“Green” UV-LED Gel Nail Polishes from Bio-Based Materials

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Abstract

Nail polishes are one of the most widely used products in the US cosmetic industry, utilized by 117 million Americans in 2016, which is going to reach 122 million by 2020. Gel nail polishes represent an advanced class of nail polishes, with the ability to cure under ultraviolet (UV) radiation, and consequently demonstrate improved properties and greater durability compared to the conventional ones. Most gel nail polishes available today are based on petrochemical based resources making them unsustainable. Bio-based materials are excellent renewable resources, with high potential of meeting final-product performance, cost and environmental needs. In addition to this, bio-based materials can be modified to make them amenable to be cured by advanced UV-LED light that consumes low energy and is very safe for human exposure compared to conventional UV-mercury lamps. There has been a clearly growing consumer preference for use of products made from bio-based sources.

According to the U.S. Department of Energy (DOE) technology roadmap, 10% of basic chemical building blocks should be derived from plant-based renewable resources by 2020 and this amount should increase to 50% by 2050. However, to the best of our knowledge, bio-based nail products has not been sufficiently explored. Therefore, considering the increasing consumption of nail polishes and to keep pace with the bio-based regulations and consumer preference, there is an unmet opportunity to develop novel sustainable nail gel polishes with considerable bio-renewable content.

In this study, two Green UV-LED curable nail gel polish prototypes; one high-solid zero-VOC and the other waterborne, both with considerable bio-renewable content have been designed, and their performance compared with a commercial petro-based benchmark. Also, both formulations were cured under both UV-mercury and UV-LED radiation sources in order to evaluate their curing efficiency under UV-LED source. The high-solid formulation demonstrated very promising performance, exceeding that of the benchmark, while waterborne formulation met most of the desirable requirements with some significant technical benefits. These novel nail gel polishes are greener alternatives to the current products in the market with promising consumer acceptance.

Introduction

Nail polishes are one of the most widely used products in the US cosmetic industry, utilized by 117 million Americans in 2016, which is going to reach 122 million by 2020. Nail lacquers are cosmetic coatings applied on human’s finger nails or toe nails for two main reasons: first, for enhancing aesthetic aspects of the nails and second for protecting and strengthening fragile nail surface, which is serving as a protecting cover for the fingertips [1,2].Conventional nail coatings usually contain various solid components dissolved or suspended in a non-reactive solvent, which build a clear or pigmented film after application and drying on the nail. These nail polishes typically have low scratch resistant and will chip or peel from the nail surface after 2-7 days in the best cases. Gel nail polishes are a specific class of nail polishes, with the ability to be cross-link under ultraviolet (UV) radiation, and consequently demonstrate improved properties and greater durability compared to the conventional ones. Gel-polishes typically last around two weeks without chipping or peeling[3].

Gel nail polishes are usually offered in 3 layers: Base-Coat, which is applied directly on the nail, with different purposes such as covering the deformities on the nail surface and making it uniform, strengthening the nail, and assisting with the adherence of the subsequent layer- polish. Polish, as the colored layer, mainly provides the aesthetic aspects. Finally, clear Top-Coat would be applied on the polish to form a hardened barrier, resistant to scratching, chipping and peeling. Each layer would be applied after curing the previous layer with UV-Radiation.

Although radiation curing offers unique features such as fast curing and low VOC emission in development of nail gel polishes, health and safety aspects of using UV nail dryers has been a controversial subject for years. Although there are some observations that announce exposure to UV nail dryers, mostly radiating UVA, as a risk factor for skin cancer development[4], in July 2017, the US Food and Drug Administration (FDA) released a statement about safety of UVA nail lamps[5], referring to a study by Dowdy and Sayre[6] indicated that even for the worst-case lamp that was evaluated, 36 minutes of daily exposure was below the occupational exposure limits for UV radiation (Note that these limits only apply to normal, healthy people and not to people who may have a condition that makes them extra sensitive to UV radiation). Dowdy and Sayre reported that nail lamp outputs ranged from 0.5% to 2.2% of the allowable monthly occupational exposure limits or 0.30 to 1.676 µW/cm2 between the range of 350 to 400 nm. As Diffey (2012) reports, this amount of risk is accepted by most of the women, and even that low risk could be reached to virtually zero by using fingerless gloves at the time of curing the gel-polish on the nails[7].

