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PAPER

Degradation behavior of carbon nanotubes/phenol-furfuryl alcohol multifunctional composites with aerospace application

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L S Conejo¹, M L Costa¹, S S Oishi² and E C Botelho¹

¹ Department of Materials and Technology, UNESP, Guaratingueta, Brazil

² National Institute for Space Research, INPE, São José dos Campos, Brazil

E-mail: luizaconejo@yahoo.com.br

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Abstract

Lightweight and highly conductive composite associated with good impact and tribological properties could be used in the aerospace industry to replace metal for an aircraft skin and still provide effective shielding against electromagnetic interference (EMI). Also, phenol-furfuryl alcohol resins (PFA) are excellent candidates to replace existing thermoset matrices used for obtaining glassy carbon, both in its pure form and reinforced with nanoscale structures. The synthesis of PFA allow obtaining a resin with better properties than that showed by conventional phenolic resins and with synthesis and cure processes more controlled than observed for the furfuryl alcohol resin. This work has as main purpose the synthesis and thermal characterization of PFA resin and its nanostructured composites with different concentrations of carbon nanotubes (0, 0.1, 0.5 and 1.0 wt%). PFA resin was synthesized with 1:2:1 molar ratio of phenol/formaldehyde/furfuryl alcohol, according to the more appropriate condition obtained previously. The specimens were evaluated by thermogravimetry (TGA) to knowledge of the temperature of thermal degradation, either by actual analyses as simulated by simulation heating rate conversion software (known as *Highway Simulation*). The introduction of CNT in PFA sample does not affect its thermal stability. The values of residual weight found for samples with CNT additions are close to the values of the phenolic resin in the literature (about 60% residual weight).

1. Introduction

Currently, nanotechnology is a major focus of research, development and innovation activities in all industrialized countries. Inside of this context, one of the trends that have been observed over the past years in the field of composite materials is the production of materials in which the interaction occurs between constituents at the nanometer scale, i.e. at least one of the nanometric constituents present are responsible to improve the mechanical, thermal and/or electrical performance of a material [1]. At first, some types of materials can be produced with nanometric sizes and shapes, but until now none of these particles has gained much attention as carbon nanotubes (CNT), discovered by Iijima in 1991 [2].

At first, the main objective of producing CNT was focused on space applications [3]. Nowadays, the use of nanotechnology for aerospace applications usually include high strength and low weight composites, improved electronics and displays with low power consumption, several kinds of physical sensors, multifunctional materials embedded sensors, and numerous others. The interests of aerospace industry are through thermal barrier and wear resistant coatings, sensors that can be perform at high temperature and other physical and chemical sensors that can perform safety inspection cost effectively [2].

One of the resins most used for aeronautical and space applications and produced on a large scale for years are phenolic resins, as they have satisfactory properties for different purposes and are relatively inexpensive. However, they have some disadvantages such as high porosity, very exothermic cure, moderate tensile and compression properties and low chemical resistance after curing [4].

The furfuryl alcohol resin, on the other hand, is considered a bioresin obtained from biomass rich in pentose, and provide interesting characteristics such as higher hardness and good mechanical and chemical resistance

[5]. However, this resin has not been commercialized on a larger scale due mainly to the difficulty in control its polycondensation reaction [6].

Therefore, phenolic and furfuryl alcohol resins may be combined in order to obtain resins with better properties than those synthesized by conventional phenolic resins and with synthesis and curing processes more controllable than those observed for furfuryl alcohol resin. This combination can be accomplished in several ways: the two resins can be prepared separately and then mixed to form a homogeneous product, or even via simultaneous synthesis of the two resins by mixing all the precursors reagents, or by adding one or more reagents for a partial or complete [6, 7] reaction. Within this context, to meet the aerospace industry needs in the search for new materials, phenol-furfuryl alcohol resins (PFA) are excellent candidates to replace existing thermoset matrices reinforced with nanoscale structures.

Nanocomposites processed from phenolic and furfuryl alcohol resins have shown to be able to exhibit excellent mechanical [8], tribological [9], and thermal [10] properties. Thus, PFA resin was chosen especially for the combination of good processing, chemical and mechanical resistance when compared to the phenolic resin [6, 7, 11]. And its synthesis is more controlled and consequently easier to apply on a large scale than the furfuryl alcohol resin [11, 12]. CNT were chosen as extra reinforcement and intercoating agents since they contribute to the improvement of thermal stability and mechanical resistance [9, 11, 13].

