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Processing of Carbon Fiber/PEI Composites Based on Aqueous Polymeric Suspension of Polyimide

Liliana Burakowski Nohara[1,2], Geraldo Maurício Cândido[2],
Evandro Luís Nohara[3] and Mirabel Cerqueira Rezende[2]
[1]*State University of São Paulo - UNESP*
[2]*Institute of Aeronautics and Space, Department of Aerospace Science and Technology*
[3]*University of Taubaté, Unitau*
[1,2,3]*Brazil*

1. Introduction

Thermoplastic composites materials are being more frequently used in a wide range and variety of structures such as automotive and aerospace components. These applications often demand a unique combination of properties including high thermal and oxidative stability, toughness, solvent resistance, and low dielectric constant, etc (Nohara, 2005).

Thermoplastic have some distinct advantages over thermoset composites such as: high ductility and toughness, facility of processing and recycling potential. For applications that require high performance, the most commonly used thermoplastic are PEI (polyether imide), PPS (polyphenylene sulfide) and PEEK (polyether ether ketone) (Kong, 1996; Nohara, 2005; Nohara et al., 2005).

Thermoplastic can be classified by their molecular structure as either amorphous or semicrystalline polymer. Semicrystalline polymers crystallize to form structures with excellent chemical resistance, mechanical properties, and high service temperature, whereas the amorphous are unable to form ordered structures, showing up either in glassy or rubbery state. The glass transition it is not just determined by the chemical structure but, also, by the available free volume between the chain, allowing its rotational movement (Cogswell, 1992; Nohara, 2005).

The term amorphous implies that the polymeric chain it is present in a "entangled" without any degree of local order, unlike the semicrystalline polymer, that has a certain crystallographic orientation (Cogswell, 1992). One of the advantages of amorphous system is that they don't crystallize, since that it shows less a "variable" to be rated in the processing. A real advantage of amorphous polymer is that there is a slight variation in its volume between the solid and molten state, since there is no change in its specific mass associated with the formation of crystalline areas. Thus, such materials are less likely to be submitted to distortion in the cooling process, in the processing operation and for the composite material, it occurs a minor level of internal stress (Cogswell, 1992).

The aerospace industry has been researching more about the amorphous thermoplastic polymer and has found a meanful usage of they in aircrafts, especially where the high temperature performance is demanded (above 200ºC), as well as a good resistance to solvents (Cogswell, 1992). Among the polymer high performance thermoplastic that has been used in aerospace industry, is the PEI, which is an amorphous polymer, transparent with amber colour that has been used since 1982.

The material is inherently flame resistant with low smoke emission, attending the established standards for the aircrafts interior and the requirements of the FAA (Federal Aviation Administration). It is soluble to solvents partially halogenated (such as the methylene chloride), but resistant to alcohol, acids and solvents made of hydrocarbon, bearing well the gama rays and ultraviolet radiation, characteristics of the semicrystalline polymer. The amorphous structure of the PEI contributes for the excellent dimensional stability and the mechanical proprieties highly isotropic, comparing to other semicrystalline (Offringa, 1996; Sroog, 1991).

Its high glassy transition temperature (217ºC) and high modulus at high temperature are resulting from the rigid imide groups in their chemical structure. However, the ether groups justify the flexibility of the molecular chain. PEI also demonstrates good electrical properties and remains stable over a wide range of temperatures and frequencies. The high glass transition temperature allows the PEI to be used intermittently to 200ºC. O PEI it stands out medical procedures, where the medical and dental equipments demand frequent sterilization. O PEI is also used for primary and secondary aircraft structure, radomes and stealth panels for military use and snow boards (Offringa, 1996; Jenkins, 1999).

The composite materials show different interfaces between its constituents which tend to govern the properties of material. This interface is defined as boundary surface between the reinforcement and the matrix and needs to be strong enough in order to allow stress transfer from the matrix to the reinforcement.

As the composite can be manufactured in high temperature and the reinforcement tends to have a lower CTE (coefficient of thermal expansion) than the matrix, the composite at room temperature tends to have residual stress, such that the reinforcement is under compression. The residual stress is particularly large when the reinforcement is in the form of fibers. The residual stress affects both the reinforcement and the interface between reinforcement and matrix (Chung, 2000).

However, besides the interface, the composite also have an interphase which is defined as the region formed by the interaction between the reinforcement and the matrix, possessing local properties different from those of the bulk matrix. The size and type of interphase varies strongly and depends on the nature of the fiber and its surface as well as on the polymer matrix. Because stress transfer in the composites should be influenced by the interphase, optimization of the mechanical properties of composites requires an extensive knowledge of the behaviour of the interphases and its effect on mechanical performance (Brodowsky et al., 2010; Pompe, Mäder, 2000; Reifsnider, 1994).

Interactions in the interphase region in thermoplastic composites depend on many factors such as matrix morphology, fiber surface conditions, presence of residual stresses, fiber and matrix elastic moduli as well as the presence of reactive functionalities. These functionalities

can be obtained by coating the reinforcement or treating its surface with an interfacial bonding agent or coupling agent (Gao, Kim, 2001; Nohara et al., 2005).

Several methods have been developed to improve the fiber surface wettability or to increase the quantity of surface functional groups. The interfacial bond between the carbon filaments and the resin matrix can be enhanced by enlarging the surface area, which provides more points of contact/anchorage between the fiber and the matrix, or by enhancing the physicochemical interaction between the components (Burakowski, 2001; Nohara et al., 2005; Zielke, et al., 1996; Pittman Jr. et al., 1997).

Oxidation methods consist of oxidizing the carbon fiber in a liquid or gas environment to form oxygen-containing functional groups such as carboxyl, carbonyl, lactone and/or hydroxyl groups on the surface of the fiber, while simultaneously increasing the surface area of the carbon fiber. All these methods contribute to improve the stress transfer from the relatively weak and compliant matrix to the strong and stiff reinforcing fibers (Burakowski, 2001; Nohara et al., 2005; Zielke, et al., 1996; Pittman Jr. et al., 1997; Yue et al., 1999; Lee, Kang, 1997).

Another method to improve the adhesion between the reinforcement and matrix consist in applying a thin polymer layer (normally in lower than 1% of total composite mass), also known as coating or sizing on the reinforcement surface. This interphase area can also be developed spontaneously, by the matrix interactions with the carbon fiber surface (Chuang & Chu, 1990; Texier, A. et al, 1993).

The most used coating in carbon fibers are made of epoxy, phenolic and, furfurylic resins among others. However, these bonding agents don't bear temperature near to high performance thermoplastic matrix processing temperature, as the PEI, PPS, PEEK (>300 °C). In these case, can either be recommended the polyimide, due to the its high solvent resistance and high service temperature like the polymers above named (Burakowski, 2001; Nohara, 2005).

Polyimides (PIs) are a class of thermally stable high performance polymers that continue to gain importance in a wide variety of applications such as high temperature adhesives, microelectronics, membranes, photosensitive materials, matrix materials for composites and as reinforcement coating (Gao & Kim, 2001; Bessonov & Zubkov, 1993; Mittal, 1984; Ghosh & Mittal, 1996).

