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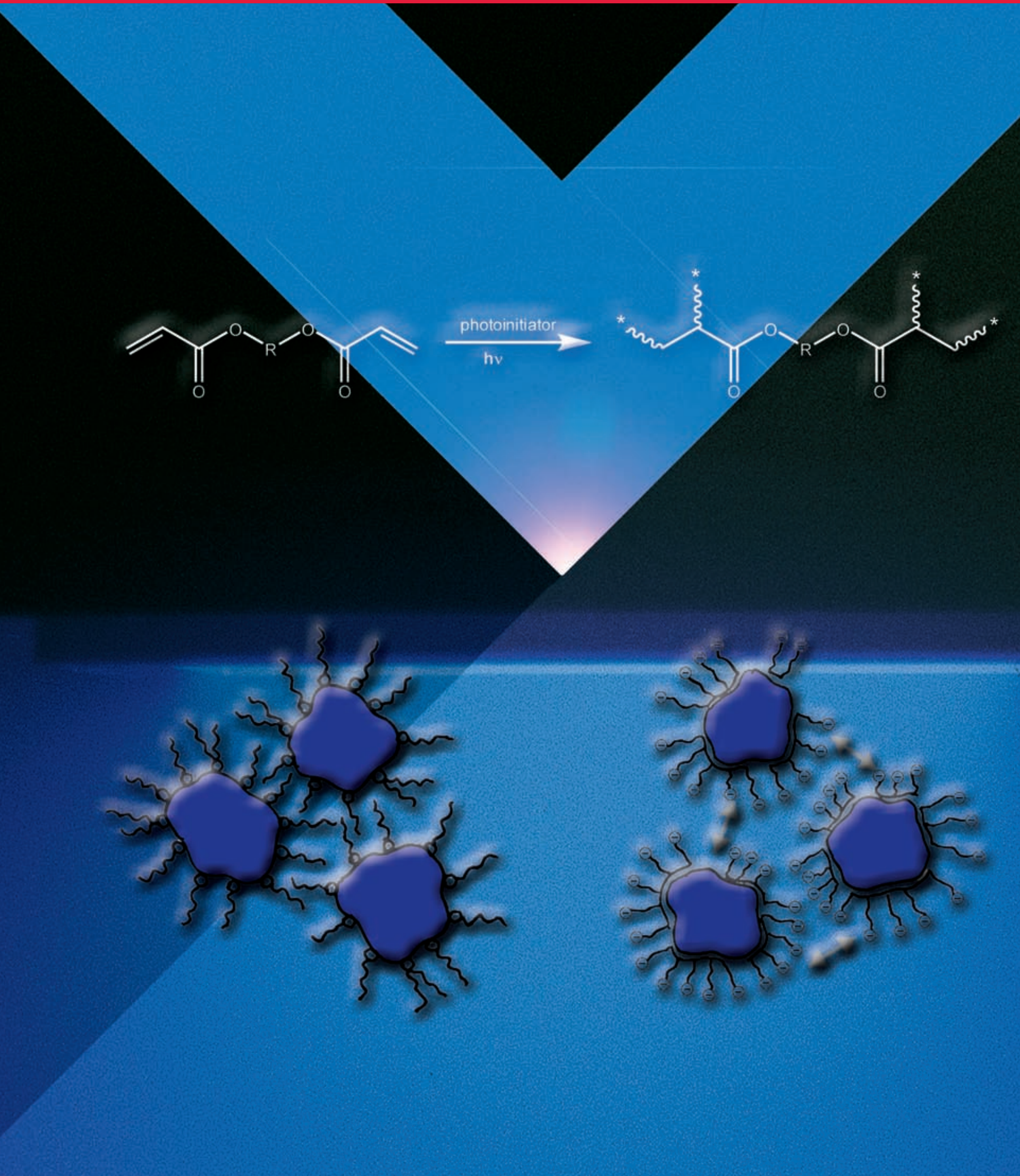
Radiation Curing

Coatings and Printing Inks



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Technical Basics, Applications and Trouble Shooting

Glöckner/Jung/Struck/Studer: Radiation Curing for Coatings and Printing Inks

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Foreword

Radiation curing is the fastest growing technology in the inks and coatings industries. It is being widely discussed in numerous publications and conferences and is being used or at least tested in all possible industrial applications.

