The durability of carbon fiber/epoxy composites under hydrothermal ageing

G. Alaimo [1]
S. Alessi [2]
D. Enea [1]
G. Pitarresi [2]
G. Przybytniak[3]
G. Spadaro[2]
D. Tumino[4]

T 61

ABSTRACT

Studies on fibre reinforced composites are now receiving greater attention. Industrial applications have been successful in areas like aerospace, automobile, marine, construction and sporting goods. The first generation of epoxy resins for use in carbon fibre composites are able to achieve optimized high stiffness modules and high heat resistance by a high crosslink density, reached through thermal curing. However, these formulations can be very toxic and brittle with low crack resistance, which was a major disadvantage for structural applications. In the last years the use of ionizing radiation as alternative to thermal curing has been proposed as an environmentally friendly process. Furthermore, in order to enhance toughness mechanical requirements for their applications, the formulation generally consists of blends of epoxy resins and engineering thermoplastics. In terms of durability (service life and reliability), in these materials it depends on different environmental conditions (temperature, moisture, etc.), and it is very important to know how their properties are modified after the exposure to different temperature and moisture absorption cycles. In this work carbon fibre composites produced by ionizing radiation induced curing of the epoxy based matrices have been subjected to thermal and moisture absorption ageing and the influence of these treatments on the thermal and mechanical properties has been investigated through dynamic mechanical thermal analysis and mechanical fracture toughness tests.

KEYWORDS
Durability, carbon fiber composites, hydrothermal ageing, fracture toughness.

---

[1] Dipartimento di Progetto e Costruzione Edilizia (DPCE), Università degli Studi di Palermo, 90128, Palermo, ITALY (alaimo@unipa.it)

[2] Dipartimento di Ingegneria Industriale, Università degli Studi di Palermo, 90128, Palermo, ITALY (alessi@dicpm.unipa.it; pitarresi@dima.unipa.it; spadaro@dicpm.unipa.it)

[3] Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195, Warsaw, POLAND (g.przybytniak@ichtj.waw.pl)

[4] Facoltà di Ingegneria e Architettura, Università degli Studi di Enna Kore, Cittadella Universitaria, 94100, Enna, ITALY (tumino@dima.unipa.it)

Alaimo G. - Alessi S. – Enea D. - Pitarresi G. – Przybytniak G.- Spadaro G. – Tumino D.

1 INTRODUCTION

Fibre reinforced composites are receiving more and more interest, due to their industrial applications in several areas, like aerospace, automobile, marine, constructions etc... Composites are usually used when high performance and light weight are needed. Among all the polymer based composites, epoxy resin/carbon fibre systems present the best performances in term of mechanical properties and thermal resistance. They are used in particular for aerospace and advanced automotive applications [Feraboli & Masini 2004; Hufenbach et al.2011].

The first generation of epoxy resins for use in carbon fibre composites optimized high modulus and high heat resistance by a high crosslink density reached through thermal curing. However, these formulations can be very toxic. In the last years the use of ionizing radiation as alternative to thermal curing has been proposed as an environmentally friendly process. In fact radiation process allows to perform curing at mild temperatures with reduced emission of organic volatile substances and the obtained materials are characterized by the absence of thermally induced mechanical stresses [Lopata et al. 1999; Goodman & Palmese 2002].

A significant drawback in the use of cross-linked epoxy resins as polymer matrices is that the material is very brittle with low crack resistance. In order to achieve the mechanical requirements in term of toughening, the used formulations generally consist of blends of epoxy resins and engineering thermoplastics [Mimura et al. 2000].

The structures made of composites materials, in general, work in more or less aggressive environments, like temperature, humidity, chemical exposition, corrosive environments, UV and ionizing radiation. Consequently, it is very important to know how their properties are modified after the exposure to these different aggressive factors.

In this work carbon fibre composites produced by the ionizing radiation induced curing of the epoxy based matrices have been subjected to thermal and moisture absorption ageing. The influence of these treatments on the thermal and mechanical properties has been investigated through dynamic mechanical thermal analysis and mechanical fracture toughness tests.

