HANSER

Sample Pages

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Electron Beam Curing of Composites

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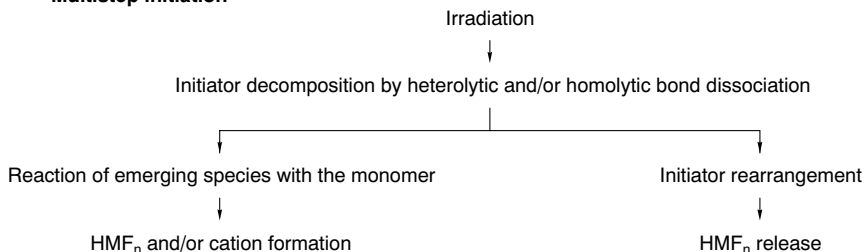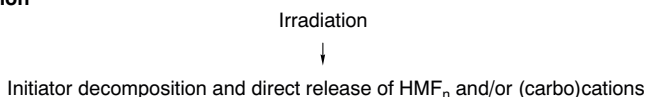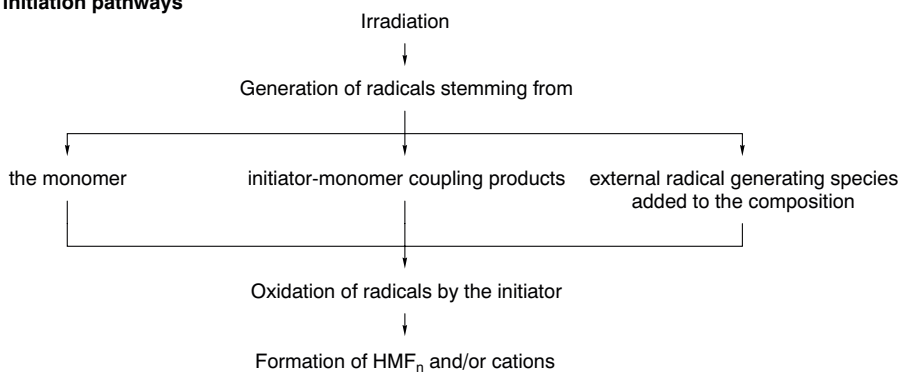# 2 Aspects of Electron Beam Curable Materials

2.1 Initiators

During the past decades, free radical electron beam curing, particularly of (meth)acrylates, was developed elaborately based on well-established technological and scientific principles [79–83]. In contrast, ionic polymerization in the field of electron beam curing was not widely investigated and the lack of suitable initiators restricted further developments in this field. The combination of conventional cationic initiators, typically Lewis or Brønsted acids, with multifunctional monomers resulted in nearly instantaneous and irreversible gelation. This high reactivity and lack of latency made it impossible to employ most of these cationically polymerizable systems in commercially important applications.

A major breakthrough in ionic curing reactions initiated by electron beam irradiation came along with the key discovery of Crivello et al. that certain onium salts, such as diaryliodonium $[Ar_2I]^+MF_n^-$ or triarylsulfonium salts $[Ar_3S]^+MF_n^-$ with weakly or non-nucleophilic anions ($MF_n^- = BF_4^-$, PF_6^-, AsF_6^- or SbF_6^-), as seen in Fig. 2.1, can act as highly efficient photoinitiators for the cationic polymerization of virtually all known types of cationically polymerizable monomers, including epoxides, vinyl ethers, oxetanes, oxazolines, styrenes, and many others [9]. Moreover, these salts display excellent latency and, after dissolving of the initiator in a multifunctional monomer, polymerization can be triggered on demand by irradiating the mixture. Initial investigations concentrated on UV curing [84–89], e.g., of coatings, and it could also be shown that these compounds are very well suited as initiators for electron beam processing [90–93], even of deep section substrates and composites [94].
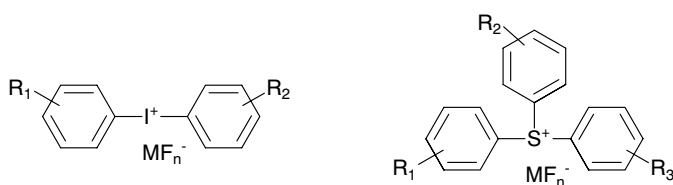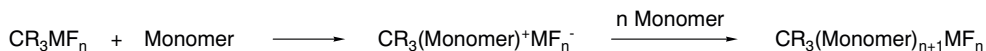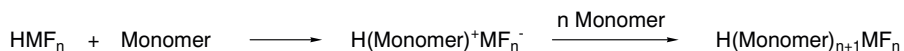

Figure 2.1: Diaryliodonium and triarylsulfonium initiators ($MF_n^- = BF_4^-$, PF_6^-, AsF_6^- or SbF_6^-)

Various initiation mechanisms resulting in the formation of very strong Brønsted acids HMF_n and/or highly reactive carbocations CR_3^+ capable of monomer activation and polymerization initiation have been discussed [95]. The dominating initiation pathways are summarized in Fig. 2.2 and can be divided into "non-redox pathways" covering HMF_n and/or cation formation in a direct or multi-step procedure and "redox initiation pathways" where the onium salt functions as an oxidant converting radicals into cationic species. A cascade of reactions can take place and, to complicate matters further, some of these mechanisms can also proceed simultaneously.

Non-redox initiation pathways

● **Multistep initiation**

Irradiation

↓

Initiator decomposition by heterolytic and/or homolytic bond dissociation

Reaction of emerging species with the monomer　　　　　　Initiator rearrangement

↓　　　　　　　　　　　　　　　　　　　　　　　　　　↓

HMF_n and/or cation formation　　　　　　　　　　　　HMF_n release

● **Direct initiation**

Irradiation

↓

Initiator decomposition and direct release of HMF_n and/or (carbo)cations

Redox initiation pathways

Irradiation

↓

Generation of radicals stemming from

the monomer　　　　initiator-monomer coupling products　　　external radical generating species
　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　added to the composition

Oxidation of radicals by the initiator

↓

Formation of HMF_n and/or cations

Figure 2.2: Main initiation pathways in iodonium and sulfonium salt-induced cationic polymerization

According to Fig. 2.2, the following monomer activation and polymerization (Fig. 2.3) is initiated by Brønsted acids and/or cations generated upon radiation-induced onium salt decomposition.

$$HMF_n \; + \; \text{Monomer} \longrightarrow H(\text{Monomer})^+MF_n^- \xrightarrow{\text{n Monomer}} H(\text{Monomer})_{n+1}MF_n$$

$$CR_3MF_n \; + \; \text{Monomer} \longrightarrow CR_3(\text{Monomer})^+MF_n^- \xrightarrow{\text{n Monomer}} CR_3(\text{Monomer})_{n+1}MF_n$$