When asked to write a comprehensive work on radiation curing, we soon realized that the need was not for a theoretical treatise but a book that could be helpful to a large number of readers in their day-to-day work. Our objective was to link theory and practice in a reference guide for formulators in the field of radiation curing. The book is also intended for students and young professionals in coatings and printing inks with no previous experience of radiation curing. In addition to the fundamental principles, therefore, we offer guidance in the selection of raw materials. The Trouble Shooting Chapter summarizes approaches to solving problems that may arise during the manufacture and processing of radiation curable systems.

The focus is on 100 % liquid coating systems that are radically or cationically curable by UV or electron beam radiation. Technologies that are still relatively unimportant are beyond the scope of this book and are discussed only briefly.

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Content

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1 Introduction

1.1 Definition

Radiation curing coatings (RC) and inks are formulations of components that contain reactive groups which react with each other after exposure to energy-rich radiation. In general there is no physical drying involved in the curing mechanism. Up-to-date formulations tend to be free of organic solvents.

Even though many kinds of radiation would theoretically be possible the industrial application is mainly limited to the cure by ultraviolet light (UV) and electron beam (EB). While in the case of EB the irradiation itself initiates the crosslinking in the case of the UV cure the radiation does not directly activate the reactive groups, but activates a light sensitive component called photoinitiator that actually starts the polymerization reaction. The cure by radiation takes place at very high speed – from parts of a second to just a few seconds.

1.2 Main differences compared to conventional coatings

Conventional coatings consist of
- binders (film forming polymer),
- volatile, organic solvents,
- pigments and fillers (if not a clear coat), and
- additives.

Conventional coatings dry by evaporation of the solvents and possibly a subsequent chemical crosslinking of the binder with itself or a hardener. This may take place at room temperature, at elevated temperatures below 100 °C (enforced drying) or above 100 °C (stoving/ baking). If no chemical reaction takes place after the evaporation of the solvent the coating is called physically drying.

The most well-known representatives are solvent-based formulations. Similar principles apply to waterborne coatings where the organic solvent is replaced by water. Here, the binders are often dispersed in water, rather than solved. In any case the solvent is primarily used to allow the manufacturing and the application of the coatings and acts as viscosity reducer. After application it leaves the film completely.

In constrast **radiation curing formulations** cure without any evaporation of solvent. Indeed normally there is no volatile solvent present at all. All components in a radiation curing formulation stay within the film. The film forming agents present are a combination of higher molecular weight oligomers and lower molecular weight monomers, all of which carry reactive groups to crosslink with each other. This means, that none of these is solely a visco-reducer, but all components become part of the final polymer network and contribute to the final film properties. Figure 1 illustrates the differences between conventional and radiation curing coatings.

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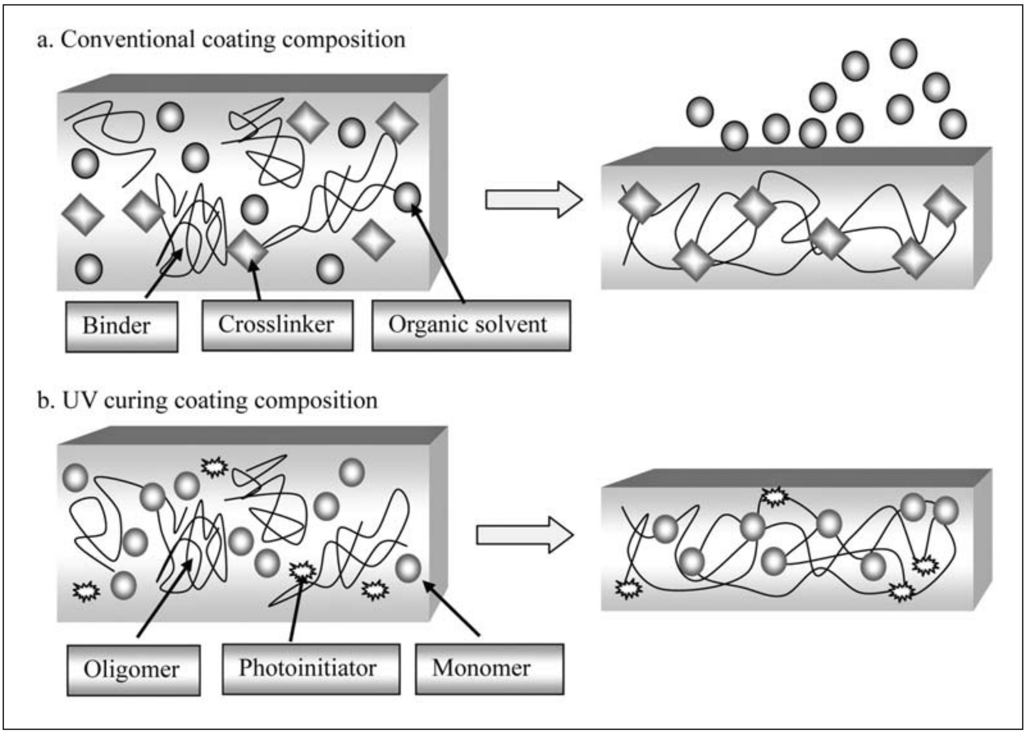

