Development of carbon fiber/phenolic resin prepregs modified with nanoclays

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Abstract

This work is focused on the study of the main variables involved in the development of phenolic/carbon prepregs and how these variables are affected by the incorporation of nanoclays. For this, phenolic resin was obtained from phenol and formaldehyde, performing the reaction under basic conditions and with formaldehyde excess. Resin curing kinetics was studied by means of Fourier transform infrared spectroscopy measurements. Organo-modified clay was added to the phenolic resin in order to evaluate their effect on the general performance of the material. Carbon fiber/phenolic resin and carbon fiber/clay modified phenolic resin prepregs were obtained by hand-layup and vacuum bagging. Prepregs were characterized in terms of fiber content, flexural stiffness, and degree of tack. In both the cases, intermediate fiber volume content, nearly 50%, was obtained. The addition of 5 wt% of clay to the phenolic resin did not produce a significant change on the prepregs stiffness but increased the degree of tack, which implies that the incorporation of such particles was useful to enhance the prepregs properties. Composite materials were obtained by compression molding of the prepregs obtained, and were characterized by its fiber content, mechanical behavior with the three-point bending test and its thermal degradation by thermogravimetry. High fiber content composites materials were obtained, nearly 75% by volume. However, modified composites showed lower fiber content, which resulted in a decrease of the flexural modulus and strength. In relation to thermal degradation, the addition of nanoclay did not change the behavior of the materials.

Keywords

Prepreg, phenolic resin, carbon fiber, curing kinetic, nanoclays, composite materials

Introduction

Fiber-reinforced polymers have emerged as a major class of structural materials and are either being used or being considered for use as substitutes for metals in many weight-critical components in the aerospace, automotive, and other industries.[1] In the specific case of the aerospace industry, the materials used must meet additional requirements such as dimensional stability, high stiffness, and high temperature resistance. Fire resistance and ablative composites are used in the construction of turbine nozzles and other components of rockets and airplane engines, exposed to very high temperatures.[2] Phenolic resin/carbon fiber reinforced composites are suitable for these applications due to their high mechanical and thermal performance. Resol-type phenolic resins are obtained by carrying out the reaction between phenol and formaldehyde under basic conditions with formaldehyde excess. One of the most

important properties of these resins is their excellent flame and high temperature resistance, which is due to the formation of a carbonaceous layer called "char", which radiates heat and acts as an insulating material, protecting the bulk material of the components.[3] Nowadays, phenolic resins are used in thermal

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protection systems, molding compounds, wood products, coatings, and different types of composite materials.[4] Regarding carbon fibers, they have been widely used as reinforcement in composites for thermal protection due to their high-dimensional stability, non-flammability, low density, and excellent mechanical properties.[5] Composite materials based on phenolic resins and carbon fibers have been used by NASA as a standard material for high-temperature applications (MX-4926). These materials also contain micron-sized powdered fillers in the formulation, which are added to stabilize the charred polymer, which can be mechanically removed by the friction action caused by the atmospheric gases during combustion. For that purpose, particles based on glass, refractory oxides, carbon, or mineral asbestos are typically used. However, traditional micron-sized ablation composites have shown a threshold in their protection capacity that cannot be surpassed unless a different approach is proposed. One of the limitations comes from the fact that chars are structurally weak and suffer mechanical erosion, thus reducing the lifetime of the ablative layer or requiring additional insulation thickness. Also, the composite-like nature of these ablatives severely limits their processability and requires them to be pattern cut, and laid in place by hand.[6] Materials with better ablative properties would allow applying relatively thinner protection layers, reducing the overall weight of aerospace systems. Thermoset polymer nanocomposites have excellent potential to be used as ablative materials because upon pyrolysis, the organic–inorganic nanostructure reinforcing the polymer can be converted into a uniform ceramic layer which may lead to significantly increased resistance to oxidation and mechanical erosion compared to traditional composite ablative materials.[7] Different nanoparticles have been used with phenolic resins to enhance their ablation and thermal resistance. Srikanth et al.[8] added nanosilica particles to carbon–phenolic composites and obtained much higher ablation resistance than conventional carbon–phenolic materials under similar testing. These authors attributed this behavior to the reaction of the nanosilica with char at high temperatures, which formed an ablation-resistant silicon carbide phase. Natali et al.[9] studied the ablative properties of highly loaded carbon black and multiwall carbon nanotubes (MWCNT)/phenolic resin composites and found that the MWCNT-based systems showed a thin charred region whereas the carbon black system was characterized by a thick and wide pyrolyzed zone, which effectively shielded the virgin material. Also, nanolayered silicates have been used in phenolic–carbon composites to improve their thermal properties. Koo et al.[10] prepared carbon–phenolic composites with different clay loads (2.5, 5, and 7.5 wt%) and found that only highly loaded materials

(with 7.5 wt% of nanoclays) decreased the erosion rate, the surface temperature and the insulation index. When comparing different nanoparticles, nanoclays have the advantage of being cheaper, abundant, and relatively easy to being chemically modified to make them more compatible with the polymer matrix. However, changes in the composition of composite materials used as thermal protection systems have a significant impact on the processability of the final components.

The ability of a formulation to be processed by the standard manufacturing techniques used in the aerospace industry is crucial for the success of any new development. The manufacturing technique that ensures the best mechanical properties is the autoclave processing, which allows obtaining composites with low porosity and high fiber content.[1] The raw materials for processing by autoclave are prepregs, which facilitate placing resin and fibers in the necessary amount in the mold. Therefore, if a new ablative material based on the incorporation of nanoclay to the neat phenolic matrix is developed, it is important to know how the manufacture and application of prepregs are affected by the presence of nanoclays. Several articles related to the obtaining and characterization of prepregs can be found in the literature. Some authors have processed and characterized prepregs in terms of mechanical and physical properties by differential scanning calorimetry (DSC), tack degree, and grade of cure, among others,[11–13] whereas other authors have studied the properties of commercial prepregs by means of dynamic mechanical analysis (DMA), DSC, and mechanical tests.[14–19] On the other hand, only very few papers are related to the processing and characterization of prepregs with nanofillers,[20,21] and in those cases epoxy/carbon nanotubes systems were studied.