Due to limited information available in the literature about the PFA/CNT composites, this work aims the synthesis of PFA resin with different molar ratio of furfuryl alcohol, producing composites with different contents of CNT and obtaining the thermal degradation temperature behavior by means of both actual and simulated TGA (thermogravimetry) curves via simulation heating rate conversion software (known Highway Simulation software). The investigation of pyrolysis process to convert PFA to disordered carbon with high carbon yield is quite important for improving the producing procedure and the quality of the resulting products [6, 7, 14].

2. Materials and methods

2.1. Materials

Multiwalled carbon nanotubes (MWCNTs) used in this study were produced by chemical vapor deposition (CVD) technique and supplied by Bayer, coded as 150 °C Baytubes P. They are characterized by an average outer diameter of 15–20 nm, number of walls 3–15; bulk density of 140–160 kg m⁻³ and less than 5% impurities.

The chemicals used in the synthesis of PFA resin and characterization of the samples were: furfuryl alcohol GC (supplied by Fluka), sulfuric acid PA, phenol PA, formaldehyde PA, hydrochloric acid PA, Karl Fischer solution without pyridine (5 mg H₂O ml⁻¹), all were supplied by Vetec; p-toluenesulfonic acid PA (PTSA) was supplied by Cromoline, sodium hydroxide PA was obtained from Nuclear and anhydrous methanol was obtained from Mallinckrodt. All the chemicals were used without previous treatment.

2.2. Methods

2.2.1. Synthesis of phenol-furfuryl alcohol (PFA) resin

The route used in this work for the synthesis of PFA resin was based on Lebach patent [6] and Oishi *et al* [15], where the process begins with the reaction of phenol and formaldehyde in the presence of a basic catalyst (NaOH). After partial reaction of the phenol-formaldehyde, furfuryl alcohol was added along with a quantity of sulfuric acid, sufficient to neutralize the basic catalyst and then catalyze the acid condensation of furfuryl alcohol [15].

The reaction was conducted in a three-necked flask equipped with a reflux condenser and magnetic stirring in a glycerin bath and a thermometer was used to better control the reaction temperature.

For the reaction of phenol and formaldehyde it was used a phenol-to-formaldehyde molar ratio of 1:2 and sodium hydroxide as catalyst. The reaction was carried out at 90–95 °C for 30 min. Then, the reaction was cooled to room temperature and added to the furfuryl alcohol. For this work, furfuryl alcohol was varied to obtain three different molar ratio phenol-furfuryl alcohol (0.5; 1.0 and 1.5 named PFA1, PFA2 and PFA3), keeping constant the phenol-to-formaldehyde molar ratio. Dilute sulfuric acid (0.6 mol l⁻¹ solution) was added dropwise to the mixture until the pH returned to acid (around pH 2–3). The mixture PFA was heated at 50 °C and the reaction was carried out until the dynamic viscosity reached about 1000 mPa · s. The resin was then cooled and neutralized with NaOH until the pH of the resin was around 6–7. The pH was measured directly on the resin using a pH meter from Metrohm AG, model 827, with a combined glass electrode Unitrode. Since polyfurfuryl alcohol needs to be neutralized to avoid continuous polymerization [15], the same procedure was applied for PFA resins.

The water present in the PFA resin samples was removed by distillation at reduced pressure at a temperature of about 50 °C. For this procedure, a rotary evaporator IKA RV 10 digital model was used adapted to a vacuum pump from Marconi, model MA-058 and to a thermostatic bath of Tecnal, model TE-184 with cooling and circulation to cool the condenser water. This procedure was repeated until the moisture was around 5 wt% (or as low as possible).

PFA resin was characterized by FT-IR analysis on a spectrometer from PerkinElmer Instruments, Spectrum 100 model, by using the technique of universal attenuated total reflectance (UATR). Free furfuryl alcohol and phenol were analyzed by gas chromatography using a Varian, model 3380, equipped with a FID detector. The capillary column used was a CP-Sil 8 CB (30 m \times 0.25 mm) from Varian, using helium as carrier gas and 0.5 μ l of injected sample. The procedure for furfuryl alcohol and phenol extraction and analyses conditions were based on the work of Oliva-Teles *et al* [16].

2.2.2. Obtaining of nanostructured composites PFA/CNT

The CNT dispersion was performed with the assistance of an ultrasonic probe (Sonics & Materials, Model VC 750, 750 W, 20 kHz, during 4 min). Using this methodology, the following nanocomposites were produced with different concentrations of CNT: 0.1, 0.5 and 1.0 wt% (denominated 0.1% CNT, 0.5% CNT and 1.0% CNT, respectively).

