Radiation Processing for Synthesis of Structural Materials

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Abstract. Radiation processing has given rise to more and more interest in the production of structural materials because of the several advantages that it can offer. Besides the economic considerations, concerning energy saving due to the short processing times, radiation curing provides a non thermal process way, thus reducing mechanical stresses in the final product. Considering that radiation curing can cause an increase of temperature, due to both the exothermic polymerization reactions and the absorption of radiating energy, depending upon process and system parameters, a right choice of operating conditions has to be done in order to obtain the thermal profile which could provide the desired final properties. In this work epoxy resins based blends, for use as matrices for advanced composites, have been cured by electron beam with a moderate temperature profile. The samples cured in different operating conditions, including a post irradiation thermal treatment out of the mould, have been characterized by both DMTA analysis. The results, discussed also in the light of the morphological analysis investigated by SEM, indicate that the required properties for such applications (in terms of Tg) can be achieved by a dual cure process consisting of irradiation at moderate temperature followed by a slight thermal treatment in order to overcome vitrification effects due to the low temperature during irradiation.

1. Introduction

Ionizing radiation induced synthesis of structural materials is an alternative way to the more traditional thermal processes. In spite of both the capital investment and the safety procedures for its use, radiation curing offers several advantages. Among others the most attractive factor is that radiation curing can be started at room temperature with several positive consequences such as energetic costs saving, the use of low cost mould materials and the improvement of mechanical properties of the cured materials due to the reduced residual thermal stresses. Furthermore radiation curing, conversely to thermal curing, does not need the use of toxic hardeners but only the presence of a very small quantity of acidic salt as initiator. This fact, together to the reduced volatile emission caused by the use of low temperatures, makes radiation curing an environmentally friendly process. Other advantages are the great flexibility of the process, in terms of both shape and curing degree of the sample, and the short curing times [1].
Nevertheless during radiation curing the temperature of the system can undergo to a significant increase due to the occurring of both exothermic polymerization reactions and radiation absorption. The extent of this phenomenon depends, for fixed components and geometry of the mould, on the component ratio and on the rate by which the energy is provided to the sample, that is the irradiation dose rate of the process [2]. The occurrence of a not expected heating causes a simultaneous thermal curing during irradiation, invalidating the beneficial effects coming out from a not thermally activated process.
Composite matrices for advanced applications are required to show at the same time high toughness, high thermal resistance (high glass transition temperature) and high stiffness. In order to satisfactorily achieve all these characteristics, epoxy resins-thermoplastics mixtures are generally used in which the epoxy components give the stiffness and the thermal resistance and the thermoplastics promote the toughening of the matrices through separation phase phenomena.

In particular matrices for advanced composites, cured by ionizing radiation, generally suffers from poor fracture toughness. This mechanical property can be enhanced by the introduction of engineering thermoplastics, having both high elastic modulus and high Tg, but it is significantly affected by the morphology and by the distribution of residual stresses in the material. Starting from an "homogeneous" blend, the occurring of separation phase phenomena between the resin and the thermoplastic gives rise to a specific morphology whose characteristics determine the distribution of stresses in the material and hence its fracture mechanisms [3,4,5]. To this regard the study of the morphological structure of these systems is essential and, considering that the morphology results not only from the components nature and their ratio, but also from the process, it is evident that a great effort has to be devoted to the individuation of the optimal parameters governing the process. It is well known from literature, concerning thermally cured epoxy systems, that co-continous type morphology at a nano-micro metric scale is very effective in improving fracture toughness, but the design of a material having specific mechanical features, tailored for specific applications, is not easy to perform, especially when several parameters are introduced in the process, such as in the case of radiation curing [6].
In addition to this problematic it has to be considered that all the properties of the cured materials, whatever the curing process used, should remain acceptable during service. In fact for structural applications a very important issue is the long-term performance of such materials under exposure to various environmental conditions during their operating life. Thermal excursion and water absorption are the most common and the most critical environmental conditions, with respect to aging, for aeronautic and automotive applications. It is well recognized that generally polymer matrix composites suffer substantial losses in their properties under cycle thermal excursions and moisture/solvents absorption-desorption [7]. For thermally cured materials several studies are reported in literature, where effects of hydrothermal induced aging are investigated [8], while there are not similar extended studies for radiation cured materials.
In this work the main results achieved in the study of radiation curing of epoxy-thermoplastic blends are presented. In particular the influence of process parameters and formulations on the structure, morphology and properties of materials are reported.

