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Thermal behavior of phenol-furfuryl alcohol resin/carbon nanotubes composites

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Abstract

Phenol-furfuryl alcohol resins (PFA) are excellent candidates to replace existing thermoset matrices used in obtaining insulating systems or carbon materials, both in its pure form and reinforced with nanoscale structures. This work had as main purpose synthesize and investigate thermal characterization of PFA resin and its nanostructured composites with different concentrations of carbon nanotubes (0, 0.1, 0.5 and 1.0 wt%). The DSC analysis was performed to estimate the specific heat (c_p) of the cured samples and thermomechanical analysis to find the linear thermal expansion coefficient (α). From these results, the c_p values found for the PFA system was similar to that described in the literature for the phenolic resin. The c_p increased with the increase in the CNT concentration in the system up to 0.5%. The coefficient of linear thermal expansion obtained by TMA technique for PFA sample was $33.10^{-6}/^{\circ}\text{C}$ which was close to the α value of phenolic resin (40 to $80.10^{-6}/^{\circ}\text{C}$).

1. Introduction

Phenolic resins are produced on a large scale for years, as they have satisfactory properties for different purposes and are relatively inexpensive. One of the uses of phenolic resin is the electro-electronic industry and electrical insulation products or those applications that require high carbon content [1, 2].

The beginning of synthetic products for insulations started with phenol-formaldehyde resins, which were used in different electrical applications. Other synthetic products such as polyvinyl chloride, polyesters, polyethylenes, polyurethane, epoxy, etc, were introduced later [1]. Composites and nanocomposites based on thermosetting resins have been widely used in electrical insulation applications, however, nanocomposites have emerged because they improve the overall characteristics (i.e. mechanical, electrical, thermal, etc) as a result of enhanced interactions at the interfaces [1, 3–5]. In addition, the greater extent of interactions can enhance the dielectric properties, which includes higher energy storage or lower dielectric loss, and improved power dissipation [4].

Nanotechnology has been very important in current research, development and innovation activities. Many nanometric fillers composed of different materials and different sizes and shapes have been used, but in particular, what gained most attention was the carbon nanotubes (CNT) discovered by Iijima [6].

Although phenolic resin has been widely used in different applications, they have some disadvantages such as high porosity, moderate values of tension and compression and low chemical resistance after curing [2]. On the other hand, the furfuryl alcohol resin is considered a bioresin obtained from biomass rich in pentose and provide interesting characteristics such as higher hardness and good mechanical and chemical resistance [7]. However, this resin has not been commercialized on a larger scale due to the difficulty in control its polycondensation reaction [8].

To resolve this issue, the phenolic and furfuryl alcohol resins can be combined to obtain resins with improved properties and methods of synthesis and cure better controlled than the separate resins.

The ‘interfaces’ between inorganic fillers and the organic polymers, such as phenolic resin systems, represent the key to understand the mechanisms and phenomena that control the properties of nanocomposites used as

advanced materials [9]. Therefore, interfacial control is critical for achieving good coupling between the inorganic filler and the base polymer. The present goal of the research studies in this field is to optimize these benefits and to provide a better understanding of the physical and chemical structure of the interface region [10].

Thus, to know the thermal properties of a nanocomposite is fundamental to understand where it can be applied, mainly in electro-electronic components. One of the properties that must be known is the specific heat and coefficient of linear thermal expansion of the material.

Specific heat is the amount of heat required for each gram of a substance to undergo a temperature change corresponding to 1 °C. This magnitude is a characteristic of each type of substance and indicates the behavior of the material when exposed to a heat source. Some factors influence specific heat, such as intermolecular forces and impurities. It is known that the greater the intermolecular bonding strength of the material, the greater the energy required for the rupture of the bonds and effective transformations of the material. Generally, materials that have hydrogen bonds in their structure have high specific heat. Impurities present in various materials may alter the specific heat value of the substance.

The major issue for determining the specific heat of a nanocomposite is to have control of the amount of heat exchanged between the different bodies when subjected to actual operating conditions. The greater the specific heat of a nanocomposite, the greater the amount of heat that must be supplied or withdrawn from it so that temperature variations occur.

In addition, it is expected that the material does not shrink or expand with use over a given temperature range. For this reason, it is important to know the coefficient of linear thermal expansion of nanocomposites that will be used in the electro-electronic industry.

