Chapter 16

FUNDAMENTAL ASPECTS OF RADIATION-INDUCED CURING OF COMPOSITES

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1. INTRODUCTION

Composites are engineered multiphase materials consisting of two or more materials with significantly different physical and/or chemical properties. The combination of these produces a material with characteristics different from the individual components which remain separate and distinct within the finished structure. By using properly selected materials in appropriate proportions, the resulting composite can exhibit new or improved properties, such as higher mechanical strength with a lower mass, specific optical, electrical, or magnetic properties, as well as many other possible functional properties, such as flame resistance. Composites are usually classified by the type of material used for the matrix [1]. Polymer matrix composites include a variety of reinforcements such as particles, aligned continuous fibers, discontinuous fibers, fabrics and braids and are by far the most widely used type of composites. The polymer matrix can either be a thermoplastic or a thermoset. The primary role of the continuous matrix is to bind together the embedded reinforcing component so that applied mechanical loads can be effectively transferred to it. The matrix also protects the reinforcing component from chemical and environmental attack.

Thermoset composites offer a number of advantages in terms of design options, ease of fabrication and mechanical performance with respect to weight. They are increasingly used to replace heavy structural parts and components, often made from metals, particularly in the aerospace and ground transportation industries. Such applications require composite materials exhibiting high glass transition temperatures and good compaction. Hence, the curing process is conducted at high temperatures under appropriate levels of pressure.

In a different area, inks and paints can be considered composite materials since they have a continuous polymer matrix and particulate fillers and pig-

ments. The formation of polymer networks using radiation-initiated crosslinking-polymerization or curing in graphic arts and industrial coating is now a well-established technology that has been rapidly expanding since the 1980s [2]. This represents an alternative to solvent-based processes that are being banned and restricted because of their detrimental impact on the environment. Radiation curing technology offers several advantages in terms of eco-design (energy saving, reduction of volatile organic compounds (VOCs) and emissions, *etc*.) [3]. *In-situ* polymerization of restorative resins infused into damaged archeological objects made of wood or into weak artistic pieces of porous structure is another illustration of the unique in-depth effects that can be induced under mild conditions by high energy radiation [4]. High energy radiation treatment from electron beam (EB) accelerators is a more suited alternative to intense ultraviolet radiation (UV) for initiating in depth the crosslinking-polymerization of solvent-free compositions including monomers and reactive pre-polymers. The rapid polymerization process is triggered by exposure to ionizing radiation. Because of the presence of multifunctional monomers in a formulation, a three--dimensional covalent network is formed, resulting in the drying of the initial formulation and yielding mechanically toughened and chemically resistant materials, as illustrated in Scheme 1.

high energy
radiation
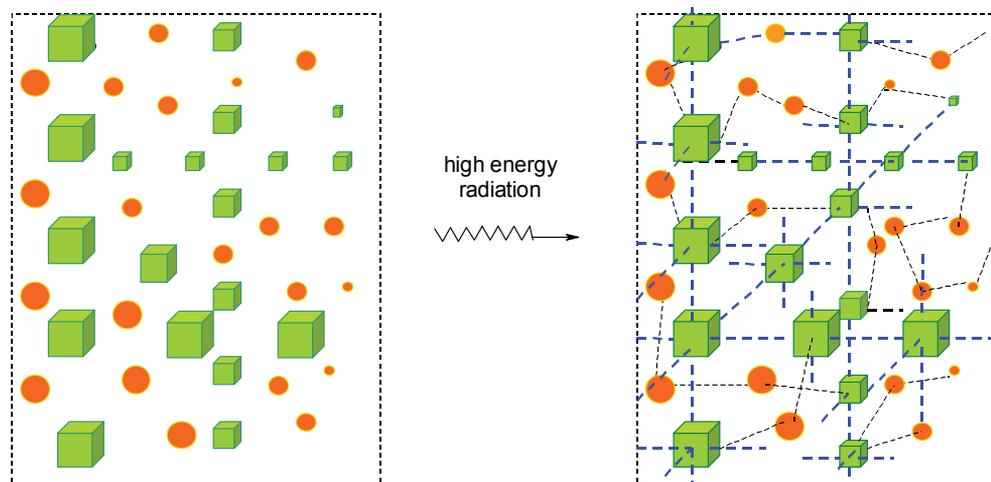
Scheme 1. Radiation-induced crosslinking-polymerization of monofunctional (○) and multifunctional (□) monomer blends.

Liquid or semi-solid formulations can be handled and applied to substrates by various means, spraying or rollor or blade coating as are solvent-based coatings. Acrylate derivatives and some vinyl aromatics are well-suited to give fast curing by free radical mechanisms. Epoxy or vinyl ether functional analogs can be cured by a cationic process requiring the addition of onium salt initiators. Pigments and additives are added to the formulation in order to facilitate the coating application, to enhance curing efficiency and to adjust performance

and end-use properties of the coating. UV radiation is extensively used for labels, cartons and containers in the packaging industry. High energy radiation curing provides additional advantages compared to ultraviolet radiation. No initiator is needed for free radical polymerization and the penetrating power of electrons is greater than photons in the ultraviolet range at usual concentrations of photoinitiator and/or in formulations with high pigment or filler concentrations. Electrons are more efficient than ultraviolet radiation in that they penetrate opaque coatings and in composites they activate monomers even after vitrification of the network which undergoes gradual curing. This results in lower amounts of unreacted monomers and other extractables. Grafting reactions can also take place at the substrate-coating interface, thus improving adhesion.

