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Thermal Properties of E-beam Cured Epoxy/ Thermoplastic Matrices for Advanced Composite Materials

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Summary: The aim of this work is to investigate the possibility to improve the thermal behaviour of epoxy based systems, cured by ionizing radiation, in order to produce matrices for advanced carbon fibres composites. Blends of two epoxy monomers, difunctional and trifunctional, have been polymerized by e-beam irradiation and the dynamic mechanical thermal properties have been investigated. The increase of the concentration of the trifunctional epoxy monomer in the blend causes a marked increase of the Tg, but strongly decreases the reactivity. Subsequently, blends of the same epoxy monomers with a high Tg thermoplastic toughening agent have been considered and their reactivity and the thermal properties of the obtained materials have been also studied. The experimental results show that the thermoplastic component increases the reactivity of the difunctional/trifunctional blends, without a significant decrease of the glass transition temperature which still satisfies the requirements for advanced composite materials.

Keywords: composite materials; electron beam irradiation; epoxy resin; thermal properties

Introduction

The interaction of ionizing radiation with matter causes the formation of excited species whose evolution can induce marked modifications in the irradiated systems. For instance polymeric materials can be formed through the polymerization reactions induced by irradiation of suitable monomers.[1,2]

Among all the studied processes, the use of ionizing radiation to initiate the ‘‘curing’’ of epoxy resin based systems, in order to produce matrices for advanced carbon fibres composites, has received a great interest because of the several advantages offered by this technology, with respect to the conventional thermal ways. It is well known in fact that radiation curing does not need thermal activation, has reduced processing times with a consequently decrease of manufacturing costs, allows a localised curing overcoming the problems related to particular shapes of the cured samples, and does not require the use of chemical hardeners.[3]

Although irradiation can be initiated at room temperature, during the process thermal effects occur due to the heat produced, related to both the polymerization reactions and the absorption of radiating energy. The temperature of the sample is then the result of the balance between the rate of the heat production and the rate of the heat releasing toward the environment.[4]

In order to perform the radiation induced cationic curing of epoxies, basic impurities such as water must be avoided, and an initiator is always added. The most effective and commercially available initiators are the so called ‘‘onium salts’’ developed by Crivello et al. for the UV

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epoxy curing.[5,6] These are acid salts consisting of a strongly electronegative group and of a cationic part whose reduction allows the epoxy ring opening with the consequent molecular chain lengthening.[5]

The principal requirements regarding carbon fibre composites for aerospace and advanced automotive applications are a high operating temperature (high Tg), a high stiffness (high elastic modulus), a high toughness (high fracture energy) as well as a high processability and solvents resistance. Like the thermal systems, the main target of the studies about radiation curable epoxy matrices, is to find the best formulations and the best processing conditions in order to optimise the properties of the products. In the recent years several blends of epoxy resin monomers, having different number of functionalities, and containing either different toughening agents or initiators have been investigated.[7–10]

In this work the possibility to improve the thermal behaviour of epoxy based systems, cured by ionizing radiation, in order to produce matrices for advanced carbon fibres composites has been investigated. In particular, the systems used consisted of blends of two epoxy monomers, difunctional and trifunctional, polymerized by e-beam irradiation. The obtained materials have been characterized through dynamic mechanical thermal analysis.

Subsequently, blends of the same epoxy monomers with a high Tg thermoplastic toughening agent have been considered and their reactivity and the thermal properties of the obtained materials have been also studied.

Experimental Part

The epoxy resins were Bis(4-glycidyloxyphenil) methane (DGEBF) as difunctional resin, supplied by Aldrich, and Tris(4-glycidyloxyphenil) methane (Tactix 742) as trifunctional resin, supplied by Vantico. The toughening agent was a high Tg and high modulus polysulphone thermoplastic ($Mw = 10000$). Cumyltolyliodonium tetra(-pentafluorophenil) borate supplied by Rhodia Silicones was used as initiator.

Blends with only epoxy monomers were prepared by mixing them with the initiator at 80 °C for 1h and then keeping the samples at the same temperature for 1h in order to eliminate the air trapped into the systems. Blends with 20, 40, 60 wt % of Tactix were prepared.

For the preparation of the epoxy/thermoplastic blends, the epoxy monomers were mixed with the thermoplastic at 80 °C for 1h. Then the blend was kept at 80 °C for 24h in order to complete homogenization. Before irradiation the same procedure before described, for the adding of the iodonium salt, was followed. For these blends the concentration of the thermoplastic was always 10 wt %, while the difunctional/trifunctional epoxy weight ratio was 60/40. For all the blends irradiated the amount of initiator was always 1% with reference to the epoxy mixture.

