

Review

To Shed Light on the UV Curable Coating Technology: Current State of the Art and Perspectives

Renuka Subhash Patil ¹, Jomin Thomas ^{1,*} , Mahesh Patil ² and Jacob John ³

¹ School of Polymer Science and Polymer Engineering, University of Akron, Akron, OH 44325, USA; rsp44@uakron.edu

² Department of Chemical and Materials Engineering, New Jersey Institute of Technology, Newark, NJ 07102, USA; mp2256@njit.edu

³ Department of Electronics Engineering, Manipal Institute of Technology, Manipal 576104, Karnataka, India

* Correspondence: jt179@uakron.edu

Abstract: The industrial application of UV curable coatings is being widely commercialized at a rapid pace with very diversified product markets. UV curing has existed for many years now, but the new commercial opportunities emerging for sustainable, and climate friendly technologies have driven demand for photo-curable coating systems. It is primarily attributed to its environmentally friendly solvent-free and energy-efficient method. Precedented UV light curable coatings are being commercialized and numerous lamp sources are being extensively studied. In such an era of predominant research evolving the UV curing technology horizon, we attempt to outline the state of the art, opportunities, and challenges. This contribution attempts to highlight, in a comprehensive way, sustainable UV coating on the basis of recent research advancements, existing challenges and prospective scope in this field. With a set of prerequisite foundational knowledge into UV curable coatings and mechanisms, the review has meticulously looked at the recent research advancements. This review contribution attempts to focus on three aspects: the known science behind UV curing coatings, coupled with the recent advancements, and future opportunities.

Keywords: UV coatings; LED cure; biobased UV coatings; sustainability; hybrid UV system



Citation: Patil, R.S.; Thomas, J.; Patil, M.; John, J. To Shed Light on the UV Curable Coating Technology: Current State of the Art and Perspectives. *J. Compos. Sci.* **2023**, *7*, 513. <https://doi.org/10.3390/jcs7120513>

Academic Editors: Tomasz Tański, Andrzej N. Wiczorek and Marcin Staszuk

Received: 1 November 2023

Revised: 24 November 2023

Accepted: 4 December 2023

Published: 7 December 2023



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1. Introduction

In the photochemistry horizon, UV curing maintains an unprecedented position among the industrially relevant new generation coating systems [1,2]. UV curing technology began in the late 1950s and the first UV precursor material to be used for coating and adhesive application was epoxy acrylate [3]. By the 1970s, UV technology gained USD 400 million sales by formulation of numerous products [4]. A quick look at the coating market statistics makes it clear that UV curing technology has indeed captured a huge amount of attention, with a heavy influx of funds and resources poured into its technical advancements [5]. In 2022, the global coating market was 5% wood and furniture, 10% electronics, 15% automotive, 21% paper and packaging, 18% industrial coating and 31% building and construction [6]. In that context, the UV-cured coating market is expected to expand from 7.28 billion in 2022 to 18 billion in 2030, according to a report by *Chemical and Material* published in 2023 [7].

Currently, environmental sustainability and climate friendliness are at the center of polymer research [8,9]. It includes the use of raw materials from renewable or biobased sources, replacing petroleum based raw materials, reducing overall curing temperature using alternate curing technology, etc. [10,11]. To that extent, polymer sustainability has been a key factor in the emergence of UV curing coating technologies [12,13]. The multi-faceted sustainable advantage in lieu of UV coating has received worldwide attention. UV-cured coatings provide energy savings, coupled with pollution prevention and excessive waste reduction [14]. Moreover, efficient, environmentally friendly, energy-saving,

enabling and economical technologies are considered to be the 5E advantages of UV curing technology [15]. The numerous industrial applications of UV curing can be attributed to its sustainable and energy-efficient coating system and shorter curing time compared to those of thermally cured systems and its ability to coat heat-sensitive substrates like wood, paper and plastics [16].

A typical curing system consists of a UV light source and UV curable formulation. Herein, the formulation consists of photoinitiators, resin/oligomers, diluent/monomers, and additives [17]. The curing process starts with the exposure of the formulation to UV light where the initiator breaks down to generate free radicals (homolytic cleavage) or breakdown of part of the molecule (electron–proton transfer), referred to as the initiation step. Next, the curing undergoes the propagation stage and finally the termination process [18]. The curing process can be either free radical or cationic, depending on the initiator and the system selected for developing the coating. In radiation curing, light not only plays a significant role, but is a mandatory trigger for the curing reaction with options of visible, UV-A, UV-B and UV-C with the wavelength ranges of 400–700, 320–400, 280–320 and 100–280 nm, respectively [1]. Depending on the wavelength required for curing, a light source can be selected and used. Figure 1 depicts an illustration of a typical UV curing system, whereas a general formulation is presented in Table 1.

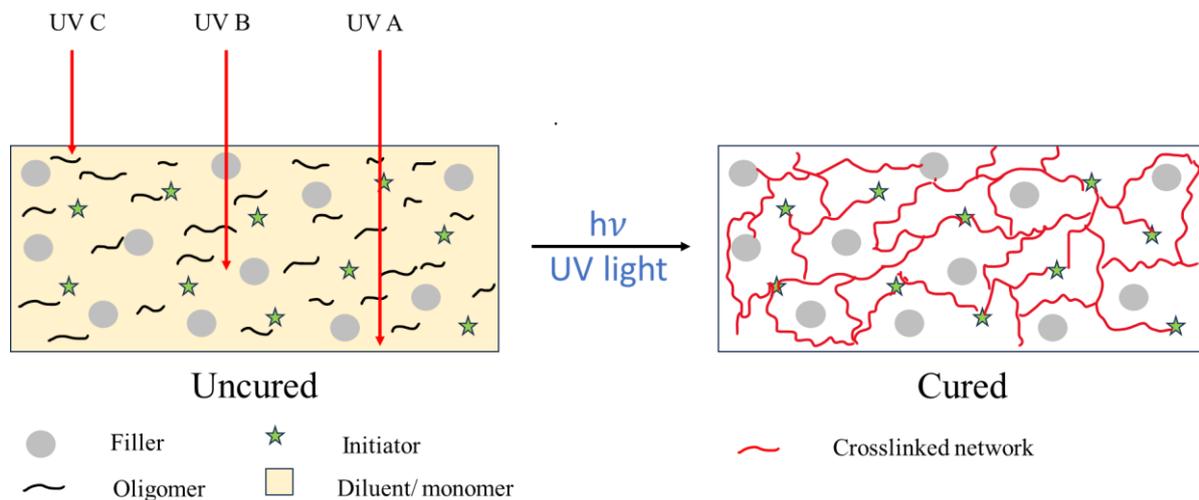


Figure 1. Illustration of a typical UV curing system.

Table 1. General formulation of UV curable coating [4,19].

Ingredient	Amount (%)
Oligomer	0–90
Monomer/diluent	0–80
Photoinitiators	0.25–5
Additives like Stabilizers, surfactant, adhesion promoter etc.	0–5
Fillers and pigment	0–45

It is important that a researcher retains strong and updated knowledge of radiation curing developments, not only on the basic foundations. In the first part of the review, a set of prerequisites for curing mechanisms are focused on before examination of each component of the curing system in depth. In the initial sections ahead, the focus is kept on proving the fundamentals of curing mechanisms coupled with pertinent commercially available precursors and technical advancements in academia. Few intrinsic UV reviews are available concentrating on very specific sectors of UV [1,20–23], but the authors believe that our meticulous and extensive review methodology can help researchers be cognizant

of the chemistry, industrial availability and significance, as well as novel academia-based innovations, and thus extend the resources needed for new product development.