2. EXPERIMENTAL

The epoxy monomer was 2,2-bis[4-(glycidyloxy)phenyl]propane, also named diglycidyl ether of bisphenol A (DGEBA), by aldrich and the toughening agent for the epoxy resin was an engineering thermoplastic, polyether sulfone (PES), produced by Sumitomo Chemicals. The initiator was an iodonium salt cumyltolyliodonium tetra(pentafluorophenil) borate rh 2047 (Rh), supplied by Rhodia Silicones.

The carbon fibers were sika unidirectional, high modulus, carbon fibers, Sikawrap 400c midmod nw, having a density: of 1.81 g/cm^3 and longitudinal young's modulus E_l of 390 GPa.

Two composite laminate panels have been prepared with two different resin blends with zero and 10 phr (per hundred of resin) of toughening agent:

<div align="center">

DGEBA- Rh-carbon fibers   (0PES)
DGEBA- 10PES-Rh-carbon fibers (10 PES)

</div>

The 0PES system has been prepared through the following procedure. A blend from DGEBF and initiator (Rh) was prepared at 60°C. First the resin was heated in an oil bath, then the initiator was added in small portions. The amount of initiator for this system was established to be 0.1 phr (per hundred resin). The blend was mixed for about 30 minutes until the initiator dissolves in the resin then it was cooled down to the room temperature. The 10PES system has been prepared through the following procedure.

The blend was prepared at 80°C. First the resin was heated at 80°C, then the toughening agent was added in order to be dissolved. After 2 hours mixing a homogeneous but unclear blend was obtained. Rising the temperature step by step it was found that 130°C is the optimal temperature for the complete dissolution of the thermoplastic in the resin. As in the previous blend, the initiator is added after cooling down to 60°C.

The impregnation of unidirectional carbon fibers was done with a hand lay-up technique, and the final

laminate lay-up is unidirectional comprised 8 laminas, $[0°]_8$. An aluminum foil strip was placed between the 4th and 5th laminas in order to introduce a delamination front. The strip orientation and dimensions were such to allow the cutting of samples for the "Double-Cantilever Beam" (DCB) test, with a delamination crack length of 50 mm. After impregnation the prepared composite was inserted between two aluminum plates, pressed by clamps in order to create an uniform thickness. The dimensions of the system were 20x25x0.4 cm.

The e-beam irradiation of the blends has been realized using the LAE 10 MeV linear, pulsed accelerator located in the laboratory of the ICHTJ (Inst. of Nuclear Chemistry and Technology) of Warsaw. The previously prepared uncured composites have been positioned in a horizontal position in the front of the pulsed beam. The temperature of the sample during the irradiation is a very important factor and it can affect the properties of the material. In order to monitor the sample's temperature a thermo-resistor was inserted in the blend and during the irradiation a thermal profile was registered. Due to the different reactivity, 0.5phr and 1phr of initiator has been used for 0PES and10PES respectively. The curing reaction has been followed by monitoring the temperature during the irradiation. After e-beam curing, the material was characterized by means of thermal and morphological analysis.

Radiation cured composites have been subjected to hydrothermal ageing by immersion of the samples in distilled water at 70 °C for two periods, 1 week and 1 month respectively. After reaching the desired ageing time, all materials have been characterized. The samples have been kept in water at room temperature until characterization tests, which were performed within few days from the end of hydrothermal treatments.

Thermal properties of both not-aged and aged materials have been determined through Dynamic Mechanical Thermal Analysis using a Rheometrics DMTA V instrument, single cantilever bending method. The test has been done in temperature swift mode, between 25-250 °C and a heating rate of 2 °C/min. The frequency was set to 1.8 Hz and the strain was 0.02 %. The storage modulus (E') and loss factor (tan δ) versus temperature (T) were recorded. The glass transition temperature was determined by tan δ peak.

Two types of beams samples were analyzed with DMTA, the first with the uniderctional fibre direction aligned with the beam axis, $[0°]_8$, and the second with the fibres direction oriented orthogonally to the beam axis, $[90°]_8$.