Recent advances in Light-Emitting Diodes (LED), i.e., high intensity of energy output and low initial costs has made 60In addition, ability to through cure, energy efficiency, longer lifetime and instant on/off ability has made UV-LEDs an environmentally friendly technology with lower carbon footprint compared to UV-curing technology.

“Bio-based materials refer to products that mainly consist of a substance(s) derived from living matter (biomass) and either occur naturally or are synthesized, or it may refer to products made by processes that use biomass.”[8] These materials, such as plant oils, are excellent renewable resources, with high potential of meeting final-product performance, cost and environmental benefits. In addition to this, bio-based materials can be modified to make them amenable to be cured by advanced UV-LED light. Thus, in recent years, there has been a growing interest for using them in the design and the development of environmentally friendly advanced coatings [9]. On the other hand, according to the U.S. DOE technology roadmap, 10% of basic chemical building blocks should be derived from plant-based renewable resources by 2020 and this amount should increase to 50% by 2050 [10]. Therefore, Bio-based materials are leading the development of the next generation of products and processes thanks to their renewable agricultural and forestry base, Bio-based materials are eco-efficient and generally economically viable. The Renewable Raw Material content (RRM %) is one of the measures of product sustainability and is calculated according to equation 1. However, although there are multiple studies on radiation-curable gel polishes, there is very limited focus on radiation-curable nail polishes based on renewable materials.

$$\text{Weight \% RRM} = 100 \times \frac{\text{Weight RRM}}{\text{Weight End Product}} \qquad (1)$$

Multiple researchers patented radiation-curable nail coating formulations. Valenty et al.[11] proposed a radiation curable top-coat composition comprising mainly of nitrocellulose, (meth) acrylate monomers, non-reactive solvents, photoinitiator, inhibitor, etc. to be applied on top of commercial nail enamels. They have reported that the proposed formulation was easily removable by standard acetone-based nail polish removers and is compatible with daily chores since it is water insoluble. Gudjil et al.[12] designed a metamorphic radiation curable nail polish consisting of a photochromic compound such as Spiroxazine or Spiropyran derivatives added to a clear polish comprised a base resin containing nitrocellulose and cellulose acetate butyrate and a photoreactive monomer, that was able to react with UV radiation or sunlight by changing color from clear to any chosen color such us violet, blue, yellow, red, etc. and going back to colorless form upon removed from the ultraviolet source. Cook et al.[13] patented UV-curable nail coating formulations containing modified cellulose esters with ethylenically unsaturated pendant groups, acrylate monomers or oligomers as copolymerizable reactants, pigments, plasticizers, organic solvent, etc. The coating was formulated to be at least partially soluble in suitable removing solvents. In another patent, Vu et al.[14] proposed an easily removable base coat consisting a 3D thermoset lattice dispersed in a network of solvent-dissolvable resin. The thermoset lattice provides durability, toughness and good adhesion, while the solvent-dissolvable resin facilitates removability. For making the 3D lattice, they used copolymers of polymethylmethacrylate and polymethacrylic acid, a solvent-sensitive monomer from polypropylene/polybutylene glycol (meth)acrylate family, and other acrylate monomers such as urethane (meth)acrylates and cellulose esters were used as the solvent-dissolvable resin. As they reported when the polymer was exposed to a solvent, it penetrated to the domains of solvent-sensitive resin, dissolved it and then more easily penetrated to the interior of thermoset matrix. Proposing a storage-stable radiation-curable nail gel coating, Kozacheck et al.[15] investigated effect of different organic and inorganic thixotropic agents on shelf life of pigmented nail gels consisting of urethane acrylate oligomers and (meth)acrylate monomers. They reported drastic difference in stability of the nail polishes (pigment settlement) with and without thixotropic agents. They also found out that by changing the rheological properties of the nail gels, thixotropic agent allows nail gels to be easily applied at lower viscosities due to shear thinning that reduces the amount of required solvent for viscosity adjustment. Chang et al.[1] patented a radiation-curable nail lacquer formulation mainly composed of aliphatic/aromatic urethane and polyester acrylate oligomers that contained no irritating reactive (meth)acrylate monomers, possessed good adhesiveness and was easily removable with a wooden or metal stick. Klang, Lu and Vappala[16] disclosed UV curable nail polish compositions based on aqueous polyurethane dispersions. They made a prepolymer using a diisocyanate compound, DMPA, a polyol and and a compound containing both ethylenic unsaturation and hydroxyl. Then after neutralization, the prepolymer was chain extended dispersed in water. Final nail compositions were prepared by addition of photoinitiator, and optionally a leveling agent and a thickener. Finally, Steffer et al. patented UV-curable nail coating formulations based on renewable polyols. This formulations consist mainly of a (meth)acrylate monomer or oligomer prepared from reacting the bio-based poyol with a (meth)acrylate monomer and a co-reactant such as diisocyanate, polyacid, polyester, cyclic lactam, cyclic lactone, epoxy compounds, etc.[17]. To sum up, to the best of our knowledge, bio-based nail products has not been sufficiently explored by the researchers. Therefore, considering the increasing consumption of nail polishes and to keep pace with the bio-based regulations and consumer preference, there is an unmet opportunity to develop novel sustainable nail gel polishes with considerable bio-renewable content.