2. Photo-Curing Polymerization Mechanism

There are two types of photocuring mechanisms, (1) free radical polymerization and (2) cationic polymerization [24,25]. In free radical polymerization, a photoinitiator absorbs the photon to generate a free radical, which then reacts with vinyl groups (primarily acrylates present in monomers, oligomers, and resin) in the system leading to chain propagation. This leads to the formation of a highly crosslinked network. On the other hand, in cationic polymerization, UV exposure leads to the formation of Bronsted or Lewis acid. Cations generated further open the ring in epoxy, oxetanes, etc., leading to a 3D crosslinked polymer network [16,26–29].

2.1. Free Radical Polymerization

The basic mechanism of free radical polymerization is shown in Scheme 1. The photoinitiated polymerization reaction follows almost the same mechanism as that of traditional radical polymerization, except the free radical from a photoinitiator is generated via the absorption of light (250–450 nm) instead of heat. Initiation occurs when the initiator absorbs the photon (Equation (1)). This photon absorption leads to excitation of electrons which eventually leads to generation of a free radical (Equation (2)). Free radical generation can follow two paths depending on the type of photoinitiator selected (type I and type II). This step is followed by subsequent addition of reactive entities leading to chain propagation (Equation (3)). The reaction is then terminated due to oxygen inhibition or absence of reacting entities or radical coupling or disproportionation (Equation (4)) [17].



Scheme 1. The type I alpha scission process.

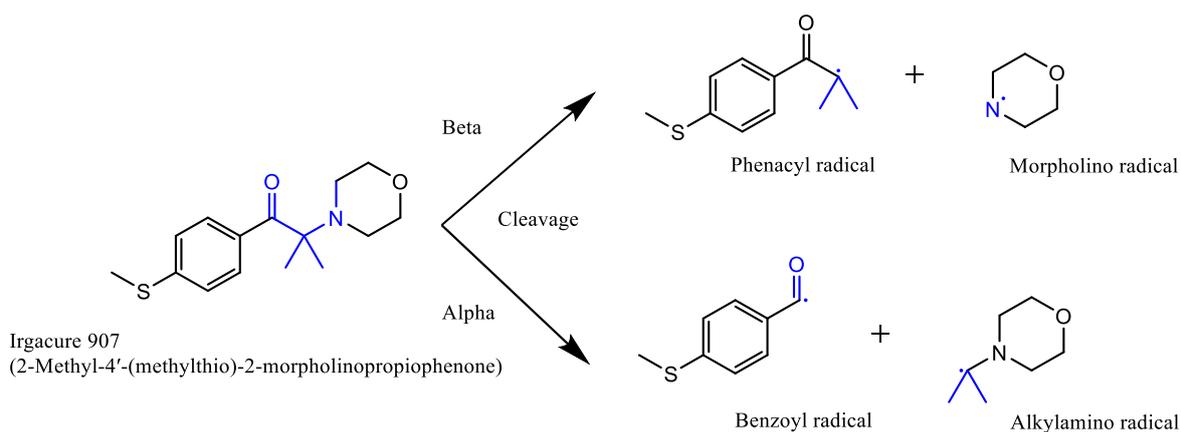
As mentioned earlier, photoinitiator (PI) used can be classified as type I and type II, i.e., unimolecular or bimolecular PI. Due to the importance the two types hold in a curing process, the next section discusses it in depth.

2.1.1. Unimolecular Photoinitiators (Type I)

These photoinitiators are also called Norrish type I photoinitiators. Type I photoinitiators generally consist of aromatic organic compounds such as ketals, benzoin derivatives, benzil derivatives, acetophenones, oxime esters, phosphine oxides and oxylates [30,31]. They undergo homolytic cleavage upon exposure to UV light. Their bond energy is low and thus they easily undergo homolytic cleavage [32]. The scission process can be either alpha or beta scission, although alpha scission is the most common mechanism in type I initiator reaction. The photoinitiator absorbs a photon that leads to the formation of two active free radicals via cleavage of a carbonyl (CO)-alkyl bond (Scheme 1). The wavelength

and rate at which this cleavage occurs depends on the substituent chemical moieties at R_1 and R_2 . Electron donor atoms like sulfur or nitrogen at R_1 shift absorption to a higher wavelength, whereas oxygen and nitrogen at R_2 increase the cleavage rate [29].

Beta scission occurs when a hetero atom is attached to an alpha carbon, e.g., C-Cl, C-S, C-N, etc. Such weak bond is more susceptible to cleavage. Compounds with N in the α position do not undergo predominantly β -cleavage (α -aminoketones as efficient photoinitiators). For example, Irgacure 907 mainly undergoes α -cleavage and very little β -cleavage (Scheme 2).



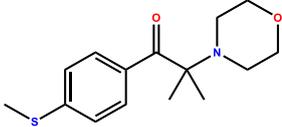
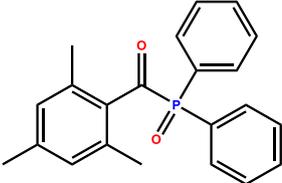
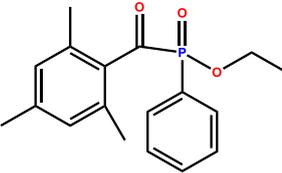
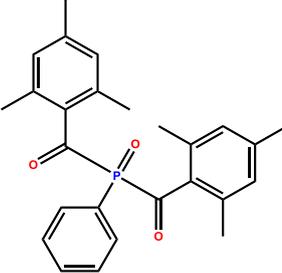
Scheme 2. Alpha and beta cleavage of Irgacure 907.

Lately, considering the use of type I photoinitiators in photopolymerization, Wu et al. and Dietlin et al. and coworkers synthesized new type I photoinitiators for light-emitting diode (LED) curing [33]. Xing and coworkers used a commercially available type I photoinitiator (Darocur1173) to develop a coating with superior flame retardancy [34]. Table 2 shows some of the common examples of type I photoinitiators. Phosphine oxides such as 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO) and bis-phosphine oxides particularly mark a new era of photoinitiators which enable UV-LED cured coatings [33]. They have an $n-\pi^*$ absorption band located at 380–410 nm and are used particularly in thick coatings where photobleaching leads to good depth cure [35]. The development of such new type I photoinitiator has enabled many researchers to improve the performance of commercially available photoinitiators. In addition, developing such new photoinitiators also provides the opportunity to tune their absorption spectra.

Table 2. A common commercially available type I photoinitiator.