The aim of this work was to study the obtaining process of carbon fiber/phenolic resin prepregs and characterize both these prepregs and their corresponding composites. To this end, bentonites were chemically modified and incorporated to the phenolic resin to evaluate their effect on the manufacturing parameters of prepregs. In a previous work, we found that the addition of nanoclays was good to improve the flame resistance of the composites.[22] In addition, relevant matrix properties, such as cure kinetics and resin viscosity, were studied and the effect of these parameters on the processing of the prepregs was analyzed. Prepregs were characterized in terms of fiber content, flexural rigidity and tack degree. Finally, the composites were characterized by their fiber content and mechanical behavior with the three-point bending test.

This study is part of a larger project aimed to develop new ablative carbon fiber reinforced polymer materials for aerospace applications.

Experimental

Materials

Resol-type phenolic resin was prepared using a formaldehyde to phenol molar ratio equal to 1.3 under basic conditions,[23] as follows. Phenol and formaldehyde water solution (37 wt%) was placed in a 1-l stainless steel reactor with a low-velocity stirrer, a thermometer, and a reflux condenser. The pH was kept at 9.0 with a 40 wt% solution of sodium hydroxide (NaOH) and the mixture was allowed to react for 2 h at 90°C. After that, the mixture was neutralized with a 7 wt% solution of boric acid (H_3BO_3) until the pH reached a value of 6.8–7.0. The resol was dehydrated in a rotary evaporator by vacuum at 70°C. During this step, viscosity was measured every 15 min to avoid an excess increase in this property which could generate problems in the processability of the materials. The resin obtained was kept at −10°C until it was used. The phenol and formaldehyde used for the synthesis were supplied by Cicarelli S.A. (Argentina).

Modified phenolic resin was obtained by adding 5 wt% of ammonium-modified bentonite, kindly supplied by Minarmco S.A. (Argentina), to the original resol. The addition was performed gradually with continuous stirring and after obtaining a homogeneous mixture it was sonicated for 30 min in an ultrasonic bath at room temperature to ensure a good dispersion of the nanoparticles on the phenolic resin. The method used to modify the clay with octadecylamine, by cation exchange reaction, is explained elsewhere.[24] Carbon fiber fabric (Toray T700SC-12000), supplied by Yixing Huaheng High Performance Fiber Textile CO (China) was used as reinforcement.

Methods

Characterization of the resin

Curing kinetics. Fourier transform infrared (FTIR) spectra of the resol and the modified resin were obtained in transmission mode in a Nicolet 6700 spectrometer using KBr windows, with 32 scans and 4 cm^{-1} of resolution in the range of 600–4000 cm^{-1}. The spectra were normalized using the band centered at 1595 cm^{-1}, corresponding to the stretching C=C of the benzene ring, which was expected to remain constant in all the samples.[23] Dynamic tests were performed from room temperature to 190°C, whereas isothermal tests were carried out at 80°C and 190°C.

Viscosity measurements. Viscosity was measured in a Brookfield cone and plate viscometer HBTDV-IICP both at room temperature and at 80°C.

Gel time. The gel time was measured using test tubes with a looped wire therein in a controlled temperature bath at 80°C, 100°C, and 120°C. The test was based on the movement of the wire inside the tube, considering the gel time as the moment at which the wire gets stuck due to the great increase in viscosity.

Clay characterization. X-ray diffraction (XRD) spectra were obtained in a PANalytical X́PERT PRO spectrometer, with CuK$_\alpha$ (λ=1.5406 Å) radiation at room temperature. The generator voltage was 40 kV and the current was 40 mA. Thermogravimetric tests were carried out in a TGA-DTGA Shimadzu 50, from room temperature to 1000°C at a heating rate of 10°C/min under a nitrogen atmosphere to avoid thermo-oxidative degradation.

Processing of prepregs. Prepregs were obtained by vacuum bag molding, which consists of six steps: mold preparation, fabric cutting, impregnation, bag closing and vacuum application, curing, and demolding. First, the mold was cleaned and a release agent (REN RP79-2) was applied to facilitate the demolding step. The release agent was needed because prepregs usually adhere to the mold after curing.[25] Then, the fibers, bleeder fabric, release film, and vacuum bag were cut. Once all materials were prepared, the carbon fabric was manually impregnated with the phenolic resin. After impregnation, the release film and the bleeder fabric were placed over the fibers and then the vacuum bag was sealed along the perimeter of the fabric area. The partial curing took place in an oven for 4 h at 80°C, and the vacuum was applied for the first 2 h.

A total of 18 prepregs were obtained: nine made with the original resin and nine made with the modified resin. Figure 1 shows one of each type. Their dimensions were 45 cm × 35 cm.

Characterization of prepregs

Density. Density was measured by means of picnometry, using the Archimedes principle, at 20°C, using water as test liquid.

Reinforcement content. The fiber content of prepregs was measured by the digestion technique, according to the ASTM D3171 standard, procedure b. The fiber content was calculated by using the following equation

$$V_f = \left(\frac{W_f}{W_0}\right) * 100 * \left(\frac{\rho_m}{\rho_f}\right) \tag{1}$$
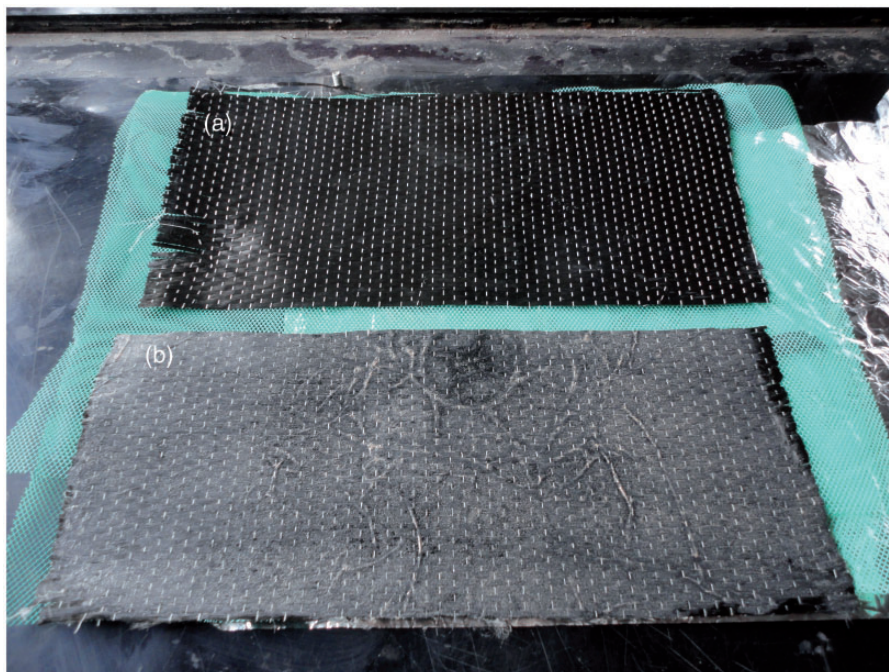
Figure 1. Photograph of (a) unmodified prepreg and (b) modified prepreg.