These applications are possible due to the many advantageous properties exhibited by polyimides, including excellent mechanical, thermal and adhesive properties, good radiation resistance, low dielectric constant, chemical resistances, there are no known organic solvent for the aromatic polyimides, and it has been used successfully in applications at temperatures as low as -269°C and as high as 400°C (Ghosh & Mittal, 1996; Saeed & Zhan, 2006; Srinivas et al., 1997).

In the case of composite applications, PIs have been successfully used as reinforcement coating between carbon fibers and high performance thermoplastic matrices such as PEEK, PEI and PPS (Chuang & Chu, 1990).

Recently, it has been possible to use PIs as interphase in structural thermoplastic composites by employing a new pre-impregnation and composite manufacture technique, namely,

aqueous suspension prepregging (Texier et al., 1993; Gardner, 1998; Nohara, 2005). With this technique has been possible to improve the mechanical and chemical properties of the interface in thermoplastic composites.

The aqueous suspension prepregging method, was first proposed by Virginia Polytechnic Institute and State University researches and there is a few literature about this subject (Texier et al., 1993; Brink, Lin, Riffle, 1993; Gardner, 1998).

The aqueous suspension prepregging technique uses PAA (polyamic acid), a polyimide precursor, allowing the polymer matrix to be applied to the reinforcement together with the interphase forming polymer during a single pre-impregnation step (Brink, Lin & Riffle, 1993).

The aqueous suspension prepregging technique uses PAA neutralized with a base to produce the PAA salt. The polymer matrix (powder form) is then dispersed in an aqueous solution of the PAA salt, which acts as a dispersant and electrostatically stabilizes the suspension via the interaction with the surface of the matrix powder particles (Texier et al., 1993). Carbon fibers or fabrics are then coated with the polymeric suspension.

In a second phase of the processing, the PAA is thermally converted in a polyimide that can form an interphase region between the reinforcement and the polymer matrix, acting as coupling agent (Texier et al., 1993; Yu & Davis, 1993).

The purpose of this study is to compare two methods of processing thermoplastic composite: hot compression molding and aqueous suspension prepregging, showing that the latter method uses the insertion of a polyimide interface in composite. For polyimide interphase had been used 5 PAA/PI: BTDA/DHPr; BTDA/ODA; BTDA/DDS; BTDA/BisP e PMDA/ODA. As polymeric matrix in the composite processing, with carbon fiber, PEI was used. The PI synthesized as dust, they were characterized by the DSC technics (Differential scanning calorimetry), TGA (thermogravimetry), SEM (Scanning electron microscopy) and FTIR (Fourier transform infrared spectroscopy). The composites obtained in both manufature processes were compared and assessed by the technics of ILSS (interlaminar shear strength) and SEM.

2. Materials and methods

2.1 Reinforcement

As reinforcement plain weave carbon fiber was used, obtained from Hexcel Composites, with sizing compatible to epoxy resin. This fabric is composed of 3,000 filaments with a diameter of about 7 μm each. The carbon fiber fabric were cut in small square pieces (50 mm X 50 mm) and washed with acetone to eliminate the sizing.

2.1.1 Surface treatment of carbon fiber

Carbon fibers surface were treated, in order to verify the improvement of interface properties. This procedure was carried out in concentred nitric acid (Synth, 97%). Enough fabric to obtain a composite lot was treated (to acquire aqueous suspension prepregging based on BTDA/ODA).

2.2 Polymeric matrix

PEI, an amorphous thermoplastic polymer, was used. The PEI has T_g (glass transition temperature) of 217°C, is marketed by GE Plastics under trade name Ultem 1000, in pellets form and transparent amber color; its structure is shown in Figure 1.
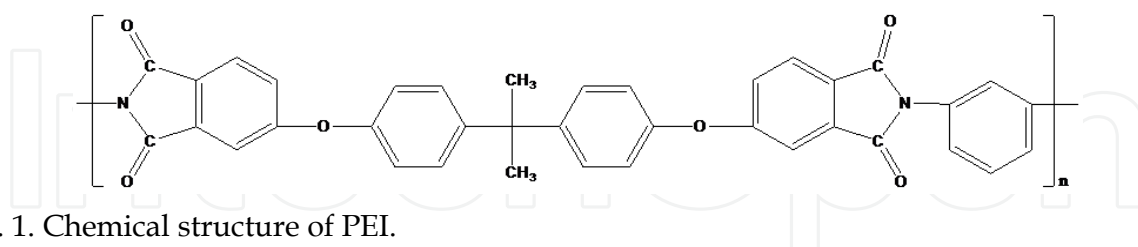

Fig. 1. Chemical structure of PEI.

2.2.1 Micronization of polymeric matrix

As the PEI was acquired commercially, in the form of pellets, it was necessary to micronize this material, so that it could be used to obtain polymeric suspension. Firstly, the PEI was grinded in a mill. For this, the pellets were immersed in N_2 liquid, for the purpose of fragilize them, in order to facilitate the milling. The grinded polymer in the mill presented a granulometry considered high (200 μm in average), to be used in the polymeric suspension technic, that is why it requires the micronization. For the micronization was used the Treu micronizer, the procedure was made three successive time.

2.2.1.1 Average size PEI measurement

The average size of the particles PEI was measured in a SEM from Zeiss, model 950 under variable pressure. The particles were sifted on a metallic specimen holder, which was covered by conductive carbon tape. The sample was blasted with compressed air to remove the excess of particles. The usage of SEM also played an important role, to observe the particles morphology after the micronization.

2.3 Polyimide interphase

2.3.1 Reagents

Dianhydrides: PMDA (pyromellitic dianhydride) and BTDA (3,3′,4,4′-benzophenonetetracarboxylic dianhydride). Diamines: DHPr (1,3-diamino-2-propyl alcohol); ODA (4,4′-diaminodiphenyl ether); DDS (4,4′-diaminodiphenyl sulfone) and BisP (4,4′-[1,4-phenylenebis(1-methylethylidene)]). Solvent: Acetone. All chemicals were purchased from Sigma Aldrich (97–99% purity) and the solvent was Merck.

2.3.2 Synthesis

The synthesis of the PI precursor, o PAA, was made according to literature (Asao, 2001; Nohara et al., 2007). Two solutions were prepared from equimolar quantities of the dianhydride and diamine in acetone (dianhydride or diamine/acetone = 0.004 mol/100mL). Both solutions were mixed at room temperature in a buchner flask at N_2 atmosphere, under ultrasonic agitation (40 kHz) for 4 hours. Monofunctional end-capper phthalic anhydride (from Vetec) was added to solution (16.10^{-5} mol). The end-capper has the function to limit

the chain growth of PAA/PI which in smaller size, as an oligomer, tends to migrate to the fiber/matrix interface, acting as an interface/interphase creator on the bonding between the components of the composite. The conclusion of the reaction was monitored by thin layer chromatography. The chemical structures of PAAs/PIs are showed on the table below (Nohara et al., 2007).
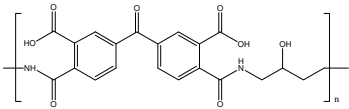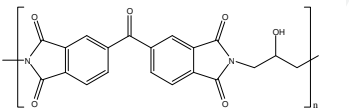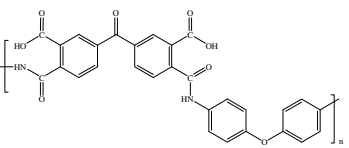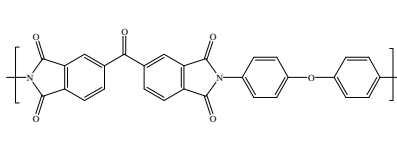
PAA Structure	PI Structure	Polyimide Designation
		BTDA/DHPr
		BTDA/ODA
		BTDA/DDS
		BTDA/Bis-P
		PMDA/ODA

Table 1. Chemical structures of PAA/PI.

