

## Radiation-induced cross-linking polymerization: Recent developments for coating and composite applications

Xavier Coqueret 💿

**Abstract.** Radiation-initiated cross-linking polymerization of multifunctional monomers is an attractive method used for drying solvent-free liquid coatings, inks, and adhesive as well as for fabricating high-performance composite materials. The method offers a number of advantages compared with thermal curing processes. Free radical and cationic polymerization have been investigated in detail over the past years. A high degree of control over curing kinetics and material properties can be exerted by adjusting the composition of matrix precursors and/or by acting on the process parameters (overall dose, dose rate, dose increment, initial temperature). Several pending issues that require deeper investigations are as follows: (i) the fast polymerization of multifunctional monomers generates micro-heterogeneous networks requiring detailed characterization and quantification by microscopic, thermal, and spectroscopic analyses; (ii) the adhesion and surface properties of radiation-cured coatings are quite sensitive to processing parameters; and (iii) significant enhancement of the toughness is needed to qualify potential matrices based on simple difunctional monomers for high-performance composites. Recent results show that the bulk and surface properties of radiation-cured materials can be improved by advanced formulation of matrix precursors and by a parametric study of the processing factors.

**Keywords:** Acrylate monomers • Coatings composites • Cross-linking polymerization • Polymer networks • V/EB curing

X. Coqueret

Université de Reims Champagne Ardenne, CNRS UMR CNRS 7312, Institut de Chimie Moléculaire de Reims BP 1039, 51687 Reims Cedex 2, France E-mail: xavier.coqueret@univ-reims.fr

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### Introduction

Cross-linking polymerization triggered by ultraviolet (UV) or electron beam (EB) radiation continues to grow and expand as a greener technology in the fields of overprinting inks and varnishes, industrial coatings, adhesives, and composite materials. Formulations that can be dried under radiation by cross-linking polymerization have experienced very significant industrial development since the 1970s. Current perspectives estimate the overall production of radiation curable formulations to 600 000 metric tons by 2025, with an annual growth of 6% in volume [1].

Triggering of drying operation is achieved by exposing the reactive liquid material to UV radiation (conventional bulbs or LED) or to a beam of accelerated electrons (EB). Both technologies offer great flexibility of implementation for a significantly lower energy cost than thermal processes used for chemical cross-linking and/or solvent evaporation. The integration of the drying operation into the production lines with a reduced and modular footprint constitutes an additional benefit. Last but not least, this technology presents, compared with conventional solvent-based processes, a large

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**Fig. 1.** Principle of radiation curing that converts liquid formulation of reactive prepolymers and reactive diluents (monomers) into solid polymer networks.

number of advantages in terms of productivity and reduction in the emission of organic vapors (Fig. 1).

Although the curing process is essentially based on the same polymerization chemistry, noticeable differences speak in favor of the ionizing radiation using accelerated electrons for high-performance applications. It is important to note that both EB curing and photopolymerization have their own advantages and limitations, and the choice between them depends on the specific requirements of the application, material properties, and production conditions [2].

EB curing generally proceeds faster than photopolymerization. This enables higher production speeds and increased productivity. EBs have the ability to penetrate deeper into materials compared with UV-visible photons used in photopolymerization. This allows for curing of thicker coatings or materials, making EB curing suitable for applications where thicker layers or substrates are involved. The feature is obviously a unique advantage for the fabrication of large parts made of thick and opaque composite materials.

Photopolymerization relies on the presence of photo-initiators which are specially designed compounds that absorb actinic light to generate active species initiating polymerization. By contrast, EB curing does not require any photosensitive additive, reducing the need for such chemicals and simplifying the curing process.

EB curing often results in improved adhesion and chemical resistance compared with photopolymerization. The high-energy electrons are expected to induce higher cross-linking density and promote better bonding to substrate or fillers having a favorable chemical constitution, leading to composites with enhanced adhesion and resistance to solvents, chemicals, and aging in various types of ambiances. Heat-sensitive substrates that may be damaged or degraded by the infrared radiation emitted by the conventional UV sources can be processed under softer conditions and with a better control of thermal effects by using the EB technology.

