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Radiation Curable Materials – Principles and New Perspectives

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SUMMARY: Increasing environmental concerns and the ensuing legislation to cut emissions of volatile organic compounds (VOCs) have been major driving forces behind the development of radiation cured coatings over the past 25 years. Today radiation cured coatings are known for their good overall performance and their excellent resistance against chemical and physical surface damages. Advanced photoinitiator systems allow the light stabilisation of UV-curable formulations and the outdoor application of the coating. The rapid curing, combined with the possibility of immediate processing of the coated objects opens the way for radiation curing – in 100%-, water based-, and dual cure systems as well as for radiation curable powder coatings - for a wide variety of application.

Introduction

Increasing environmental concerns and the ensuing legislation to cut emissions of volatile organic compounds (VOCs) have been the major driving force behind the development of radiation-curing coatings over the past 25 years. Technical advances have also played an important role in the spread of this fascinating field of coatings technology. The need to cut energy and raw material costs meant that new binder types, coatings formulations, as well as application and curing techniques, had to be found.

Often success was only possible through close co-operation of scientists and engineers in allied industries. As research expanded, so did knowledge about the relationships between the chemistry of the curing process and the application properties of the cured film. Apart from the environmental and technological aspects, economics has played a deciding role in the direction radiation curing has developed.

In the early years the main applications were limited to the coating of flat substrates such as boards, paper and wood. In the past decade, however, the range of applications has expanded considerably. Today, the technology has been applied to plastics, glass and even 3D objects. Coatings for metals and exterior applications are growing in importance.

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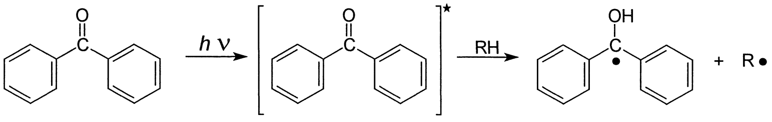
Principles of Radiation Curing

Radiation curing formulations can be grouped according to the polymerisation mechanism in radical systems and, less importantly, cationic cured systems, which will not be covered in this paper. The radical systems are based on low viscosity acrylate binders which are usually formulated solvent free and applied to substrates by various techniques. The curing is performed by exposure to high energy radiation, such as ultraviolet (UV) light or an electron beam (EB). Curing with UV radiation requires a photoinitiator in the coating formulation which starts the radical polymerisation. The main advantage of radiation curing to initiate the curing lies in the very high polymerisation rates reached under intense illumination, so that the transition from the liquid formulation to the solid coating takes place in a fraction of a second. Today UV-curing accounts for 90% of the radiation curing market, as the technical requirements for EB curing and the investment costs involved are much higher. However, apart from the photoinitiator, the raw materials used in EB- and UV-curing techniques are identical.

There are two classes of **photoinitiator** employed in UV curing, those which form radicals by hydrogen abstraction of a H-donor, e.g. as in the case with benzophenone **1**, or by homolytic cleavage of C-C-bonds, e.g. as in the case with 2,4,6-trimethylbenzoyldiphenylphosphin oxide **2** (Lucirin®-TPO).



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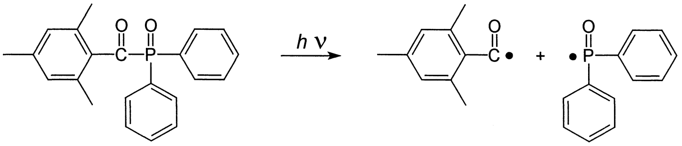

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Acylphosphine oxides have absorption bands extending up to the near UV/visible region, which make them especially suitable for the curing of thick films. The long wavelength absorption of this type of photoinitiator allows the use of light stabilisers in the UV-curable formulations, necessary for outdoor applications.

Photoinitiators are usually applied in concentration between one and 5% in the coating formulation, however, they significantly contribute to the costs of the coating formulation.

Radiation curable resins are most commonly based on acrylates as the reactive functional group. The acrylate groups are attached to oligomeric or monomeric compounds, to yield resins/binders or functional monomers/reactive thinners.

Functional monomers or reactive thinners are used to adjust the working viscosity of the coatings and the film properties, which depend on the crosslinking density, which can be controlled by the functionality of the monomers. Mono-, di-, tri and polyfunctional compounds are known. Monofunctional thinners, owing to their very strong odour, are only used in small amounts for special applications such as plastic coatings. The most important thinners contain two acrylic groups, such as hexanediol diacrylate (HDDA), dipropylene glycol diacrylate (DPGDA) and tripropylene glycol diacrylate (TPGDA). One commonly used trifunctional monomer is trimethylolpropane triacrylate (TMPTA).

