

Radiation curing: coatings and composites

Anthony J. Berejka,
Daniel Montoney,
Marshall R. Cleland,
Loïc Loiseau

Abstract. The initial experiments conducted in the late 1960's at Radiation Dynamics, Inc. (now IBA Industrial, Inc.) showed that by removing the pigment from a radiation curable coating formulation, the same binder system could be used as a matrix system for electron beam (EB) cured fiber reinforced composites. Recently, the binder systems used for EB curable coatings have also been successfully used (without pigments) as the matrices for EB and X-ray cured fiber composites. Insights gained from the development of coatings were translated into desirable properties for matrix materials. For example, understanding the surface wetting characteristics of a coating facilitated the development of a matrix that would wet fibers; the development of coatings that would adhere to rigid substrates as metal while being bent, as for coil coatings, and which would exhibit impact resistance when cured on a metal also imparted impact resistance to cured composite materials. Thermal analyses conducted on the coating binder cured at low energies were consistent with analyses performed on thick cross-sections as used for matrices. The configuration of the final product then dictated the modality of curing, be it low-energy EB for coatings or higher energy EB or X-ray curing for composites. In industrial radiation chemistry, one deals with monomers and oligomers ($\sim 10^2$ and $\sim 10^3$ to 10^4 Daltons molecular weight, respectively). Thus, one can approach the development of coating binders or matrix systems as one would approach the synthesis of organic polymers. The desired final material is a fully cured and cross-linked polymer. In contrast, concepts involved in "formulating" are often derived from dealing with high molecular weight polymers ($\sim 10^5$ + Daltons) in which intense mechanical mixing is used to bring different ingredients together. When synthesizing a radiation curable coating or matrix system, greater attention is given to microphase compatibility as reflected in the microhomogeneity of the entire material.

Key words: radiation curing • fiber composites • coatings • electron beam • X-ray • matrices

A. J. Berejka[✉]
Ionicorp⁺,
4 Watch Way,
Huntington, New York 11743, USA,
Tel: +1 631 549 8517, Fax: +1 631 549 8517,
E-mail: berejka@msn.com

D. Montoney
Strathmore Products, Incorporated,
1970 West Fayette Str.,
Syracuse, New York 13204, USA

M. R. Cleland
IBA Industrial, Incorporated,
151 Heartland Boulevard,
Edgewood, New York 11717, USA

L. Loiseau
IBA Industrial,
Chemin du Cyclotron, 3,
1348 Louvain-la-Neuve, Belgium

Received: 10 June 2009
Accepted: 18 August 2009

Industrial electron beam processing

There are >1400 high current (typically >10 s of milliamps), EB accelerators used in manufacturing on a world-wide basis. Some accelerators used in research facilities, such as ~ 550 Van de Graaff generators and low current linear accelerators, linacs, are not included in this estimate. The pie chart of Fig. 1 below illustrates the major market end-use categories for industrial accelerators. Since accelerator energy governs beam penetration, different end-use applications have found different beam energies more suitable for their needs. Table 1 highlights the major segments of the EB industrial radiation processing business based on accelerator energy, with electron penetration being expressed on an equal-entrance, equal-exit basis (surface dose = dose on exit from the material) in unit density materials. Industrial accelerators are limited to a maximum energy of 10 MeV so as to preclude inducing any radioactivity in the target material [10].

Of these market segments, the fastest growing area over the past decade has been in the use for surface curing. New lower cost, low-energy self-shielded EB



Fig. 1. Industrial electron beam end-use markets.

Table 1. Electron beam energy by industrial market segment

Market segment	Typical energy	Electron penetration
Surface curing	80–300 keV	0.4 mm
Shrink film	300–800 keV	2 mm
Wire & cable	0.4–3 MeV	11 mm
Sterilization	4–10 MeV	38 mm
Composites (carbon fiber)	10 MeV	24 mm or less

units have made EB processing more accessible to the end-user market.

Electron beam curing of composites – historical background

The initial experiments that demonstrated the efficacy of EB curing for composite materials were conducted in the late 1960's by Dr Walter Brenner, a professor of chemistry at New York University and then a consultant to the accelerator manufacturer, Radiation Dynamics, Inc. (RDI, now IBA Industrial, Inc.). W. Brenner was working on developing high gloss, pigmented coatings that could be applied to bricks and, when EB cured, would give the bricks the appearance of higher priced glazed ceramics. Removing the pigment from his coatings, he prepared three ply, 3 mm thick wet lay-ups using different then available fiberglass cloth and mat with unsaturated polyesters as the matrix material. Using a 1.5 MeV RDI Dynamitron™, these wet lay-ups were cured at 40 to 50 kGy in air without catalysts being added. Dose profiles were run as well as comparative tests with thermally cured, peroxide initiated, fiber glass reinforced materials of the same matrix material. Results showed that EB curing was comparable in flexural strength and in the retention of flexural strength after immersion in hot water and hot acid solutions for up to a month. These EB and thermally cured systems were also comparable in flexural modulus at room temperature and at elevated temperatures, 80°C and 120°C. A paper covering this work won Brenner and his RDI collaborator, William Oliver, a “Best Paper Award” from the Society of the Plastics Industry's Reinforced Plastics Division in 1967 [5].

In the 1970's, Brenner collaborated with Frank Campbell at the US Naval Research Laboratory. They explored the use of graphite fibers and of polyimide

Table 2. Advantages of radiation curing (Brenner and Campbell – 1970's)

Room temperature cure
stress-free joints
no thermal distortion
Saves energy
eliminates need for autoclave
Avoids air pollution
solvent is cured as part of resin
no volatile by-products
Spot bonding capability
Ideal for weld bonding

precursors as well as the use of EB curing for adhesive systems. Using thermomechanical analysis (TMA) with a compressing probe, their EB cured (25 to 150 kGy) imide systems showed TMA transitions ~ 340°C to 360°C [7]. Toughness was enhanced by using low dose levels and by incorporating an elastomer into the matrix system. The advantages of EB curing of composites, as seen by Brenner and Campbell in the mid-1970's, are presented in Table 2 [6]. These still hold true today: EB curing is free of thermal stresses, it is energy saving and it is non-polluting – issues more relevant in today's manufacturing environment.

Coatings development to composite matrix materials

In 1998, Strathmore Products, Inc., a family owned coatings company in Syracuse, New York, began to investigate the use of radiation curing for metal coil coatings. EB curing tests of developmental, solvent free materials were conducted using the first low-energy laboratory unit made by Advanced Electron Beams [12]. The demands placed on the coil coating material for excellent adhesion to metal, for coating flexibility, for durability in environmental tests and for curing at low doses were shown to be beneficial in taking essentially the same formulation, but without pigments, and using it as a matrix for EB cured composites. A free radical curing metal coating based on an epoxy diacrylate was demonstrated to cure at low doses at speeds up to 305 m per min (the maximum speed attainable on the coating/curing line being used) [1].