where V_f is the fiber volume content (%), W_f and W_0 are the final and initial sample weight respectively, and ρ_m and ρ_f are the sample and filler densities respectively.

Flexural stiffness tests. Flexural stiffness tests were performed at room temperature in a universal testing machine Instron 4467, according to ASTM D1388, procedure A. To carry out the test, it was necessary to build a special device that allowed the prepreg displacement to record the distance at which it curves 41.5°. The prepregs were cut in strips of $2.5\,cm \times 45\,cm$ for testing; four samples in both sides were tested for each material. The displacement was carried out parallel to the fiber direction.

Prepreg tack testing. Prepreg tack was measured at room temperature according to the ASTM D3167 standard, in a universal testing machine Instron 4467.

Processing of the composites. Composite materials were obtained by compression molding of prepregs in a heated press. For that, laminates were cut in $10\,cm \times 12\,cm$ rectangles, and then placed into a steel mold with a release agent that was added to facilitate the demolding step. Twelve sheets were staked in the same direction to obtain 2-mm-thick materials. The thermal curing cycle was 15 min at 45°C, 1 h at 60°C, 4 h at 80°C, 1 h at 110°C, 1 h at 150°C, and 2 h at 190°C. To achieve the correct compaction of the prepregs, 1 bar of pressure was applied throughout the cycle.

A total of four plates were obtained: two made with the original prepregs and two made with the modified prepregs.

Characterization of the composites. The density and the reinforcement content were measured with the same methods as those used for prepregs.

Thermogravimetry. Thermal degradation of the composites was studied by thermogravimetry (TGA). Measurements were performed in a Q500 TA Instrument thermogravimetric analyzer. Tests were carried out at a heating rate of 10°C/min from 30°C to 900°C, in atmospheres of nitrogen and air, respectively. The samples were about 50 mg in all cases.

Three-point bending test. The mechanical properties of composites were measured by the three-point bending test; tests were performed in a universal testing machine Instron 4467 with a 30 kN load cell, according to the ASTM D790 standard. At least five specimens of each type of composite material were tested and the average modulus and strength were calculated.

Results and discussion

Characterization of the modified clay

Figure 2 shows the XRD spectra of the original and modified bentonite with their respective interlaminar spacing (d_{001}). It can be observed that the modified
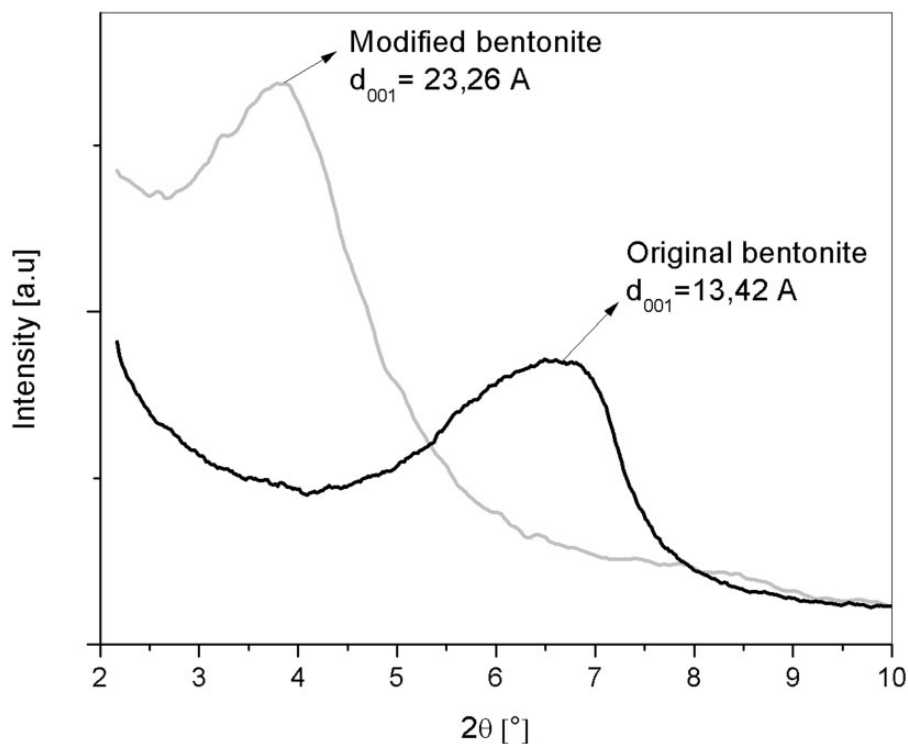
Figure 2. XRD diffraction spectra of original and modified bentonite.

bentonite suffered a displacement of the 001 peak to a lower angle and, therefore, an increase in the interlayer distance compared to the original clay. Furthermore, a single diffraction peak, which indicates a uniform spacing, can be seen.[26] Regarding the thermogravimetric test (TGA), the mass loss curve as a function of temperature (Figure 3) of the unmodified bentonite shows two thermal degradation transitions: (a) the surface-adsorbed water, which volatilizes at low temperatures and (b) crystallization water, which does so at higher temperatures.[27] In the case of modified bentonites, four regions of mass loss were distinguished: (a) the evolution of water and gaseous species physically adsorbed (below 150°C); (b) the decomposition of organic substances (between 150°C and 550°C); (c) the dehydroxylation of the bentonite by loss of structural water (between 550°C and 700°C); and (d) the evolution of organic carbonaceous products (between 700°C and 800°C). Both results demonstrate that the clay was successfully modified and that its interlaminar space was expanded (XRD) by the incorporation of organic chains (TGA), which should be beneficial to promote its dispersion in the phenolic resin. Additionally, the disappearance of the first water peak indicates that the modified bentonite is less hydrophilic than the original one, which would increase the compatibility with thermosetting resins, even considering that, among the different polymeric systems, phenolic resins present a low degree of hydrophobicity. Once the modified

bentonite was obtained, it was added to the resin in a proportion of 5 wt%, as explained in the "Experimental" section.

