKOH/g) and a GPC molecular weight M_w above 1000 Da. While short fatty acids and glycerin can be sourced from vegetable oils, Succinic Acid is conveniently derived from grapes by fermentation. Since polycondensation reaction is allowed as a synthetic tool for synthetic Natural Origin ingredients [3], the intermediate proved extremely appropriate for the scope of the project.

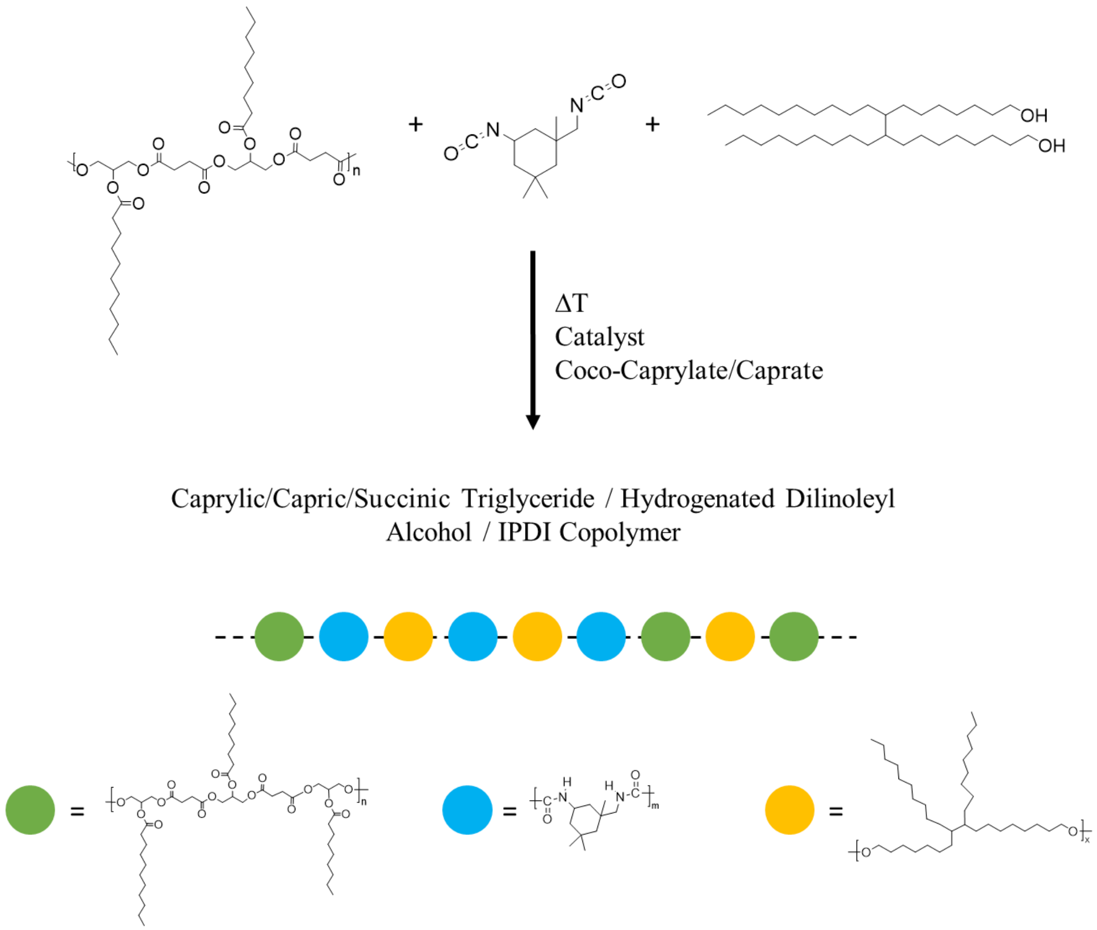


Figure 2 – Reaction scheme of the new biobased polyurethane family

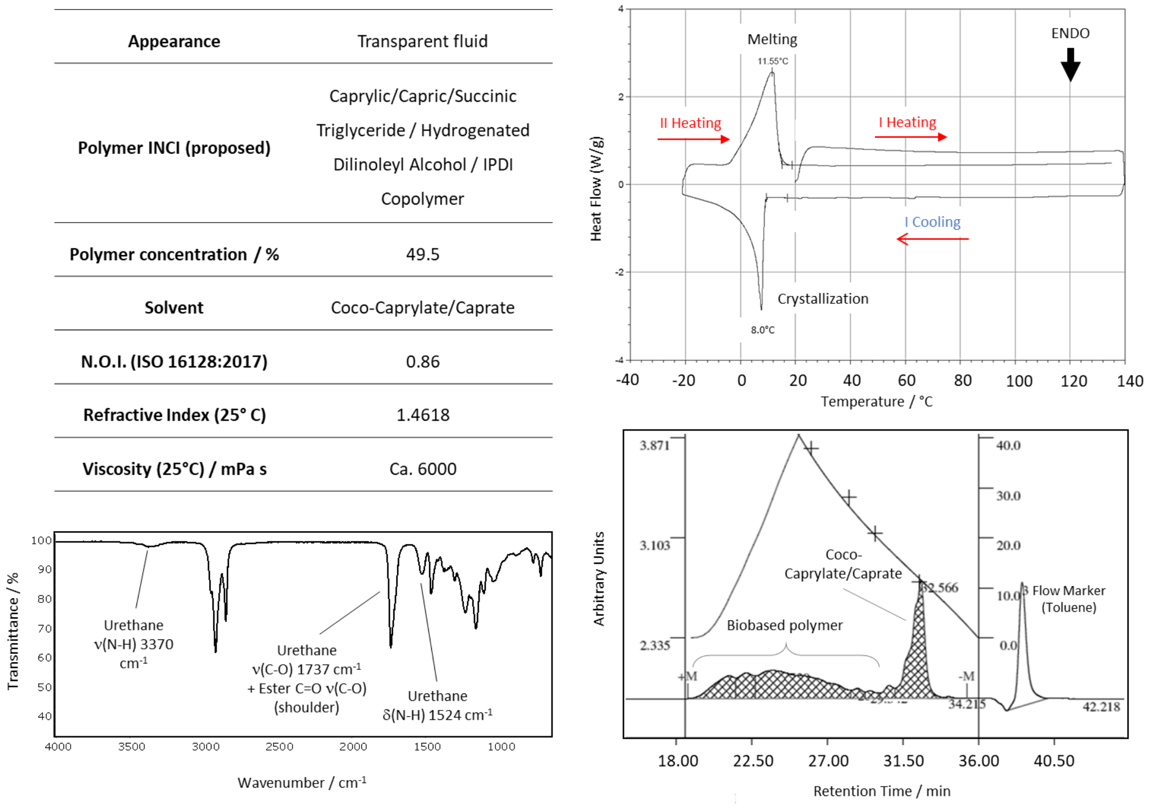
The polyurethane synthesis was performed at various content of Hydrogenated Dilinoleyl Alcohol, from 0 to 100% eqOH. Since reacting HDI with Hydrogenated Dilinoleyl

Alcohol is known to yield polymers with oil gelling properties [7]; IPDI was selected as building block for its tendency to form liquid polymers with the same diol (Figure 2).

Reaction stoichiometry between overall hydroxyl and isocyanate group was adjusted to obtain a range of molecular weights and ultimately various viscosities. Lastly, the concentration of polymeric material in the reaction medium (Coco-Caprylate/Caprate) was maintained constant (50%wt) to draw comparisons and allow the interpretation of synthetic conditions.

The disappearance of NCO signal in the IR spectrum of the reaction mixture and the appearance of the peaks associated to the urethane group demonstrates the conversion of isocyanates and the formation of the expected polyurethane. GPC molecular weights showed highly polydisperse polymers with average molecular weight M_w ranging from 10 to 100 kDa. The polymer obtained was named, after analogy with existing INCIs, with the tentative Caprylic/Capric/Succinic Triglyceride / Hydrogenated Dilinoleyl Alcohol / IPDI Copolymer name.

