

Radiation Curing of Thermosetting-Thermoplastic Blends as Matrices for Structural Carbon Fibre Composites

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1. Introduction

Radiation processing indicates all the processes based on the use of ionizing radiation that cause chemical changes in the matter. Practical application of radiation processing have been evolved since the introduction of this technology nearly fifty years ago. The earliest developments are represented by the sterilization of disposable medical products, preservation of food and crosslinking of plastic materials, while the curing of monomeric coatings was developed somewhat later (Woods, 2000; Cleland et al. 2003). In the last years the use of these and other processes has grown more and more and they are widely practiced today to produce heat-shrinkable plastic films for packaging foods or insulation on electrical wires and jackets on multi-conductor cables in order to increase heat tolerance and to improve the resistance to abrasion and solvents. Other important applications include the reduction of the molecular weight by scissoring of polymers, the grafting of monomers into polymers in order to modify their surface properties and the curing of fibre-reinforced polymer composite materials, whose main applications are in automotive and aeronautic/aerospace industries (Clough, 2001; Singh et al. 1996; Lopata et al. 1999; Goodman & Palmese, 2002; Jhonson, 2006; Berejka, 2010). Due to its behaviour regarding the possibility to involve very small particles, like electrons or heavy ions, radiation processing is the ideal way to produce nano-structured systems. Different examples are reported in literature, such as nano-lithography devices (Woods, 2000) and nano-hydrogels especially in the biomedical area (Singh & Kuma, 2008; Chmielewski, 2010).

The radiation sources generally used in radiation processing applications can be divided into two main groups, that one regarding the use of natural or artificial isotopes and the other one in which particle accelerators are employed. In the first group artificial radioisotopes, like Cobalt-60 and Cesium-137, are included and the second group comprises electron accelerators, accelerators for the production of positive ions and x-ray generators (Woods & Pikaev, 1990; Spinks & Woods, 1990).

Currently the most widely used sources of ionizing radiations in the industrial processes are Cobalt-60 and electron accelerators.

Cobalt-60 produces γ photons of two discrete energy values, 1.332 and 1.173 MeV. Since γ photons tend to lose the greater part of their energy through a single interaction, during irradiation a fraction of them are completely absorbed, but the remaining photons are transmitted with their full initial energy.

Electron beams produced by accelerators are mono-energetic and they may be pulsed or continuous. Unlike γ photons, electrons lose their energy gradually, through a number of small energy transfers, so that they are slowed down by thin absorbers.

The use of γ or e-beam radiations depends upon different considerations, such as the nature and size of the objects to irradiate, the penetration to be realized and the productivity required. For a fixed material and for a fixed distance from the radiation source, the radiation is characterized by the penetration in the material and the rate by which the energy is absorbed by the material. The first parameter depends on the nature and energy of radiation and can be related to the absorbed dose, i.e. the energy absorbed by the unit of weight of the material, measured in Gray (Gy), or more commonly in kGy ($1 \text{ J/Kg} = 1 \text{ Gy}$). The second parameter is the dose rate that is the energy absorbed by the unit of weight of the material per unit of time, measured in Gy/s or more commonly in kGy/h.

In particular gamma rays are more penetrating than electron beams, but generally they are characterized by a lower dose rate. On the other hand γ sources offer the advantage of a very simple process, but they suffer from a low flexibility of the plant and from degradation during the time owing to the decrease of the activity of the source. Due to all these considerations γ radiation is normally used when high penetration is required without any productivity problems, while for low penetration and high productivity e-beam process is advisable.

The interaction of electromagnetic and particle radiations with matter occurs by means of different processes, even if it always produces fast charged particles, which generate a mixture of ionized and excited species. The overall effect of both types of ionizing radiation is qualitatively similar, since the same types of ionized and excited species are formed in both cases.

When a moving charged particle interacts with the matter, its energy loss gives rise to a trail of excited and ionized atoms and molecules in the same path of the particles. The same effect is caused by an electromagnetic radiation since the energy absorbed is transferred to electrons and positrons and then dissipated along the paths of these particles. In this way the overall result of the absorption of any type of ionizing radiation by matter is the formation of excited and ionized species, giving rise to similar chemical effects.

As already observed, radiation processing finds several applications in different fields. In particular it has been subjected to a very marked interest for the synthesis and modifications of polymeric materials. In fact, the interaction of ionizing radiation with apt monomers can give rise to radical or ionic (mainly cationic) polymerizations.

Radical polymerization of vinyl monomers is easily performed, while cationic process is more difficult due to the possibility that the cationic species can be neutralised by even very small amount of basic impurities (Chapiro, 1962; Crivello, 1999).