In 2004, Strathmore Products collaborated with IBA Industrial, Inc. and an independent consulting firm, Ionicorp+, to work on matrix systems for composites [4]. This evolved into a feasibility of using X-rays derived from IBA's high current Dynamitron accelerator to cure fiber reinforced composites while they were maintained within molds. The objective was to demonstrate that X-rays, with their far greater penetration than electrons from industrial EB accelerators, could cure materials while in a mold. The binder systems developed for coil coating applications were used as matrix materials [3].

Surface wetting

In order to attain durable adhesion to metals (steel and aluminum), a goniometer was used to investigate the surface tension of variations of a free radical curing for-

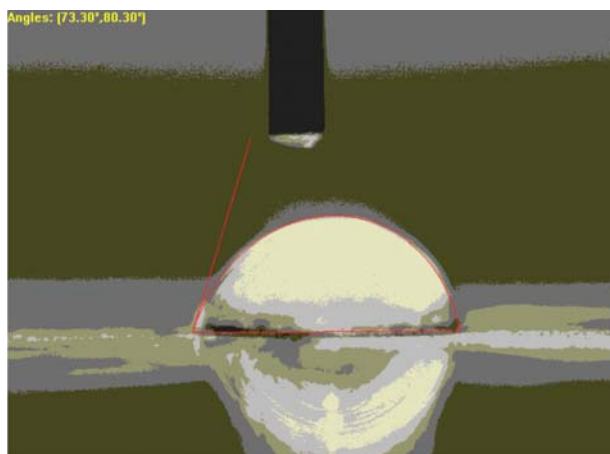


Fig. 2. Goniometer pictures of surface wetting on steel.

mulation based on an epoxy diacrylate. Figure 2 shows pictures for a control of a high surface tension drop of water and of an EB curable formulation tailored to wet the metal substrate. Figure 3 then correlates the contact angle measurements with surface tension [14].

When shifting focus to the development of EB curable matrix materials for reinforced composites a few years later, this understanding of surface wetting properties was found to be of benefit in an EB curable matrix system based on the formulation technology that was developed for coil coatings. It was found that a coating binder when used as a matrix binder could

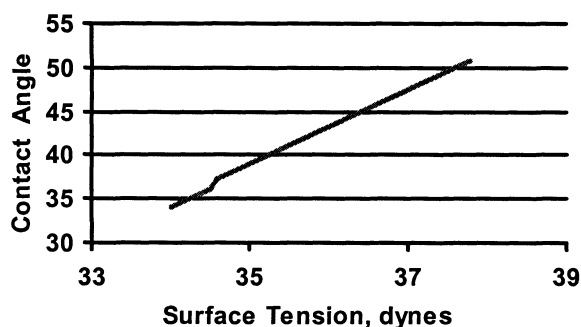


Fig. 3. Relationship between contact angle and surface tension.

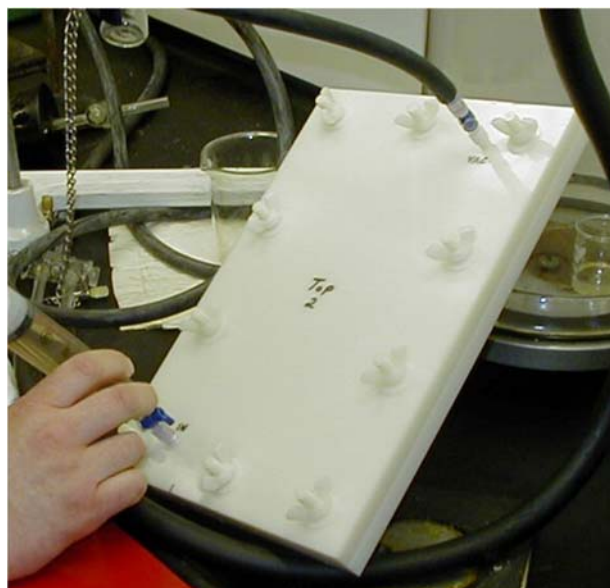
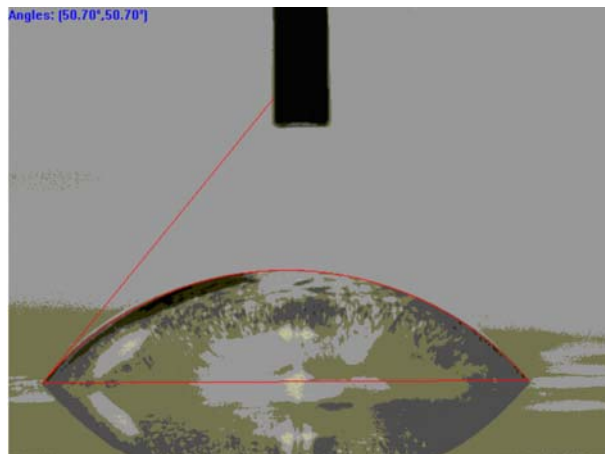


Fig. 4. VARTM with HDPE platens.



readily wet and saturate carbon fiber twill being used for composites development. The advantage of having a coating system that could be sprayable, requiring a viscosity of ~ 550 centipoises, not only facilitated wetting, but also enabled its use when drawing the liquid into a vacuum assisted resin transfer mold (VARTM). Figure 4 shows the liquid matrix material being drawn into a mold constructed of two high density polyethylene platens (HDPE was used to facilitate mold release), in which the carbon fiber had been previously placed between the platens [2]. When using a mold with a clear polycarbonate (PC) upper platen, this matrix material was observed to flow up and into the carbon fibers by capillary action even after the vacuum had been turned off, as shown in Fig. 5. The higher gloss on the carbon fiber twill indicates where the fibers had been wet.