Among the products synthesized, a transparent, though slightly hazy, dispersion having a room temperature viscosity of around 6000 mPa s and strikingly glossy appearance was selected as a candidate to fill the portfolio gap of a bio-based glossy polyurethane film former, and therefore studied (Figure 3). The combination of medium body and a refractive index of n_D~1.46 gave a material able to produce films with a good setting and thickness, displaying smooth self-leveling surface with remarkable specular reflection. The gloss of the films of the polyurethane dispersion, as spread with a controlled thickness automatic spreader (thickness: 100 μm) equals 105 GU. The molecular weight distribution curve of the material spans several orders of magnitudes (1000 kDa < M_w < 1 kDa) with a high polydispersity index and average M_w of around 60 kDa. DSC analysis on Caprylic/Capric/Succinic Triglyceride / Hydrogenated Dilinoleyl Alcohol / IPDI Copolymer in Coco-Caprylate/Caprate shows that the mixture undergoes crystallization and melting associated with the solvent: this observation gives a hint on possible instabilities arising from freeze-thaw during the storage of the ingredient. However, the ingredient itself proved to be stable at the organoleptic and chemical-physical level for over 12 months at 5, 25 and 50°C ensuring that no separation occurs even during prolonged storage at low temperature.



Appearance	Transparent fluid
Polymer INCI (proposed)	Caprylic/Capric/Succinic Triglyceride / Hydrogenated Dilinoleyl Alcohol / IPDI Copolymer
Polymer concentration / %	49.5
Solvent	Coco-Caprylate/Caprate
N.O.I. (ISO 16128:2017)	0.86
Refractive Index (25° C)	1.4618
Viscosity (25°C) / mPa s	Ca. 6000

Figure 3 – Top left: characteristics of the new biobased polyurethane. Low left: ATR-FTIR spectrum. Top right: DSC thermogram. Low right: GPC chromatogram.

The compatibility between the newly synthesized structure and common cosmetic oils (Table 1) was investigated and evidenced how the ingredient has good miscibility with polar esters and fatty alcohols at a 1:1 ratio, however when mixed with alkanes of various volatilities such as Undecane/Tridecane or C13-15 Alkane, it forms a two phases systems with evident separation. Interesting, Coco-Caprylate/Caprate, used as a vehicle for the polyurethane, causes the polymer to separate when it is added to the dispersion. The result is counterintuitive and can be ascribed to an incomplete solvent capability of Coco-Caprylate/Caprate due to the cohesive forces present among hydrogen bonded polymer backbones that the ester is not able to fully take apart. The slight haziness of the pristine polymeric dispersion hints that the solvent medium could be further optimized, for instance moving to light triglycerides such as Triheptanoin.

Table 1 – Compatibility of the novel biobased polyurethane with a selection of cosmetic oils. The ingredient was mixed with oil in a 1:1 ratio and mixture evaluated above 60°C and at Room Temperature after cooling down. C = Compatible, I = Incompatible

INCI	***Hot evaluation***	***Room Temperaure evaluation***
Undecane and Tridecane	I (Opaque)	I
C13-15 Alkane	I (Opaque)	I
Coco-Caprylate/Caprate	I (Opaque)	I
Triheptanoin	C	C
Hexyl Laurate	C	I (Turbid)
Octyldodecanol	C	C
Caprylic/Capric Triglyceride	C	C
C12-15 Alkyl Benzoate	C	C

Next, recognizing that the function of the newly synthesized ingredient may fit into the "film-former" category, it was first admixed to fully compatible Octyldodecanol, an ubiquitous oil in anhydrous formulations, and combined to a set of biobased and petrochemical-derived waxes to probe the overall compatibility with structuring agents of various categories (Table 2). Almost all tested waxes are compatible (clear melt) and among those compatible in the melt, Sunflower Wax generated a well-structured, homogeneous, and smooth anhydrous intermediate. However, Rice Bran Wax hinted incompatibility due to a sweating surface. Coherently with the incompatibility of the new polyurethane with alkanes, both Synthetic Wax and Polyethylene showed signs of incompatibility either in the turbid melt (Polyethylene) or after cooling (incomplete structuring of Synthetic Wax, producing a soft structure). These results are convenient guidelines for formulators in selecting the proper composition for stable anhydrous products.