Advances in formulations as well as in process control of radiation curing allow for major industrial developments in the food packaging industry and for industrial coatings (flooring, outdoor building parts, and such). Curing of fiber-reinforced polymer composites using high energy electron beams offers similar significant advantages for making a variety of aerospace, water vessels and ground vehicle components, as demonstrated by the Technicopolis programme [5]. The EB/X-ray curing process greatly reduces the time required to crosslink the polymer matrix compared to conventional heat curing. This process allows for curing without external thermal activation that results in high throughput. Radiation curing yields materials with reduced residual stresses for good part dimensional stability and fitting. Curing times are shorter and the curable formulations have long storage stability. The absence of highly volatile monomers renders the industrial process safer and more environmentally friendly.

Multifunctional monomers as aromatic acrylates or epoxies can be used as the resin matrix in high-performance composites due to their good mechanical, thermal, and electrical properties. Both types of monomers react according to specific mechanisms and yield networks with properties that can be adjusted by formulating the resin and by using the appropriate treatment under the radiation source.

2. RADIATION CURING

Ionizing radiation, EB, gamma or X-rays, is non-selectively absorbed by matter and thus generates at random a mixture of ionic species, free radicals, molecules in an excited state and solvated electrons. Depending on the medium subjected to irradiation, those active species can induce various types of chemical reactions, namely polymerization, crosslinking or scissioning of polymeric chains, grafting, oxidation, *etc*. [6]. Under irradiation, molecules with carbon-carbon

double bonds, such as vinyl or acrylate monomers, undergo fast polymerization *via* a free radical mechanism. The cationic polymerization of epoxies, oxetanes and vinyl ethers requires a suitable initiator, as an onium salt.

2.1. RADIATION-INDUCED POLYMERIZATION

Chain reactions are efficiently initiated with moderate radiation doses or exposure because modest exotherms result in the amplification of the kinetics of radiation-induced initiation. Processes involving single steps or short kinetic chain length reactions require much higher doses. This is generally the case for the radiation crosslinking of rubbers and thermoplastics. The matrices dedicated to electron beam processing of composites are generally designed for a specific application. In filament wound structures, where the properties of the roving are optimized to reach the maximum tensile strength of the fiber, the overall tensile properties are less important. But for other applications where the loading is complex, the off-axis material properties, such as transverse and shear, are important. These materials need to be developed to provide the maximum tensile yield, but the transverse properties of these composites are generally limited with radiation-cured materials. Two criteria are known to be of prime importance to improve the composite transverse properties: the transfer of the loading from the matrix to the fiber through an optimized fiber-matrix interface and a sufficient matrix toughness to avoid matrix dominated failure. In view of the broadening of electron beam curing applications, the search for materials with improved properties is actively ongoing in different research groups and companies worldwide.

2.2. RESIN SYSTEMS

A variety of monomers and pre-polymers either with ethylenic unsaturations, mainly acrylates, or with epoxy functionality are commercially available. The molecular architecture, backbone and functionality of these monomers and pre-polymers influence both the reactivity of the radiation-sensitive composition and the physical properties of the resulting material.

The molecular architectures, shown in Scheme 2, exist for several classes of pre-polymers (polyurethanes, polyesters, polyethers, silicones and aromatic epoxies) with various molecular weights and functionalities. The degree of flexibility (or rigidity) of the pre-polymer backbone has a strong impact on the thermomechanical properties of the resulting network. Depending on the technical needs of the application, the viscosity of the pre-polymer blend can be adjusted by reactive diluents. Generally, the resin systems selected for high-performance applications must endure high service temperatures and exhibit high
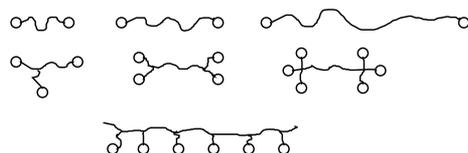
Scheme 2. Typical architecture of monomers and pre-polymers available for radiation curable compositions.

mechanical properties together with a high toughness to avoid matrix dominated failure. For service temperatures higher than 120°C, resins based on aromatic monomers resembling or derived from the bisphenol A component of conventional thermosets are needed. Two representative monomers are shown in Scheme 3.
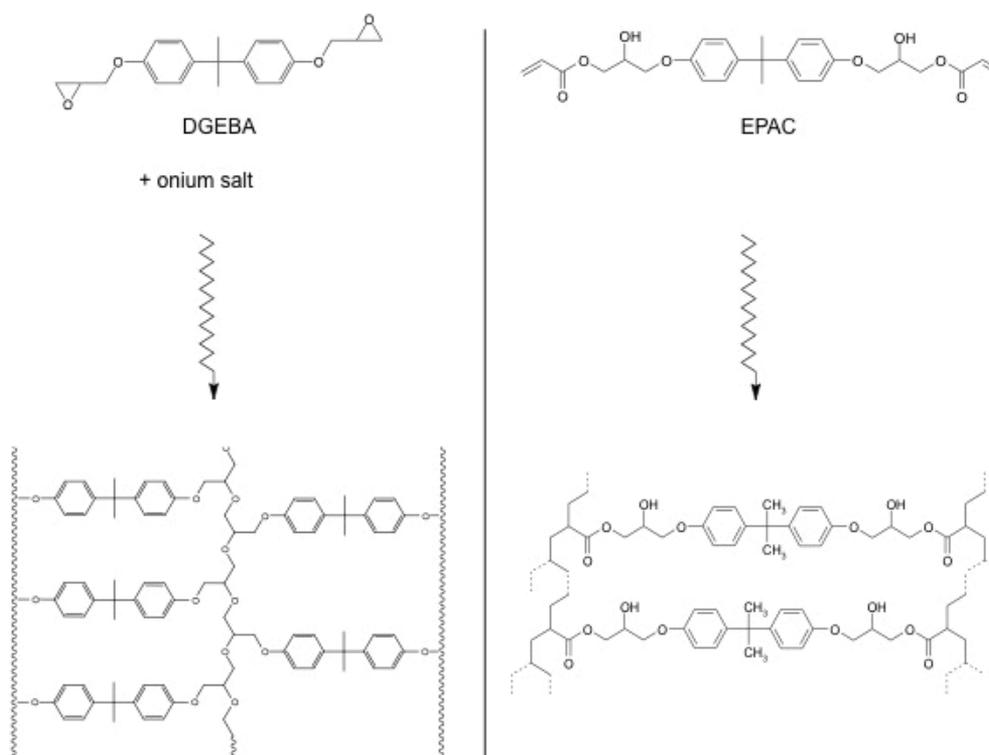
Scheme 3. Molecular structure of bisphenol A diglycidyl ether (DGEBA), of bisphenol A epoxy acrylate (EPAC) and of the networks resulting from their radiation-initiated crosslinking-polymerization.

