THERMAL AND MECHANICAL PROPERTIES OF POLYMER MATRICES FOR CARBON FIBRE COMPOSITES PRODUCED BY RADIATION CURING OF EPOXY-PES BLENDS

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ABSTRACT

A model poly(ethersulfone) (PES) - epoxy resin has been prepared to be cured by means of electron beam irradiation. The influence of temperature mixing of the two components, PES and diglycidyl ether of bisphenol F (DGEBF), on thermal and mechanical properties of the cured material has been investigated through Dynamic Mechanical Thermal Analysis (DMTA) and single-edge notched three point bending tests, in order to determine glass transition temperature and calculate fracture toughness, respectively. These results have been discussed in the light of the observed co-continuous morphologies obtained for the cured material upon e-beam irradiation. Finally the effect of a thermal postcure process, carried on the demoulded samples at moderate temperature, has been also investigated.

1. INTRODUCTION

Radiation processing is proposed as an alternative methodology to cure composite materials for aerospace and advanced automotive applications, whose main requirements are high thermal resistance (high Tg) and high toughness [1]. The most interesting aspect of this process, with respect to thermal curing, lies in the fact that it does not need thermal activation, so that it can be performed near to room temperature neither it does the use of toxic hardeners. This bring about several positive consequences such as improvement of thermal and mechanical properties of the cured materials, that are free of thermal stresses, environment preservation and energetic costs saving. Other advantages are the short curing times and the possible recourse to low cost mould materials [2].

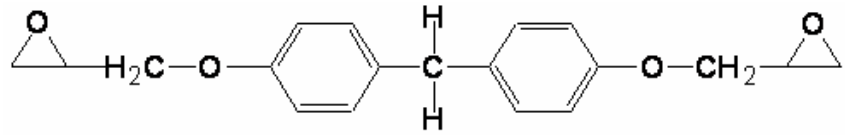
Epoxy polymers are widely used as matrices of fibre reinforced composite materials and adhesives. When cured, epoxies are amorphous and highly-crosslinked polymers. This microstructure results in many useful properties for structural engineering applications, such as high modulus and failure strength, low creep and good mechanical performance at elevated temperatures. However, the structure of such thermosetting polymers also leads to a highly undesirable property in that they are relatively brittle materials, with a poor resistance to crack initiation and growth. Nevertheless, it has been well established for many years that the incorporation of a second micro-phase of a dispersed rubber [3], or a thermoplastic polymer [4] into the epoxy polymer can increase its toughness.

The aims of the present work is to investigate the behaviour of epoxy-thermoplastic blends, cured by e-beam radiation and to establish the processing-structure-properties relationships.

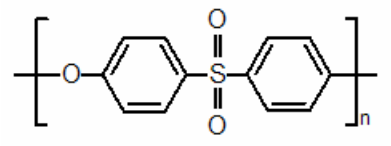
2. EXPERIMENTS

2.1 Materials

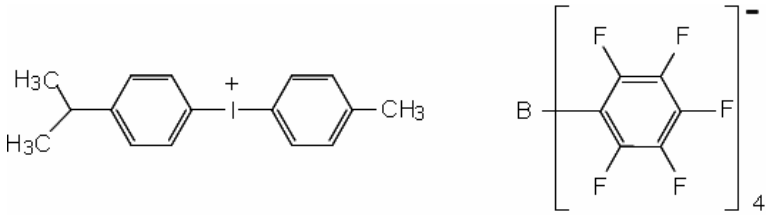
The epoxy resin used in our experiments was Bis(4-glycidyloxyphenyl) methane (DGEBF) supplied by Aldrich. The thermoplastic was a commercial polyethersulphone (PES), Mw=25000 by Sumitomo Chemicals and Cumyltolyliodonium tetra(pentafluorophenyl) borate (Rh), supplied by Rhodia Silicones, was used as initiator (Figure 1).