The laminate material has been also tested in order to evaluate its delamination fracture toughness in Mode I crack opening on DCB ("Double Cantilever Beam") samples [Reeder 1992]; this resulted in the evaluation of the critical Strain Energy Release Rate, G_{IC}, i.e. the value at which crack propagation in the material is started. The DCB samples (shown in Figure 1) had dimensions complying with the standard [ASTM D5528], and in particular: $B = 20$ mm, $2h = 4$ mm, $L > 125$ mm, $a_0 = 35$ mm.
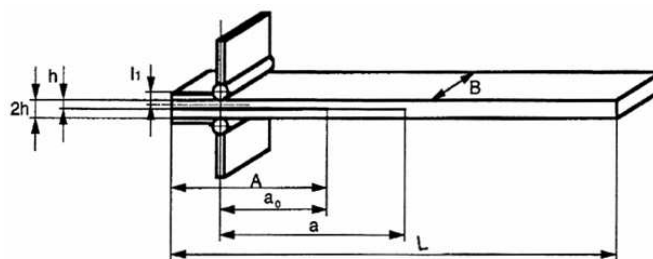

Figure. 1 Scheme of a DCB test for delamination fracture toughness characterisation

The initial crack length, obtained with the embedded thin aluminium foil, has length *A*, and is placed at the middle panel thickness. Two hinges are bonded at the far end of the delaminated fronts by using a bi-component cyanoacrilate adhesive applied, after the adhered surfaces were grinded with thin emery paper and cleaned and degreased with an opportune solvent. A white paint was applied upon the thickness surface on one side of each DCB sample in order to enhance the visual contrast with vertical lines drawn with a marker pen at one mm distance. This drawn scale is used to monitor the crack length changes during the crack propagation (see Figure 2).

The DCB samples where then mounted on the loading machine by gripping the free wing of the

hinges on common wedge grips employed for tensile tests. The testing machine employed was an electric Instron 3367 rig equipped with a 1 kN load cell and controlled with the Instron Blue Hill software which allowed the synchronous measure of the load *P* and the crosshead displacement which is also the separating displacement between the two delamination fronts at the hinge location, *d*. The load versus displacement curve is measured by running each test in displacement control, i.e. at a given fixed crosshead rate. The length of the growing crack *a* is measured manually by the operator by locating the crack tip on the zoomed images of the sample painted side, taken with a digital video camera. Images where captured at determined displacement values, monitored by means of the testing machine software, in order to synchronise the crack length measurements with the corresponding load and displacement values.
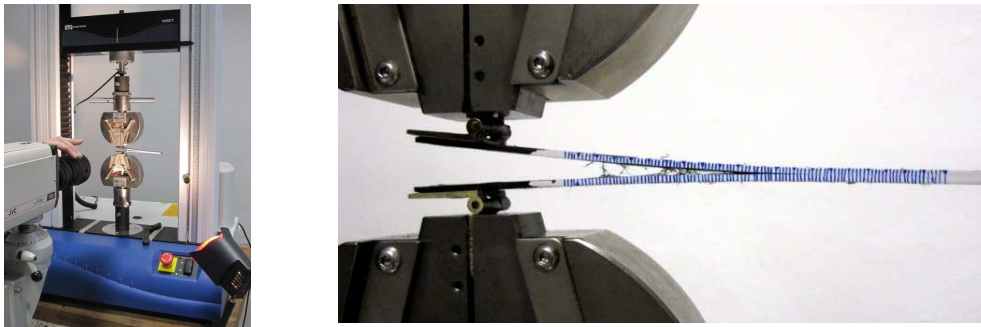

Figure. 2 Images of the DCB test set-up and of a DCB sample during propagation of the delamination

3 RESULTS AND DISCUSSION

As it is well known, e-beam curing can be considered a "cold" process because it does not need thermal activation, but during irradiation the temperature can significantly increase due to different thermal effects [Alessi et al. 2005]. For this reason the temperature of the irradiated sample is recorded during irradiation.

The thermal profiles, i.e. the temperature values as function of the irradiated dose, (here not reported) are very similar for both 0PES and 10PES systems and do not pass over 70 °C during the whole curing process. In these irradiation conditions the influence of the temperature is minimal and the curing is realized mainly by the e-beam process.