From the understanding of surface wetting characteristics and how different ingredients in a formulation affect wetting, problems reported with the adhesion to carbon fibers, albeit they are sized for thermally cured matrix materials, can be minimized. The carbon fiber materials produced within these thick plastic molds were cured using X-rays derived from a high-current, 3.0 MeV electron beam. The X-rays penetrated the

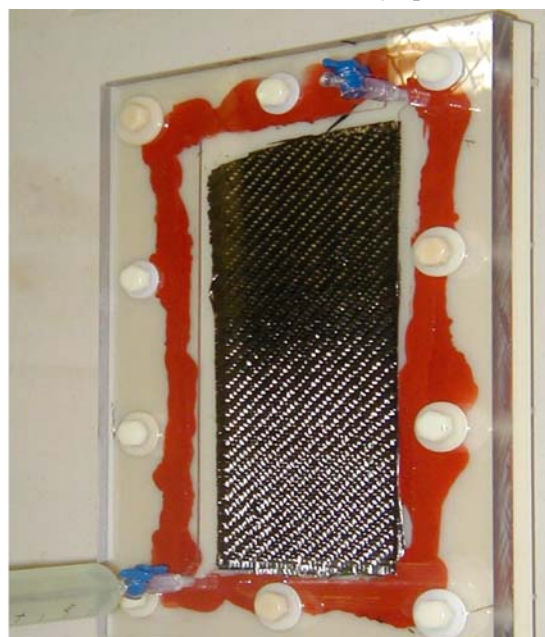


Fig. 5. Wetting carbon fibers.

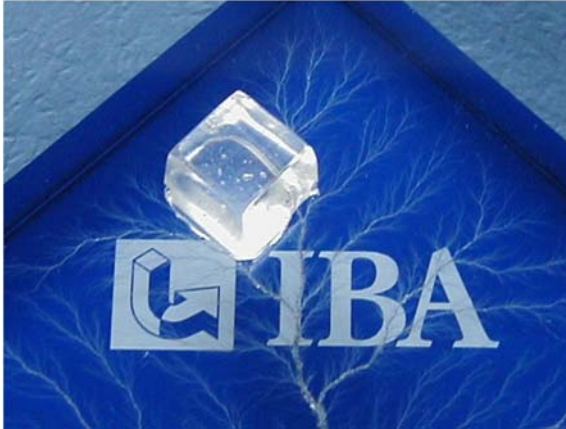


Fig. 6. EB/X-ray cured epoxy diacrylate sample.

mold walls and carbon fibers and then cured the matrix system.

Solubility

A material is deemed to be cross-linked if it is insoluble in solvents that would dissolve its precursors. A pragmatic technique used when conducting the coil coating trial at 305 m/min was to use a cloth moistened with methyl ethyl ketone (MEK) and rub it against the coating as it exited the low-energy EB unit to see if any could be dissolved or removed. If no coating dissolved onto the cloth, the coating was deemed cured. More formal ways of conducting MEK rub tests are defined by ASTM International in D-5402, "Standard practice for assessing the solvent resistance of organic coatings using solvent rubs". An automated version of this test that eliminates the differences in pressure applied by different persons performing this type of test is ASTM International D-7244, "Standard test method for relative cure of energy-cured inks and coatings".

To study the dose response of the base material, bis-phenol-A diacrylate, as used in the coil coating formulations which would also be used in the matrix systems, this material itself was poured into small plastic molds and X-ray cured with both 3 MeV electrons and X-rays derived from the 3.0 MeV beam. Figure 6 shows a 1.3 cm³ X-ray cured test sample. Two grams from such pieces were immersed in an aggressive solvent, methyl-

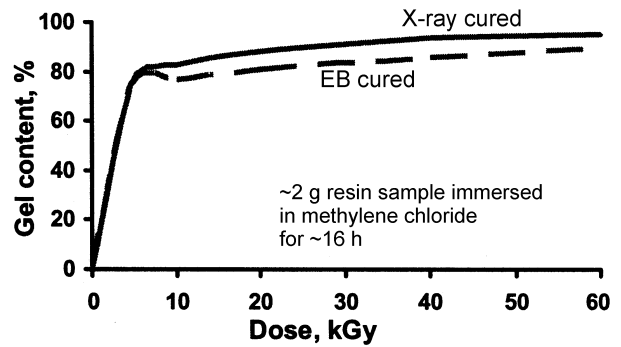
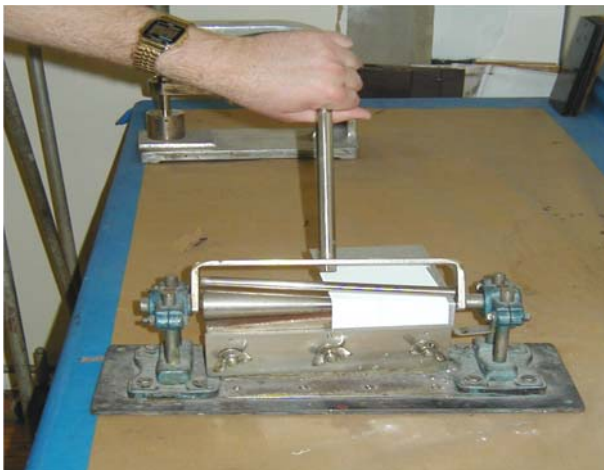


Fig. 7. Gel content vs. dose for EB and X-ray cured epoxy diacrylate.

ene chloride, in closed containers for 16 h and the per cent gel or insolubles was determined. The methylene chloride evaporated quickly so the weights of the immersed materials could also be quickly determined. From the results, as shown in Fig. 7, this difunctional material had a broad dose range for curing. > 75% gel formation was observed at as low as 5 kGy for both EB and X-ray exposure. At 60 kGy, > 90% was insoluble. At all data points, the X-ray cured material exhibited slightly higher gel formation than the EB cured materials. In the formulated systems that were used as binders in the coil coatings and which would be used as matrix systems, tri-functional acrylates were incorporated to assure more complete conversion and cross-linking of the oligomer.

Flexibility and impact resistance

In the coil coating industry, metal is coated at a factory, wound into a reel and then shipped to a user who will fabricate coated metal components from it. The precoated metal eliminates a coating operation in the fabricator's factory. Such components will be bent and formed into desired shapes by the fabricator. ASTM International has two tests which are used to determine the flexibility of coated metals, such that they can subsequently be used in fabrication operations: ASTM D-522, "Standard test methods for mandrel bend test of attached organic coatings" and ASTM D-4145, "Standard test method for coating flexibility of prepainted sheet". Figure 8 shows the mandrel bend test and the bent test piece. Figure 9 shows the EB cured coating on steel after having being subjected to the severe OT-bend



Fig. 8. Mandrel bend test.