Table 2 – Compatibility with a selection of cosmetic waxes. The new polyurethane was mixed in a 1:7 ratio with compatible oil (Octyldodecanol) and 1:2 ratio with the selected wax. The mixture was brought above the melting temperature of the wax and then it was evaluated at high temperature and room temperature for compatibility. C = Compatible, I = Incompatible

INCI	***Appearance of the mixture***	
	Above Melting Temperature of wax	***Room Temperature***
Helianthus Annuus (Sunflower) Seed Wax	C	Homogeneous, Smooth surface
Rice Bran Wax	C	Sweating surface
Synthetic Wax And Copernica Cerifera (Carnauba) Wax	C	Homogeneous, Smooth surface
Polyethylene	I (Opaque)	Homogeneous, Smooth surface
Synthetic Wax	C	Homogeneous, soft structure, Smooth surface

Discussion

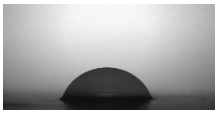
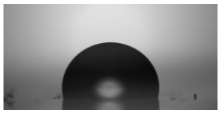
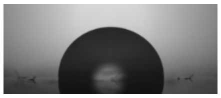
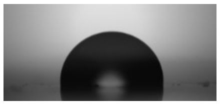
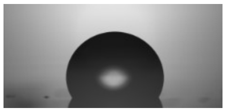
The novel Caprylic/Capric/Succinic Triglyceride / Hydrogenated Dilinoleyl Alcohol / IPDI Copolymer can be compared to the state-of-the-art film formers belonging to the Alkyl Tartrate based polyurethanes (Table 3) to understand benefits, relative improvement and suggest further developments [7]. Among these, HDI/Di-C12-14 Alkyl Tartrate/Hydrogenated Dilinoleyl Alcohol Copolymer represents the most similar analogue. This polyurethane is conveniently delivered through Isododecane/Ethanol volatile mixtures, leaving a shiny, non-self-consistent sticky film with remarkable adhesion. However, the overall N.O.I. of the HDI/Di-C12-14 Alkyl Tartrate/Hydrogenated Dilinoleyl Alcohol Copolymer is zero and represents a burden when high Natural Origin Content is required in formulations. The novel material instead, delivers a N.O.I. = 0.86 opening unprecedented opportunities to formulators. Moreover, the gloss value of 105 GU outperforms the one of HDI/Di-C12-14 Alkyl Tartrate/Hydrogenated Dilinoleyl Alcohol Copolymer, showing the cosmetic potential for the development of shiny finishes. IPDI/Di-C12-13 Alkyl Tartrate/Bis-Hydroxyethoxypropyl Dimethicone Copolymer and Polyurethane-102, both built around similar chemistries, can cast a self-consistent film which is relatively glossy and endowed with no-transfer properties: they represent a target to further tweak the structure of the novel Caprylic/Capric/Succinic Triglyceride-based polyurethanes to obtain similar performance.

Another target to address is the resistance to water and oils for the waterproof and food-proof claims of make-up products. These characteristics can be probed using water contact angle on thin film layers to compare the surface energy of the polymers and score them accordingly. Alkyl Tartrate-based polyurethanes display water contact angles in the 100°-110° range, associated to overall hydrophobic surfaces with good oil resistance. For comparison, Bis-Hydroxyethoxypropyl Dimethicone/IPDI Copolymer Ethylcarbamate, a silicone-based polyurethane, scores a water contact angle of more than 120°, thanks to the presence of polydimethylsiloxane functionalities and is a "golden standard" as film former for no-transfer food-resistant lip products. In this regard, the new biobased polyurethane has a water contact angle of only 72°, namely it is more polar in nature: it can be concluded that oil-proof is still a challenge but water-proofing is ensured by water immiscibility and polymer viscosity. On the other hand, higher polarity is advantageous because adhesive forces are mediated by polar interactions.