3.1 DMTA Tests

The dynamic mechanical thermal behaviour has been studied for all e-beam cured carbon fiber composites (0PES and 10PES), considering both longitudinal and transversal samples. In the comparison between the samples differently cut it has to be taken into account that in the longitudinal samples the main response comes from fibers (high modulus) while for perpendicular samples the response is mainly generated by the epoxy matrix and the matrix-fiber interface.

In Figure. 3 DMTA curves for 0PES and 10PES samples produced by irradiation and transversally cut are reported. Similar qualitative behaviour are presented by longitudinally cut samples.

In all cases two main relaxation peaks in tanδ/T curves have been observed, with a broader extension for the peak at low temperature. The presence of two relaxation peaks can be attributed to the formation of a "not uniform" structure, consisting of portions having different cross-linking densities, which relax at different temperatures. This behaviour has been already observed for radiation cured epoxy matrices and is related to vitrification effects of the polymerizing resin due to the low process temperature [Alessi et al. 2005, 2007-a, 2007-b]. In fact when radiation curing is performed at mild temperature, as in this case, the glass transition temperature of the material soon approximates the cure temperature and the cure reactions become controlled by diffusion processes.
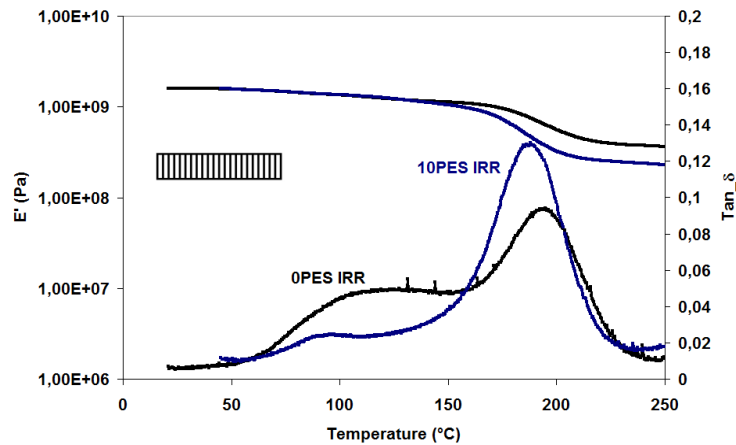
Figure. 3 Tan δ and storage modulus vs temperature for 0PES and 10PES transversal, only irradiated

In Tab.1 the water uptake values of the irradiated samples are reported as M_t, with $M_t = (m_t-m_0)*100/m_0$, where m_t was the weight at immersion time t and m_0 that one before immersion.

Tab. 1 Water uptake for irradiated systems as $M_t = (m_t-m_0)*100/m_0$

Systems	1 week hydrothermal ageing	1 month hydrothermal ageing
0 PES	1 %	1.5 %
10 PES	3 %	5 %

In Figure. 4 DMTA curves are presented for 0PES e-beam cured carbon fiber/epoxy transversal composites, after performing hydrothermal ageing for 1 week All the other DMTA curves, for 10 PES and for longitudinally and transversally cut samples, show similar qualitative behaviour.

After 1 week hydrothermal ageing the systems show only one relaxation peak at an intermediate temperature between the initial peaks. This effect is similar to that already observed in epoxy matrices hydrothermally aged after e-beam curing [Alessi et al. 2010]. It can be interpreted by the occurring of a combined effects of plasticization and degradation of the matrix, responsible of the decrease of the peak from high temperature, and a thermal post-curing which causes an increase of the peak from low temperature [Colombini et al. 2002], [Zhou and Lucas 1999].

