

# Monitoring of Nylon 6,6/Carbon Fiber Composites Processing by X-ray Diffraction and Thermal Analysis

Edson Cocchieri Botelho,<sup>1</sup> Clara Leal Nogueira,<sup>2</sup> Mirabel Cerqueira Rezende<sup>2</sup>

<sup>1</sup>Departamento de Engenharia Aeronáutica e Mecânica, Instituto Tecnológico de Aeronáutica, Centro Técnico Aeroespacial, São José dos Campos, São Paulo, Brazil, CEP:12228-905

<sup>2</sup>Divisão de Materiais, Instituto de Aeronáutica e Espaço, Centro Técnico Aeroespacial, São José dos Campos, São Paulo, Brazil, CEP:12228-904

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**ABSTRACT:** This work reports a study made to obtain carbon fiber/nylon 6,6 prepreg composites by hot-compression molding. Thermogravimetric analysis (TG) and crystallinity degree determination were carried out to monitor the nylon 6,6 behavior during the different steps of the composite processing. The homogeneity of the carbon fiber/polymer matrix distribution was verified using microscopic analyses and the fiber content was determined by the acid-digestion method. The results show that the processing

parameters employed were adequate, allowing the manufacture of laminates with good texture and an adequate reinforcement/matrix relation (60/40). However, improvements need be done to minimize the pullout effect observed in the tensile specimens. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3114–3119, 2002

**Key words:** composites; polyamides; X-ray; processing

## INTRODUCTION

Polymers reinforced with carbon fibers exhibit the highest values of both specific mechanical strength and rigidity among the available materials. Therefore, the substitution of aluminum by polymeric composites allows a weight reduction of 20–30%, besides a decrease in the processing final cost of nearly 25%.<sup>1–4</sup>

Thermoplastics reinforced with continuous fibers present some advantages when compared to the conventional thermoset composites, such as higher rigidity and impact energy values, a higher service temperature, and great versatility in a serial production. Although most of the polymeric composites are obtained by reinforcement impregnation with thermoset resins, this kind of polymeric matrix presents some disadvantages. Among them are tensions originated during the material processing enhanced by the brittle nature of the thermoset resin, low erosion resistance, and chemical and structural changes caused by excessive heating during use. These disadvantages limit the application of thermoset composites in some areas of higher service temperature, for example, in aircraft.<sup>5–10</sup> Figure 1 shows applications of composite materials in

aircraft produced by EMBRAER (Aeronautical Brazilian Co.).<sup>11</sup>

Nowadays, the use of thermoplastic composites in structural applications has increased considerably. In the aeronautical area, they have been employed in the manufacture of internal components and parts of wings in Boeing aircraft, doors of landing trains, floor panels, mobile surfaces such as the elevators of Fokker airplanes, Hercules radome, and flaps among others.<sup>12–15</sup> In this context, polyamidic polymers are good candidates to be used as polymeric matrix in thermoplastic composites processing due to their low cost and ease of handling. Nylon 6,6 is a semicrystalline polyamidic polymer, with a melting point near 265°C. Its physicochemical and mechanical behaviors have allowed its use in several industrial areas, such as in aeronautics and space.<sup>16–18</sup>

In these areas, structural composites are obtained by consolidation of several preimpregnated sheets, through the use of pressure and heat. Preimpregnated (prepreg) manufacture can be obtained by placing the reinforcement fibers in contact with the thermoplastic polymer in several ways: polymeric solution, polymer casting, powder, or granules spreading on the reinforcement followed by polymer melting or by consolidation of hybrid fabric previously obtained by weaving polymer and reinforcement tows.<sup>19–21</sup> Independent of the way used to impregnate the reinforcement, some processing parameters, such as the heating and cooling rates, compression pressure and crystallinity degree, and melting temperature of the polymeric ma-

Correspondence to: M. C. Rezende (mirabel@iae.cta.br).