Chemical Name	Structure	Activation Wavelength (nm)	Physical Form	Ref.
2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Omnirad 2959)		276	White powder	[36,37]
2-Hydroxy-2-methylpropiophenone (Omnirad 1173)		245	Colorless to slightly yellow	[36,38,39]

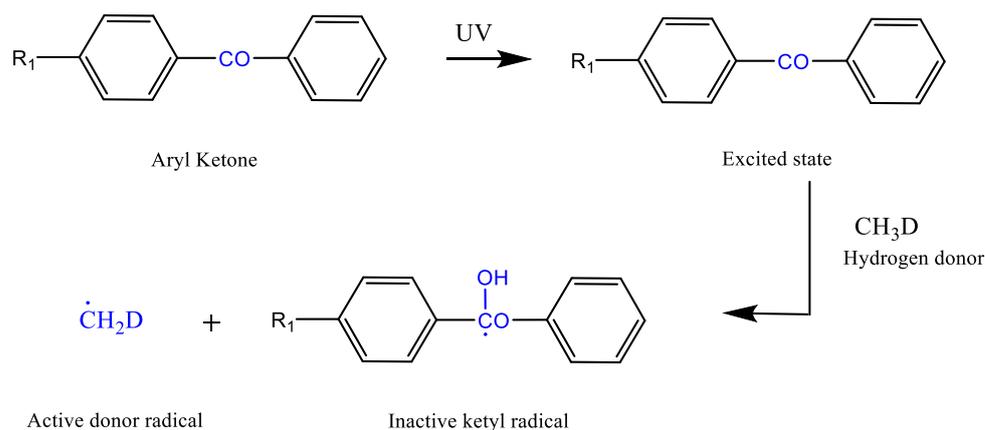
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Chemical Name	Structure	Activation Wavelength (nm)	Physical Form	Ref.
2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (Omnirad 907)		230, 303	Off-white powder	[40]
diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO)		275, 379	Pale yellow crystal powder	[32,36,40]
Ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (TPO-L)		299, 366, 380, 393	Yellow liquid	[36,40,41]
Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Omnirad 819)		295, 370	Light yellow powder	[38,40]

2.1.2. Bimolecular Photoinitiator (Type II)

These photoinitiators are also called Norrish type II photoinitiators. Type II photoinitiators generally consist of benzophenones and their substituent derivatives, thioxanones, anthraquinones, benzoylformate ester and camphor quinones [29]. They do not cleave themselves to generate free radicals owing to their high bond energy. Instead, they absorb the photon to reach an excited state enabling abstraction of hydrogen from the hydrogen donor molecule to generate a free radical [42,43]. When a CO bond absorbs the photon in such molecules, the UV energy is not sufficient to break the bond. Therefore, by virtue of a donor molecules (e.g., tertiary amine), excited CO can then abstract the hydrogen atom (Scheme 3). It is important to note that these coinitiators are sometimes erroneously referred to as sensitizers (which react with energy transfer instead).

Sanai and coworkers used benzophenone (BP) as type II photoinitiator to cure acrylate coating to achieve high solvent resistance [44]. Balta and coworkers further utilized type II photoinitiators to cure the coating formulation with Quinoxalines dyes along with *N*-methyl diethanol amine (MDEA) as hydrogen donor [45]. Like in the case with type I photoinitiator, researchers are interested in developing a new type II photoinitiator which can provide flexibility over the absorption spectra as well as solubility of the initiator. Lately, the idea of developing a single molecule with both donor and acceptor entities has emerged, which can enable use of a single photoinitiator in the system to achieve complete curing [43,46,47]. Table 3 shows some of the common examples of type II photoinitiator.



Scheme 3. The type II hydrogen abstraction process.

Table 3. Common examples of type II photoinitiator.

Chemical Name	Structure	Physical Form	Activation Wavelength (nm)	Ref.
Benzophenone (BP)		White flakes	250	
4-Phenylbenzophenone (PBZ)		White powder	248	
Methyl 2-Benzoylbenzoate (OMBB)		liquid	260	[40,48,49]
Isopropylthioxanthone (ITX)		Pale yellow powder	244, 330	
1-[4-(4-Benzoylphenylsulfanyl)-2-methyl-2-[(4-methylphenyl)sulfonyl]propan-1-one (Esacure 1001 M)		Off-white to pale pink	315	

2.1.3. Oxygen Inhibition

In addition to the two types of photoinitiators in free radical photopolymerization, it is critical that another key factor, oxygen inhibition, is discussed. In order to understand the significance of oxygen inhibition in the curing process, let us first understand the mechanism of the process. The first step is when propagating radicals (P-M^{*}) react with atmospheric oxygen to generate peroxide radicals (POO^{*}) and the peroxide then forms a bridge (POOP) by recombination of two peroxy radicals. These newly formed radicals are less reactive comparatively and thus form a tacky surface. In consequence, oxygen inhibition arises as one of the major issues associated with free radical polymerization [50]. Further, the high surface area of the coating leads to high oxygen exposure which needs to be tackled for an effective defect-free coating system.

Physical approaches like curing under inert gas, using wax barriers, etc., are few of the proposed solutions [51]. Further, chemical strategies include incorporating a high concentration of photoinitiator which consequently helps generate a high concentration of free radicals. These free radicals can then consume oxygen and reduce its concentration [52]. Incorporation of (1) hydrogen donors into the formulation like amine, thiols, etc., (2) oxygen scavengers like diphenyl furan, dibutyl anthracene, etc., (3) phosphine and phosphite, which are also used as antioxidants, and (4) CO₂ generating molecules like N-phenyl glycine (NPG) are some of the approaches that have been reported to eliminate the effect of oxygen inhibition [53]. Husár and coworkers noted that antioxidants affect storage stability, hydrogen donors affect hydrophobicity and viscosity, whereas CO₂ generating molecule incorporation is not that effective, and an alternative inert atmosphere is deemed just too expensive for industrial applications [52]. Oxime esters are not designed to overcome oxygen inhibition by CO₂ formation, since the amount formed is far too low to result in initiation. Another strategy to tackle this problem by industrial researchers was to incorporate acrylated amine oligomers into the formulation which can serve two purposes: (1) act as an abstractable hydrogen site for a type II initiator and (2) react with oxygen present in the system [54]. Incorporating multifunctional acrylate and highly reactive acrylate can also help reduce oxygen inhibition [26]. In retrospect, despite the above-discussed strategies recommended in the literature as well as the ones being currently developed, there still exists no clear solution to the problem, and it warrants further research.

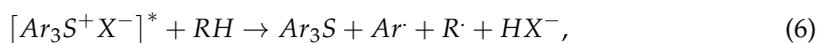
2.2. Cationic Polymerization

The industrial popularity for a cost-effective free radical photopolymerization is frequently offset by the oxygen inhibition constraint. To that extent, cationic polymerization is therefore a good alternative. Unaffected by the oxygen inhibition factor, however, it does have a lower cure speed compared to free radical polymerization [55]. Further, cationic polymerization is inhibited by humidity. It was first discovered in the 1970s by Crivello [56]. This process involves generation of protonic acid using UV light from cationic photoinitiators. Cationic polymerization generally follows the ring-opening mechanism [57,58]. The reaction can even continue for several days after irradiation due to acid generated during UV curing, a phenomenon commonly referred to as “dark curing”.

Currently, onium salts are popular in cationic UV polymerization [59]. Figure 2 shows some of the common onium salts for UV-cationic polymerization reactions. These onium salts are formed with bulky group 5A, 6A and 7A elements and their counterions. A counterion is an inorganic anion, and the efficiency of the initiator is determined by the nucleophilicity of a counterion [60]. Photo decomposition of these salts generates Lewis acid that can initiate cationic polymerization. This polymerization is terminated with water and alcohols. Termination is also accompanied by generation of protons that can lead to chain transfer. The general mechanism of cationic photopolymerization with onium salt is shown below in Equations (5)–(9) [61]. Scheme 4 shows the ring-opening polymerization of the epoxy moieties which are one of the most common chemistries in UV-based cationic polymerization.