### Principles of radiation-initiated curing by cross-linking polymerization

### Technological aspects of EB curing

A step-by-step explanation of how EB curing works starts with the extraction of electrons from a metal cathode (e.g., tungsten) heated under vacuum and their injection into the acceleration chamber forming the electron gun. The beam of charged particles extracted from a point-shape is then focused and shaped using electromagnetic effects to create a narrow and controlled beam of electrons which is directed toward the target material [3].

Linear accelerators (LINACs) and cyclotrons form the two main classes of high-energy EB sources. LINACs consist of a long straight tube or waveguide through which the electrons are accelerated in a linear path. LINACs can generate high-energy EBs ranging from a few kiloelectron-volts (keV) to several megaelectron-volts (MeV). Cyclotrons accelerate electrons in a circular path using a combination of electric and magnetic fields. They can generate high-energy EBs, typically in the range of a few MeV. Cyclotrons are often used for large-scale industrial applications where high beam power is required.

Electron curtain units form a separate class of low-energy accelerators used for drying flat substrates with a continuous beam of electrons (i.e., non-pulsed) extracted from one or several linear filaments with a high current (from several milliamperes to few amperes), but of relatively low energies (from some dozen keV to a few MeV). This type of compact size accelerators can produce a large beam area, typically in the range of several square centimeters to several square meters, well suitable for industrial applications such as surface modification, curing, and sterilization.

When the high-energy beam strikes the target material, ionization of the atoms presents in the irradiated organic molecules which will form the final solid material results in excited species, radical ions, and thermalized electrons that further interact and form active species, ionic, or electrically neutral as free radicals, capable of initiating polymerization processes [4].

# Chemical composition of radiation curable formulations

Radiation curable formulations for coatings and composites typically consist of reactive oligomers of low to medium molecular weight, fitted with polymerizable and/or pendant-groups. Acrylate, methacrylate, epoxy, and vinyl ether are the most common functionalities used to confer a sufficient reactivity to this prime component of the curable formulation. Depending on the nature and length of the prepolymer backbone and the average number of attached functional groups, the reactivity, flexibility, adhesion, and durability to the cured coating or composite can be adjusted to the technical needs. Common oligomers used in radiation curable formulations include functionalized aliphatic or aromatic polyepoxies, polyesters, polyurethane, and silicones (Fig. 2).

Reactive diluents based on the same types of monomer groups present in numbers of units attached to a same molecule between 1 and 3 (and sometimes up to 6) are added to the prepolymer to reduce the viscosity so as to be compatible with Generic architecture and structural features of reactive prepolymers

- Chemical nature of the main chain and monomer units (-O)
- Size (molecular weight)
- Functionality (number of monomer units per molecule)

Examples of representative components fitted with acrylate functions



Fig. 2. Generic structure and examples of prepolymers and monomers bearing acrylate functionalities that are typically used in radiation curable formulations polymerized by a free radical mechanism.

the technology of deposition in the case of coating, or impregnation of the fiber-reinforced composite precursor. The average functionality of the reactive diluents used in a formulation also affect its reactivity, generally by enhancing the initial polymerization rate but also by reduction of its ultimate degree of monomer conversion.

Various additives can be included in radiation curable formulations to enhance specific properties or provide additional functionalities. These additives can include antioxidants, UV stabilizers, flow agents, leveling agents, adhesion promoters, and pigments. The selection and concentration of additives depend on the desired performance and application requirements. In most cases, fillers and reinforcements may be added to radiation curable formulations to improve mechanical properties, such as strength, stiffness, and impact resistance. Besides pigments and matting agents, common fillers and reinforcements used in coatings and composites include silica nanoparticles or flour as well as natural, glass, or carbon fibers.