2.3.2.1 Characterization of PI

The glass transition temperature from each PI was determined by DSC Pyris 1 Perkin Elmer under N_2 purge (20 mL/min). From each sample, approximately 13mg, was firstly imidized in the equipment and submitted to the cycle of : 1h-100°C, 1h-200°C and 1h-300°C at 10°C/min. After, the samples were cooled at ~100°C/min up to 150°C and submitted to a new cycle up to 550°C (20°C/min).

The thermal stability of the PIs was analyzed by the TGA. The sample were imidized in the equipment, following the same procedure applied on the DSC analysis. After this, the samples were cooled at room temperature. Subsequently, imidized samples were analyzed from room temperature up to 1000°C (10°C/min) to obtain T_d.

Fourier transform infrared spectroscopy (FT-IR) was used to confirm the presence of functional groups within both PAAs and PIs (BTDA/DHPr, BTDA/ODA, BTDA/DDS, BTDA/BisP and PMDA/ODA). Measurements were carried out on a FT-IR spectrometer Spectrum 2000 from Perkin Elmer, using the potassium bromide disk technique (1:400 mg).

2.4 Composites preparation

2.4.1 Hot compression molding

The preparation of composites using hot compression molding consist in spread the powdered polymeric over the carbon fiber fabrics, as showed on the Figure 2. In a mold, eighteen layers of carbon fiber fabrics (cleaned with acetone) were used intercalated with PEI micronized in an aluminum mold, in the ratio reinforcement:matrix of 50/50 (v/v) (Nohara et al., 2007).
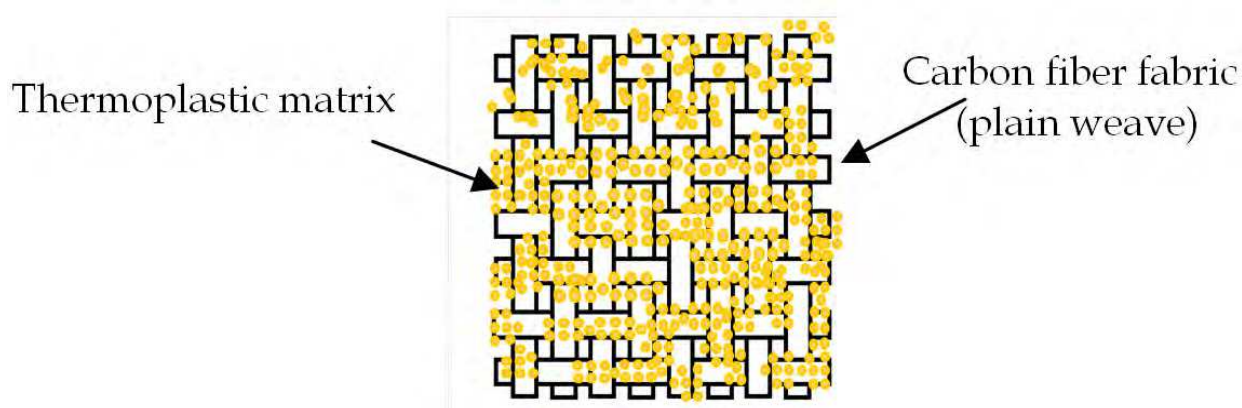

Fig. 2. Schematic diagram showing the carbon fiber/matrix composite assembly by hot compression molding.

2.4.2 Aqueous suspension prepregging

2.4.2.1 Preparation of poly(amic acid) salt

For the composites manufacture through aqueous suspension prepregging technic, were used PAAs (showed on the Table 1) as dispersants, with purpose of induce the matrix suspension of the polymeric particles (PEI) in solution PAA salt (obtained by the solubilization of PAA in NH_4OH) and so, obtain an effective wettability of carbon fiber fabrics by the system. In addition, the PAA played a very important role in the composites processed by this method: the interphase between the reinforcement and the matrix.

This method of composites processing it had already been studied previously by other scientist (Texier et al., 1993; Gardner, 1998). The last scientist mentioned in his work, he used three different bases: ammonium hydroxide (NH_4OH); tetramethyl ammonium hydroxide – (TMAH - ($N(CH_3)_4OH$)) and tripropylamine hydroxide (TPA - ($NH((CH_2CH_2CH_3)_3OH$)) to obtain the composites based in PPS (poly(phenylene sulfide)) and PEEK (poly(ether ether ketone)) and he studied the influence of these three bases in the molar mass distribution, in the thermal properties and viscosity of interphase formed by Ultem and BTDA/Bis-P type polyimide interphase. Gardner noticed that, the bigger the size of the counterion ($NH_4^+<$

TMA$^+$<TPA$^+$) the better is the thermal properties interphase PI, bigger is the molar mass distribution and smaller is the viscosity molten. These results confirm that final properties of the interphase can be controlled and tailored according to the requirements and the usage of the composites.

In the current article, was choosen to use a single base or counterion: NH$_4$OH, since the main objective of this study is to identify the affinity of the PEI with the 5 PIs synthesized. With the purpose to study the effects of pH in the salt solutions of PAA in polymeric suspension of PEI, seven different solutions of NH$_4$OH were patterned, in the following pH: 11.70; 11.80; 11.90; 12.00; 12.10; 12.20, and 12.30.

It was used NH$_4$OH from the Synth (28-30%) and deionized water was added to the NH$_4$OH, to correct pHs. Then, salt solutions were prepared from PAA (NH$_4$PAA), from solubilization of each PAA in solution NH$_4$OH from pHs 11.70 to 12.30. The NH$_4$OH was used with stoichiometric ratio of 1.25:1 for the functionalities of PAA (two per unit). The 25% of stoichiometric excess of the base were used to assure the neutralization of the functionalities of amic acid to and keep the salt stability of polyamic acid, as studied by Texier and Gardner (Texier et al., 1993; Gardner, 1998).

2.4.2.2 Preparation of the polymeric suspension

After obtaining NH$_4$PAA, each beaker with salt was covered with a polymer film and heated at 60°C for 30 minutes, under magnetic stirring. Then, the solution was cooled up to room temperature. After this phase, the micronized PEI was added to NH$_4$PAA solution, and then homogenized with a magnetic stirrer for 30 minutes (Texier et al., 1993; Gardner, 1998; Nohara et al., 2007). The NH4PAA/PEI mass ratio was 0.05 and the concentration of PEI in the suspension was 10% mass (Gardner, 1998).