Also the modification of polymers by ionizing radiation has been subject of studies and several industrial applications. The interaction of ionizing radiation with polymeric materials causes the formation of free radicals that further evolve towards chain scission, with molecular degradation, chain branching and cross-linking with molecular weight increase (Woods & Pikaev, 1990). All these effects coexist, their extent depending on many factors, such as the molecular structure of the irradiated polymer, the presence of air or

other gases during irradiation and the operating conditions (temperature, dose rate, etc.). The molecular modifications induced by irradiation can strongly modify the mechanical, electrical and thermal properties of the polymers. Crosslinking for the production of electrical insulating materials or tubes for both high thermal and mechanical resistance are among the most important applications (Jansen & Brocardo Machado, 2005).

Among the ionising radiation induced polymerization processes, one the most stimulating and studied application is the radiation curing of epoxy resins in order to produce polymeric matrices for carbon fibre structural composites, in both aerospace and advanced automotive industries. Compared to thermal curing, the main advantages lie in the reduced curing time, the ambient curing temperature, the greater design flexibility and the higher materials shelf life (Singh et al., 1996; Lopata et al. 1999; Jhonson, 2006). In particular the possibility to carry out the process at mild temperature derives from the fact that it does not need thermal activation. This behaviour makes the process environmentally friendly, energy saving and induces positive effects on the properties of the synthesised materials. In fact the significant reduction of thermally induced mechanical stresses derived from the use of mild process temperature leads to an improvement of the mechanical properties of the cured materials.

The use of polymeric composite materials for transport applications has considerably increased in the last few decades for their favourable strength/weight ratio, with respect to low weight metallic materials traditionally employed in such structures. Other advantages coming from the use of polymeric composites are the improvement of the resistance to both corrosion and chemicals.

The standard thermal cure process induces high quality and performance in these materials and it has been extensively studied and optimized for each specific application (Ellis, 1994; Di Pasquale et al., 1997; Mimura et al., 2000). On the other hand radiation processing has become more and more promising for advanced structures for the several advantages offered. Lopata, Saunders and Singh widely discussed the benefits of electron beam curing for the manufacture of high performance composites and in particular Lopata suggested the importance of this process also for the repairing of such structures (Lopata et al., 1999; Singh et al., 1996; Lopata & Sidwell, 2003).

The first successful attempts of radiation curing were developed on acrylic derivative epoxies, which undergo to polymerization via radical mechanism, but the obtained materials did not meet the required thermal (high glass transition temperature, T_g) and mechanical properties (high elastic modulus and high fracture energy) for aerospace and advanced automotive applications (Woods & Pikaev, 1990).

Materials with enhanced thermal and mechanical behaviours, similar to that of the materials realized via thermal curing, were obtained when the cationic polymerization of epoxy resins was performed through the use of suitable onium salts, already successfully used in the UV induced epoxy curing (Lopata et al. 1999; Crivello, 1999; Crivello, 2002; Crivello, 2005; Bulut & Crivello, 2005). Due to the presence of strongly electronegative groups, onium salts are very acid and make possible the epoxy ring opening and the further cationic attack to the other epoxy monomers with the increase of the chain length.

Most of the commercially available initiators are diaryliodonium or triarylsulfonium salts of weak bases. Several mechanisms for polymerization of epoxies have been suggested (Decker & Moussa, 1991; Crivello, 1999, 2002 and 2005; Bulut & Crivello, 2005) and probably radiation induced polymerization of epoxies can proceed via different mechanisms whose relative contributions might vary from one formulation to another.

During radiation curing, several parameters can greatly influence the final properties of the cured materials. In particular parameters such as the composition of the epoxy resin system (including the catalyst species, the chemical structure of the epoxy, other modification agents etc.), and those related to the process such as irradiation dose, dose rate and curing temperature have a key role in determining the properties of these materials (Fengmei et al. 2002; Degrand et al., 2003 ; Nho et al., 2004; Raghavan, 2009).

A general problem for epoxy cured systems, either thermally or by irradiation, is that both high glass transition temperature and high elastic modulus are accompanied by a brittle behaviour and by a decrease of the toughness, with a poor resistance of the material to crack initiation and growth and with a low fracture energy value (Ellis, 1994; Broek, 1986; Riew & Kinloch, 1993).

The basic goal in toughening crosslinked epoxy resins is to improve their crack resistance and toughness without a significant decreasing of the other important inherent properties, such as the flexural modulus and the thermo-mechanical properties (T_g) of the original epoxy resins. A way to improve the toughness is the incorporation in the monomer of a second component. This has been successfully done for thermally cured systems, incorporating in the monomer a second component into the continuous matrix of epoxy resins through physical blending or chemical reactions (Kim et al., 1999; Mimura et al., 2000).