2. Experimental

The epoxy resin was Bis(4-glycidyloxyphenil) methane (DGEBF) supplied by Aldrich. The thermoplastic toughening agent was a polyether sulfone based polymer, Mw 10000, and the initiator was an onium salt, Cumyltolyliodonium tetra(pentafluorophenil) borate, supplied by Rhodia Silicones.
Blends were prepared mixing the thermoplastic with the epoxy resin at 80°C for 2 hours. Then, after cooling at 60°C, the initiator was added. System with 10 phr of thermoplastic and with 1 phr of salt were prepared. E-beam irradiation has been carried out in closed steel moulds (150x150x4mm) at the ISOF-CNR laboratory in Bologna with the 12-MeV Vickers type linear accelerator [9]. The irradiation dose was 80 kGy and the dose rate 90-103 kGy/h. During irradiation the temperature inside the sample has been recorded through a thermo resistor connected to a computer. Post irradiation thermal curing has been carried out at 100°C for 2 hours.
Thermal behaviour has been studied by dynamic mechanical thermal analysis (DMTA) through a Rheometrics DMTA V apparatus, equipped with a three point bending fixture, in a temperature swift mode in the 25-300 °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 morphology of the cured materials has been analysed by a scanning electron microscopy (SEM: Philips 505). The surfaces have been etched in super-acid solution and then gold coated.

3. Results and discussion

Radiation curing of epoxy based blends can be started at room temperature but their temperature during irradiation can increase, due to either the exothermic polymerization reactions or the energy absorption, up to significant levels. For this reason a monitoring of the temperature inside the sample is always advisable.
In Fig. 1 the thermal profile of samples, consisting of the epoxy resin and the thermoplastic, are reported against the irradiation dose for two different dose rate values. It is noticeable that a slight increase of the dose rate causes a well evident enhancement of the temperature. In any case, starting from room temperature, the system undergoes toward a heating after an induction dose that is higher at higher dose rate. The effect of the dose rate on the induction dose, as already discussed in our previous works [2,10], is related to the presence in the system of the impurities whose consumption, through chemical reactions, needs a finite time to be carried out, corresponding to different dose values. The extent of the heating of the system depends, for fixed geometry and formulation, on the rate of reactive species production, that is the process rate, and hence higher the dose rate, higher the heating. The thermal profile, after a peak temperature, tends toward a plateau, whose value is strongly dependent on the heating due to the absorption of radiating energy, that is higher at higher dose rate. The system irradiated at higher dose rate is therefore subjected to a proper thermal treatment simultaneous to radiation with not positive consequences on the material properties and on the overall costs of the process. Similar thermal effects have been also evidenced in epoxy systems increasing the initiator concentration, because also in this case the rate of production of reactive species increases [2].