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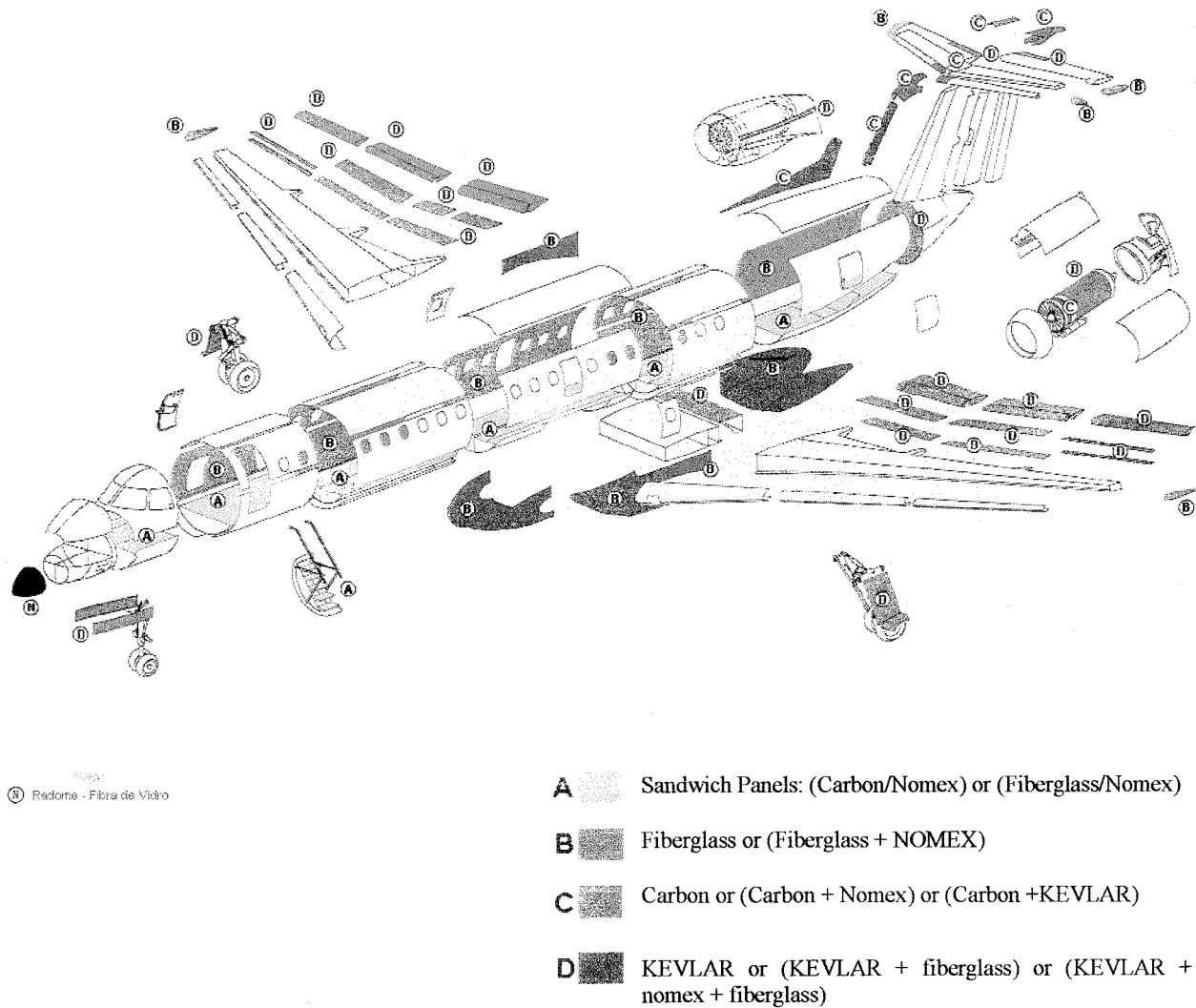


Figure 1 Applications of polymeric composites in the EMB-145 aircraft produced by EMBRAER.<sup>11</sup>

trix must be taken into account to guarantee the success of thermoplastic prepreg manufacture. The control of these parameters is important to minimize polymer degradation and also any undesirable growth of the crystallinity region around the fiber, increasing the fragile behavior of the matrix. The objective of this study was to evaluate the processing of nylon 6,6/carbon fiber prepreps by hot-compression molding, following any possible change in the polymeric matrix by X-ray diffraction (crystallinity degree) and thermogravimetry analysis. The carbon fiber/polymer interface was analyzed by optical and scanning electronic microscopies.

**EXPERIMENTAL**

The thermoplastic composite manufacture was carried out by adapting a mold (600 × 600 mm) in a press with a capacity of 100 tons. The inferior and superior parts of the mold were heated by an electrical-resis-

tance system, controlled by software. Figure 2 shows the scheme used for obtaining the thermoplastic composite prepreg sheets.

