RSC Smart Materials

Photocured Materials

Edited by Atul Tiwari and Alexander Polykarpov

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Photocured Materials

RSC Smart Materials

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Preface

Synthetic polymers have been conventionally hardened by heating them at elevated temperatures. The properties and service life span of such synthetic materials largely depends on the degree of cure and crosslinking. In some cases, hardening of polymeric materials can be achieved in ambient conditions with the aid of catalysts. However, postcuring of such materials at higher temperature imparts better strength and resistance to harsh environmental conditions. The heating or hardening of such materials at higher temperature demands a high level of safety, excessive energy, and often a large working space.

The invention of photocuring technology is deemed to revolutionize the materials industry. This technique is considered as one of the most effective ways to rapidly transform a liquid polymeric resin into a dense crosslinked stable product without the release of harmful volatile organic components. Curing and crosslinking reactions triggered by light occur extremely rapidly that saves significant time required in conventional hardening of the materials. The ability to rapidly cure at low temperature, high spatial resolution, and use of stable single-component systems without the need for solvents continue to fuel industrial and academic interest in photocured materials. The past decade has noticed significant research and development activities in the curing technology as well as chemical ingredients. A wide array of photoinitiators, polymer precursors, fillers, and light devices has been discovered for the newer developments. Market survey studies have suggested that interest in photocured materials is gaining wide acceptance in academia as well as industry. It is thought that the market of photocured materials such as acrylic resins would grow at a rapid pace and reached approximately US$ 4.94 billion in year 2012. It clearly demonstrates the applicability and usefulness of the materials and technology. This staunch

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effort could help educating young scholars about the unforeseen applications that may originate from the interdisciplinary approach.

This book is a collection of excellent chapters written by the experts utilizing the technology in various innovative areas of materials science and engineering. Chapters dedicated to the synthesis of new monomers and resulting polymeric precursors are included to lay the foundation for novice. The utility of photocuring in coatings is the fastest growing area and has been extensively highlighted in the book. Besides traditional photocuring using UV lamps, LED and lasers a two-photon curing technique will impart new research directions for innovative developments. Chapters on the utility of photocuring technology in obtaining complex 3D structures, composite curing, and functional polymers will be of enormous interest to the readers of many research areas. The utilization of commercially successful polymers in microscale structures fabrication is well demonstrated in three interrelated chapters. The chapter on migration from cured coatings in food-contact applications reminds the researchers to consider the levels of residual photoinitiators and other low molecular weight species while designing their materials for faster curing and better properties.

We are confident that this book will be of interest to readers from diverse backgrounds in chemistry, physics, biology, materials science and engineering, and chemical engineering. It can serve as a reference book for students and research scholars and as a unique guide for the industrial technologists.

Atul Tiwari
Alexander Polykarpov

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CHAPTER 1

Photocured Materials: A General Perspective

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1.1 Current Trends and Future Avenues

1.1.1 Photocured Applications

Photocured materials are obtained by photoinduced hardening or cross-linking of various monomer-, oligomer-, and polymer-based compositions. Most commonly these materials are cured by UV, visible light, and electron beam (EB). A wide range of inexpensive UV photoinitiators coupled with the compactness, simplicity, and relatively low cost of UV equipment allows UV-cured materials to be used much more often and the interest in photocured materials has continued to grow[1] in recent years.

Photocured materials are commonly used as coatings, inks[2] and adhesives. The global consumption of photocurable coatings, inks and adhesives was 868 million pounds in 2012 worth $4.94 billion, according to a recent study from Kusumgar, Nerlfi & Growney Inc.[3] Photocured materials have also been the mainstay of photolithographic applications playing an important role in the creation of microchips and printed circuit boards. Due to the very rapid and low-temperature cure these single-component systems also found uses in biomedical applications from nail polish and dental

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restorations to providing scaffolds for tissue and organ regeneration. Increasing demands for higher productivity and lower emissions of volatile organic chemicals (VOC) continue to support the expansion of photocured materials into various areas of human activities.

1.1.2 Graphic Arts

As the printing market declined due to reduced use of newspapers, magazines, and paper books the growth in the UV and electron beam (EB) -curable printing inks and coatings continued to be in the packaging applications. Especially attractive has been the use in food packaging where there is a continued need for safer, faster, and cheaper inks, functional coatings, and overprint varnishes.

