Synthesis of Polyamide 6/6 by Interfacial Polycondensation with the Simultaneous Impregnation of Carbon Fibers

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ABSTRACT: The present study shows the synthesis of polyamide 6/6 (nylon 6/6) via interfacial polycondensation of hexamethylenediamine and adipoyl chloride, at room temperature, with the simultaneous impregnation of carbon fibers, using the reaction injection pultrusion (RIP) process. The polyamide 6/6 obtained was characterized by infrared spectroscopy, differential scanning calorimetry, and viscosity measurements. The impregnation of the carbon fibers was evaluated by scanning electron microscopy assisted by electron dispersive spectroscopy showing good carbon fiber/polymer matrix interface. These results show that the combination of the synthesis of polyamide 6/6, at room temperature, with simultaneous impregnation of carbon fiber amplifies the application of this structural thermoplastic composite with different arrangements of the reinforcement.

Introduction

Recently the thermoplastic composites have increased their use in several applications. In the aeronautical area this kind of composite has found utilization in internal artifacts and wings of Boeing's aircraft, landing gear doors, floor panels, and mobile surfaces such as elevators, radomes, flaps, among others.[1−9] Among the thermoplastics, the polyamidic type is a good candidate due to its low cost and its ease of handling.[10−15] The nylon 6/6 is a semicrystalline polymer, with a melting point near 265 °C. The physicochemical and mechanical characteristics of polyamide have allowed its use in several types of industries, among them can be cited the aeronautical and the space ones.[16−18]

The polyamides can be obtained by several ways.[19−22] In the present work the synthesis of the polyamide 6/6 was accomplished via interfacial polycondensation. This, is a chemical method carried out in the interface between water and an organic solvent that are immiscible. This method can be used to impregnate reinforcements, crossing the filament through the interface of the nylon reaction chamber.[23] Generally, when diamine monomers and diacid chloride are used in this process, the synthesis product, polyamide, is present in a good yield and high molecular weight.[23]

This work shows the study of impregnation of carbon fibers with freshly synthesized polyamide 6/6, aiming to obtain a good fiber/matrix interface, making viable the manufacture of thermoplastic composites with different arrangements of the impregnated fibers and good mechanical properties. For this, polyamide 6/6 was synthesized by interfacial polycondensation, at room temperature. The obtained polymer was characterized by infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and viscosimetry. The carbon fiber impregnation was evaluated by scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDS) analysis of the carbon fiber/polyamide interface.

Reaction Mechanisms

In the same way that the carboxylic acids and their derived react with amines, resulting in amides, the dicarboxylic acids react with diamines, producing an intermediate called nylon salt. Figure 1 shows the synthesis of the polyamide 6/6 mechanism starting from adipic acid and hexamethylenediamine. This reaction occurs at high temperature (∼220 °C) and under vacuum to decrease the water liberated concentration during the reaction, respecting Le Chatelier's law.[24]

However, it is possible to obtain polyamide 6/6 at room temperature, avoiding the use of vacuum. This reaction can be conducted using simple laboratory systems producing polymers with high molecular weight. In this route, the adipic acid is substituted by adipoyl chloride (Figure 2) producing the polyamide 6/6 via interfacial polymerization.

Experimental Section

Adipoyl Chloride Synthesis. In this work, the adipoyl chloride was synthesized in our laboratory. For this, was used a reaction flask with 25 g of adipic acid and 50 g of thionyl chloride in benzene connected to a condensation system. The purity of these reagents was verified by FTIR analysis. With

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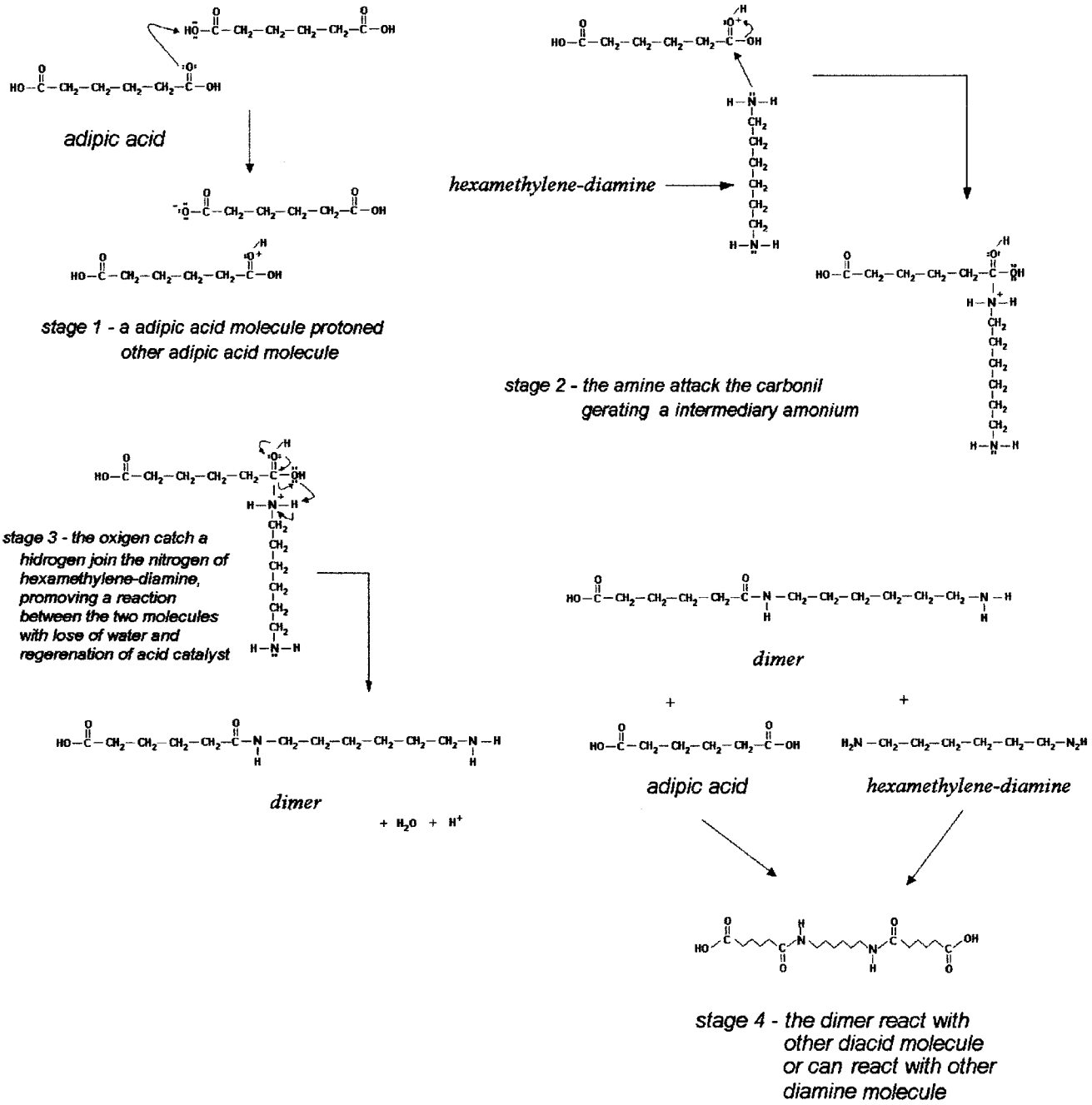