Beyond the mentioned differences in monomer structure and in polymerization mechanisms, a number of other contrasting features may exert, in a direct or indirect manner, an adverse or a beneficial influence on the structure and on the properties of the final crosslinked materials.

The interaction between high energy radiation and organic materials generates free radical species that are efficient in initiating polymerization. The

free radical process follows the same pathway as that of conventional crosslinking-polymerization initiated by thermal or redox processes. However, the dose rate of the irradiation source may strongly affect the efficiency of the process. At low dose rates, inhibition by oxygen may reduce the efficiency of initiation, and even completely preclude polymerization.

There are specific aspects of the cationic polymerization of epoxies. Radiation-initiated cationic polymerization of epoxies and vinylethers requires the use of onium salts with a low nucleophilicity anion. Aryl sulfonium or iodonium cations, as shown in Scheme 4, will be reduced by thermalized electrons or by the free radicals generated *in situ* as a consequence of radiation interaction with organic matter, yielding active cationic species (Bronsted acid, oxonium or carbenium ions).

$Y^- = PF_6^-, AsF_6^-, SbF_6^-, B(C_6F_5)_4^-$
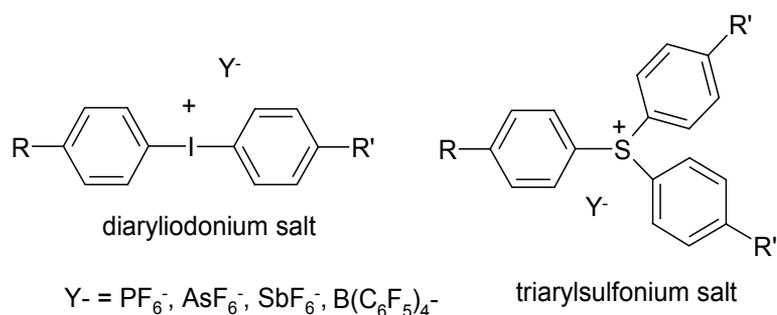
Scheme 4. Examples of onium salts used for radiation-initiated cationic polymerization.

Cationic chain propagation proceeds *via* the reaction of the oxonium ions with epoxy monomers by the activated chain end (ACE) or activated monomer (AM) mechanisms [7]. The ACE mechanism consists of the repeated addition of monomer to the growing chain by the nucleophilic attack of the oxygen from the epoxy monomer on the carbon atom adjacent to the oxonium ion. The AM mechanism takes place in presence of hydroxyl containing species and involves their addition to the protonated monomer followed by a charge transfer; the activated monomer is then regenerated and can react again with a hydroxyl compound. As the epoxy ring opens, hydroxyl groups are formed which favor the AM mechanism. Others transfer reactions can take place between an active chain and nucleophilic species such as water, alcohol or any other hydroxyl compounds resulting in the liberation of a proton and an inactive oligomer [8].

As two cationic species cannot react together, no termination reaction occurs as a result of the self-quenching of active centers, as in the case of free radical processes. Once irradiation has ceased, cationic polymerization will continue without new initiation, by the so-called dark cure phenomenon [9], until the active centers are trapped in the glassy network or quenched by some inhibitor entering the material. This pseudo-living behavior enables further thermal activation giving rise to some beneficial post-cure effects [10].

2.3. NETWORK FORMATION AND VITRIFICATION

Radiation curing is generally achieved by processing composites at room temperature. During the process, the temperature rises a bit due to the absorption of radiation and to the exotherm of polymerization which generates typically 60 to 80 kJ per mole of reacted monomer group. The temperature reached by a sample increases when the dose, dose rate and/or initiator content increases resulting in a higher monomer mobility and a higher final conversion. The dimensions and the geometry of the cured sample are also very important since they control the kinetics of heat transfer. This explains why it is possible to achieve a high degree of conversion in vitreous samples, which have a glassy form. The curing of bisphenol A epoxy acrylate (EPAC)-based materials can yield networks with glass temperatures, T_g, as high a 180°C. The conversion dependence of T_g determined by dynamic mechanical analysis (DMA) of thin films treated under various conditions, as shown in Fig.1, exhibits a monotonous, unchanging increase suggesting a continuous build-up of the network as a consequence of increasing crosslinked density. The variations can be satisfactorily described by the Pascault-Williams relation:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1 - (1 - \lambda)x}$$