Recent research in the photocurable inks area has been focused on replacing mercury-vapor-based UV lamps with UV LED cure sources and developing better performing systems with low migration and low odor for use in food packaging. Acrylate oligomers developed for use in UV/EB curable inks have to be fast curing, disperse multiple pigments well, and provide suitable rheology to the ink formulations. Most commonly these are polyester acrylates,[4] though aliphatic epoxy acrylates and polyurethane acrylates are also used. Various special effect inks continue to be developed.[5]

UV inkjet inks are being used to make packaging labels and typically suffer from fewer delamination issues than conventional inks. These inks also allow for easy inline processing such as hot stamping, die cutting, embossing and others.[6] Plastic films are well suited for UV inkjet printing.[7]

EB cure often provides a viable alternative to UV for inks and overprint varnishes.[8] EB cure has been found to be especially effective in food-packaging applications where it leads to higher conversions of photocurable materials, while also removing the need for migrating photoinitiators and cure accelerators. Being an ionizing radiation with higher depth of penetration EB allows for much better through cure of pigmented coatings and inks. EB also enables cure through opaque to UV and visible-light multilayered substrates. EB coatings can be sufficiently durable to replace more expensive film lamination in paper-bag packaging.[9]

1.1.3 Adhesives and Sealants

Photocured materials are being used in laminating and pressure-sensitive adhesives and even as structural adhesives.[10] However, they still face a tough competition with the often less expensive on the per weight unit basis solvent, waterborne, and 100% solids two-component systems. Providing a low migration bonding layer for substrates used in food packaging presents an additional level of challenge due to the lower functionality of the oligomers and monomers used in adhesives than in coatings. This is often coupled with the difficulties in curing through opaque bonded substrates.

EB-curable adhesives have recently seen better growth due to superior properties and better process control of EB cure.[11]

Due to the speed of cure and ease of application UV-curable sealants found use in manufacturing of ammunition rounds.[12] In this application UV-curable sealant is applied to the joint between the brass casing and the projectile of the ammunition cartridge after the cartridge has been fully assembled and crimped. The sealant penetrates into the joint by capillary action and is then UV cured to form a waterproof joint. A specially designed LED UV source is used to obtain a narrow strip of UV exposure with well-controlled uniformity.

UV-curable hot melt adhesives continue to be developed and often have superior properties to the conventional systems. UV-cured hot melt adhesives find uses in specialty pressure sensitive tapes, construction, and medical applications.

1.1.4 Barrier Coatings

Films and plastic containers with gas barrier coatings found multiple uses in food packaging where protection of flavor and extension of the life of packaged food and beverages is of great importance. Photopolymerizable thiol–ene systems were shown to form films with oxygen permeability that can be dialed from very low to very high depending on the glass-transition temperature of the created polymer network. Modification of these networks with amine functional groups was found to create very good oxygen barrier films.[13] Surface modification of clays with acrylate or thiol-functional groups coupled with the selection of suitable exfoliating surfactants was shown to lead to UV-curable formulations with improved mechanical properties. Such formulations were also shown to result in better gas and water barrier properties.[14]

Various other barrier and sensor applications became possible *via* printing of the functional components using UV- and EB-cure processes.[15] The opportunity in gas and especially oxygen barrier coatings remains to be open for photocured coatings with high flexibility and adhesion to various plastic substrates.

1.1.5 Release Coatings

Release coatings are usually applied either on film or paper[16] substrates and used as removable liners for pressure-sensitive adhesive films or as protective films for various displays. Modern UV-curable release coatings are based on acrylated or epoxy functional polysiloxanes.[17]

1.1.6 UV Powder Coatings

UV powders are typically based on methacrylates and unsaturated polyesters. These formulations are applied by electrostatic spray to a substrate followed by melting of the powder in an oven and UV cure of the melt. The temperature required for melting is lower than what is required for thermally cured powder coatings and is typically around 120 °C.[18] UV powder coatings are used on a variety of substrates such as metals, medium density fiberboard (MDF), structural foams, plastics, composites and other heat-sensitive materials.[19] Creating cost-effective photocurable polymer powders with better resistance to sintering during storage and shipment remains an industry challenge.

1.1.7 Corrosion-Protection Coatings

UV-cure technology capabilities have been extended to the high-performance corrosion protection of steel and aluminum surfaces in industrial applications. Thinner and faster to cure UV coatings were shown to have corrosion protection similar to solvent based two-component urethane and epoxy systems.[20] Adhesion is often a challenge for UV-cured protective coatings on metal and some materials were suggested to address this issue.[21] Very large commercial opportunities for coatings with corrosion protection for metal remain in marine, automotive and aerospace uses, where there is a strong desire to move to rapidly curing, solvent-free and isocyanate-free systems. One of the key challenges remains to be the need for a well-working system that would combine exceptional durability and weatherability of the cured coatings with easy to use and relatively inexpensive curing and application devices. Recent developments in robotic UV systems have been made that allow precision application and cure of UV coatings on surfaces with various curvature and complexity including large vertically positioned surfaces.[22]

UV-curable coatings based on halogenated phenyl acrylates were shown to inhibit biofouling and biocorrosion on plastic panels immersed in waste water.[23]

1.1.8 Automotive Refinish

UV coatings are slowly making way into the automotive refinish area.[24] Among the challenges is the need to cure around corners and in cracks. Dual cure and photolatent catalyst approaches have been used to address these issues.[25] Recent advances in UV LED resulted in creation of hand-held cure devices that do not emit in the UVB and UVC range of the spectrum and do not generate ozone, which is expected to accelerate the adoption of the UV-cure technology by the automotive refinish and other applications where the materials are field applied and cured.