Nylon 6,6, also called polyamide 6,6, in the form of pellets with a 40% crystallinity degree, was supplied by South America Polyamide Rhodia (São Paulo), and the reinforcement of carbon fiber fabric, style 282, plain weave, standard modulus, was supplied by Hex-

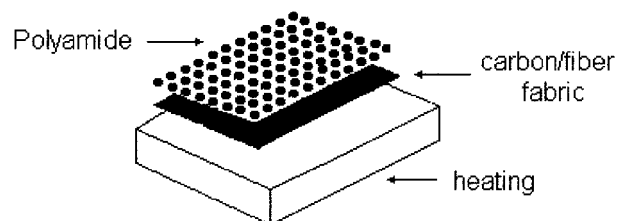


Figure 2 Scheme of preparation of thermoplastic preimpregnated polyamide 6,6/carbon fabric by hot-compression molding.

TABLE I  
Melting Temperature and Enthalpy Values of the Polyamide 6,6 Studied

Sample	Peak (°C)	Enthalpy (J/g)
01	263.2	73.6
02	262.1	73.5
03	263.1	69.4
Average value	262.8 ± 0.6	72.2 ± 2.4

cel Composites (São Paulo). For the preparation of each prepreg sheet, 25 g of nylon 6,6 was homogeneously spread on the surface of the carbon fiber fabric (450 × 450 mm) placed into the mold. The thermal cycle was carried out in two steps: First, the raw materials (fabric + nylon 6,6) were heated to 150°C, at a heating rate of 4°C/min, maintaining this temperature for 10 min. Soon afterward, the system was heated to 290°C, at a rate of 3°C/min. At this temperature, a pressure of 3.0 ± 0.1 MPa for 10 min was applied. The mold cooling was done naturally, to the room temperature, taking nearly 15 h.

Thermal analysis of the nylon 6,6 sample was carried out using a differential scanning calorimeter (DSC-Pyris) and a thermogravimeter (TGA 7), both equipment of Perkin-Elmer. Both analyses were carried out using a heating rate of 10°C/min under a constant nitrogen flow. X-ray diffraction analysis was carried out using Philips equipment, Model PW 1830, to evaluate possible changes of the crystallization degree. The polymer/reinforcement interface of the prepreg was observed using an optical microscope, Olympus Model BH, with a tungsten lamp of 50 W, through the analysis of the sample cross section. The interface was also observed by a scanning electron microscope (SEM), LEO I, Model VPi 43, analyzing the fractured surface after recovering it with a gold film. The prepreg fiber content was determined by the matrix acid-digestion method, according to ASTM-C611.<sup>22</sup>

## RESULTS AND DISCUSSION

DSC analyses were carried out to determine the polymer melting point (Table I). These data show a clear endothermic peak around 263°C with an enthalpy value of 72.2 ± 2.4 J/g. The good repeatability of the measurements shows that nylon 6,6 samples are homogeneous. The melting-point values determined agree with those presented in the literature, that is, in the range of 255–265°C.<sup>23</sup>

Figure 3 shows the nylon 6,6 TG curve. It is observed that the polymer presents two regions of weight loss. The first one, in the range of 100–340°C, with a weight loss of 3.84%, is due to the presence of moisture in the polymer sample, adsorbed during nylon

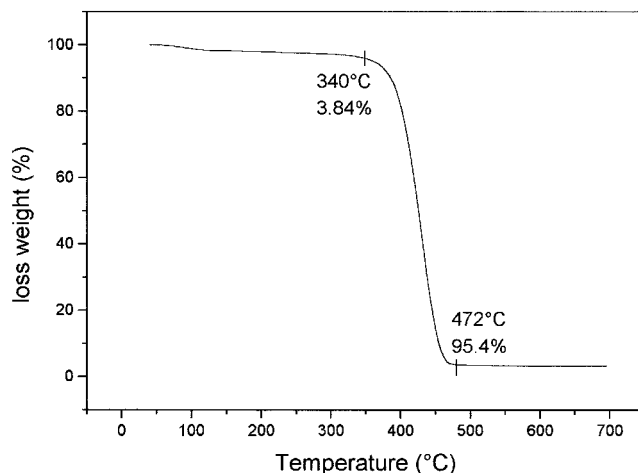


Figure 3 Thermogravimetric analyses of the polyamide 6,6 studied.