After 1 month ageing DMTA curves show a further decrease of the relaxation temperatures even if with a minor extension compared to that observed after 1 week.
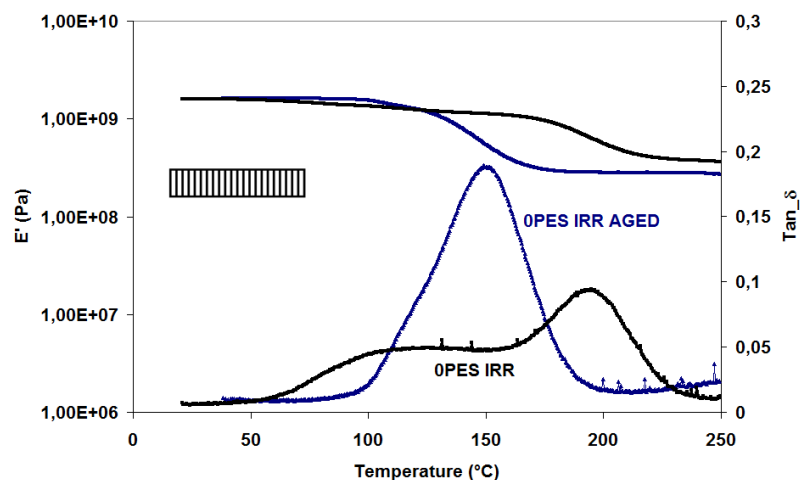

Figure. 4 Tan δ and storage modulus vs temperature for 0PES transversal irradiated and 1 week aged

In Table 2 a summary of the relaxation temperatures for all studied samples is presented.
In general, after hydrothermal ageing, a more marked effect is observed for longitudinal samples than transversal ones, probably due to a strong decrease of interaction between fiber and matrix. In this respect it is worth to note that fiber sizing of the used fibers was designed for thermal curing and then the optimization for radiation curing should be considered in order to reach better hydrothermal ageing resistance.

Table 2. Glass transition temperatures for 0PES and 10PES

Systems	Cure conditions	Sample type	Relaxation temperatures (not aged) [°C]	Relaxation temperature (after 1 week ageing) [°C]	Relaxation temperature (after 1 month ageing) [°C]
0 PES	Irradiated	Transv.	120, 195	152	150
		Long.	109, 200	150	145
10 PES	Irradiated	Transv.	95, 188	156	145
		Long.	125, 198	144	140

3.2 DCB Tests

Figure 5 shows the load vs displacement curves from Double Cantilever Beam tests on not aged samples. Although several tests were carried out for each beam type and aging condition, only one curve for each sample is reported for clarity.
In the case of untoughened samples (i.e. CFRP laminates adopting the untoughened resin batch) it is observed (see Figure. 5(a)) that after the first pseudo-linear stage the curve decreases with a rather irregular trend. This is probably caused by a non uniform and gradual crack growth accompanying the hinges displacement.
The same rough trend is still observable and even more marked in toughened samples (see Figure. 5(b)). One possible explanation is given the presence of PES agglomerates dispersed within the matrix, and observed by means of SEM micrographs. The tougher behaviour of this clustered PES rich phases act as an obstacle to a continuous smooth crack propagation. This determines the mechanical energy to accumulate, e.g. when the crack front reaches a PES reach area, as suggested by the load/displacement curve growing again after crack propagation onset. As soon as enough mechanical energy is stored then this is suddenly released generating a crack pop-in mechanism of crack growth (see Figure. 5(b)). When enough energy is accumulated the sudden crack pop-in releases the load very rapidly. By post-processing the measured load, displacement and crack growth data for the DCB geometry it is possible to evaluate the delamination crack resistance R-Curve of the material for the different analysed conditions. Figure 6 shows the curves of the energy G versus the crack length a.
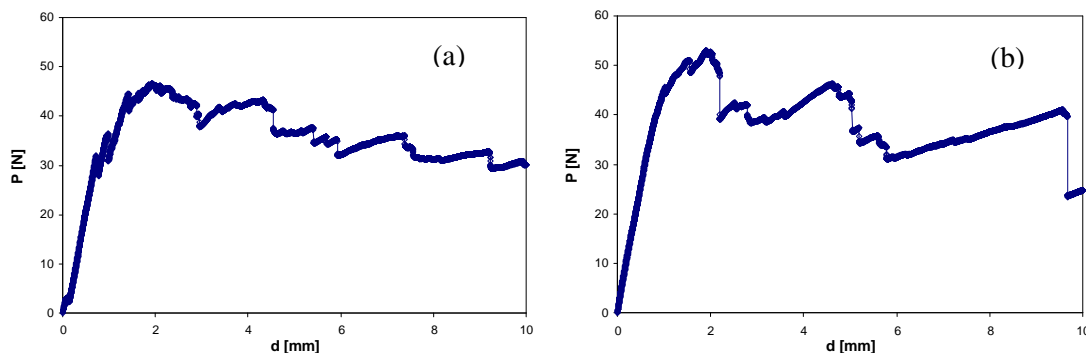