Figure 1: a) In case of conventional coatings organic solvents leave the film during drying and crosslinking; b) UV curing formulations crosslink without emitting any organic solvents

Table 1: Some properties of conventional and radiation curing coatings and inks

	Conventional coating	Radiation curing coating
physical drying	yes	no
chemical crosslinking	yes (depending on binder)	yes
volatile solvents	yes	no
drying times	minutes to days	parts of a second

Radiation curing coatings consist of
- oligomers,
- monomers,
- photoinitiators (in case of UV curing),
- pigments and fillers (if not a clear coat), and
- additives.

In Table 1 some properties of conventional and radiation curing coatings and inks are listed and compared. A detailed explanation of the formulation components can be found in Chapter 3 of this book.

1.3 Advantages and disadvantages

Radiation curing is distinctly different to conventional coating technologies. The nearly immediate cure and the absence of solvents allow obtaining a dry and fully cured film in just a few seconds. There is no need for long flash-off times or time- and energy-consuming drying tunnels in application lines. Cured surfaces can immediately be processed. Printed goods can be coated, cut, embossed, etc. right away; coated surfaces can be sanded, recoated, glued and assembled without waiting time. Radiation curing is the ideal technology for curing coatings on flat (two-dimensional) substrates. Especially when the substrate is fed from a web like in graphic arts applications or flat substrates moved on a conveyor belt through the application line like in wood coatings applications a radiation curing unit is easy to install and operate. Figure 2 shows the principle of a web-fed UV coating unit. The most important advantages and disadvantages of radiation curing over conventional coating technology are summarized in Table 2.

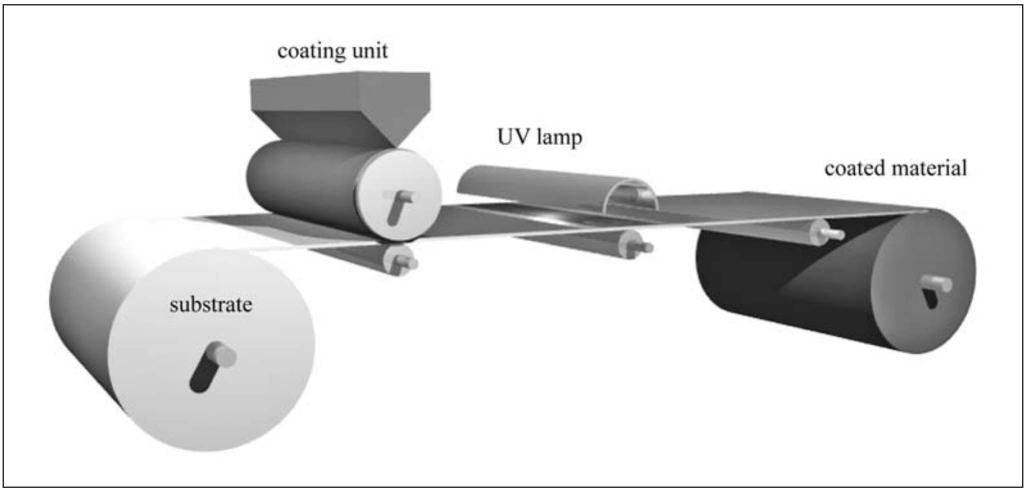

Figure 2: Principle of a web-fed UV coating unit, source: EVONIK TEGO

Table 2: Main advantages and disadvantages of radiation curing over conventional coating technology