Finally, the ingredient was tested in two make-up applications: a powder compact and a lip lacquer. In eyeshadows powders with frost finish, at 1.5-2.0%wt of overall formulation, the new polymer was used to improve successfully the adherence and long-wear of the cosmetic film, contributing in the same time to the luminous appearance of the pearl pigments, substituting effectively petrochemical-derived setting ingredients (Hydrogenated Styrene/Isoprene Copolymer). Instead, in the lip lacquer the new ingredient was used at a remarkable 25%wt content to exploit its full potential as a gloss-promoting agent. The choice of the other ingredients comprised the synergic use of PLA-derived fluids and waxes [6] to modulate the texture (20%wt overall) and selected oils and pigments to generate a formulation boasting a Natural Origin Content up to 96%, depending on the shade. The lip fluid delivers an even, comfortable, and flexible film with deep color impact and shine.

Future developments involve mainly addressing no-transfer and compatibility with biobased volatile ingredients, for all-round formulation versatility achieving the ultimate long-lasting performance at the level of traditional polyurethanes. In this regards, successful prototypal syntheses have been carried out using a modified macro-diol where Succinic Acid is formally replaced by Azelaic Acid (Nonanedioic Acid).

Table 3 – Comparison of the new polyurethane with notable non-biobased film-forming polyurethanes: gloss and water contact angles and N.O.I.

INCI	***Silicone content / %***	***Gloss (GU)***	***Water Contact Angles (°)***		***N.O.I.***
Caprylic/Capric/Succinic Triglyceride / Hydrogenated Dilinoleyl Alcohol / IPDI Copolymer	0	105	72		0.86
Polyurethane-102	2	71	106		0
HDI/Di-C12-14 Alkyl Tartrate/Hydrogenated Dilinoleyl Alcohol Copolymer	0	65	96		0
IPDI/Di-C12-13 Alkyl Tartrate/Bis-Hydroxyethoxypropyl Dimethicone Copolymer	2	62	96		0
Bis-Hydroxyethoxypropyl Dimethicone/IPDI Copolymer Ethylcarbamate	89	67	123		0

Caprylic/Capric/Azelaic Triglyceride conveniently exploits Azelaic Acid as a biobased building block obtained from biorefineries transforming biomass from a non-edible vegetable source (Cynara cardunculus) that grows in arid areas unfit for food cultures. The formal replacement of Succinic Acid with Azelaic Acid allows to obtain a biobased polyurethane that has similar properties (gloss and viscosity) but endowed with a more aliphatic character (9 vs 4 carbon atoms) that can improve the compatibility with non-polar ingredients. This easy modification of the chemical synthesis truly demonstrates the flexibility of the new platform that has been developed and will surely lead to successful new ingredients in full compliance with the current and future sustainability trends.

Conclusion

The present research represents a step towards the synthesis of biobased cosmetic ingredients with the desirable properties of adhesion and film-forming capabilities. The research was meant to address the need for high gloss fluid endowed with skin adherence, comfortable sensoriality and low tackiness, aiming to uncompromised performance. A whole range of polyurethanes exploiting vegetable-derived triglycerides of Caprylic, Capric and diacids as building blocks was synthesized and a promising ingredient was selected for characterization, comparison with the state-of-the-art polyurethane ingredients and applied to novel make-up formulations. A lip lacquer synergistically using various exclusive biobased ingredients was created, boasting comfortable wear, high gloss, deep chroma and a Natural Origin Content of up to 95%.

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Conflict of Interest Statement. NONE.

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