

THE SCIENCE OF UV CURE NAIL GELS: A SHORT REVIEW

Liz Pavlovic, PhD

Nail Division Coty, Inc.

INTRODUCTION

UV gels are based on UV cure acrylate chemistry. The hard coats resulting from acrylate polymerization under UV light have been used in a first place for sculpting artificial nail extensions. Because of their rheology, these homogenous mixtures of monomers and oligomers were assimilated to “gels”, which became the general denomination for the category. Softer soak-off gels were developed later on, with application and appearance similar to solvent based lacquers but displaying a higher gloss, longer wear and chipping resistance. Current high performance UV nail products claim 14+ days of gloss and wear while chipping and peeling of their lacquer counterparts occurs as early as 2 days after application. The UV nail gel systems are normally composed of three parts: base coat, color coat, and top coat. The base coat provides the adhesion and protects the nail, the color coat delivers a variety of colors, and the top coat provides gloss and damage resistance. The coats are cured using specifically designed UV lamps and removal is performed by soaking soft gels in acetone, while hard gels require a file off process.

HISTORY

The idea of using acrylate chemistry in the nail industry was born in the US in the 1950s when a dentist, Dr Frederick Slack, fixed his broken nail with a dental acrylic material for crown molding. In the late 1970s, another dentist, CND founder Dr Stuart Nordstrom, made the first professional liquid and powder acrylic system for nails. In the 1970s as well, UV cure dental systems appeared in the dental material industry and made their debut as nail products. Nevertheless, UV cure nail gels did not become successful until the late 1990s, the main reason being the UV lamp manufacturers were not aligned with the nail industry and the wavelength of the emission light did not match the photoinitiators in the gels. In addition, not enough education was available for nail technicians to promote UV nail gels as mainstream products. By the end of the 1990s, brands like OPI launched professional UV nail gel lines including UV lamps with appropriate wavelength and light intensity. Development of formulations with improved properties continued in the 2000s, notably with lacquer-gel hybrids displaying an easier and faster removal. Nowadays, UV nail gel manicures are offered in the vast majority of nail salons.

CHEMISTRY

The base composition of UV nail gels is a blend of (meth)acrylate monomers, (meth)acrylated oligomers and photo-initiators, as well as various additives [1]. In addition to achieving targeted product properties, chemical functionalities of ingredients are selected in order to meet compatibility with the nail tissue as well as regulations for use in cosmetic products.

Monomers and Oligomers

Hard gels with high Tg typically require a higher crosslinking density which is achieved using di-, tri- or tetrafunctional monomers [2]. Flexible soft gels usually use monofunctional monomers for a lower crosslinking density [2]. The most common monomers are shown in Figure 1. Some monomers are also known to be adhesion promoters and are used in base coats to ensure a strong interaction between the UV nail gel and the nail tissue. They are designed to react or interact specifically with chemical groups present on the nail surface. Oligomers with (meth)acrylated ends (Figure 2) provide flexibility and ease of removal by lowering the crosslinking density [3,4]. Most common oligomer backbones are urethanes, acrylics and polyesters [5]. The choice of molecular weight and backbone composition will result in specific bulk properties leading to optimal performance.