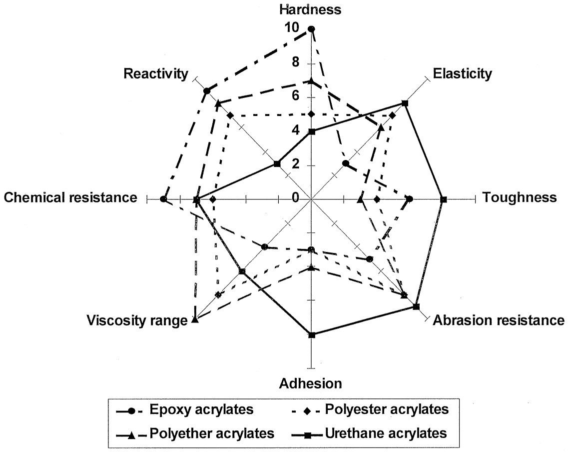


Fig. 1: Comparison of coating properties by binder classes.

Epoxy acrylates dominate the binder market, despite the fact that the viscous aromatic epoxy moieties have to be thinned with the potentially hazardous functional monomers. The more expensive aliphatic epoxy resins, on the other hand, are only used in special applications.

The wide choice of **polyester acrylates** available enables a broad range of demands to be met by the coating. These are generally low-viscous resins, requiring little or no reactive thinner.

Polyether acrylates, the least viscous group of resins, are made by esterfication of polyetherols with acrylic acid. These, too, usually do not require thinners. They can be made more reactive by tagging on amine groups.

Urethane acrylates are produced by reacting isocyanates with hydroxy alkyl acrylates, usually along with other hydroxy compounds to give the desired set of properties. Aliphatic urethane acrylates are the most expensive class of materials, however, due to their excellent weather resistance, they have become an important class of binders for outdoor applications.

Initiation	Photo-Initiation	PI	$\xrightarrow{h\nu}$	$R\bullet$
	Chain-Start	$R\bullet + M$	$\longrightarrow$	$R{-}M\bullet$
Propagation		$R{-}M\bullet + M$	$\longrightarrow$	$R{-}M_n\bullet$
Transfer		$R{-}M_n\bullet + TH$	$\longrightarrow$	$R{-}M_n{-}H + T\bullet$
Termination	Recombination	$R{-}M_n\bullet + T/R\bullet$	$\longrightarrow$	$R{-}M_n{-}T/R$
	Quenching	$R{-}M_n\bullet + Q{-}H$	$\longrightarrow$	$R{-}M_n{-}H + Q$
	Disproportionation	$2\ R{-}CH_2{-}CHX\bullet$	$\longrightarrow$	$R{-}CH_2{-}CH_2X + R{-}CH{=}CHX$

Fig. 2: Principle steps for a radical photopolymerisation.

During the process of curing, the photoinitiator absorbs UV light and forms radicals which add to an acrylic group of a binder or thinner to start the radical chain reaction. Within a fraction of a second thousands of acrylic groups are consumed, before the reaction stops by recombination, disproportionation or quenching. The radiation curing follows the mechanism of a radical chain polymerisation, figure 2. While monofunctional acrylic monomers give a linear polymer, higher functional binders give a polymer network.

The network density, together with the chemical structure of the polymer chains determines the properties of the coating. It is important to follow the mechanism of UV-curing, e.g. by real-time infrared (IR) spectroscopy, to learn about the reactivity of binders and to know the conversion. The degree of cure is known to correlate with the chemical resistance of the final coatings. Figure 3 depicts the network formation of a bifunctional thinner.

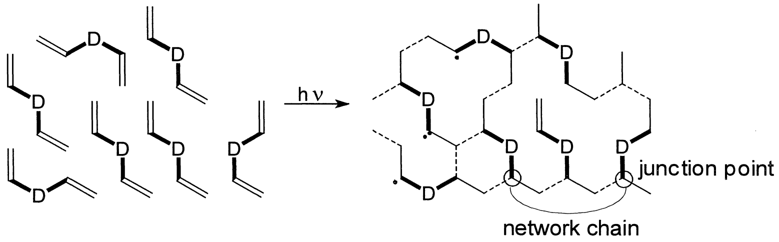


Fig. 3: Network formation with a bifunctional thinner.

While there is a good knowledge about the correlation of the mechanical properties of a polymer network with its structure, there is only a loose relationship of the polymer-network properties and the application properties of the final coating. The product properties like chemical resitstance, adhesion, hardness, toughness, elasticity, abrasion or scratch and mar resistance, influence each other and form a complex property matrix for the coatings.

New Perspectives

While the coating of wood, wood products and furniture finishing films will remain the main application area for radiation cured coatings, the coating of other substrates like plastics and metal come in focus for UV-coatings.

