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Irradiation and annealing effects on delamination toughness in carbon/epoxy composite

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ABSTRACT

Gamma irradiation to various doses (4.8–27.2 MGy) was performed on unidirectional carbon fiber/epoxy resin composite plates. Unidirectional composite coupons irradiated to various doses were annealed at 180 and 250 °C, in vacuum. The strain energy release rate G_{IC}, as a measure of delamination fracture toughness, was determined by Mode I fracture testing on double cantilever beam coupons. The glass transition temperature (T_g) of the tested coupons matrices was determined in DMA tests. The effects of irradiation and annealing on G_{IC} values – the mean values of 10 propagation points ($G_{IC,mean}$) and that of fracture initiation ($G_{IC,init}$) – were established. These values were analyzed as a function of irradiation dose and annealing temperatures, having in mind glass transition temperature values changes, as well as the possible mechanisms and phenomena of irradiation and annealing.

1. Introduction

Delamination is one of the major fracture modes of many advanced laminated composite structures. Therefore, better understanding of the laminates delamination resistance is very useful for structural design and development of the materials. In continuous fibers reinforced plastics the value of delamination critical strain energy release rate G_{IC} is used as a measure of the fracture toughness. Mode I double cantilever beam (DCB) test is commonly used for determination of G_{IC} values [1–4]. Pereira and de Morais [3] and Brunner et al. [4] devoted special attention to the phenomenon of fiber bridging and its effects on calculated G_{IC} values. Pereira and de Morias [3] ascertained that when the pronounced fibers bridging takes place during crack propagation in DCB Mode I test, it significantly increases the $G_{IC,mean}$ values. In these circumstances, Pereira and de Morias recommended the use of $G_{IC,init}$ values of the crack initiation from the film generated starter crack as the only true interlaminar properties. Moreover, they found $G_{IC,init}$ to be fairly independent of the delaminating interface.

The increased polymer matrices composite (PMC) industrial applications involving high radiation fields (such as adhesives, structural composite matrices, coating of nuclear waste, parts of structures in nuclear power plants environment, airplane and space-crafts, sterilization irradiators and accelerators) made the knowledge of the resin radiation induced aging indispensable.

A lot of data on irradiations and less on annealing effects on mechanical (dominated by matrix or by fiber/matrix interface) and thermo-mechanical properties of carbon fiber reinforced epoxy resin are present in this literature. The effects are known for many different cases, but the doubts remain about the dominating mechanisms of the phenomena. The changes in the properties of polymeric materials caused by ionizing radiation have been mainly ascribed to the chemical reactions, like chain scission and/or formation of cross links [5,6]. It has been suggested that the real situations connected with radiation effects on PMC are, however, far more complex, due to high sensitivity of the matrix to its environment (oxygen) and to the resin system composition (antioxidants, additives, plasticizers, processing agents, etc.) [5]. Milkovich and Herakovich [6] pointed out, too, that the radiation degrades the in-plane elastic and strength properties by increasing the plasticity of the epoxy matrix, more at elevated than at lower temperatures.

During the study of radiation and post-irradiation annealing effects, many authors followed the changes of glass transition temperature T_g, by linking them to chain scission to explain both the degradation improvement of properties. For low temperature epoxy resin, irradiation to high doses can increase the T_g, while at low doses (2.0–5.0 MGy) T_g decreases. Annealing at temperatures close to, but lower than T_g, increases the glass transition temperature [7,8]. Egusa et al. [9] performed the irradiation up to 20.0 MGy and the subsequent annealing in vacuum, for 2 h at 180 °C, on cloth-filled organic composites, including carbon/epoxy PMC. After annealing of coupons irradiated to higher doses, they

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observed the degradation of the matrix and fiber/matrix dominated properties.

The data concerning of the radiation and annealing effects on fracture propagation in carbon/epoxy composites, are unreliable [9] and scarce. Hummer et al. [10] reported that both specific energies released in the crack opening and in interlaminar shear mode initiation, in glass fiber PMC, measured at 77 K, show the degradation after gamma irradiation at 77 K, up to 0.18 MGy dose. The degradation is slightly intensified when the irradiated samples were subjected to warm-up cycles at room temperature, before testing at 77 K.