Figure 1. Reaction mechanism for the polyamide 6/6 synthesis using adipic acid and hexamethylenediamine.[24]

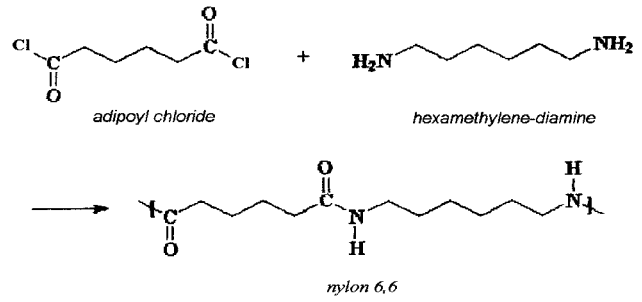

Figure 2. Polyamide 6/6 synthesis using adipoyl chloride and hexamethylenediamine.

the purpose being to trap the delivered byproducts of the reaction (SO_2 and HCl), the condenser was connected to a wash bottle containing distilled water. During the reaction the flask was heated to 80 °C in an oil bath (di-*n*-butyl sebacate) for approximately 2 h. The SO_2 and HCl liberation was monitored by bubbling these gases in water. When the bubbling stopped, the synthesis was interrupted. Then, the reaction flask contending the adipoyl chloride was connected to a distillation system. The benzene was eliminated heating the system at 80 °C for 10 min. After this, this temperature was increased up to 140 °C and the system was connected to a vacuum pump (50 mmHg). The extraction of the byproducts was performed for nearly 1 h.

Polyamide 6/6 Synthesis. The polyamide 6/6 synthesis by interfacial polycondensation was accomplished with 1.5 mL of adipoyl chloride in 50 mL of dichloromethane (solution 1). Over this solution was added solution 2, containing 2.20 g of hexamethylenediamine and 4.0 g of sodium carbonate in 50 mL of distilled water. The polymerization reaction starts immediately before the addition of solution 2.

Impregnation of the Carbon Fibers. Simultaneously with the addition of solution 2, carbon fibers are pulled through the interface, producing the impregnation of this reinforcement within the freshly synthesized polyamide 6/6 (Figure 3). This

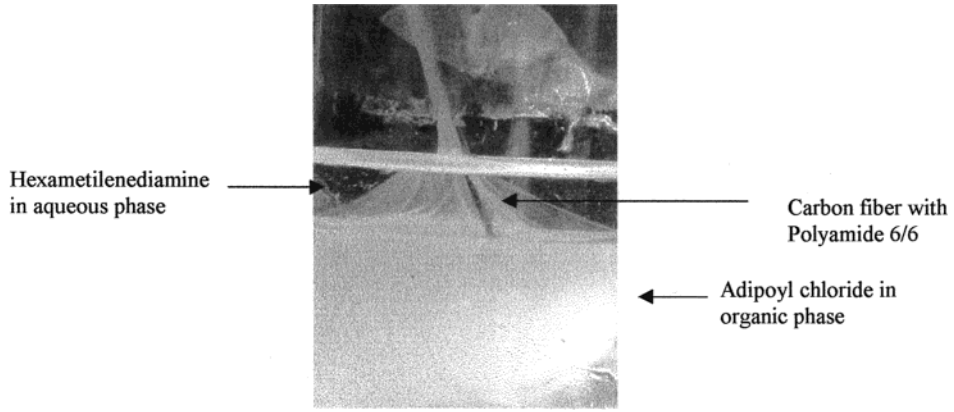

Figure 3. Scheme of the polyamide 6/6 interfacial polymerization on carbon.