Unmodified epoxy resins are usually single-phase materials, while the addition of modifiers can turn the toughened epoxy resins into multiphase systems. When modifier domains are correctly dispersed in discrete forms throughout the epoxy matrix, the fracture energy or toughness can be greatly improved.

Among the toughening agents studied for thermally cured systems, the best improvement of toughness, without losing thermal and mechanical properties, has been obtained by engineering thermoplastics, like poly(ether sulfone), poly(ether imide), poly(aryl ether ketone), poly(phenylene oxide), polyamide etc. (Unnikrishnan & Thachil, 2006; Mimura et al., 2000; Blanco et al. 2003, Park & Jin, 2007). The thermoplastic toughened epoxies form homogeneous blends in the uncured state and can lead to phase separation on curing. The curing and phase separation processes were studied in many papers (Gan et al., 2003; Giannotti et al., 2003; Montserrat et al., 2003; Swier & Van Mele, 1999 and 2003; Tang et al., 2004; Xu et al., 2004; Li et al., 2004; Wang et al., 2004).

In particular the phase diagrams temperature/compositions for epoxy/toughening agent systems as function of the epoxy curing degree are of fundamental importance. In fact, the use of engineering thermoplastics as a method for toughening high performance, thermally curable epoxies, can cause different morphologies (Inoue, 1995; Mimura et al., 2000; Swier & Van Mele, 1999 and 2003). The "homogeneous" morphology results from a single phase that requires the dissolution of the thermoplastic into the epoxy with a curing process without phase separation. This method effectively reduces the crosslinking density of the epoxies, but it provides only modest improvement of the toughness in thermally cured systems. Another kind of morphology that can be obtained is the "second phase" morphology, resulting from two phases formed. In a first type the thermoplastic is the discontinuous phase (thermoplastic particles) and the epoxy the continuous phase. It generally occurs at thermoplastic loadings of about 15% or less, and it provides only modest improvement of toughness in thermally cured systems. A second type of the particulate consists of the epoxy which forms a discontinuous phase (epoxy particles) distributed in a thermoplastic continuous phase (phase inversion) and it generally occurs with a thermoplastic loadings of

more than 15-20%. Also in this case there is only modest improvement of toughness in thermally cured systems.

The preferred morphology which allows to realize high fracture toughness in epoxy based systems is the "co-continuous" morphology, which consists of an epoxy continuous phase and a thermoplastic continuous phase. These phases have nanometer or micrometer dimensions and require thermoplastic loading exceeding 15-20%, while the phase size and the toughness are controlled by the thermoplastic backbone, by its reactive end groups, its molecular weight and obviously by the epoxy nature (Mimura et al., 2000).

Up to 2000 the majority of studies and programs focused on the development of ionising radiation curable resin systems that could match the performance of thermally cured matrices for structural composites, while the understanding of how radiation curing takes place and its dependence on both system and process parameters was limited (Singh et al. 1996; Berejka & Eberl, 2002; Singh, 2001; Decker, 1999). On the contrary in the latest years many research efforts have been done toward other directions, in particular investigating the influencing factors of this process in order to provide a careful foundation of radiation curable epoxy based systems. In particular the influence of the catalyst (type and content), the effect of the nature of epoxy resins and of the processing parameters, such as dose and temperature, on the curing degree of the systems, the EB curing mechanism, the role of the onium salt and the influence of the monomer conversion on the glass transition temperature have been investigated (Fengmei et al. 2002; Gang et al., 2002; Degrand et al., 2003; Nho et al., 2004; Raghavan, 2009; Coqueret et al. 2010).

A very important work has been performed by the "Cooperative Research and Development Agreement" (CRADA) sponsored by the Department of Energy Office of Science, NASA Langley Research Center, U.S. Air Force Research Laboratory, U.S. Army Research Laboratory, and several industrial partners. Several epoxy resins systems in the presence or not of toughening agents and cured by electron beam irradiation have been realised. These resin systems showed mechanical, thermal, and physical properties that are significantly better than earlier electron beam curable resins, and are comparable to many thermally cured, high performance, toughened and untoughened epoxies (Janke et al., 2001). This review presents the results obtained by the authors in the study of e-beam curing of epoxy resin systems in order to produce polymeric matrices for carbon fibre composites (Alessi et al., 2005, 2007, a,b and 2010).

The influence of the processing parameters on both the curing reactions and the properties of the obtained materials is presented. In particular the possibility to really perform the process at mild temperature is critically discussed and the consequences of the low-temperature process on the final structures and properties of the cured materials are evidenced.

Also the influence of engineering thermoplastics in the toughening of the cured matrices is illustrated.