To the best of our knowledge the only data on irradiation effects on interlaminar strain energy release rate, determined according to ISO standard method, are those presented by the authors of this paper recently [11].

In the frame of this study, the effects of irradiation to the doses from 4.8 to 27.2 MGy, and subsequent annealing under vacuum at temperatures below (180 °C) and above (250 °C) of the matrix glass transition temperature are studied. The Mode I delamination strain energy release rate of unidirectional composite (UDC) was tested at room temperature, before and after irradiation and annealing.

The variations of G_{IC} values with irradiation and annealing were correlated with irradiation doses and glass transition temperature values. The observed effects on G_{IC} values were explained by concurrent mechanisms and phenomena: chain scission or cross-linking, gas products formation and evacuation, changes of matrix plasticity or changes in fiber/matrix interface ability to transfer the load. In assessing the dominating mechanisms of irradiation and annealing changes, the $G_{IC,init}$ values of crack initiation from the film generated starter crack were included into consideration, too.

2. Experimental

2.1. Materials

The laminated plates were prepared from a unidirectional high strength carbon fiber (Twaron HTS/epoxy prepreg, commercially available under the trade name HexPly 6376 NCHR), supplied by Hexcel. The epoxy resin was a tetraglycidyl-*p*-aminophenol derivative of metilenedianiline. The plates were prepared by hot (175 °C) platen pressing, according to the processing conditions recommended by the supplier. The laminate sheets of the composites before and after irradiation were cut into coupons of appropriate shape and dimensions for testing of Mode I crack propagation as the DCB.

2.2. Irradiation, annealing and tests

The ^{60}Co γ-ray irradiations, up to the doses of 4.8–27.2 MGy, were conducted in air, at ambient temperature, with a dose rate of 12.0 kGy/h. Some part of the tested none irradiated and irradiated coupons were annealed for 2 h, under vacuum, at the temperatures of 180 and 250 °C.

The double cantilever specimens (Fig. 1) were cut from the plates with nominal dimensions (3.6 × 25.0 × 125.0 mm). A 13.0-μm thick PTFE film was used to generate the starter crack. Piano hinges were glued to the specimens for load transmission. The procedures followed current ISO 15024 standard guidelines. Both lateral edges of specimens were coated with the white paint (the typewriter correction fluid) and several marks were made to facilitate the monitoring of crack position. The specimens were dried at 75 °C for 24 h and then stored in desiccators for 24 h before testing.

The DCB test was performed on a Universal Testing Machine INSTRON M 1185, at a crosshead speed of 1.0 mm/min, at room temperature and atmospheric pressure. The force and displacement signals of the testing machine were recorded on the chart recorder. The delamination length was measured visually on the specimen edges. The point, at which the onset of delamination movement from the starter film occurred on the edge of the specimen, was marked on the force–displacement curve. The pre-crack loading was stopped at a delamination length increment of 5.0 mm. The position of the pre-crack tip was marked on both edges of the specimen, after unloading. In these tests the strain energy release rate G_{IC} values were determined before and after gamma irradiation to various doses, as well as after thermal treatments.

The data processing was carried out according to Method B of ISO 15024 standard. The critical energy release rate G_{IC} was calculated by the following equation

$$G_{IC} = \frac{3m}{2(2h)}\left(\frac{P}{B}\right)^2 (\delta \cdot C)^{2/3} \quad (1)$$

where P is the load, δ is the opening displacement, B is the specimen width, and $2h$ is the specimen thickness. The compliance C is equal to δ/P and m represents the slope of $(bC)^{1/3}$ versus $a/2h$ plot. The G_{IC} values for none irradiated, irradiated and annealed coupons were presented as the mean values from 10 different propagation distances ($G_{IC,mean}$) (Figs. 3, 4 and 6–8). Their standard deviation is measure of span between the G_{IC} values of the onset and the end of crack propagation, as it can be seen from R curves (Figs. 4 and 6). The G_{IC} values of every 10 propagation points were calculated as mean values from data obtained on five tested coupons and their coefficient of variation (CV) is a measure of the measurement precision and homogeneity of tested materials.