By leveraging the environmental and health benefits of UV-LED curing and bio-based oligomers/monomers, this study proposes new UV-LED curable gel-polish compositions with high Bio-Renewable Content. In this effort, a Zero-VOC High-solid (HS) UV-LED curable nail gel formulation and a UV-LED waterborne (WB) nail polish, both with considerable bio-renewable content were designed and their performance compared with a petro-based product as benchmark. Also, both formulations were cured under both UV-mercury and UV-LED radiation sources in order to evaluate the curing efficiency of the designed formulations by UV-LED.

Experimental

Materials

Aliphatic polyester polyol (Stepanpol pc-205P-160, Stepan), Bisphenol A epoxydiacrylate (Genomer 2252, Rahn USA Corp.), pigment dispersions both aqueous and in reactive diluents (Chromaflo Technologies), Garamite 1958 (BYK), Cellosize QP-300 (Dow Chemical), TEGO Foamex 822, Evonik), TEGO Twin 4200 Evonik, Toluene Diisocyante (TDI, Byer), Genocure TPO-L (Rahn USA Corp), and isopropyl thioxanthone (ITX, BASF) were supplied by the manufacturers. Dimethylolpropionic Acid (DMPA), Acetone, N-Methyl-2-Pyrrolidone (NMP), triethylamine (TEA), 4-methoxyphenol (MEHQ) and Diethylene glycol diethyl ether were purchased from Sigma Aldrich. Mercapto-modified polyester acrylate resin (Ebecryl LED-02), hexafunctional aliphatic urethane acrylate oligomer (Ebecryl 1290), hexafunctional aromatic urethane acrylate oligomer (Ebecryl 220), Pentaerithritoltriacrylate (PETA), copolymerizable amine synergist (Ebecryl P115), Acrylated Epoxidized-Soybean Oil (AESO, Ebecryl 860) and Trimethylolpropane triacrylate (TMPTA) were provided by Allnex. Finally, isopropylideneglycerol methacrylate (Bisomer IPGMA) and a two functional acryalte oligomer (Bomar BR-952) were supplied by GEO specialty chemicals and Dymax respectively.

Synthesis of aqueous polyurethane dispersion for WB nail gel polish

DMPA, aliphatic polyester polyol, Bisphenol A epoxy diacrylate, acetone and NMP were charged into a three-neck flask equipped with agitator, nitrogen flushing tube, temperature controller and water-cooled condenser. The contents were heated to 80°C and held until the solution was homogeneous. Then, TDI, was added drop-wise, and the batch was reheated to 80°C and held for one hour. After one hour, the temperature was increased to 90ºC and held for the % NCO target point. % NCO was determined by the di-n-butylamine back titration method according to ASTM D2572. After that, PETA) and AESO were added to the mixture to introduce acrylate functionality at the chain-ends. Reaction was continued until reaching to the NCO% near zero. Then, at 40-50°C, TEA was charged to the flask for neutralization and mixed for 5-10 minutes. Pre-polymer was transferred to the dispersing vessels equipped with high-speed dispersing agitator. Before dispersing the prepolymer in DI water, it was divided to three proportions. The first one was dispersed as was; to the second one 10% TMPTA, and to the third one 10% of the two functional acrylate oligomer was added. Agitator speed was increased to 1000-1500 rpm and de-ionized water was started to add at a rate sufficient to maintain a vortex. After the complete addition of DI water, agitator speed was reduced to 300-400 rpm and mixing was continued for an additional 20 minutes. Finally, the PUD was filtered and transferred to plastic container for storage.