So, due to limited information available in the literature about the composites PFA/CNT and to describe the scientific development of nanocomposites electrical features desired in power engineering, the present article is focused on the thermal properties of phenol-furfuryl alcohol (PFA) composites with different percentages of carbon nanotubes. Specific heat was determined by differential scanning calorimetry (DSC) and the linear thermal expansion coefficient via thermomechanical analysis (TMA).

2. Experimental

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

The synthesis route used in this work is described in previous work [11]. Briefly, first phenol and formaldehyde (supplied by Vetec) is reacted in the presence of a sodium hydroxide (from Nuclear) for 30 min at 90 °C–95 °C. Then, furfuryl alcohol (supplied by Fluka) is added along with a quantity of dilute sulfuric acid (from Vetec) sufficient to neutralize the basic catalyst and then catalyze the acid condensation of furfuryl alcohol until viscosity around 1000 mPa.s. The synthesized PFA resin was neutralized with NaOH until pH around 6–7. The presence of water in the PFA resin was removed using a rotary evaporator at reduced pressure until moisture of around 5%.

2.2. Obtaining of nanostructured composites PFA/CNT

Multiwalled carbon nanotubes (MWCNTs) used in this study were supplied by Bayer, coded as 150 C Baytubes P. Samples of PFA containing CNT concentrations of 0.1, 0.5 and 1.0 wt% were prepared with the assistance of an ultrasonic probe (Sonics & Materials, Model VC 750, 750 W, 20 kHz, for 4 min). PFA samples was then catalyzed with 4% w/w of p-toluenesulfonic acid solution (60% w/v) and cured in a vacuum oven with step heating at 60, 90, 120, 150, and 180 °C (each for 2 h).

2.3. Differential scanning calorimetry (DSC)

The equipment used for the analyzes was the DSC brand TA Instruments model 2940 previously calibrated with indium. Cured samples of approximately 2 mg were used in a standard-hermetically sealed aluminum sample under constant nitrogen flow (20 ml min⁻¹) at a heating rate of 20 °C min⁻¹, the temperature ranging from 25 °C to 300 °C. The initial temperature was maintained for 4 min to establish thermal equilibrium.

The procedure adopted to determine the specific heat of the studied material consisted of 3 steps:

- (1) testing of samples (three for each type), the empty pan and reference material (sapphire), by differential scanning calorimetry (DSC);
- (2) subtracting the DSC curves of the samples and sapphire curve relative to baseline; and
- (3) determination of c_p . All conditions used in this step follow the ASTM E1269-11 (*Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry*) [12].

2.4. Thermomechanical analysis (TMA)

TMA/SS 6100 (Thermo Mechanical Analysis) SII Nanotechnology Inc. - Seiko model EXSTAR6000 was used in the present work. Analyzes were performed according to ASTM E831, to understand the behavior of the linear thermal expansion coefficient of samples cured PFA and its nanostructured composites. Following the standard, samples were heated from 25 to 300 °C at a heating rate of 3 °C min⁻¹ and each sample was shaped to the dimensions of (8 × 8 × 3) mm.

Each sample was analyzed twice, that is, the same sample was heated and cooled, heated again, as mentioned in the standard [13]. This procedure was performed for PFA resin with different percentages of CNT (0; 0.1; 0.5 and 1.0% w/w). All analyzes were performed in triplicate. To calculate the coefficient of expansion (α), the second run curve was used.

3. Results and discussions

3.1. Specific heat (c_p)

The physical properties of a material are related to changes in temperature and are responsible for possible suitability of a material for a particular purpose [14]. The specific heat evaluates the energy required to accomplish an increase of 1 °C on a sample of 1 g [15].

We can thus assume in general: 'The higher the specific heat, the lower the temperature variation as a given amount of heat is absorbed'. But specific heat does not tell us just how much heat must be absorbed by a material before its temperature varies; it also describes the material's ability to release heat to cool an object. So, the smaller the heat capacity, the greater the material's ability to release heat so that it cools.