Figure 2.3: Cationic polymerization initiated by strong Brønsted acids HMF_n or carbocations CR_3^+

It was demonstrated that various essential characteristics of iodonium and sulfonium salt initiators can be assigned to the respective cation and anion moieties of these compounds [9, 96]. For the efficient initiation of polymerization by Brønsted acids, super acids derived from the initiator anion with Hammett acidities [97] (H_0 values) in the range of –15 down to –30 are required. One of the strongest Brønsted acids known and thus one of the most powerful initiating species for cationic polymerization is $HSbF_6$ [97, 98]. This acid is readily generated *in situ* by photolysis of onium salt initiators bearing the SbF_6^- anion. Fluorinated tetraphenylborates, e.g., $B(C_6F_5)_4^-$ or $B[C_6H_3(CF_3)_2]_4^-$, represent another class of highly efficient anions and onium salt initiators bearing these anions exhibit activities similar to the corresponding hexafluoroantimonate compounds [99]. The rate of chain propagation depends on the basicity and nucleophilicity of the anion and polymerization rates increase with decreasing basicity and nucleophilicity of the anion [95]. Thus, within a series of photoinitiators with structurally identical cations but different anions MF_n^- or $B(C_6R_5)_4^-$, initiator activities increase in the order

$$BF_4^- < PF_6^- < AsF_6^- < SbF_6^- \approx B(C_6F_5)_4^- \approx B[C_6H_3(CF_3)_2]_4^-$$

Therefore, the nature of the anion and its stability determines the strength of the acid formed during photolysis and its corresponding initiation efficiency. The nature of the anion also determines the character of the propagating ion pair. This affects directly the polymerization kinetics and whether termination can occur by anion-splitting reactions.

On the other hand, several important initiator properties, e.g., radiation absorption characteristics, radiation sensitivity, compatibility with other additives such as photosensitizers, solubility in the monomers, toxicity, or thermal stability strongly depend on the cation type and substituents at the cation framework. The thermal stability, for instance, has a direct impact on the latency of these photoinitiators and determines, ultimately, whether they can be employed in industrial applications.

Besides the onium initiators, a radically different class of cationic photoinitiators was developed by the research department of the Ciba-Geigy Corporation. It was found that cyclopentadienyl iron(II) arene complexes generate Lewis acidic iron species upon irradiation by release of the arene ligand [100]. Subsequently, the arene ligand is substituted by monomer species and ring-opening polymerization starts in the coordination sphere of the metal. However, the use of these initiators appears restricted to monomers that can effectively bind to the coordinatively unsaturated iron centre, e.g., epoxides. Very recently, another class of metal complex initiators for cationic polymerization was described. It was shown that silver olefin complexes are highly efficient initiators, especially for the electron beam processing of epoxy resins [101].

The most important initiators, both onium salt and metal complex initiators, their preparation, commercial availability, and initiation mechanisms are discussed in details in the following sections.
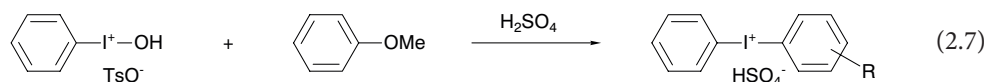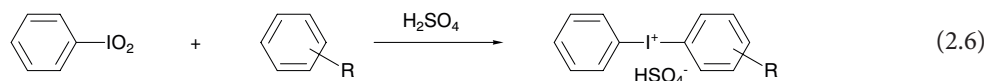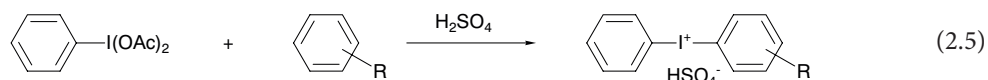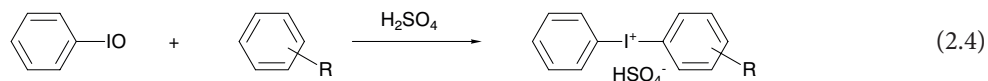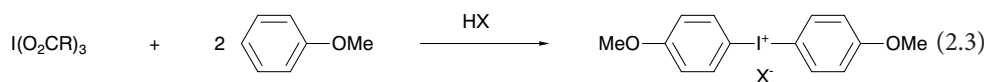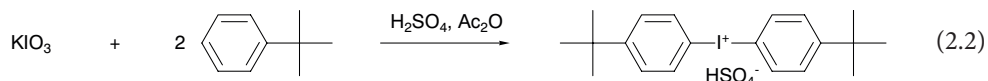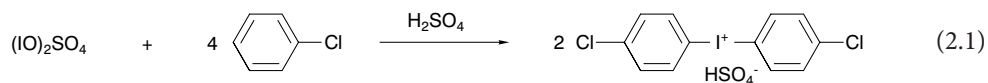
2.1.1   Onium Salt Initiators

The discovery that diaryliodonium and triarylsulfonium salts are easily accessible and efficient photoinitiators for cationic polymerization led to the development of various other onium salt initiators [95], mainly based on nitrogen, sulfur, or phosphorus compounds. However, most of the commercially available initiators for electron beam processing are diaryliodonium and triarylsulfonium salts of weak bases, due to their outstanding performance.

Many parallels exist between diaryliodonium and triarylsulfonium salts [9]. For example, the initiation mechanisms of diaryliodonium salts follow a course very similar to that observed for triarylsulfonium salts. Triarylsulfonium salts undergo electron-transfer photosensitization like diaryliodonium salts, but they are not as readily photosensitized as diaryliodonium salts, due to their significantly lower (less positive) reduction potentials. However, the relatively low reduction potentials of the triarylsulfonium salts contribute markedly to the excellent thermal stability of these compounds even in the presence of the most nucleophilic and reactive monomers.
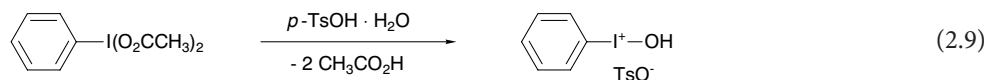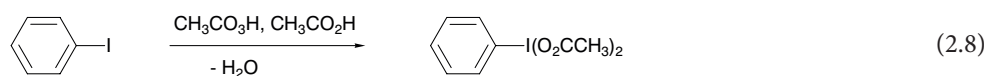
As mentioned above, some key features of these initiators are governed by the substituents at the cation and can be tuned by appropriate choice. Therefore, a variety of synthesis strategies have been developed facilitating access to a series of onium salts with the desired substituents and properties.