6,6 storage and handling. The second region is observed between 340 and 472°C, with a weight loss of 95.4%, attributed to the polymer degradation, leaving a residue of 4.62%. The TG results together with the nylon 6,6 melting point determined by DSC were used to establish the thermal cycle used for heating the mold during the prepreg processing (Fig. 4).

The first step of the thermal cycle was heating the mold containing the nylon 6,6 pellets plus the carbon fiber to 150°C (4°C/min), keeping this temperature for 10 min. This step was done to minimize the effect of the thermal inertia of the mold and also to eliminate moisture present in the polymer and in the carbon fiber reinforcement. Afterward, the mold was heated to 290°C, nearly 27°C above the melting point of nylon 6,6. This temperature is enough to guarantee the melting of the polymer without causing its degradation, which starts close to 345°C.

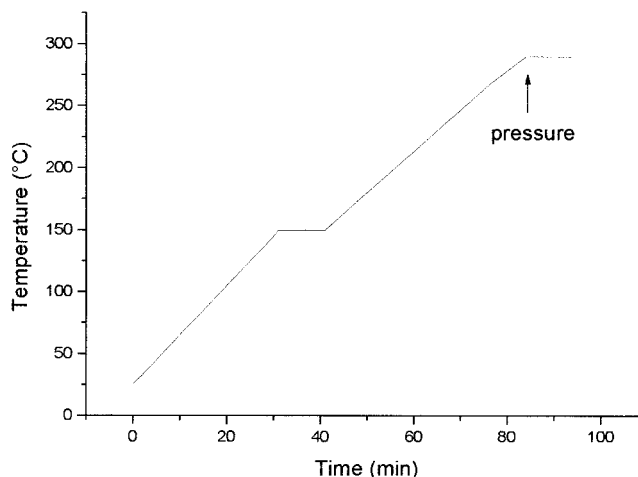
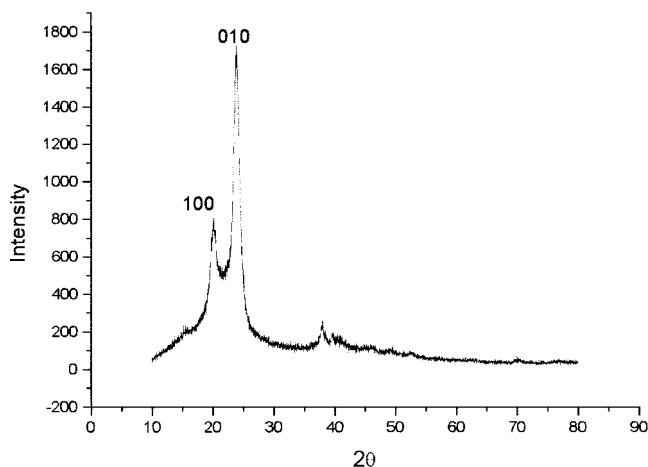


Figure 4 Thermal cycle used in the carbon fiber/polyamide 6,6 composite manufacture by hot-compression molding.

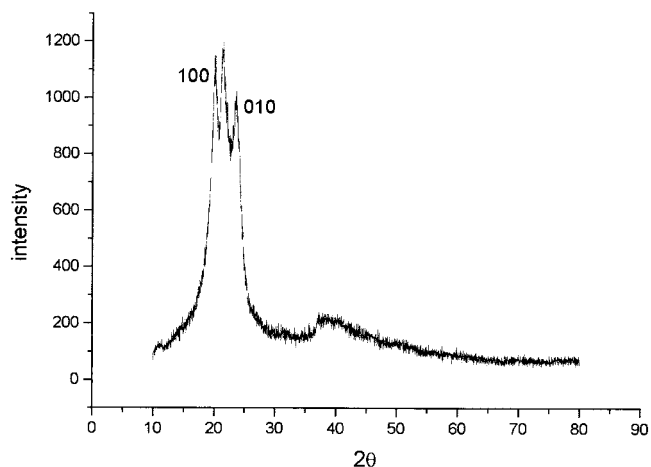


**Figure 5** X-ray diffractogram of the polyamide 6,6 used as the matrix.

The absence of degradation during prepreg manufacture was checked by TG analysis. The TG curves of nylon 6,6, obtained before and after prepreg manufacture, present exactly the same profile, with the curves superimposing one another. These results show that no significant changes occurred in the nylon 6,6 during the prepreg manufacture.