where: T_g – the glass transition temperature of network at conversion degree x, T_{g0} – the glass transition temperature of the uncured resin (x = 0), $T_{g\infty}$ – the glass transition temperature of the fully reacted resin (x = 1), λ – a structure--dependent parameter with value between 0 and 1, as represented by the continuous line in Fig.1 [11].
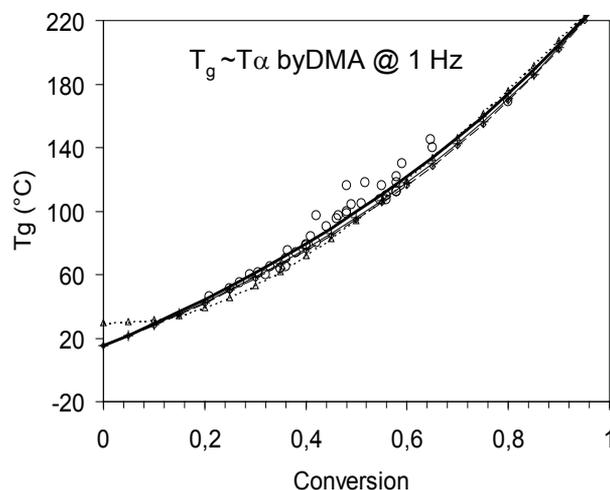
Fig.1. Plot of the T_g (tan δ maximum in DMA spectrogram) as a function of acrylate conversion for EB-cured EPAC films (for various EB doses, dose rates and dose increments).
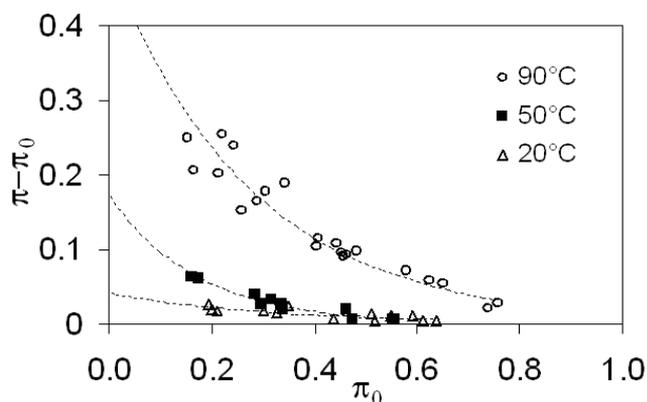
Fig.2. Conversion increase upon thermal aging *vs.* initial conversion (π_0) for EB-cured EPAC resin (35 days of aging).

The variation of acrylate conversion after thermal treatment *vs.* acrylate conversion after EB processing is illustrated in Fig.2 for EPAC resin aged at three different temperatures for 35 days. Post-polymerization increases with increasing temperature and with increasing residual unsaturation after EB processing, but is limited to less than 5% for EB-cured materials that have high conversions. Furthermore, no oxidation by-products (hydroxyl or carbonyl) were detected by FTIR after 3 months at 90°C.

Temperature monitoring during irradiation gives insight into the progress of network build-up. A thermocouple was placed in bulk bisphenol A diglycidyl ether (DGEBA) samples which included various amounts of initiator (diaryliodonium tetrakis(pentafluorophenyl)borate, Rhodorsil 2074). A 3 cm thick epoxy sample in an aluminum box was moved in front of a 10 MeV electron beam so as to receive a dose of 25 kGy per pass. The temperature profiles recorded during the EB processing of the DGEBA samples contained different amounts of an onium salt initiator and provided interesting and useful information, as shown in Fig.3. The thermal energy that caused the temperature rise in the irradiated samples not only came from the deposition of radiative energy by the electron beam into the samples, but also from the exotherm of polymerization.

With the lowest amount of initiator (0.1 wt%), one observes during the first 25 kGy pass a simple temperature step attributed to the conversion of the absorbed radiation into heat, since a similar step is recorded in the cured samples during the third and following passes. In the presence of this rather low amount of initiator, it is likely that the cationic species generated during the first pass are quenched by the nucleophilic contaminants contained in the unformulated resin itself which act as inhibitors. DGEBA resins are synthesized under basic conditions. The potentially initiating entities are not produced in sufficient concentration and the polymerization of epoxy functions does not start before the second pass.

Fig.3. Temperature profiles recorded during the dynamic EB irradiation of DGEBA samples with 0.1, 0.25 and 0.5 wt% of treated diaryliodonium salt by a dose increment of 25 kGy per pass (3 first passes shown in this figure).

The polymerization proceeds during the second exposure to the electron beam in a medium almost free of inhibitor and brought to a temperature of around 50°C. The temperature peak rises up to 180°C within approximately 10 s, just on exiting the irradiation zone.

The third pass does not lead to any significant polymerization exotherm, the temperature rise being limited to the absorbed radiation energy. With an onium salt content of 0.5 wt%, the polymerization starts and proceeds to completion during the first pass in front of the beam. The amount of initiator is sufficient to allow efficient consumption of the inhibiting species early during the first pass. The number of active centers produced is high enough to initiate the fast exotherm process that reaches completion in spite of the increase den-

0.5 wt% initiator:
1 - Heating due to radiation absorption, inhibitor consumption
2 - Exothermal polymerization, heating due to radiation absorption
3 - Heating due to radiation energy absorption (fully cured material)

0.25 wt% initiator:
1 - Heating due to radiation absorption, inhibitor consumption
2 - Kick off of the polymerization (partial cure), heating due to radiation absorption
2' - Vitrification
3 - Heating due to the radiation absorption, vitrified material: uncomplete curing

0.1 wt% initiator:
1 - Heating due to radiation absorption, inhibitor consumption
2 - Polymerization (total cure), heating due to radiation absorption
3 - Heating due to radiation absorption

sity of the network. The maximum temperature reached under these conditions is greater than 225°C. This impedes the vitrification of the sample at incomplete conversion, as observed for the intermediate content of onium salt (0.25 wt%). In this last case, the start of the exotherm from polymerization is delayed compared to the thermal effect due to the radiative energy deposition.

Polymerization is likely initiated by a smaller amount of cationic additive, possibly quenched by some residual inhibitors after some propagation steps. This results in a lower temperature rise and in a lower conversion following the first dose exposure. An important temperature decrease occurs by energy dissipation before the second pass which leads to a sample in the glassy state at 80°C. In the vitreous network, the propagation is expected to be slow and to generate a weak exotherm. As a consequence, the polymerization does not resume during the second 25 kGy pass, in spite of a significant amount of residual monomer functionality.

