Investigation of the Effect of Electron Beam Radiation on Carbon Fiber / Polyamide-6,6 and Carbon Fiber / Polyamide-6 Composites

The aim of this work was to investigate the effect of electron beam radiation on carbon fiber reinforced thermoplastic composites, with polyamide-6,6 (PA66) and polyamide-6 (PA6) as matrix. In order to achieve a matrix cross-linking after irradiation a cross-linking agent was incorporated into the polymer. Further experiments were conducted using additional nanoclay in the matrix material. After irradiation, important changes in the thermal properties and in the creep behavior were measured.
INVESTIGATION OF THE EFFECT OF ELECTRON BEAM RADIATION ON CARBON FIBER /POLYAMIDE-6,6 AND CARBON FIBER/POLYAMIDE-6 COMPOSITES

Dipl.- Ing. S. Wiedmer, Dipl.-Ing. D. Gellner, Prof. Dr.-Ing. Dr. h.c. K. Friedrich

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1 INTRODUCTION

Polymer materials can undergo structural changes under radiation, e.g. due to Infrared [IR], Microwave, Ultraviolet [UV] as well as Gamma-Ray or Electron-Beam [EB] exposure. Depending on the irradiation type and on the polymer materials, cross-linking reactions or degradation can take place in the polymer [1].

Since the 1960s, Electron-beam radiation has been used to cure thermosetting polymers. Compared to conventional curing methods, it permits to cure rapidly thicker parts at low temperature and to reduce the emission of volatile agents [2]. In contrast to thermosetting resins, thermoplastic materials are not cross-linked. They can be melted and consolidated reversibly by changing the temperature. However, they do not exhibit the advantages of cross-linked structures such as high stiffness, high strength, as well as temperature resistance [3]. In order to reach these requirements, EB cross-linking processes of thermoplastic systems have been successfully developed and introduced. The first developments were conducted on polyolefins, and the process is now well established. EB irradiation is applied for instance to polyethylene pipes used for gas and water transport [4, 5] resulting in a higher creep resistance, higher resistance to external impact, higher tolerance to notches and grooves or higher chemical and temperature resistance. However it should be pointed out, that irradiation can induce chain scission in the polymer, which can deteriorate its mechanical properties. For instance
polypropylene is known to undergo chain scission under irradiation. In this case, improvements in the properties could be achieved after addition of a cross-linking agent as well as a radical scavenger [6]. On the other hand, Krause and al. [7] applied electron beam irradiation on polypropylene in the molten state. Formation of long chain branching and molar mass degradation took place, however, irradiation in the molten state led definitely to a higher degree of chain branching than irradiation in the solid state, without using any additives.

Numerous works have been also conducted on thermoplastic and thermoplastic composites materials. For instance, the effect of EB radiation on several aromatic polymers such as polyimide, poly(etherimide) [8], poly(etheretherketone) as well as poly(ethersulfone) [9] and on some glass and carbon fiber reinforced poly(etheretherketone) and poly(phenyl sulfide) laminates [10] was investigated. Recently, polyamide-6, polyamide-6,6 and poly(butylene terephthalate), reinforced with short glass fibers, were successfully cross-linked and exhibited enhanced thermal properties and chemical stability [11]. This opens up new application fields for the materials, e.g. in the electronic industry.

However a real up-turn of the EB cross-linking of thermoplastic is still limited, due to the fact that most of the thermoplastic polymers need the presence of a cross-linking agent, in order to develop radiation sensitivity.

In previous works from the same authors [12, 13] the effect of EB radiation on different carbon fiber reinforced thermoplastic composites, namely carbon fiber reinforced poly(butylene terephthalate) (PBT), polyamide-46 (PA46) and polyamide-6,6 (PA66) respectively laminates was still investigated. Despite the presence of a cross-linking agent, no significant changes in the properties could be register in CF/PBT and CF/PA46. However, cross-linking reactions could be successfully induced in the case of CF/PA66. Some efforts were made in order to achieve a homogeneous repartition of the cross-linking agent into the polymer. Using the chill-roll-extrusion process, PA66 films containing cross-linking agent in different proportion were produced. Depending on the proportion of the cross-linking agent and on the irradiation dose, different degrees of cross-linking were achieved. Significant changes in the melting point, glass transition temperature as well in the creep properties were observed.