2.2.3. Cure of PFA/CNT

The curing of PFA/CNT specimens was made using 4% (w/w) of an aqueous solution of PTSA (p-toluene-sulfonic-acid) catalyst 60% w/v. The samples were cured in an oven from VacuCell, VUK/VU 55 model, following 5 steps heating: the temperature was raised from room temperature to 60, 90, 120, 150 and 180 $^{\circ}$ C at a heating rate of 2.0 $^{\circ}$ C min $^{-1}$ and isotherms of 2 h in each temperature, all with vacuum (50 psi).

2.2.4. Morphological analysis

The specimens with CNT were characterized using transmission electron microscopy (TEM) from JEOL, JEM-2100 model. The samples were microtomed with a diamond knife at room temperature and the nominal slice thickness of 50 nm, and the voltage used was 200 kV.

2.2.5. Thermogravimetric analysis (TGA)

Analyses were performed in triplicate using the TGA/DTA 6200 equipment, EXSTAR6000 model by SII Nanotechnology. For all analyses a weight of about 8.0 mg, platinum-sample holder and alumina as reference material were used.

The samples were heated using heating rates of 2.0; 5.0; 10 and 20 $^{\circ}$ C min $^{-1}$ under constant nitrogen flow of 100 ml min $^{-1}$ and at a temperature range between 25 and 1000 $^{\circ}$ C. The setting and calibration was performed according to the manufacturer's specifications.

2.2.6. Simulation heating rate conversion software

Using the simulation heating rate conversion software known *Highway Simulation* curves were simulated at 2, 5 and 10 $^{\circ}$ C min $^{-1}$ for each type of sample from the experimental curve performed at 20 $^{\circ}$ C min $^{-1}$. According to ASTM E2550-11, the reproducibility results from the TGA can consider the curves obtained by simulation as valid or not, from the following parameters [17]:

- The reproducibility standard deviation for TGA onset temperature is 54 $^{\circ}$ C;
- The reproducibility standard deviation for TGA mass change is 2.3%;
- The reproducibility standard deviation for DTG onset temperature is 18 $^{\circ}$ C.

If all these three conditions are satisfied, simulation can be considered valid and reproductive.

3. Results and discussions

3.1. Evaluation of the synthesis of phenol-furfuryl alcohol (PFA) resin

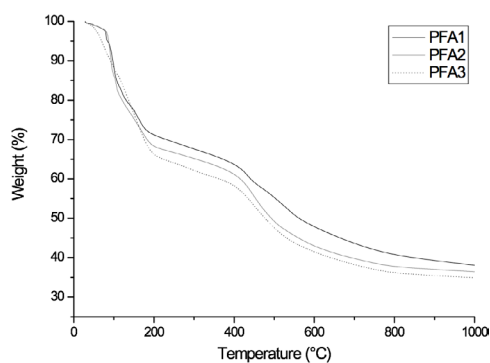
Table 1 shows the physicochemical characterization of PFA resins. Free furfuryl alcohol and phenol were quantified by gas chromatography. As can be observed in this table, increasing furfuryl alcohol content in the PFA resin formulation increases the free furfuryl alcohol while free phenol remains almost the same. The presence of moisture and free monomers are directly related to the residual weight obtained from thermogravimetric analysis at 1000 $^{\circ}$ C. Although free monomers are easily volatilized, some of them can still react during heating, especially furfuryl alcohol that is more reactive than phenol.

The moisture must be below 10% to avoid breakage and excess bubbles in the cured sample. With distillation of the resin could remain below 6% moisture. An important point is also the viscosity of the resin, it cannot be too high or too low, so that it can flow into the mold without leaking and interact with the CNTs easily. Therefore the range was chosen between 1600–2600 mPa \cdot s.

Figure 1 present the thermogravimetric analyses of PFA resins with different molar ratio of furfuryl alcohol. The resins exhibit a similar profile with two main weight losses related to curing and carbonization. The initial weight loss in the temperature range between 80–200 $^{\circ}$ C, indicate a rapid curing reaction along the presence of

Table 1. Physicochemical characteristics of synthesized PFA resins.

Parameters	Resins		
	PFA1	PFA2	PFA3
Moisture	5.17 ± 0.04	4.70 ± 0.05	5.69 ± 0.06
Viscosity (mPa · s)	1650	2465	1800
Free furfuryl alcohol (w/w%)	6.40	7.20	8.45
Free phenol (w/w%)	2.51	2.70	2.71
Residual weight (%)	38.1	36.4	34.9

**Figure 1.** Thermogravimetric curves of PFA1, PFA2 e PFA3 resins.

water, monomers of phenol and furfuryl alcohol and products of low molecular weight that are easily volatilized. Increasing furfuryl alcohol content the weight loss increase, due probably to an increased in free furfuryl alcohol as shown before. The cured samples undergo a gradual decomposition after 200 °C and leads to carbonization [18]. According to Zhang and Solomon [19], most reactions should occur below 600 °C, where the second weight loss is located (between 400–600 °C). Also, similar tendency of weight loss during carbonization was obtained, in which curves with higher furfuryl alcohol content presented higher weight losses.