Radiation Curing

SUNUV 48W UV-LED dryer machine with wavelengths in 365 and 405 nm, and radiation intensity of 0.691 J/cm^2 for each 60s of radiation measured by a compact radiometer (UVPS), was used for curing of the nail gel polishes. In addition, in order to evaluate the efficacy of UV-LED curing of the designed formulations, a UV-mercury system (Fusion UV) with an H-bulb with the conveyor belt speed set to 12 feet/min and energy density of ~0.70 J/cm^2 per pass was also used.

All the samples were applied with 2 mil wet film thickness on standard Aluminum panels, and were cured three times under 60s radiation period, or three passes under UV mercury source at 12 feet/min. The WB formulation were first dried in the oven at 60 °C for 10 min to remove water before being polymerized under the UV-LED or the UV-mercury lamp. The hardening and eventual full curing of the films were evaluated using a thumb twist procedure - the fully cured films did not leave any observable mark from placing a thumb on the film and twisting[19].

Testing and Evaluation

The following tests were performed in order to evaluate the bio-based nail gel polishes and compare their performance with the petro-based benchmark: Tack-free time, opacity, Acetone double rub, pendulum hardness test, pencil hardness. In addition, blush test (or water resistance) was evaluated by immersion of half coated plates in tap water for 4 hours, and then inspect them visually after the drying. Moreover, the removability of the nail gel polishes were assessed after 10 minutes of immersion in acetone[13,14].

Furthermore, extent of cure versus time for both curing methods was studied by time-based FTIR analysis using a Bruker Tensor 27 FTIR analyzer. 8 scans were recorded in the range of 400 - 4000 cm^{-1}. Thin films of nail polishes were applied on prepared KBr pallets and IR spectroscopy was performed after each pass of curing. To calculate the acrylate double bond conversion, the area of the acrylate band at 810 cm^{-1} was used. It was normalized using the carbonyl band (1720 cm^{-1}), which is constant throughout the polymerization, as a reference peak. A comparison of the ratio of these areas for both the cured and the uncured sample allows to calculate the acrylate conversion degree after polymerization according to equation 2 [20]. Finally both HS and WB nail gel polishes were characterized for gloss at 60º using a micro-TRI Gardco gloss meter.

$$\text{Conversion (\%)} = 100 \times 1 - \left(\frac{\left(A_{810\,cm^{-1}}/A_{1720\,cm^{-1}}\right)_{cured}}{\left(A_{810\,cm^{-1}}/A_{1720\,cm^{-1}}\right)_{uncured}} \right) \qquad (2)$$

Result and Discussion

Formulation Design

Material selection

Several factors should generally be considered in material selection for developing nail gel polish formulations. First, the monomers and oligomers should not be selected from high skin irritating acrylate monomers and oligomers. Second, the nail gel polish should be fast cure under radiation, i.e., a tack-free film should be achieved in about one minute. Third, in order to prevent oxygen inhibition, which is highly probable in UV-LED curing, acrylate content and reactivity should be controlled since compositions with low reactivity or low acrylate content would be prone to oxygen inhibition. oxygen inhibition could also be mitigated by using reactive chemicals such as amines or copolymerizable amines, which contain easily abstractable hydrogen atoms[18] and can react with proxy radicals. Copolymerizable amines are preferred in this study since acrylate functionality insures that the materials become a part of backbone, reduce its odor and prevent amine bloom to the surface. Another requirement is that, the gel polish should be easily removable by common nail-polish removers. To meet the aforementioned requirement each of the main components including binder, photoinitiator(s), pigments and additives should be carefully selected for both HS and WB formulations, as described in more detail in the later section.