2.4.2.3 Preparation of the laminate

The carbon fiber fabrics were immersed in a beaker with polymeric suspension under stirring. The fabrics impregnated with NH4PAA were kept in room temperature for 24 hours. Thereupon, were taken to an oven under vacuum, were they preimidized under the following cycle: 1h-100°C; 1h-200°C e 1h-250°C a 10°C/min (the complete imidization of the PAA, occurred together the polymer matrix, in the consolidation of the composites). Next, the impregnated fabrics, were placed (in 18 layers), into a mold and were taken to a hydraulic hot press for the consolidation, that started heating from room temperature (~30°C) up to 310°C (10°C/min). It was established a ramp of 1h at 310°C, and applied in a pressure of 9.8 MPa for 30 minutes in this temperature.

The same procedure (consolidation) was applied to obtain the composites via hot compression molding.

2.4.3 Characterization of the composites

2.4.3.1 Interlaminar Shear Strength (ILSS)

The ILSS test was conducted according to ASTM D 2344. The test was made using 10 specimens obtained for each composites type, through the methods by the hot compression

molding and aqueous suspension prepregging. The values of ILSS were calculated by the use of equation 1. The test was conducted by a test machine from universal Instron, in a test speed of 1.3 mm/min and a load cell of 5 tons.

$$F^{sbs} = 0.75 \times \frac{P_m}{b \times h} \tag{1}$$

where: F^{sbs} = is the short-beam strength (MPa)

P_m = is the maximum load during the test (N);

b = is specimen width (mm);

h = is the thickness (mm).

2.4.3.2 Scanning electron microscopy

The microscopic analysis of the composites surface fracture was made from sample submitted to interlaminar test shear strength. The surfaces for analysis by SEM were generated through a process that consisted in loading in shear, under very low speed until material rupture by delamination. Thereafter, the specimens generated during the loading were immersed in an isopropyl alcohol solution and distilled water (50:50 v/v) in a ultrasonic bath for 5 minutes. Then the specimens were blasted with compressed air for drying and were placed in a suitable holder. Carbon tapes and conductive silver ink were used to the electrical contact with the microscope. These analyses were accomplished in SEM Zeiss 950 and the results were registered with magnifications of 1000 and 2000 times.

3. Results and discussion

3.1 Reinforcement

3.1.1 Surface treatment of carbon fiber

The chemical attack of the carbon fiber, was accomplished to promote the surface changes, by a reliable introduction of the chemical polar groups and for the roughness rise (Nohara et al., 2005).

In the chemical treatment, carbon fiber fabrics (as received) were treated with a concentred nitric acid solution for 10 minutes at 103ºC, with heating plate without agitation. The exposition time was chosen based on studies of Nohara et al. (Burakowski, 2001; Nohara et al., 2005) who concluded that the fibers treated superficially with nitric acid shown an increase roughness (measured by Atomic force microscopy and SEM) and a small decrease in tensile strength of single filaments of the carbon fiber (2143 ± 471MPa to 1924 ± 658MPa) – ASTM D-3379, due to removal of surface layers weakly attached to the fiber surface and the reduction of critical failures, that act as stress concentration. Analysis by XPS (X-ray photoelectron spectroscopy) it was also used and found the introduction of polar groups such as C-OH, C=O and COOH at the fiber surface treated with nitric acid (Burakowski, 2001; Nohara, et al., 2005).

After the chemical treatment, the fibers were thoroughly washed with freshly boiled deionized water and dried in an oven at 105ºC for 2 hours. Carbon fiber fabrics treated were

immediately kept in a desiccator under vacuum until its usage in composites preparation. Just one family was chosen for the research of carbon fiber fabrics with changed surface (carbon fiber-BTDA/ODA-PEI).

3.2 Polymeric matrix

3.2.1 Micronization of polymeric matrix

The polymeric matrix of PEI, after being grinded, passed through three micronizations consecutive and it was observed that this procedure led to the breakage of the particles, as expected and the smaller the particles size the more accentuated became the phenomenon of attraction among them and consequently, the packing. The micronized particles were separated by sieve 200–400 mesh coupled to a sieving machine with ultrasonic agitation. Just the obtained part in sieve 400 mesh was used in aqueous suspension prepregging.

3.2.1.1 Average size PEI measurement

The PEI particles, analyzed by MEV (Figures 3-a and -b) showed a rounded grain, like a cabbage, composed by many foils. This morphology of thin "foils" it was obtained probably due to the successive micronization suffered by the particles that made them to stick to one another, at the milling, they originated a packing of polymer layers. The PEI, as it can be observed on Figures 3-a and –b, showed after the micronization, the majority of its particles with sizes over than 30 μm.
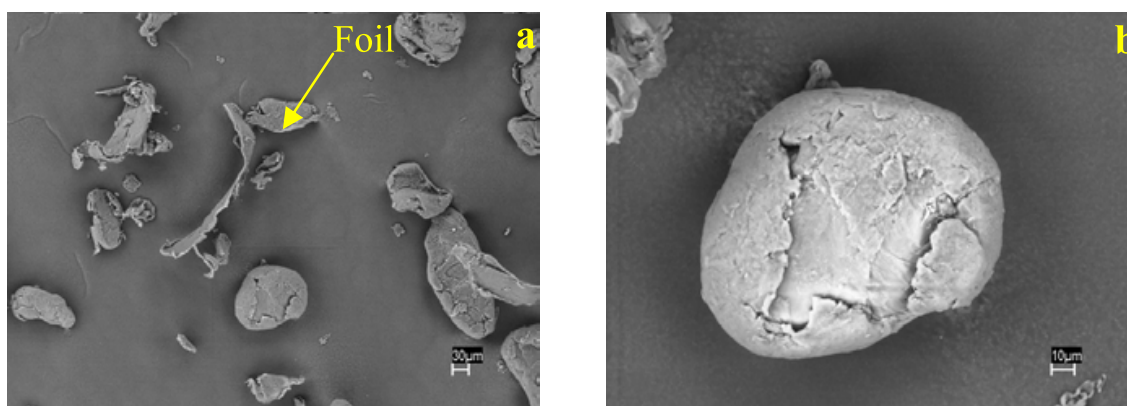

Fig. 3. Particle of PEI – a) 120X and b) 1000X.

3.3 Polyimide interphase

The synthesized PAAs showed the following colors: BTDA/DHPr = pale yellow; BTDA/ODA = yellow; BTDA/DDS = orange; BTDA/BisP = bright yellow and PMDA/ODA = golden yellow. Next, will be presented the analyses made by DSC, TGA and FT-IR of PAA and PI.

3.3.1 Characterization of PI

The measured glass transition temperature, Tg, of PI: BTDA/DHPr, BTDA/ODA, BTDA/DDS, BTDA/BisP, PMDA/ODA were measured by DSC, as showed on the table 2. T_g obtained for the PIs showed a slight difference from the one found in the literature, due to

the changes in variable of the synthesis, such as: different solvents, methods and cycles of imidization, among others. There is a very interesting case to be emphasized, is the PI PMDA/ODA from literature (Sroog, 1991), which indicates a value of T_g = 399°C and a temperature of theoretical melting temperature of 595°C. However, as described in the same literature, at 510°C already occurs a mass loss of ~5%, which probably compromise the fusion identification by the overlap of the thermal events. The values found here, for this polyimide were different (T_g=437°C e T_d=498°C) due to a likely difference of the solvents and synthesis method used.