The effects of the thermal history on the glass transition and on monomer conversion in EB-cured DGEBA materials with diaryliodonium salts have been examined in some detail [12]. A series of samples containing various amounts of initiator were exposed to various doses so as to cover a broad conversion range. The plot of T_g variations as function of the monomer conversion exhibits a monotonous increase for low to medium conversion, up to a conversion degree of about 0.8 (the open circles in Fig.4), followed by an anomalous decrease of the T_g for conversion degrees exceeding that critical value (the open squares in Fig.4).
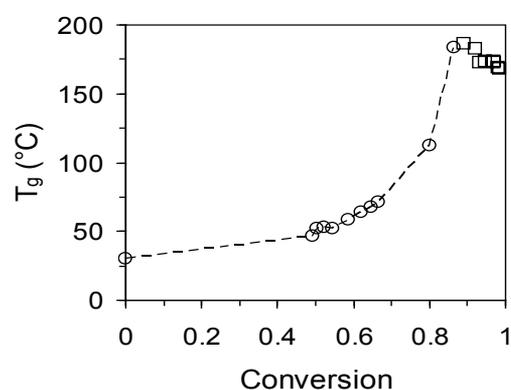
Fig.4. Plot of the T_g (E" maximum) as a function of epoxide conversion for EB-cured DGEBA samples with various initiator contents (diaryliodonium tetrakis(pentafluorophenyl)borate), EB doses, dose rates and dose increments.

Post-curing at a higher temperature than the glass transition pointed out that this decrease in the glass temperature is correlated to the amount of initiators used in the matrix.

This anomalous behavior can be explained by the relaxation of weak ion pair clusters. The build or increased density of the network likely traps the
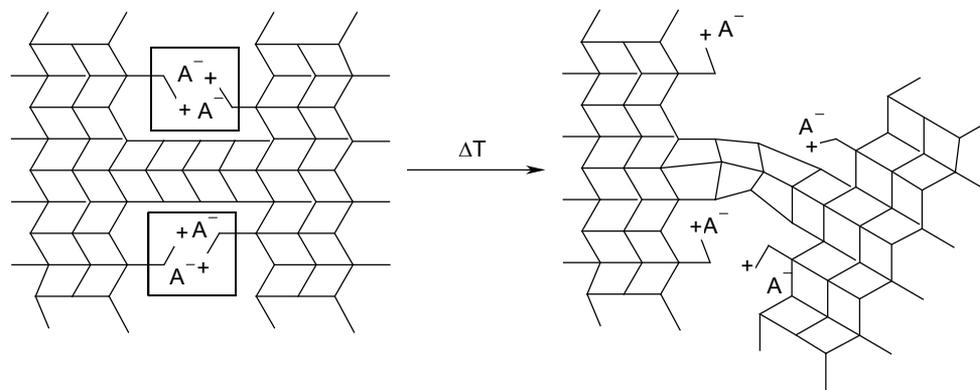
Scheme 5. Simplified representation of the effect of a thermal treatment above T$_g$ on the associated ion pairs within a poly(epoxy) network.

propagating oxonium and the counter-ion in vitreous clusters that contribute to the crosslinks of the network. A thermal treatment above T$_g$ is thought to bring some segment mobility allowing for a rearrangement of the ionic clusters into ion pairs to take place. The total amount of crosslinks within the sample would decrease with amplitude correlated to the amount of ionic end groups in the network, which is observed experimentally. A simplified representation of this is illustrated in Scheme 5.

2.4. NETWORK PROPERTIES

2.4.1. Flexibilizing the matrix: the case of epoxy resins

As with thermosets, radiation curable resins can be formulated with various comonomers, reactive diluents or transfer agents to adjust the final properties of the matrix. The influence of hydroxyl compounds on the properties of the cured network has been studied by different groups [13-15]. The presence of hydroxyl groups as impurities or as additives affects the curing kinetics and, among other features of the material, the network T$_g$ (as shown in Fig.5). Chain transfer which occurs by the activated monomer mechanism leads to shorter polymer chains and increases the mobility of the reactive species. This results in an accelerated curing, in higher final conversion of monomers, and in some decrease of T$_g$. It is possible to tailor the network structure of such systems by exploiting intrinsic differences in hydroxyl group reactivity. Water as a nucleophilic species is also a transfer agent which alters the polymeric network. A 23°C decrease of the T$_g$ was observed when 1% of water was present in the matrix compared to a dry system [8].

The use of reactive diluents can facilitate the impregnation process by significantly reducing the viscosity of paste-like formulations. Reactive diluents also have an influence on the cure rate and on the final properties [16]. If the
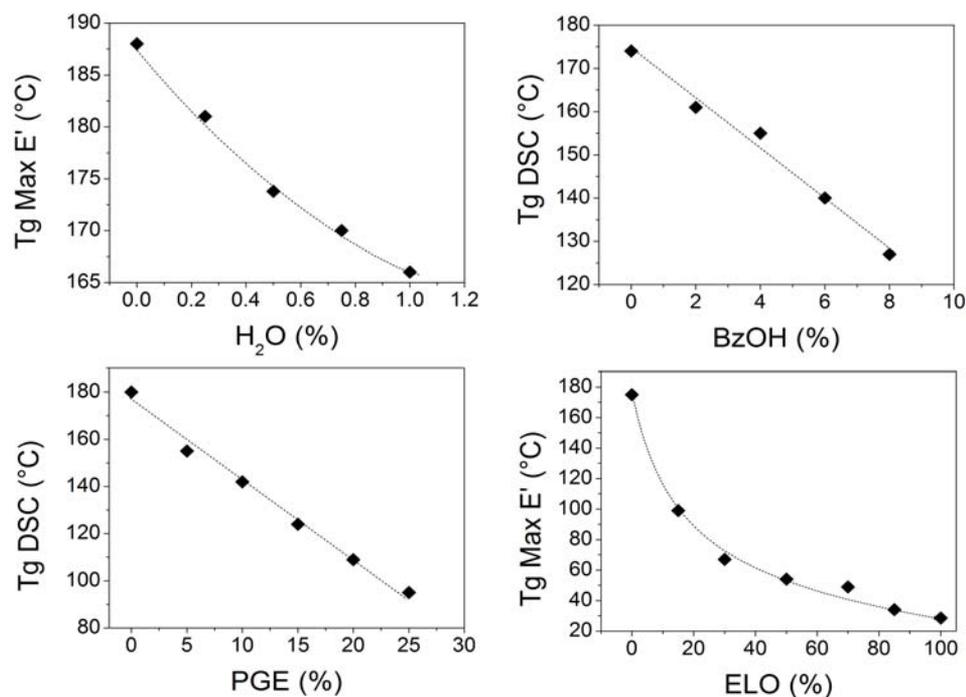
Fig.5. Influence of some reactive additives (water, benzyl alcohol (BzOH), phenyl-glycidyl ether (PGE) and epoxidized linseed oil (ELO)) for flexibilizing EB-cured DGEBA containing 0.5 wt% of an initiator (T_g determined by DSC (differential scanning calorimetry) or by DMA at 1 Hz).