2.1.1.1   Iodonium Salt Initiators

Compared to diaryliodonium salts, dialkyliodonium and alkylaryliodonium salts are much more difficult to prepare and to handle. Hence, alkyl-substituted iodonium salts, in contrast to alkyl-substituted sulfonium salts, did not find practical applications as initiators [102]. Figure 2.4 shows several strategies that have been developed to synthesize diaryliodonium salts in high yields via electrophilic aromatic substitution employing iodyl sulfate $(IO)_2SO_4$ (Eq. 2.1), potassium iodate KIO_3 (Eq. 2.2), iodine(III)acylates $I(OOCR)_3$ (Eq. 2.3), aromatic iodoso compounds ArIO (Eq. 2.4), iodoso diacetates $ArI(OAc)_2$ (Eq. 2.5), or aromatic iodoxy compounds $ArIO_2$ (Eq. 2.6) as iodine source [102–105]. The synthesis route depends on the desired substituents at the aryl moieties and diaryliodonium salts bearing electron-withdrawing groups are favorably prepared starting from iodylsulfate, whereas iodonium salts with electron-donating groups are advantageously obtained using potassium iodate. Another efficient method to couple electron rich aromatic substrates is their electrophilic substitution reaction with hydroxy(tosyloxy)iodobenzene ArI(OH)OTs (Eq. 2.7) [106]. The reagent can be obtained in a one pot synthesis (Fig. 2.5) by oxidation of iodobenzene with peracetic acid, yielding the iodoso diacetate and subsequent addition of p-toluenesulfonic acid (Eqs. 2.8 and 2.9) [107]. Furthermore, reactions of hydroxy(tosyloxy)iodoarenes with aryltrimethylsilanes proceed with silicon carbon bond cleavage and offer a very selective pathway to diaryliodonium salts with tunable substituent placement in both rings [108]. Symmetrical iodonium salts with the same substituents at both aryl groups are obtained via reactions (2.1) to (2.3) whereas unsymmetrical substituted iodonium salts can be prepared according to equations (2.4) to (2.7).

$(IO)_2SO_4$ + 4 (phenyl)—Cl →[H_2SO_4] 2 Cl—(phenyl)—I^+—(phenyl)—Cl, HSO_4^- (2.1)

KIO_3 + 2 (phenyl)—C(CH_3)_3 →[H_2SO_4, Ac_2O] (CH_3)_3C—(phenyl)—I^+—(phenyl)—C(CH_3)_3, HSO_4^- (2.2)

$I(O_2CR)_3$ + 2 (phenyl)—OMe →[HX] MeO—(phenyl)—I^+—(phenyl)—OMe, X^- (2.3)

(phenyl)—IO + (phenyl)—R →[H_2SO_4] (phenyl)—I^+—(phenyl)—R, HSO_4^- (2.4)

(phenyl)—$I(OAc)_2$ + (phenyl)—R →[H_2SO_4] (phenyl)—I^+—(phenyl)—R, HSO_4^- (2.5)

(phenyl)—IO_2 + (phenyl)—R →[H_2SO_4] (phenyl)—I^+—(phenyl)—R, HSO_4^- (2.6)

(phenyl)—I^+—OH, TsO^- + (phenyl)—OMe →[H_2SO_4] (phenyl)—I^+—(phenyl)—R, HSO_4^- (2.7)

Figure 2.4: Synthesis strategies for the preparation of diaryliodonium salts via electrophilic aromatic substitution: Eq. 2.1 to 2.7

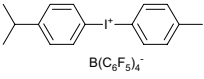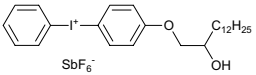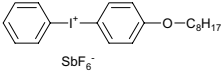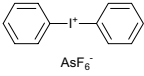(phenyl)—I →[CH_3CO_3H, CH_3CO_2H; $-H_2O$] (phenyl)—$I(O_2CCH_3)_2$ (2.8)

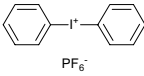(phenyl)—$I(O_2CCH_3)_2$ →[p-TsOH · H_2O; $-2\ CH_3CO_2H$] (phenyl)—I^+—OH, TsO^- (2.9)
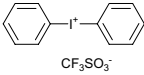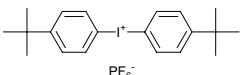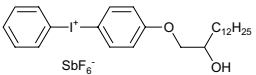
Figure 2.5: Synthesis of hydroxy(tosyloxy)iodobenzene: Eq. 2.8 and 2.9
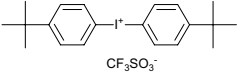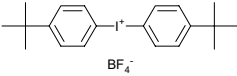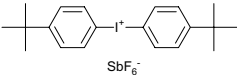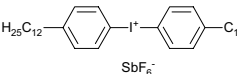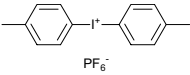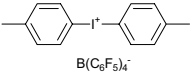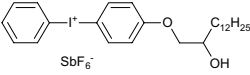
According to the procedures outlined in Fig. 2.4, iodonium salts with hydrogen sulfate, halogenides, or p-toluolsulfonate as counterions are obtained in most cases. These are not compatible with a cationic polymerization pathway due to the nucleophilicity of the anions. The anions combine with emerging cationic species thus interfering with the polymerization reaction. Anion exchange (Eq. 2.10) with bulky, non- or extremely low-nucleophilic complex metal fluorides MF_n^-, such as BF_4^-, PF_6^-, AsF_6^- and SbF_6^-, or fluorinated tetraphenylborates, such as $B(C_6F_5)_4^-$ or $B[C_6H_3(CF_3)_2]_4^-$, yield highly active polymerization initiators. Some commercially available iodonium salts are listed in Table 2.1.