The present work must complete the results achieved in previous works [12, 13] about EB radiation of CF/PA66 laminates. In this aim not only a cross-linking agent but also nano-particles will be incorporated to the PA66 matrix in order to enhance the effect of the CLA. Additionally carbon fiber reinforced PA6 laminates, with matrices containing cross-linking agent and also some nano-particles will also be investigated. In each case, the thermal and mechanical properties, in particular the creep properties will be determined before and after irradiation.
2 EXPERIMENTAL

2.1 Material

Carbon fiber reinforced thermoplastic laminates were processed according to the so-called “film-stacking-process”, where polymer films and textile fabrics were stacked together in a defined sequence. As mentioned before a cross-linking agent has been used, it will be referred in the following part as CLA. The name and composition of the CLA can here not be published. PA66 films without and with CLA in different proportions were used. Some films including CLA and nano-particles were also produced. In the same manner PA6 films without as well as with 3% in weight of CLA and 3% in weight of nano-particles were produced. Organic modified silicate particles were used as nano-particles. The production of the polymer films using the chill-roll film extrusion process is described in [13]. The impregnation of the fibers and the consolidation of the laminates using the “film-stacking-process” were conducted in a static press under heat, pressure and time. The values of heat, pressure and time can again not be unveiled. Table 1 gives an overview of the properties of the polymer films, the carbon fabrics as well as the final laminates. Here one should note that the weight content of CLA and nano-particles indicated in Table 1 refers to the proportion contained in the polymer (and not in the entire composite).

<table>
<thead>
<tr>
<th>Polymer Film</th>
<th>Carbon Fabric</th>
<th>Laminates</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66</td>
<td>Number of Polymer Film Layers: 10</td>
<td>Area Weight: 200 g.m⁻²</td>
</tr>
<tr>
<td>PA66 + 2wt%, 3wt%, 3,5wt% cross-link agent (CLA)</td>
<td>Weave: Köper 2/2</td>
<td></td>
</tr>
<tr>
<td>PA66 + 3wt% CLA + 3wt% nano-particles</td>
<td>Fiber volume content: 50%</td>
<td></td>
</tr>
<tr>
<td>PA6 + 3wt% CLA + 3wt% nano-particles</td>
<td>Thickness: 100 μm</td>
<td>Carbon Yarn: 3K</td>
</tr>
<tr>
<td></td>
<td>Number of Carbon Fabric Layers: 9</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Overview of laminates composition
2.2 Irradiation

Irradiation experiments were carried out by the company Beta-Gamma-Service GmbH, Bruchsal, Germany. As irradiation source, an electron-beam accelerator with 150 kW power setting and 5 MeV energy was used. The irradiation was performed in air at ambient temperature. There was no need for a particularly pre-treatment of the laminates before irradiation. Irradiation doses of 99 kGy and 132 kGy were applied. Based on previous work [13] and on the know-how of the company Beta-Gamma-Service, these irradiation doses are the most appropriate doses for polyamide. They should lead to the highest cross-linking degree.

2.3 Thermal Characterization

2.3.1 Differential Scanning Calorimetry

Changes in the thermal properties of the materials were determined by differential scanning calorimetry (DSC), using a DSC 821 apparatus from Mettler Toledo, Germany. Samples were heated up under nitrogen atmosphere from room temperature up to 290°C at a heating rate of 10K/min. Only one heating-up was applied to the sample since it reflects its thermal history. The heat flow was recorded as a function of temperature, and the melting temperatures were determined from the thermograms.