Figure 2 presents FT-IR spectra of PFA resins where the following structures from a phenolic resin could be identified [20–23]: OH stretching at 3300 cm^{-1} ; methylene C–H stretching vibration at 2948 and 2885 cm^{-1} ; C–C stretching of aromatic ring at 1610 cm^{-1} ; C–H bending of aliphatic bridge structure at 1477 cm^{-1} ; phenolic OH in-plane deformation at 1360 cm^{-1} ; and aromatic C–H out-of-plane deformation vibrations at 888 , 817 and 755 cm^{-1} . Some bands attributed to furfuryl alcohol are [15, 24, 25]: OH stretching at 3300 cm^{-1} which become larger with increasing furfuryl alcohol; 1142 cm^{-1} related to furan ring and 1001 cm^{-1} attributed to C–O stretching of furan ring. The bands at 2948 and 2885 cm^{-1} can also indicate the reaction between hydroxymethylol from phenolic resin and furfuryl alcohol, forming methyl groups.

The selection phenol-to-formaldehyde molar ratio (1:2) was based on the results obtain from the work of Lin and Teg [23], where increasing formaldehyde ratio the resin yield decreased, while the carbon yield increased. Therefore, the average value selected is between 1–4 formaldehyde-to-phenol molar ratio. From the results varying the furfuryl alcohol molar ratio, PFA 2 was chosen as the condition for processing the PFA composites owing to the tendency to decrease residual weight as furfuryl alcohol content increase.

3.2. TEM

After synthesis and characterization of the PFA resin samples, the addition of different percentages of CNT was made in the selected PFA2 resin. For the dispersion the ultrasonic tip was used, and then after curing TEM analyzes were performed to evaluate this dispersion.

In figures 3–5, the presence of CNT can be observed with the TEM technique, and note that these are mostly agglomerated and forming islands. This suggests that the method for dispersion of the CNT must be improved.

The use of CNT did not cause major changes in the results obtained. This may be related to the percolation limit of nanostructured composites, as some literature [26–28] suggests, which needs to be analyzed with rheological studies to verify this limit.

3.3. TGA

Figures 6–10 show representative TGA curves of PFA/CNT samples, at different heating rates, 2.0; 5.0; 10 and 20 °C min^{-1} . In figure 6, it was found that neat PFA resin presents at least four stages of thermal degradation in the presence of nitrogen, between room temperature—200 °C, 200–400 °C, 400–620 °C, and 620–800 °C showing a

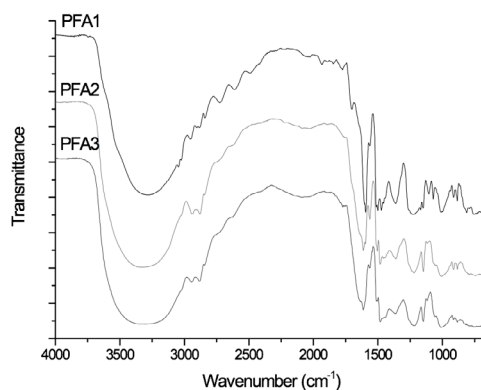


Figure 2. FT-IR spectra of PFA1, PFA2 e PFA3 resins.

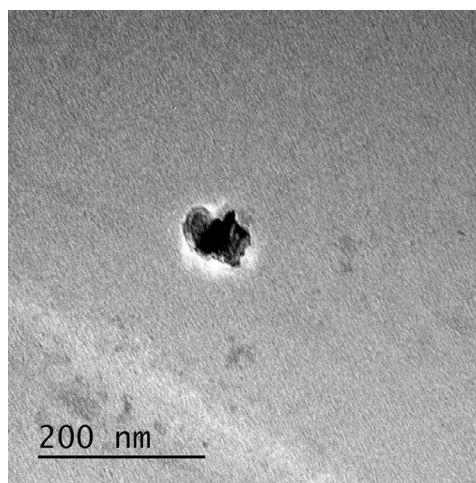


Figure 3. TEM of the sample PFA/CNT 0.1%.

residual weight of 61% at 850 °C (table 2). Moreover, the initial stabilization region is very small, between room temperature to 200 °C, suggesting that the cured sample still has some associated volatiles and adsorbed water. To study the decomposition one can compare the PFA resin with a phenolic resin, since both have phenol in the formulation. According to the literature, during pyrolysis of the phenolic resin, between 300 and 500 °C, water and a mixture of phenol and cresol are released with only a small amount of carbon dioxide. During this process, water production is attributed to competing reactions of hydroxymethyl groups condensation, from residual curing process and the condensation of hydroxyl groups. Between 400 and 800 °C, the major products eliminated are hydrogen, methane, carbon monoxide, water and small amounts of carbon dioxide and ethane. In the range between 560 and 900 °C, most of the product formed is hydrogen, resulting from separation of hydrogen atoms bonded directly to the benzene nuclei [29].