Mean CV for the G_{IC} values of all propagation points of tested coupons was 7.2 ± 3.9%. Besides the $G_{IC} = G_{IC,mean}$ values, the

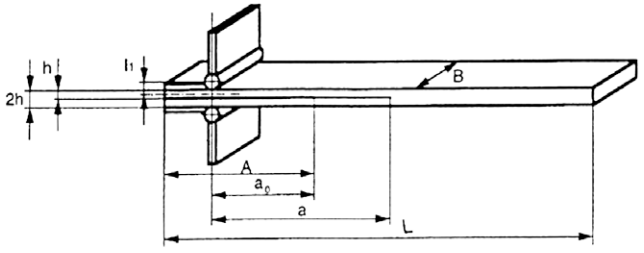

Fig. 1. Geometry for the DCB specimen with PTFE insert (doted line) as a starter of delamination and with piano hinges for load introduction. B is the specimen width, a_0 is the initial delamination length, A is the insert length, l_1 is the distance from centre of piano hinge axis to mid-plane of specimen, $2h$ is the specimen thickness, a is the total delamination length and L is the specimen length.

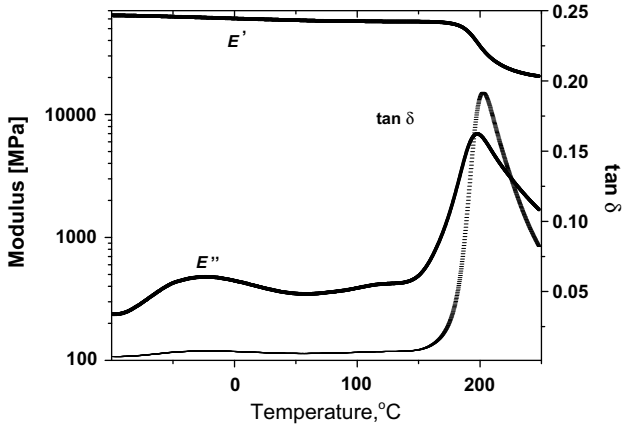

Fig. 2. Characteristic DMA diagram of tested coupons: storage modulus – upper line, loss modulus – middle line and tan δ – the lowest line.

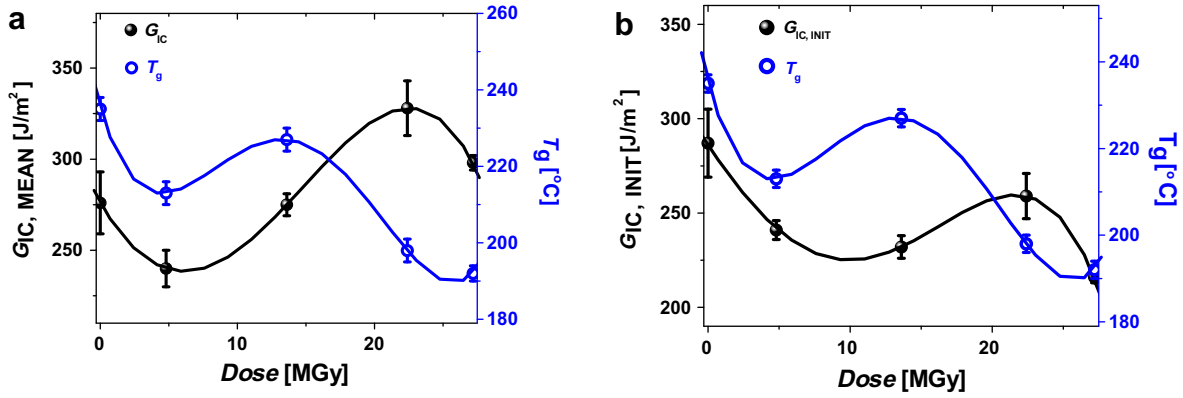

Fig. 3. T_g and G_{IC} versus dose plot of (a) present study and (b) previous results [14].