2. Radiation curing of epoxies as matrices for advanced composites

The occurrence of curing reactions has been checked by the monitoring of the temperature during samples irradiation. The temperature of the irradiated samples depends on different thermal events, whose rate depends on the processing parameters. The temperature increase is due to both the absorption of radiation energy and the heat developed by the exothermic curing reactions, while the temperature decrease is due to heat releasing from the irradiated samples to the environment. The balance of these phenomena determines the temperature of

the epoxy resin during irradiation. The heat production rate is low when both the concentration of iodonium salt and the dose rate are low, while the heat released to the environment is mainly related to the surface/volume ratio.

2.1 Untoughened epoxies

E-beam curing of blends of various epoxies/iodonium salts has been carried out.

One example is reported in Fig 1, where the temperature as function of the absorbed dose for Bis(4diglycidiloxy-phenil) methane (DGEBF)/iodonium salt samples (Alessi et al., 2005) is reported. The iodonium salt concentration is constant (0.1 phr) and the experiments have been performed at different dose rates (84, 420 and 840 kGy/h). At low dose rate (84 kGy/h) the temperature curve has a very slight increase and tends to a plateau value of about 50°C. On the contrary at high dose rates (420 and 840 kGy/h) the temperature increases up to 180°C and after decreases, but toward higher values than that reached during the correspondent irradiation at low dose rate.

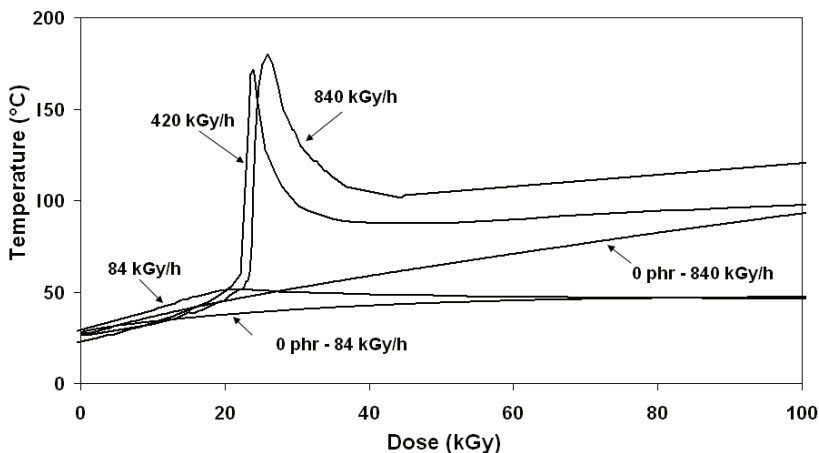


Fig. 1. Temperature as a function of irradiation dose at different dose rates.

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In the same figure the thermal profiles of the system without initiator, i.e. without polymerization reactions, are reported for two dose rates conditions, revealing that the major contribution to the plateau value is essentially due to the heat evolved by the radiation absorption. Since during curing very different temperature profiles can be obtained, the production of materials with marked different properties is realized. In fact, in conditions apt to produce marked temperature increase, the epoxy monomer undergoes to a simultaneous radiation and thermal curing, while when the irradiation is performed at low temperature the systems undergoes only to radiation curing.

Dynamic mechanical thermal analysis (DMTA) tests, carried out on samples cured in different processing conditions, and at different temperature profiles, evidence the different

structure and properties of the synthesised materials. In Fig. 2 elastic modulus, E' , and loss factor, $\tan\delta$, as function of the temperature for the materials cured in the conditions of Fig. 1 are reported. The sample cured at low temperature presents two broad relaxation peaks. This is an indication of a not uniform structure with networks of different cross linking degrees. This phenomenon can be related to vitrification phenomena during irradiation. In fact polymerization reactions cause the increase of the glass transition temperature of the irradiated system, which soon reaches the low processing temperature. In these conditions the structure becomes rigid and further curing reactions are controlled by the diffusion of the reactive species in the bulk of the polymerising system. Furthermore the storage modulus/temperature curve reported in the same figure presents an increase between the two relaxation temperatures. This can be attributed to post-irradiation thermal curing due to the heating during the DMTA test itself. We can conclude that the low temperature radiation curing is not complete and that the second relaxation peak can be considered the result of the combined effect of radiation and post-irradiation thermal curing. DMTA tests relative to the sample cured at high temperature presents only one relaxation peak, due to the high temperature reached during irradiation, which allows to overcome the vitrification phenomena, giving rise to the formation of a more "uniform" structure. In these conditions a simultaneous radiation and thermal curing is performed. It is interesting to note that the relaxation temperature is significantly lower than the second relaxation temperature of the material cured at low temperature. This can be explained with the more efficient thermal treatment (due to the test itself) when the structure is less rigid.