Let us take $Ar_3S^+X^-$ as an example:



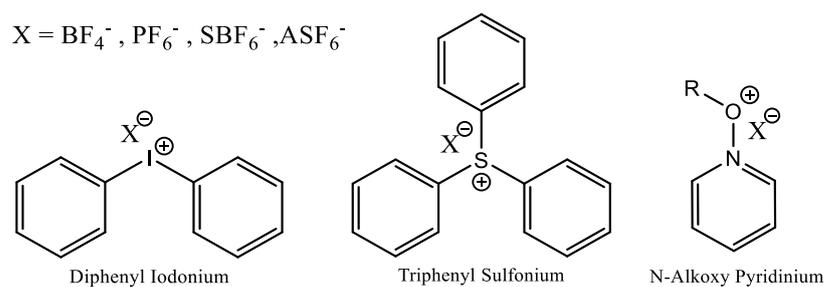
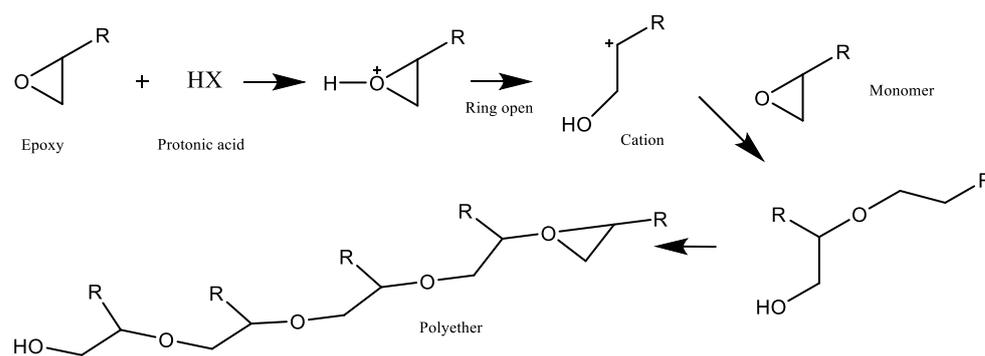


Figure 2. Common onium salts for cationic photo-polymerization reactions.



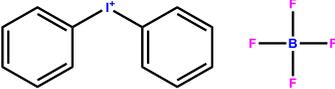
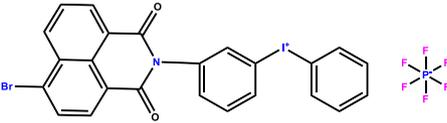
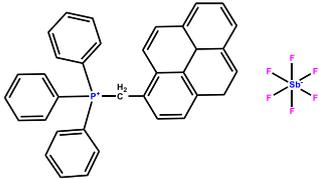
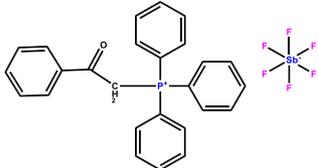
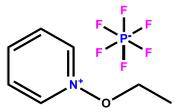
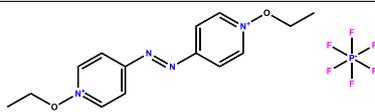
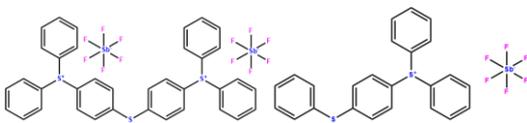
Scheme 4. Ring-opening epoxy polymerization.

Early research work was reported by Crivello and coworkers, where triarylsulfonium salt was used as a cationic photoinitiator for photopolymerization [62]. Since then, various researchers have worked on different systems as part of cationic polymerization. Martysz and coworkers used polyester resin and epoxy resin as candidates for this cationic polymerization [63]. Isin and coworkers developed silica modified nanocomposite coating using cationic polymerization to improve abrasion strength of the coating system [64]. Oxenate groups were cured using cationic polymerization to develop coating with a hardness of 6H [65]. Very recently, even biobased linseed, soybean, and tung oil were reported to have been used in cationically polymerized systems [12,66,67]. The cationic polymerization initiator list is extensive; some initiators are presented in Table 4.

Table 4. Examples of cationic photo-polymerization initiators.

Chemical Name	Structure	Activation Wavelength (nm)	Ref.
triarylsulfonium hexafluorophosphate		350	[68]
Iodonium, (4-methylphenyl)[4-(2-methylpropyl) phenyl]-, hexafluorophosphate		240	[68]

Table 4. Cont.

Chemical Name	Structure	Activation Wavelength (nm)	Ref.
diphenyliodonium borontetrafluoride		227	
6-bromobenzo[de]isochromene-1,3-dione Diphenyliodonium Hexafluorophosphate		340, 360	
pyrenylmethyl triphenylphosphonium hexafluoroantimonate		280, 350	
benzoyl triphenylphosphonium Hexafluoroantimonate		257	[22]
methoxy pyridinium hexafluorophosphate		266	
N,N'-diethoxy-4,4'-azobis(pyridinium) hexafluorophosphate		289, 459	
diphenyl [4-(phenylthio)phenyl]sulfonium Hexafluoroantimonate salts		245, 312	[68]

3. Lamps for UV-Curable Systems

Lately, several lamp sources have been explored to utilize the potential of the UV curing technologies to its maximum [17,69]. UV irradiance is one the key factor that needs to be considered while choosing the UV energy source for curing. Irradiance is the power per unit area expressed as W/cm^2 , and the depth of curing is affected by irradiance. The power supplied to coating during curing is called Dose or UV energy and is expressed as J/cm^2 . These two power factors are important, and while specifying irradiance, dosage integrated over time can also be used [5,70]. Generally, when UV sources emit light, it consists of different wavelengths. The graph of radiance vs wavelength is called spectral distribution and becomes a key piece of information in curing equipment setup. Some commonly used lamps are mercury lamp (low, medium, and high pressure), electrodeless lamp, excimer lamp, and LED (Figure 3).