Resol synthesis (original and modified with clay)

The formaldehyde to phenol molar ratio was chosen equal to 1.3 because it was found in a previous work[23] that the resol resin synthetized with this molar ratio has the highest methylene bridge concentration and, as a consequence, the highest crosslinking density. The rheological properties and cure characteristics of the resin are crucial processing parameters for composite preparation. Regarding rheology, a suitable resin viscosity for prepreg processing is considered to be around 1100 cP. To achieve this value, the synthesized resin was gradually dehydrated in a rotary evaporator. To avoid an excessive increase in viscosity by water loss during dehydration, viscosity was measured repeatedly every short times as explained in the experimental section.

Prepreg processing design

Resin viscosity is a very important parameter in a prepreg because it determines the correct processing of the composite material. Very low resin viscosity can cause resin draining and excessive tack, while very high viscosity can reduce void and resin excess elimination. One common way to achieve the right resin viscosity is to
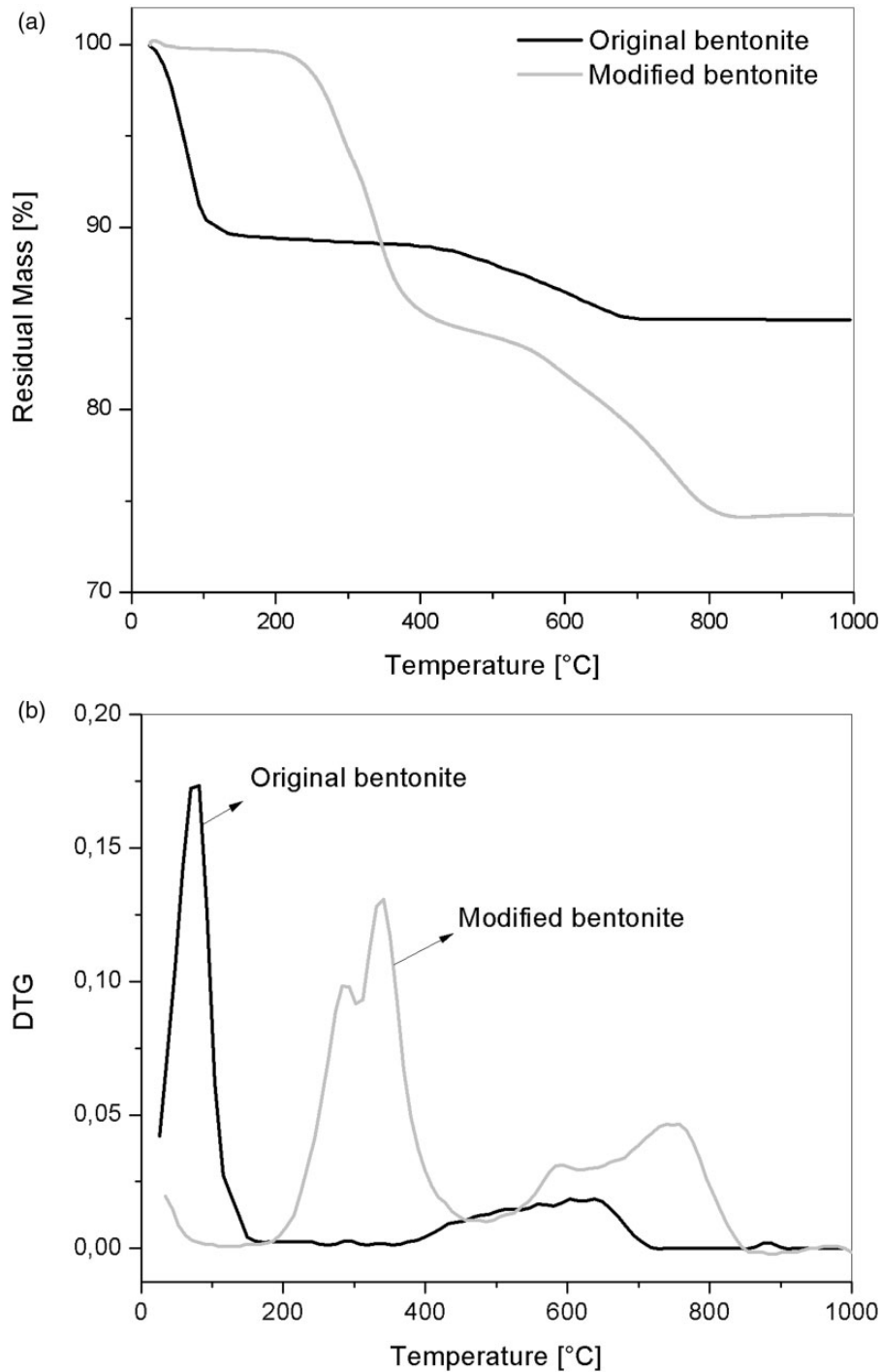
Figure 3. TGA (a) and DTGA (b) thermograms of original and modified bentonite.