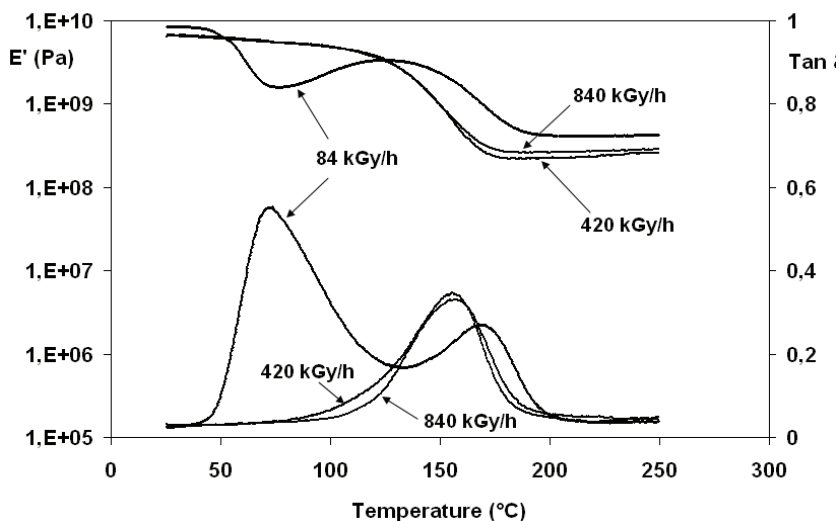


Fig. 2. Dynamical mechanical thermal curves at an irradiation dose of 150 kGy and at different dose rates.

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As the results indicate that not always radiation process allows to complete curing reactions, in order to check their completeness, samples radiation cured in various conditions have been subjected to post-irradiation thermal treatments.

In Fig. 3 DMTA curves of the sample cured at 150 kGy - 84 kGy/h and of the sample also subjected to a post-irradiation thermal treatment at 175°C for 2 hours are reported. In the last case a single relaxation peak is observed, thus indicating the formation of an uniform structure. Comparing the two curves reported in Fig.3, it is possible to note that the sample post cured after irradiation at low temperature presents a relaxation temperature very close to that of the second relaxation peak related to the only irradiation process, while not significant increase of Tg after thermal curing has been observed for sample irradiated at high temperature, whose correspondent comparison is not here reported. It is possible to conclude that the way to optimise the curing degree and the thermal properties of the radiation cured materials is a suitable combination of radiation curing at low temperature and a post-irradiation thermal treatment. It is important to consider that the post-irradiation thermal curing is performed on already polymerised solid materials, in an oven and out of the mould. In these conditions thermal treatment does not create environmental problems (no volatile emission) and the obtained materials do not present thermally induced mechanical stresses.

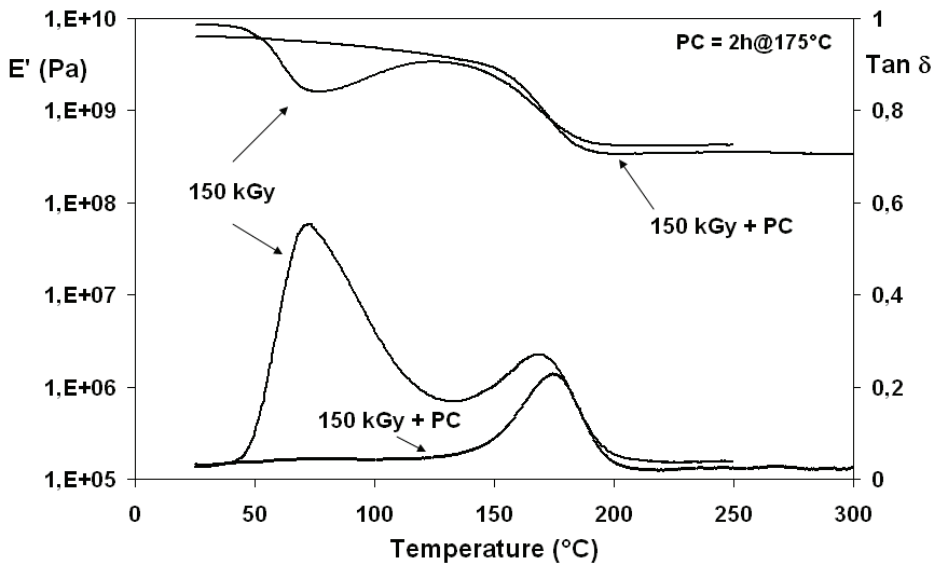


Fig. 3. Dynamical mechanical thermal curves for blends cured at 150 kGy and 84 kGy/h with and without post irradiation thermal curing. Iodonium salt concentration: 0.1phr (per hundred of resin).