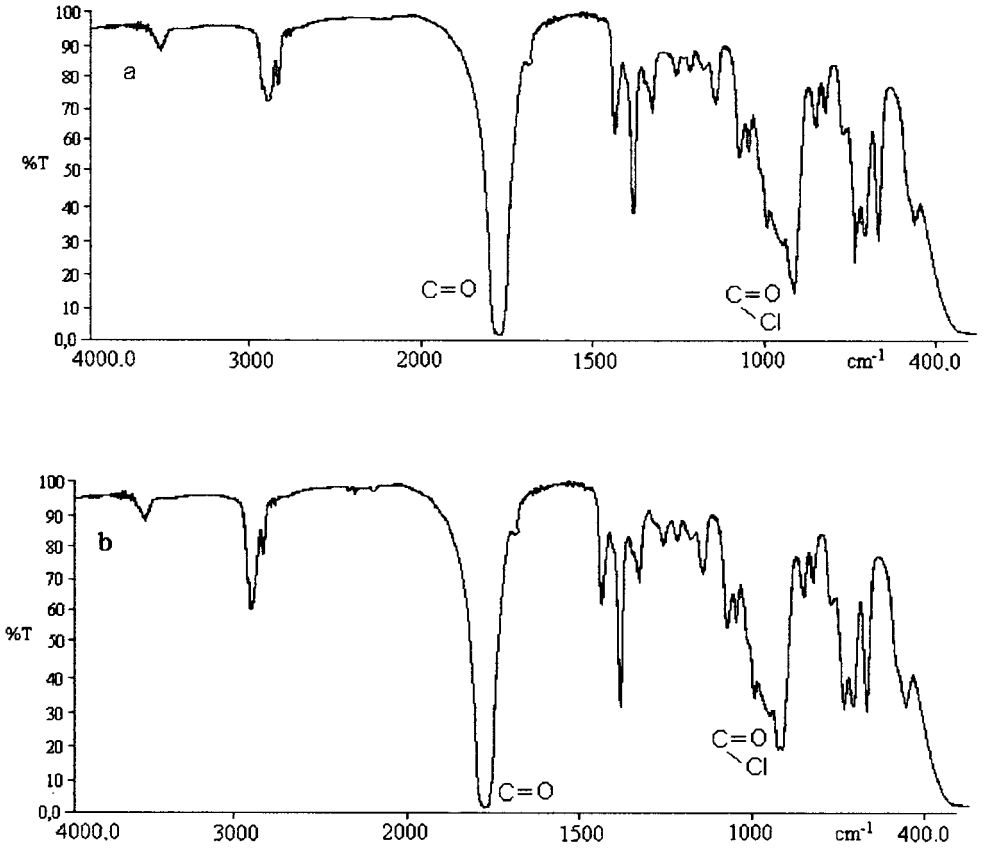

Figure 4. FTIR spectra of adipoyl chloride: synthesized (a) and reference (b).

procedure was accomplished in a glovebox, with N_2 atmosphere to avoid hydrolysis of the adipoyl chloride used.

Characterization. Samples of adipoyl chloride synthesized and the reference (Fluka, with 99% of purity) and polyamide 6/6 synthesized and the reference (provided by Rhodia) were characterized by FTIR analysis, using a spectrometer Perkin-Elmer 1750 spectrometer(range of 4000−500 cm^{-1}, gain 1, resolution 4 cm^{-1}, and 40 scanning). The FTIR analyses of the polyamide 6/6 synthesized involved two techniques to prepare the sample: KBr pellets with a 1:400 mg ratio and films obtained from formic acid solution.

The ^1H NMR spectroscopy analysis involved the dilution of the adipoyl chloride (reference and synthesized) samples in isotopic methanol (solutions at 1%, w/w). These samples were examined at a nominal frequency of 200 MHz and for ^{13}C NMR at a nominal frequency of 50 MHz.

Analyses of gas chromatography/mass spectra (GC/MS) were carried out with the reference and synthesized adipoyl chloride samples, washing them in ethanolic ether after dissolution in acetone. The equipment used was a gaseous chromatograph, HP 6890, with quadrupole mass detector.

The viscosity analysis were carried out using a Schott viscometer, model AVS-500, and polyamide 6/6 solutions (0.05% w/w) in formic acid with purity of 99.9%.

The carbon fibers used are from Toray Co. with 3000 filaments, without surface treatment. After impregnation, these samples were characterized by SEM using a LEO microscope, I model VPi 435 assisted by EDS model Oxford.

Results and Discussion

Adipoyl Chloride Synthesis. In agreement with the synthesis methodology used, the yield of the adipoyl chloride reaction was 70%. Figure 4 shows the FTIR spectra of the reference and the synthesized adipoyl chloride samples. Comparing these results, it is observed that the spectra presents several coincident peaks showing the success of this synthesis. For the adipoyl chloride (reference and synthesized) samples, the main absorptions observed and its probable attributions are as follows: bands at 1797−1798 cm^{-1} (groups