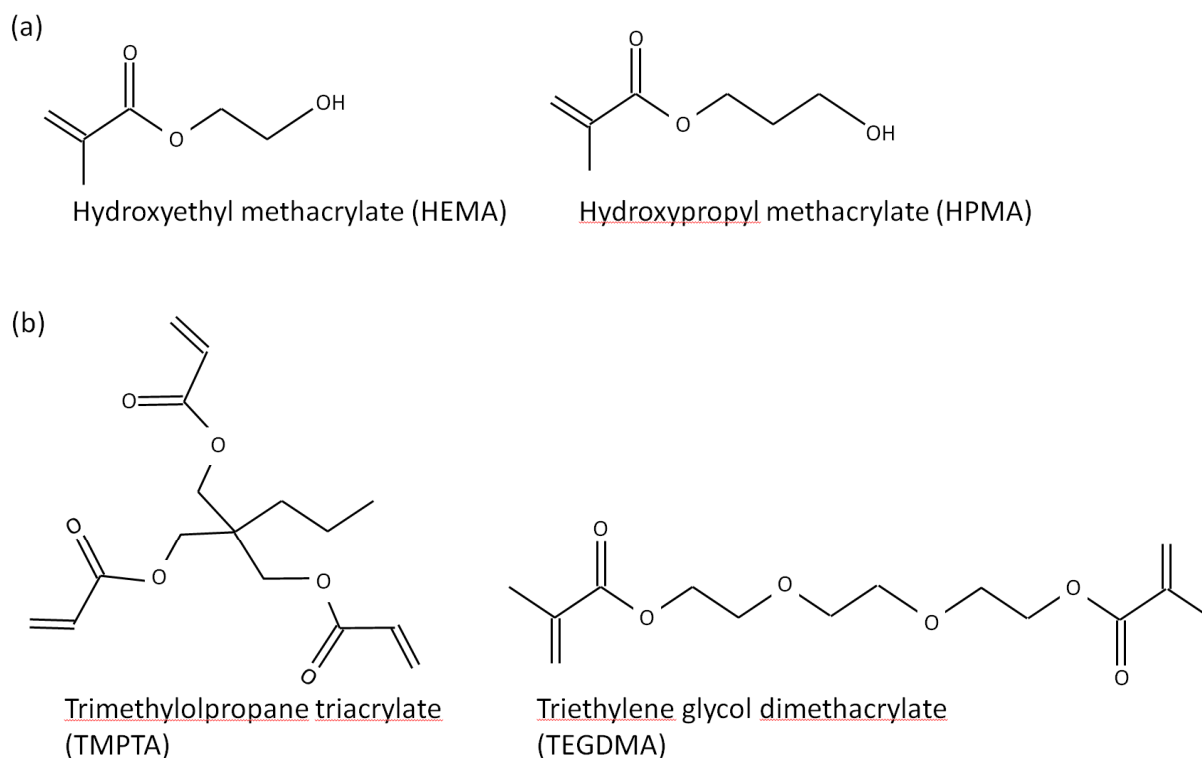


Figure 1. Monofunctional (a) and multifunctional (b) (meth)acrylate monomers used in UV nail gels

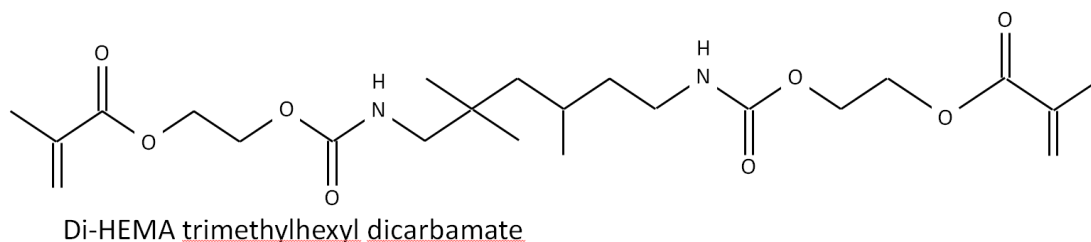
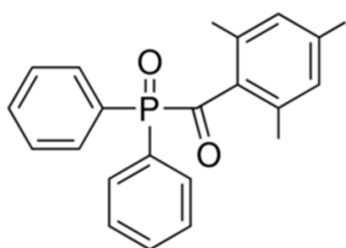


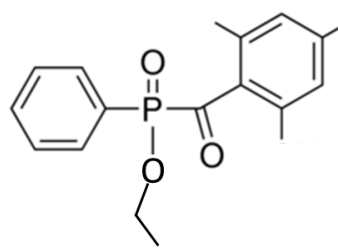
Figure 2. Base unit of Di-HEMA trimethylhexyl dicarbamate oligomers used in soft UV nail gels

Photoinitiators

UV nail gels are cured under wavelengths, intensities and exposure times presenting a very low risk of harm in humans [6,7]. The range of wavelengths is 325-435 nm [1]. The most common clear photoinitiators used for UV nail gels, shown in Figure 3, are diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO) and its liquid form, ethyl (2,4,6 trimethylbenzoyl) phenylphosphinate (TPO-L). Although the regulatory limit of use for TPO in cosmetic products is set to 5% [8], the amount of photoinitiator in the UV nail gels is usually ca. 2%. Other photoinitiators absorbing in this range are phenyl bis (2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO), 1-hydroxycyclohexyl phenyl ketone (HCPK) and 2,2-dimethoxy-2-phenylacetophenone (BDK).



Diphenyl (2,4,6-trimethylbenzoyl)
phosphine oxide (TPO)



Ethyl (2,4,6 trimethylbenzoyl)
phenylphosphinate (TPO-L)

Figure 3. Common photoinitiators used in UV nail gels

Other additives

Uncured UV nail gels have to show enough chemical stability to ensure a shelf-life of 12 to 36 months after opening. Therefore, the formulations are stabilized using polymerization inhibitors hydroquinone (HQ) or 4-methoxyphenol (MeHQ). The antioxidant preservative butylated hydroxytoluene (BHT) is also used to avoid color fading. These additives are regulated

for use in cosmetic products. Color coat formulations contain pigments which are under FDA regulation in the US. More recently developed polish-gel hybrid formulations also contain cellulose derivatives and plasticizers [3] as well as solvents.

PROPERTIES

The compositions are tailored to satisfy to the right viscosity and stability before UV curing and the required mechanical properties after curing. A successful UV nail gel is the result of a combination of several factors: adhesion to the nail surface, which should be strong enough to lifting; compromise between flexibility and stiffness, to avoid delamination due to stress and withstand deformation while providing gloss and durability.