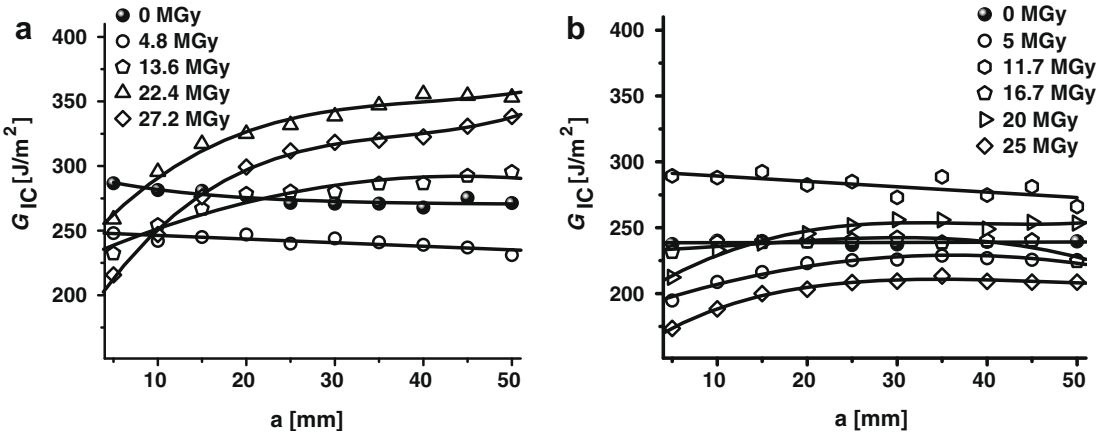

Fig. 4. *R* curves of (a) present results and (b) previous results [14].

$G_{IC,init}$ values of crack initiation from the film generated starter crack, were determined and included into consideration during the assessment of the mechanisms responsible for change of properties during the irradiation and annealing (Figs. 5, 7 and 8). Mean CV for the $G_{IC,init}$ values of all tested coupons was 6.3 ± 3.9%.

The diagrams with related calculations were drawn in Origin 7.5. Last one includes a standard error of determination of G_{IC} from n measurements s_{ERR} (J/m^2), via relation

$$s_{ERR} = \frac{\sigma}{\sqrt{n}} \tag{2}$$

This relation is valid for Gaussian normal distribution of statistical errors. The G_{IC} values for every point of crack propagation, from pre-crack tip to the propagation end were calculated from measurements on five coupons. Symbol σ is the standard deviation of these measurements.

The matrix glass transition temperature values (Figs. 3, 5, 7 and 8) were determined by DMA in the single cantilever mode using multi-frequency 2980 dynamic mechanical analyzer from TA instruments, (New Castle, DE), at frequency of 10.0 Hz. The tests were performed in the temperature range −100 to 250 °C and the storage modulus, loss modulus and tan delta curves were recorded. The matrix glass transition temperature was deduced from the position of alpha (highest temperature) peak on the loss modulus curve (Fig. 2).

3. Discussion

3.1. Irradiation effects

By comparing our present and previous [11] results one can observes the differences in T_g and G_{IC} properties values (Fig. 3), in spite of the fact that the supplier for both prepregs was the same. The conditions of curing were identical, but all T_g values of none irradiated and irradiated coupons are remarkably higher in new UDC (Fig. 3(a)). The G_{IC} mean values of UDC, obtained with the older prepreg [11], are lower (Fig. 3(b)) and have lower standard deviation. Different T_g values for the tested UDC obtained from two Hex Ply NCHR prepregs, both based on the tetraglycidyl-*p*-aminophenol derivative of metilenedianiline, can be ascribed to the different resin systems composition or to different degree of prepreg ageing. These composition differences are not available, because the producers treated them as confidential information.