Binder. *HS nail gel polish formulation.* AESO and IPGMA were used as bio-renewable based oligomer and monomer respectively. AESO, as a soft segment can also contribute in easy removability of the nail gel polish. A mercapto-modified polyester acrylate was used to mitigate oxygen inhibition by increasing the cure speed. A hexafunctional aliphatic urethane acrylate oligomer and a hexafunctional aromatic urethane acrylate oligomer) were used to provide desired acrylate content and also good chemical properties.

WB nail gel polish formulation. Regarding the WB binder, it should be noted that TDI and Bisphenol A epoxy acrylate were used in the PUD development to bring proper hardness, and AESO was used to bring bio-renewable content and acrylate functionality for UV-Curing.

Photoinitiators. UV-LED lamps emit very intense light in a very narrow range of UVA and Visible light wavelengths, therefore the number of useable photoinitiators is highly limited compared to those for conventional UV-Mercury platforms. Experiments have shown that using a combination of Type I and Type II photoinitiators can reduce oxygen inhibition more effectively[18]. After several preliminary experiments, a mixture of Type I, Type II and an amine synergist was found as the best choice for initiator package, in terms of faster curing (shorter tack-free time), lower oxygen inhibition, accepted level of yellowing, and other properties such as scratchability of the surface. Genocure TPO-L (type I), ITX (type II), and Ebecryl P115 (the synergist) were used as the initiator package in this study.

Pigment dispersion. In order to get an effective tint in the final coating, commercial pre-milled pigments in monomer carrier, specially formulated for radiation curable systems, were utilized. Among the available options, Tripropylene Glycol Diacrylate (TPGDA) was chosen as the proper monomer carrier for pigment dispersion in this study. For similar reasons, aqueous pigment dispersions used for the WB formulation.

Additives. In both formulations, MEHQ was used as an inhibitor to increase the shelf life of the nail gel polishes. MEHQ amount was kept very low, first to prevent poor cure and second because of its skin sensitivity effects. In the HS formulation, Garamite 1958 was used as a rheology modifier to prevent settling of pigments in long term. In the WB formulation, Cellosize QP-300, was used as the thixotropic agent. Other additives in the WB formulation include defoamer, anti-crater and wetting agent, and coalescing agent.

Composition

As mentioned before, nail gels typically comprise three layers including base coat, color coat and top coat. In this research, two three-layer bio-renewable based nail-gel formulations were prepared and their performance was compared to a petro-based commercial three-layer nail gel polish as the benchmark. Tables 1 to 3 demonstrate the final composition of HS basecoat, polish and top coat respectively and Table 4 demonstrates the formulation of WB nail gel polish. It should be noted that a small quantity of acetone, as a VOC exempt solvent, was used in all formulations for dissolving ITX.

Cure Study and Performance Properties

Although time-based FTIR studies was carried out for all the formulation, whole FTIR spectra are not included since they would occupy too much space for the purposes of this article. Thus, only the FTIR spectra for the HS formulation (Figure 1) will be represented here as an illustration. Figure 2 compares the extent of cure in WB and HS nail gel polishes by UV-Mercury and UV-LED calculated by equation 2. Based on these results, the extent of cure for each of HS and WB polishes is in a similar range in both curing methods. This shows that UV-LED is an efficient curing method for the designed formulations. According to Figure 1, the majority of acrylic bond conversion occurs in the first pass of curing for both formulations regardless of the curing method. In addition, in UV-LED curing the extent of cure is more than the UV-Mercury in the first and second passes for both formulations. In addition, in contrast to the waterborne formulation, in the HS polish the extent of cure by UC-Mercury exceeded the UV-LED.