DGEBF – diglycidyl ether of bisphenol F



PES – polyethersulfone



INITIATOR- cumyltolyliodonium tetra(pentafluorophenyl) borate

Figure 1. Chemical structures of the materials

2.2 Preparation of blends and e-beam irradiation

DGEBF-PES blends were prepared according to the following procedure. PES powder was mixed with the resin at room temperature in two beckers, each one was then heated at different temperatures, 80°C and 130°C respectively, for 1hour, under continuous stirring. The resulted blends were cooled down to room temperature and the corresponding quantity of initiator was added.

Finally the blends were transferred in a closed steel moulds and irradiated with a dose rate of approximately 70 kGy/h and a total absorbed dose of 80 kGy. E-beam irradiation was carried out at the ISOF-CNR laboratory in Bologna with 12-MeV Vickers type linear accelerator.

A post-irradiation thermal treatment was carried out at 120°C for 2 hours for all systems after demoulding.

2.3 Characterisation

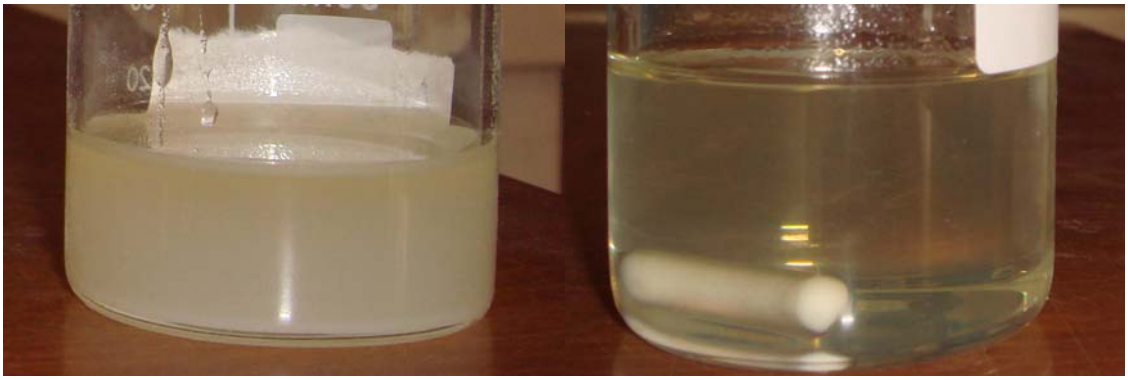
Dynamic Mechanical Thermal Analysis (DMTA) was done on both e-beam cured and thermally postcured samples, through a Rheometrics DMTA V apparatus, equipped with a single cantilever bending fixture, in temperature sweep mode from 25 °C to 300 °C range at a heating rate of 2°C /min. The strain level was set at 0.02% and the frequency was 1.8 Hz. Storage modulus (E') and loss factor (tanδ) vs temperature were recorded. The glass transition temperatures were determined from tanδ curves.

The mechanical tests (fracture toughness determination) were performed by an Instron 3367 having a loading cell of 1 kN using the ASTM D5045 96 standard. Critical stress intensity factor (K_{IC}) was calculated using the single-edge notched three point bending method. Dimensions of the specimens were 48.4 mm × 11 mm × 4 mm. Cracks were introduced by first cutting a notch, then hammering in a razor blade to perform a sharp crack.

The morphology of the cured materials were analysed by Scanning Electron Microscope (SEM: Philips 505). The surfaces obtained after cutting and polishing were etched in super-acid solution and then gold coated.

3. RESULTS

As discussed above, a blend of resin and thermoplastic were to be prepared prior to irradiation. In the Figure 2 the photos of the blends prepared at 80 °C (a) and 130 °C (b) are presented. A hazy yet uniform system, was obtained by 1 hour stirring at 80 °C suggesting that the PES is not totally dissolved in the colourless and transparent epoxy resin and part of it is only homogeneously dispersed while in the case of system prepared at 130 °C a clearer and transparent blend is obtained.



a) b)

Figure2. Blends of epoxy monomer and PES prepared at a) 80 °C and b) 130 °C

The initiator was then added to the blend and the resin mixtures were subject of e-beam irradiation, in the same conditions (80 kGy-70kGy/h).