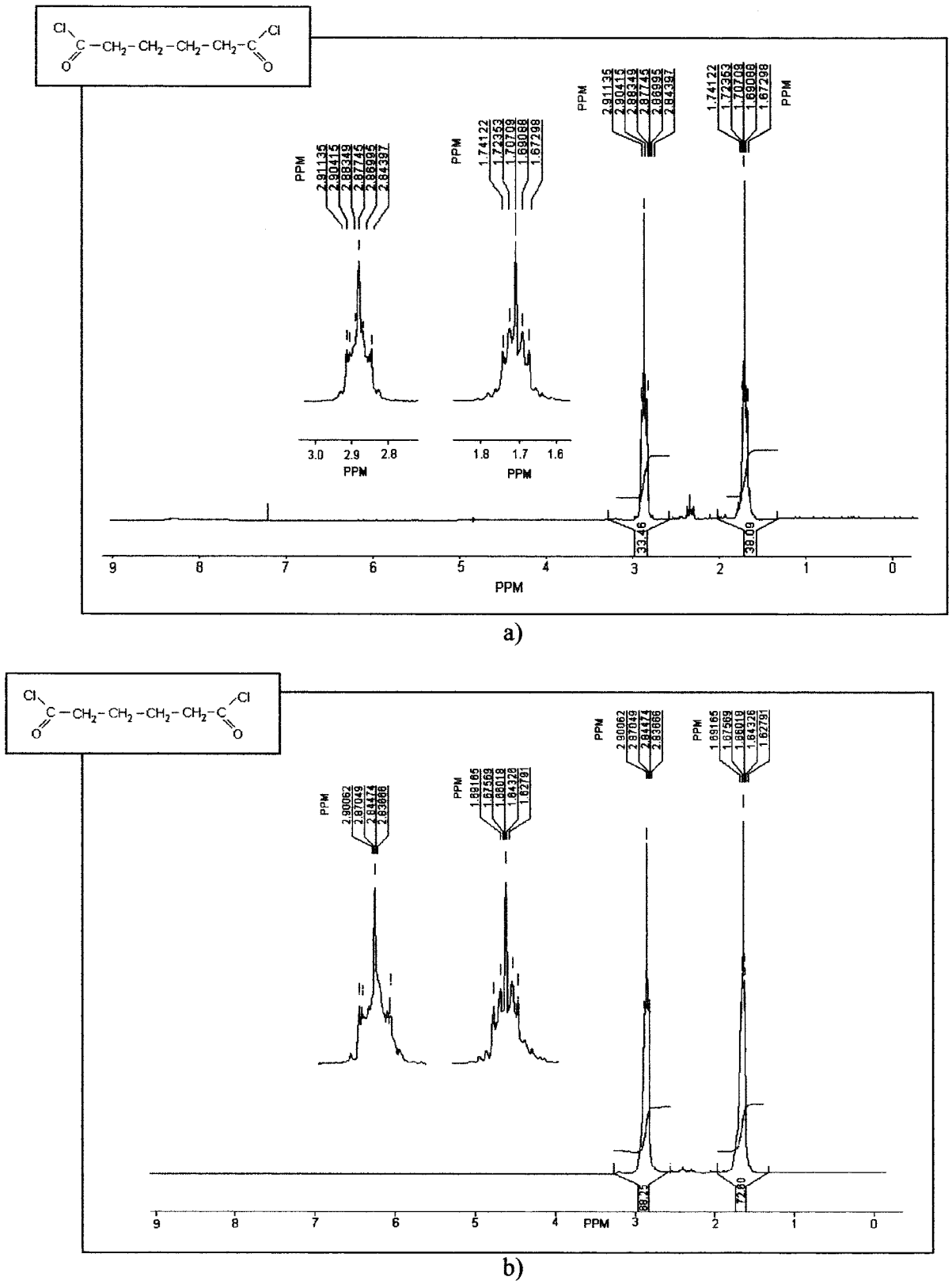

Figure 5. ^{1}H NMR spectra of reference (a) and synthesized adipoyl chloride (b) samples.

C═O) and 930−932 cm^{-1} (groups CO−Cl), confirming the chlorination of the adipic acid. The other bands present are due to the contributions of the unreacted adipic acid.

Figure 5 shows the ^{1}H NMR spectra for the synthesized and reference adipoyl chloride samples. Two peaks can be observed for the adipoyl chloride reference: a multiplet in the range $\delta = 1.62-1.69$, presenting a median value of $\delta = 1.65$ and other multiplet in the range $\delta = 2.81-2.88$, with a median value of $\delta = 2.85$. For the synthesized adipoyl chloride sample, it is possible to observe a multiplet in the range $\delta = 1.63-1.69$, presenting a median value of $\delta = 1.66$ and another multiplet at $\delta = 2.84-2.90$, with a median value of $\delta = 2.87$. These results are close but differ slightly from the literature values,[20] where the adipoyl chloride shows