Viscosity

It is essential for the formulation viscosity before curing to enable an application process using a brush. Soft UV gels require the lowest viscosities [3,4], typically 1000-5000 mPas, with self-leveling preventing streaking. Hard sculpting gels are much thicker, with viscosities between 25000 mPas and 70000 mPas.

Heat Spike

During UV exposure, users can experience a heat spike due to the exothermic polymerization reaction. To avoid increased and uncomfortable heat spikes above 70 degrees Celsius [4], slower curing rates are ensured by lowering the concentration of reactive monomers as well as light intensity, resulting in longer exposure times.

Elastic Modulus

Hard sculpting gels must have a high elastic modulus to enable durable nail extensions. The stiffness gives wear resistance and cracking is prevented by the coating thickness. These gels interact very strongly with the nail surface and have to be filed off at removal. Fracture of extensions may occur and cause nail injury. Soft soak-off gels are thinner and hence must be flexible to avoid cracking and ensure adhesion. The transversal and longitudinal elastic moduli of the nail were determined to be 4.3 and 2.1 GPa, respectively [9]. To match these values, it was shown that an elastic modulus of ca. 700 MPa results in good wear as well as good adhesion [4].

Gloss

High gloss and gloss retention over time are two essential features of UV nail gels. Microhardness of the coating surface is an indicator of gloss retention over time [3,4]. The level of gloss is mostly driven by the monomer content, photoinitiator, UV light intensity and the resulting conversion rate [5]. While fast curing rates favor high gloss and durability through

high conversion rate, slower curing rates are essential to achieve acceptable stability and heat spike.

Oxygen Inhibition

Tacky layers are caused by oxygen quenching the activated photoinitiator and scavenging carbon radicals, resulting in an uncured layer at the coating-air interface [10]. This phenomenon is favored by short wavelengths (UVA), known for absorbing near the substrate, combined with a low light intensity. Tacky layers are observed for soft gel top coats which display a lower surface gloss compared to hard gel top coats which are usually tack-free. Increasing the concentration of (meth)acrylates results in a tack-free coat, as the increased number of carbon radicals counteracts the effect of oxygen.

UV/LED LAMPS

The first lamps used for UV curing of nail gels were Compact Fluorescent Tube (CFL) lamps emitting a continuous spectrum of UVA, very little to no UVB and no UVC light [11]. Emission peaks for these lamps were around 365-370nm and required one to three minutes curing time because of their low intensity. The invention of LEDs allowed for higher intensity emission of narrower UVA ranges, making curing faster and more efficient. Exposure times with LED lamps are typically in the 5-45 seconds range. The available LED wavelengths are 365-385nm and 395-405nm. The first LED lamps emitted a 405nm peak wavelength [12] and were not able to cure hard gels. Later on, LED emitting at 365nm became cheaper and were added to UV nail lamps to improve surface cure efficiency, increase surface gloss and allow curing of hard gels.

CHALLENGES AND OPPORTUNITIES

In general, there are many opportunities for innovation in the entire manicure process – make up and removal. For example, fast application time, decrease in number of steps during application (preferably just one step) and lastly, quick and easy of removal.

REFERENCES

- [1] Douglas Schoon, *Cosmetic Dermatology*, Zoe D Draelos ed. (2010) Part 2, Chapter 28, 215-221
- [2] Dapawan Kunwong *et al*, *Songklanakar J. Sci. Technol.* (2011) 33 (2) 201-207
- [3] Z Grigale-Sorocina *et al*, *Proceedings of the Estonian Academy of Sciences*, (2015) 64 (1S) 88–93
- [4] Z Grigale-Sorocina *et al*, 2016 *IOP Conf. Ser.: Mater. Sci. Eng.* 111 012008

- [5] Viera Jancovicova *et al*, *Chem. Pap.* (2007) 61 (5) 383-390
- [6] B L Diffey, *Br J Dermatol.* (2012) 167 (5) 1175-8
- [7] John C Dowdy and Robert M Sayre, *Photochemistry and Photobiology*, (2013) 89 961-967
- [8] SCCS, Opinion on the Safety of Trimethylbenzoyl Diphenylphosphine Oxide (TPO) in Cosmetic Products, Submission I, 27 March 2014, SCCS/1528/14
- [9] Howard P Baden, *Journal of Investigative Dermatology*, (1970) 55 (2) 115-122
- [10] Jo Ann Arceneaux, Mitigation of Oxygen Inhibition in UV LED,UVA, and Low Intensity UV Cure, *Proceedings*, Radtech 2014
- [11] Douglas Schoon, Understanding UV lamps, www.schoonscientific.com
- [12] Douglas Schoon, *Cosmetic Dermatology Second Edition*, Zoe D Draelos ed. (2016) Part 3, Section 2, Chapter 26, 226-233

ACKNOWLEDGEMENTS

I would like to thank my colleagues from the Nail Division Coty, Inc.: Mr Dhaval Patel, Dr Yuemei Zhang, Dr Paul Bryson and Ms Sunan Yuvavanich, for their input on the history, chemistry, challenges and opportunities in UV nail gels.