Radiation cured coatings on plastic substrates give a **scratch/mar resistance** comparable with high-performance organic-inorganic hybrid coatings, as shown in Figure 4. Cured under a normal atmosphere the scratch/mar resistance of pure binder systems is better than conventional 2K formulations used as automotive topcoats. Radiation curing under normal atmosphere struggles with the inhibition of the radical chain reaction by oxygen diffusing into the film. Besides using an inert atmosphere which seems inapplicable for radiation curing in some cases, surface active additives can be used to build a oxygen barrier at the uncured film surface.

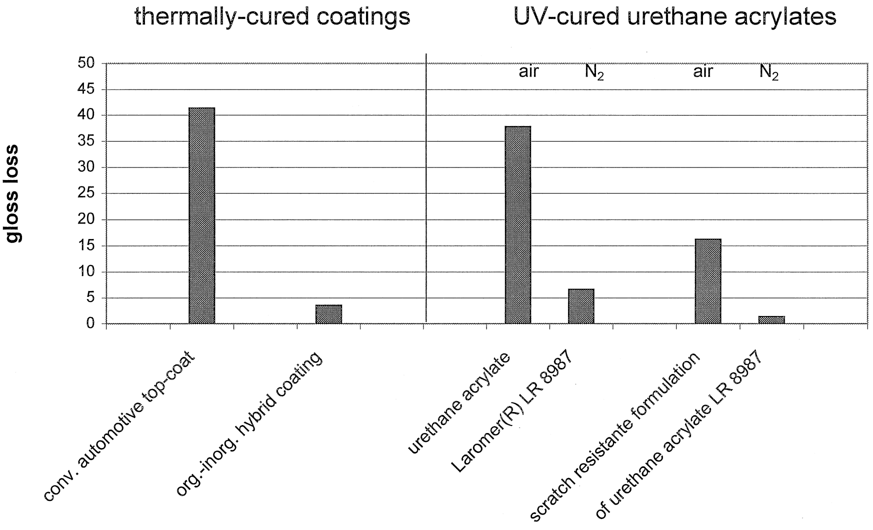


Fig. 4: Comparison of the scratch/mar resistance of coatings. The coatings have been physically damaged by a Scotch-Brite® fleece with a normal force of 84 g/cm² for 50 cycles. The scratch/resistance is inversely proportional to the gloss found.

The promising properties of radiation cured coatings give reasons for the reconsideration of paradigm that radiation curing can not be used for **three-dimensional objects** as the UV-light can not reach shaded regions and therefore will be left with some wet or sticky areas which will lose the protection by the coating with time. It looks as if the manufacturers of UV-equipment will offer a technical solution to this problem within the next years.

Today **dual cure systems**, combining radiation curing with a second curing mechanism are very attractive, adding excellent surface resistance against chemical and mechanical damages to the properties of a conventional coating. In most cases the areas with the highest demand on resistance can easily be reached by UV light. In principle any combination of curing mechanisms, e.g. thermal-, oxidative-, UV-cationic-curing or physical drying can be combined with UV-curing. In all cases it is necessary to balance the properties of the two networks formed. The UV curing equipment are compact and occupy relatively little space so that they may be added to an existing coating line. In comparison to thermal curing, they consume less energy and besides the environmental reasons there are economical reasons in favour of radiation curing.

Another paradigm to UV-curing is, that UV-absorbers used for light stabilisation of the final coating can not be used for UV-coatings, as the UV-absorber competes with the photoinitiator for the UV-light. This has two drawbacks for the coating, that is, that the film is not thoroughly cured and/or that the film is not stable enough for **outdoor applications**. Normal sunlight induces the photo-oxidation and degradation of the coating. UV-absorbers absorb the sunlight in the UV-region and transfer the energy to thermal relaxation rather than to radical formation. The new class of photoinitiators, the bisacylphosphine oxide have a longer wavelength absorption band and allow coating formulations for light-stabilised UV-coatings.

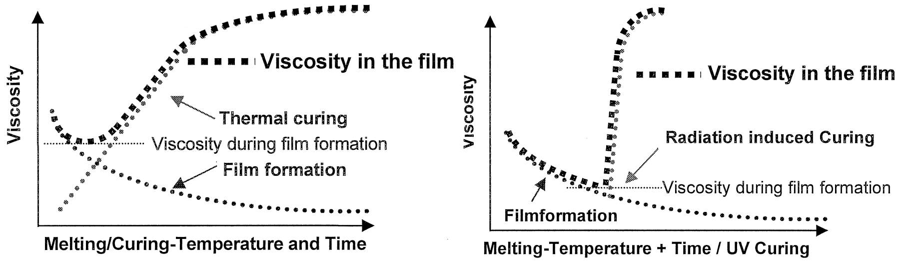
Based on aliphatic urethane acrylates coatings the coatings show little yellowing and a weather resistance comparable to 2K-PUR automotive coatings.