$$Ar_2I^+X^- + NaMF_n \rightarrow Ar_2I^+MF_n^- + NaX \qquad (2.10)$$

Table 2.1: Commercially Available Aryliodonium Salts

Iodonium salt	CAS-No.	Company[a]	Name or order number
$B(C_6F_5)_4^-$	178233-72-2	Rhodia Silicones S.A.S. TCI Europe N.V. ABCR GmbH & Co. KG Gelest, Inc.	Rhodorsil 2074 I0591 AB134236 OMBO037
SbF_6^- ($C_{12}H_{25}$, OH)	139301-16-9	Sartomer Co., Inc. Aldrich	SarCat® CD-1012 445835
SbF_6^- ($O-C_8H_{17}$)	121239-75-6	ABCR GmbH & Co. KG Hampford Research, Inc. GE Silicones	AB154263 OPPI OPPI
AsF_6^-	62613-15-4	TCI Europe N.V. Apollo Scientific Ltd. 3B Scientific Corporation Fluorochem Ltd. ABCR GmbH & Co. KG	D2248 PC0756 3B3-063894 009164 AB142786
PF_6^-	58109-40-3	TCI Europe N.V. Aldrich 3B Scientific Corporation Pfaltz & Bauer Chemicals Carbone Scientific Apollo Scientific Ltd. Alfa Aesar Fluorochem Ltd. ABCR GmbH & Co. KG PCI Synthesis	D2238 548014 3B3-017307 D51230 C-22159 PC8214 A17934 009165 AB129475 600013
$CF_3SO_3^-$	66003-76-7	TCI Europe N.V. Aldrich 3B Scientific Corporation Apollo Scientific Ltd. Alfa Aesar Fluorochem Ltd. ABCR GmbH & Co. KG	D2253 530972 3B3-063895 PC5029 L17444 009166 AB180350
PF_6^-	61358-25-6	Midori Kagaku Co., Ltd. ABCR GmbH & Co. KG TCI Europe N.V.	BBI-102 AB171136 B2380
SbF_6^- ($C_{12}H_{25}$, OH)	139301-16-9	Sartomer Co., Inc. Aldrich	SarCat® CD-1012 445835

**Table 2.1:** (continued) Commercially Available Aryliodonium Salts

Iodonium salt	CAS-No.	Company[a]	Name or order number
$CF_3SO_3^-$	84563-54-2	Midori Kagaku Co., Ltd. Aldrich Acros Organics 3B Scientific Corporation ABCR GmbH & Co. KG TCI Europe N.V.	BBI-105 530999 37503 3B3-073732 AB171137 B2381
BF_4^-	62051-09-6	Midori Kagaku Co., Ltd.	BBI-101
SbF_6^-	61358-23-4	Midori Kagaku Co., Ltd.	BBI-103
$H_{25}C_{12}$ — I^+ — $C_{12}H_{25}$ SbF_6^-	71786-70-4	Deuteron GmbH UFC Corporation Nanjing Chemlin Chemical Industry Co., Ltd.	UV 1242 DDHA NP50764
PF_6^-	69842-75-7	Deuteron GmbH	UV 2257
$B(C_6F_5)_4^-$	153699-26-4	Nanjing Chemlin Chemical Industry Co., Ltd.	NP43110
I^+ — O — $C_{12}H_{25}$, OH, SbF_6^-	139301-16-9	Sartomer Co., Inc. Aldrich	SarCat® CD-1012 445835

[a]   Some selected suppliers

Several further developments in the field of iodonium salt initiators have been described and promising results were obtained using initiators adapted to the respective requirements by incorporation of irradiation-sensitive substituents, e.g., fluorenones [109]. Other strategies comprised the development of polymers containing iodonium salt moieties in the main chain [110] or the use of tailored sensitizers [111], e.g., dyes [112].

The mechanism of UV-induced cationic polymerization, especially of epoxy resin monomers, employing diaryliodonium salt initiators was intensely investigated by several research groups [84–89, 113–117] and electron beam initiation proceeds via similar reaction pathways [90–94]. The process is complex and comprises a cascade of reactions (Fig. 2.6), starting with photoexcitation of the iodonium salt, followed by heterolytic and homolytic carbon-iodine bond dissociation. The resulting aryl cations, aryliodine cation radicals, and aryl radicals are highly reactive and give rise to the formation of Brønsted acids HMF_n in subsequent reactions.
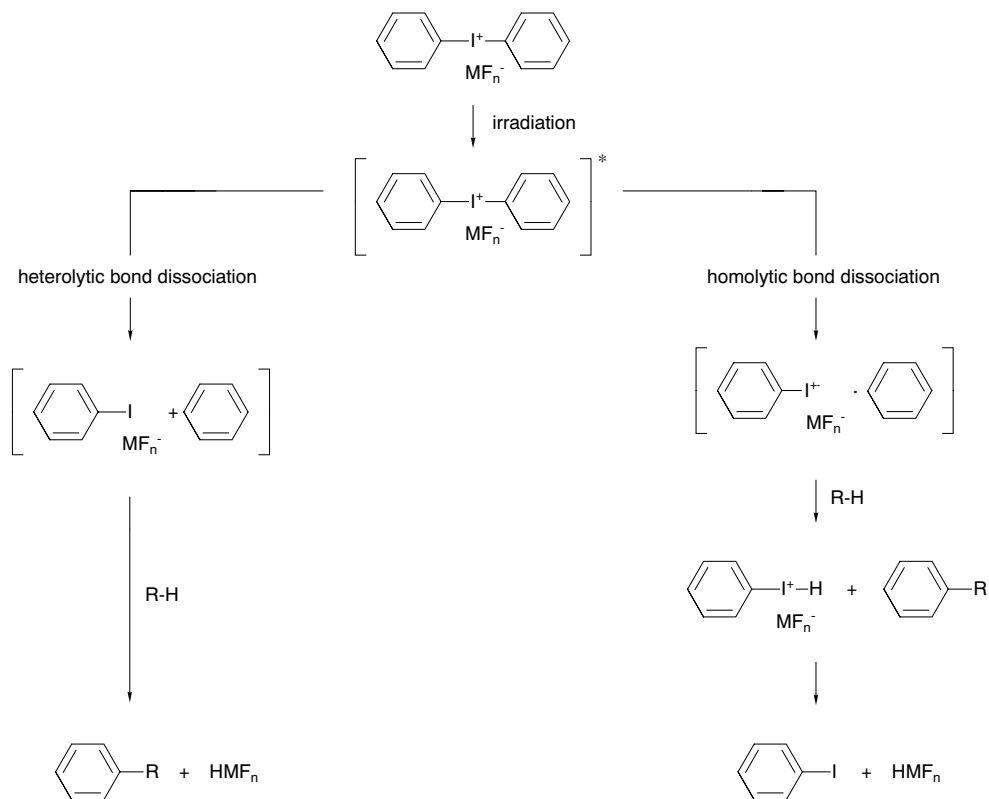
Figure 2.6: Interaction of diaryliodonium salts with radiation and formation of super acidic species HMF$_n$

Depending on the anion MF_n^-, superacids, such as $HSbF_6$ with Hammett acidities down to H_0 values around −30, can emerge upon irradiation, capable of monomer protonation and thus starting cationic polymerization.