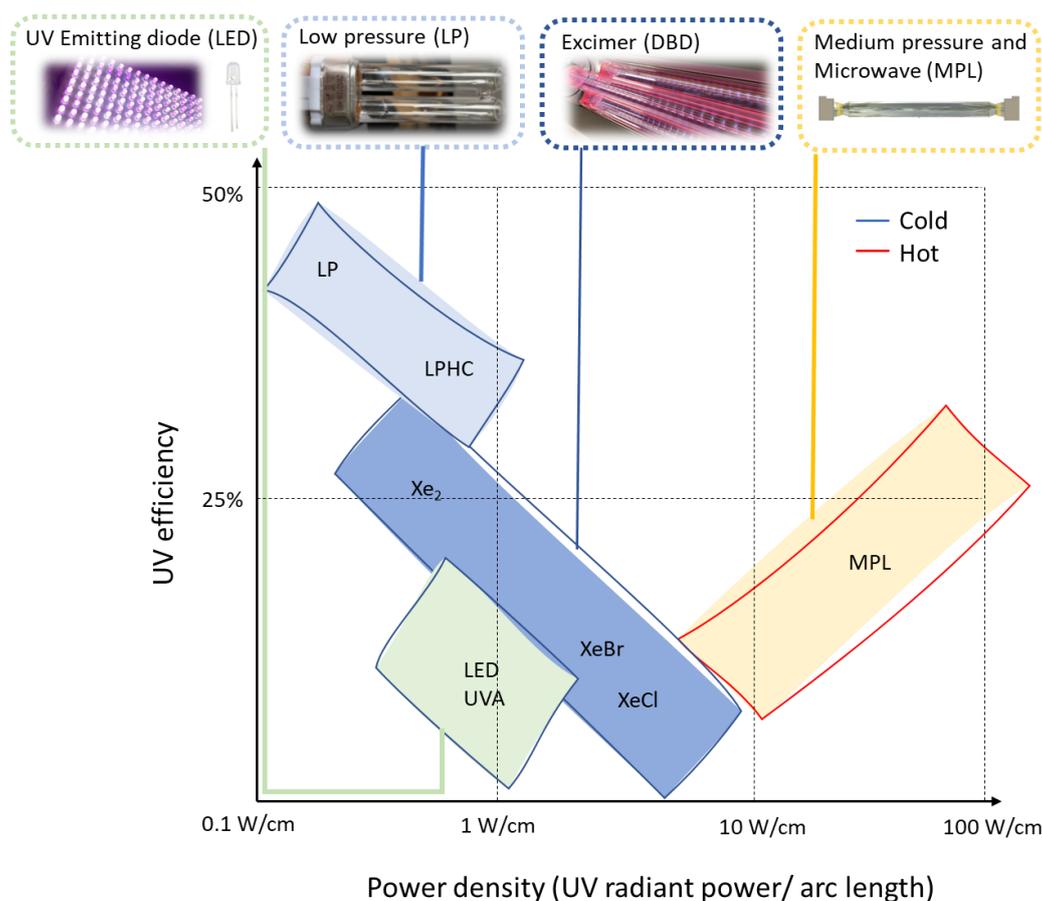


Figure 3. Comparison between different lamps and efficiency over power.

First, three types of mercury lamps are introduced, low-pressure, medium-pressure, and high-pressure mercury lamps operating at 12 W/cm, 80 W/cm, and 240–360 W/cm, respectively, excited by a microwave or an electrode. Mercury is enclosed in a quartz tube at $\sim 10^{-6}$ bar for low pressure, 1 bar for medium pressure and 100 bar for high pressure. A medium-pressure lamp is more popular amongst the three types of mercury lamps [71,72]. The higher the pressure, the more powerful the emission as a result of more collision. A point to note is that the UV source output must be tuned properly in such a way that pigment and fillers in UV formulation absorb minimum or no energy output from UV lamp. In this way, most of the energy is absorbed by the PI and utilized for photopolymerization [73], which reiterates the importance of the selection process of PI. Schwalm et al. reported a highly filled or pigmented system cured with UV-C (200–280 nm) [28]. In several instances, mercury lamps are doped with different metal halides to obtain a certain spectral output. Furthermore, iron doping (D bulb) has its maximum radiated powder in the range of 350–400 nm, whereas gallium (V bulb) has the maximum radiated power of 400–450 nm. Low-pressure mercury lamps are hardly used in industrial radiation curing. Emitting at short wavelengths, they are less safe than other lamps, produce ozone, and the short wavelength light has very poor penetration into the formulation.

Next, excimer lamps, unlike mercury lamps, generate quasi-monochromatic light. The word “Excimer” originated from “excited dimer”, and as the name implies the fact that light is generated through excitation of a dimer. Excimer lasers have very limited commercial applications. They are generally used in printing applications [28,29]. Rare gases (He₂, Ne₂, Ar₂, Kr₂, Xe₂) along with rare halides (ArF, KrF, XeCl, XeF) are used in excimer lamps [71]. Different wavelengths of light can be achieved by choosing different gas fills. UV light is generated through electrical gas discharge between two concentric

quartz tubes [74–77]. An added advantage is that these lamps do not generate ozone as opposed to mercury lamps. Scherzer and coworkers utilized an excimer laser to cure thin coating without incorporating any photoinitiators [78].

Next in line is the much-acclaimed LED lamp source. LED was commercially introduced in 2002 [72,79]. Since then, it has gained a lot of popularity. Herein, an electric current passes through semiconductor devices to generate energy that is emitted in the form of photons. It provides many advantages over mercury and excimer lamps. Low heat production, low power consumption, curing without generating ozone, mercury-free and longer life are only a few of the advantages of LED lamps [80]. Commercially available LED sources have lower output than medium-pressure UV mercury lamps and laser [81]. According to the paper published by Marcon and coworker, there has been significant development in LED output irradiance over the years. With time, it is expected to catch up with UV-mercury lamp sources [79]. Due to the industrial significance of the LED cure system, further discussions are provided in the future perspective section. To summarize the lamp sources for UV curable coatings, Figure 3 shows a comparison between different lamps and efficiency over power [81].

4. UV Curing Chemistries

As mentioned earlier, the UV curing system consists of a UV light source, a photoinitiator, oligomer/resin, and a diluent. We already discussed photoinitiators and UV light sources. Let us now have a look at the resin and diluent chemistry that determine the final properties of the system. Monofunctional and multifunctional molecules are used in UV curing systems as a diluent and a crosslinking agent, respectively [82,83]. They can help control the viscosity of the system. However, there are several variations and functional molecules being researched for optimization of UV coating properties [84,85]. Among the resin system, acrylate and methacrylate are widely popular UV system precursors. Methacrylate is less reactive compared to acrylate. Epoxy acrylate, urethane acrylate, polyester acrylates, silicon acrylates, and polyether acrylates are some of the examples of acrylic oligomers that are used in a UV-cured system [5,28]. Vinyl esters are also polymerized using this mechanism for UV curable coatings. Thiol-ene is another revolutionizing class of UV-curable chemistry mitigating the oxygen inhibition constraints of free radical systems [86]. In free radical systems, alkylperoxy radicals formed by adding oxygen to the growing polymer chain retard the polymerization process as it lacks sufficient energy to react with a monomeric double bond. However, the alkylperoxy radicals in thiol-ene polymerizations still possess sufficient reactivity to abstract hydrogen atoms from thiols and thus regenerate thiol radicals, resulting in the additional chain transfer reaction [87]. However, one challenge that exists is the unpleasant odors of low-molecular-weight thiols which has limited their commercial utilization. General chemistries involved in cationic systems are shown in Figure 4. It is important to know the advantages of the above-mentioned polymer precursors as they define the final performance of the coatings (Table 5).