From the results presented in figure 6, it is possible to identify four peaks of loss weight in the derivative of neat phenol-furfuryl alcohol cured resin, being the first between room temperature and 200 °C and the others between 200 and 620 °C. The first peak probably is related to some adsorbed water, while the others peaks can be attributed to the release of water from condensation reactions, carbon monoxide, carbon dioxide and hydrogen.

The addition of CNT in the samples neither modify the peaks of degradation and nor significantly the amount of final residue. Therefore when adding CNT in the PFA does not thermally modify the composite.

From the results shown in table 2, it can be concluded that the residual weight for PFA/CNT nanocomposites are not significantly affected by the amount of CNT in the composition and no trend was observed which might be due to inhomogeneity on CNT dispersion. Also, the samples did not show a great variation due to differences in heating rates used, as expected. The residual weight for most samples remained between 60–65%, which is higher than phenolic resin [4], although residual weight includes carbon and ash.

3.4. Simulation heating rate conversion software

The simulation heating rate conversion software known *Highway Software* produce the prediction data by combining following four steps:

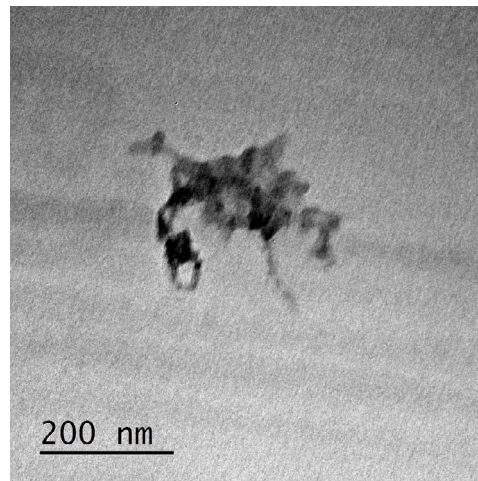


Figure 4. TEM of the sample PFA/CNT 0.5%.

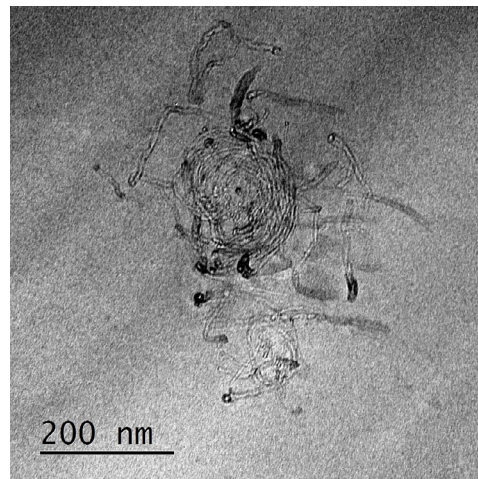


Figure 5. TEM of the sample PFA/CNT 1.0%.

1. Data is measured at a certain heating rate.
2. Separation of peaks (when multiple peaks are overlapping).
3. Activation energy (ΔE) calculation.
4. Time-temperature conversion based on the Arrhenius' equation.

The principle of the time-temperature conversion based on Arrhenius' equation is shown figure 11 below [30].

A rate change can be converted into temperature change in the kinetic events which obey the Arrhenius' equation.

T : Absolute Temperature

B : Heating Rate

ΔE : Activation energy

R : Gas constant

Actually, the original measured temperature is calculated to conversion temperature based on the equation (1) [30]

$$T' = \frac{1}{\frac{1}{T} + \frac{R}{\Delta E} \cdot \ln\left(\frac{B}{B'}\right)} \quad (1)$$