2.3.2 Dynamic Mechanical Thermal Analysis

The glass transition temperatures were measured using a dynamic mechanical thermal analyzer (DMTA), Eplexor 150N (Gabo Qualimeter, Ahlden, Germany). The specimens were subjected to oscillating dynamic loading, consisting of a static load of 40 N, on which a sinusoidal wave of 20 N was superimposed at a constant frequency. The measurements were performed under 3-point-bending loading at a frequency of 1Hz. Heating rate was set up to 1K/min from −100°C to ca. 280°C. The glass transition temperatures were determined from the peak of the mechanical loss factor, tan δ.
2.4 Mechanical Characterization

2.4.1 Flexural Test

A universal testing machine, Zwick 1474 (Ulm, Germany) with a 10 kN load-cell was used for determining the flexural properties. The test method was based on DIN EN ISO 178 [14]. 5 specimens with fiber orientation $0^\circ/90^\circ$ (warp direction) were tested in each case. Cross-head speeds, varying from 1.9-2.1 mm/min, were applied, depending on the sample thickness. Software was used in order to transmit on-line the data to force-displacement or stress-strain curves.

2.4.2 Creep Measurement

In order to evaluate the creep behavior of the cross-linked polymer composites, creep experiments were performed using a creep apparatus Modell 2002 from Coesfeld, Germany. Samples with a $+/45^\circ$ fiber orientation, having dimensions of 120 mm by 10 mm, were cut out of the laminates. In this case the tensile creep properties are matrix dominated. Two strips were bonded onto the surface of each specimen at a distance of 30 mm in order to measure the longitudinal deformation. The test specimens were mechanically clamped between the jigs, and tension loads were applied. The strain between the strips was continuously recorded by a camera. Experiments were conducted at room temperature as well as at a temperature of 70°C, using different stress levels.

3 RESULTS AND DISCUSSION

In a previous work [13], gel content measurements were made using the solvent extraction method on unreinforced polyamide 66 sheets, produced with the same PA66 films as used for the laminates. It was then proved that cross-linking was successfully induced in the PA66 matrix containing CLA. Corresponding results are shown in figure 1. The increase in the cross-linking degree was accompanied by a decrease of the melting point of the polymer. Due to the high carbon loading in the composite material, the determination of the degree of cross-linking induced by EB radiation in the CF/PA66 laminates turns out to be difficult. However we supposed that a cross-linking was also successfully induced after radiation. This supposition was then confirmed by the decrease of the melting point and the increase of the glass transition temperature. The possible effect of the carbon fiber on the cross-linking behavior of the matrix was here not considered.

Table 2 presents the results of the melting points of the different materials tested here before and after irradiation were. Before irradiation the melting point lies at
around 260°C and 220°C for the CF/PA66 and CF/PA6 laminates, respectively. For PA66 based laminates, the melting point after irradiation in presence of CLA and CLA with nano-particles, decreased down to 255°C or 252°C. The decrease was more pronounced at higher irradiation doses and higher CLA contents. The addition of nano-particles doesn’t seem to have any particular effect on the melting point before irradiation, except a slightly smaller value. Regarding the gel content presented on figure 1, the melting point seems to be directly related to the cross-linking degree. The higher the gel content is, the lower is the melting temperature. After irradiation, CF/PA6 laminates containing CLA and nano-particles exhibited a melting point of around 206°C. Although the cross-linking degree could not be directly determined, we can suppose, from the decrease in the melting point, that cross-linking was successfully induced in CF/PA6. Further explications will be given below.

Figure 1: Gel content in the PA66 matrix without and with CLA versus irradiation dose [13]
The glass transition temperatures ($T_g$) of the different systems before and after irradiation were measured using the DMTA analysis. The results are summarized in Table 3. Here it is evident that the EB irradiation led to an increase of the glass transition temperature for each system. For the CF/PA66 laminates with CLA, the $T_g$ increases by 10°C, independently of the CLA content. An explication for this behavior will be given below. The addition of nano-particles to the PA66 with CLA doesn’t influence significantly the $T_g$ before irradiation, however after irradiation an increase of 20°C was recorded. In the same manner the $T_g$ of CF/PA6 increases from 64°C to 85°C after EB radiation in the presence of CLA and nano-particles. This represents an interesting aspect regarding the future application of this composite.