This property can be determined by the technique of differential scanning calorimetry according to ASTM E1269-11. Specific heat being an intrinsic property of the material, for composites, it is expected that this property is influenced as the reinforcement is added to the matrix. In the case of nanostructured composite PFA/CNT, the CNT being a good thermal conductor, it is expected that its introduction decrease the specific heat of the composite as its concentration increases.

For each sample, the curve to calculate the specific heat is generated from the empty sample holder, which is then used to initially confine sapphire and after the sample. In the present work to avoid repetition, only one representative DSC curve is shown in figure 1 for the standard sapphire.

Figure 1 also shows the thermal profile of the cured PFA and with 0.1, 0.5 and 1 wt% of reinforcement. It is observed that the sample presents a deviation from the baseline in the temperature range studied (50 °C to 300 °C) of approximately 0.24 mW for pure PFA and 0.63 mW, 0.75 mW, and 0.50 mW for PFA samples with 0.1, 0.5, and 1 wt% of CNT, respectively. This suggests that the PFA samples suffer thermal change when given certain quantity of heat, and this variation in the case of PFA is not constant, because it increases with increasing CNT% until the concentration of 0.5%.

Based on the data of figure 1, the c_p values were calculated in accordance with equations (1) and (2) and the results are shown in table 1. In addition, figure 2 shows a better view of the results for different concentrations of CNT.

For the calculation of c_p , the equations (1) and (2) were used [19]:

$$E = \left[\frac{b}{60.Dst} \right] \cdot [Wst.cp(st) + \Delta W.cp(c)] \quad (1)$$

Where:

b = heating rate, K/min;

$c_p(st)$ = specific heat capacity of the sapphire standard, J(g.K)⁻¹;

$c_p(c)$ = specific heat capacity of the specimen holder, J(g.K)⁻¹;

E = calorimetric sensitivity of the DSC apparatus;

Dst = vertical displacement between the specimen holder and the sapphire DSC thermal curves at a given temperature, mW;

Wst = mass of sapphire, mg; and

ΔW = difference in mass between the empty specimen holder and the standard specimen holder, mg [12].

Using calorimetric sensitivity, E , calculated in equation (1), the specific heat capacity of the test specimen was calculated as follows equation (2) [12]:

$$c_p(s) = \frac{(60.E.Ds)}{Ws.b} - \frac{\Delta W.cp(c)}{Ws} \quad (2)$$

Where:

$c_p(s)$ = specific heat capacity of the specimen, J(g.K)⁻¹;