Table 1. Composition of the Basecoat

Basecoat Ingredients		**Weight (gr)**	**Weight %**
Binder	Bio-based acrylate compound	50	45.02
	Acrylate oligomer	40	36.01
	Reactive diluent	10	9
	Subtotal = 100		
Amine synergist	Copolymerizable amine synergist	5	4.5
Photoinitiator Package	Type I	3	2.7
	Type II	3	2.7
Inhibitor	Inhibitor	0.01	0.0001
Total = 111.06 100			

*RRM% in total formulation = 54%

Table 2. Composition of the polish

Polish Ingredients		**Weight (gr)**	**Weight %**
binder	Bio-based acrylate compound	40	28.64
	Acrylate oligomer	40	35.80
	Reactive diluent	10	7.16
	Subtotal = 100		
Amine synergist	Copolymerizable amine synergist	5	3.58
Photoinitiator Package	Type I	3	2.15
	Type II	3	2.15
pigments	White pigment dispersion	5.35	3.83
	Colored pigment dispersion	1.24	0.88
Inhibitor	Inhibitor	0.06	0.0001
Additives	Thixotropic agent	13.1	0.75
Total = 139.65* 100			

*RRM% in total formulation = 35.8%

**Garamite 1958 was dispersed in the binder by 8 wt.% before adding to the final formulation.

Table 3. Composition of the Topcoat

Topcoat Ingredients		**Weight (gr)**	**Weight %**
binder	Bio-based acrylate compound	46	41.4
	Acrylate oligomer	34	39.6
	Reactive diluent	10	9
	Subtotal = 100		
Amine synergist	Copolymerizable amine synergist	5	4.5
Photoinitiator Package	Type I	3	2.7
	Type II	3	2.7
Inhibitor	Inhibitor	0.011	0.0001
	Total* =	111.06	100

*RRM% in total formulation = 50.4%

Table 4. Formulation of waterborne nail polish

Polish Ingredients		**Weight (gr)**	**Weight %**
UV-PUD	Bio-based acrylated polyurethane dispersion	500	80
Amine synergist	Copolymerizable amine synergist	24.39	3.90
Photoinitiator Package	Type I	15	2.40
	Type II	15	2.40
pigments	White pigment dispersion	30	4.80
	Colored pigment dispersion	9	1.44
Additives	Thixotropic agent	5.3	0.85
	Defoamer emulsion	0.62	0.13
	Substrate wetting and anti-crater additive	0.6	0.09
	Coalescing agent	9.37	1.5
	Total** =	625	100

*RRM% in PUD (solid) = 58.98%

**RRM% in total formulation (solid) = 43.56%

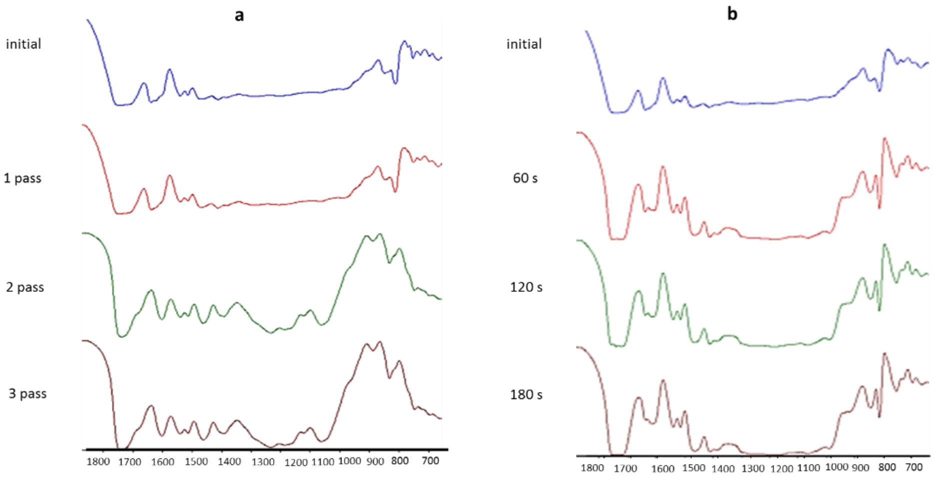

Figure 1. Studying the extent of cure using time-based FTIR curing of HS nail gel polish a) under UV-LED light b) under UV-mercury lamp