From the G_{IC} versus dose plots (Fig. 3), one can say, at first sight, that the shapes of G_{IC} – dose curves of two groups (current and previous) are similar. Both curves have minimum at a low dose (around 5.0 MGy), followed by the increase of mean G_{IC} values up to the maximum, and a steady G_{IC} decrease afterwards. The peak on the curve obtained from previous results appears at lower doses (11.6 MGy) (Fig. 3(b)), comparing to present results (22.4 MGy), which show a less steep rise toward maximum G_{IC} value. By following the variation of T_g and G_{IC} with dose at the same time (Fig. 3), it is easy to see that irradiation behaviour of two UDC

is not the same. In the previous study, the sign of T_g and G_{IC} changes during irradiations was the same for all the doses (minus–plus–minus) (Fig. 3(b)), while in this study it is not the case. The effect of gamma irradiation dose on T_g and G_{IC} values, as shown in Fig. 3(a), demonstrates a decrease of both properties at a low dose (4.8 MGy). The measured T_g values follow the trend of G_{IC} change with the rising irradiation dose up to the dose of 13.6 MGy. After this dose, the proportionality between G_{IC} and T_g values ceases – at 22.4 MGy a decrease of T_g corresponds to the increase of G_{IC}. This rise of the mean G_{IC} values with the increasing irradiation dose, followed by T_g values decrease, could be ascribed to the increase of matrix plasticity and consequently to a higher contribution of plastic deformation to the crack propagation. The same was concluded by Reis and Ferreira [12] during their study of freeze-thaw and thermal degradation influence on the fracture properties of carbon and glass fiber reinforced polymer concrete.

The shape of *R* curves of the two groups of tested coupons, the present one and that studied before [11], both presented in Fig. 4, differ a little for the lowest irradiation doses.

The differences exist at higher doses, but they are significant only in the shape of *R* curve (Fig. 4(b)) of coupons irradiated up to 11.7 MGy. This delamination resistance curve is atypical (according to the criteria given in the ISO 15024 standard) by displaying decreasing resistance to crack propagation with the growth of delamination length. The *R* curves for other irradiated coupons are typical, showing the increasing delamination resistance with the increase of delamination length.

It is evident from the *R* curves (Fig. 4(a) and (b)) that the span between G_{IC} values at crack initiation ($G_{IC,init}$) and at the end of crack propagation ($G_{IC,end}$), for coupons irradiated to a higher doses, is large enough. According Pereira and de Morais [3], it means that the *R* curves of coupons irradiated with the doses higher than 13.6 MGy, are influenced by the pronounced fibers bridging. By the way, pronounced fibers bridging is visible by a macroscopic observation of cracked surfaces of these coupons. At the same time, it means that the $G_{IC,mean}$ values are increased due to the fibers bridging as well.

By comparing the T_g–$G_{IC,mean}$ and T_g–$G_{IC,init}$ plots, it can be stated for previous results that the decrease of $G_{IC,init}$ is more evident than for $G_{IC,mean}$ at the doses of 16.7 and 20.0 MGy (Figs. 5(b) and 3(b)). The contribution of the fiber bridging effect to the $G_{IC,mean}$ values was the reason for this statement. Due to the same reason, the peak $G_{IC,mean}$ value in the current study is higher, and $G_{IC,init}$ value (both for the dose of 22.4 MGy) (Figs. 3(a) and 5(a)) is lover than the corresponding values of none irradiated coupons. During our former study of irradiation effects, both peak values (for the 11.6 MGy dose) were higher than the corresponding values of none irradiated coupons (Figs. 3(b) and 5(b)). However, this can be explained by the fact that the irradiation at the dose of 11.6 MGy [11] was carried out at four times lower gamma ray flux. This explanation agrees with the conclusions in Refs. [13,14].

Concerning the present results, after irradiation with the dose of 4.8 MGy all $G_{IC,mean}$, $G_{IC,init}$ and T_g values decrease (Figs. 3(a) and 5(a)). At doses equal and higher than 13.6 MGy, due to the lack of crack propagation contribution, all $G_{IC,init}$ values are lower than the corresponding $G_{IC,mean}$ values. After dose of 13.6 MGy the increase of T_g is followed by $G_{IC,mean}$ value increase and $G_{IC,init}$ value decrease. The irradiation up to 22.4 MGy dose causes the decrease