As mentioned earlier in this paper, coating research in academia is becoming further inclined towards biobased or renewable raw material sources [9,88]. This is true for UV curable coatings, too [89–91]. Biobased thio-ene systems like lipoic acid, isosorbide diallyl monomers, and vegetable oil precursors are also being researched lately [92]. Ma and coworkers developed a gallic acid-based crosslinking agent for UV-cured coatings. Gallic acid, commonly found in tea leaves, hazel, oak bark, etc., and acrylated epoxidized soyabean oil were used for the system with >88% biobased content. Coating with superior mechanical property and crosslink density was obtained compared to those of petroleum-based precursors, but the cure time for the formulation was 45 min [90]. Further research into UV curable coatings has been performed by Soucek and coworkers, wherein modified derivatives of vegetable/seed oils like tung oil, linseed oil and soybean oil were used as alkyds, non-isocyanate polyurethanes, epoxy derivatives and reactive functional precursors, both in free radical and cationic UV polymerization [12,66,93,94]. Li and coworkers used castor oil to develop a polyurethane acrylate-based UV coating with a 40 sec cure time

Aqueous dispersion allows the use of high-molecular-weight resin which can be directly crosslinked with UV radiation [97,98]. Whereas solvent-based systems can have water soluble resins, emulsions, or dispersions, completely water-based coatings offer several advantages like low toxicity, better viscosity control, easy clean up, low cost and better adhesion, but they are constrained with low crosslink density and high shrinkage. In waterborne formulations, water is evaporated before curing. Although there are some disadvantages of such a system, such as (1) humidity sensitivity due to polar components and (2) time and energy consumption during drying step [27,28], incorporating acrylic functionality in the resin can be beneficial. This particular acrylate attachment step is called capping, with hydroxyl capping being the most common. Some of the recent developments in the field of waterborne coating use polyurethane, polyacrylate, epoxy and polyester to develop such coatings [99–105]. Substantial development in UV-cure coatings to overcome inherent limitations of free-radical-type curing systems has paved the way to dual-cure systems [106]. Typically manufactured as a two-component system, dual-cure technology, as the name suggests, is an amalgamation of UV curing combined with either thermal or moisture curing. Furthermore, dual-cure technology is currently being successfully adopted for many industrial products, especially in wood coatings, circuit boards and automotive coatings [107,108]. Examples of such dual-cure coating include a system with dimethacrylate–chalcone moiety (University) and dual-cure conformal coating 9482 (Commercial-Dymax) [109].

High solid UV coatings are liquid in their uncured state and do not contain solvents. However, these formulations use a reactive diluent, which consists of mono- or multifunctional monomers. They help control viscosity and also take part in curing reactions [28]. Bednarczyk and coworkers used trimethylolpropane triacrylate (TMPTA) and eugenol to develop antimicrobial coating. Reactive diluent eugenol incorporated into the coating inhibited microorganism growth [110]. Lee and coworkers used isobornyl acrylate (IBOA) as a reactive diluent to develop UV coating [111], whereas Seo and coworkers used TMPTA as a reactive diluent to achieve coating with better chemical and mechanical properties [112]. Cheon and coworkers used trimethylolpropane ethoxylate triacrylate (TMPEOTA) and IBOA as a reactive diluent in their system to study the effect of TMPEOTA amount on the system. It was reported that the mechanical properties as well as reactivity of the system increases with an increase in concentration of TMPEOTA [113]. It is very clear that the property of coating can be manipulated and tuned by selection of an appropriate reactive diluent and its amount in the formulation. In addition, as mentioned before, viscosity can also be tuned with the help of a reactive diluent. Since these diluents take part in the reaction, there is no VOC. One of the disadvantages of such a system is the toxicity of these acrylic diluents. However, once the curing is complete, they are not considered toxic.

UV curable powder coatings are a relatively new area of research, and they are gaining attention due to their unique properties. As opposed to conventional liquid coating, powder coating offers high efficiency, fast curing and low cost [114]. With its inception rooted to the 1970s by Vincent D. McGinniss at Glidden coatings company, Cleveland, OH, USA (currently Glidden® brand by PPG, Pittsburgh, PA, USA), several companies had to step up for a concerted attempt at commercialization in the 1990s [115]. Czachor-Jadacka et al. recently evaluated the deblocking process of various isocyanate crosslinker enabling low-temperature curing types [116] and determined that a potential substrate can be medium-density fiberboard (MDF). When using UV curable powder, coating is transformed into a film with infrared heat and later exposed to high-intensity UV light [117]. Lower-molecular-weight resins with low melt viscosity and high glass transition temperature are preferred in view of the need for physical storage stability [28]. However, UV durability for exterior applications still remains a concern, limiting its application. To that extent, Misev and coworkers previously studied weather stabilization and pigmentation relating to UV curable powder coating, where a combination of a bis-acylphosphineoxide and an α -hydroxy-acetophenone photoinitiator was suggested [118].

Another class of UV cure coating technologies that are making significant inroads on novel products and applications is UV-sol-gel coatings [119]. There, photoacid/photo base organic UV absorber molecules entrapped in hybrid organic-inorganic matrices are capable of drastically reducing the amount of UV light reaching the substrate [120]. This functional coating technology has facilitated hybrid anti-yellowing UV coatings on polystyrene substrate, aeronautical protection coatings, hydrophobic silica anti-reflective coatings, primer-less corrosion-resistant pretreatment coatings, etc. [121–124]. Figure 5 shows the different UV coating technologies and evolving opportunities which are discussed in the following section.

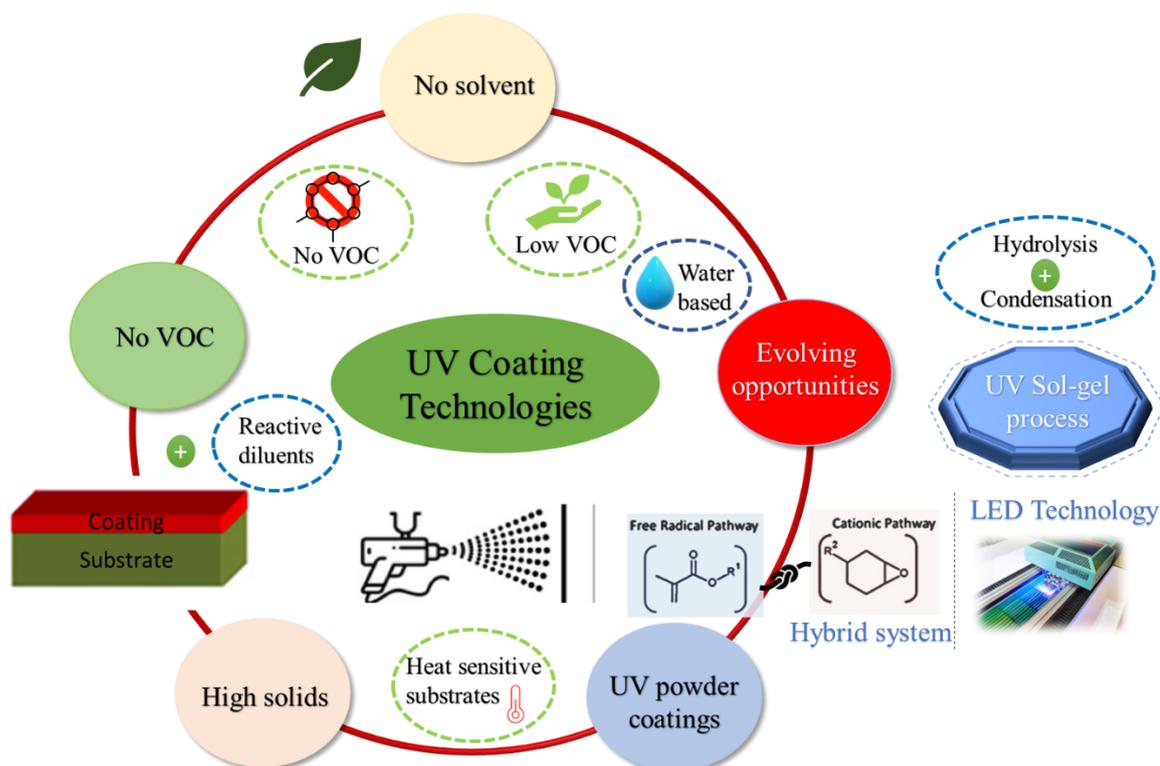


Figure 5. Depiction of UV coating technologies and evolving opportunities.