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As already cited in the introduction, the polymer matrices for structural carbon fibre composites for advanced automotive and aerospace applications need to meet severe requirements in terms of thermal and mechanical properties. The optimal combination of a “dual curing” process, radiation curing at moderate temperature, followed by a post-irradiation thermal treatment at high temperature, allows to obtain materials with high thermal performances, indicated by glass transition temperatures higher than 170°C.

An alternative way to increase the T_g of the polymer matrix is to use epoxy resins with higher degrees of functionalities. Blends of difunctional DGEBF and trifunctional Tris(4-glycidiloxyphenyl) methane (Tactix) resins have been cured by ionizing radiation in the presence of an iodonium salt (Alessi et al., 2007, a).

In table 1, for difunctional/trifunctional blends at different composition, glass transition temperatures, elastic modulus in the rubbery state (at $T=T_g+30^\circ\text{C}$) and $\tan\delta$ maximum are reported. With respect to the 100% DGEBF system, the presence of a trifunctional monomer allows to perform T_g increase up to about 70°C. This effect is related to a strong increase of cross-linking degree, as confirmed by the values of the elastic moduli in the rubbery state and of the maximum of $\tan\delta$, also reported in the same table.

System	T_g (°C)	$E_{\text{rubbery state}}^*$ (MPa)	$\text{Tan}\delta_{\text{max}}$
100D	157	70	0.35
80D-20T	175	600	0.20
60D-40T	230	800	0.11
90D-10t.a.	139	50	0.45
54D-36T-10t.a.	212	800	0.13

Table 1. Relaxation temperatures (T_g), elastic modulus in the rubbery state (* at $T=T_g+30^\circ\text{C}$) and $\tan\delta$ maximum for epoxy based systems at different difunctional/trifunctional ratios, e-beam cured at 150 kGy and 840 kGy/h. D: difunctional epoxy resin (DGEBF); T: trifunctional epoxy resin (Tactix); t.a.: toughening agent (Polyethersulfone based).

“Alessi, S., Dispenza, C., Spadaro, G.. Thermal Properties of E-beam Cured Epoxy/Thermoplastic Matrices for Advanced Composite Materials. Macromolecular Symposia. 2007. 247. 238-243. Copyright Wiley_VCH Verlag GmbH & Co. KGaA. Reproduced with permission”

2.2 Toughened epoxies

The increase of crosslinking degree obtained by either the combination of radiation and thermal curing or by the mixing of epoxy monomers at different functionalities, causes improvement of thermal properties and significant increase of the elastic modulus. Unfortunately such molecular behaviour can give rise to very brittle materials. As discussed in the introduction the toughness can be increased by the use of apt toughening agents, like high modulus and high T_g thermoplastics.

This has been done in Alessi et al., 2007b, where blends of difunctional DGEBF, polyethersulphone (PES) and iodonium salts have been e-beam cured by ionizing radiation.

First of all it is shown that the presence of PES does not interfere with radiation curing process and that similar results with respect to systems without thermoplastic are obtained. In particular a similar effect of the processing parameters and more specifically of the irradiation dose rate on the temperature during irradiation is observed, with the obtaining of mild temperature profiles at low dose rates and a dramatic temperature increase at high dose rates. Similar comments can be made also for the molecular structure and thermal properties of the cured materials, as shown in Fig. 4 by DMTA curves, where data relative to a DGEBF/PES blends cured at different dose and dose rates are reported. Also in this case, a post irradiation thermal curing allows to uniform the structure and to obtain a sufficiently high value of glass transition temperature.

In the same table 1 glass transition temperatures, elastic modulus in the rubbery state and $\tan\delta$ maximum are reported, for difunctional/trifunctional blends toughened by a PES based thermoplastic. Also in this case the introduction of the trifunctional epoxy monomer causes a marked increase of T_g value, indicating an increase of the cross linking degree, confirmed by the correspondent values of $\tan\delta$ maximum and of the elastic modulus in the rubbery state.