increase the degree of conversion of the polymeric system, without reaching the gel point (which is called the B-stage). Gelation is an irreversible transformation of the polymer state from a viscous liquid to an elastic solid when the resin reaches a certain degree of conversion.[28] So, it is necessary to avoid reaching gelation while preparing the prepreg because the resin must be able to flow during composite manufacturing. Gel times

for the original and modified phenolic resin were measured at three different temperatures: 80°C, 100°C, and 120°C and the results are presented in Table 1. It was observed that the phenolic resin reached the gel point after 41 min at 120°C as well as after 2 h 57 min at 100°C. However, the resin did not reach the gel point during the first 4 h at 80°C. To corroborate this test, viscosity was measured every 30 min for 4 h at 80°C (the

initial viscosity, measured at room temperature, was 1108 cP for the original resin and of 4143 cP for the modified resin). The evolution of this parameter was plotted as a function of time and is shown in Figure 4. It can be seen that the viscosity increased as time passed but did not reach the sharp increase corresponding to the gel point before 250 min. A similar behavior was observed for the resin modified with bentonite, even though higher viscosity values were measured. Therefore, 4 h at 80°C were chosen as the processing time and temperature for the consolidation step of both types of prepregs (with and without bentonite). During that step, resin viscosity increased and the excess of resin was removed.

Another important parameter to be considered is the resin stability during prepreg storage at −18°C.

Table 1. Gel time of original and modified phenolic resin determines at different temperatures.

Temperature (°C)	Average gel time	
	Original resin	Modified resin
80	More than 4 h	More than 4 h
100	2 h 57 min	2 h 5 min
120	41 min	34 min

Although it is relevant for other resins, it has been demonstrated that the curing reaction of phenolic resins does not proceed at such a low temperature.[29]

After obtaining the processing parameters of prepregs, it was important to determine the degree of conversion achieved by the resin after being under such conditions. It must be taken into account that a disadvantage of phenolic resins is that they exhibit a complex process of polymerization reactions with the evolution of water and formaldehyde. Therefore, having control of the cure kinetics is very important to ensure obtaining good parts with low defect concentration, such as porosity. The curing kinetics of phenolic resins (novolac and resol) has been studied by different techniques: high-performance liquid chromatography (HPLC),[30] DSC,[31] solid-state ^{13}C NMR and FTIR,[32,33] and DSC and ^{1}H and ^{13}C NMR spectroscopy.[34] In our work, the evolution of the degree of curing as a function of time at 80°C was determined from FTIR spectra of the neat and modified resol resins. Theoretically, the principle of kinetic building by FTIR consists in following the evolution of a reactive vibration band of the resin versus cure treatments, time and temperature. This evolution is related to the intensity of a reference vibration band, which does not vary during the curing process.[35] This methodology is known as the internal reference method, and is
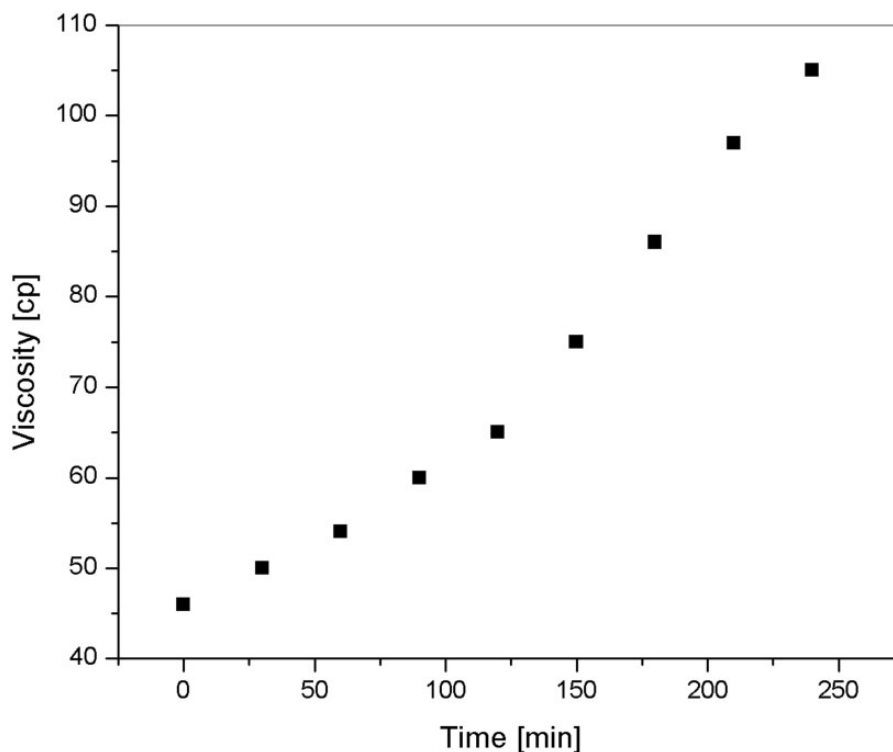
**Figure 4.** Resol viscosity as a function of time measured at 80°C.
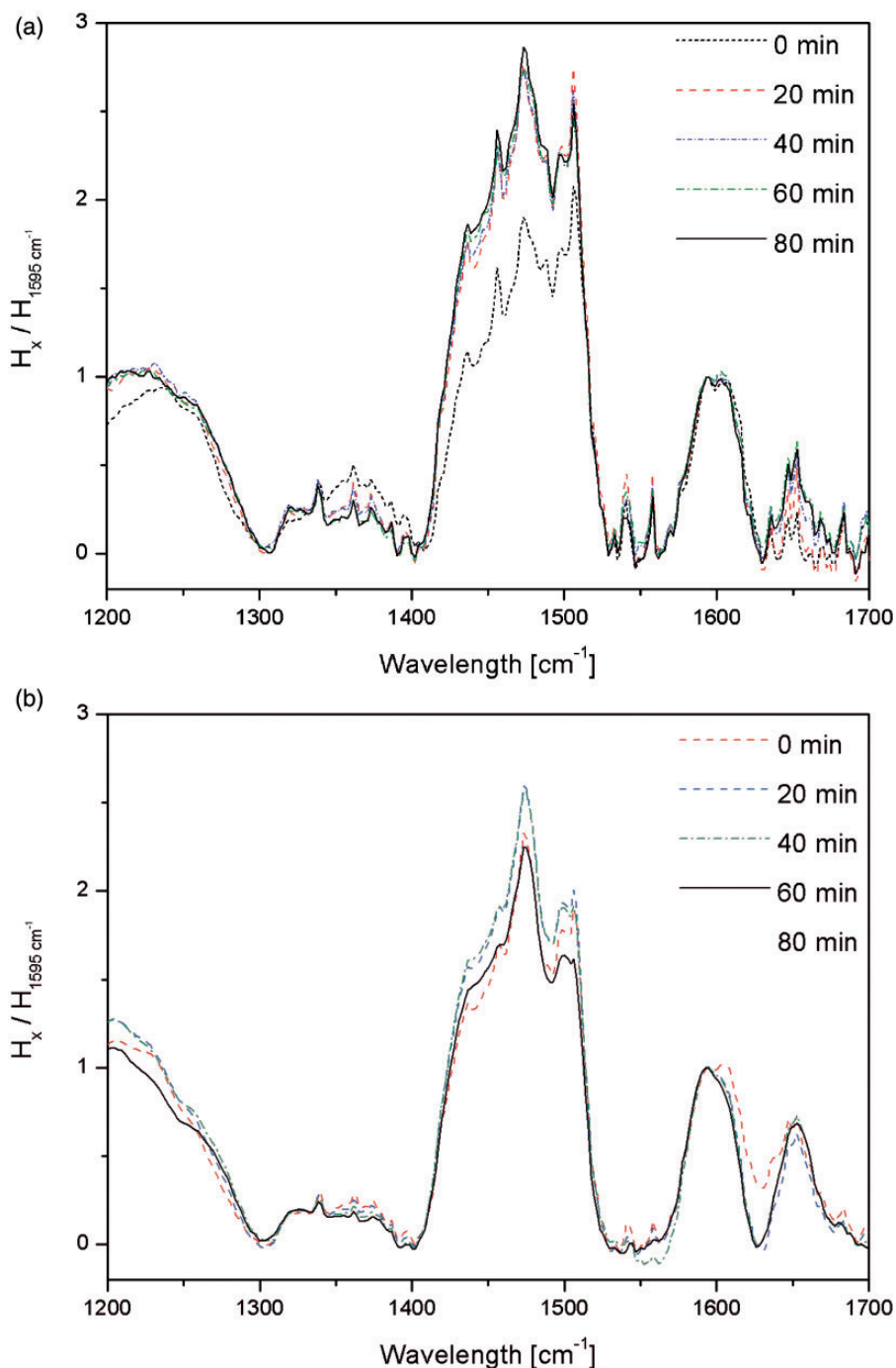
Figure 5. FTIR spectra obtained at different times at 190°C in the 1200–1700 cm^{-1} region of: (a) neat resol and (b) modified resol.