Figure. 5 DCB test: load *vs* displ. curves for unaged DGEBA (a) and DGEBA+10phr PES (b) based composites.

In particular Figure 6(a) compares all curves from untoughened samples with different aging periods; it is noticed that this curves have a rather irregular but clearly growing trend. It seems that the curves become smoother at longer aging times, and this might be due to plasticizing phenomena induced in

the resin matrix as aging is prolonged.

In Figure 6(b) the toughened material is considered. Again the curves evidence a general growing trend. Irregularity is now more marked then the untoughened material but it decreases significantly as the aging period is longer.
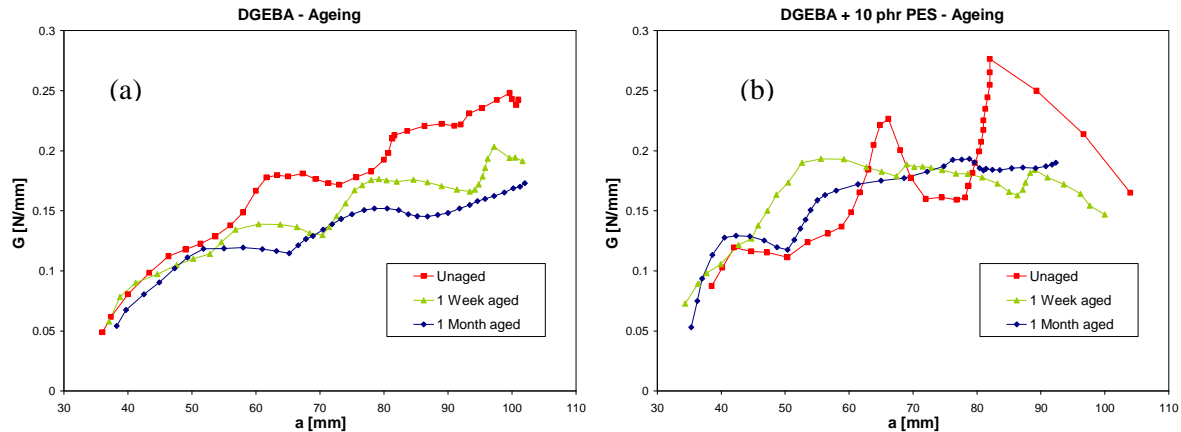

Figure. 6 DCB test: resistance curves for DGEBA (a) and DGEBA+10phr PES (b) based composites.

Values of fracture toughness G_{IC} at crack propagation onset (i.e. at $a=a_0$) are summarised in Figure 7. This diagram shows that for the same aging time the toughened material has a higher delamination resistance than the untoughened one. The results obtained in this work show also that for the same material the implemented aging procedure has not determined a meaningful variation of the initial crack resistance, i.e. of the critical fracture toughness.
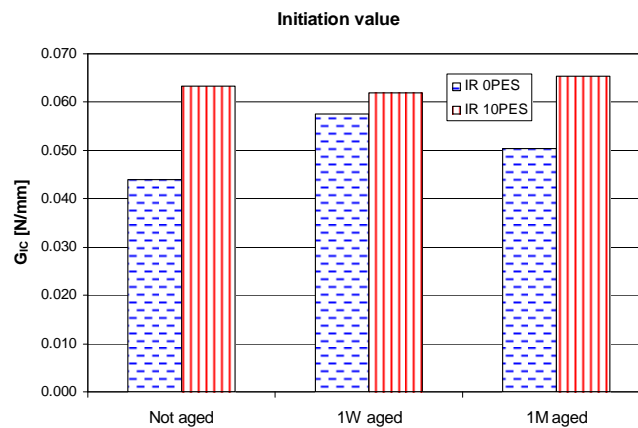

Figure. 7 DCB test: initiation values of crack resistance.