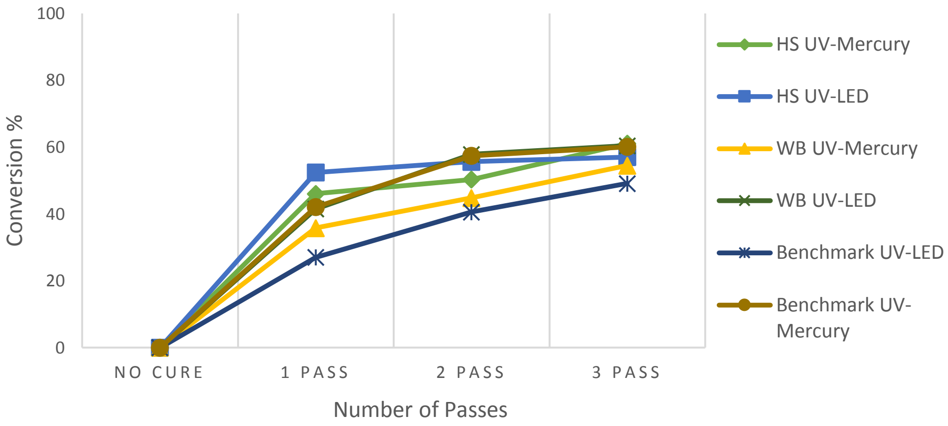

Figure 2. Extent of cure of HS and WB formulations versus time by UV-LED and UV-Mercury methods

Table 5 demonstrates the results of evaluation of the commercial benchmark. Basecoat, topcoat and polish were tacky after 3 passes (60s each) under UV-LED dryer, and the tackiness problem was not solved even after curing for 10 passes. Thus, after three passes and before the characterization, the very thin tacky layer was wiped off with a paper towel soaked with acetone, as is common in beauty salons, and is recommended in other studies [14]. The tackiness, most probably caused by oxygen inhibition, was not observed in UV-mercury curing method.

Table 5. Properties of the benchmark

	Acetone double rubs		**König Hardness (Oscillations)**		**Pencil Hardness**	
Method of Curing	UV-Mercury	UV-LED	UV-Mercury	UV-LED	UV-Mercury	UV-LED
Base coat	105	100	34	26	3H	HB
Polish	43	20	51	45	F	F
Top Coat	>200	>200	42	29	6H	2H

The HS designed nail gel polish layers, on the other hand (Table 6), became tack-free after one minute under UV-LED dryer, which is a considerably superior performance compared to the benchmark. As can be seen for the results, acetone double rubs were in similar range for the layers regardless of the curing method, which shows that curing was performed efficiently under UV-LED light. However, the three layers demonstrated higher hardness when cured under UV-mercury lamps, which might be caused by inevitable oxygen inhibition on the surface.

Table 6. Properties of the High-solid nail gel system

	Acetone double rubs		**König Hardness (Oscillations)**		**Pencil Hardness**	
Method of Curing	UV-Mercury	UV-LED	UV-Mercury	UV-LED	UV-Mercury	UV-LED
Base coat	170	180	126	110	H	2H
Polish	>200	>200	120	114	F	F
Top Coat	>200	>200	136	120	3H	5H

Waterborne nail polish was also completely tack-free after the first 60s of curing under UV-LED. Table 7 summarizes the evaluation results of waterborne nail polish. According to the results, acetone double rub enhanced considerably by addition of acrylate monomer/oligomer, inducing more crosslink density. In this hardness measurements were in a similar range, which shows oxygen inhibition is much less in case of WB formulation. This is consistent with other studies that found out there is less or no oxygen inhibition in aqueous systems because of lower solubility of oxygen in water compared to oil-based ones[21].

All the HS layers including base coat, polish and topcoat passed the blush test regardless of the curing method. However, waterborne polish and benchmark layers failed this test and became hazy after immersion. Moreover, addition of 10% TMPTA to the waterborne formulation, improved the water resistance, drastically, which shows water resistance improves by increasing of crosslink density.

As shown in Fig. 3, LED-cured HS nail polish was glossy, showing 88.8% gloss at 60º. However, WB polish and benchmark polish were semi-gloss showing 71.5% and 20.6% gloss at 60º, respectively. All the formulations showed good adhesion to the surface and on the other hand were easily removable from the nail surfaces after 10 minutes of immersion in acetone. Figure 4 compares the overall performance of UV-LED cured HS, WB and benchmark polishes and also 3-layer system.