Using water as a carrier system higher molecular weight binders can be applied to a substrate in relatively low viscous formulations. The introduction of water as a ‘solvent’ in radiation curing contradicts the idea of a 100%-systems, and in addition lacks the advantages of a conventional aqueous coating systems introducing the more expensive UV-systems. However, higher molecular weight UV-curable binders can be used in this aqueous systems without the addition of low molecular weight thinners, which migrate into porous substrates, e.g. wood. Therefor the extractable parts of uncured monomers is significantly lower than in 100%-UV coating systems.

UV-dispersions overcome problems of classical dispersion, too, which lack chemical and surface physical resistance and show low gloss and poor blocking resistance. The higher molecular weight binders need less crosslinking during the UV-curing step to give a coating with good properties. Therefore the volume reduction during the UV-curing step is lower than with conventional systems. This results in reduced mechanical stress in the coating and a better adhesion of the coating to the substrate.

In principle it seems possible to transfer all conventional radiation curable resins into water, either as they are water soluble, or by stabilisation with an emulsifier or by addition of e.g. ionic groups allowing the resin to disperse in water. Most recently air-drying urethane acrylates dispersions were introduced which exhibit relatively good blocking resistance even before radiation curing, enabling the coated article to be handled before the final crosslinking.

The field of **radiation curable powder coatings** is still in its beginning but offers interesting perspectives. Like in the case of UV-dispersions, higher molecular weight binders can be used in the coating. Instead of the physical drying of the film to evaporate the water, the UV-curable powder is molten. The advantage to conventional thermal cured powder coatings is the separation of the melting/film-formation step and the final curing.



a) b)

Figure 5: Profiles of the viscosity in the film during film formation for thermal a) and radiation b) induced curing of powder coating.

Figure 5 depicts the viscosity temperature profiles for conventional a) and radiation curable b) powder coatings. While in the first case the thermal curing starts already during the film formation, secondly, in the case of the much quicker radiation curing process the time of initiation can be choosen indepentently to the melting process of the resins. This promises advantages in terms of the levelling and the coating appearance. In combination with a fast heating IR-radiation source it seems possible to use radiation curable powder coatings for heat sensitive substrates, e.g. plastic and wood.

Outlook and Summary

Figure 6 shows the prospects of the coating markets, where radiation curable products compete with solvent based systems, with high solid, water-based and powder coatings. The relative importance of solvent based systems is declining in favour of the others, of which radiation cured products have the lowest market share. However, they promise the highest growth rate.

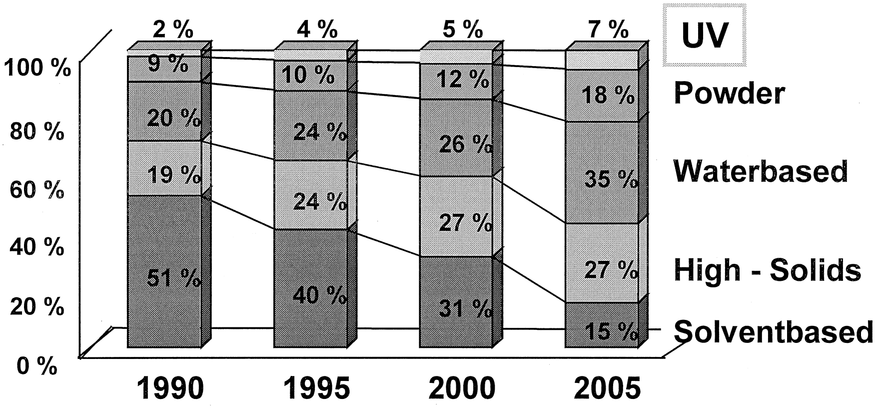


Figure 6: Market prospects for coatings as for the European paint industry. (Source: Information Research Ltd.).

In recent years, radiation curing has established itself as an environmentally friendly technology that saves both energy and material resources. In Western Europe the greatest penetration has been in the wood coatings and graphic arts sector. There is a clear trend towards low-monomer-content products that are potentially less harmful. The prospects for further expansion and introduction of radiation-curing technology into new applications look good but depends on the following becoming available commercially:

- low-viscosity, monomer-free oligomers
- low VOC raw materials
- oligomers that adhere well to critical substrates
- weathering resistant products
- improved curing equipment

The long-term success of radiation curing will require a concerned effort from all parts of the coatings industry. Problems can no longer be solved alone, but by adopting a joint approach of the raw material together with the coating formulation suppliers in close cooperation with the manufacturers of equipment for coating application and curing.