The majority of the physical, mechanical, and thermodynamic properties of thermoplastic materials are correlated to the crystallization degree and to the morphology of the crystalline areas. Increasing crystallinity favors improvements in some physicochemical properties, such as higher density, rigidity, melting and glass temperatures values, dimensional stability, and higher chemical and abrasion resistance. On the other hand, a higher crystallinity degree reduces properties such as the impact resistance, elongation, swelling, and mechanical damping. The presence of polar groups in the molecule is not necessary to initiate the crystallization, but the presence of polar groups favors the approaching of the chains, resulting in a higher crystallinity degree.<sup>24–26</sup> In the case of nylon 6,6, the presence of carbonyl groups (CO) induces the formation of intermolecular hydrogen bonds, which increases the degree of crystallinity and the melting temperature. According to the literature, the highest crystallinity values of polyamide 6,6 is nearly 60%,<sup>24–26</sup> but in this work, the polyamide used had a 40% crystallinity degree. A higher degree of crystallinity is also favored by a slow cooling rate of the melted polymer.

In this work, the cooling of the mold was done by natural convection, taking nearly 15 h. This procedure is usually slow due to the large weight of the mold and can affect the crystallinity degree of the polymer matrix as discussed previously. The degree of crystallinity of the nylon 6,6 was determined by X-ray diffraction analyses. Figures 5 and 6 show the X-ray



**Figure 6** X-ray diffractogram of the polyamide 6,6 used as the matrix after it was compressed.

diffractograms of the nylon 6,6 sample before and after prepreg processing, respectively. As expected, Figure 5 presents two peaks, one located at  $2\theta = 20.1^\circ$  and the other one at  $2\theta = 23.8^\circ$  (Table II).

The crystallinity value (CV) determination can be obtained using eq. (1), available in the literature,<sup>24</sup> where  $d_{100}$  and  $d_{010}$  are the interplanar distances related to the planes (100) and (010), respectively:

$$CV = \frac{[d_{010}/d_{100}] - 1}{0.189} \times 100 \quad (1)$$

Equation (1) can be simplified and expressed as eq. (2), where  $\theta_{100}$  and  $\theta_{010}$  are the angles related to the (100) and (010) interplanar distances ( $d$ ); 546.7 is a constant and 0.40 is the other constant related to the crystallinity indicated by the supplier. The CV values were 39.8 and 38.9%, before and after processing, respectively:

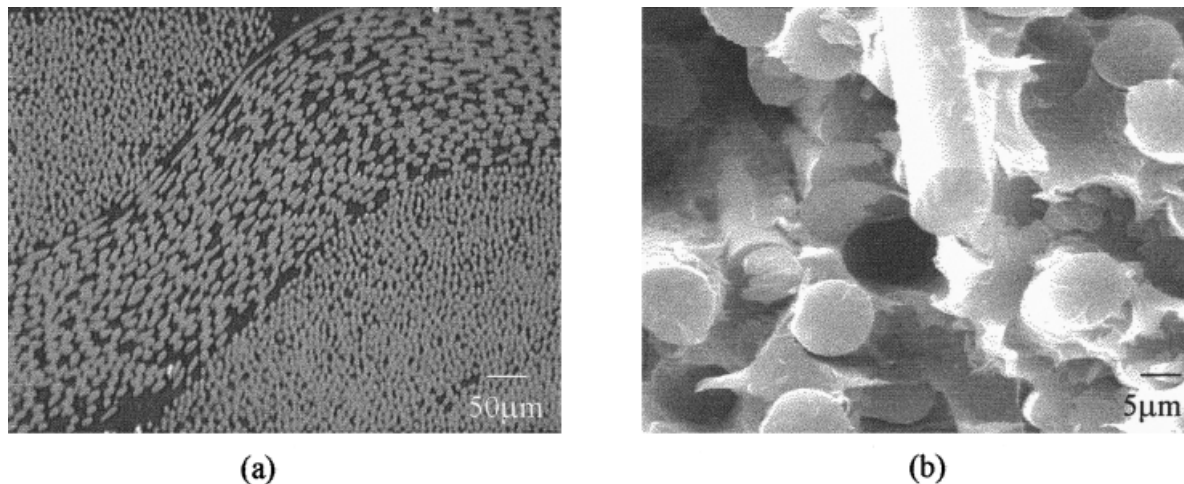
$$CV = \left( \frac{2\theta_{010}}{2\theta_{100}} - 1 \right) \times 546.7 \times 0.40 \quad (2)$$