1.1.9 Aircraft Coatings

UV coatings have found uses in aircraft exterior applications where faster process flow for coatings is often sought.[26] Since the aircraft exterior finishing takes place at the end of the build process the urgency to avoid delivery delays while holding a very expensive inventory pushes the manufacturers to selection of faster curing coatings and UV is one of the options being considered.[27] UV coatings are also being considered as replacement for thermally cured coatings for the exhaust vent areas,[28] where the coatings can be subjected to temperatures as high as 150 °C. Recent developments in UVA LED cure sources and matching photoinitiating systems resulted in increased interest in field repair and stencil coatings for aircraft. These UVA-curable coatings have been shown to have performance that rivals that of the conventional 2K urethane systems.[29]

The idea of creating shark-skin-inspired microscale patterns on the surface of aircraft to improve fuel economy by reducing drag was recently tested using UV-curable materials.[30]

1.1.10 Coatings for Plastics

Creation of stable dispersions based on submicrometer scale particles of alumina and silica[31] along with the improvements in polyurethane acrylates led to creation of a new generation of scratch-resistant coatings with exceptional wear resistance. More recent developments in functionalized silicas, hybrid alkoxysilane-epoxy and acrylate systems,[32] and waterborne polyurethane acrylates[33] made UV-curable coatings especially useful for such easy to scratch plastics like polycarbonate, which is widely used in automotive headlamps. Various consumer electronics devices, optical discs, eye glasses, and even vinyl flooring have also benefited from UV-cured scratch- and abrasion-resistant coatings.

Photocured coatings are typically praised for their high gloss. Matte finish or low gloss photocured coatings have been less common due to the challenges in their formulation.[34] Recently, there has been an increased interest in matte UV coatings driven in part by the increasing demand for matte finishes in plastic packaging. There is also a need, particularly for the automotive and consumer electronics markets, for "soft touch" rapidly cured at low-temperature coatings where despite multiple attempts the balance of the soft to touch, velvety texture with high chemical resistance has not yet been attained.

UV-cured coatings are also used as base and top coats for metallization of substrates using physical vapor deposition techniques.[35] The "chrome look" has found uses in automotive, cosmetics and home-appliances markets.

1.1.11 Can Coatings

UV coatings found use in protection of beverage can rims from abrasion damage. The coating also allows for easier movement of the cans on conveyors during manufacturing and filling.[36] UV inks are also used in metal container decoration, although to a smaller extent than solvent-based inks.

1.1.12 Wood Coatings

Modern coatings for parquet flooring are based on UV-curable formulations. These coatings are multilayered systems consisting of the bottom layer, which is typically a water borne UV-curable formulation, followed by 100% solids UV-curable formulations layers to provide the necessary abrasion and scratch resistance.[37] UV-cured coatings are still used in multiple furniture and kitchen cabinetry applications. 100% solids UV lacquer was found to be the best alternative from an environmental point of view as a surface coating for wood furniture.[38]

1.1.13 Concrete Coatings

UV-curable formulations have been developed for coating concrete floors.[39] While these coatings provide almost instantaneous cure and are zero to low VOC they continue to face tough competition with the two-component rapid-cure technologies. Repair of rail seat abrasions on concrete ties has been shown to be very effective when using UV-cured materials.[40]

1.1.14 Alkyd Paints

Alkyd paints are based on oxidative drying of the unsaturated fatty acid esters and are used in households to paint doors, trim, and cabinets. Cobalt salts are typically used to accelerate the drying that otherwise can take more than 24 h. Recent studies showed that cobalt salts could be linked to adverse health and environmental effects, which forced the paint industry to seek alternatives to cobalt-based accelerators of the drying. A photochemical system was shown to be a viable candidate for a photoassisted autoxidation drying process in alkyds.[41]

1.1.15 Photochromic and Imaging Materials

A full-color imaging system based on photopolymerizable pressure-sensitive microcapsules was invented in 1984 for use in color copying.[42] The system was later developed into a visible light and pressure-sensitive single-sheet full-color printing medium.[43] More recent systems were developed to color irreversibly directly upon the exposure of photopolymerizable materials to UV and even EB without requiring secondary mechanisms such as heat or pressure for color development.[44] These systems found uses as cure indicators in photopolymerizable systems, as sensors and dosimeters for UV and EB radiometry,[45] and presented an opportunity for various photocured formulations to develop color as part of the curing process. Photocurable color imaging systems based on structural color using magnetically tunable photonic crystals are also being developed.[46]

Photocured materials can also be used as parts of the image forming or transferring devices. UV-curable formulations containing carbon nanotubes found uses in electrostatographic devices as transfer belts.[47] Such formulations were shown to have better control over the uniformity of electrical resistivity and superior mechanical properties to solvent-based thermoplastic and thermosetting systems.