For the TGA analysis, the samples were imidized in the equipment, and it was checked, during the imidization cycle, that each one of them lost 21% of mass, concerning to the loss of solvents and to the water release from the synthesis and imidization. Next, the samples were cooled up to room temperature, were submitted to a second scanning, so that the thermal stability could be evaluated from each one of them (Table 2). The TGA analysis of the PIs synthesized show a beginning of decomposition temperature almost the same the found in the literature. The PI from the type BTDA/BisP, for example, shows a beginning of T_d decomposition temperature of 401°C (Table 2). Gardner (Gardner, 1998) explains the acquirement of this PI com T_d at about 489°C. The biggest difference found between the T_d it is due to a likely difference of the solvents and synthesis used: Gardner (Gardner, 1998) used NMP (n-methyl-2-pyrrolidone), a solvent of high boiling point solvent (202°C), while the current study was used acetone (56.5°C), with the purpose to obtain PI directly in powder form.

Polyimide	T_g (°C)		T_d (°C)	
		Reference		Reference
BTDA/DHPr	213	201*	310	310*
BTDA/ODA	305	329*	422	532*
BTDA/DDS	300	307**	396	400**
BTDA/Bis-P	248	270***	401	489***
PMDA/ODA	437	400**	498	505**

*Asao & Saito, 2001; **Sroog, 1991; ***Gardner, 1998.

Table 2. Glass transition temperature (T_g) and decomposition temperature (T_d) for the PI of the types: BTDA/DHPr, BTDA/ODA, BTDA/DDS, BTDA/BisP, PMDA/ODA.

The FT-IR analysis was used for the identification of synthesis of PAA or from the possible incomplete reaction found from the used reagents – which is characterized, mainly by carboxylic acid remaining group of dianhydride - and PI. PAA samples show similar absorption spectra in Figure 4-a, wherein bands near 1719-1740 cm^{-1} were assigned to the vibrational modes of acid groups for all samples. Bands near 1660 and 1537-1542 cm^{-1} were assigned to the vibrational modes of amide groups.

The bands related to acid and amide groups disappeared after imidization (Figure 4-b). The characteristic absorption bands of imide groups near 1780, 1722-1724, 1380 and 721-725 cm^{-1}, were present in the spectra (Figure 4-b). These absorption bands confirm the presence of imide groups. Table 3 presents the Infrared absorption bands of amides, imides and related compounds.
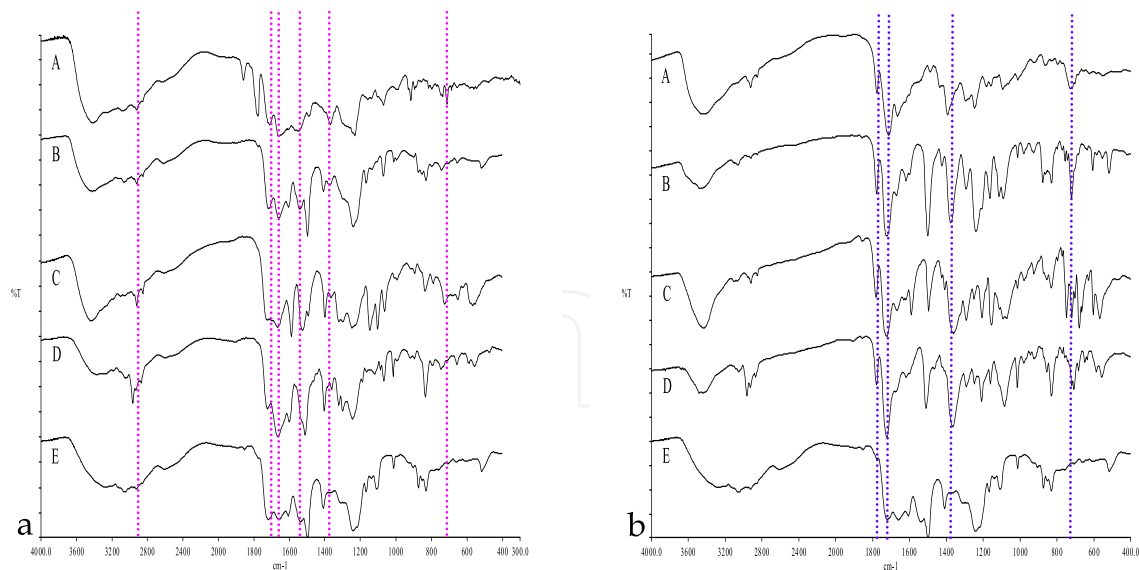
Fig. 4. FTIR spectrum of: a) PAA and b) PI: A) BTDA/DHPr, B) BTDA/ODA, C) BTDA/DDS, D) BTDA/BisP e E) PMDA/ODA.

	Absorption band (cm⁻¹)	Origin
Aromatic imides	1780	C=O asymmetric stretch
	1720	C=O symmetric stretch
	1380	C-N stretch
	725	C=O bending
Amic acids	2900-3300	COOH and NH_2
	1710	C=O (COOH)
	1660	C=O (CONH)
	1550	C-NH
Anhydrides	1820	C=O
	1780	C=O
	720	C=O

Table 3. Infrared absorption bands of imides and related compounds.

3.4 Preparation of the composites

3.4.1 Hot compression molding

The obtained composites from molding compression were retired of the mold and cutted according to the test specification of ILSS.

3.4.2 Aqueous suspension prepregging

3.4.2.1 Preparation of the polymeric suspension

For the composites manufacture, through the aqueous suspension prepregging, 5 different PAAs were used as dispersant, with the purpose of causing suspension of polymeric matrix particles of the PEI in the salt solution in the PAA thus, obtaining a effectively wettability of the carbon fiber fabric by the system.

3.4.2.1.1 Investigation of the polymeric suspension behavior due to the use of pH different

The polymeric suspensions based in PEI were evaluated in relation to interaction with the 5 PAAs, under seven different values of pH: 11.70; 11.80; 11.90; 12.00; 12.10; 12.20; 12.30. The Figure 5 shows the polymeric suspensions of the PEI, prepared from the PAA type BTDA/ODA, which is representative for all the PAAs studied.

Observing the obtained suspensions from the PAA type BTDA/ODA, there was not found any evidence, related to the material suspension quantity – in the system there after the immediate agitation. Can also be observed that, the tonality of the seven solutions, under seven different pH did not suffer any color alteration. Despite of this, the original color of PAA-BTDA/ODA, obtained from the synthesis, is bright yellow, while the one from PEI it is bright amber, indicating that all the systems, suffered the same tonality changing. It was also observed the rise of the pH value, did not influence the NH$_4$PAA-PEI interaction and quantity of polymer in suspension. The same procedure was applied in 4 different PAAs and no meanful change was found. Thus, it was chosen the usage of pH 12 to obtain all composites by aqueous suspension prepregging.

Fig. 5. Polymeric suspension of NH$_4$PAA-PEI type BTDA/ODA.