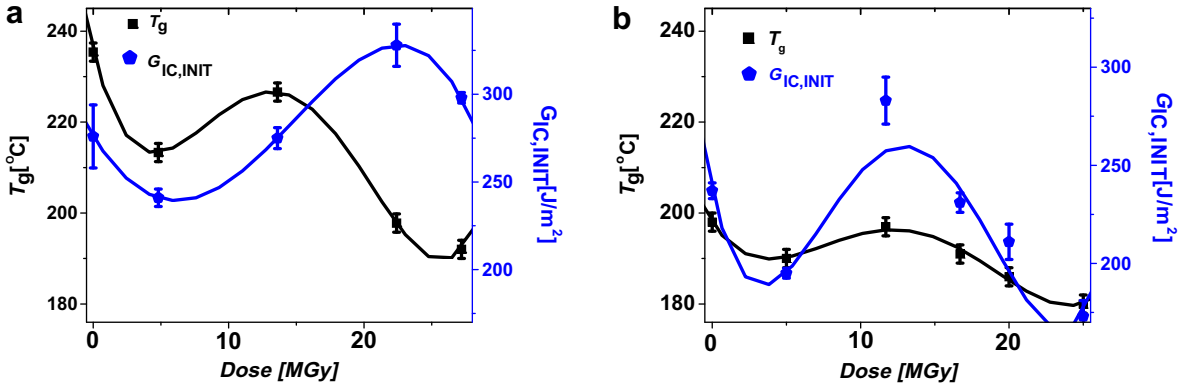

Fig. 5. T_g and $G_{IC,init}$ versus dose plot of (a) present study and (b) previous results [14].

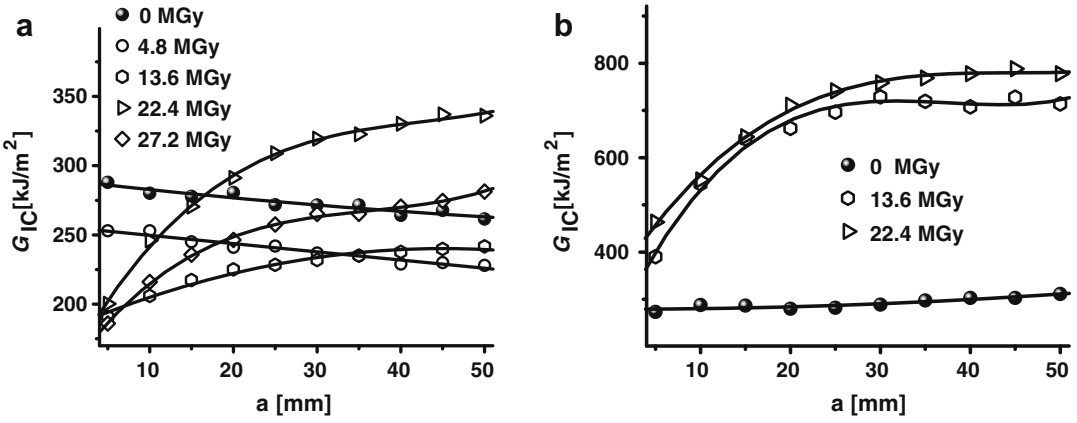

Fig. 6. *R* curves for annealed coupons: (a) at 180 °C and (b) at 250 °C.

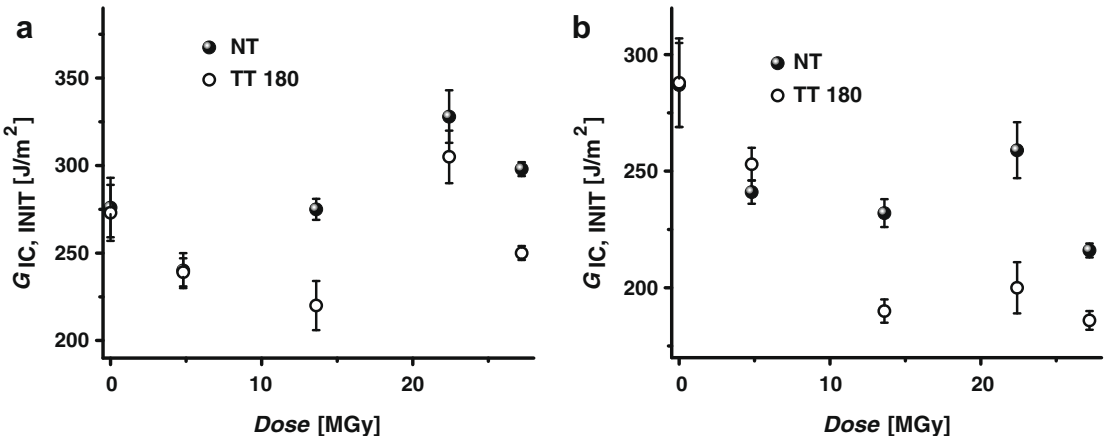

Fig. 7. $G_{IC,mean}$ (a) and $G_{IC,init}$ (b) values as function of irradiation dose before and after performed annealing at 180 °C.