<table>
<thead>
<tr>
<th>CF/PA66</th>
<th>CF/PA66</th>
<th>CF/PA66</th>
<th>CF/PA66</th>
<th>CF/PA66</th>
<th>CF/PA6</th>
<th>CF/PA6</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% CLA</td>
<td>3% CLA</td>
<td>3.5% CLA</td>
<td>3% CLA, 3% Nano</td>
<td>3% CLA, 3% Nano</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unirradiated</td>
<td>262.5°C</td>
<td>260.9°C</td>
<td>260.3°C</td>
<td>260.7°C</td>
<td>259.6°C</td>
<td>220.4°C</td>
</tr>
<tr>
<td>Irradiated with 99 kGy</td>
<td>262.1°C</td>
<td>255.1°C</td>
<td>253.5°C</td>
<td>252.6°C</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Irradiated with 132 kGy</td>
<td>261.3°C</td>
<td>254.7°C</td>
<td>253.8°C</td>
<td>252.9°C</td>
<td>252.4°C</td>
<td>205.7°C</td>
</tr>
</tbody>
</table>

Table 2: Melting temperature of the different laminates versus irradiation dose

In the results presented above, it can be observed that the EB radiations cause some change of the melting point as well as of the glass transition temperature. In previous work conducted on PA66 matrix [13], the presence of cross-linking reaction was proved after irradiation and this was accompanied by a decrease of the melting point. Due to the changes in the thermal properties observed before,
we can then suppose that cross-linking reactions are also induced in CF/PA66 and CF/PA6 laminates, even if the effects of the carbon fiber and of their finish were not investigated. Changes of the melting point as well as of the glass transition temperature let suppose that the crystalline regions as well as the amorphous ones are both affected by the irradiation. Different conclusions have already been published concerning the mechanisms involved during irradiation. Some authors [9] claimed that irradiation causes scission and cross-linking reactions, and that the melting point is controlled by chain scission effect. Cross-linking is likely to occur in the amorphous regions [7, 15] which leads to a reduction of the free-volume content and restricts movements. Dadbin et al. [15] investigated the case of polyethylene. As the both amorphous-crystalline phases are pinned together by the macromolecules, they concluded that crystalline regions can be easily intermingled in the cross-linked network. Additionally they pointed out that irradiation can create minor defect in the crystals. Following these conclusions, one can assume that the cross-linking in the amorphous region (which was reflected by the increase of $T_g$ in Table 2) affects somehow the crystalline regions, thus leading to a shift of the melting point to a lower temperature.

Additionally we stated above that the increase of the $T_g$ of CF/PA66 is identical, independently of the CLA content. This can be due to the fact that the cross-linking degree achieved after irradiation is the same for each CLA proportion. It is possible however, regarding the figure 1, a higher cross-linking degree was expected with a higher cross-linking agent content. We can more likely suppose that the reduction of the free-volume and the movement restriction due to the cross-linking are approximately identical at 20% or 40% gel content degree.

The effect of CLA seems to be enhanced by using nano-particles. The further increase of the $T_g$ using nano-particles is due to a further decrease of the molecule mobility. One can suppose that the nano-particles act as cross-link points and then contribute to increasing the cross-linking packing. These are only assumptions, since the mechanisms involved have not been investigated in the details within the scope of this study. Further investigations should be required in the future.