1.1.16 Photoresists

Photocure can be used to prepare negative-tone photoresists, where photopolymerization or crosslinking can be used to render the material insoluble in the developer. Positive-tone photoresists, where the polymer is rendered soluble in the developer after the exposure, are typically not prepared by photopolymerization and can be classified as photosensitive, rather than photocurable materials.

Relatively simple photopolymerizable systems can be used to make low-resolution stencils and masks for etching glass and ceramics. Flexography is based on the use of the printing plates prepared from photocurable materials image wise exposed by UV.[48] Stencils for screen printing can also be prepared using photoresists.

High-resolution nanolithography and patterning is obtained using immersion 193 nm systems in making microchips.[49] EUV (extreme UV), EB, X-ray, and other imaging technologies are under different stages of evaluation and development for fabricating even smaller nanometer scale patterns for next-generation microchips.

1.1.17 Stereolithography

UV-curable formulations find use in stereolithography – a process of printing 3D objects using a computer-controlled laser layer-by-layer using photocurable materials. The photopolymerization takes place using a 355 nm laser and features as small as 40 μm in the lateral direction can be obtained.[50] Two-photon absorption-induced photopolymerization allowed to further expand the capabilities in creating 3D microstructures using photocured materials – features as small as 120 nm can be created.[51]

1.1.18 Optics and Electronics

UV-curable coatings for optical fiber have very stringent requirements for resistance to humidity and temperature variations. Acrylate monomers used in such formulations also have very high purity requirements to help minimize potential data transmission losses. As optical fiber began to be used in subterranean exploration for natural resources additional requirements for the coatings were added such as resistance to high pressure and corrosive environment of the drilling wells.[52]

Radiation-curable materials are used in integrated optical and optoelectronic applications (optical discs, diffraction gratings, antireflective coatings, imaging sensors and photonic devices).[53] UV-curable conductive inks are very suitable for making printed electronics for uses in RFID tags and OLED displays.[54]

UV-curable formulations found use in liquid-crystal displays.[55] Anti-reflective coatings for displays can also be obtained by using UV-cured coatings and films.[56]

1.1.19 Photovoltaics

UV-curable materials were shown to be capable of meeting the performance requirements for use in photovoltaic structures as adhesives.[57] UV-curable hard coatings found use in silvered films used in production of lead-free mirrors, where they greatly reduced the weight and cost of the system.[58]

1.1.20 EB Crosslinked Polymers and Composites

Low-energy EB (120 keV to 300 keV) is typically used to cure inks, coatings and adhesives. Medium-energy EB (300 keV to 5 MeV) is used to crosslink wire and cable insulation and to modify and cure fiber and composites.[59] High-energy (10 MeV) EB crosslinking of high density polyethylene was shown to result in superior dielectric properties *vs.* thermal crosslinking using peroxides.[60] Although, low-energy EB has also been found to be useful in crosslinking low-density polyethylene.[61] EB crosslinked wood–plastic composites are being developed to present a sustainable and nontoxic alternative to pressure-treated lumber for building materials.[62]

1.1.21 Nail Polish

UV-curable coatings have been a common alternative to solvent-based formulations in nail-polish applications. Polyurethane methacrylates are typically the basis of these formulations.[63] Renewable UV-curable coating materials are sought for this use.[64]

1.1.22 Dental Work

Photocured materials have been used in restorative dentistry since 1969.[65] The cure is now done using visible light, typically the blue region of the electromagnetic spectrum and often blue 450 nm LEDs are used.[66] Camphorquinone-based photoinitiating systems are most common, though other photoinitiating systems are constantly being developed in order to obtain faster and better curing composite systems with minimum shrinkage.[67]

1.1.23 Biomaterials

Photocured materials can be used in stereolithography based construction of artificial joints[68] or as scaffolds supporting tissue repair. Hydrogels are used as scaffolds for tissue engineering and can be obtained from photocured materials.[69] The use of UV-cured materials for creation of nerve-implanting surfaces with high spatial resolution may lead to creation of prosthetic materials with better outcomes for patients.[70]

1.2 An Overview of Chapter Contributions

Section 1.1 described several interesting applications of photocured materials. It was difficult to cover all the mentioned areas due to scarce of available literature and proprietary nature of technologies. This section briefly details the technical articles included in this book.