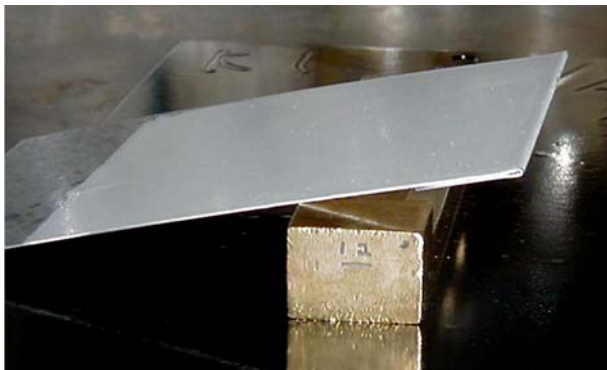


Fig. 9. OT bend of EB cured coating.

of D-4145. The ability of an EB cured epoxy diacrylate formulation to pass these flexibility tests reflects the inherent toughness of the binder system.

Another test used to determine the ability of coil coatings to deform is a falling tup impact test, ASTM 2794, “Standard test method for resistance of organic coatings to the effects of rapid deformation (Impact)”, as pictured in Figs. 10 and 11. A hemispherical steel tup is raised to different heights and allowed to fall with a prescribed load atop onto the substrate below. The force that will shatter the coating, beyond which it will no longer deform on impact, is recorded. The same test was



Fig. 10. Falling tup impact tester.



Fig. 11. Impact tup.

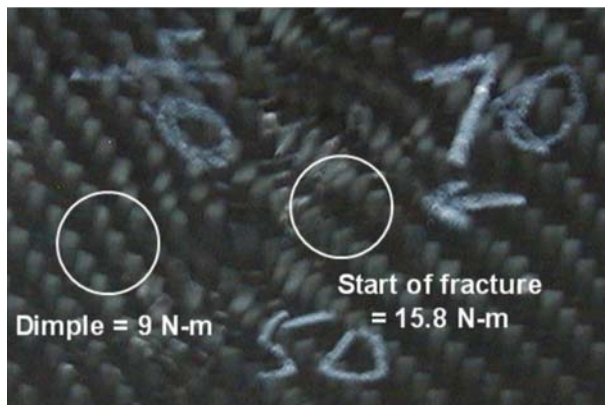


Fig. 12. 8 ply X-ray cured carbon fiber impact resistance from falling tup.

used to illustrate the impact resistance of carbon fiber reinforced composites. Eight ply carbon fiber specimens were prepared using the same binder system as used in the free radical cured coatings. To attain this thick a construction, 2.7 mm, materials were cured in molds made of flat aluminum platens (3.2 mm) with interior PE sheet (0.9 mm) using X-rays derived from a high current EB (3.0 MeV) unit to 20 kGy. Figure 12 shows that it took 15.8 N-m to initiate surface fracture on the composite. Figure 13 shows that a four ply carbon fiber composite has greater impact resistance than aluminum of the same gauge thickness (0.6 mm). 13.6 N-m force fractured the aluminum, but only created a surface dimple or dent in the composite. The aluminum (2.7 density) has a 1.7 times greater density than the carbon fiber composite (1.6 density).

The toughness and flexibility required for a coil coating binder were thus successfully translated into performance benefits for a fiber reinforced composite. To attain this toughness, these proprietary formulations contained a multi-functional oligomer that could itself be considered an elastomeric precursor. A more common plastics impact test, the izod swinging pendulum impact test, ASTM International D-256 “Standard test methods for determining the izod pendulum impact resistance of plastics”, was also used. Six ply carbon fiber samples X-ray cured to 24 kGy while in a mold

Table 3. Impact resistance of X-ray cured formulations

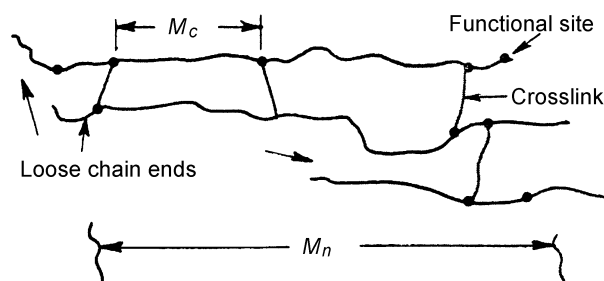
X-ray cured formulations	ASTM D-2794	ASTM D-256
	Initial tup indentation	Izod impact
Epoxy diacrylate without additive	6.8 N-m	901 J/m
Epoxy diacrylate with impact additive	15.8 N-m	1043 J/m

**Fig. 13.** 4 ply X-ray cured carbon fiber composite and aluminum panel of the same thickness impacted at 13.6 N-m.

were used. Comparisons in the two impact tests were made between formulations that contained the impact additive and ones that did not. Table 3 summarizes these results.

Developing molecular structures

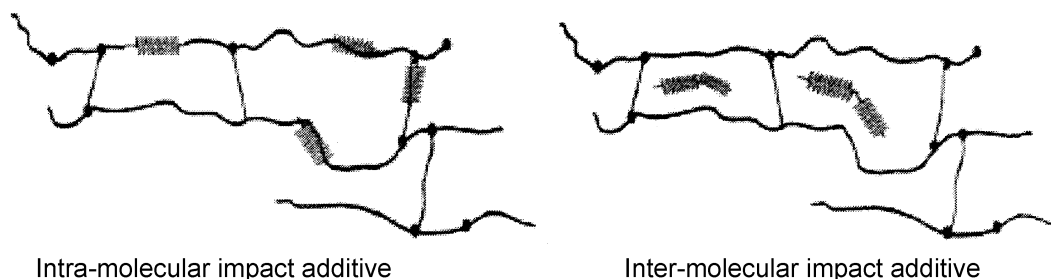
With radiation chemistry, as used in coating binders and for composite matrices, one starts with monomers and oligomers and can thus tailor the molecular architecture of the final cured, cross-linked polymer. The choice of oligomer molecular weight, M_n , impacts the monomer content needed to reduce viscosity to a given level. The selection of oligomer type, epoxy, urethane, or acrylate, governs some final performance properties, such as durability. Low viscosity, in the hundreds of centipoises, facilitates coating application, surface wetting and the ability of a material to wet and be drawn through and around fibers. Monomer and oligomer functionality, especially the use of multi- or trifunctional monomers, can assure network completion and more thorough cross-linking and enhanced cure rates. An adroit combination of constituents can then be polymerized into a fully cross-linked network. With EB and X-ray curing, there is no need for added initiators. The polymerization and cross-linking takes place when secondary electrons hit the functional groups on the monomers and oligomers themselves. The dose or degree of exposure to EB or X-rays can govern the

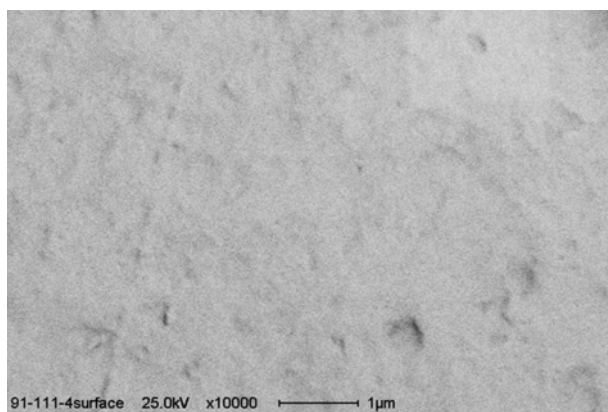
**Fig. 14.** Cross-linking and molecular weight between crosslinks, M_c .

tightness or cross-linked density of the final material. Figure 14 illustrates cross-linking and the molecular weight between crosslinks, M_c .