where,

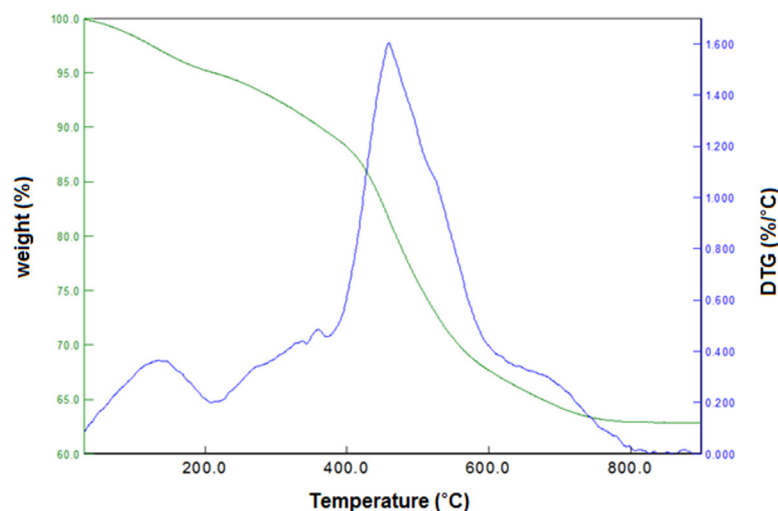


Figure 6. TGA/DTG curve of PFA/CNT 0.0% with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

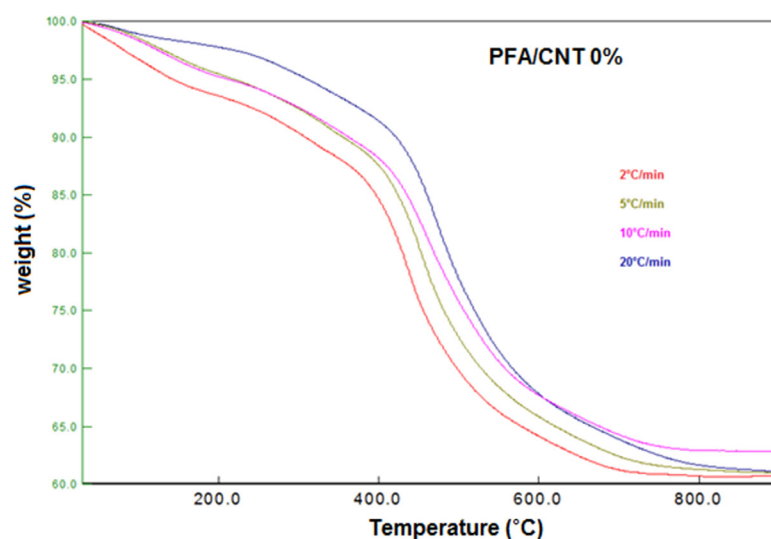


Figure 7. TGA curves PFA/CNT 0% comparative rates of heating.

T : Original Temperature (Absolute Temperature)

T' : Converted Temperature (Absolute Temperature)

ΔE : Activation Energy (calculated or entered value)

R : Gas Constant

B : Original Heating Rate ($^{\circ}\text{C min}^{-1}$)

B' : Converted Heating Rate ($^{\circ}\text{C min}^{-1}$)

Figure 12 shows a real and simulated curve representation of the PFA/CNT 0.1 wt% sample to $10\text{ }^{\circ}\text{C min}^{-1}$.

As can be seen the points where the values were compared for reproducibility check according to ASTM E2550.

Table 3 shows the onset temperature from the TGA curve to the real and simulated curves of each of the samples. The same for the mass percentage of the TGA curve in table 4 and the onset temperature of DTG curve in table 5.

Based on the analysis of tables and the values established by the ASTM E2550-11 the method used can be validated to simulate the TGA curves since all are within the acceptable and consistent pattern with real curves performed.

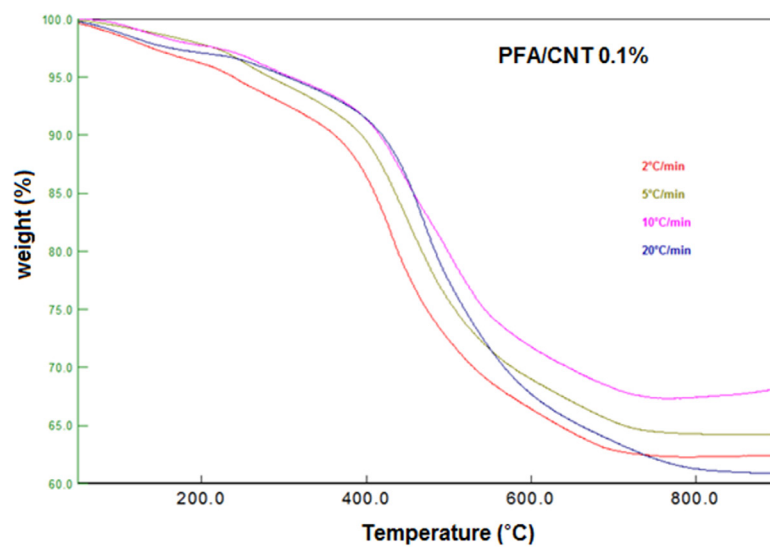


Figure 8. TGA curves PFA/CNT 0.1% comparative rates of heating.