The area of UV light-cured coatings has been well established, and the coating industry was probably the beginner to adopt the use of photocuring. Soucek *et al*., in Chapter 2 describes the fundamentals, the chemical components and their use in the development of photocured coatings. The authors also detail the mechanism of cationic photopolymerization and free-radical photopolymerization along with the advantages and disadvantages of both the methods. Novel synthesis of photocrosslinkable polymers containing pendant chalcone moieties with different substituents has been described by Kumar *et al*., in Chapter 3. The authors utilized the free-radical polymerization method for the development and claimed that polymers containing pendant chalcone moiety exhibits liquid-crystalline behavior.

Torgersen *et al*., in Chapter 4 briefly describe laser-assisted two-photon polymerization. Their precise fabrication technique enabled the authors to create three-dimensional micro- and nanostructures. The chapter provides insight into optimization of photoinitiators to absorb two photons for the radical formation leading to photopolymerization. Formation of polymer liquid-crystalline composite material by a photoinduced inhomogeneous curing pattern has been shown by Veltri *et al*. in Chapter 5. The authors found that two parameters related to diffusion and curing intensity primarily governed the structures of the final product.

It is worth mentioning that photosensitive materials are now playing a vital role in precise fabrication of micro/nanocomponents and devices. Chen, in Chapter 6, comprehensively reviews the fundamental principles and interdisciplinary approach behind the development of miniaturized objects. The author also describes various schemes of microfabrication in photolithography, light stereolithography, soft lithography and inkjet printing. The developments of UV-curable scratch-resistant, functional coatings are detailed by Sangermano *et al*. in Chapter 7. Several variations of coating containing series of nanoparticles were achieved by photocuring technique. Zhou *et al*. in Chapter 8 demonstrate a photoimmobilization technology that uses photoreactive and nonbiofouling polymers for the preparation of microarray biochips. The authors expect that use of this technology will assist in understanding the fundamental aspects of biological interactions, along with other useful applications in clinical analysis. Cakmakci *et al*., study the flame-retardant photocurable coating containing boron and phosphorous in Chapter 9. The effectiveness of various monomers and additives in flame retardancy is discussed in detail. Similar to Veltri *et al.*, in Chapter 10, Sio *et al.*, demonstrated the fabrication of curved periodic microstructures containing self-aligned liquid crystals. The holography and lithography techniques assisted the authors in developing periodic nano-/microcomposite gratings. The diversified nature of polymer liquid-crystal polymer slices (POLYCRIPS) technology is mentioned by Sio *et al.* as well as in Chapter 11 by Caputo *et al.* The author's study suggested that POLYCRIPS technology is valuable for switchable diffraction phase grating, switchable optical phase modulator, arrays of mirrorless optical micro-resonators for tunable lasing effects and a one-step fabrication of fork gratings.

The use of photocuring in fabrication of thick high aspect ratio structures is shown by Chiu *et al.*, in Chapter 12. The authors have selected a negative-tone photoresist to fabricate complex three-dimensional structures. The basic material properties and fundamentals of the fabrication process related to the selected negative photoresists are summarized. In Chapter 13, Morales *et al.* adopted a unique approach for rapid crosslinking and stabilization of carbon fibers. The authors noticed that with the use of short UV treatment, precursor fibers could be thermo-oxidatively stabilized and successfully carbonized rapidly. The resulted fibers retained a higher extent of molecular orientation and displayed higher tensile modulus.

Although photocured technologies have demonstrated extremely high potential in various commercial arenas, they show limitations when used in food contact. The photoinitiators from packaging materials tend to leach out into food products that poses serious human-health issues. Lago *et al.*, in Chapter 14 review the methods available for the detection and determination of photoinitiators in food packaging and foodstuffs. The authors comprehensively summarize the state-of-the-art systems for the determination of nonintentionally added substances derived from the photoinitiators.

Apart from conventional UV light lamps for photocuring and photopolymerization, LED light curing and polymerization show significant promises. Vallo *et al.*, in Chapter 15 suggest that since spectral output of LED sources is concentrated in a comparatively narrow wavelength range, more efficient curing is possible, resulting in reduced curing time and increased depth of cure compared to conventional light sources. Moreover, with LED curing there will be less heat transfer to the substrate without the possibility of harmful UV rays. Finally, in Chapter 16, Barrera *et al.*, discusses the importance of gamma-radiation technology for the structural and physicochemical modification of waste materials such as PET bottles, TetraPak® packing containers and tire rubbers. Additionally, the utilization of such modified waste as fillers and reinforcement in concrete is emphasized.