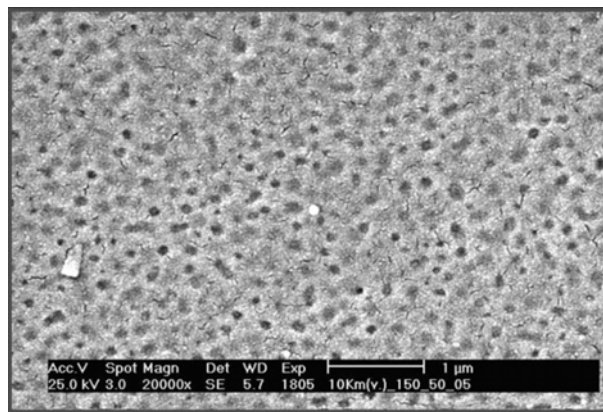
The coating binders and matrix systems developed were based on the bis-phenol-A diacrylate at ~ 60%. Extended salt spray testing of coatings showed this epoxy backbone to have excellent environmental resistance. It also contributes hardness to the cross-linked network. The impact additive chosen has both elastic properties when cured and is multi-functional. As a result, the impact additive will copolymerize into the cross-linked polymer network and be an intramolecular constituent, much as complementary monomers are added to other polymers to enhance impact resistance. For example, butadiene is incorporated into styrene polymerization to produce impact polystyrene; ethylene is incorporated into propylene polymerization to produce impact polypropylene. Conventional formulating of epoxies for composite matrices often uses thermoplastic additives that do not incorporate into the cross-linked network. Figure 15 illustrates the differences between intra- and inter-molecular impact additives. Figure 16 presents scanning electron micrographs (SEM's) of the coating binder/matrix system that was developed and for a system using a phase incompatible thermoplastic impact additive for an EB curable composite matrix system [2, 3, 17].

Such microphase separation has also been found on the micron scale for amine cured epoxies, as shown in Fig. 17 [18]. This is not surprising given the disparity in solubility parameters between amines and epoxies. Atomic force microscopy (AFM) has also shown phase differences on a nanoscale for photoinitiated epoxy-acrylates that were cured with ultraviolet radiation (UV), Fig. 18 [16]. In UV curing, microgels form within

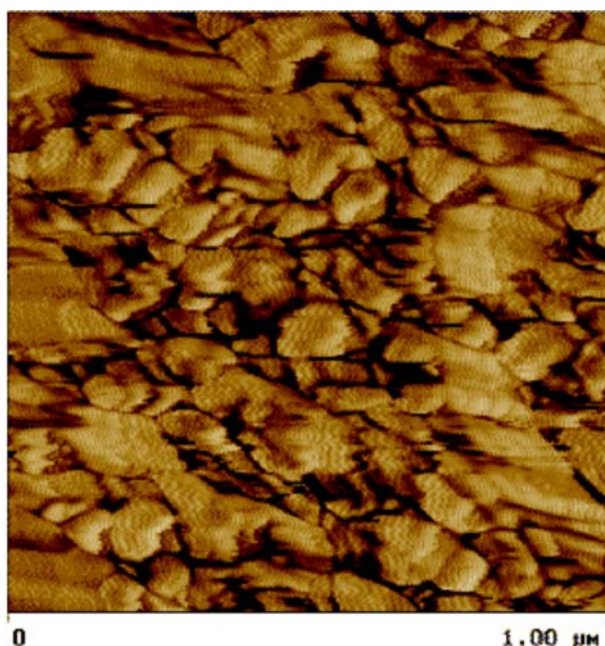
**Fig. 15.** Schematic of impact additives in matrix systems.



Intra-molecular impact additive

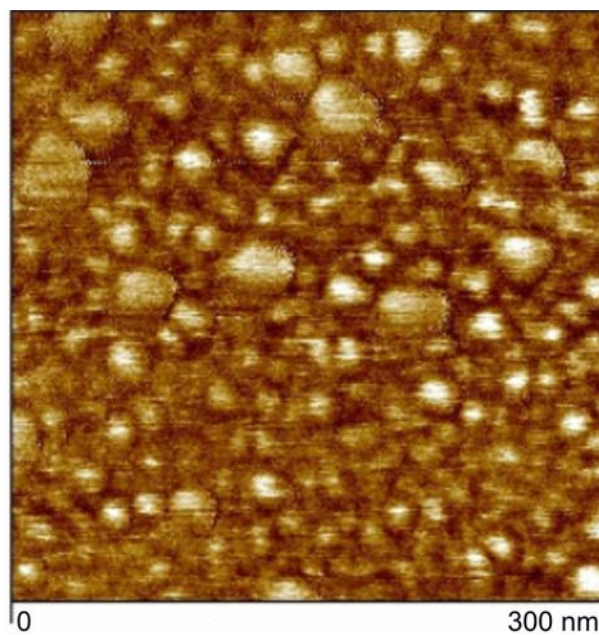


Inter-molecular impact additive [17]

Fig. 16. SEM's to same scale for matrix materials with impact additives.**Fig. 17.** SEM microphase separation in amine cured epoxy system.

a softer polymer matrix [15]. Whether or not this microstructure holds for systems cured with a continuous exposure to electrons or photons from X-rays generated from an electron beam remains to be determined. The secondary electron spurs or tracks do not depend upon affecting an initiator which can be a point of nucleation for gel formation.

In the development of the coating binder/composite matrix material, great attention was given to the compatibility of all of the constituents used in building the cross-linked polymer network. In designing this polymer, attention was given to the compatibility of the base oligomer, the epoxy diacrylate, and the impact additive. Besides the use of a tri-functional acrylate to enhance cross-linking and cure rate, monomers were incorporated to enhance adhesion (as to metal for the coil coating application) and to render all of the constituents more microcompatible. A testament to the phase compatibility of the binder/matrix free radical epoxy diacrylate material is that after over 40 months of standing, there is no indication of any phase separation in the liquid and that it still cures to the same properties as originally determined, yielding clear cross-linked materials.