Further the flexural modulus and the flexural strength of the different systems before and after irradiation were determined. Since the flexural modulus is mainly dependent on the fiber volume content, it did not exhibit significant changes after EB radiation. Its value lies between 38 GPa and 41 GPa for CF/PA66 laminates with CLA. A slight improvement of the moduli of the CF/PA66 and CF/PA6 laminates are observed due to the addition of nano-particles. CF/PA66 and CF/PA6 laminates with CLA and nano-particles exhibit a modulus around 44 GPa and 43 GPa respectively. The flexural strength is given on figure 2. A slightly increase is observed by addition of CLA. After irradiation a slightly increase is observed for laminated containing CLA, however a slightly decrease is recorded for laminates containing nano-particles.
Thermoplastic polymers possess a very temperature-sensitive creep behavior, even at room temperature. The results of the tensile creep measurements are displayed in figures 3, 4 and 5. Figure 3 shows the results of CF/PA66 samples containing 3,5% CLA before and after radiation tested at room temperature. At each stress level applied, the cross-linked specimens exhibit a better creep resistance as the non-cross-linked specimen. However, this improvement in the creep behavior is more obvious at high stress level. In figure 4 one can see that the creep resistance of unirradiated and then non-cross-linked CF/PA66 laminates is decreasing by increasing the temperature from room temperature to 70°C, due to the vicinity of the glass transition temperature. For cross-linked laminates however, the creep resistance at 70°C remains in the same order of magnitude as at room temperature. This is without a doubt due to the fact that the glass transition temperatures of the cross-linked systems lie at around 84°C. In any case, the irradiated specimens exhibit smaller strain as unirradiated specimen. From figure 5 one can also note an improvement in the creep properties of CF/PA6 laminates after irradiation. A comparison between figure 4 and figure 5 permits to show that, under the same conditions of temperature and of load (50 MPa), unirradiated
Figure 3: Strain versus time for +45° fiber angle specimen of CF/PA66 with 3.5% cross-linking agent at room temperature and at 3 different tension loads.

Figure 4: Strain versus time for +45° fiber angle specimen of CF/PA66 with 3.5% cross-linking agent at room temperature and 70°C under a tension load of 50 MPa.
CF/PA6 laminates exhibit a much larger creep as unirradiated CF/PA66 laminated. After irradiation the both materials exhibit approximately the same creep behavior.

Figure 5: Strain versus time for +-45° fiber angle specimen of CF/PA6 with 3 wt% cross-linking agent and 3 wt% nano-particles under a tension load of 50 MPa at room temperature

4 CONCLUSIONS

In this study the influence of EB radiation on the properties of carbon fiber reinforced Polyamide 66 and carbon fiber reinforced Polyamide 6 laminates was investigated. In presence of a cross-linking agent, some changes in the thermal properties were observed after irradiation, e.g. a decrease in the melting point as well as an increase in the glass transition temperature. This let suppose that cross-linking was successfully induced after irradiation. The addition of nano-particles to the both matrix was particularly advantageous, it enhanced the positive effect of the CLA, since it did not affect the melting point but led to a further increase of the glass transition temperature after EB radiation. Within the scope of this study, the flexural properties were not particularly influenced by the presence of the cross-linking agent and nano-particles, except the decrease of the flexural strength observed after irradiation of the laminates containing nano-particles. Remarkable improvements of the creep properties after irradiation were observed, at room
temperature but also at 70°C, which is directly related to the increase of the glass transition temperature. This represents an important feature, which can definitely open new application fields for thermoplastic and thermoplastic composites materials. The potential of nano-particles should be further exploited in the future.

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Autors:
Dipl.-Ing. S. Wiedmer*, Dipl.-Ing. D. Gellner**, Prof. Dr.-Ing. Dr. h.c. K. Friedrich*
*Institut für Verbundwerkstoffe GmbH (IVW)
Erwin-Schrödingerstr. 58, Technische Universität Kaiserslautern
D-67633 Kaiserslautern, Deutschland
** Bond Laminates, Am Patbergschen Dorn, 9
D-59929 Brilon, Deutschland

E-Mail-Adresse: sandrine.wiedmer@ivw.uni-kl.de