It is important to note that the specific composition of radiation curable formulations can vary significantly depending on the application and desired properties. Different industries and manufacturers may have their own proprietary formulations tailored to specific needs. A selection of examples from studies carried out at our Institute can highlight the importance of these various factors on the properties of materials polymerized under UV radiation or under EB with particular interest in questions relating to the adhesion (release and low-adhesion coatings, resins for micro- and nano-lithography, 3D-printing and microsystems, matrices for composite materials). For thin layer applications, drying occurs in a fraction of a second upon exposure to radiation of formulations deposited by coating, projection, or spraying. These formulations comprise monomers and prepolymers with an average functionality  $\geq 2$ ; a three-dimensional network is formed, the physical and mechanical characteristics of which strongly depend on the degree of conversion achieved and the nature of the constituents. The polymerization mechanism in industrial processes is mainly free radical, with acrylate or methacrylate monomers. Cationic curing of epoxy- or vinylether-based formulations are also used in specific applications [5].

### Radiation treatment

The penetration of radiation into the material to be treated and its effective use for initiation are the first two conditions to be satisfied to obtain drying of the deep layers. For pigmented formulations or formulations loaded with fibers and solid particles, inks, or paints, photochemical activation in-depth is severely reduced in efficiency by the optical diffusion of the incident beam, reflection, and refraction, as well as by the absorption specific to the pigments or fillers [2]. In this case, EB irradiation presents an obvious advantage [4].

As an ionizing radiation, accelerated electrons are absorbed non-selectively by the irradiated formulations. The initiation mechanisms are therefore quite different from those described for photopolymerizations. With acrylates, the ionization cascade results in thermalized electrons which reduce the monomer function to an anion radical [6]. After dimerization and protonation, the formed radical initiates the polymerization. In the case of cationically polymerizable formulations, such as epoxies, the presence of an onium salt is necessary to obtain active initiator centers in sufficient amounts [5].

#### Control and monitoring of EB curing

The EB curing process is carefully controlled and monitored to ensure that the desired level of curing is achieved. Parameters such as beam energy, beam current, exposure time, and material thickness are adjusted to optimize the curing process. A convenient method consists in exposing repeatedly a thin sample deposited onto an infrared-transparent window to a low-energy EB and monitoring by transmission infrared spectroscopy the decrease in the absorbance of a band assigned to the reactive function. In the case of acrylates the elongation of the C=C unsaturation is at 1409 cm<sup>-1</sup> or the outof-plane deformation of the ethylenic C–H is at 810 cm<sup>-1</sup> [4, 7].

The plot representing the variations of absorbance at one of these wavenumbers as a function of time or dose reflects the evolution of the conversion rate during irradiation and makes it possible to determine three important parameters: (i) an eventual induction period that may occur before the effective start of polymerization, delayed by the inhibitory effects of stabilizers and dissolved oxygen; (ii) the polymerization rate *Rp*, deduced at any time from the slope of the recorded curve; and (iii) the final content in unreacted monomer functions in the sample. During cross-linking polymerization, numerous physical evolutions accompany the chemical processes. The initial polymerization speed depends mainly on the reactivity of the monomer group and the initiation rate, the latter being controlled by the quantity of energy absorbed per unit of time. In the case of a radical mechanism, the increase in viscosity



leads to the self-acceleration effect (Trommsdorff effect), resulting from a strong decrease in the termination rate constant  $k_t$  following the diffusion of more and more slow macroradicals. This effect is clearly demonstrated by comparing the kinetic profiles of thin films of bulk mono- and difunctional acrylate monomers exhibiting similar initial unsaturation concentrations (7–8 equiv. kg<sup>-1</sup> of acrylate) polymerized under low-energy EB radiation under similar exposure conditions (Fig. 3). The models describing the kinetics of radical polymerizations were adapted to the initiation mode under radiation. The instantaneous polymerization rate can be related to the initiation rate and the termination constant, by application of the steady-state approximation in propagating active centers [8].