Apart from the basic reactions outlined in Fig. 2.6, a series of other initiation reactions [118], e.g., release of protons via radiation-induced decomposition and rearrangement reactions of the initiators (Fig. 2.7) [117], have been discussed.
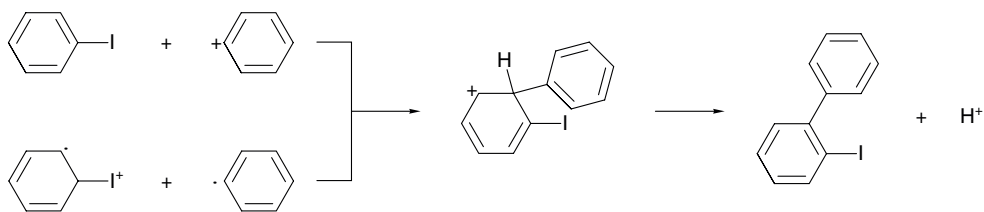
Figure 2.7: Generation of Brønsted acids via radiation-induced decomposition and rearrangement reactions of iodonium salts

Reactions where the iodonium salts serve as efficient oxidants (Fig. 2.1 and Fig. 2.8), e.g., oxidation of radicals emerging after high-energy electron irradiation and stemming from the monomer (Eq,.2.11) [91, 93, 94], direct reaction of aryliodine cation radicals with the monomer followed by oxidation of the coupling product (Eq. 2.12) [118–199], or generation of reactive carbocations by reaction of iodonium salts with easily oxidizable free radical photoinitiators (Eq. 2.13) [115, 120–122] yield highly reactive cationic species and have been observed particularly in the case of electron beam irradiation. In this context, reduction of the iodonium salt initiator by low-energy electrons followed by formation of protonic acids (Eq. 2.14) was also proposed as another probable mechanism [91, 92, 94].

As mentioned above, some of these mechanisms can also proceed simultaneously and superpose. Thus, electron beam curing of an epoxy acrylate in the presence of diphenyliodonium hexafluorophosphate was investigated and it was shown that acrylate as well as epoxide groups were involved in the polymerization [123]. The results lead to the assumption that acrylate polymerization proceeds via a radical process induced by slow electrons and phenyl radicals, whereas epoxide polymerization was induced by hydrogen fluoride, stemming from the decomposition of preliminarily generated HPF_6.

(2.11)

(2.12)

(2.13)

(2.14)
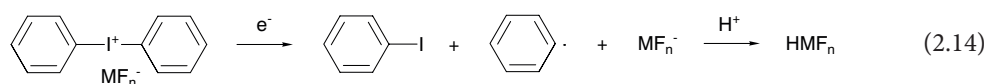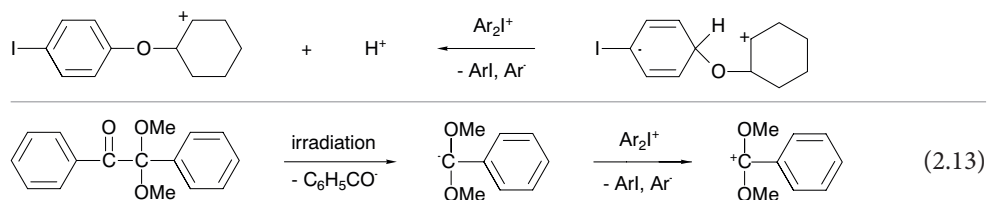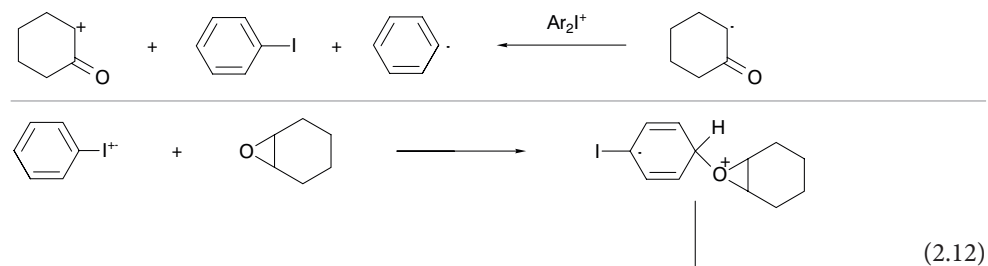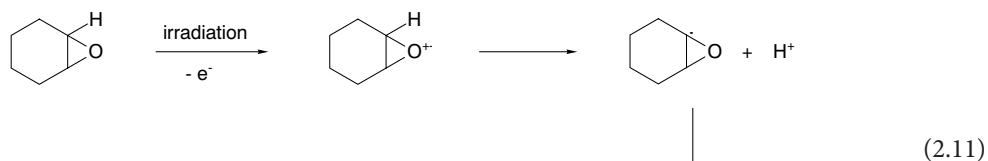
Figure 2.8: Formation of cationic species via reduction of iodonium salts

A detailed study on the electron beam-induced cationic polymerization of epoxide monomers using iodonium salt initiators showed that polymerization depends mainly on the type of epoxide monomer, the onium salt concentration, the counterion, and the radiation dose [124]. A mechanism according to Eqs. 2.11 and 2.14 in Fig. 2.8 was proposed and it was concluded that the polymerization proceeds mainly via ion pairs, rather than free ionic species. Cationic polymerization of vinylether monomers was also investigated (Fig. 2.9) and the reaction proceeds via α-alkoxy radicals [91, 92, 124], analogous to the mechanisms outlined in Eqs. 2.11 and 2.14 related to cyclohexene oxide as monomer.
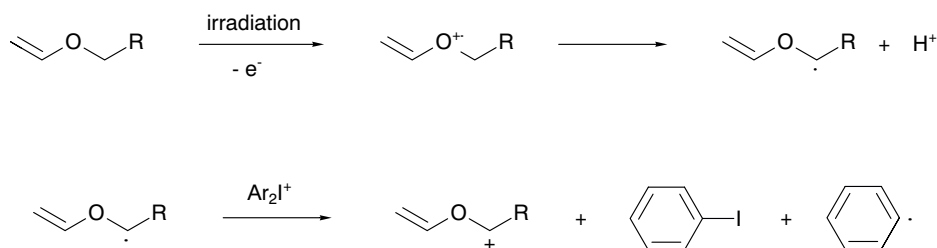
Figure 2.9: Generation of cationic species upon electron beam irradiation of vinylether monomers in the presence of diaryliodonium salts

Recent research on the electron beam curing of iodonium salt-containing compositions focused on the use of epoxide monomers. The technology was compared to thermal and UV curing [125, 126] and the influence of various parameters such as resin type [55, 64, 127], initiator type and concentration [55, 64, 127–129], the presence of coinitiators [130], impurities [64], diluents [129] or hydroxyl containing compounds [62], dose and dose rate [55, 64, 127, 128], temperature [64], thermal treatment after irradiation [55, 128], as well as the influence of fiber surfaces [131] in the case of composites were studied. It should be pointed out that iodonium salts are among the most efficient initiators for electron beam processing. The compounds are meanwhile, like in UV curing, well-established and some of the most promising material features could be obtained employing these initiators [132–134].