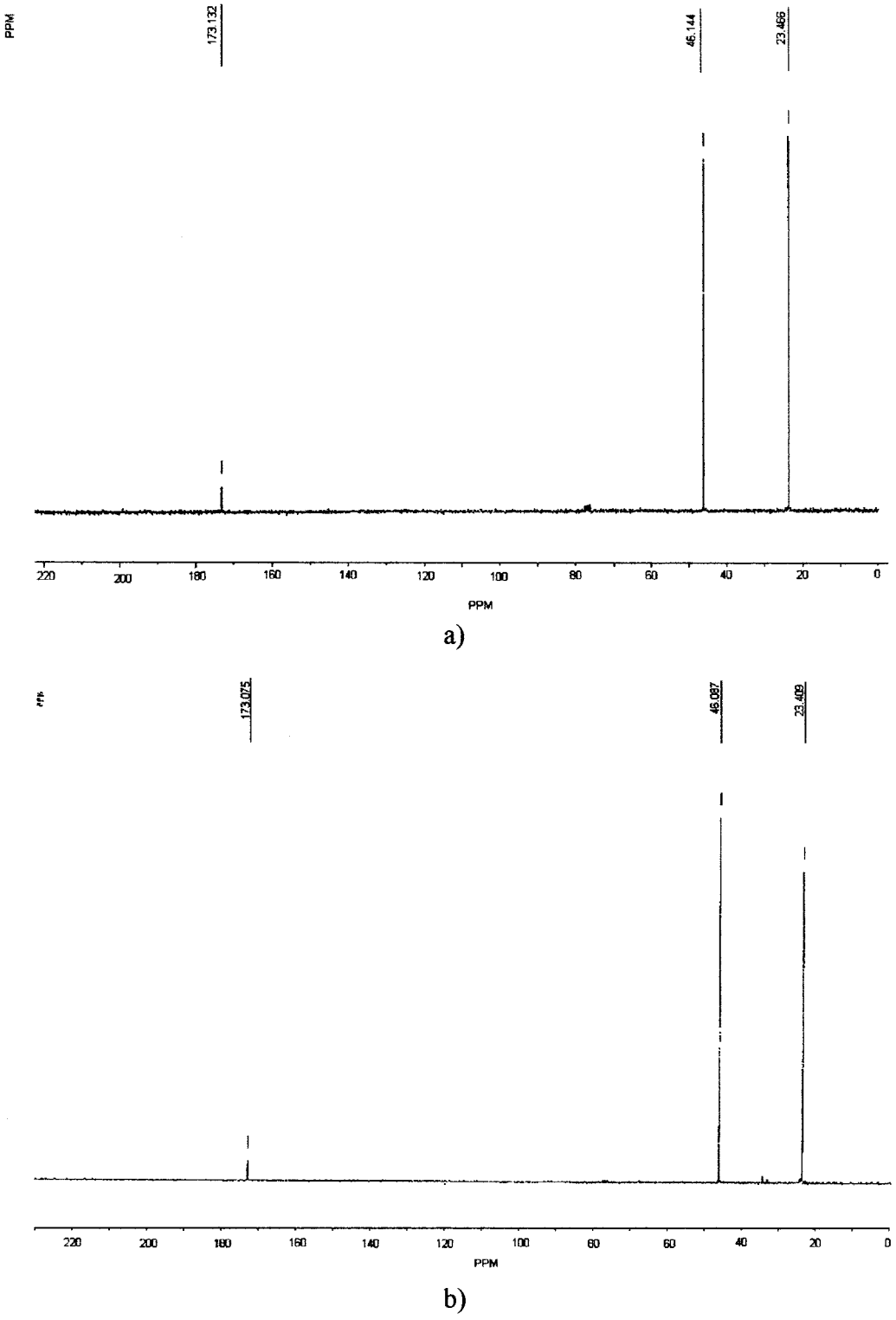

Figure 6. ^{13}C NMR spectra of reference (a) and synthesized adipoyl chloride (b) samples.

two peaks: the first one at $\delta = 1.95$ and other one at $\delta = 2.80$. This deviation of the values is not significant and can be attributed to small amounts of byproducts. This way, one can conclude that both analyzed samples present close displacements, showing that the product of the synthesis of thionyl chloride and adipic acid is the adipoyl chloride.

Figure 6 shows the ^{13}C NMR spectra of the adipoyl chloride synthesized and reference samples, and Table 1 compares the literature values of ^{1}H NMR and ^{13}C NMR[20] with that one determined.

The spectra of ^{13}C NMR of the adipoyl chloride synthesized samples present three peaks: the first one at $\delta = 23.41$, the second at $\delta = 46.09$, and the third one, due to the carbonyl group, at $\delta = 173.08$. For the adipoyl chloride reference sample, the analysis shows peaks at $\delta = 23.47$, another at $\delta = 46.15$ and a third one due to the carbonyl group at $\delta = 173.13$. As can be