**Fig. 18.** AFM nanophase gel formation in UV cured system.

Thermal analysis

ASTM International D-4762, "Standard guide for testing polymer matrix composite materials", suggests the use of differential scanning calorimetry, as in ASTM D-3418, "Standard test method for transition temperatures and enthalpies of fusion and crystallization of polymers by differential scanning calorimetry". An advantage to DSC is that it requires only very small samples, 20 mg, so that even thin gauged test specimens prepared using low-energy EB laboratory units can be evaluated. This was useful in indicating that an alternative to the epoxy diacrylate, an acrylated epoxy-phenolic, could be used to notably increase the transition temperature of a cured matrix system, as shown in Table 4. A disadvantage to using DSC is that this methodology was developed for other purposes, such as showing reaction kinetics or the transitions of thermoplastics. However, with cross-linked materials, transitions are very subtle, often only being able to be determined through computer analysis of output curves of heat flow vs. temperature. For example, the DSC for an EB or X-ray cross-linked matrix material

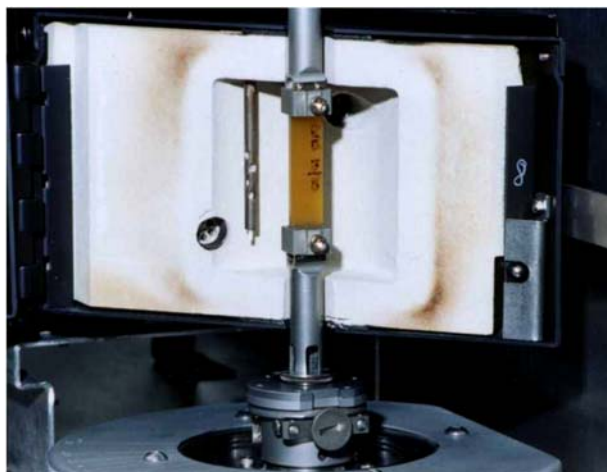
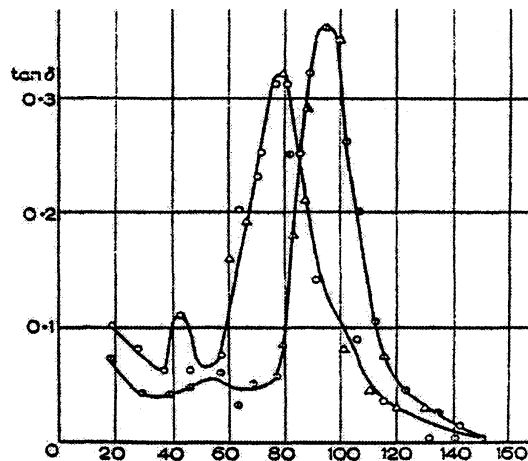
Table 4. T_g of X-ray cured base resins

Resin X-ray cured at 20 kGy	DSC T _g	TMA T _g
Bis-phenol-A diacrylate (M _n = 452)	54°C	66°C
Ethoxylated bis-phenol-A diacrylate (M _n = 572)	–	67°C
Diluted acrylated epoxy-phenolic	92°C	69°C

showed heat flow at computer analyzed transitions of $<< 0.1$ W/g, whereas the heat flow at the melt transition for a same weight of sample of high density polyethylene was ~ 2 W/g, more than an order of magnitude greater. When using thermal expansion in thermal mechanical analysis (TMA), per ASTM International E-1545, “Standard test method for assignment of the glass transition temperature by thermomechanical analysis”, the task of determining transitions in these cross-linked materials is even more arduous Table 4 shows that DSC was more discerning than TMA in assessing the glass transition temperature, T_g , for some oligomers.

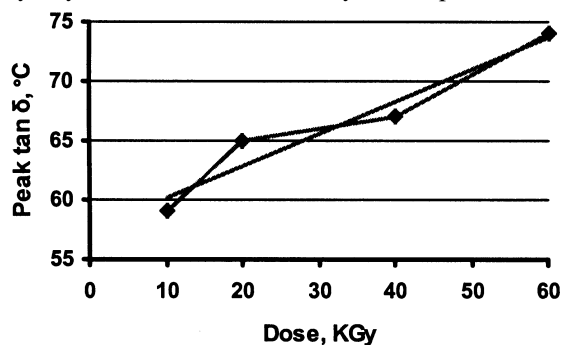
Much of the literature for composite matrices reports transitions using dynamic mechanical analysis (DMA), as per ASTM International E-1640, “Standard test method for assignment of the glass transition temperature by dynamic mechanical analysis”. DMA, as do DSC and TMA, involves increasing the test temperature at a prescribed rate. An oscillating strain is placed on a test specimen and the modulus response is recorded. When a material significantly begins to absorb input energy, it is damping the input vibrations and the output modulus is out of phase with the input force. This damping phenomenon is called the loss tangent or $\tan \delta$. The peak of the $\tan \delta$ with respect to temperature is considered to be a glass transition temperature, T_g . Figure 19 shows the interior of a DMA tester with its oven open. DMA was used by one of the pioneers of radiation chemistry, Arthur Charlesby, to show the influence of styrene concentration in two blends in an unsaturated polyester, with both materials being irradiated to approximately the same dose [9]. The blend with a higher styrene concentration (40% vs. 20%) showed both a slightly higher peak $\tan \delta$ and a shift closer to the peak $\tan \delta$ for polystyrene itself, Fig. 20.

DMA can be used with thin films, as prepared using low-energy electron beams, or with thicker specimens cured using higher energy EB or X-rays. The composi-

**Fig. 19.** DMA test equipment.**Fig. 20.** Irradiated styrene-polyester.

tion that was used both as a binder in coatings and as a matrix for fiber reinforced composites was X-ray cured in the aluminum plate/PE molds at different doses. While solubility tests showed little change with respect to dose (Fig. 7), there was a noticeable increase in temperature at which the peak $\tan \delta$ or T_g was observed with increasing dose, as summarized in Fig. 21. Since all materials were cross-linked, this shift represents an increase in cross-linked density which is a decrease in the molecular weight between crosslinks, M_c .