diluent is a monofonctional monomer, the dilution causes a decrease of the crosslinked density. Some flexibilizing effect can be expected for the network.

The series of graphs shown in Fig.5 illustrate various possible formulations for adjusting the T_g of DGEBA-based resins cured by EB after an exposition to a dose 100 kGy (0.5 wt% of diaryliodonium tetrakis(pentafluorophenyl)borate, Rhodorsil 2074) with the presence of limited amounts of water or benzyl alcohol (BzOH) as transfer agents, of phenyl glycidyl ether (PGE) as a monofunctional reactive diluent and of epoxidized linseed oil (ELO) as multifunctional monomers with flexible alkyl side groups.

2.4.2. Micro-heterogeneities in matrix networks

The crosslinking-polymerization of multifunctional monomers is known to yield more brittle matrices, thus limiting the development of using such for the production of high-performance composite materials. A possible cause of such brittleness is the spontaneous formation of nano-heterogeneities during radiation-initiated polymerization, which is supported by atomic force microscopic imaging and by calorimetric analyses.

The local topography of samples cured by exposure to ultraviolet or EB radiation on NaCl plates was analyzed by atomic force microscopy (AFM).
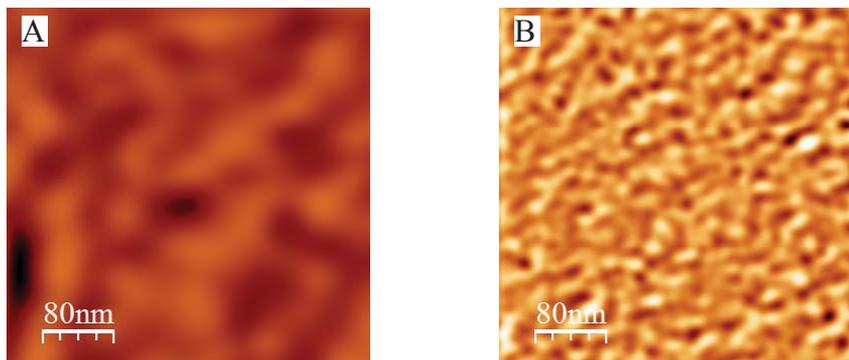
Fig.6. Height (A) and phase contrast (B) AFM images recorded in the tapping mode of partially EB-cured (20 kGy, conversion $\pi = 0.41$) epoxy diacrylate network.

The control of monomer conversion in the samples was determined by transmission FTIR to appraise simultaneously the local topography along with variations of crosslinked density as a function of the progress of the reaction. The pictures in Fig.6 show both the height and the phase contrast images the polymer network of a film made of bisphenol A epoxy diacrylate cured under an electron beam to a dose of 20 kGy yielding a conversion level of $\pi = 0.41$ for the acrylate functionality. The topographical image shows a very flat surface with a root mean square (RMS) roughness of 0.2 nm, whereas the phase contrast image highlights the more complex and heterogeneous structure of the network [17].

The sample morphology appears to be made of very stiff domains corresponding to the lower phase values, whereas the darker zones correspond to much more compliant material. Stiff domains can be reasonably associated with what can be named as clusters, originating from the initial microgels. Such clusters exhibit a densely crosslinked structure which contrasts with the softer interstitial zones that likely correspond to the loosely crosslinked and swollen portions of the matrix. This type of imaging reveals without ambiguity dense nodules with a mean diameter of about 15 nm. The description and understanding of structure-properties relationships in multi-acrylate networks by taking

Progress of cross-linking polymerization
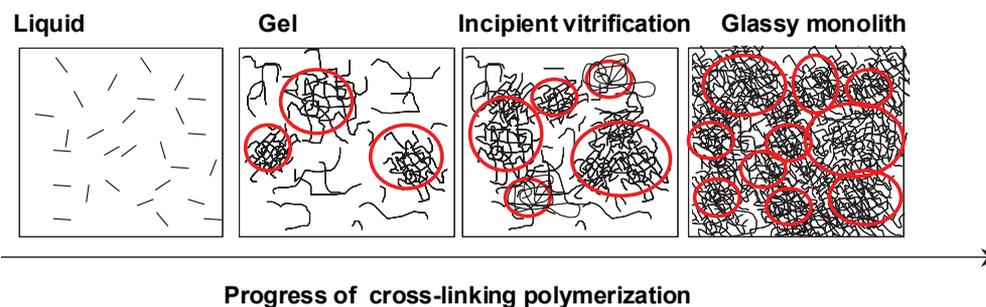
Scheme 6. Sketch representing the heterogeneous build-up of networks prepared by radiation-induced chain polymerization of aromatic diacrylates.

into account their micro-heterogeneity is essential from both a fundamental and a practical viewpoint [18].