6. Evolving Opportunities

It is understood that amidst the multiple opportunities that exist in UV-based research, including UV degradation study and weatherability data compilation, UV coatings are still at its center [125–128]. In the context of the UV curable coating area, this section first discusses some of the most important coatings in terms of the latest advancements and industrial significance. The first system is the LED cure. LEDs are commercially available lamps, and many studies have been published on LED curing [22,79,129–132]. As discussed before, its low energy consumption, low heat generation, low cost and long life have gained huge attention worldwide. Furthermore, LEDs are quicker to reach full power and do not generate ozone unlike mercury lamps, which contain mercury, and special care must be taken if such a lamp breaks. Most important of all, LED helps reduce carbon footprint [79]. Currently, LED outputs of 365 nm, 395 nm, 405 nm and 455 nm are used for curing [133,134]. It can be used to carry out both free radical photopolymerization and cationic photopolymerization. Although LED offers huge advantages over mercury lamps, it is challenging to produce a surface cure, which explains its future perspective rationale. There is a two-faceted justification for this observation. The first point is that LED light sources have lower intensity compared to mercury lamps. It is well understood that when high-intensity lamps are used, a higher concentration of free radicals is generated, which rapidly combines with oxygen there by reducing its concentration [50]. Therefore, the

oxygen inhibition effect is more significant in an LED cured system compared to that in mercury lamps. The second point is that the LED light source is more concentrated in the UV-vis side. In this side, there is more surface generation resulting in wavelengths offered in LEDs that are more favorable for through cure rather than surface cure. Researchers are continuing to develop new photoinitiators to increase efficiency and initiators that can absorb wavelengths over 365 nm to match LED lamp output [134,135]. A cationic photoinitiator absorbing at the emission of LED lamps is required for radical photoinitiators. One example of such LED-triggered cationic polymerization system consists of onium salt with a radical source, or a formation of charge transfer complex with an electron donor helping to minimize the effect of oxygen inhibition [59].

Another important opportunity lies in a free radical/cationic hybrid system. As discussed earlier, free radical polymerization has many advantages: it uses a commercially available acrylate-based system, has high reactivity and moderate cost [136]. However, oxygen inhibition still exists as one of the major limitations of free radical photopolymerization [19]. Along similar lines, cationic photopolymerization with dark cure advantage is a good alternative for free radical photo curing. As the name suggests, the photopolymerization reaction can continue even after the light source is removed. Furthermore, monomers used in cationic polymerization have relatively low toxicity and low shrinkage [21]. However, water sensitivity is one of the limitations in the cationic polymerization system [60]. In addition, the most commonly used onium salt may decompose/reduce in the presence of a carbon radical [60]. As a result, to overcome limitations of free radical and cationic polymerization, they are proposed to be utilized together to gain their combined advantages. This thought process led to the inception of the concept of hybrid polymerization [137,138]. Oxman and coworkers used acrylates along with epoxy to develop a free radical/cationic hybrid system [139]. In more recent studies, Hasa and coworkers developed a hybrid system using difunctional oxetane and butyl acrylate. However, during the curing process, the system led to phase separation. By controlling the kinetics of free radical and cationic polymerization, Hasa and coworkers were able to develop a polymer network with superior mechanical properties [140]. Another possible breakthrough in a hybrid system involves research from Mannari and coworkers [120,124,141]. The research spanned the photo-initiated sol-gel process for corrosion-resistant hybrid pretreatments and ambient temperature UV-curable hybrid acetoacetylated non-isocyanate polyurethanes systems. Even though it is perceived that a hybrid system can result in novel coatings with enhanced properties, there is a scope of further meticulous research and optimization to facilitate its full potential.

7. The Aspect of Academia and Industry Research

It is important that academia and industry work in collaboration for the most effective product development route. It is equally critical that either party are cognizant of the recent works happening in both portfolios. This section serves the purpose of such a consolidation and comparison in terms of UV curable coating. Some of the papers published in 2022–23 talk about utilizing UV light to develop coating. In addition to the recent research reported in the earlier sections, various coating chemistries developed for substrates like wood, glass, metal, and plastic are presented in Table 6 for easy reference. Different types of lamps were used to cure these coatings like the mercury lamp, LED and excimer lamp as discussed before.

Table 6. Compilation of some of UV cure systems, lamp sources and application areas.

UV System and Lamp	Substrate and Application	Ref.
Urethane and epoxy acrylate coating cured by a mercury lamp	Multilayer protective wood coating	[142]
Polyurethane acrylate cured using an excimer lamp and a UV mercury lamp	Anti-fingerprint coating for wood application	[71]
Polyurethane methacrylate coating cured using LED	Anti-icing coating for tin	[143]
Water-based polyurethane acrylate coating cured using LED	Corrosion resistance for metal; can also be applied on glass	[99]
Siloxymethyl-modified silicone acrylate cured using a mercury lamp and a moisture cure	Anti-smudge coating and ant fingerprint coating for PET film	[144]
Silsesquioxanes and an acidic silica sol composite coating film cured by a mercury lamp	Antireflection coating for a PET substrate	[145]
Epoxy-functionalized siloxane hybrid coating matrix cured using LED	Glass fabric-reinforced siloxane hybrid composite	[146]
Polyurethane acrylate coating	Antifogging coating for plastic substrates like PET, PC, PMMA, PBS	[147]
Polyurethan coating cured using a mercury lamp	Anti-smudge coating for glass, wood, tin thermoplastic urethanes	[148]
Acrylic-styrene coating cured using a mercury lamp	Varnish coating for glass	[149]
Fluorinated polyoxetane and polysiloxane coating cured using LED	Antifouling coating for glass and PET	[150]

In contrast to most common filler/pigment/additive free academia research, recently published patents (Table 7) show that an industrially viable UV-cured coating system has oligomers, diluents, fillers, and additives. We note that even if major academic research disregards this complex system for the understanding of basic and foundational science, some of the papers published do focus on UV curable composite coatings. Chen and coworkers talked about the effect of TiO_2 as a filler on the curing of the urethane and epoxy acrylate coating, as well as the performance of the cured coating when exposed to UV light, i.e., weatherability. They were able to conclude that an optimum amount of filler along with controlled thickness can improve UV blocking of coating [73]. Cataldi and coworkers further developed a UV curable nano cellulose composite for wood. They used methacrylic siloxane in their system and deemed nanocellulose filler to be the choice for overall better performance compared to micro cellulose, especially in terms of water absorption, hardness and thermal properties [151]. Moreover, Barletta and coworkers developed UV curable coating using cationic polymerization technique. They used polycarbonate as substrate and amino-functional graphene oxide as fillers for this epoxy based UV coating to improve the scratch resistance [152]. From the product standpoint, there were many patents published in the recent years that revolves around UV-cured coatings (Table 7). In terms of application industries, UV curable technologies are being applied to smaller parts commercially with tubes, pipes, circuit boards, 3D printed applications and specialty coatings in medical, industrial, protective, and automotive industries. A combination of Tables 6 and 7 provides the significance of UV cure coatings in numerous new and novel areas of applications. Further, the compilation of Tables 6 and 7 shows that all the technical papers are written by experts in academia, whereas all the patents are filed by inventors from the industries, with no significant inter-collaboration observed.