### Vitrification and thermal effects affecting radiation--initiated polymerizations

When the reaction mixture includes monomers whose structure tends to form a glassy network, the progressive reduction in the local mobility of the active centers and the monomer functions has the effect of limiting the speed of propagation and modifying the nature of the termination mechanism. The latter, initially bimolecular, with self-destruction of the active centers by combination or by dismutation, evolves toward a process of pseudo-termination by occlusion. Occluded free radicals, which do not necessarily have the structure of the propagating radical, can continue polymerization after heating the sample above the glass transition temperature.

It may happen that vitrification takes place at low conversion, as in the case of prepolymers with a bisphenol-A type skeleton, which is more rigid than that of aliphatic polyurethanes. The corresponding kinetic profiles are strongly affected by this phenomenon, when curing is carried out with samples initially at room temperature. This is clearly evidenced by the kinetic profiles plotted in Fig. 4 for aliphatic polyurethane triacrylate and bisphenol-A epoxy diacrylate.



**Fig. 3.** Plots representing the progress of monomer conversions as a function of the absorbed dose of radiation for (a) hexanediol diacrylate and (b) n-butyl acrylate treated as thin layers of monomer coated on an NaCl window covered with a 25  $\mu$ m-thick polyethylene terephthalate (PET) film, 150 keV electron accelerator.

**Fig. 4.** Plots representing the evolution of the fractional conversion of acrylate monomer units as a function of the absorbed dose of radiation in EB-irradiated thin layers of resin coated on an NaCl window and treated with 150 keV electron accelerator (various dose increments, same dose rate): (a) aliphatic polyurethanes triacrylate and (b) bisphenol-A epoxy diacrylate.

The polyurethane triacrylate possesses a flexible backbone, which yields a relatively soft material in the cured state, whereas the rigid aromatic epoxy acrylate tends to form a glassy network even at low conversion levels. The kinetic profiles are affected by the occurrence of vitrification that occurs at different conversion levels for both prepolymers processed at the same temperature. The acrylate plot shows a steep increase in monomer conversion to 0.75 for a dose lower than 10 kGy. The curve then levels off to a plateau with a conversion value of about 0.9. The plot for the aromatic epoxy diacrylate indicates that the fast-initial stage has abated at a low conversion level of 0.2, the conversion approaching 0.4 only for a dose of 60 kGy. The tangent to the initial segment of the kinetic profiles is quite steep for both prepolymers, but for the epoxy acrylate, soon after the beginning of the curing process, at a fractional conversion of about 0.2, the plot levels off, with polymerization proceeding quite tediously by continuing the radiation treatment. At this stage, the concentration of unreacted acrylates is 3.6 equiv.  $kg^{-1}$ , a value that is even higher than the acrylate concentration in the polyurethane triacrylate sample before starting the treatment. The very low reactivity observed in partially cured aromatic epoxy diacrylate in spite of the still important content in monomer units is strong evidence of the influence of incipient vitrification that hinders further polymerization at the working temperature. The horizontal dashed line corresponds to the degree of conversion at which the formed network exhibits a glass transition temperature  $(T_g)$  of 25°C (room temperature) for the type of acrylate prepolymer. This corresponds precisely to the point where the curves show a strong decrease in their slope [8].

The exothermicity of the polymerization of the monomers used, of the order of 80 kJ per mole of acrylate function, however, induced an elevation of the sample temperature that depends on monomer content, dose increment, polymerization rate, and heat exchanges with the environment. The rise in temperature can be a few to some dozens of degrees for thin films treated under industrial polymerization conditions, for example, as high as 200°C, in the case of massive samples treated to a high absorbed dose of radiation. The plots drawn in Fig. 5 show the strong thermal effects observed in a bulk sample of aromatic epoxy diacrylate treated with a 50 kGy dose.