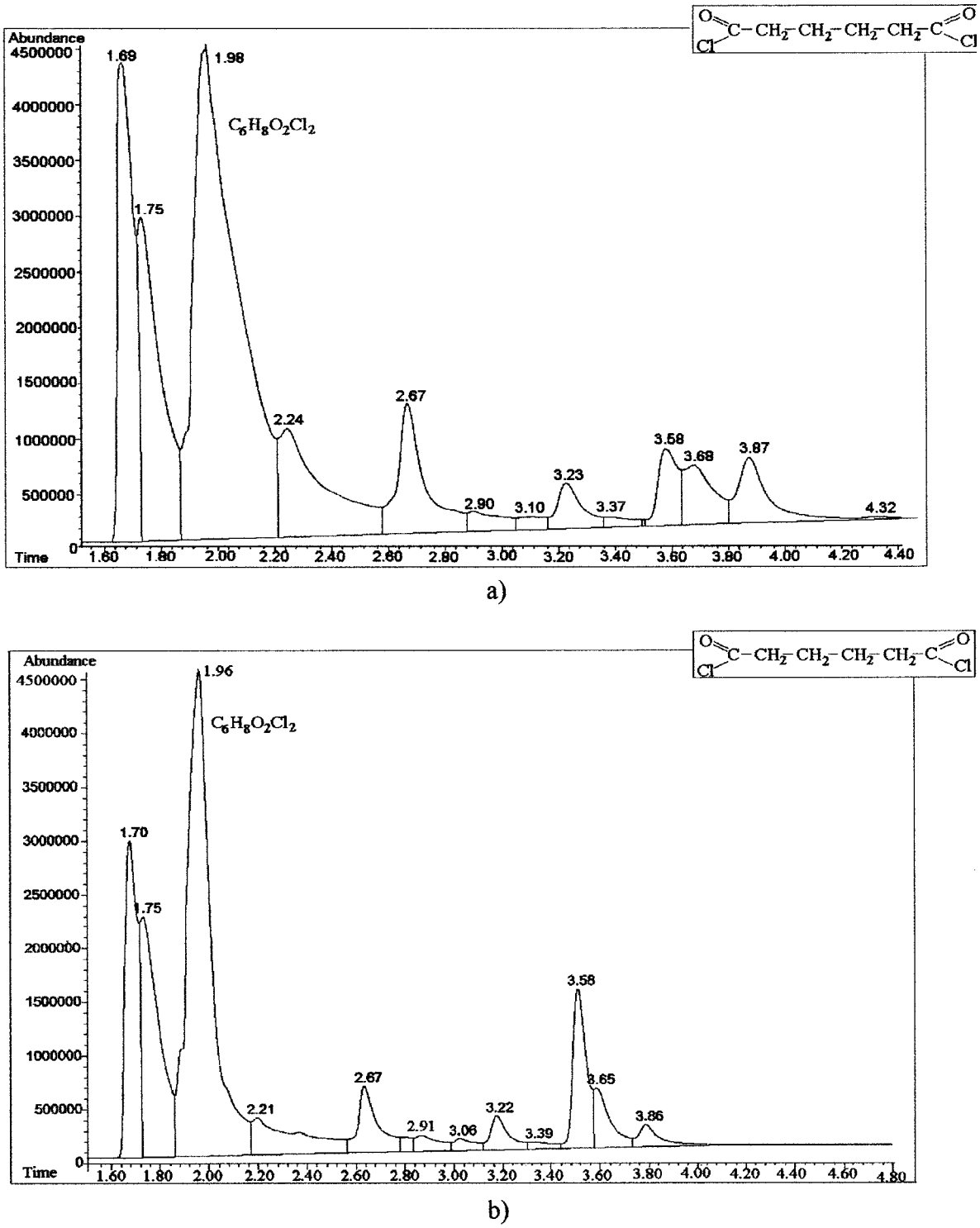

Figure 7. Gas chromatography of the reference (a) and the synthesized adipoyl chloride (b).

Table 1. ^{1}H and ^{13}C NMR Chemical Shifts of Adipoyl Chloride

	adipoyl chloride[20]			synthesized adipoyl chloride			reference adipoyl chloride		
site	a	b	carbonyl	a	b	carbonyl	a	b	carbonyl
$\delta(^1H)$	2.80	1.95	2.87(m)	1.66(m)	2.85(m)	1.65 (m)			
$\delta(^{13}C)$	35.2	26.5	180.4	46.9	23.4	173.1	46.2	23.5	173.1

observed, the results of ^{13}C NMR present a very good concordance for both samples. These results are close to those found in the literature, with three peaks: the first one at $\delta = 26.5$, the second at $\delta = 35.2$, and the third one, due to the carbonyl group, at $\delta = 180.4$.[20]

The nomenclature used for each site refers to protons or carbons located at α, β or carbonyl positions within the respective moieties.

Figure 7 shows the gas chromatograms of the adipoyl chloride samples, reference (a) and synthesized (b). As