E-beam irradiation has been carried out, in closed steel moulds, at the ISOF-CNR laboratory in Bologna with the 12-MeV Vickers type linear accelerator whose technical characteristics are reported elsewhere.[11] The pulse frequency used was 50 Hz corresponding to the irradiation dose rate of 840 kGy/h. The dimensions of the samples were $4 \times 150 \times 150$ mm.

During irradiation the temperature of the polymerizing resin has been recorded, through a thermo resistor dipped in the sample and wired to a data acquisition system interfaced to a computer.

Dynamic mechanical thermal analysis has been performed on samples cured at 150 kGy through a Rheometrics DMTA V apparatus, equipped with a three point bending fixture, in a temperature swift mode in the 25–250 °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 ($\tan \delta$) vs temperature were recorded.

Results and Discussion

A way to monitor the occurrence of curing reactions is the temperature measurement of the system during irradiation.

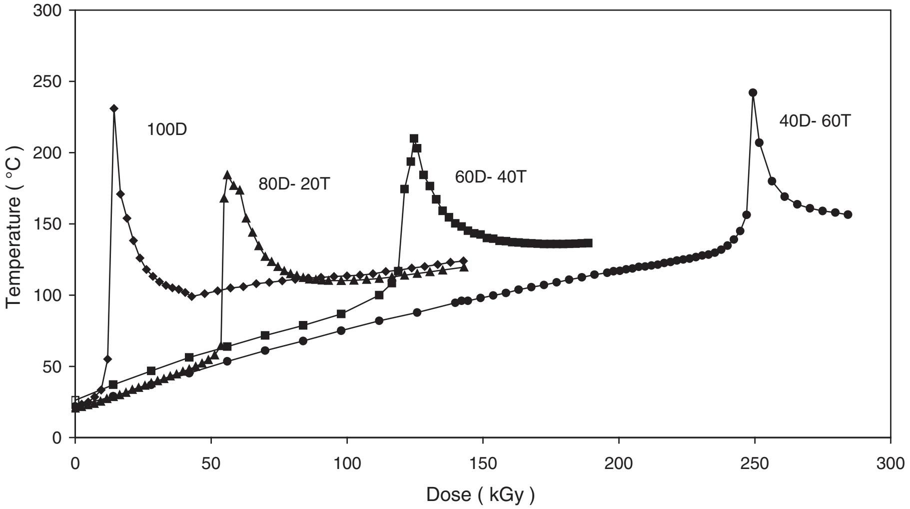

Figure 1.
Thermal profiles of blends at different difunctional/trifunctional ratios. D: DGBEF; T: Tactix.

In Figure 1 the temperature values as function of the irradiation dose for epoxy resin blends with different difunctional/trifunctional ratios are reported. As general behaviour, after the absorption of an induction dose, a temperature increase occurs, due to the exothermic effect of the polymerization reactions. Considering that the geometry of the irradiated system is always the same, and that the conditions of heat releasing can be considered essentially unmodified, the temperature profiles allow to compare the reactivity of the different irradiated systems. It can be observed that, increasing the Tactix concentration, the absorbed induction dose increases. The induction dose can be related to kinetics reasons; then it is reasonable that changing the system composition a modification of the activation energy can occur.[12] The different reactivity can be related to both the chemical structure and the diffusion phenomena due to the significant difference of the viscosity of the two epoxies.

According to the reduced reactivity, the presence of the trifunctional epoxy reduces the temperature increase, due to the polymerization reactions, with respect to the difunctional system.

For the further characterizations, samples polymerized at 150 kGy have been chosen. As evidenced by Figure1 the blend with 60% Tactix did not polymerise at this dose and it was not subjected to our investigation.

In Figure 2 DMTA spectra for all the polymerized blends are reported. Always tan δ/temperature curves present one relaxation peak, in correspondence to a flex in the storage modulus, whose correspondent temperature value can be related to the glass transition temperature of the material. This indicates that the polymerized resin has an almost uniform crosslinking degree, due to the contribution of the temperature increase simultaneous to irradiation. In fact it has been already observed that, if the system is irradiated at low temperature, a structure with a not-uniform crosslinking density is obtained with the presence of additional relaxation peaks at low temperature.[4]

Looking at the influence of the blend composition, increasing the Tactix content a marked increase of the glass transition temperature is obtained up to 230°C, according to the foreseeable positive effect of the trifunctional epoxy component on the crosslinking density.