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CHAPTER 2

UV-Curable Coating Technologies

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2.1 Introduction to UV Curing

It has been acknowledged for decades that the presence of volatile organic compounds (VOCs) in the atmosphere can not only contribute to serious air-pollution problems due to their toxic or carcinogenic characteristics, but also lead to global warming indirectly.[1] Due to concern over these problems, regulations regarding emission of VOCs into the atmosphere were established. Most solvents have been classified by the US Environmental Protection Agency (EPA) as photochemically reactive, and their usage has been regulated since the 1970s to reduce air pollution.[2] In 1990, the US Congress listed certain common solvents as hazardous air pollutants (HAPs), limiting their usage and creating pressure on the coatings industry to look for solutions in order to reduce solvent emissions.[3]

Besides the regulation of VOCs the coating industry is facing today, energy is another concern, especially the consumption of fossil-fuel resources since polymer and coatings fields depend mainly on petrochemical products derived from crude oil that will become scarce in the future. As a result, new technologies were invented and many efforts have been directed toward the area of renewable resources. A solution for the VOC restriction and energy problem is to employ a high-technology UV-curable system that is solvent free, and low in energy consumption.[4,5]

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UV curing is the process of film transformation from a reactive liquid (except a powder coating) into a solid by radiation in the ultraviolet-energy region rather than by heat. UV cure coatings involve the polymerization and crosslinked polymer network induced by photons. UV cure coatings are one of the most important classes of radiation-cure coatings.

Introduced commercially in the 1970s, the UV-curing industry has enjoyed a steady growth and has become one of the most rapidly developing fields in the entire coatings industry. UV-curable coatings have found application for the surface protection of all kinds of materials such as metals, plastics, glass, paper, wood, *etc*.[6] Today, the use of UV-curable formulations is progressing at a fast rate. The main reason for such a rapid technological growth of UV curing is due to its advantages, which could account for its popularity.

2.1.1 Advantages

(i) Fast cure. UV-curing technology uses the energy of photons from a radiation source to form reactive species, such as free radicals or cations, which can initiate a fast chain-growth polymerization of monomers and oligomers. UV-induced curing allows fast transformation of a liquid resin into a solid material by polymerization of a solvent-free formulation at ambient temperature.[7] The curing time of UV-curable coatings is of the order of magnitude of seconds or minutes rather than hours in thermal curing, which means a significant reduction in cycle time.

(ii) Ambient curing temperatures. Heating in UV curing is not required, thus the overall energy consumption is lower than the thermally initiated curing processes.[7] This contributes to not only lower thermal stresses, but less expensive tooling. Ambient-temperature curing is imperative for heat-sensitive substrates, including paper, some plastics, and wood.

(iii) Space and energy efficiency. The UV-curing requires smaller curing units as compared with ovens for baking in thermal cure, which saves building space.

(iv) Solvent-free formulations. Reduced solvent emission is an important motivation for use of UV-curable coatings. Generally, the formulations contain no solvent and VOC emissions are negligible.

(v) Improved coating properties. Functionalized monomers and oligomers can be easily formulated to meet a variety of applications. Due to the wide range of viscosities inherent in the reactive oligomers used in UV-curable components, coatings can be readily formulated to meet demanding viscosity required by certain coatings applications.

All of the aspects listed above combine together to make UV curing a unique coating means that can be tailored for any application normally met by thermally cured coatings, but with less complication. UV-radiation curing has become a well-accepted technology that has found a large variety of industrial applications because of those distinct advantages. UV polymerization is commonly used for curing of relatively thin polymer films in applications such as fast drying of varnishes, paints, printing inks and adhesives, as well as in the production of printing plates, microcircuits, and optical disks.

2.1.2 Disadvantages

There are also some drawbacks for UV-curing technology as follows:

The radiant power of the UV lamp decreases with the square of the distance, which limits the UV-curing technology to three-dimensional products that lead to no curing in the shadow areas. As a result, UV curing cannot be used to cure complex-shaped parts.

UV radiation is most limited in terms of penetration into matter, thus it has difficulty with pigmented coatings. Rapid shrinkage during curing can create adhesion problems. In composites processing, the use of UV curing has so far been limited to open-mold processes and relatively thin laminates.

UV radiation is best known for its deleterious effects on organic compounds, particularly upon prolonged sunlight exposure. By breaking chemical bonds, UV radiation causes severe changes in the mechanical and optical properties of polymer materials, thereby reducing their service life in outdoor applications.

2.2 UV Energy and its Properties

Ultraviolet radiation, part of the electromagnetic spectrum, shows wavelength in the range from 40 to 400 nm with wavelengths below those of visible blue light (see Figure 2.1). It is divided into the following four regions:

1. vacuum UV: 40–200 nm;
2. UV C: 200–280 nm;
3. UV B: 280–315 nm;
4. UV A: 315–400 nm.[7]

Vacuum UV is strongly absorbed by the oxygen in air and most common materials such as quartz. Vacuum UV has a small penetration depth. Thus, vacuum UV is not suitable for the usual radiation curing.