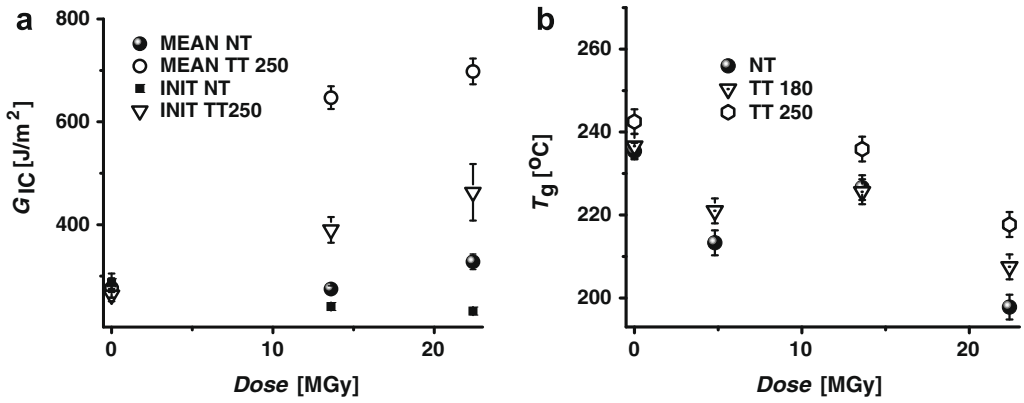

Fig. 8. G_{IC} (a) and T_g (b) values as function of irradiation dose before and after performed annealing.

of T_g and the increase of $G_{IC,init}$ value. The irradiation dose of 27.2 MGy causes again the decrease of all three $G_{IC,init}$, $G_{IC,mean}$ and T_g values (Figs. 3(a) and 5(a)). For the doses 4.8 and 27.2 MGy it can be safely stated that the chain scission under irradiation is the dominant mechanism responsible for all properties changes. However, for 13.6 and 22.4 MGy doses it is not possible to say that the change of $G_{IC,init}$ value is the consequence of either the chain scission or cross-linking only. The dominating mechanism responsible for this change of $G_{IC,init}$ is ascribed to the matrix plasticity variation, i.e., the decrease of plasticity for 13.6 MGy and increase for 22.4 MGy dose.

3.2. Annealing effects

From *R* curves of the annealed coupons (Fig. 6) one can see that the curve slope from $G_{IC,init}$ to $G_{IC,max}$ is high for higher irradiation doses. It means that contribution of the fiber bridging to the rise of $G_{IC,mean}$ values is evident as well. It was the reason why our attention was directed to a dose variation of annealed $G_{IC,mean}$ and $G_{IC,init}$ value.

The annealing at both temperatures (180 and 250 °C) carried out after irradiation to doses higher than 4.8 MGy, caused a variation of $G_{IC,mean}$ values. After annealing for 2 h in vacuum, at 180 °C (TT 180 °C) (Fig. 7(a)), the $G_{IC,mean}$ values of none irradiated (NT) and samples irradiated at 4.8 MGy are the same as before annealing (Fig. 7(a)). The coupons irradiated at higher doses have lower $G_{IC,mean}$ after annealing at 180 °C than before. However, the $G_{IC,mean}$ error bars for coupons irradiated up to 22.4 MGy before and after annealing are overlapping (Fig. 7(a)).

The coupons irradiated at 13.6 and 22.4 MGy have significantly higher $G_{IC,mean}$ (Fig. 8(a)) and T_g values after annealing in vacuum, for 2 h, at 250 °C (TT 250), than before annealing (Fig. 8(b)).