2.1.1.2   Sulfonium Salt Initiators

Aryl-substituted sulfonium salts, both symmetrically and unsymmetrically substituted, can be prepared using readily available diarylsulfides Ar_2S, thiophenols ArSH, or diarylsulfoxides Ar_2SO as starting materials. Among a variety of synthetic procedures [135–140] some strategies turned out to be superior in terms of applicability, versatility, scope, efficiency, yields, and costs (Fig. 2.10). These comprise, with respect to diarylsulfides and thiophenols as substrates, copper-catalyzed arylations using diaryliodonium salts (Eqs. 2.15 and 12.6) [141, 142]. Another approach is the self-condensation of diarylsulfides (Eq. 2.17), resulting in thiophenoxy-substituted triarylsulfonium salts [143, 144]. Considering diarylsulfoxides as substrates, reactions with aryl and alkyl Grignard reagents [145], favorably in the presence of trialkylsilyl triflates $RSiMe_2OTf$ [146] (Eq. 2.18) as well as reactions with aromatic hydrocarbons in the presence of aluminum halides [147] (Eq. 2.19), or phosphorus pentoxide-methanesulfonic acid
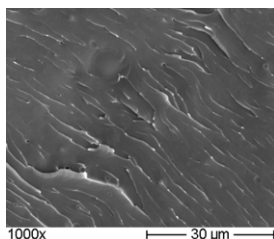
Figure 2.64: Fracture surface of the resin formulation DEN438
+ 5 wt.% A610 cured with 1 wt.% Ag(1,7-octadiene)$_{1.5}$]SbF$_6$

Incorporation of nano-silica particles in the resin results in an improvement in fracture toughness. Figure 2.64 shows the fracture surface of the resin DEN438 modified with 5 wt.% A610.

Agglomerates of silica particles are not observed, showing a very good dispersion of the nano-particles in the resin. On the fracture surface, it is possible to identify some voids in the matrix caused by the debonding and pulling-out of the particles during crack propagation. Besides debonding, the main toughening mechanism seen here relates to crack deviation and crack pinning. Unfortunately, due to the high crosslinking density, there is no evidence for plastic void formation and growth around the particles, which would lead to a significant increase in toughness. This justifies the minor improvement in fracture toughness observed here.

2.3.6   Hyperbranched Polymers

Hyperbranched polymers are highly branched macromolecules based on AB$_x$ ($x \geq 2$) monomers, which have lately obtained much attention. They are not perfectly branched, as dendrimers are, but they are more easily produced due to simpler synthetic routes.

A study of Glauser et al. [71] showed that, in order to obtain a fine blending of the electron beam curable resin and the hyperbranched additive, it was necessary to add a solvent in order to lower the viscosity. Both dichloromethane and ether were investigated. The phase separation worked well when using dichloromethane, but complete removal of the solvent required high vacuum that strongly increased the risk for gelling. Dichloromethane also turned out to be disadvantageous for electron beam curing of the resin, because the cure was highly affected by small amounts of residual solvent. Ether was preferred because of its lower boiling point and its lesser affinity for the hyperbranched additive. This also increased the driving force for phase separation.

Unfortunately, reaction-induced phase separation, as performed by Boogh et al. [250], was not possible by electron beam curing because the cure process is too fast. The phase separation was governed by several factors. First, the viscosity had to be lowered by adding a solvent, so diffusion could occur on a reasonable time scale. But on the other hand, the solvent had to be evaporated in order to obtain phase separation. A compromise was found by evaporating the solvent until the resin had a syrup-like consistence. The phase separation first provided

very small particles, which were too small to provide an increase in toughness. Time was the second factor. Sufficient time was not only necessary for phase separation to occur, but also for the particles to mature, or grow to a size in the micrometer range.

Toughness increased slightly for these hyperbranched particles modified electron beam curable resins, as cracks simply propagated through the hyperbranched particles or as secondary cracking was initiated from the hyperbranched polymers.

2.4   Interfacial Properties Between Fibers and Matrix

All reinforcing fibers that are traditionally used for advanced composites can be employed for electron beam cured composites. Carbon fibers have shown to be particularly suited for electron beam processing, since they exhibit excellent radiation stability, tolerating about 1000 times the typical curing dose, and as a good electrical conductors they ensure that no charge is built up in thicker composite structures. Aramid fibers are also unaffected by electron beam treatment up to the typical curing doses, a consequence of its highly aromatic structure. The effect of electron beam treatment on the mechanical properties, density, and chemical durability of glass fibers was shown to be negligible up to a dose of 3 MGy. The only visible effect was discoloration [66]. The use of organic fibers, such as polyethylene or nylon fibers, for reinforcing electron beam cured composites must be considered with caution, since the properties of the fibers are affected by the electron beam irradiation.

Designers must be aware that special fibers might affect the electron beam curing process, if at all, and consider these changes in the design. It is known that the fiber properties, such as thermal conductivity and heat capacity, may directly influence the curing of the matrix and consequently the final properties of the composite.

As already discussed in Section 1.3.4, the type and amount of reinforcing fibers also influences the maximal temperature (T_{max}) reached during curing, due to the capacity of the fiber to transfer heat to cooler zones. When comparing the same loading of glass fibers with carbon fibers, a higher T_{max} was reached. The relatively low conductivity of the glass fibers leads to less cooling of the curing zone.

Historically, much work was conducted to improve the interfacial strength between carbon fibers and thermally cured epoxy systems. Proper surface treatment and sizing materials were developed to optimize this critical aspect of composite performance. The solutions relied initially on trial and error and more recently have been based on a fundamental understanding of the chemical and physical processes that occur in the interphase region. It is well known that fibers have the potential to perturb the polymer network structure in the vicinity of the surface.

Several studies have shown that the interfacial shear strength, as measured by debonding fibers from the matrix, is typically 30–60% lower than that of thermally cured analogs [42, 59]. These results associated the interfacial properties as a consequence of the new mechanisms of curing related to electron beam irradiation. These range from chemical incompatibility

to physical phenomena linked only to irradiation. In the following section, chemical aspects (fiber surface treatment and use of sizings) as well as processing conditions of electron beam curable composites are discussed in regard to the resulting interfacial properties.