Because the energy of radiation increases with increasing frequency or decreasing wavelength, radiation with short waves contains a large amount of energy. This energy is capable of bringing about certain chemical reactions in a system that is sensitive to light and the absorbed energy can then generate species that are capable of initiating polymerization or crosslink reactions.

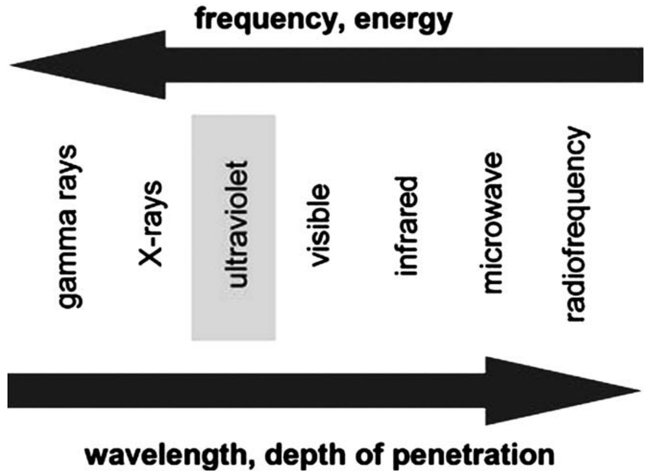

Figure 2.1 Electromagnetic spectrum.[7]

One of the requirements for UV curing is a UV source that produces high-intensity UV radiation without generating excessive infrared radiation. Major radiation sources in commercial use are medium-pressure mercury vapor lamps. For initiation *via* any lamp source, there must be absorption of radiation by the photoinitiator or substance that leads to the generation of an initiator.

The fraction of radiation absorbed within a coating film, I_A/I_0, is related to the molar absorptivity ε, concentration of photoinitiator C, and optical path length of radiation in the film X. Assuming that no other absorber is present and neglecting surface reflection, the fraction of radiation of a given wavelength absorbed is expressed as $I_A/I_0 = 1 - 10^{\varepsilon CX}$.

When a photoinitiator absorbs a photon, it is raised to an excited state, which leads to generation of an initiating species.[8] The efficiency of generation of initiating species is an important factor in the selection of a photoinitiator.

2.3 Equipment

The UV-curing equipment consists essentially of three components: the lamp, lamp housing, and the power supply. The electrical energy supplied to the bulb is converted into UV energy inside the lamp. The housing is designed to direct and deliver to the substrate or the part to be irradiated. The lamp housing reflects and focuses the UV energy generated by the lamp. The power supply delivers the energy needed to operate the UV lamp.[9]

A typical UV-curing unit might house one or more lamps. In most situations, the materials to be cured are passed by or under one or more lamps *via* a moving belt. The speed determines how long the surface is exposed to the light. The light generated by the lamp is reflected by a reflector that can either focus or defocus it depending on the process.[9]

Figure 2.2 FUSION LC-6B Benchtop Conveyor UV Curing System (http://www.caeonline.com/listing/product/182588/axcelis-fusion-lc-6b).

A FUSION LC-6B Curing System is shown in Figure 2.2. The LC6 Benchtop Conveyor is a production UV-curing unit that is suitable for laboratory and R&D applications. It can also be used in testing of adhesives, inks and coatings for qualification, cure response testing, or performance evaluation. It can handle a variety of substrates up to 7.5 inches wide with an effective curing width up to 6 inches. The lamp and housing are adjustable to accommodate parts up to 3 inches high.

2.3.1 Light Sources

UV-curable coatings require a specific type of energy with a wavelength of approximately 400 nm in the UV spectrum to initiate chemical crosslinking of the coating components. One of the most important factors in the success of a UV-curing operation is in the correct choice of the lamp system.

2.3.1.1 Mercury Lamp

By far the most popular source for UV curing has traditionally been the medium-pressure mercury lamp with output at specific lines from the deep UV to the visible, superimposed on a low-level continuous band. The standard mercury lamp is used in most of the existing applications. Such electrode lamps are tubes with different length and outputs. The radiation has continuous wavelength distribution with different major peaks (see Figure 2.3), and the main spectral output is in the wavelength range below 300 nm and at 365 nm (H-bulb). In transparent clearcoat application, this spectrum can well be used to tune the spectral output with photoinitiator absorption. By adding iron to the mercury lamp, the lamp spectrum contains additional bands in the range of 350 to 400 nm, thus in the UV-A range (D-bulb). Such types of lamps are used when additives in the coating have strong absorption in the UV-C range, like UV absorbers, and the best overlap with the photoinitiators has to be tuned to longer-wavelength ranges. A further shift to longer-wavelength absorption can be done with gallium and indium addition. Here, intense output is added in the wavelength range of 400–450 nm (V-bulb). Such lamp systems are mainly used for pigmented coatings (see Figure 2.3).[10]