Advantages	**Disadvantages**
very fast cure speed	cure of three-dimensional objectives requires complex curing units (shadow areas)
time and cost savings	skin irritation in case of some raw materials
absence of volatile solvents (VOC), zero to low emissions of VOC	very matte finishes difficult to obtain
cured films display outstanding resistance properties and gloss	high pigmentation levels at high film thicknesses can create cure problems
reduced energy consumption for cure (environment and cost)	inherent viscosity of radiation curing formulations makes certain application methods impossible at room temperature
relatively small capital investment in case of UV unit	running and maintaining the curing unit requires qualified personnel
little space requirements (especially in case of UV units)	partly high raw material costs
application on heat-sensitive substrates possible	relatively high investment costs in case of EB
no pot-life = coating/ink does not dry before irradiation (no problems in case of machine stop; easy to clean and easy recycling)	adhesion especially to metal or some plastic substrates
	odor of formulations

Table 3: Main differences between UV and EB curing

	UV	EB
curing possible in the presence of oxygen	+	-
little capital investment necessary	+	-
fast cure	+	++
low content of extractables	o	+
little space required for curing unit	++	-
easy curing of highly pigmented formulations	-	++

1.4 EB versus UV Curing

So far we have been discussing radiation curing in general, summarizing UV and EB technology. However there are distinct differences between these two which will be discussed further in detail in Chapter 2.3 (Table 5). The main difference from a formulator's perspective is the absence of photoinitiator in EB curing formulations. The high energy level of electron beam radiation initiates polymerization directly.

From a technology standpoint the main difference between the two processes is the kind of radiation. For the UV cure very energy-rich radiation with a wavelength from approx. 180 nm (UV-C) up to 380 nm close to visible light is used.

In EB cure electrons are shot onto the coating by the use of an electron accelerator. Oxygen needs to be excluded efficiently to allow proper cure. Whereas UV curing can take place under atmospheric conditions, EB units need inertization, meaning the surface to cure must be flooded with nitrogen.

The final decision which technology is most suitable for a certain application depends on the specific requirements. As a matter of fact UV curing is much more widely used today than EB curing. In Europe EB technology is used very little overall. But since this technology has its distinct advantages it waits to be seen if this picture will change in the future.

1.5 Historical development

Since the beginning of the 20th century the initiation of a curing process by the exposure to UV light had been known. Already 1946 first patents were filed describing the cure of coatings respectively printing inks by ultraviolet radiation. It was also in 1940s when first wood coatings were cured by irradiation by UV light. First industrial application of electron beam curing coatings took place in the early 1970s. It had taken many experiments and pilot plants until the first commercial electron beam curing unit was installed. It was the Ford Motor Company in the US who started off with EB curing of plastic coatings for interior trim applications [1]. Soon followed furniture coating applications in Germany and the Netherlands. In these early years of radiation curing there was a strong focus on electron beam curing. Numerous patents published in the late 60s in 20th century apply this technology to different applications. In the 80s and 90s UV curing appeared to be the technology of choice. Except for North America EB curing was hardly present in industrial applications.

In any case both technologies have proven successful on a long-term basis in all applications where flat substrates were involved and fast cure speed offered major advantages.

1.6 Market figures and main applications

Accurate global figures are difficult to obtain. But scanning through various market studies and summarizing the findings the following picture is created. Over the last decade radiation curing coatings and inks have enjoyed a global growth of 6 to 10 % every year. The estimated global market size for radiation curing formulations is currently (2007) exceeding 300,000 metric tonnes on a global basis.