2.4.1   Fiber Surface Treatment and Use of Sizings

Concerning the chemical aspects, it is well known that the functional groups on the surface of the fibers play an important role in improving the surface free energy or the work of adhesion between the fiber and the matrix, which affect the mechanical properties of the composites [131]. In thermally cured epoxy-amine resins the reaction of the amine with the carbon fiber surface is as little as 3% of chemical bonding, but this can account for a 25% increase of the interfacial shear strength [252, 253].

The French company Aerospatiale was the first to realize the need for new fiber sizings to improve the adhesion of EB-curable resins to carbon fibers during the development of EB-curable acrylate filament wound rocket motors. They developed specialized coupling agents that improved the fiber-matrix interface by creating covalent bonds between the fiber and the resin. The hydroxyl groups on the carbon fibers reacted with an isocyanate group on the sizing, and the hydrogen bonds on the sizing's acrylate group are free to crosslink with the resin during electron beam curing.

(6-Isocyanato n-hexyl) carbamoyloxyethyl methacrylate was used as a sizing agent [254] in an acrylic matrix reinforced with carbon fibers. The level of interlaminar shear strength (ILSS) was higher when using fibers sized with the acrylic-isocyanate formulation, compared to unsized fibers or epoxy sized fibers.

Zhang et al. [131] evaluated the sizing of carbon fiber in reinforced epoxy resins cured by electron beam irradiation. Unsized carbon fibers were oxidized in acid, alkaline, and neutral electrolytes. From ILSS test results it was concluded that H_2SO_4 and $NaHCO_3$ as electrolytes increased the adhesion; whereas NaOH reduced ILSS of electron beam cured composites. It had been shown that chemical bonding, also in electron beam curing, takes great importance in the increase of adhesion between the carbon fibers and the matrix resin.

H_2SO_4 electrolyte seems to improve the adhesion much better than an alkaline one. The reason for this result is assumed as the following: it is the proton acid that really initiates the cationic polymerization of the electron beam curable resin. When H_2SO_4 was taken as the electrolyte, many oxygen-containing groups were added to the carbon fiber surface. In addition, the carbon fiber surface chemisorberd some acidic functional groups. These acidic functional groups and oxygen-containing groups benefit the electron beam curing through strengthening the action of proton acid and the reaction with matrix resin during electron beam process. With NaOH as the electrolyte, the active carbon atoms on the carbon fiber surface chemisorbed the OH- groups. It is known that the OH- can be neutralized with the proton.

Studies concerning glass fibers can also be found in the literature. In the work of Goodman et al [61], glass fibers from Owens Corning, have been sized with coatings designed for use with specific epoxy resin systems. These fibers show high interfacial properties with thermally cured epoxy resin. However, poor properties were obtained when these composites were cured

by electron beam irradiation. The authors associated these results with the fact that the rapid EB cure may not allow the unbound components of the fibers to diffuse into the bulk resin and react with coupling agents. An alternative explanation was that reactivity in the vicinity of the fiber surface might be decreased due to particular compounds present in the sizing, which may locally inhibit cationically curing reactions.

Surface treatments on carbon fibers and a sizing suitable for cationically cured epoxy resins have been developed during a CRADA project, developed by a number of companies and research institutes in North America. In chapter 5 this project is described in greater details. This approach was based on the modification of the chemistry at the fiber-matrix interface during radiation curing, and resulted in proprietary formulations. The major results showed that [59]:

- Sol-gel, dialdehyde and isocyanates sizings can improve adhesion;
- Plasma treatment can be very efficient to increase adhesion in carbon fiber reinforced epoxy composites;
- Epoxy-novolac sizing has a limited efficiency to increase adhesion;
- Epoxy sizing with high photoinitiator concentration can significantly increase adhesion.

Employing the above-mentioned methods, it was shown, in the frame of this project, that the interfacial shear strength of electron beam curable composites could be increased in the range of 30 to 50%.

2.4.2   Processing Conditions

The low adhesion of electron beam curable resins to reinforcement fibers has also been investigated and evaluated in terms of the irradiation conditions during processing. The effects of dose-time and temperature-time profiles during the curing were investigated. A large number of experiments showed that fiber-adhesion is relatively insensitive to the irradiation procedure [255]. However, within this same study, the thermal post-curing of the irradiated samples showed to increase appreciably the adhesion between fibers and matrix and consequently the properties of the composite. Therefore, the absence of high temperature treatment was identified as a negative aspect influencing the adhesion between the matrix and the fiber surface.

Resin cure shrinkage was also evoked as a responsible effect for the low interfacial adhesion in electron beam curable composites. Increased resin cure shrinkage, although a source of residual stresses and dimensional instabilities in laminates, is also identified as a viable method of achieving incremental improvements in composite transverse strength because interfacial debonding is delayed [256].

It is clear that differences exist in interfacial behavior of electron beam versus thermally cured systems. These differences may stem from altered cure mechanisms as well as the novel chemistry of these new resin systems. Although comparable properties between thermal and electron beam curable composites are found in the literature [59], further investigations into interfacial effects of electron beam curable systems are still required. These investigations are

currently advancing, mainly focusing on the elucidation of the new mechanisms for interface/interphase formation related to electron beam curing.

2.5   Residual Stresses

Large temperature gradients in the resin during cure can cause the build-up of non-uniform residual stresses that may influence resin properties under service conditions, because temperature is the main parameter to control the conversion rate. Also, nonuniform cure due to severe temperature gradients can lead to nonhomogeneous thermo-mechanical properties within the resin and deteriorate the quality of the material. This can cause severe warping of unbalanced structures.

The thermal curing process typically requires a complex heating and pressure cycle that ultimately must reach temperatures ranging from 150–250 °C and pressures as high as 700 kPa. As a result of the large difference between the curing temperature and the operating temperature for most structures, thermally cured composites contain large residual stresses.

Considering that one of the most appealing characteristics of electron beam processing is that it can be considered a "cold" process, the products cured by this technique should also show beneficial effects on the final properties, as they should be free of residual thermal stresses [6].

However, it is known that during polymerization reaction, which is an exothermic reaction, high temperatures may be reached. Therefore, it is of great importance to predict and minimize temperature gradients within the resin during electron beam irradiation. A minimization of the temperature gradient inside the sample will also lead to minimized gradients in the degree of cure, establishing a more homogeneous crosslinked structure.