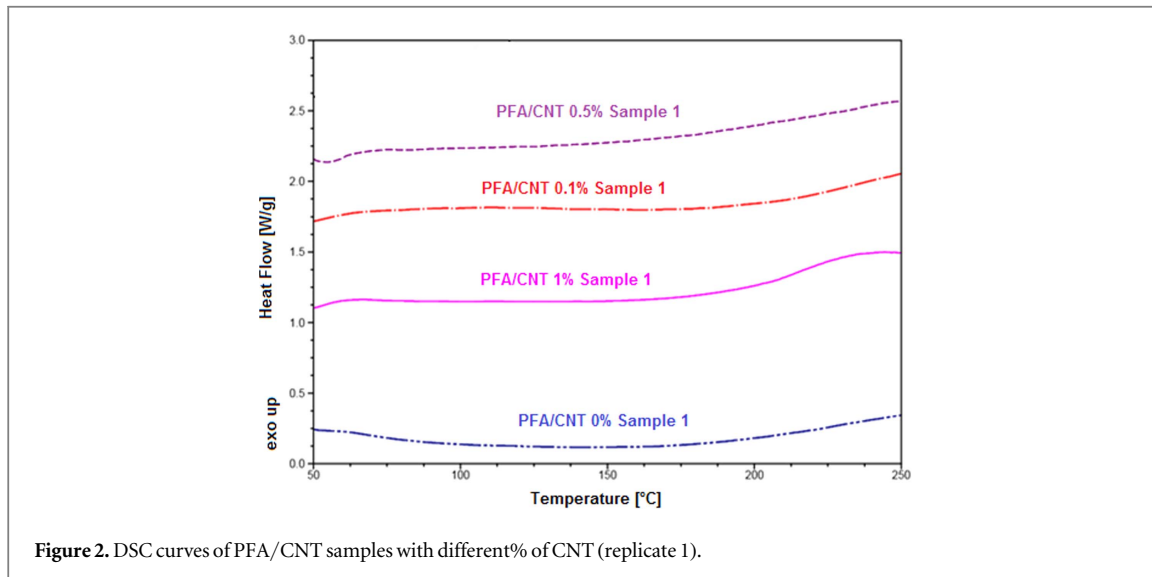
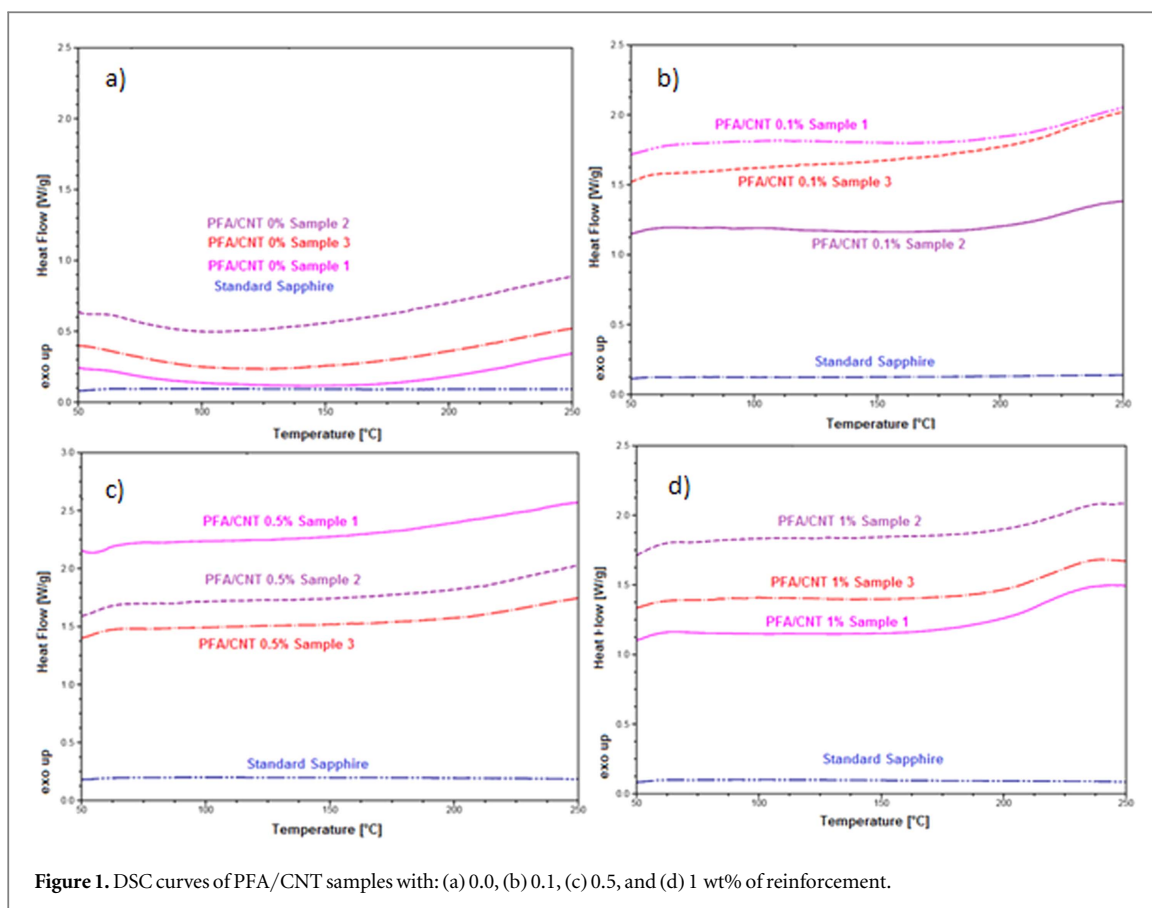


Table 1. c_p values calculated for cured PFA and its nanocomposites PFA/CNT.

Sample (PFA/CNT)	c_p [J/g.K] (Temperature 370 K)
0% ^a	1.91 ± 0.18
0.1% ^a	3.15 ± 0.61
0.5% ^a	3.66 ± 0.40
1.0% ^a	2.11 ± 0.26

^a performed in triplicate.