Globally the biggest applications for radiation curing formulations appear to be the

- wood coatings
- overprint varnishes (OPV)
- pigmented printing inks
- other industrial coatings (incl. automotive coatings)
- electronics and telecommunication
- adhesives

A rough estimation utilizing figures from various sources indicate the following global volume distributions:

According to an SRI Study from 2005 Asia has the largest consumption of radiation curable materials, closely followed by Europe and North America [2]. Other studies still claim Asia to have a lower consumption than Europe and America. But anyhow Asia is expected to draw at least level very soon.

The growth perspective is excellent. Depending on the sources a further global growth of 6 to 8 % annually is forecasted for radiation curing formulations. China and South East Asia are expected to grow over-proportionally with double digit numbers, North America following with 7 to 8 % per year and Europe and Japan falling behind with 5 respectively 4 % per year.

Even though the volume distribution by region currently appears relatively homogeneous the distribution of these end uses for radiation curing is not. Whereas the usage of RC formulati-

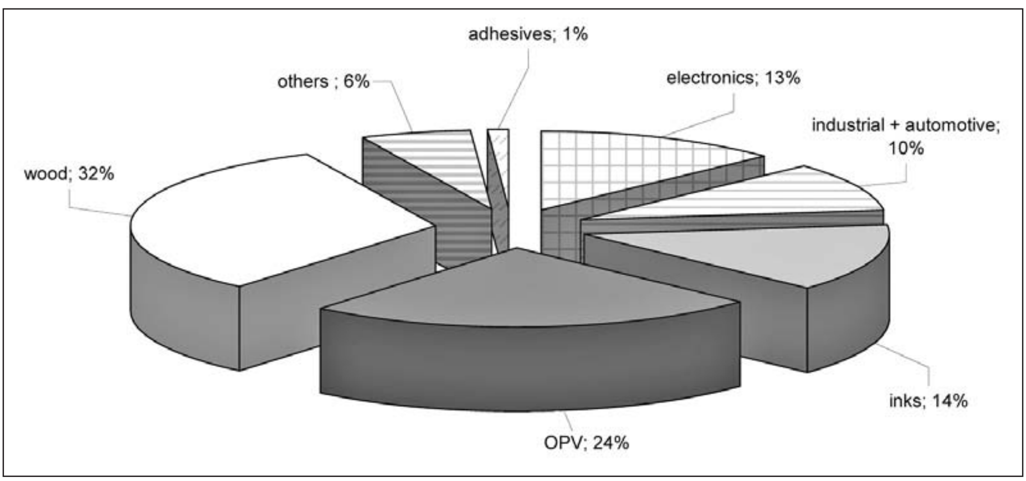

Figure 3a: Estimated volume share of applications for RC formulations

Table 4: Consumption of radiation curable materials by major region [2]

	2001 1,000 metric tonnes	2004 1,000 metric tonnes	2009 1,000 metric tonnes
Europe	84	102	129
North America	68	79	118
Asia (incl. Japan and China)	unknown	120	167
Japan	42	45	56
China	unknown	33	53

ons in Europe is strongly dominated by wood coatings, the graphic arts applications are much more dominant in the NAFTA. Also the applications of plastic coatings, release coatings, optical fibre coatings, and vinyl flooring have a higher share than in Europe. In Japan, still the largest producer of RC formulations in Asia [3], the share of opto-electronic coatings is significantly higher than indicated in the graph above. Details about these applications will be discussed in Chapter 5 of this book.

By far the largest share of the current 300,000 tonnes of the total radiation curable formulations are cured by UV light. EB technology has only captured 10 to 12 % of the market with the main applications in adhesive laminations, high-gloss varnishes, silicone release coatings, decorative furniture foils and papers, and low odor coatings for flexible food packaging materials.