The scenario currently proposed for the build-up of the network is represented in Scheme 6. These sketches illustrate the measured variations of T_g and the broadness of the transitions in relation to the variety of defects and heterogeneities in the spatial distribution of crosslinks and their density [19, 20].

2.4.3. Matrix toughening with high T_g thermoplastics

The presence of nanoscale heterogeneities in the resulting vitreous monolithic material is one of the reasons for the brittle behavior generally observed when such materials are subjected to elongation or shear strain. The localized intensity of stress on incipient cracks results in the catastrophic failure of the material. In order to overcome this limitation, thermoplastic toughening agents have been introduced in an approach similar in some ways to the improvement of fracture resistance in thermosets with rubbers or with high T_g aromatic polyethersulfone (PES). Two notable differences with respect to the toughening methodology compared to heat curable networks are related to the particular thermal profile and kinetic conditions of radiation curing. Irradiation is generally conducted on materials at room temperature and subjected to the sudden initiation of chain polymerization with the generation of heat from the radiation energy itself and from the strong exotherm of polymerization. These two distinct features should favor the early occurrence of thermoplastic phase separation upon the polymerization of the reactive diluents and pre-polymers and should as well limit the growth of the nucleated thermoplastic domains, if the system starts vitrifying during the early stages of curing. This perspective seems particularly attractive for designing advanced radiation curable formulations.

The controlled polymerization-induced phase separation of nano-sized clusters of polyethersulfone was evaluated as a means for alleviating the inherent tendency of the diacrylate materials to brittle fracture, as shown in Fig.7.
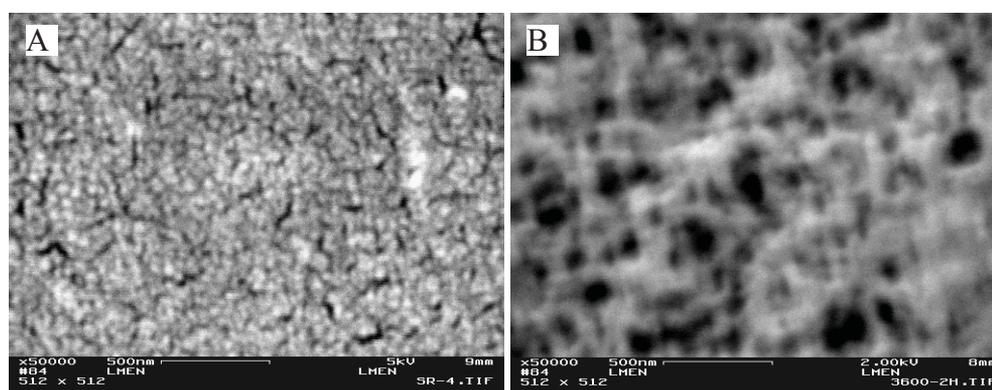
Fig.7. SEM micrographs showing the nano-sized morphology of neat (A) and toughened acrylate-based system including commercial high T_g thermoplastic (B) that exhibits typical K_{Ic} values of 2 MPa·m$^{1/2}$.

Various homogeneous formulations including aromatic diacrylate monomers, polyethersulfone together with a compatible reactive diluent were prepared and polymerized by electron beam irradiation. The resulting toughened materials showed optimized critical stress intensity factor (K_{Ic}) over 2 MPa·m$^{1/2}$, whereas the K_{Ic} value is about 1 MPa·m$^{1/2}$ for the unmodified reference resin [21].

2.5. COMPARING EPOXY AND ACRYLATE CHEMISTRIES

On the basis of the knowledge and experience gained by academic and industrial research on networks with potential applications in coatings and in structural composites, the main features of the two types of chemistries, free radical and cationic, can be compared on a number of points including pre-cure properties, reactivity during cure, change of physical properties, mechanical properties and aging after curing [22]. Some of the general properties associated with each system are listed in Table 1.

Table 1. Comparison of acrylate- and epoxy-based radiation-cured formulations.

	Free-radical (acrylates)		Cationic (epoxies)	
	Advantages	Drawbacks	Advantages	Drawbacks
Pre-cure properties	Low cost chemicals, shelf stability		Compatibility with thermoplastic additives	Poor initiator compatibility, low stability
During curing	No initiator required, easier control of the reaction	Sensitivity to oxygen, high volume contraction	Insensitivity to oxygen, low volume contraction	Sensitivity to bases and nucleophiles (water)
Post-cure properties		Brittleness (strong), current carbon sizings not adapted	Toughness, flexibility, adhesion	No termination

This comparison reasonably leads to a conclusion that acrylates exhibit some advantages for conveniently handling and curing by a free radical process in spite of their sensitivity to oxygen inhibition. Such oxygen inhibition is limited to the surfaces that are in contact with air.

Cationic systems, in spite of their more complex and environmentally sensitive chemistry, being very sensitive to trace amounts moisture or humidity and to nucleophilic impurities, offer, in principle, a much more attractive set of cured physical properties, essentially associated with their low volume contraction and their molecular interaction parameters. A beneficial influence on mechanical properties of the matrix, as well as on fiber-matrix interactions can be expected and is effectively observed in several coating applications. This anticipated advantage on mechanical properties does not seem to be eas-

ily transferred to fiber-reinforced composites [23]. However, appropriate surface treatments have been proposed and validated for improving the interfacial properties of radiation curable carbon fiber-reinforced acrylate matrices [24].