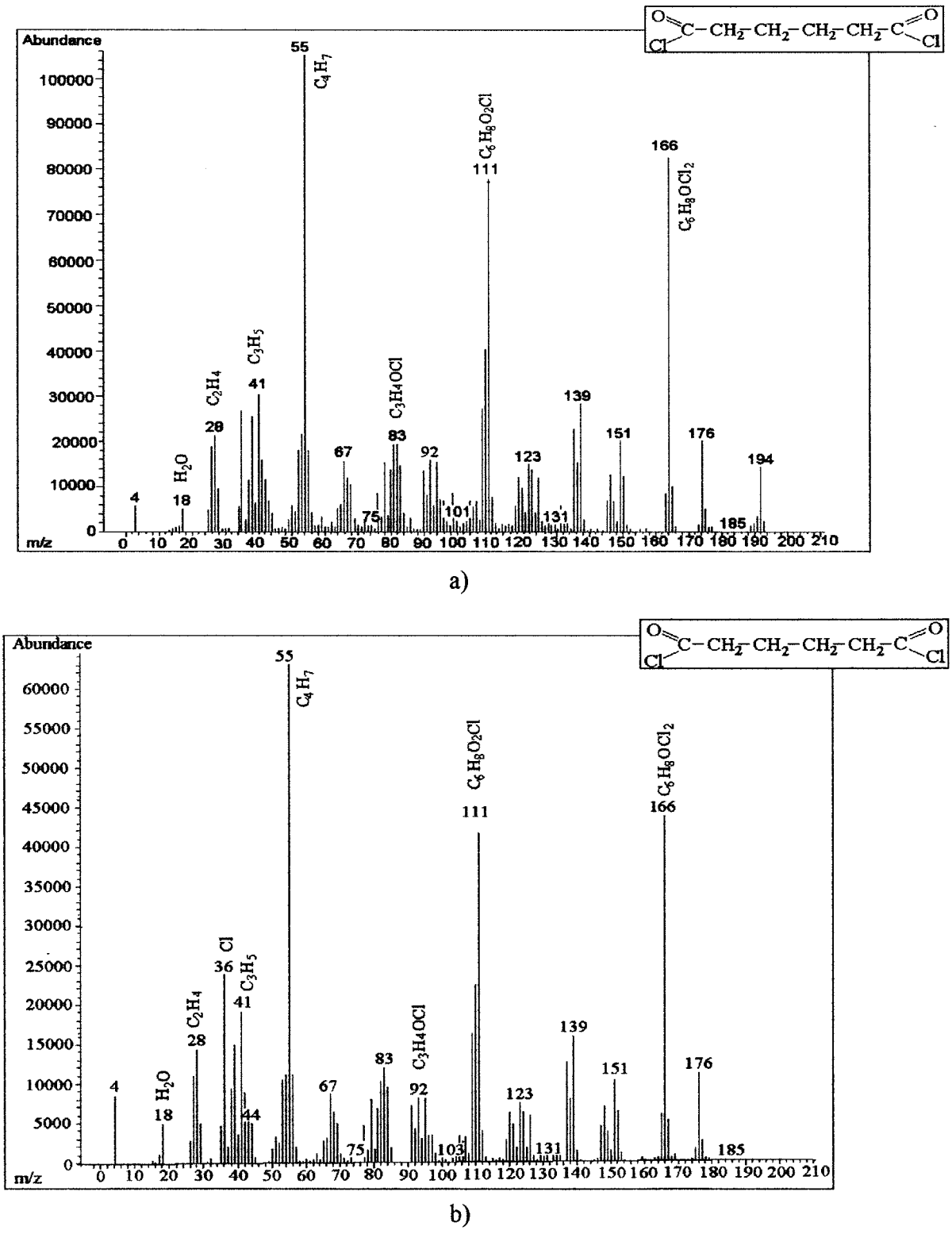

Figure 8. Mass spectroscopy of the reference (a) and the synthesized adipoyl chloride (b).

can be observed, the spectra present similar behaviors. The first peaks that appeared are due to solvents used in the analysis (ether at 1.70 min and acetone at 1.75 min). The more intense peaks at 1.96 and 1.98 min are due to the synthesized and reference samples, respectively. These peaks in this position are a contribution of the adipoyl chloride. However, the adipoyl chloride used as reference (supplied by Fluka) and that one synthesized presented sludges of the synthesis (peaks after 1.98 min). The peak positioned at 2.24 min is observed to be coming from the hydrochloric acid.

Figure 8 shows the spectra of mass of the adipoyl chloride samples synthesized (a) and used as reference (b). The analysis of these spectra show that results present similar behaviors. The main peaks are 55, 111, and 166.

The correlation of the ^{1}H and ^{13}C NMR, FTIR, and CG/MS results confirms that the product obtained in

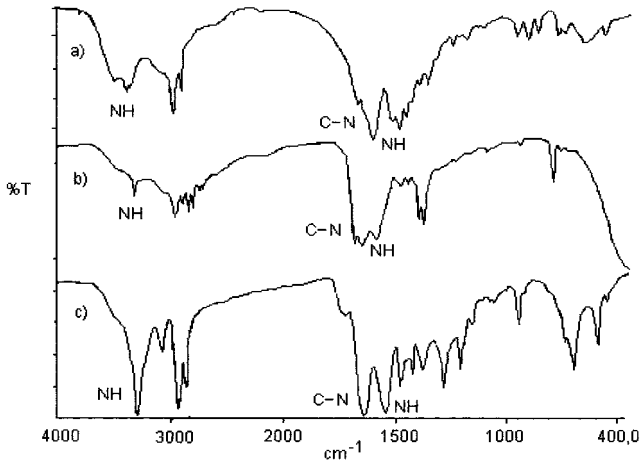

Figure 9. FTIR spectra: (a) KBr pellets, (b) drained film of the polyamide 6/6 synthesized, and (c) that taken from the literature using KBr pellets.

the adipic acid chlorination reaction is the adipoyl chloride.

Polyamide 6/6 Synthesis. The synthesized polyamide 6/6 sample was analyzed by FTIR spectroscopy using the following techniques: (a) KBr pellets and (b) drained film using formic acid. Figure 9 compares these two obtained spectra with one from the literature[25] used as reference (spectrum c obtained using KBr pellets).

The main absorptions observed in polyamides are those due to the peptidic bonds of these molecules. As can be observed in spectrum c, the main absorptions for polyamide 6/6 are as follows: contributions of the NH group (3300 cm^{-1}), the stretching of the amidic carbonyl (1650 cm^{-1}), and the NH deformations (1550 cm^{-1}). Bands positioned below 1000 cm^{-1} allow that different types of polyamides be differentiated from each other, since these samples do not have other components that absorb in the same region.

The synthesized polyamide 6/6 samples were analyzed by FTIR spectroscopy and the absorption bands obtained differed from the one expected, indicating that other components were present simultaneously with the analyzed samples. Probably these components are composed of intermediaries, oligomers (low molecular weight compounds), and unreacted precursors of the synthesis. These absorptions appear in the region of CH_2, C═N, C−N, and NH_2 groups.

The thermal properties of the polyamides were studied by differential scanning calorimetry. The DSC measurements were carried out to determine the melting point. For the polyamide 6/6 reference sample is observed a clear endothermic peak at 260.6 °C (57.82 J/g), agreeing with the literature values located in the range 255−265 °C.[26] However, the synthesized sample showed a peak at lower temperature, 249.5 °C (2.43 J/g). This fact probably occurs due to the presence of the oligomers and the sludge in the synthesized sample, as observed in the FTIR analysis, dislocating the melting point to a lower value.

The viscosimetric analysis showed that the viscosity index is equal to 40.5 mL/g and M_v is 5772 g/mol. This value of the molecular weight is low as expected, because the synthesized sample was not subjected to posterior thermal treatment.