Due to possible thermal effects, caused by both the exothermic polymerization reaction and the absorption of radiation energy, during irradiation the temperature of the samples has been recorded, through a thermo-resistor dipped in the sample and wired to a data

acquisition system interfaced to a computer. Having fixed the geometry of the irradiated systems, the thermal profiles measured for each of the sample prepared at the two temperatures, give an indication of their relative reactivity (see Figure 3).

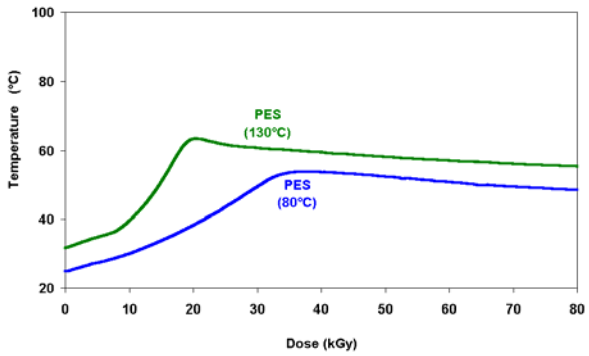
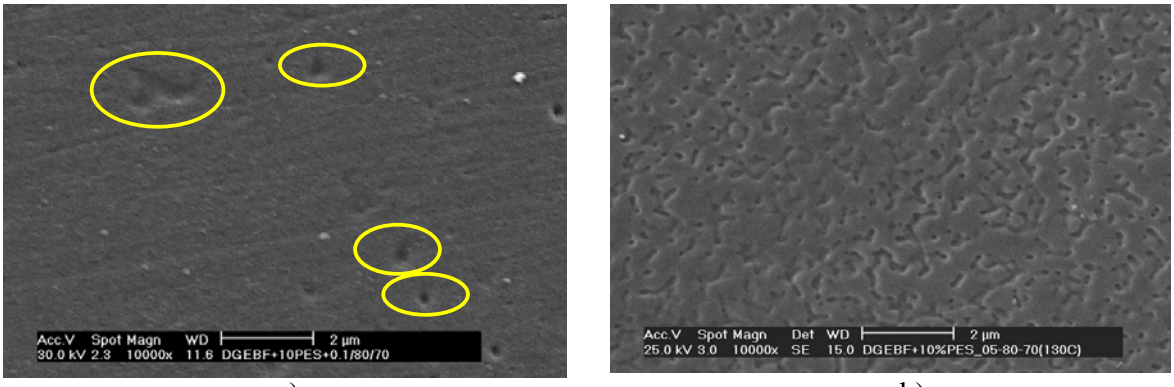


Figure 3. Thermal profiles obtained during e-beam radiation of DGEBF/PES blends

It can be observed that in both cases temperatures recorded are fairly low with peaks at 50°C and 65 °C for mixing temperatures of 80 °C and 130 °C, respectively. According to this evidence, the influence of the thermal curing on the structural modifications of the irradiated materials is very limited.

In the figure 4 SEM micrographs for the two systems are presented. The first one,referring to the blend prepared at a lower temperature, shows only some holes, with different sizes, caused by the extraction of PES by the acid solution (etching). This means that PES agglomerate and phase-separate in some regions, having a not uniform distribution. In the second image a typical co-continuous morphology is observed. It belongs to the system in which the PES was totally soluble in the resin and the blend was transparent. Based on this results it is expected that the e-beam cured materials with the co-continuous morphology will have better mechanical properties .



a) b)

Figure 4. SEM micrographs e-beam cured materials of which blends (DGEBF+PES) were prepared at 80 °C (a) and 130 °C (b)

Thermal properties of the e-beam cured materials were measured by means of DMTA. The glass transitions temperatures were determined from the tan δ peak.
The loss tangent curve presents two main relaxation peaks, corresponding to the glass transition of clusters with different network density. As already discussed [5], this behaviour is related to vitrification phenomena occurring during irradiation when the glass transition temperature of the polymerising resin becomes higher than the processing temperature. This usually occurs also for thermal curing process, but it is enhanced in this case, as curing is carried out at a much lower temperature. Moreover the system prepared at 80 °C presents also a third peak at a temperature higher than 250 °C. It can be attributed to the glass transition of the coarse phase separated PES.