currently used instead of DSC because the high degree of volatiles evolved during the curing reaction alters the DSC curves, making them difficult to analyze. The FTIR bands corresponding to the methylene bridges of the neat and modified phenolic resins were taken as the reactive vibration bands to follow the evolution of the resin curing process. These bands appear at 1456

and 1473 cm^{-1}, for the "para–para" and "ortho–para" bridges, respectively.[23] It is well known that methylene bridges are indicative of the polymerization reaction advance and the polymer crosslinking density of resol resins. Additionally, it has been reported that after heating the resol up to 190°C a completely cured resin is obtained.[23] Then, the evolution of the conversion at
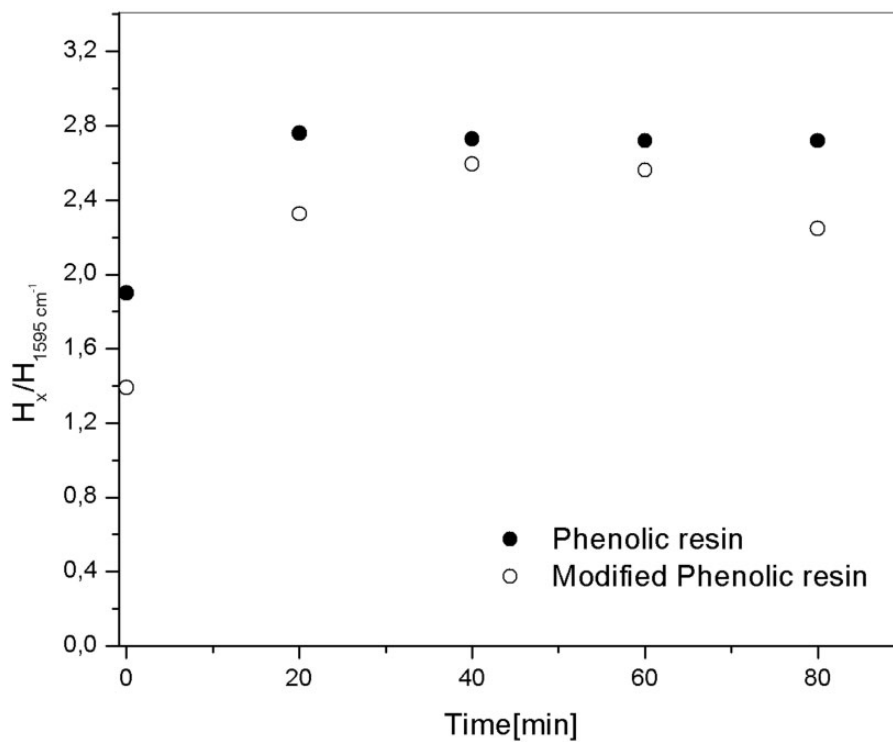
Figure 6. Peak height ($1473 \, cm^{-1}$) as a function of time at $190°C$, for the neat and modified phenolic resin.
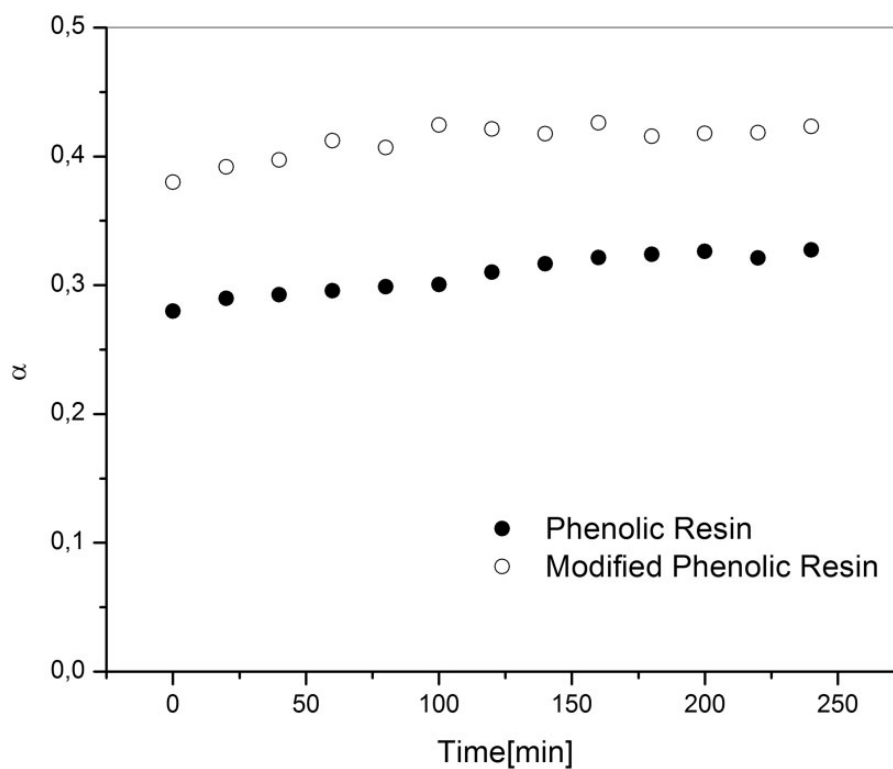
Figure 7. Degree of conversion as a function o time obtained from isothermal FTIR test at $80°C$ for neat and modified phenolic resin. Both measured from the $1456 \, cm^{-1}$ peak.