Finally, both acrylate and cationic systems have their advantages and drawbacks. Whatever system is used, the knowledge of electron beam-induced chemistry and of the curing process is essential to attain and control the desired final materials properties. Ongoing research projects are focusing on the improvement of the transverse properties of composite materials through a better understanding of the fiber-matrix interface.

3. COMPOSITE PROPERTIES

Interfaces are among the most important yet poorly understood aspects of composite materials. There is a lack of understanding of processes occurring at the atomic level of interfaces and how those processes influence the behavior and the properties of the composite, whatever the chemical make-up (carbon, inorganic) and the geometry of the reinforcing component (short or long fibers, micro- or nanoparticles). There is a need for global understanding of the processes that take place on the atomic, microscopic, and macroscopic levels.

A weakness of radiation-cured carbon fiber-reinforced composite materials is their low transverse properties [24, 25], which are the result of a poor quality interface between fibers and the surrounding matrix. Several potential causes of this have been investigated.

Cure-induced volume shrinkage may, in some cases, influence adhesion between carbon fibers and the matrix. EB curable acrylate formulations have a higher cure-induced volume shrinkage (in the range of 3 to 5% for high-performance formulations) compared to thermally cured epoxy amine systems used for similar applications (commonly around 2 to 3%) [26]. This volume shrinkage is due to the polymerization process itself and can have a negative effect on the fiber-matrix adhesion. A low profile additive approach using polyvinyl acetate in some formulations resulted in a decrease of the cure-induced shrinkage from 6 to around 4.5% of the initial material volume. Such an improvement was attained without a significant decrease in the network's T_g and opens an interesting path for upgrading transverse properties.

Fiber treatment using plasma treatment is another interesting approach [27]. Plasma treatment of fibers resulted in an interlaminar shear strength increase of 20 to 30% of composite samples. Adhesion improvement was demonstrated to be related to the oxidation of carbon fibers. X-ray photoelectron spectroscopy (XPS) analyses of the fibers show more than 15 to 20% of oxygen on the carbon surface after plasma processing.
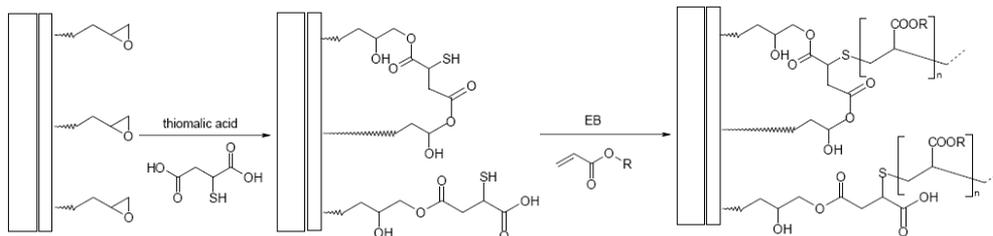
Scheme 7. Schematic view of carbon fiber surface modification aimed at strengthening fiber-matrix interface.

Laboratory experiments were conducted on model formulations to try to reproduce in solution the chemistry that takes place at the fiber-matrix interface. The results emphasized the critical inhibiting influence of some chemical groups such as aromatic hydroxyls or amines. At the opposite end, the sensitizing effects of thiol groups on acrylate polymerization were also demonstrated. This led to the development of a treatment of the carbon fibers with thiomalic acid and an epoxy type sizing that yields a reactive coating particularly adapted to matrices curable by EB-initiated free radical mechanisms, as illustrated on Scheme 7. Covalent bonds between the carbon fiber sizing and the matrix are created with a great efficiency, as a result of the chain transfer reactions between grafted thiol groups and the growing polymer network [28-30].

Elementary composites using treated fibers and an epoxy acrylate formulation were found to exhibit transverse properties, measured by the transverse tensile strength, that were more than doubled ($\sigma_2 = 70$ MPa) compared to the same composite using fibers without treatment ($\sigma_2 = 29$ MPa) (Scheme 8).
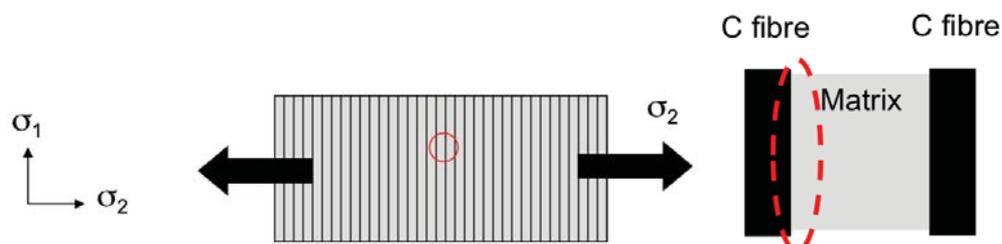
Scheme 8. Principle of mechanical testing of the interface between carbon fiber and the radiation-cured matrix.

4. CONCLUSION AND PERSPECTIVES

Over the past 10 years, the knowledge of EB and X-ray processing has considerably increased. Curing kinetics, control and modeling of radiation processing, aging of EB-cured composites are now better understood on the basis of a

multiscale investigation of network construction and of material properties. A variety of technical issues concerning EB curing have been addressed through a basic approach to radiation physics, radiation chemistry and materials science. Advanced studies aimed at the improvement of matrix toughness, at the reduction of the matrix cure-induced shrinkage, and at the design of fiber surface functionality have been addressed and significant results have been achieved with regard to each of these topics. Solutions for matrix toughening with greater processability and compatible with environmental considerations are under development. A next step will consist in aggregating the technical solutions developed for improving isolated aspects of curing, examined from the viewpoints of processing, of curing kinetics, of polymer network performance and of fiber-matrix interactions. Radiation-induced composite curing technology is being demonstrated that meets demanding product specifications. Encouraging results envision the mass production of structural composites as well as functional materials by means of a reliable, cleaner and more productive out-of-autoclave approach to manufacturing [31].

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