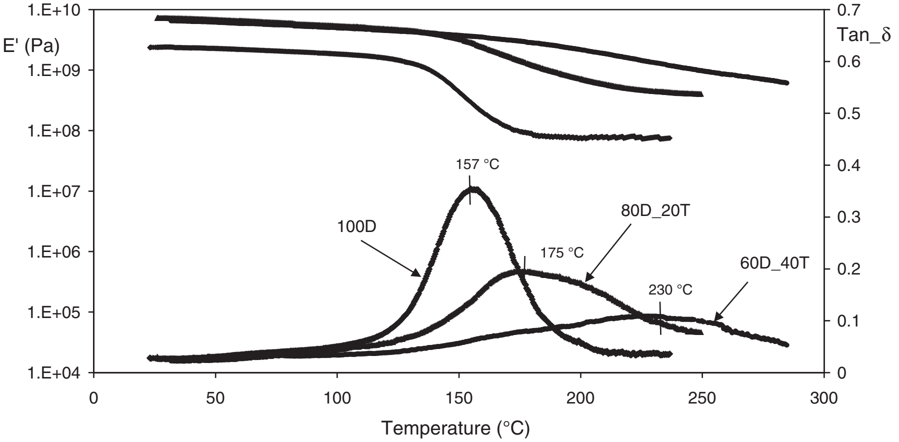

Figure 2.
DMTA analysis of cured blends at different difunctional/trifunctional ratios. D: difunctional; T: trifunctional.

The increase of the crosslinking degree is also confirmed either by the maximum tan δ values, that show a marked decrease with the Tactix content, or by the storage modulus both before and after the glass transition. In particular, in the rubbery region, the elastic modulus goes toward three different plateaux, which can be related to different average molecular weights between crosslinks.[13]

The influence of the toughening thermoplastic on the reactivity is shown in Figure 3 where the temperature profiles of the difunctional system and the 60/40% wt difunctional/trifunctional blend are compared with the correspondent systems containing 10% of thermoplastic.

A different effect of thermoplastic can be observed for the difunctional resin and for the blend. The adding of thermoplastic to the pure difunctional epoxy decreases the reactivity, as evidenced by both the increase of the induction dose and the decrease of the maximum temperature

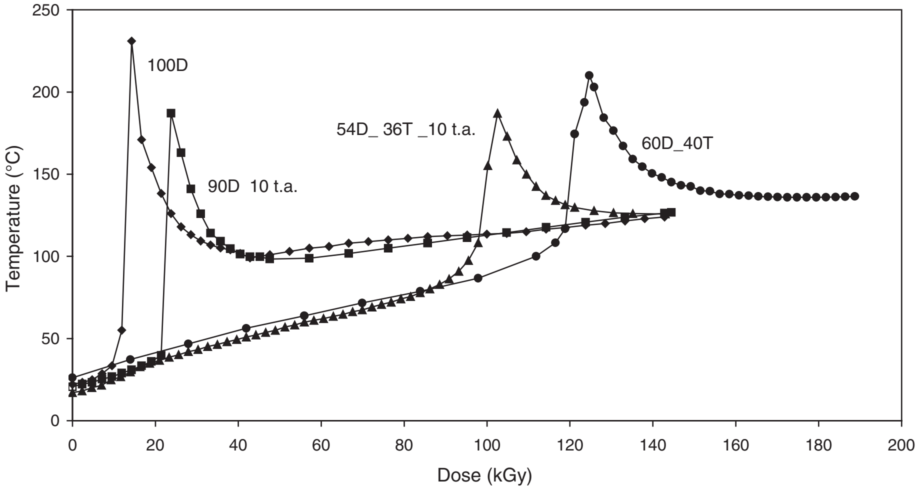

Figure 3.
Thermal profiles of toughened and not toughened systems. D: difunctional; T: trifunctional; t.a.: toughening agent.