During electron beam curing, the temperature gradient may be reduced by controlling processing parameters such as processing temperature (laboratory temperature), temperature and properties of tooling materials, forced convection heat transfer around the curing materials, time between passes, and others.

Concerning the irradiation doses, it was shown that a lower dose per pass leads to higher cure levels and lower residual stresses at a given dose level. In addition, cure-shrinkage induces residual stresses that can be appreciable in electron beam cured multidirectional laminates. In summary, there are much less residual stresses induced during electron beam curing as observed with thermally cured composite [257].

A homogeneous dispersion of the initiator for cationically cured materials is essential to assure cure homogeneity, therefore decreasing the temperature gradient of the materials and reducing internal stresses. At the same time, a higher initiator concentration caused a larger temperature gradient within the resin system because of larger heat release due to a higher cure rate.

Usually, for electron beam curable resins, the maximum temperature during cure, due to the exothermic polymerization reaction, is found in the core of the material. This is due to conduction and convection boundary effects, as the process is achieved in ambient temperature.

Therefore, the material's properties of the mold used will exert a high effect on temperature gradients. For instance, in a mold made from glass, the maximum temperature appears in the centre of the core; however, an aluminum mold plate caused the maximum temperature to appear close to the open interface subject to surroundings. This is explained by the high value of thermal conductivity of aluminum [69].

Therefore, a balance between irradiation dose, number of passes, amount of initiator, initiator dispersion, and mold properties should be met in order to minimize the effect of internal stresses in electron beam cured composite materials and structures.

2.6   Effect of Post-Curing

Post-curing consists of subsequent steps after samples have been irradiated by an electron beam. The thermal treatment of the samples may improve some final properties of the materials. However, post-curing of electron beam curable resins is not interesting from an economical point of view.

In the literature, there is no conformity concerning the efficiency of thermal post-curing of electron beam curable thermosetting polymers. In some cases, improvement of properties was observed; however other studies showed properties to be independent to thermal post-treatment. A literature review presenting these distinct results and main conclusions is presented in this section.

Zhang et al. [258] studied DGEBA epoxy resins cured in presence of diphenyliodonium hexafluorophosphate. The gel fraction of the irradiated samples increased after heat treatment, and the increased extent of gel fraction in the samples was inversely proportional to the radiation dose. This is a result of the existence of residual active centers and reactive functional groups in the resin systems after electron beam irradiation. Curing reactions were difficult to sustain because of the glassy and compact crosslinking structures in the resin systems. When the irradiated samples were heated at high temperature, the trapped active centers acquired enough mobility to induce a further curing reaction, involving residual epoxy groups. Only if the temperature of heat treatment was above the glass transition temperature of the irradiated samples, the heat treatment could play a role through the collision and reaction of residual active centers and reactive groups, which can be devitrified by the heating process.

Similar observations were made by Sui et al. [55]. Moreover, it was observed that the post curing of DGEBA resins caused not only increased gel fraction and glass transition temperature, but also mechanical properties, such as Young's modulus. Post-curing was also related to the fact that residual active centers and epoxy groups still exist after radiation and was found to be more significant for low initiator concentrations. This can be explained by higher concentration of unreacted groups and a significantly lower temperature rise during EB irradiation at lower initiator concentration, which limited the mobility of residual monomers. At higher initiator concentration (thus at higher resin temperature) a larger portion of the reactive species was consumed before being trapped in the vitrified system [69].

Therefore, increasing the polymerization reaction level during the irradiation step decreases the effect of post-curing on the final properties. As mentioned, one way to increase the speed of reaction is to increase the amount of initiator. There are two other methods to improve the polymerization by electron beam irradiation, one is to use more reactive initiators, and another is to increase the irradiation dose.

As shown by Janke et al. [63], the glass transition temperature (T_g) of resins incorporating very efficient initiators does not change, even after several thermal post-cures. On the other hand, the T_g's of resins having inefficient initiators do change after thermal post-cure. However, and more importantly, even after several thermal post-cures, the T_g's for these resin systems incorporating less efficient initiators never approach the T_g's of the same resin systems incorporating highly efficient initiators.

Defoort et al. [255] observed that a higher dose is required to reach a fully reacted state when electron beam processing is done with low dose increments. This is mostly due to the temperature profile during electron beam processing and to the vitrification of the material after the first passes under the beam.

For the materials that were undercured after electron beam curing, the thermal treatment leads to a completion of the polymerization and subsequently to a significant increase of the glass transition temperature. It is also noticeable that the materials that were partially cured by electron beam and by thermal treatment exhibit lower shear modulus than the materials that were fully cured under electron beam.

Some negative effects of thermal post-curing of irradiated samples are also reported in the literature [128, 255]. In highly cured samples, the thermal treatment seems to reduce the crosslinking density of the network. The magnitude of T_g's decrease after a thermal treatment seems to be more correlated to the initiator concentration in the electron beam cured materials than to any other change during reaction. A tentative explanation of this phenomenon is based on the relaxation of the interactions through ionic pairs. The progress of the cationic polymerization in the vitrifying network is believed to be early affected by the difficult segmental diffusion of the bulky counter-anion. Clusters of weak ion pairs could be formed in the glassy material that could then relax to tight but independent ion pairs if some mobility is authorized by a thermal treatment.

In respect to fiber/matrix adhesion, thermal post-cure treatment by electron beam curing increased the interfacial shear strength between the fiber and the matrix. The thermal post-cure even increased the fiber/matrix adhesion of materials that were cured with an electron beam up to a high level of curing. The increase of the interfacial shear strength after thermal treatment is not related to a change in the properties of the bulk matrix. The increase of adhesion might be due to two phenomena. The thermal treatment may induce some beneficial thermal stresses in the composite material that was not induced during electron beam curing because of the limited temperature increase during processing. This thermal stress is beneficial to fiber matrix adhesion measured at room temperature. Alternatively, thermal treatment at high temperature might induce chemical bonding between the carbon fibers and the matrix that was not present during the high-speed low-temperature electron beam curing. Even a few unreacted epoxy functions remaining in the matrix after electron beam processing could

significantly increase the adhesion to the carbon fibers if they react during the thermal post-treatment [255].

To conclude, owing to the pseudo-living character of electron beam curing, the active centers occluded in the glassy samples are ready to resume propagation upon any temperature rise that would provide the network with some mobility [259]. However, thermal post curing of electron beam cured neat resins is only required for low reactive systems. That means that highly crosslinked networks obtained directly by electron beam curing are not positively affected by thermal post-curing. On the other hand, due to a lack of suitable fibers adapted to electron beam curing, thermal post-curing may still improve some of the interphase properties of such composites.