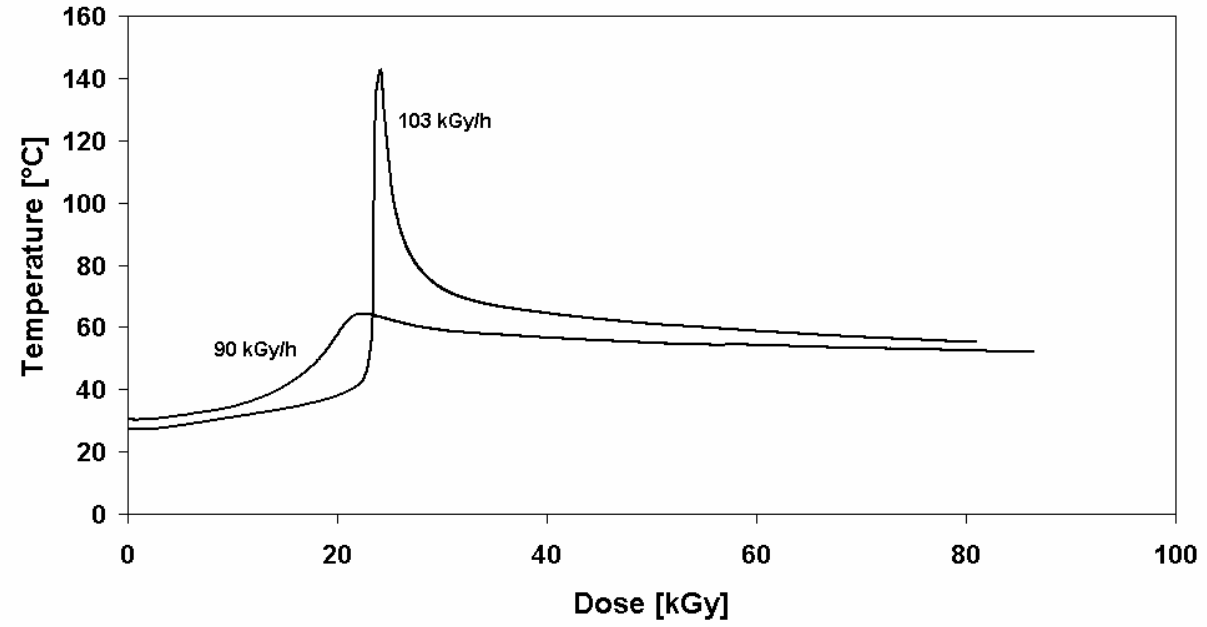


FIG. 1. Thermal profiles of toughened systems obtained during irradiation.

Our previous studies on radiation cured epoxy resin systems have pointed out that the optimal way to obtain advanced materials through irradiation consists in the use of a not very high rate of the process, choosing a compromise between the dose rate and the initiator concentration, followed by a mild thermal treatment out of the mould in order to complete the polymerization reactions.
In Fig. 2 tanδ curve from DMTA analysis performed on the sample irradiated with the lower thermal profile of Fig.1 is reported. The curve shows the characteristic presence of more than one relaxation peak which attests the formation of clusters having different crosslinking densities. This effect is related to vitrification phenomena due to the temperature profile during irradiation which soon becomes lower than the glass transition temperature of the forming crosslinked agglomerations, making the reactions controlled by diffusion of the reactive species [11]. We cannot exclude that the second relaxation peak is also due to the thermal curing related to the analysis itself, since the elastic modulus curve, reported in the same figure, shows an increase after the first tand peak. The occurring of a thermal treatment after irradiation in fact induces mobility in the formed molecular chains, favouring the curing reactions which lead to a denser network, having a higher Tg. For this reason a post irradiation thermal curing is always recommended on such samples. Moreover this treatment is performed on already solid samples and hence out of the mould, avoiding thermal stresses in the material.