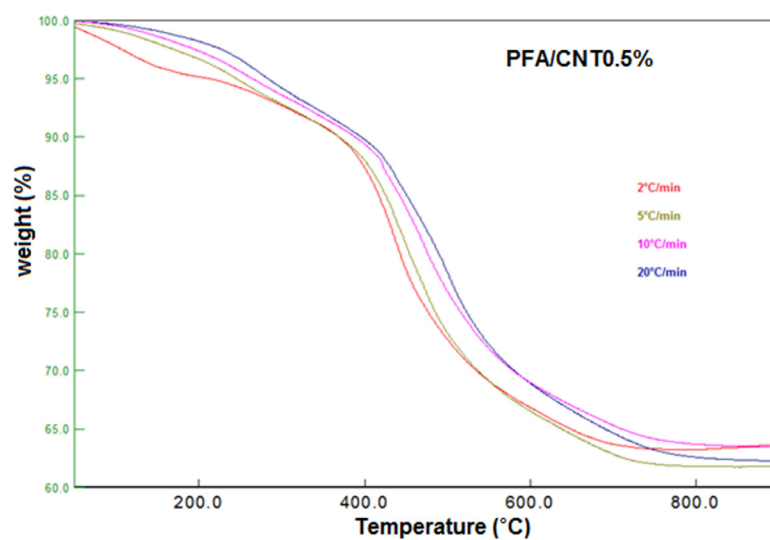


Figure 9. TGA curves PFA/CNT 0.5% comparative rates of heating.

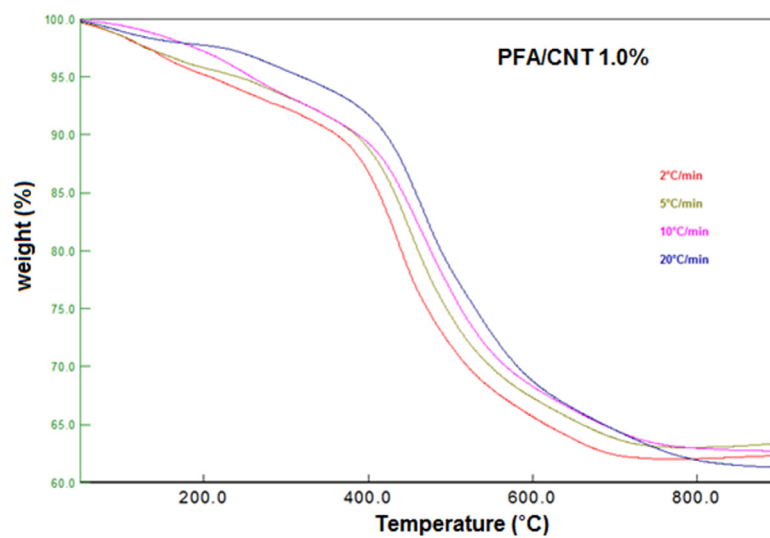
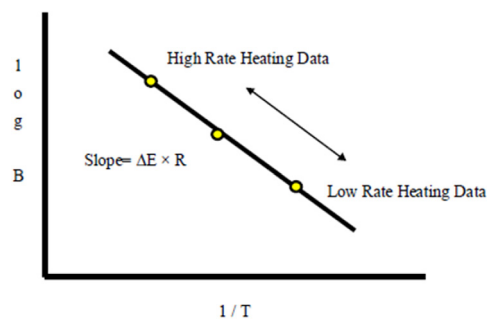
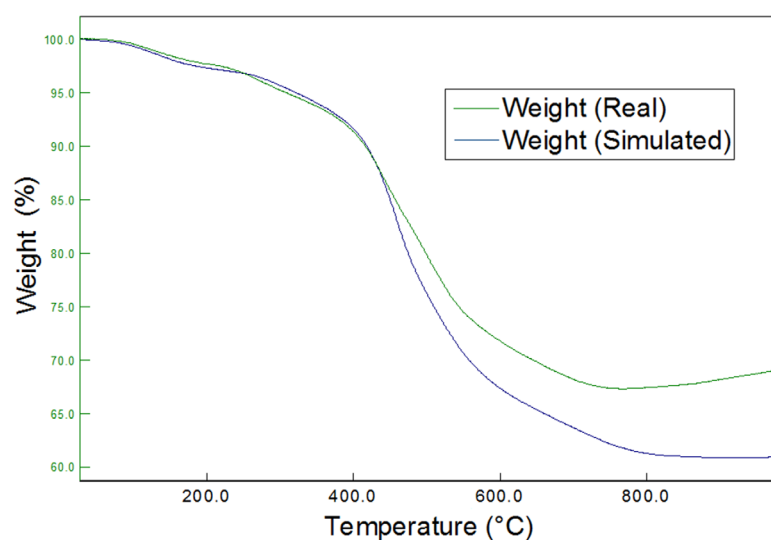


Figure 10. TGA curves PFA/CNT 1.0% comparative rates of heating.