4 CONCLUSIONS

In this work CFRP panels with a unidirectional fibre stacking sequence have been characterised after conditioning with different aging conditions. The tested material in particular uses a resin formulation suitable for radiation curing and has been manufacture by hand lay-up and cured with an e-beam accelerator. Two resin formulations have also been adopted, an untoughned DGEBA system and a toughened system obtained by mixing DGEBA with 10 phr of a PES monomer. Characterisation has been carried out through DMTA tests and mechanical delamination tests on DCB samples for fracture propagation in mode I. The aging influence on toughened and untoughened systems was then studied by characterising the materials glass transition temperature Tg, the critical initial fracture toughness at delamination and the crack resistance curve.

In general it was observed that dispersion of PES rich phases can have a strong influence on the crack propagation behaviour. The use of a toughened resin seems to promote an increase in the critical fracture toughness while this value was not significantly affected by the ageing procedure.

REFERENCES

Alessi S., Calderaro E., Parlato A., Fuochi P., Lavalle M., Corda U., Dispenza C., Spadaro G. 2005, 'Ionizing radiation induced curing of epoxy resin for advanced composites matrices.', *Nuclear Instruments and Methods in Physics Research B*, **236**, 55-60 .

Alessi S., Parlato A., Dispenza C., De Maria M., Spadaro G. 2007, 'The influence of the processing temperature on gamma curing of epoxy resins for the production of advanced composites', *Radiat. Phys. and Chem.***76,** 1347-1350.a

Alessi, S., Dispenza, C., Spadaro, G. 2007 , 'Thermal properties of e-beam cured epoxy/thermoplastic matrices for advanced composite materials', *Macromolecular Symposia* **247,** 238-243. b

Alessi S., Conduruta D., Pitarresi G., Dispenza C., Spadaro G., 2010, 'Hydrothermal ageing of radiation cured epoxy resin-polyether sulfone blends as matrices for structural composites', *Polymer Degradation and Stability* **95**, 677-683.

ASTM Standard D5528-01, 'Standard Test Method for Mode I Interlaminar Fracture Toughness of Unidirectional FiberReinforced Polymer Matrix Composites'. USA, 2001.

Colombini D., Martinez-Vega J.J., Merle G., 2002, 'Dynamic mechanical investigations of the effects of water sorption and physical ageing on an epoxy resin system', *Polymer* **43**, 4479-4485.

Feraboli P., Masini A., 2004, 'Development of carbon/epoxy structural components for a high performance vehicle'**,** Composites: Part B, **35,** 323–330 .

Goodman, D. L. & Palmese, G. R., 2002, 'Curing and Bonding of Composites using Electron Beam', in *Handbook of polymer blends & composites*, Kulshreshtha, A. K. and Vasile, C. vol. 1, ch. 11, RAPRA Technology Ltd, Shropshire, UK

Hufenbach W., Böhm R., Thieme M., Winkler A., Mäder E., Rausch J., Schade M., 2011, Polypropylene/glass fibre 3D-textile reinforced composites for automotive applications', *Materials and Design* **32**, 1468–1476.

Lopata, V., Saunders, C.B., Singh, A., Janke J.C., Wrenn**,** G.E., Havens, S.J.,1999, 'Electron-beam curable epoxy resins for the manufacture of high-performance composites', *Radiation Physics and Chemistry*, **56**, 405-415.

Mimura, K., Ito, H., Fujioka, H., 2000, ' Improvement of thermal and mechanical properties by control of morphologies in PES-modified epoxy resins', *Polymer*, **41**, 4451-4459.

Reeder, JR., 1992, 'An evaluation of mixed-Mode delamination failure criteria', Technical Memorandum-1992-104210, NASA Langley Research Center.

Zhou J., Lucas J.P., 1999, 'Hygrothermal effects of epoxy resin. Part II: variations of glass transition temperature', *Polymer* **40**, 5513-5522.