The breadth of the half-height of the $\tan \delta$ is also used to indicate the heterogeneity of some cross-linked systems [15]. The greater the width of the half-height means the greater the heterogeneity of the cross-linked system. For heterogeneous systems, half-heights of 80°C and greater have been noted. When UV cured under comparable conditions, monomer rich (55%) compositions based on a urethane diacrylate and di- and tri-functional acrylate monomers exhibited DMA half-height widths of $\sim 109^\circ\text{C}$. Systems with less monomer (35%) exhibited narrower DMA half-height widths of $\sim 74^\circ\text{C}$. The broader $\tan \delta$ half-heights for the monomer rich formulation were indicative of a higher cross-linked density. In developing coating binders and composite matrix materials that are to withstand impact and to be EB or X-ray cured, the cross-linked density, M_c , is controlled by oligomer type and dose, as well as monomer concentration. Figure 22 is the DMA for the binder/matrix system used in the formulations described above. This is for the oligomer/monomer material only that was X-ray cured between aluminum platens and polyethylene to a dose of 60 kGy with a peak $\tan \delta$ T_g

**Fig. 21.** Effect of dose on T_g for the X-ray cured epoxy diacrylate formulation.

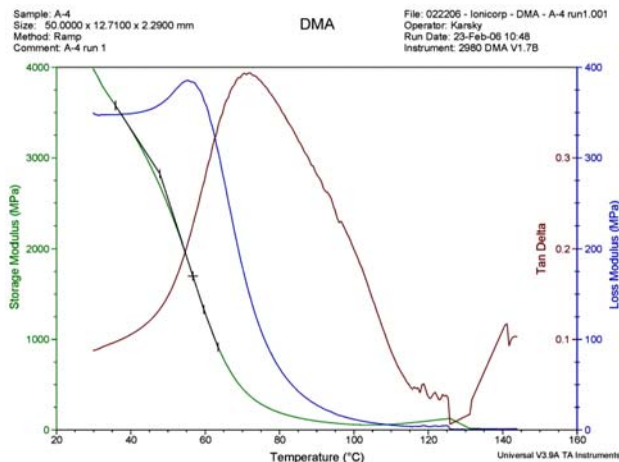


Fig. 22. DMA binder/matrix material X-ray cured to 60 kGy. of 73°C. The half-height width of the tan δ peak is 42°C, indicative of the controlled cross-linked density needed to attain the balance of desired end-use properties.

When used as the matrix in an eight ply carbon fiber twill reinforced composite that was also cured between aluminum/polyethylene platens but to only 20 kGy, the DMA showed a T_g of 58°C based on the peak of the tan δ curve, as shown in Fig. 23. Based on the data presented in Fig. 21, the lower T_g would be expected with lower dose. The half-height width of the tan δ curve is also narrower, 34°C, than that shown in Fig. 22, reflecting a lower cross-linked density, as would be anticipated from the use of a lower dose.

Several methods of thermal analysis can be used to characterize coating binders and matrix systems to be used with reinforced composites. These materials can be prepared using low-energy laboratory EB units or higher energy industrial equipment. Information on materials obtained using low cost EB laboratory equipment can be used to scaled up for use with higher current, low-energy EB units, as for coatings, or to higher current, mid-energy EB or X-ray systems for composites curing.

Pragmatic implications

While diverse analytical tests can help describe materials that will be used in radiation curable coatings or

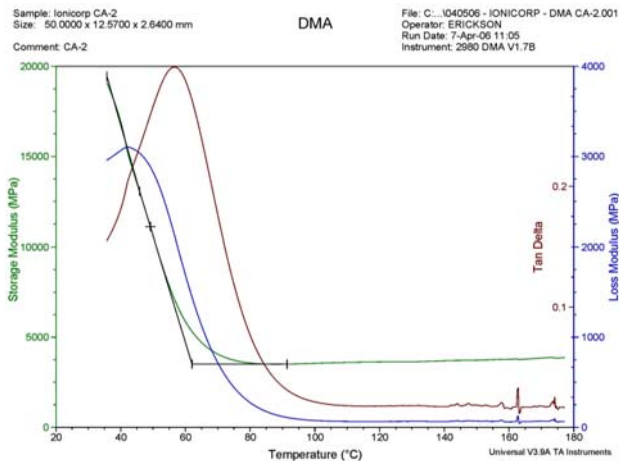


Fig. 23. Eight ply carbon fiber composite X-ray cured to 20 kGy.

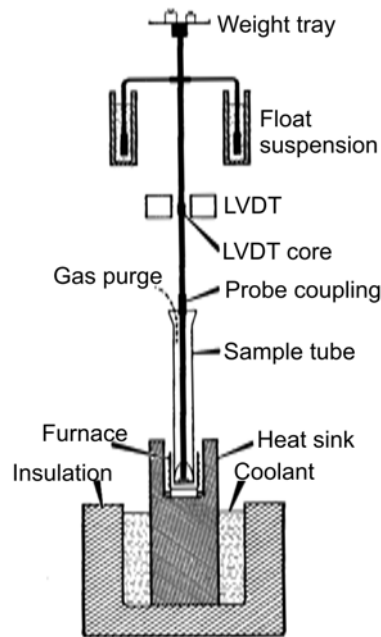


Fig. 24. TMA in compression mode.

as matrix systems for EB or X-ray cured composites, they should be complemented with other performance oriented tests. Some of the tests described above, such as the ability of a material to wet a substrate and, when cured, to exhibit impact resistance, have direct bearing on performance. When assessing thermal properties, care must be given to understanding the implications on performance, especially for cross-linked materials. With cross-linked materials, polymer chain mobility is constrained. Such materials are insoluble and cannot melt. When evaluating a thermoplastic adhesive formulation based on an ethylene-vinyl acetate copolymer (EVA), the crystallinity in the polymer was sufficient to restrict flow or creep below a melt transition, $T_m = 72^\circ\text{C}$. When such material was crosslinked, the flow above its melt was restricted. As the dose increased to provide a very tightly cross-linked network (200 kGy), there was no creep or flow when under a constant load in TMA testing well above the T_m (at 100°C), as shown in Figs. 24 and 25 [8].

A six ply carbon fiber composite made with the same matrix resin as used in the tests above (DMA $T_g = 58^\circ\text{C}$ when cured at 20 kGy) was X-ray cured between the aluminum/PE platens to 30 kGy and subjected to a heat deflection test as described in ASTM International D-648, “Standard test method for deflection temperature of plastics under flexural load in the

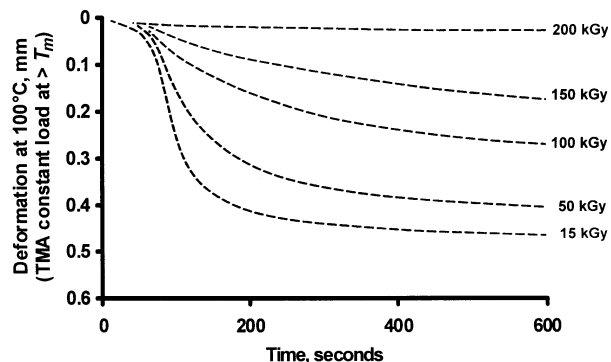


Fig. 25. Creep of cross-linked EVA, $T_m = 72^\circ\text{C}$, at 100°C .