The change of $G_{IC,mean}$ with annealing does not have the same sign as that for T_g in case of the annealing at 180 °C: the coupons irradiated at 4.8 MGy have the same $G_{IC,mean}$, and a higher T_g values after annealing (Fig. 8(b)). Samples irradiated at 13.6 MGy have equal T_g and a lower $G_{IC,mean}$ values after annealing (Figs. 7(a) and 8(b)). For higher doses, during 180 °C annealing, the decrease of $G_{IC,mean}$ values is followed by the increase of T_g (Fig. 8(b)).

The $G_{IC,mean}$ increase during 250 °C annealing, could be attributed to cross-linking. However, the $G_{IC,mean}$ values changes due to annealing at 180 °C, cannot be connected directly to the processes like chain scission or cross-linking only.

As expected, all $G_{IC,init}$ values after the annealing are lower than those for $G_{IC,mean}$. The ratio between the $G_{IC,init}$ before and after annealing at both temperatures is the same as for $G_{IC,mean}$ values (Figs. 7 and 8). After annealing at 180 °C, for irradiation dose equal or higher than 13.6 MGy (Fig. 7(b)), $G_{IC,init}$ values are considerably lower than before annealing and any overlaps of the error bars was not observed (Fig. 7(b)). The effect of annealing is reduced at 250 °C, but the increase of $G_{IC,init}$ values is evident (Fig. 8(a)).

All statements concerning the dominant mechanisms of annealing changes deduced with $G_{IC,mean}$ data can be justified and improved through the analysis of $G_{IC,init}$ values. Since the sign of $G_{IC,init}$ and T_g changes (Fig. 8(b)) remains the same during annealing at 250 °C, the cross-linking during this process can be stated as the dominant mechanism. The changes of $G_{IC,init}$ with annealing at

180 °C do not have the same sign as those of T_g (Figs. 7(b) and 8(b)) so these changes cannot be related directly to chain scission or chain cross-linking.

The obtained G_{IC}, results after annealing at 180 °C in vacuum, both $G_{IC,mean}$ and $G_{IC,init}$ (Fig. 7), are in a full agreement with the findings of Egusa et al. [9]. They found that for organic composite materials (including carbon/epoxy composites), irradiated with gamma rays up to the doses of 20.0 MGy, the decrease of polymer dominated properties occurred after annealing conditions identical to ours. They suggested that the mechanism of annealing-activated degradation of irradiated composites is due to the rearrangement of polymer chains that have been entangled and loosened, thus decreasing the number of polymer chains for load transfer at the fiber/matrix interface. Annealing of irradiated composites, therefore, is considered to activate latent radiation damage near the fiber/matrix interface, thus causing a decrease in the load transfer capacity at the fiber/matrix interface.

4. Conclusions

The effects of gamma irradiation, in the dose interval from 4.8 to 27.2 MGy, on mean and initial values of strain energy release rate (G_{IC}) in carbon/epoxy UDC, with high glass transition temperature matrix, have been studied. The G_{IC} variation after annealing of irradiated coupons, at the temperatures 180 and 250 °C in vacuum, has been investigated too.

The R curves for higher irradiation doses indicate that, during the crack propagation, fiber bridging plays an important role, thus increasing the $G_{IC,mean}$ values. $G_{IC,init}$ values related to crack initiation, proved to be used in the assessment of dominant mechanisms responsible for irradiation and annealing changes.

$G_{IC,init}$ decrease with the dose follows the change of T_g at the lowest (4.8 MGy) and a maximum (27.2 MGy) dose. The measured T_g value does not follow the trend of $G_{IC,init}$ change after irradiation of up to 13.6 and 22.4 MGy.

The annealing of coupon at 180 °C for doses higher than 13.6 MGy, induces a decrease of both G_{IC} values, causing a decrease in the load transfer capacity at the fiber/matrix interface. This G_{IC} values decrease can as well be related to the gas product evacuation of under vacuum.

The 250 °C annealing, leading to the pure increase of $G_{IC,init}$ values, followed with T_g values increase, can be associated with the reticulation process.

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