The CV calculated for nylon 6,6 before prepreg processing is close to the value of 40% indicated by supplier and found in the literature<sup>25</sup> and corresponding to a triclinic lattice. It means that the nylon 6,6 used in this study does not present crystallographic changes induced during its syntheses. Figure 6 shows an X-ray

**TABLE II**  
Crystallographic Results of the Polyamide 6,6 Studied

Interplanar distances	Before processing		After processing	
	$2\theta$ (°)	$\theta$ (°)	$2\theta$ (°)	$\theta$ (°)
100	20.14	10.07	20.12	10.06
010	23.82	11.91	23.80	11.90
Unknown	—	—	22.60	11.30





**Figure 7** Photomicrographs by (a) optical microscopy 200 $\times$  and (b) scanning electron microscopy 2000 $\times$  of the polyamide 6,6/carbon fiber composites.

diffractogram of the polyamide 6,6 sample after prepreg processing. It shows three peaks, with two of them at  $2\theta = 20.1^\circ$  and  $23.7^\circ$ , similar to those observed in Figure 5, and a third peak located at  $22.6^\circ$ . Using only the two first peaks, the CV for nylon 6,6 after processing is equal to 38.9%. This value is slightly lower than the one found before processing. This small difference has been attributed to the appearance of the third peak, formed due to the fast cooling rate of the mold (in the beginning of the natural cooling). This hypothesis was confirmed by doing two experiments concerning the cooling rate of nylon 6,6. In the first one, a sample of the melted polymer was cooled by the same conditions used in the prepreg manufacturing, and in the second one, the sample was cooled in a quicker manner, by dropping it into a water bath. The X-ray diffraction measurements confirm that the fast cooling rate leads to the appearance of the third peak. On the other hand, the sample subjected to the lower cooling shows the same diffractogram of the nylon 6,6 before processing. Thus, the third peak is caused by the fast cooling rate used after the prepreg processing, and it has been attributed to the formation of a new crystallographic phase. However, it must not be representative because no change was verified in the melting point of nylon 6,6 after the prepreg processing.

Figure 7(a) shows a representative texture of the prepreg composite observed by optical microscopy. The image shows that the processing parameters adopted for the prepreg led to the formation of a homogeneous composite, with a good distribution of the nylon 6,6 on the carbon fibers, without voids and microcracks. This observation was confirmed by quantitative determination of the fiber and matrix contents by matrix acid digestion. A carbon fiber content of 62.3% and a nylon 6,6 content of 37.7% were deter-

mined. These values are close to those found in the literature for structural composites, that is, around 60% of the reinforcement and 40% of the polymeric matrix.

Figure 7(b) shows the fracture surface of the prepreg composite obtained by scanning electron microscopy. This image confirms the observation done by optical microscopy, revealing the good infiltration of the polymer in the reinforcement and the good reinforcement/polymer interface. Although in a very small scale, the pullout effect of the fibers, due to the weak polymer/carbon fiber interface, was also observed. This can be attributed either to the presence of traces of moisture in the raw materials, even after heating the mold for 10 min at  $150^\circ\text{C}$ , or due to an inadequate surface treatment of the carbon fiber.

## CONCLUSIONS

The processing of nylon 6,6/carbon fiber prepreps, made by hot-compression molding, was evaluated. DSC analysis shows that the melting point and crystallinity value (enthalpy) of nylon 6,6 is nearly the same before and after the prepreg processing. Thermogravimetric analysis shows that the weight-loss profile of nylon 6,6 does not change after being submitted to the heating cycle of the prepreg preparation. X-ray diffraction shows the formation of a new crystallographic phase, attributed to the slow cooling rate of the mold. Optical microscopy analysis shows that the processing parameters adopted for the prepreg preparation led to the formation of a homogeneous composite, with a good distribution of the nylon 6,6 on the carbon fibers, without voids and microcracks. Scanning electronic microscopy analysis revealed the good infiltration of nylon 6,6 into the carbon fiber reinforcement and a good reinforcement/polymer in-

terface. Although in a very small scale, the pullout effect of the fibers, due to the weak polymer/carbon fiber interface, was also observed in the composites obtained. The results obtained in this study show the viability of using hot-compression molding for obtaining preregs of nylon 6,6 reinforced with carbon fiber.

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