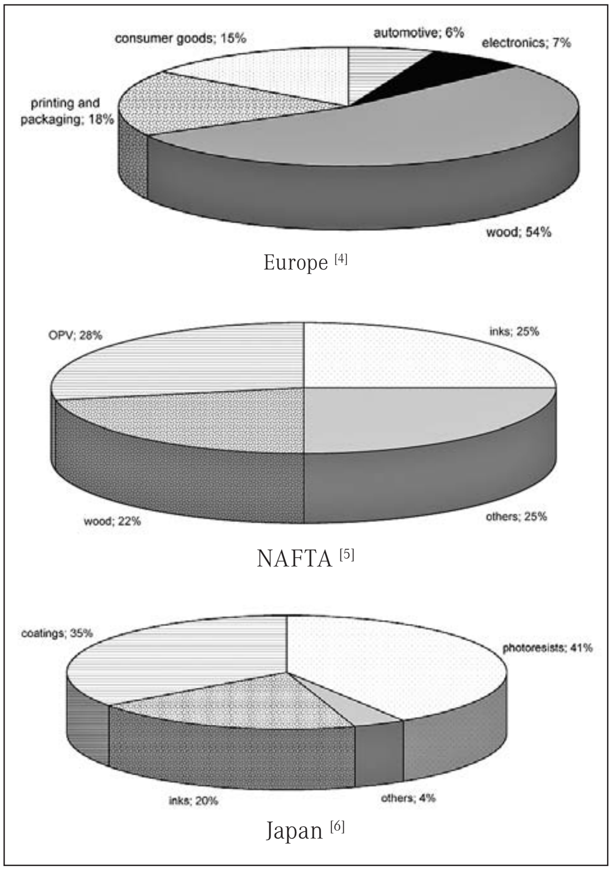

Figure 3b: Split of applications for RC formulations in 2005/2006

Cationic curing systems serve mostly specialized niche markets including can and coil coating due to their superior adhesion to metal and sterilizable packaging materials. Their market share is estimated arround 1 and 2 % by volume.

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2 Basics of radiation curing technology

Radiation curing is an ultrafast and efficient method to convert a liquid film into a solid material by exposure to radiation [1, 2]. This technology developed in the 1960's gained progressively importance and reached new markets to finally become state-of-the-art in many applications including the coating and ink industry as well as electronic applications. Key features responsible for this growth are the availability of 100 % liquid systems with no VOC and low energy consumption, which are both distinct ecological and economical advantages over thermal or physical drying processes. Additional unique benefits include in the case of radical polymerization an ultrafast process [3, 4], reduced space requirements in a production line, an easy control of the reaction and a curing step performed at "cool" temperature (room temperature) which allows this technology to be applied for applications involving heat-sensitive substrates. Use of light further opens the possibility of image-wise curing, which is at the base of all imaging applications such as printing plate fabrication or electronic applications including chip production, electronic materials or the fabrication of flat panel displays. Final materials cured by this way are strongly crosslinked and exhibit outstanding properties as well as excellent physical and chemical resistances.

Two radiation curing technologies are currently employed in the coating and ink industry: UV curing and electron-beam (EB) curing. Curing induced by UV light currently represents about 90 % of the radiation-curing market in Europe. UV curing, in other terms photoinitiated polymerization, photopolymerization or photocrosslinking, is a polymerization reaction involving a functionalized oligomer (Figure 4) leading to the formation of a solid crosslinked film [5]. The cure mechanism is initiated by a light sensitive molecule called a photoinitiator and can be a cationic [6] or a free radical polymerization reaction [7] as well as a catalyzed polyaddition. Light sources which activate the process are usually medium pressure mercury lamps, xenon lamps, lasers or electrodless vapor lamps emitting mostly between 200 and 500 nm. Near-visible light sources (e.g. sunlight, fluorescent lamp, LED) are currently used for niche applications but are raising interest because of their low toxicity.

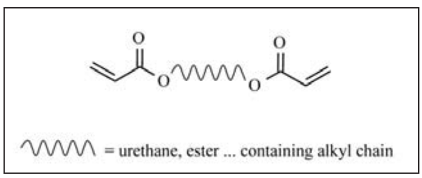

Figure 4: Example of a functionalized monomer contained in a radiation-curable formulation cured by a radical polymerization

Electron-beam curing involves an electron beam which directly induces the curing process of a functionalized oligomer [8] by a free radical mechanism in absence of a photoinitiator. In the case of cationic polymerization induced by electron beam, an initiator is required.

In this chapter, an overview of the UV curing technology will be outlined first, together with the different curing mechanisms, their advantages and limitations. The influence of the cure parameters on the cure speed and the material performances will then be discussed. Basic principles of EB curing will be reviewed in a second part.

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