3.4.2.1.2 Evaluation of the adhesion PEI/interphase/reinforcement

The Figures 6 a–b show the carbon fiber fabrics that were impregnated with the polymeric suspension of the NH$_4$PAA-PEI from the types: BTDA/ODA e PMDA/ODA, respectively, after imidization. Can be observed on the Figure 6-a there was a significant adherence of the polymeric matrix PEI to the carbon fiber fabrics, by the usage of the PAA/PI interphase type BTDA/ODA; since, placing the semipreg in vertical position no particle was displaced.

It was also identified that, pre-impregnation allowed the handling of the semipreg, by the perfect adherence of the particles, besides the perfect distribution of these particles. The Figure 6-b shows the aqueous suspension prepregging process provides a formation of a polymeric film stuck to the carbon fiber, easy to be seen by the strong adhesion of PEI particles each other, by the usage of PAA/PI type PMDA/ODA. Can also be observed that, polymeric film part can be unstuck and handling with the spatula. So, can be presumed that this system offers a perfect compatibility between PAA-BTDA/ODA or PMDA/ODA and PEI.
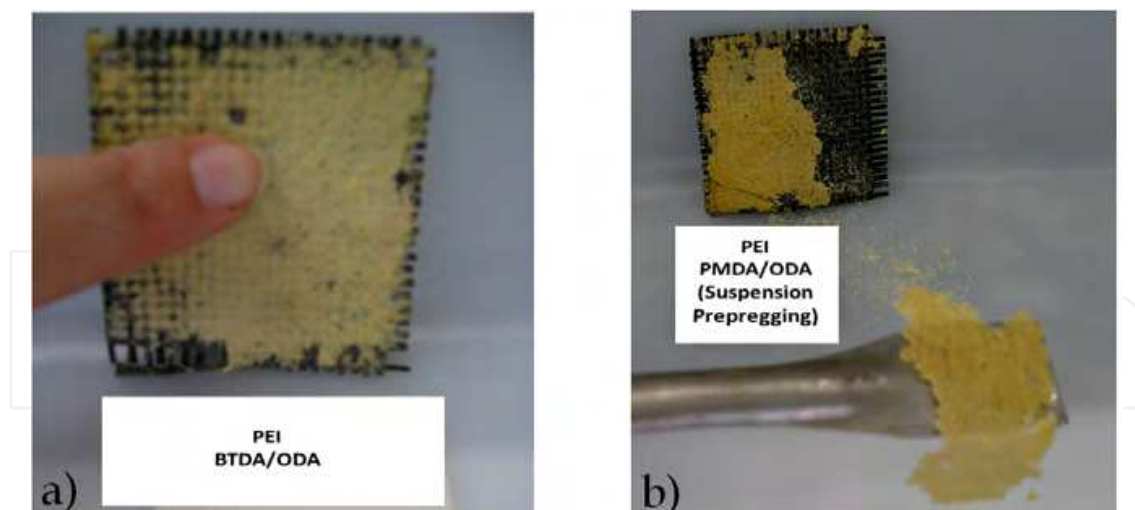
Fig. 6. The semipregs sample pre-imidized, obtained through a pre-impregnation via polymeric suspension – a) PAA-PEI type BTDA/ODA e b) PAA-PEI type PMDA/ODA.

3.4.2.1.3 Composites preparation – Hot compression molding X aqueous suspension prepregging

The main objective of the current study is to compare the acquirement process of composites by the hot compression molding and aqueous suspension prepregging. Once, interface/interphase region obtained by two processing methods can have a meanful difference and, considering that this region is one the composites components with meanful importance, all the variables must be considered.

At first, the obtained composites by aqueous suspension prepregging have a differential related with obtained composites by hot compression molding method: the PI interface/interphase. It is expected that the mechanical properties – that in the current study are evaluated by interlaminar shear strength – have an increase in values, using the method that makes use PI interphase.

However, as can be seen, some information related to both processing methods can also be obtained, by the simple observation of the contact between the carbon fiber fabric and the polymeric matrix, as shown on Figures 7-a and –b which show (1) fabric impregnated with the polymeric suspension of PEI-PMDA/ODA and (2) the covered fabric with the polymer PEI powder.

The Figure 7-a (2) shows that when fabric "2" (would be the hot compression molding method) it stands on horizontal position, all the polymer remains spread on the reinforcement. However, when the fabric is exposed to the vertical position (Figure 7-b(2)), can be noticed that the polymer matrix loose itself easily from the fiber fabric. It happens because the lamination process, for the composites acquirement by the hot compression molding method, it consist on spread the polymeric matrix in the reinforcement; while, the pre-impregnation method (Figure 7-a (1) e 7-b (1)) consist in use of an interphase. In this case, it favors adhesion between the polymeric matrix and the reinforcement, like an adhesive type. It allows the best spreading of polymer matrix on the fabrics, besides to favour the adherence and wettability before the composites consolidation.

The Figures 7-a (2) e –b (2) also show that the method that consist on spread the polymeric matrix on the fabric has one more interference: spreading the powder over the fabric, it enters easily through of weft and warp, not allowing a uniform spread of the polymer matrix on the fabric layer, by introducing a different quantities of matrix, of a layer to another of composite.
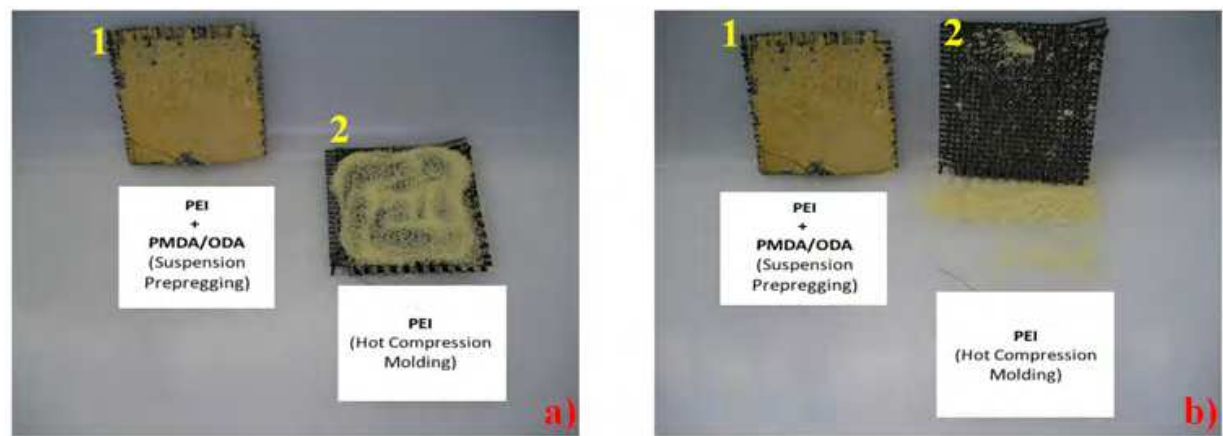

Fig. 7. (1) Impregnated fabrics with polymeric suspension PEI-PAA type PMDA/ODA e (2) PEI was spreaded on the carbon fiber fabric – hot compression molding.

3.4.3 Characterization of the composites

3.4.3.1 Interlaminar shear strength (ILSS)

The Table 4 relates the ILSS values and the respective standard deviations from the 7 lots of composites based in PEI, obtained by hot compression molding and aqueous suspension prepregging.