The presence of the thermoplastic can induce a marked effect in the mechanical properties. The presence of PES does not significantly affect the tensile elastic modulus. Our experiments give for difunctional epoxy formulations containing 10PES, e-beam cured at 80 kGy-90kGy/h, a value of the elastic modulus of about 3.6 GPa, very close to the values of

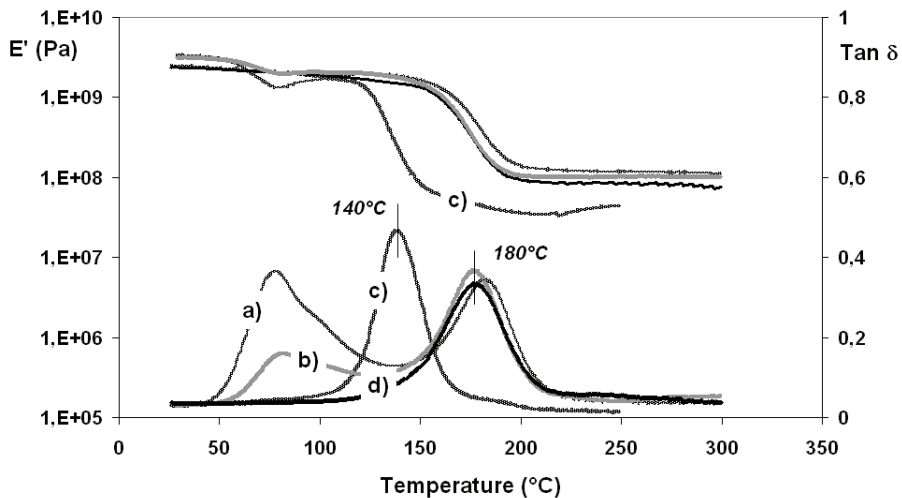


Fig. 4. Dynamical mechanical thermal curves for blends, toughened by PES, cured at different process conditions: a) 80 kGy, 84 kGy/h; b) 150 kGy and 84 kGy/h; c) 150 kGy and 840kGy/h; d) 80 kGy and 84 kGy/h and thermally post-cured for 2 h@ 100°C . Iodinium salt concentration: 1phr (per hundred of resin).

“Reprinted from *Radiation Physics and Chemistry*, 76, Alessi, S., Dispenza, C., Fuochi, P.G., Corda, U., Lavalle, M., Spadaro, G. E-beam curing of epoxy-based blends in order to produce high-performance composites, 1308-1311, Copyright (2007), with the permission from Elsevier”

similar untoughened epoxy resins (Janke et al., 2001). On the contrary a marked toughness increase is observed. In table 2 the results of the fracture toughness test in terms of the critical intensity factor K_{IC} (Broeck, 1986; ASTM D 695-02a., 2002), for both DGEBF neat resin and DGEBF/PES blends, are reported (Alessi et al. 2010). Passing from neat epoxy resin systems to blends, a general K_{IC} increase is observed. It is worth to note that the K_{IC} values relative to the toughened materials are not very far from the best results obtained by thermally cured systems (Janke et al., 2001).

In Fig. 5a-b the images of the specimens tested on tensile and three point bending testing machines are shown.

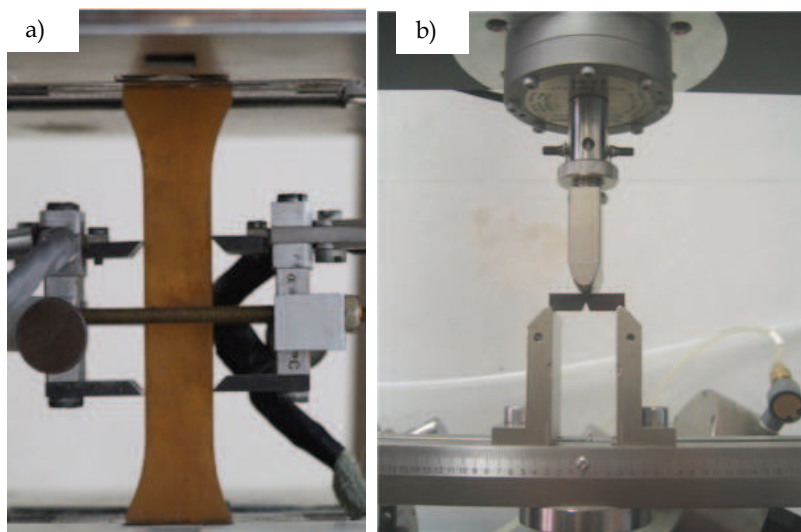


Fig. 5. Mechanical tests. a) Tensile: specimen gripped on a testing machine.; b) Fracture toughness: SENB (Single Edged Notched Bending) specimen in a three point bending configuration.

System	K_{IC} (MPa*m ^{1/2})
0 PES	0.6 ± 0.1
10 PES	1.5 ± 0.2
20 PES	1.2 ± 0.1

Table 2. K_{IC} values for different epoxy resin based systems irradiated at 80kGy and 70kGy/h.

“*Polymer Degradation and Stability*, 95, Alessi, S., Conduruta, D., Pitarresi, G., Dispenza, C., Spadaro, G. Hydrothermal ageing of radiation cured epoxy resin-polyether sulfone blends as matrices for structural composites, 677-683, Copyright (2009), with the permission from Elsevier”.