80°C was obtained following the FTIR peaks at 1456 and 1473 cm^{-1}. The degree of conversion (α) at each time (t) was calculated from the following

$$\alpha = \frac{H_{T,t}}{H_{max}} \qquad (2)$$

where $H_{T,t}$ is the height of the peaks (at 1456 and 1473 cm^{-1}) in the FTIR spectra obtained at 80°C at a certain time, and H_{max} is the height of those peaks in the isothermal test at 190°C, i.e. the maximum conversion. It was considered that the reaction for both systems was completed after 20 min at 190°C because after that time the variation in the peaks height was negligible. Figure 5 shows the 1200–1700 cm^{-1} region of the FTIR spectra at 190°C for the neat and modified resol resins at different times whereas Figure 6 shows the evolution in the height of the 1473 cm^{-1} peak with time. The peak centered at 1456 cm^{-1} showed the same behavior.

The evolution of the conversion as a function of time at 80°C for the neat and modified resins is shown in Figure 7; it can be observed that similar results were obtained for both systems. However, the initial conversion of the modified resin was higher than that of the neat resin. This could be related to the accelerating effect on the polymerization reaction produced by sonication, which is a necessary processing step in the case of the bentonite-modified resin. From that point, the

conversion increased at the same rate during the isothermal treatment at 80°C for both systems. Whereas the neat resin reached around 35% of conversion (Figure 7), the modified one achieved a value of approximately 40% after 4 h at 80°C. This increase in resin conversion is important to increase the resin viscosity and avoid resin draining in the final prepregs, keeping the matrix below the gel point. Additionally, both systems reached a comparable crosslinking density when they were completely cured (Figure 5). Similar results were reported in a previous work, where it was found that the addition of modified montmorillonites to phenolic resins produces a cured network with crosslinking density similar to that of the neat resin.[36]

Characterization of the prepregs

The fiber content and density of the prepregs obtained are presented in Table 2. As expected, the addition of clay produced an increase in the density of the phenolic resin prepregs while the fiber content was similar in both types of prepregs. In general, 45% by volume is a common value for the fiber content in prepregs[37] because it allows forming pieces by removing the excess of resin, without leaving dry spots and increasing the fraction of fibers in the final component.

Another important property of prepregs is stiffness, which indicates their ability to form pieces with sharp angles. The test sequence is shown in Figure 8; it can be seen that as the prepreg advances horizontally with increasing load (a), the curvature becomes more pronounced (b), the test ends when the sample reaches the angle given by the holder. Results are shown in Table 2 and it is difficult to make a categorical conclusion because the values obtained for the modified prepregs fell within the error range of the values obtained for the unmodified prepregs. However, the stiffness of the nanoclay-modified prepregs decreased slightly, which can be attributed to the higher viscosity of the phenolic–bentonite system, which reduces the amount of

Table 2. Prepregs fiber content, density, and stiffness.

	Unmodified prepregs	Modified prepregs
Density (g/mL)	1.01 ± 0.19	1.26 ± 0.10
Fiber content (vol.%)	43 ± 8	45 ± 4
Stiffness (mJ/m)	18.5 ± 6.0	13.8 ± 2.8
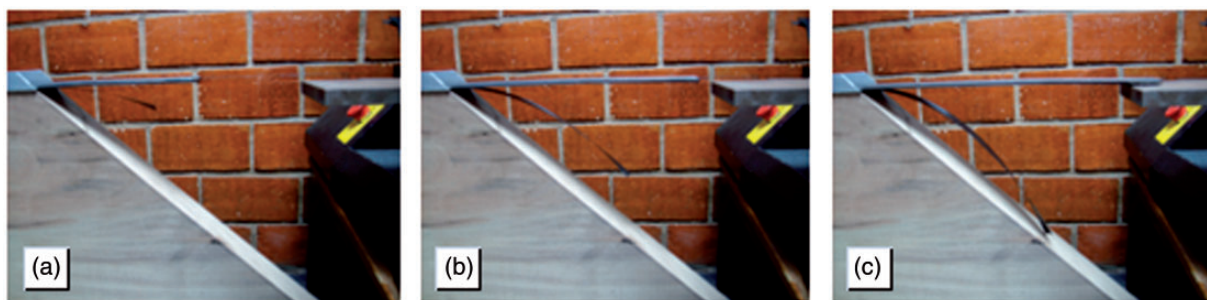
Figure 8. Prepregs stiffness test sequence: (a) the prepreg starts to advance horizontally, (b) the curvature becomes more pronounced, (c) the test ends when the sample reaches the angle given by the holder.

resin that flows to the outer part of the prepreg. The higher amount of resin accumulated in the other face of the laminate increases the moment of inertia for bending, decreasing drapability.