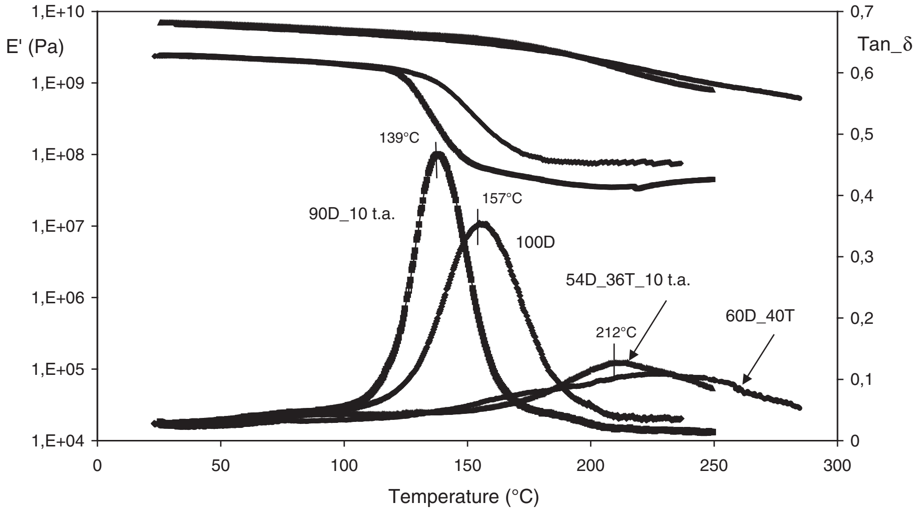

Figure 4.
DMTA analysis of cured toughened and untoughened blends at different bifunctional/trifunctional ratios. B: bifunctional; T: trifunctional; t.a.: toughening agent.

value reached when the polymerization reactions start. This could be related to a dilution effect of the thermoplastic on the epoxy groups and also to the increase of the viscosity of the resulting system.

On the contrary, for the difunctional/trifunctional blend, the introduction of the same content of thermoplastic increases the reactivity of the system. A possible explanation can be derived by the very high viscosity of the systems containing the trifunctional component. In fact, as said above, for these blends, before an appreciable starting of the polymerization reactions, revealed by the peak temperature, a large dose has to be absorbed that corresponds to a high temperature value in the thermal profile (about 100 °C). At this point of the process we can not exclude that some "pre-curing" reactions have already occurred with a consequent slight increase of the viscosity of these systems. In these conditions we can suppose that the use of the thermoplastic, having always a dilution effect, causes a lower extent of the "pre-curing" reactions, allowing the true polymerization to start after a shorter induction time, giving rise to a more reactive system with respect to that one without thermoplastic.

In Figure 4 the comparison of the dynamic mechanical thermal behaviour for the toughened and not toughened systems is reported. In agreement to the already discussed dilution effect due to the presence of the thermoplastic component, either in the difunctional epoxy or in the difunctional/trifunctional epoxy blend, the adding of the thermoplastic gives rise to a decrease of the glass transition temperature and to an increase of the maximum tanδ value, corresponding to a less crosslinked structure.

Conclusions

Radiation curing is an alternative way to the more traditional thermal processes in order to produce epoxy resin based matrices for advanced composites, for aerospace and automotive applications.

In order to increase the glass transition temperature, blends of difunctional and trifunctional epoxy resins have been polymerized. The results indicate that a strong Tg increase can be obtained, thus satisfying very well the severe requirements for the above mentioned applications.

In order to obtain materials at high fracture energy a high Tg and high modulus thermoplastic has to be considered, especially in the presence of a trifunctional component because of the markedly increase of the crosslinking density reached.

For this purpose in the second part of this work the influence of a thermoplastic component, on the reactivity and on the thermal behaviour of the obtained materials blends, has been studied. The results indicate that the thermoplastic increases the reactivity, with a reduction of the induction dose. Moreover the values of the glass transition temperature still satisfy the requirements for advanced applications.

[1] R. J. Woods, A. K. Pikaev,in: ''*Applied Radiation Chemistry. Radiation Processing*'', Wiley, New York, **1994**.

[2] A. Singh, J. Silvermanin: ''*Radiation Processing of Polymers*'', Hanser, **1992**.

[3] A. Singh, C. Saunders, V. J. Lopata et al., *Radiation Phisics and Chemistry* **1996**, *48*, 153–170.

[4] S. Alessi, E. Calderaro, A. Parlato, P. Fuochi, M. Lavalle, U. Corda, C. Dispenza, G. Nuclear, *Instruments and Methods in Physics Research B* **2005**, *236*, 55–60.

[5] J. V. Crivello, *Nuclear Instruments and Methods in Physic Research B* **1999**, *151*, 8–21.

[6] J. V. Crivello, *Radiation Phisics and Chemistry* **2002**, *63*, 21–27.

[7] Janke, R. D. Lomax, V. J. Lopata et al., *International Symposium SAMPE* **2001**.

[8] H. Degrand et al., *Radiation Phisics and Chemistry* **2003**, *68*, 885–891.

[9] L. Fengmei, B. Jianwen et al., *Radiation Phisics and Chemistry* **2002**, *63*, 557–561.

[10] G. Sui, Z. G. Zhang et al., *Materials Chemistry and Phisics* **2002**, *78*, 349–357.

[11] P. Fuochi, M. Lavalle, Proceedings of the Workshop RADECS **2002**, 19-20 September, Padova, Italy 209–212.

[12] U. Bulut, J. V. Crivello, *Macromol.* **2005**, *38*, 3584–3595.

[13] P. J. Flory in: ''*Principles of Polymer Chemistry*'', Cornell University Press, Ithaca, New York **1953**.