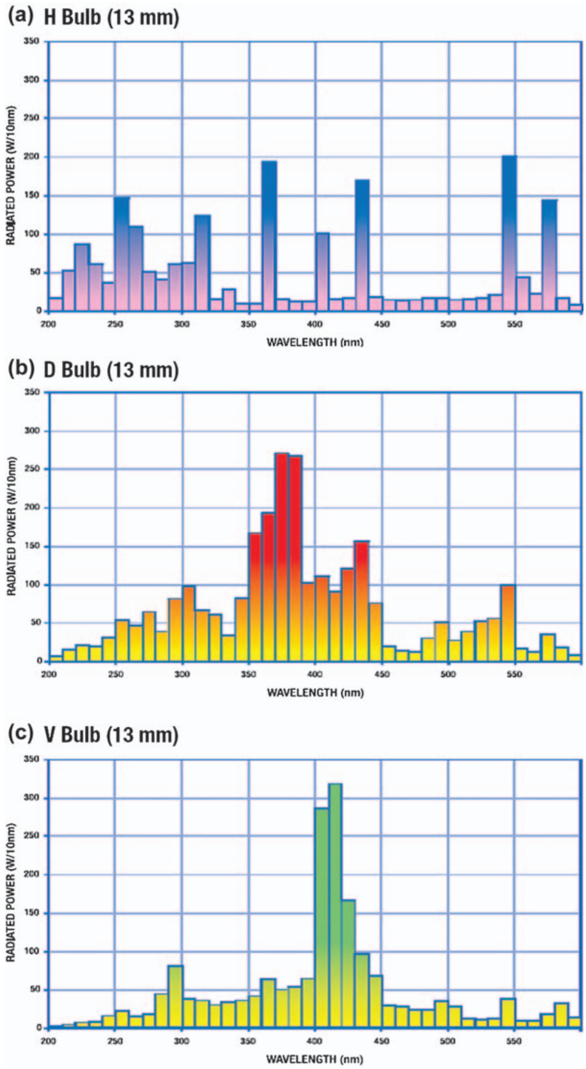

Figure 2.3 Spectral power of different mercury bulbs.

A limitation of UV curing is that the distance between the lamp and the coating on various parts of the object being coated must be fairly uniform. Hence, UV curing is most easily applicable to coating flat sheets or webs that can be moved under the UV lamps or cylindrical objects that can be rotated under or in front of the lamps.

2.3.1.2 Electrodeless Lamps

In recent years, a number of UV operations have turned to the use of the electrodeless lamp systems. Electrodeless lamps are powered by microwaves and are more suitable for doping, since the lifetime of lamp electrodes is generally reduced by dopants. Electrodeless lamps have the further advantage of essentially instantaneous start-up and restart. However, electrodeless lamps are more expensive.[9]

2.3.2 Coating Methods

A variety of methods are used to apply liquid systems to different surfaces in UV-curable coatings.

1. Roll coating. Roll coating is widely used as an efficient way to coat uniform, generally flat or cylindrical, surfaces of rigid or flexible substrates. Direct roll coating and reverse coating are two of the most commonly used types of roll coating systems. The typical UV formulations are in a viscosity range (<4000 mPa s) to be used preferably in roll and curtain coating applications.[9,10]
2. Curtain coating. Curtain coating is widely used in coating of flat sheets of substrate, such as wood panels. A coating is pumped through a slot in the coating head so that it flows as a continuous curtain of liquid. The material to be coated is moved under the curtain by a conveyor belt. The film thickness is controlled by the width of the slot and the speed of the substrate being coated.
3. Airless or conventional spray guns, used for three-dimensional or shaped objects.
4. Vacuum coaters.
5. Electrostatic application.

Spay application; dip coating, flow coating, spin coating, and rod coating are some other application methods.[9,10]

2.4 Components

UV-curable coatings are very different from conventional solvent or water-based coatings. They are up to 100% solids, containing little or no solvent or water carrier. The main components of such formulations are: photoinitiators, reactive oligomer, reactive diluent, and additives.

2.4.1 Photoinitiator

A photoinitiator is a compound-generating reactive species that will initiate polymerization or crosslinking. Photoinitiators are the basic link in the UV-curable formulation between the lamp source and the resin system. The function of a photoinitiator is:

1. absorbing the incident UV radiation;
2. generation of reactive species (free radical or ions);
3. initiation of photopolymerization.[11]