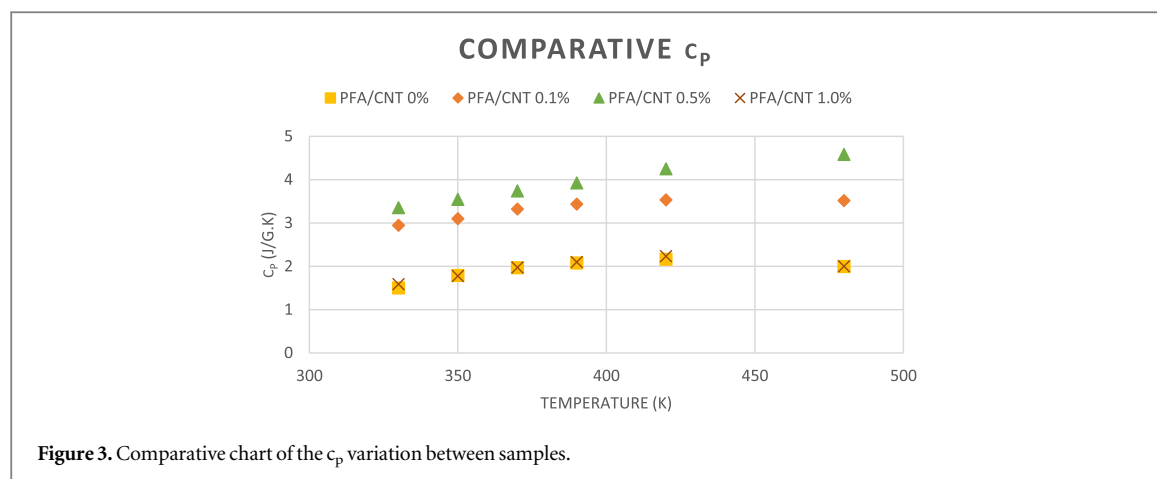


Figure 3. Comparative chart of the c_p variation between samples.

D_s = vertical displacement between the specimen holder and the specimen DSC thermal curves at a given temperature, mW;

ΔW = difference in mass between the empty specimen holder and the test specimen holder if the same holder is not used for both runs (In the case of this experiment is used the same sample holder for both runs).

Other symbols are defined in equation (1) [12].

According to the data available in the literature [16] the c_p of phenolic resin is $1.92 \text{ J g}^{-1} \cdot \text{K}$ at 370 K (96.85°C), and as can be seen in table 1, the value of c_p found for the PFA (approximately $1.91 \text{ J g}^{-1} \cdot \text{K}$) is close to the value of the phenolic.

c_p value tends to increase with increasing concentration of CNT until 0.5%, above this concentration the c_p value decreases. An increase of 65% in the c_p value can be observed when only 0.1% CNT is added to the composite. That is, the introduction of CNTs into the composites increases the c_p value, and the higher the composite specific heat, the greater the amount of heat that must be supplied or withdrawn for temperature variations. Thus, because the thermal conductivity is inversely proportional to the c_p , according to equation (3), [17] (ASTM E 1952-11 *Standard Test Method for Conductivity and Thermal Diffusivity by Modulated Temperature Differential Scanning Calorimetry*) it is verified that the introduction of CNT makes the composite a better thermal insulation than the polymer matrix itself.

$$\lambda_0 = \frac{(8LC^2)}{(c_p \cdot m \cdot d^2 \cdot P)} \quad (3)$$

Where:

λ_0 = thermal conductivity ($\text{W}/(\text{K} \cdot \text{m})$);

L = sample thickness (mm);

C = thermal capacity (mJ/K);

c_p = specific heat ($\text{J}/(\text{g} \cdot \text{K})$);

m = sample mass (mg);

d = sample diameter (mm); and

P = time course (s) [24].

In figure 3 the comparative chart of c_p variations as a function of temperature in the samples of PFA/CNT is presented in different concentrations of carbon nanotubes. It is observed that the samples have similar profiles in terms of c_p , and the increase in the c_p value is checked with increasing the temperature until approximately 150°C . After this temperature the c_p tends to a slight decrease or presents the tendency to stabilize to a constant value. It is worth mentioning that the highest c_p value is obtained with the addition of 0.5% CNT followed by the 0.1% CNT concentration. The value of c_p found for sample with 1.0% CNT was the same for sample without CNT. This suggests that samples produced with CNT concentration higher than 0.5% does not present the same homogeneous dispersion in the polymer matrix, thus losing its function in the thermal property. This fact CNT dispersion for different concentrations behave differently for each material is described by the literature [18, 19].