Interlaminar shear strength (ILSS) (MPa)	
Hot compression molding	
Carbono fiber/PEI composite	66.1 ± 5
Aqueous suspension prepregging	
PI-BTDA/DHPr	40.6 ± 3
PI-BTDA/ODA	52.5 ± 2
PI-BTDA/ODA/ fabric treated by HNO_3	80.6 ± 8
PI-BTDA/DDS	57.4 ± 5
PI-BTDA/Bis-P	74.7 ± 6
PI-PMDA/ODA	78.1 ± 7

Table 4. Interlaminar shear strength (ILSS) values of the thermoplastic composites manufactured by the hot compression molding method and aqueous suspension prepregging.

The analysis of curves (stress x displacement) showed, for all the composites, the occurrence of failure not catastrophic, in other words, didn't happen an abrupt break of the sample,

after reach the maximum stress value. The composites showed interlaminar fracture, i.e. the crack formation in horizontal way.

The observation of Table 4 shows, in general way, that the obtained composites by the aqueous suspension prepregging method presented an improvement in the interlaminar shear strength values compared to the prepared composites using the hot compression molding. This is due to the usage of PAA/PI, besides acting as dispersant in the polymeric suspension, they also had an important role for the composites: as interphase creators.

The PI usage also favored the interdiffusion possibility of the PI into polymeric matrix, which resulted in a gradient of properties in the matrix, as it was evidenced by different ILSS values found, due to different PI polymeric chains.

The interphase material can have best and differentiated properties from the ones found in the matrix bulk. This is exactly the purpose of using the aqueous suspension prepregging in the current study: improve the interface/interphase. Thus, the 7 lots of composites were analyzed.

The PEI composites prepared by hot compression molding process, presented higher ILSS values, comparing from the ones prepared with aqueous suspension prepregging, just for the samples obtained PI-BTDA/DHPr interface. The decrease in ILSS values for the processed composites with this interphase, comparing to the hot compression molding process, it is related, probably, to the chemical structure of the PI. This is the only PI, among the 5 used in this study, that present less aromaticity, due to the structure of diamine (linear - DHPr).

Observing the lots of sample, it was proved that the prepared composites with the polymeric suspension based in PI-PMDA/ODA and BTDA/ODA/treated fabrics with HNO$_3$, they had better results of ILSS (18.1 and 21.9% respectively), comparing to the composites obtained by hot compression molding.

The difference of the ILSS values of the composites with different PI interphases, can be explained by a slight difference of polymeric chains. The PEI it is a polymer from the polyimides class and has part of its chemical structure similar to the PIs studied, with p-phenylene and imide groups that provide the stiffness to a part of the structure. PI BTDA/ODA, however, it is considered a flexible chain, due to the carbonyl group "bridges", between the benzene rings of the dianhydride and the ether between the benzene rings of diamines. This flexibility allows a better interfacial contact with the carbon fiber, resulting in stronger bond strength. In fact, in the last case, it is important to observe that there is a difference meanful between the ILSS values found for the composites that used PI-BTDA/ODA, related to the composite obtained with PI interphase equal, but which made the use of the treated reinforcement with HNO$_3$. The meanful increase of the ILSS property for this composite, comparing to the prepared composite with the same interphase, it is due to the probable interdiffusion chains mechanism of the PI into PEI, because when it is in contact with the treated fibers (now with high quantity of polar group and rugosity – as shown on the item 3.1.1) they were able to favour a strong chemical bond and mechanical anchorage.

It is important to emphasize, by using the aqueous suspension prepregging the PAA/PI is present as a oligomer in the system thus, it shows a tendency to the migrate to the interface

between matrix and reinforcement. This facilitates the fiber wettability by PAA/PI, changing the interfacial resistance with the matrix.

The PMDA/ODA, unlike the BTDA/ODA, is PI the more rigid among the studied (it has 4 carbonyl groups attached to the same benzene ring in a coplanar conformation) it would be expected that had a smaller interaction with the carbon fiber. However, the difference in ILSS values of this interphase comparing to the others (BTDA/DDS, BTDA/BisP), it might be related to the interaction of part of its molecule with PEI, once these molecular structures can be overlapped, due to the conformation of its molecules can lead to points of attraction between chains and thus providing a strong interaction.

3.4.3.2 Electronic scanning microscopy

After the interlaminar shear strength test, the samples were analyzed, with respect the morphology of their fracture surfaces by SEM.

The samples for the analysis were obtained by loading in shear, with a very low speed, until the final charge for the production of a fracture surface by delamination. In overall, different morphologies were observed from 7 different manufactured composites (Figures 8 a-g).

The figure 8-a (FC/PEI – hot compression molding) shows the micrography of fracture surface of the laminate obtained by loading to failure. This micrography shows that there was disruption of the laminate in the fiber direction and that there is the presence of channels and ridges on the surface of fracture, which may have been occasioned by the forced loading. Can be observed (red arrow) which the outline of most of the carbon fiber filaments; it is covered with a thin PEI layer, suggesting that there was a wettability of reinforcement by the matrix, but there are also discovered fibers.

The Fig. 8-b shows a fracture surface (caused by the loading) from the obtained composites with a PI-BTDA/DHPr interphase. The micrography shows that there are carbon fiber filaments discovered, probably due to the effort of loading. In this case, seems to have a slight excess matrix among the fiber filaments, it maybe might contribute for the low ILSS values obtained. It can also be observed that the polymer presents aspect more dry and fragile, related to the carbon fiber sample/PEI without the PI interphase (Fig. 8-a) which looks have behavior more ductile.

The Fig. 8-c shows (interphase BTDA/ODA), the presence of uncovered fibers free from polymeric matrix on the laminated surface and also matrix excess in other regions. These observations don't match with ILSS values found in this composites lot. What could have happened is that the region was selected for microscopy observation wasn't representative for the composite as a whole.