The kinetic behavior during polymerization and the thermomechanical characteristics of the material obtained can be modeled, by combining the following three approaches:

- a detailed study of the kinetics of polymerization under ionizing radiation according to the parameters considered influential (dose, dose rate, temperature);
- correlation between the chemical progress of the reaction and the evolution of the thermomechanical properties of the polymer material, in particular the glass transition temperature of the network;
- development of a model with equations describing the observed previous kinetics based on mechanistic considerations.

A selection of examples taken from studies carried out at our Institute highlight the importance of various chemical and structural factors on the properties of materials polymerized under EB, with particular interest in questions relating to mechanical performances and adhesion [4, 9].

# Structure-property relationships and performances of radiation-cured materials

Heterogeneity of the networks produced by radiation-initiated cross-linking polymerization

Curing by cross-linking polymerization of multifunctional prepolymers and reactive diluents yields brittle matrices, a strong limitation with the view to producing high-performance composite materi-



**Fig. 5.** Plots representing the evolution of temperature in a bulk sample of an epoxy diacrylate resin sample placed in an aluminum box fitted with seven thermocouple probes (numbered 1–7) and submitted to an irradiation with a 10 MeV EB to ensure a 50 kGy dose in the front domain of the sample (the dotted line represents the relative dose vs. depth deposition of energy).



**Fig. 6.** Sketch representing the structure of the network obtained by cross-linking polymerization of a rigid diacrylate at various dimension scales (a) repeat unit, (b) cross-links and entanglements in the network, (c) incipient formation of rigid nanoclusters, (d) nanoheterogeneous description at mesoscopic scale of the cured material to be compared with the (e) phase contrast image obtained by atomic force microscopy in the tapping mode that reveals the presence of rigid clusters (brighter zones of cross-section 10–15 nm) in an EB-cured aromatic epoxy diacrylate network with a degree of conversion of about 0.4.

als. Among the various possible causes for this poor resistance to impact and/or to stress propagation, the formation of nano-heterogeneities during radiation-initiated polymerization was suspected and then explored in some detail by our group. Solid-state proton  $T_2$  nuclear magnetic resonance (NMR) relaxation experiments and temperature--modulated calorimetric analyses performed on radiation-cured materials prepared from model difunctional monomers with controlled degrees of monomer conversion allowed us to distinguish two types of domains inside the materials: one consisting in rigid domains, and a second one with higher local mobility and distinct relaxation features [10]. Considering a two-component description of the network microstructure, both techniques provide consistent sets of data quantifying the amount of matter in each type of domain (weight fraction of soft and rigid domains) together with specific physical parameters related to the local cross-link density in each network (relaxation time  $T_2$ , glass transition temperature  $T_g$  in each type of domains).

Imaging by atomic force microscopy of the aromatic epoxy acrylate samples in the phase mode provides a complementary picture of the network microstructure, particularly in terms of dimensions and local mechanical properties. Samples exhibiting a topographically flat aspect showed phase contrast pictures revealing a complex structure made of dense nodules with a mean cross-section of about 10–20 nm and interstitial zones that correspond to loosely cross-linked domains [11] (Fig. 6).

By measuring the evolution of surface density, Feret's diameter and cross-sectional area of the rigid domains present in series of samples covering the entire range of conversion, the early formation of nanoclusters embedded in a soft gel, essentially showing the nucleation of new clusters and limited growth and aggregation up to a certain size at higher fractional conversion in monomer. Polymerization then continues in interstitial domains, generating a more uniform network structure, yet with some discrete domains having a low degree of conversion. These observations and measurements support the following scenario depicting the gradual build-up of the network by the following step-by-step sequence: the liquid nucleation of softly interconnected gel nanoparticles within the swollen loose network at the beginning of the irradiation treatment, increase in the number of clusters by additional nucleation, and concomitant increase in size by aggregation while the cross-link density rises up to form glassy nanoclusters. Percolation of the nanoclusters induces the syneresis of the material, which results in a monolithic glassy solid [4].