It is known that c_p varies with temperature. According to the quantum theory of thermodynamics, c_p tends to increase with increasing temperature until it reaches a certain temperature known as the Debye temperature, where c_p becomes relatively constant. Thus these values of c_p are very close to each other because probably 150°C is the temperature considered as the Debye temperature for the studied materials and, therefore, the values for c_p should be approximately equal, or according to the classical theory and the Law of Dulong and Petit equal to $3R[(3)(8, 31 \text{ J mol}^{-1} \cdot \text{K}) = 24.9 \text{ J mol}^{-1} \cdot \text{K}]$ [20–22]. The thermal conductivity is inversely proportional

to the specific heat. Metals are the best heat conductors, i.e., have higher thermal conductivity values (lower c_p) and polymers are the best insulators (higher c_p).

3.2. Coefficient of linear thermal expansion (α)

Within a limited linear range of temperature, one may consider that there is a linear relationship between thermal deformation (ε_T) expansion (+) or contraction (−) suffered by a material and the change in temperature (ΔT) imposed to it. It should be noted that the normal component of strain is dimensionless and represents the ratio of a length variation relative to the initial length of it. The linear relationship of these two quantities being ($\varepsilon_T/\Delta T$), is defined by a coefficient of linear thermal expansion (α) of the material [17].

Typically for $\Delta T > 0$ the material expands and $\Delta T < 0$ is a contraction, since in most cases α is positive. Materials that exhibit this negative variation can mention the non-isotropic aramid fibers ($-2.33 \cdot 10^{-6}/^\circ\text{C}$ (longitudinal) and $41 \cdot 10^{-6}/^\circ\text{C}$ (transverse)) and carbon, in which α is negative in the longitudinal direction and positive in the transverse position of the filament. The thermoset matrices used in polymer composites exhibit positive thermal expansion coefficients and reasonably high [23].

The ASTM E831 suggests that the samples should be between 2 and 10 mm in length and width, and thickness can not be larger than 10 mm. Initially the sample must be measured with an instrument with a maximum error of $\pm 25 \mu\text{m}$ to a temperature between 20 and 25 $^\circ\text{C}$ [12].

The equipment must be calibrated and reset to zero when the tip stays in height zero. The sample shall be placed under the tip and centralized. It should be selected a force compatible with the sample material between 1 and 10 mN. The heating rate chosen should be a maximum of 5 $^\circ\text{C min}^{-1}$, the lower the better feedback. After completion of the first analysis, a new race with the same sample tested should be performed, and so, the α can be calculated with greater confidence and accuracy [12].

For the calculation of α are used the equations (4) and (5) [12]:

$$\alpha_m = \frac{\Delta L_{sp} \times k}{L \times \Delta T} \quad (4)$$

$$k = \frac{\alpha_{ref} \times L_{ref} \times \Delta T_{ref}}{\Delta L_{ref}} \quad (5)$$

Where:

α_m = mean coefficient of linear thermal expansion, $\mu\text{m}/(\text{m} \cdot ^\circ\text{C})$;

α_{ref} = mean coefficient of linear thermal expansion, for reference material, $\mu\text{m}/(\text{m} \cdot ^\circ\text{C})$;

k = calibration coefficient, from Test Method E 2113;

L = specimen length at room temperature, m,

ΔL_{ref} = change of reference material length due to heating, μm ;

L_{ref} = reference material length at room temperature, m;

ΔL_{sp} = change of specimen length, μm ;

ΔT_{ref} = temperature difference over which the change in reference material length is measured, $^\circ\text{C}$;

ΔT = temperature difference over which the change in specimen length is measured, $^\circ\text{C}$;

T = midpoint temperature of the temperature range ΔT .

Figure 4 shows the comparison between the curves of different concentrations of carbon nanotubes for better visualization of the results obtained.

From these results, the thermal profile determined by the TMA technique for the PFA and their nanostructured composites are similar, i.e., with increasing temperature, there is a slight expansion of the material, but it was not possible to achieve a glass transition temperature of the material in the temperature range evaluated.