As discussed in the introduction the toughness is strongly related to the blend morphology. In Fig 6 the SEM micrographs of the toughened materials, on fractured surfaces of the tested specimens (table 2), are shown (Alessi et al., 2010). It can be observed that in both cases a co-continuous morphology is obtained, where two phases, one epoxy-rich and the second one PES-rich, are interconnected each other.

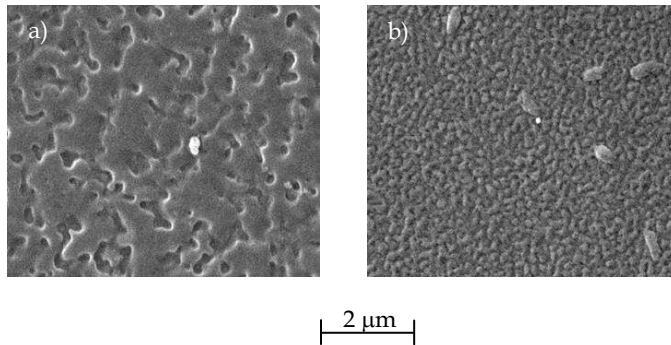


Fig. 6. SEM micrographs for epoxy resin based systems toughened by PES irradiated at 80 kGy and 70 kGy/h. a) PES content : 10 phr; b) PES content : 20 phr.

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3. Conclusions

In this review the application of radiation processing to the synthesis of epoxy based polymeric matrices for carbon fibre composites is presented.

In the introduction the general fundamentals of radiation processing, with reference to its use in the science and technology of polymer materials and in particular to radiation curing of epoxy resin systems, are discussed.

The most important results obtained by our research group are reviewed. The aim of our research is to improve both thermal and mechanical properties of the e-beam cured materials, relating them to the processing parameters for a full scale production in the aerospace and automotive industries.

It is shown that strong differences can be observed in the temperature of the epoxy systems during irradiation. The temperature depends on several parameters, such as the system formulation, the dose rate and the geometry of the irradiated sample. Varying these parameters, the temperature ranges from low to very high values. In these last conditions simultaneous thermal and radiation curing is performed. DMTA analyses evidence that the different temperature profiles during irradiation cause the formation of very different network structures with consequent different thermal behaviour. It is concluded that the best thermal performances are obtained by a combined “dual cure” process, consisting in e-beam irradiation at moderate dose rates and temperatures, followed by an “out of mould” post-irradiation thermal curing on already solid materials. It is very important to note that the heat released from the irradiated systems toward the environment, which is one of the

parameters which affects the temperature profile during irradiation, depends, among others, on the geometry of the irradiated system and in particular on the surface/volume ratio. This means that the irradiation of samples with the same formulation and at the same dose rate, but with different geometry, can have different temperature profiles and the cured materials can have different properties. This is a very important point in the scale up from laboratory to full scale industrial production. The reference parameter can be the temperature profile during irradiation which must be kept constant in the scaling up.

Regarding the mechanical properties, it is shown that blends of epoxy resins with engineering thermoplastics, similar to that used for thermally cured formulations, can be successfully cured by e-beam irradiation and the fracture energy values are not far from the best performances obtained through the more traditional thermal curing.

Finally SEM analysis shows that the toughness improvement is strictly related to the formation of co-continuous morphologies.

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"Radiation Physics and Chemistry, 76, Alessi, S., Dispenza, C., Fuochi, P.G., Corda, U., Lavalle, M., Spadaro, G. E-beam curing of epoxy-based blends in order to produce high-performance composites, 1308-1311, Copyright (2007), with the permission from Elsevier"

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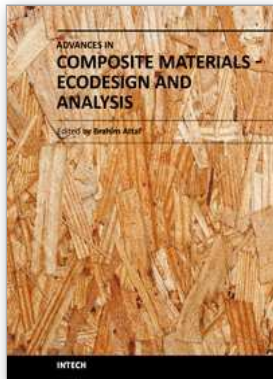
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By adopting the principles of sustainable design and cleaner production, this important book opens a new challenge in the world of composite materials and explores the achieved advancements of specialists in their respective areas of research and innovation. Contributions coming from both spaces of academia and industry were so diversified that the 28 chapters composing the book have been grouped into the following main parts: sustainable materials and ecodesign aspects, composite materials and curing processes, modelling and testing, strength of adhesive joints, characterization and thermal behaviour, all of which provides an invaluable overview of this fascinating subject area. Results achieved from theoretical, numerical and experimental investigations can help designers, manufacturers and suppliers involved with high-tech composite materials to boost competitiveness and innovation productivity.

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