Table 7. Properties of the waterborne nail polish

	Acetone double rubs		**König Hardness (Oscillations)**		**Pencil Hardness**	
Method of Curing	UV-Mercury	UV-LED	UV-Mercury	UV-LED	UV-Mercury	UV-LED
Polish	15	12	86	90	HB	HB
Polish including 10 wt.% TMPTA	45	40	87	94	F	F
Polish including 10 wt.% Bomar BR 952	15	20	76	76	F	F
Non-pigmented formulation including 10 wt.% TMPTA	40	38	85	90	H	H

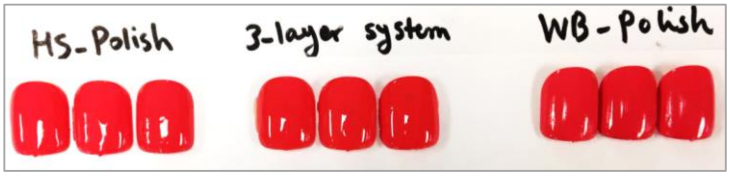

Figure 3.Appearance of the nail gel polishes applied on artificial nails

Based on these results, HS Zero-VOC polish can be applied even as a single coat and meet the required properties for nail gels. In addition WB formulation offers significant technical benefits including low odor, the highest RRM% and the lowest oxygen inhibition. However, similar benchmark the waterborne nail gel polish need to be applied in 3-layer system to demonstrate enough durability.

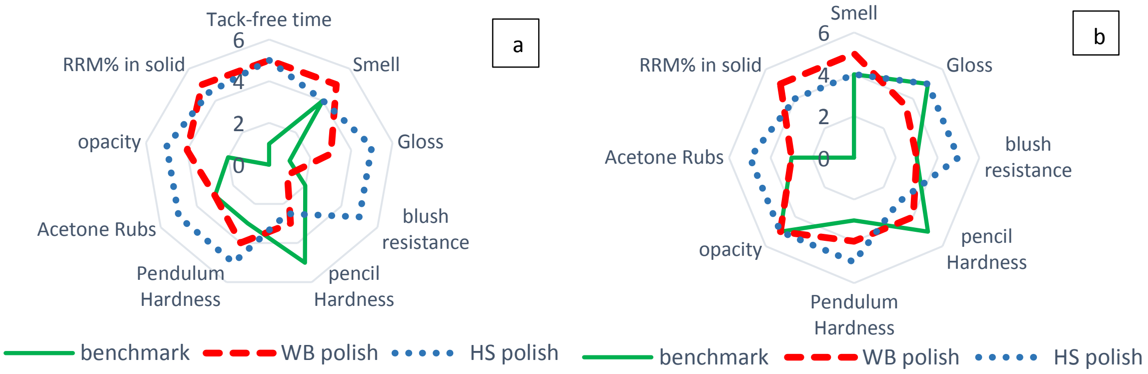

Figure 4. Overall performance of UV-LED cured HS, WB and benchmark polishes (a), and 3-layer system (b).

Conclusion

In this study, sustainable compositions containing more than 50 wt % of bio-renewable materials were designed and developed using two different approaches: through a Zero-VOC High-solid solvent-borne formulation, and via a low VOC water-borne formulation. The formulations were fine-tuned to rapidly and efficiently cure under UV-LED radiation (as a safer source of radiation for human health and environment compared to UV-mercury sources) to obtain completely tack-free surface after one-two minute of radiation using commercially available low-cost UV-LED systems. In addition, use of irritating (meth)acrylate monomers that could cause adverse allergic reactions, was avoided in formulation of the nail-gels. Moreover, the nail gel polishes were easily removable after being soaked in acetone for a few minutes.

According to the evaluation results, the zero-VOC high-solid formulation demonstrated promising performance, exceeding the petro-based commercial benchmark, and waterborne samples in most of the required properties, and showed the possibility to be applied as a single layer nail polish system, while the waterborne formulation met most of the desirable requirements with some significant technical benefits. These novel nail gel polishes are greener alternatives to the current products in the market with promising consumer acceptance.

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