Table 2 shows the values of α for the material found in the present work in two temperature ranges, the first between 70 and 130 $^\circ\text{C}$ and the second between 150 and 200 $^\circ\text{C}$ for all samples.

From this study the α ranged between $30 \cdot 10^{-6}/^\circ\text{C}$ and $43 \cdot 10^{-6}/^\circ\text{C}$. If we consider the standard deviation, it can be observed that the introduction of CNT practically does not affect the values of linear thermal expansion coefficient. The value found for the α PFA resin is within the range described in the literature for the thermoset resin systems used in polymer composites, such as epoxy resin (varying from 15 to $100 \cdot 10^{-6}/^\circ\text{C}$) and the phenolic resin (40 to $80 \cdot 10^{-6}/^\circ\text{C}$) [24].

The coefficient of linear thermal expansion consists of the fractional change of volume or linear dimension by temperature degree. Thus, from an atomic perspective, alpha expresses the average distance between atoms, the thermal expansion being an increase in the amplitude of vibration of the atoms leading to an expansion of the crystalline lattice. As this property is related to the structure and chemical bonds we can say that since we have in all the cases of the PFA matrix with carbon nanotubes, it is expected that the alpha values do not vary much.

Some polymeric materials undergo very large thermal expansions upon being heated, as is apparent from their linear coefficients of thermal expansion, ranging from about $50 \cdot 10^{-6}/^\circ\text{C}$ and $400 \cdot 10^{-6}/^\circ\text{C}$. The highest α

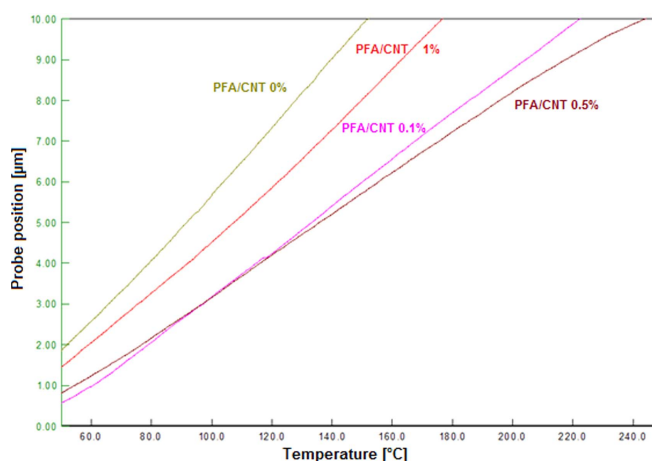


Figure 4. TMA curve of comparative of the sample PFA/CNT.

Table 2. Average values of α for PFA resin with different percentages of CNT.

Material	Average value α (70 °C–130 °C) ($10^{-6}/^{\circ}\text{C}$)	Average value α (150 °C–200 °C) ($10^{-6}/^{\circ}\text{C}$)
PFA/CNT 0.0%	43.15 ± 12.98	29.89 ± 8.73
PFA/CNT 0.1%	36.76 ± 3.54	39.53 ± 7.65
PFA/CNT 0.5%	35.42 ± 5.10	38.06 ± 8.49
PFA/CNT 1.0%	41.15 ± 1.98	42.02 ± 3.17

values are found for linear and branched polymers, since the secondary intermolecular bonds are weak, in addition to having a minimal amount of crosslinking. As the amount of crosslinking increases, the magnitude of the expansion coefficient decreases; the lower coefficients are found for thermosetting network polymers, such as phenol formaldehyde, where the bonds are almost entirely covalent.

Therefore, it can be observed that the alpha values for the studied materials practically do not vary, even for different ranges of temperature.

4. Conclusion

With the use of DSC it was possible to determine the c_p of PFA sample and their PFA/CNT nanostructured composites. The c_p value of PFA sample is like the phenolic resin. Furthermore, it was found that c_p increases with the introduction of the CNT in the PFA system until the concentration of 0.5%. Above this (1.0%), no change was observed in c_p value.