### Improvement of matrix toughness

Our current efforts to overcome the brittleness associated with the heterogeneities described above, are focused on new formulations including a high  $T_g$ thermoplastic toughener, such as polyethersulfone (PES). Starting from a fluid and homogeneous formulation, the fast radiation-initiated polymerization of the blends was shown to induce the phase separation of PES nanoparticles, strongly enhancing the critical stress intensity factor ( $K_{\rm IC}$ ) by up to 2.2 MPa m<sup>0.5</sup> and improving dramatically the current status of this technology [12, 13].

## Overcoming inhibition reactions occurring at the C fiber-matrix interface

Compared with thermally cured composites prepared according to the state-of-the-art, radiation-cured composites generally exhibit lower transverse mechanical properties. Various potential causes of these issues were investigated: matrix shrinkage upon curing, low wettability of carbon fibers, and undesirable chemical reactions at the interface between the fibers and matrix. Studies of the reactivity under EB of various acrylate monomers in the presence of aromatic chemicals bearing the chemical functions present at the surface of C fibers demonstrate that the inhibiting behavior of these functions can be overcome by introducing in the formulations various sensitizing and coupling agents. Significant improvements were achieved on transverse strain at break by applying original surface treatments onto the fibers so as to induce covalent coupling with the matrix [14, 15].

#### Recent achievements in the coil coating industry

The coil industry produces protected and pre-painted steel panels in the form of rolled strips using various types of organic coatings and various curing technologies. While the vast majority of coil coatings cured worldwide use gas-fired ovens, several efforts have been made to overcome the conventional energy consuming evaporation and/or curing thermal processes by installing lines infrared or induction heating and UV cure. The latest industrial achievement in the current race for low volatile organic compound (VOC) emission and reduced energy consumption is the EB curing of the top coat of steel coils to be used in the building sector as cladding material.

While the primer and backer applied to the steel are normally applied in much thinner layers (typically 5–10  $\mu$ m in thickness), topcoats normally consist of dry and heavily pigmented films of thickness close to 20  $\mu$ m. The specifications are very demanding at each stage: production and storage of the paint, application and curing, and structural and functional properties of the coating on the steel strip. These include stability on storage, rheological properties, high reactivity in the curing area, robustness in terms of processing, adhesion on steel or primer, resistance to scratch and impact, soft deformation on bending, anticorrosion performances, gloss, and weathering in outdoor conditions. Formulation of solvent-free EB-curable paints and optimization of their processing to meet the highly demanding specifications require a high degree of control over a number of properties [16].

Recent industrial ventures indicate that the challenges in this domain have been tackled during the past 15 years to provide viable large-scale implementation. The project led by Arcelor Mittal in partnership with Beckers Industrial Coatings for deploying radiation technologies in coil coating lines has been successfully transferred to its Contrisson's plant (France) where the process has been put into operation (February 2023) [17].

The project provides multiple environmental benefits. It reduces the energy and carbon intensity of the process by using electron radiation instead of incineration (saving up to 31% in greenhouse gas emissions compared with a conventional technology) and will also reduce considerably the amount of VOCs emissions by using solvent-free solid paint.

### Conclusions

Radiation-induced polymerization was initially established in the sectors of printing, electronics, packaging, and coatings on tolerant substrates, which provide ephemeral objects produced in very large number of units. In these applications, photochemical activation under UV radiation is still predominant but low-energy EB continues to increase its share as an alternative technology due to its specific assets in terms of performance for inks, coatings, and adhesives.

Various technological issues pertaining to the EB curing of composites have been addressed through a combination basic approach of radiation chemistry and polymer science. A step further will consist in aggregating the technological solutions developed for improving matrix toughness, decreasing the shrinkage of networks upon their build-up, and designing cohesive fiber–matrix interfaces. Encouraging results allow envisioning mass production of structural composites as well as functional materials by means of a reliable, cleaner, and more productive out-of-autoclave manufacturing.

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### ORCID

X. Coqueret D http://orcid.org/0000-0002-9645-5506

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