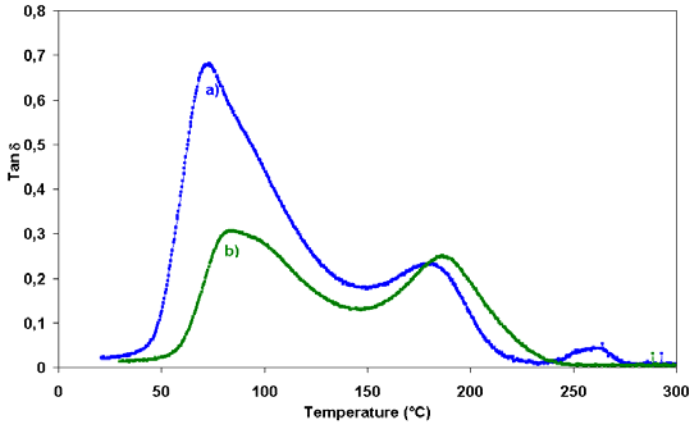


Figure 5. Loss tangent vs Temperature curves for the only e-beam irradiated systems

In order to optimize the thermal properties a thermal postcuring was performed on e-beam cured materials at 120 °C for 2h. In figure 6 it can be observed that after thermal postcuring the tanδ peak at low temperature disappeared. The main peak at high temperature is still present indicating a quite uniform crosslinking density. The highest temperature peak related to the Tg of PES is still present, laying above 250 °C.

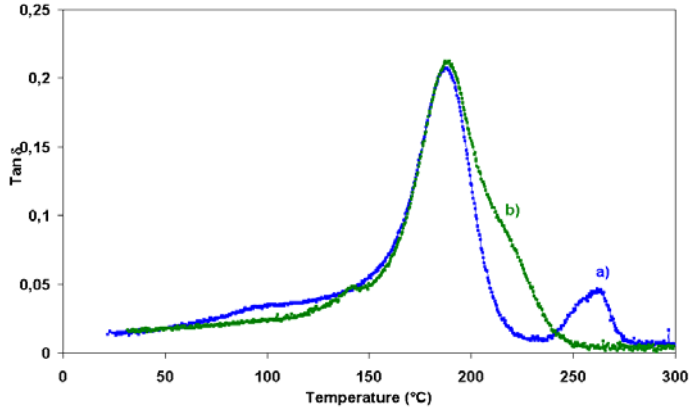


Figure 6. Loss tangent vs Temperature curves for thermally postcured systems

In the table 1 the K_{IC} values for the neat resin and the resin with thermoplastic prepared at 80 °C and at 130 °C are reported. As expected the lowest values are obtained for the resin without toughening agent. A slight increase of K_{IC} is observed in the system prepared at 80°C, while the highest values are obtained for the system where the blend, prior to cure, was transparent and the samples morphologies, upon cure, were co-continuous type (130 °C)

	Neat resin (DGEBF)	**DGEBF+10%PES (blend at 80 ºC)**	**DGEBF+10%PES (blend at 130 ºC)**
K_{IC} (MPa x $m^{1/2}$)	**0.5±0.2**	**0.65±0.15**	**1.5±0.2**

Table 1. K_{IC} values for the neat resin and thermoplastic modified systems

6. CONCLUSIONS

In this work the behaviour of one single resin-thermoplastic formulation, prepared at two different mixing temperatures is studied. Electron-beam radiation is used for curing. It was observed that a better solubility of the PES in the resin leads to a drastic improvement of the mechanical properties and toughness in particular. A more uniform phase-separation like co-continuous morphology, can also induce a better fracture toughness.

ACKNOWLEDGEMENTS

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