Table 7. Compilation of some of the UV cure system-based patents published in 2020–23.

UV System and Lamp	Substrate and Application	Ref.
Polyacrylate cured using an LED lamp	Medical implants	[153]
Carbamate acrylate cured with a mercury lamp	Coating for computer and mobile devices	[154]
Epoxy acrylate coating cured with an LED lamp	Concrete floor	[155]
Polyester and polyurethane acrylate cured with an LED lamp	Scratch-resistant coating for automotive headlight	[156]
Waterborne coating cured with a mercury lamp	Wood, metal, paper, ceramic, leather, fabric substrate	[157]
Polymethacrylate coating cured using a mercury lamp	Paint application on paper	[158]
Waterborne polyurethane paint cured using a mercury lamp	Paint application for wood, paper, metal, and plastic	[159]

8. Summary

In this review paper, we summarized some basic concepts of UV coating with recent developments in the field of UV coating, both in academia and industry. Figure 6 outlines some of UV curable coating aspects and technologies discussed. UV technology offers many advantages over commercially available coating curing techniques: it has (1) a solvent-free system, (2) no VOC, (3) a low-temperature fast-curing system for conventional and heat-sensitive substrates, (4) low energy losses and capital cost, etc. Due to the set of advantages offered by UV technology, there is constant growing interest in the field.

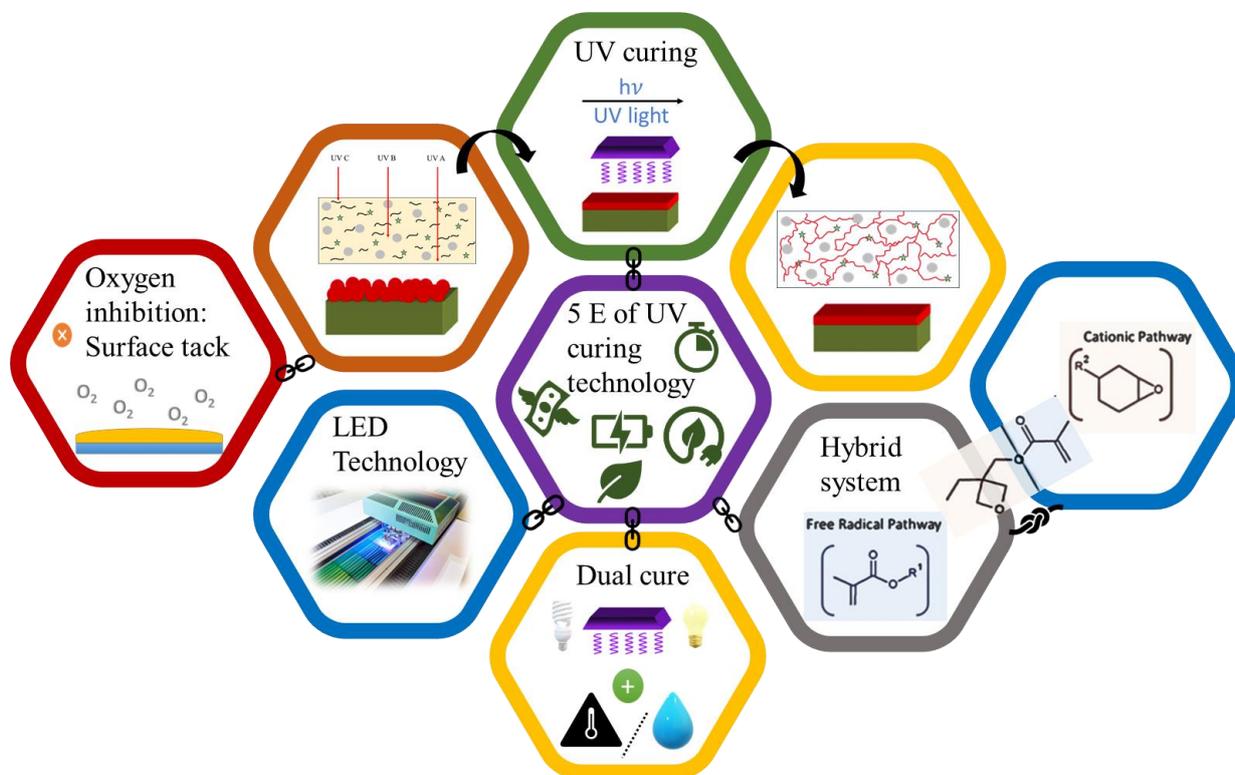


Figure 6. Illustration of UV curable coating aspects.

As discussed earlier, much of the recent academic research focuses on developing coatings from renewable raw material resources as alternative to petroleum-based raw ma-

materials, while many others concentrate on model components. These systems do not contain any fillers or additives, which is ubiquitous in an industry/commercial product. Evaluation of such systems on an industrial criteria basis is very important for assessing their commercial viability. Some of the published research discusses coating composites with fillers and additives incorporated. However, apart from evaluation of coating properties after it is cured, it is also important that the stability of the system is evaluated before it is cured. This is a vital criterion when working with new raw materials and a new coating system altogether, especially if the system does not have any additives like antioxidants. Some published works that discuss the synthesis of prepolymers and initiators for a UV coating system even use solvents. Using solvents to develop a prepolymer for UV coating and then categorizing it to be environment friendly is questionable. The purpose of synthesizing such a new UV curable coating route is to provide a good alternative for commercially available material and open new possibilities to overcome the current challenges. It is understandable that many academia researchers study fundamental science and try to understand the in-depth structure property effects of a new system. However, if a new product possibility is claimed in application-based research, it is important to evaluate the possibility of scaling-up and commercialization of such newly developed pre-polymers or initiators. The presence of very defined industry-relevant tests and evaluation methods would go great lengths when studying a new technology for industrial feasibility. Some of the synergistic systems at a nascent stage also need to be explored extensively. Furthermore, even though there are numerous advantages of UV curable coating technology, challenges to commercialization exist, too. Highly filled systems or pigmented systems that are very common in industry settings face major disadvantages when it comes to cure depth. UV light can only penetrate to a certain depth when its path is hindered by fillers. New photoinitiators with higher efficiency and lower cost need to be developed in the near future to facilitate easier commercialization. Further, UV-cured coatings react very fast and have higher susceptibility to shrinkage. This shrinkage can lead to adhesion issues. Although cationic or cationic/free radical hybrid systems can overcome some of these limitations, the high cost of photoinitiators and acrylic toxicity is still a challenge. Only a strong industry-academic collaboration can overcome this challenge in the future and needs to be implemented further. The authors hope that this review encompasses technical aspects of all strata of UV cure technologies for researchers exploring sustainable and climate-friendly coating technologies.

Author Contributions: Conceptualization, investigation, writing—original draft preparation, editing, review, and supervision, J.T. and R.S.P.; investigation and writing—original draft preparation, J.J. and M.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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