The Fig. 8-d shows a composite obtained from the same interphase (BTDA/ODA) but, was used carbon fiber fabrics treated with HNO_3. In this case, are observed regions where the polymeric matrix was removed (red arrow) with the interphase, from the loading to the rupture. It was also observed, a differentiated texture from the fracture surface, with respect to found in other composites, suggesting that there was good wettability of reinforcement by the matrix and consequently, a strong adherence, which was confirmed by the interlaminar shear strength test.
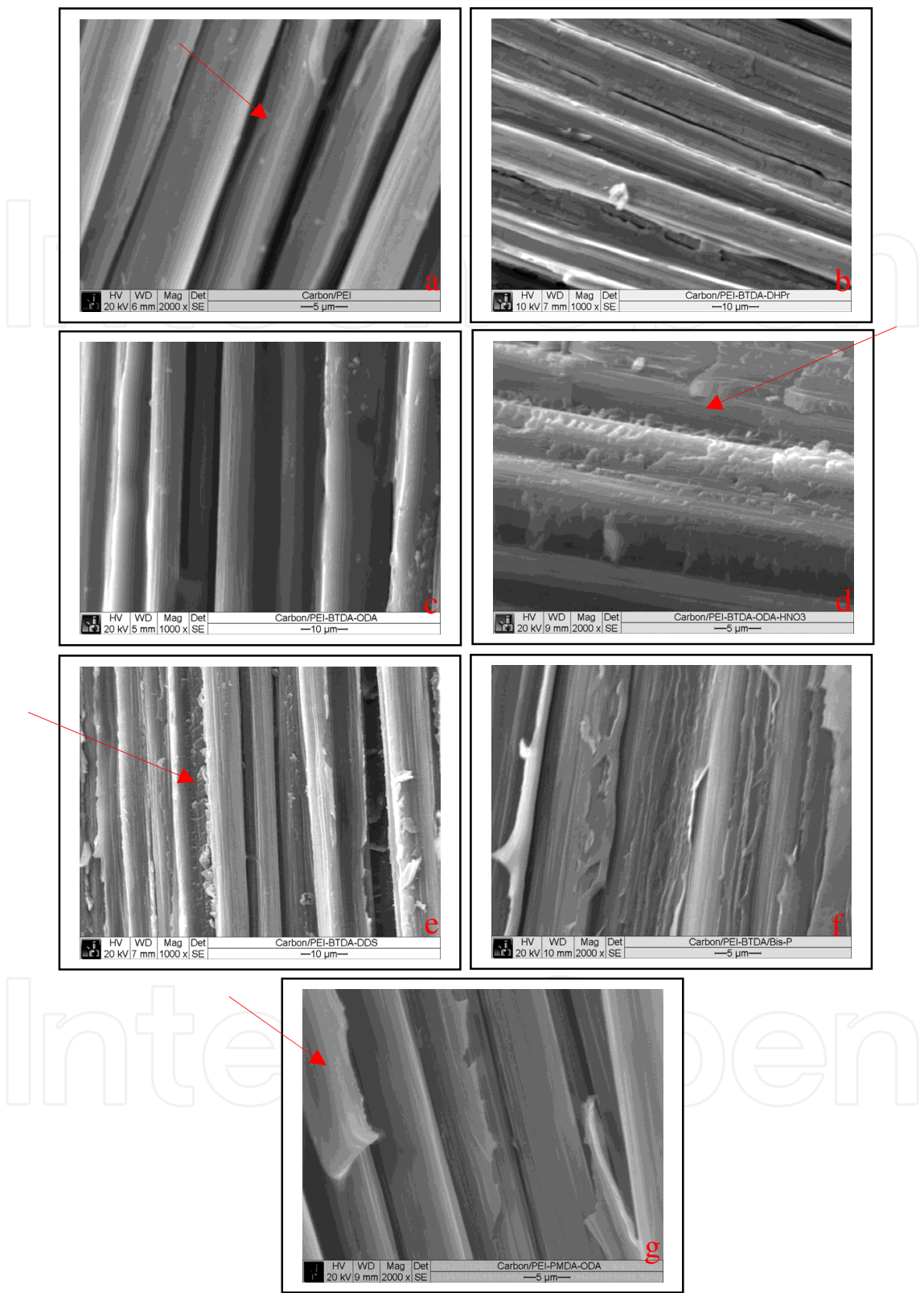
Fig. 8. The fracture surface of the manufactured composites with: a) the hot compression molding and aqueous suspension prepregging b) PI-BTDA/DHPr; c) PI-BTDA/ODA; d) PI-BTDA/ODA-treated fiber with HNO$_3$; e) PI-BTDA/DDS; f) PI-BTDA/BisP and, g) PI-PMDA/ODA.

The Fig. 8-e shows a micrography obtained from the composite of interphase BTDA/DDS. Can also be observed that there was pull out of carbon fiber filament (caused by loading) which left a gap among them (channels). Cleaned carbon fiber were found, that was not wet by the PEI with the interphase BTDA/DDS and in some places, matrix excess (red arrow). These results match with the ILSS test, as the values found in this lot were very low (lower than the ones found for the obtained composites with hot compression molding).

The Fig. 8-f shows a composites made using the PI-BTDA/BisP interphase. It Can be observed that there was not any failure on interface fiber/matrix. There are places where the polymer was pulled out, leaving the uncovered fiber, but can also be observed that, the polymer covered the fibers in many layers. The fiber wettability with system PI-BTDA/BisP-PEI interface seemed to be satisfactory.

The Fig. 8-g shows uncovered fibers, but suggesting that were covered by the system PMDA/ODA performed prior to loading to generate the fracture surface for analysis by SEM. The micrography shows clearly that PEI shows a ductile behavior (red arrow). This situation could have been generated at the loading moment; which may have introduced a certain temperature the composites by the force applied to the material.

For all these cases it was not possible to check a bondary between PI and the polymer matrix PEI, indicating that there was an interdiffusion between both polymers.

4. Conclusion

In this chapter were evaluated the thermoplastic carbon fiber composites/PEI with respect to its performance, through two different processing technics: hot compression molding and aqueous suspension prepregging. The processing technic by hot compression molding can be considered mastered, in terms of obtaining composites, that is why, did not have a further explanation in this study, as it was the aqueous suspension prepregging, which is about the recent procedure and there is a few studies about this in the literature. Thus, much attention was given to the development, knowledge and description of this process.

Firstly, the carbon fiber fabric used in this study were superficially treated with nitric acid, based on the previews studies (Burakowski, 2001; Nohara, 2005), aiming the polar groups insertion on the fiber surface and pitting, responsible for a better mechanical anchorage of the matrix on the reinforcement. The treated carbon fibers were used only in the manufacture of composite type BTDA/ODA.

All the phases that comprise the method of aqueous suspension prepregging were analyzed; started by analyzing the different suspension behavior under pH. This investigation method had the objective to verify the suspensions that presented some behavior changes: color changing due to the pH or the deposition of the most polymeric matrix in the container, that could indicate the interaction or not of the PAAs to the polymeric matrix. Did not present changes in the analyzed systems, thus it was chose to use the pH 12. The best results were obtained for the composites PEI-PMDA/ODA, PEI-BTDA/ODA/fabric treated with HNO3 which presented a substantial increase in the ILSS values (18.1 and 21.9% respectively) compared to composite without interphase. This occurred probably, due to a interdiffusion between the PEI chains and the PIs, when found in oligomer form, in the polymeric suspension. The pre-impregnated PI-PMDA/ODA and PI-BTDA/ODA/treated fabrics

presented the highest matrix adherence level to fiber fabrics, it was evidenced through a "polymeric film" on the fabric surface and a slight difficulty to be removed.

The 7 composites lots were analyzed to the fracture surface after the interlaminar shear strength. In general, it was observed shear failure occurred at the bulk the matrix and not in interface, indicating that this region was not responsible for the composites rupture. It was also a good wettability of fibers by the polymeric matrix has not been identified large quantities of dry fibers in the fracture surfaces of laminates.
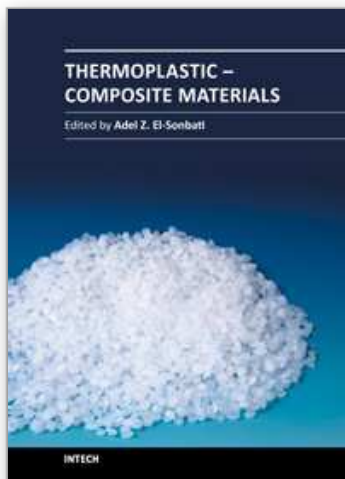
5. Acknowledgment

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