The coefficient of linear thermal expansion obtained by TMA technique for PFA/CNT nanocomposites was $38.10^{-6}/^{\circ}\text{C}$ ($\pm 3.17.10^{-6}$), which is close to the α value of phenolic resin (40 to $80.10^{-6}/^{\circ}\text{C}$). In addition, the introduction of the CNT in PFA systems did not affect the α values, so the amount of CNT depends on the intended application and not by the dependence of the α values.

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References

- [1] Pleša I et al 2016 Properties of polymer composites used in high-voltage applications *Polymers* **8** 173
- [2] Reghunadhan Nair C P 2004 Advances in addition-cure phenolic resins *Prog. Polym. Sci.* **29** 401–98
- [3] Lau K Y, Vaughan A S and Chen G 2015 Nanodielectrics: opportunities and challenges *IEEE Electr. Insul. Mag.* **31** 45–54
- [4] Tomer V, Polizos G, Randall C A and Manias E 2011 Polyethylene nanocomposite dielectrics: implications of nanofiller orientation on high field properties and energy storage *J. Appl. Phys.* **109** 074113
- [5] Paramane A S and Kumar K S 2016 A review on nanocomposite based electrical insulations *Trans. Electr. Electron. Mater.* **17** 239–51
- [6] Fiedler B, Gojny F H, Wichmann M H G, Nolte M C M and Schulte K 2006 Fundamental aspects of nano-reinforced composites *Compos. Sci. Technol.* **66** 3115–25
- [7] Domínguez J C, Grivel J C and Madsen B 2012 Study on the non-isothermal curing kinetics of a polyfurfuryl alcohol bioresin by DSC using different amounts of catalyst *Thermochimica Acta* **529** 29–35
- [8] Lebach H H 1949 Furfuryl alcohol-phenol aldehyde resinous products and method of making the same *United States Patent Office* 2,471,631
- [9] Oriakhi C O 2000 Polymer nanocomposition approach to advanced materials *J. Chem. Educ.* **77** 1138–46
- [10] Fiedler B et al 2006 Fundamental aspects of nano-reinforced composites *Compos. Sci. Technol.* **66** 3115–25
- [11] Conejo L S et al 2017 *Mater. Res. Express* **4** 105701
- [12] ASTM-E1269 2011 *Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry* (West Conshohocken, PA: ASTM International) (<https://doi.org/10.1520/E1269-11>)
- [13] ASTM-E831 2012 *Standard Test Method for Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis* (West Conshohocken, PA: ASTM International) (<https://doi.org/10.1520/E0831-12>)
- [14] Santos W N et al 2004 Hot wire technique in the determination of thermal properties of polymers *Polymer* **14** 354–9
- [15] Resnick R, Halliday D E and Walker J 2007 *Fundamentals of Physics* vol 2 (New Jersey: Wiley)
- [16] Wang R M, Zheng S R and Zheng Y P 2011 *Polymer Matrix Composites and Technology* (USA: Woodhead Published)
- [17] ASTM E1952 2017 *Standard Test Method for Thermal Conductivity and Thermal Diffusivity by Modulated Temperature Differential Scanning Calorimetry* (West Conshohocken, PA: ASTM International) (<https://doi.org/10.1520/E1952-17>)
- [18] Santos L F P et al 2017 *Mater. Res. Express* **4** 115037
- [19] Untem F O et al 2014 Benzoxazine resin/carbon nanotube nanostructured composite's degradation kinetic *J. Nanosci. Nanotechnol.* **14** 5145–50
- [20] Çengel Y A and Boles M A 1989 *Thermodynamics: An Engineering Approach* 5th edn 2006 (New York: McGraw-Hill)
- [21] Goswami M and Sumpter B G 2009 Effect of polymer-filler interaction strengths on the thermodynamic and dynamic properties of polymer nanocomposites *The Journal of Chemical Physics* **130** 134910
- [22] Higaki Y, Otsuka H and Takahara A 2006 A thermodynamic polymer cross-linking system based on radically exchangeable covalent bonds *Macromolecules* **39** 2121–5
- [23] Neto F L and Pardini L C 2006 *Compósitos Estruturais: Ciência e Tecnologia* 1 edn (São Paulo: Edgard Blücher)
- [24] Oliveira A C M 2011 Avaliação dos parâmetros de processo de reticulação do polietileno de baixa densidade *MSc Thesis* (Universidade Estadual Paulista)