Table 2. Residual weight of PFA/CNT.

Rate of heating: sample (%)	2 °C min ⁻¹ (%)	5 °C min ⁻¹ (%)	10 °C min ⁻¹ (%)	20 °C min ⁻¹ (%)
PFA/CNT 0.0	60.8	60.9	63.3	60.9
PFA/CNT 0.1	62.3	64.3	69.2	60.9
PFA/CNT 0.5	64.0	61.9	63.7	62.2
PFA/CNT 1.0	62.5	63.9	62.9	61.1

**Figure 11.** Arrhenius' plot.**Figure 12.** Real and Simulated curve of the sample PFA/CNT 0.1% at 10 °C min⁻¹.**Table 3.** Onset temperature of the TGA curves.

Sample	Real (°C)	Simulated (°C)	Difference (°C)
PFA/CNT 0%_2	105.8	105.1	0.7
PFA/CNT 0%_5	108.5	98.5	10.0
PFA/CNT 0%_10	116.5	96.7	19.8
PFA/CNT 0.1%_2	128.9	133.5	4.6
PFA/CNT 0.1%_5	143.7	141.9	1.8
PFA/CNT 0.1%_10	140.9	136.3	4.6
PFA/CNT 0.5%_2	109.7	110.5	0.8
PFA/CNT 0.5%_5	124.1	123.7	0.4
PFA/CNT 0.5%_10	91.9	111.5	19.6
PFA/CNT 1%_2	100.1	109.5	9.4
PFA/CNT 1%_5	99.2	102.0	2.8
PFA/CNT 1%_10	126.3	117.9	8.4

Table 4. Values of mass percentages at the onset temperature.

Sample	Real (%)	Simulated (%)	Difference (°C)
PFA/CNT 0%_2	97.4	98.9	1.5
PFA/CNT 0%_5	97.9	99.0	1.1
PFA/CNT 0%_10	97.8	99.2	1.4
PFA/CNT 0.1%_2	98.2	98.1	0.1
PFA/CNT 0.1%_5	98.1	98.1	0.0
PFA/CNT 0.1%_10	98.4	98.5	0.1
PFA/CNT 0.5%_2	98.3	99.8	1.5
PFA/CNT 0.5%_5	98.6	99.7	1.1
PFA/CNT 0.5%_10	99.6	99.8	0.2
PFA/CNT 1%_2	98.6	98.5	0.1
PFA/CNT 1%_5	98.9	98.8	0.1
PFA/CNT 1%_10	98.7	98.8	0.1

Table 5. Onset temperature from the DTG curves.

Sample	Real (°C)	Simulated (°C)	Difference (°C)
PFA/CNT 0%_2	337.4	351.3	13.9
PFA/CNT 0%_5	353.4	343.7	9.7
PFA/CNT 0%_10	370.6	369.1	1.5
PFA/CNT 0.1%_2	342.8	341.0	1.8
PFA/CNT 0.1%_5	354.0	343.8	10.2
PFA/CNT 0.1%_10	367.9	367.1	0.8
PFA/CNT 0.5%_2	319.6	306.9	12.7
PFA/CNT 0.5%_5	328.3	330.3	2.0
PFA/CNT 0.5%_10	353.9	345.3	8.6
PFA/CNT 1%_2	307.0	319.2	12.2
PFA/CNT 1%_5	332.2	332.2	0.0
PFA/CNT 1%_10	349.2	347.3	1.9

4. Conclusion

The synthesis of the phenol-furfuryl resin was successful, as can be seen from the results of characterization. Thermogravimetric analyses showed that samples produced have associated volatiles, since the samples lose weight at relatively low temperatures. The thermal degradation behavior of PFA is similar to the phenolic resin and the high residual weight (60–65%) is appropriate for carbonaceous materials processing.

The introduction of CNT in PFA sample does not affect its thermal stability. The simulation via simulation heating rate conversion software known *Highway Simulation software* is valid in accordance with ASTM E2550, as all conditions are satisfied and the onset temperatures and mass percentages at onset temperatures are within the acceptable standard related to the samples reproducibility. TEM analysis shows the dispersion of CNT must be improved since they agglomerated in the PFA/CNT samples.

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ORCID iDs

L S Conejo  <https://orcid.org/0000-0001-5533-1374>

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