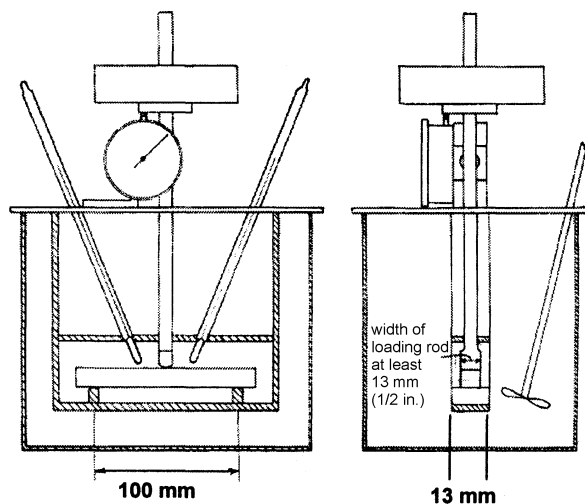


Fig. 26. ASTM D-648 heat deflection test apparatus.

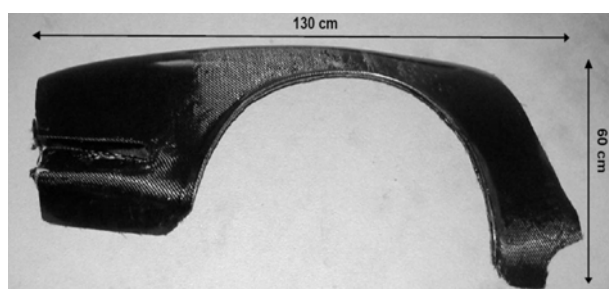


Fig. 27. Carbon fiber sports car fender X-ray cured in a mold.

edgewise position" and shown in Fig. 26. After the load of 1.82 MPa was placed on the carbon fiber test bar, the temperature of the bath was increased at 2°C/min. After reaching the maximum of the temperature of the heating fluid, 180°C, the test was terminated since there was no movement on the dial indicator. The cross-linked composite did not deflect at a test temperature well above its T_g .

Summary and conclusions

As Brenner had done in his pioneering work in the late 1960's, materials developed for coating binders can be translated into use as matrix systems for reinforced composites.

Some properties are common to needs in both the coatings area and for use in composite matrix materials such as surface wetting for adhesion and as impact resistance and toughness. In many instances, the same tests can be used for coatings and for fiber reinforced composites.

Development work can be conducted using low-energy EB equipment to produce materials for testing. The results can be used with higher energy EB or X-ray curing to produce reinforced composites [11]. Figure 27 shows a sports car fender that was X-ray cured in a vacuum bagged polyester mold using as its matrix the same free radical curing epoxy diacrylate formulation that had been used to produce coil coatings with good flexibility [13].

References

- Berejka AJ (2003) Electron beam curing of coil coatings. The RadTech Report, (September/October 2003), pp 47–53
- Berejka AJ (2007) Barriers to the commercial acceptance of radiation processing in the manufacture of fiber reinforced composites. In: Proc of SAMPE 2007, June 3–7, 2007, Baltimore, MD, USA
- Berejka AJ (2007) X-ray curing of fiber composites – feasibility study. Co-funded study for the New York State Energy Research and Development Authority. Contract 9097 (November 9, 2007), Albany, NY, USA
- Berejka AJ, Cleland MR, Galloway RA, Gregoire O (2005) X-ray curing of composite materials. Nucl Instrum Methods Phys Res B 241:847–849
- Brenner W, Oliver WF (1967) Commercial aspects of instantaneous radiation cure of reinforced plastics. SPE Journal 23;4:33ff
- Campbell FJ, Brenner W, Johnson LM, White ME (1979) Radiation curing (Task D), (part of a Naval Research Laboratory report), USA
- Campbell FJ, Brenner W, Johnson LM, White ME (1979) Radiation curable resins, (part of a larger report), USA, pp 79–92
- Canady V, Berejka AJ, Whitney W (1975) Report on creep and flow characterization of Raychem adhesives. Submittal to the Trans-Alaskan Pipeline System, Raychem Corporation, Menlo Park, California, USA
- Charlesby A (1960) Atomic radiation and polymers. Pergamon Press, New York, p 417
- Cleland MR, Berejka AJ, Sampa MH *et al.* (2010) Industrial electron beam processing. International Atomic Energy Agency Working Material – rev. 3. IAEA, Vienna, Austria (February 2010)
- Coqueret X, Defoort B, Dupillier JM, Larnac G (2003) Polymerization kinetics of acrylate monomers under UV/EB radiation: from lab scale monitoring to the modeling of industrial curing. In: Proc of the UV/EB – Meeting the Challenge, Radtech Europe, November 3–5, 2003, Berlin, Germany
- Felis K, Avnery T, Berejka AJ (2002) Innovative energy efficient low voltage electron beam emitters. Radiat Phys Chem 63:605–608
- Herer A, Galloway RA, Cleland MR *et al.* (2009) X-ray cured carbon-fiber composites for vehicle use. Radiat Phys Chem 78:531–534
- Larsen LS (2000) Electron beam cured coatings for metals. Student award presentation to the Council on Ionizing Radiation Measurements and Standards (November 1, 2000)
- Morales T, Rueda E, Christmas B (2008) The relative effects of AC- and DC-powered UV lamp systems on the properties of UV-polymerized films. In: Proc of the RadTech International North America UV& EB Curing Technology Conf, May 4–7, 2008, Chicago, IL, USA
- Ponsaud P, Defoort B, Coqueret X (2005) A microstructural investigation of UV and EB-cured bisphenol-A ethoxy diacrylate by ^1H NMR relaxation measurements. In: Proc of the SAMPE 2005, May 1–5, 2005, Long Beach, CA, USA
- Spadaro G, Dispenza C, Fuochi P, Lavallo M, Corda U, Alessi S (2005) Epoxy based matrices for structural composites prepared by ionizing radiation. In: Proc of the IAEA Consultants Meeting on Radiation Curing of Composites, August 8–11, 2005, Sao Paulo, Brazil
- VanLandingham MR, Eduljee RF, Cillespie Jr JW (1999) Relationships between stoichiometry, microstructure, and properties for amine-cured epoxies. J Appl Polym Sci 71:699–712