The microscopic analysis of the impregnated carbon fibers shows that the impregnation happened in a homogeneous way with an adequate infiltration of the

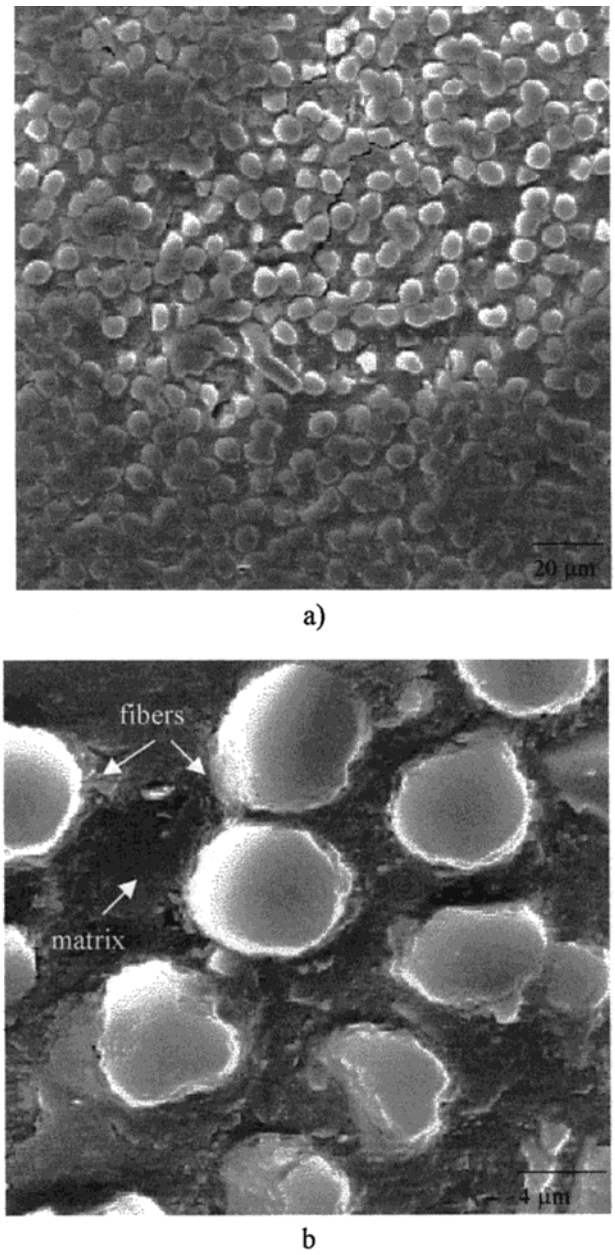

Figure 10. Photomicrography of impregnated carbon fibers with freshly synthesized polyamide 6/6: (a) 500×; (b) 3000×.

polymer in carbon fiber cables, Figure 10, parts a and b. This occurs, probably, due to the low molecular weight and, consequently, the low viscosity. As well, a good carbon fiber/polyamide 6/6 interface is observed, showing that the freshly synthesized polymer presented an adequate compatibility with the surface of the carbon fiber.

During the fiber impregnation the formation of particles occurred on the surface of the coated fiber. This observation was made by MEV, Figure 10. Analyzing this region by EDS, Figure 11, parts a and b, it is observed that these particles present more intense peaks of carbon, sodium, and chloride, when compared with the EDS spectrum obtained from a coated fiber region free of particles. This phenomenon is due to the sodium chloride formation during the polycondensation reaction. This observation indicates that the coated fibers need to be washed before the impregnation to clean their surfaces.

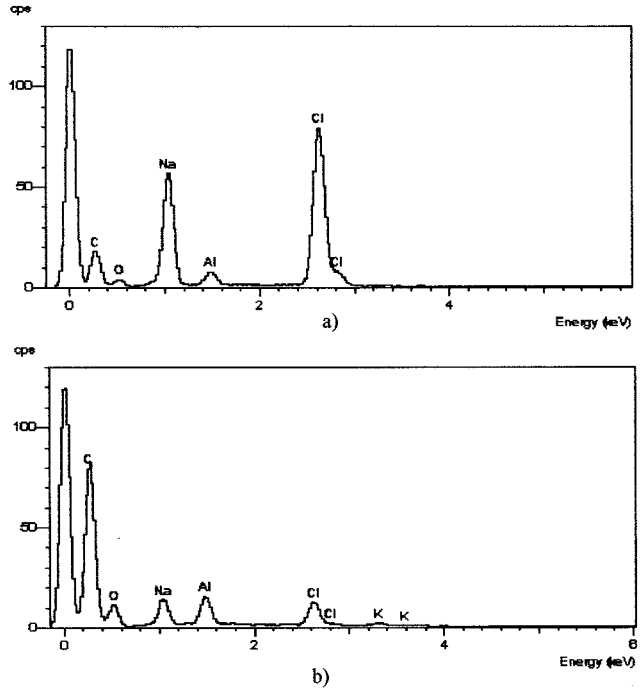

Figure 11. EDS analyses of the impregnated carbon fibers: (a) region with particles and (b) region free of particles.

Conclusions

The adipoyl chloride intermediate used in the polyamide 6/6 synthesis was obtained with success using adipic acid and thionyl chloride. The FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopies confirmed the adequate preparation of this reagent.

Samples of polyamide 6/6 obtained via interfacial polycondensation of the adipoyl chloride and hexamethylenediamine were analyzed by FTIR spectroscopy presenting characteristic absorptions. The FTIR results correlated to gas chromatography and mass spectroscopy analyses confirm the polymer synthesis.

However, different FTIR absorption bands besides the expected ones were observed, indicating that other components were present in final product of synthesis, probably intermediaries, oligomers, or byproducts of the synthesis. This observation was confirmed by dislocating of the polyamide 6/6 melting temperature to a lower value (249.5 °C).

The microscopic analysis showed that the carbon fiber impregnation by freshly synthesized polyamide 6/6 was adequate with a good reinforcement/matrix polymer interface, with any improvements being necessary during the processing to eliminate the byproducts formed during the synthesis.

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