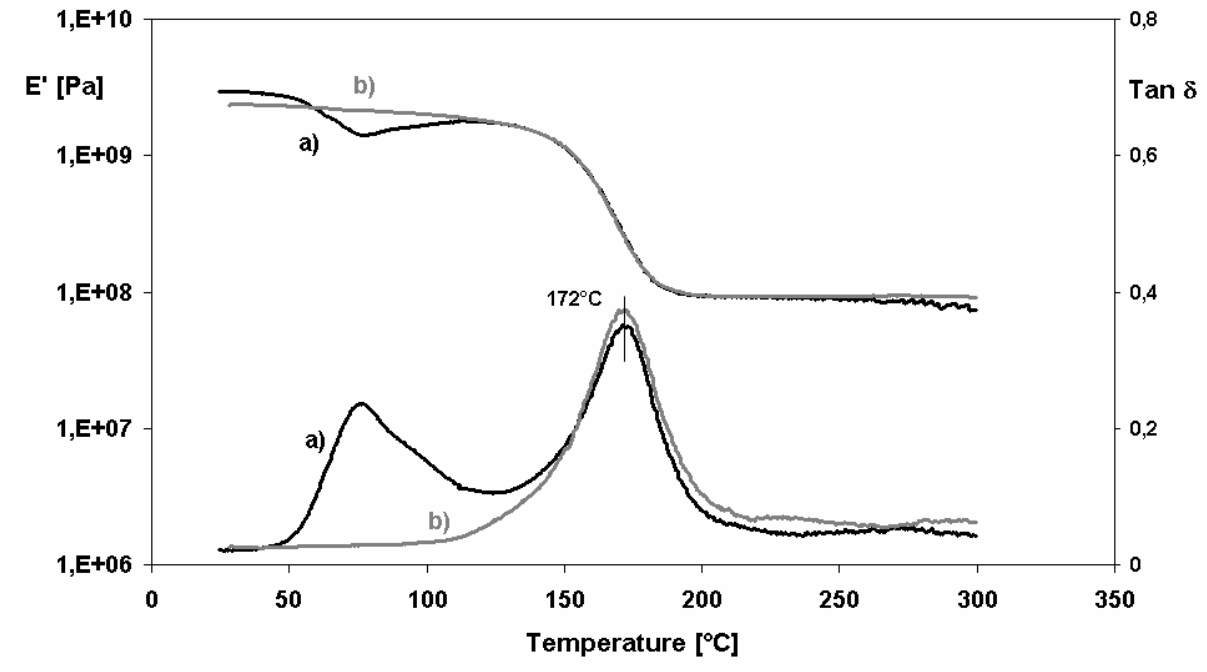
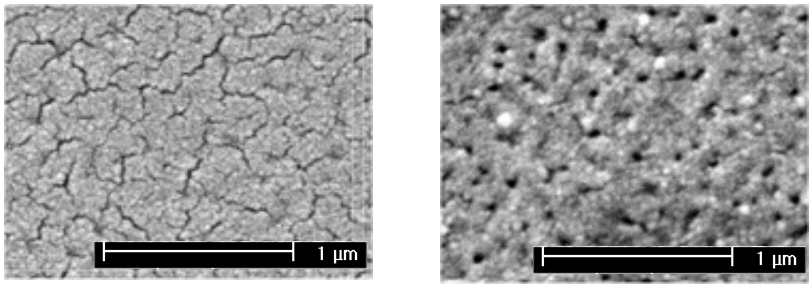


FIG. 2. DMTA of toughened systems. a) irradiated; b) post irradiation thermally cured.

The tanδ curve related to the post irradiation thermal treatment is reported in the same Fig.2.It is well evident the disappearance of the first relaxation peak and the presence of only one peak at a high temperature. This value is correspondent to the second peak of the only irradiated sample that is an acceptable value for structural applications. The peak correspondent to the thermoplastic, having a Tg of about 220°C, is not evident in both tanδ curves, indicating that the two phases, epoxy and thermoplastic, are intimately distributed in the sample.

Morphological analysis results are shown by micrographs reported in Fig.3a,b. The irradiated sample shows a "homogeneous" morphology in which the dark lines are cracks related to the surface gold layer used for the analysis.



a) b)

FIG. 3. SEM micrographs of toughened systems. a) irradiated; b) post irradiation thermally cured.

The not presence of separation phase phenomena can be related to the low process temperature, in correspondence of which is present a single phase in the phase diagram. On the contrary the micrograph for post irradiation thermally cured sample show a sea island type morphology at nanoscale due to the phase separation phenomena induced by temperature increase.

4. Conclusions

In this work radiation curing of epoxy-thermoplastic blends for structural composites polymer matrices is described. On the basis of previously reported results irradiation conditions have been chosen in order to have mild temperature processing conditions.
The corresponding thermal analysis shows the presence of cluster having different network densities. The post-irradiation thermal treatment allows an "homogenization" of the structure, as revealed by just one relaxation peak at high temperature.
Finally, morphological investigation evidences the formation of a single phase after radiation curing, followed by a nano-scale separation after thermal treatment.

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