Figure 9. Device used to measure the degree of tack of the prepregs.

Table 3. Composite properties.

Property	Unmodified composite	Modified composite
Fiber content (vol.%)	82 ± 1	73 ± 4
Density (g/mL)	1.60 ± 0.04	1.70 ± 0.02
Flexural modulus (GPa)	130 ± 7	104 ± 6
Flexural strength (GPa)	1.0 ± 0.7	0.68 ± 0.09

Finally, the degree of tack of the prepregs is another important property, because it determines their ability to adhere during the processing of the composite material. If the tack is too low, the plies do not remain in place when the sheets are placed, but too much tack makes the material difficult to handle as it sticks to everything that it comes in contact.[20] There is not a standardized method to determine the degree of tack of prepregs; commercially tack levels are specified by high, medium, or low; the ASTM D3167 floating roller peel test is often used to measure the tack of "pressure sensitive" adhesives and has also been used by prepreg manufacturers.[17] The device used to determine the degree of tack is shown in Figure 9.

The tack of unmodified prepregs could not be measured because they did not adhere to the device used for the measurement. On the other hand, the tack of modified prepregs was correctly measured and the value was 4.4 N/m $\pm$ 0.79 N/m. The increase in the degree of tack is attributed to the increasing degree of conversion and viscosity caused by the addition of clay to the resin, which is desirable because the plies can adhere properly during the posterior processing of the composite material.

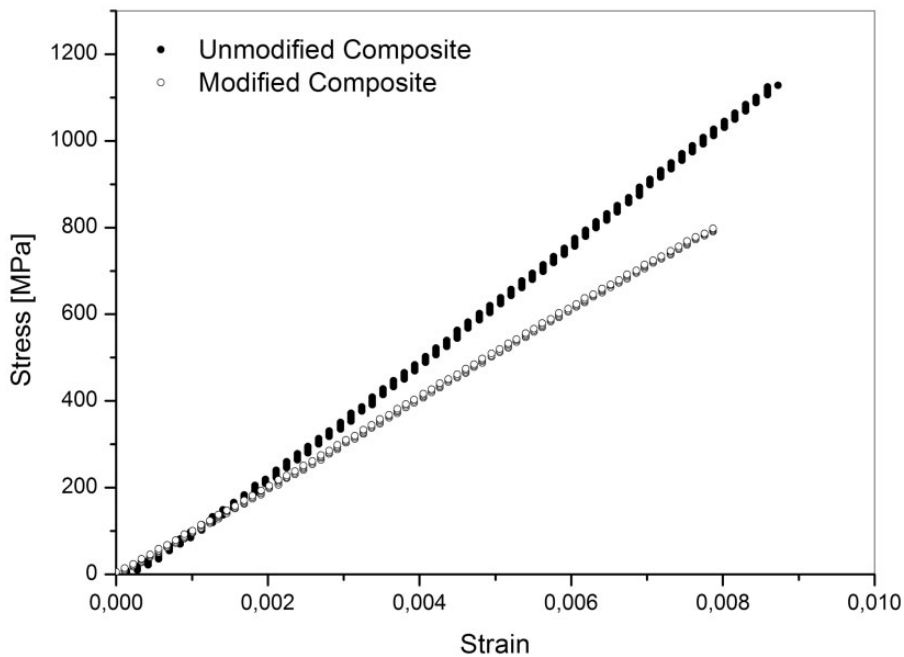## Characterization of the composites

The physical and mechanical properties of the composites manufactured with the prepregs are summarized in Table 3. In both cases, composite materials with high fiber content, near 75 % by volume, were obtained.
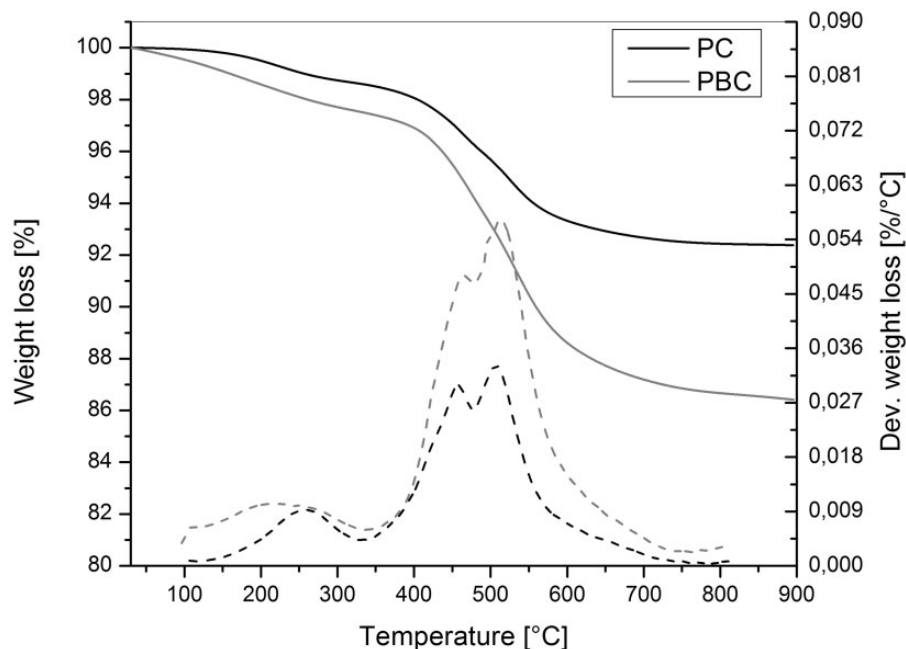
Figure 10. Thermogravimetric curves at 10°C/min of the composites in nitrogen.
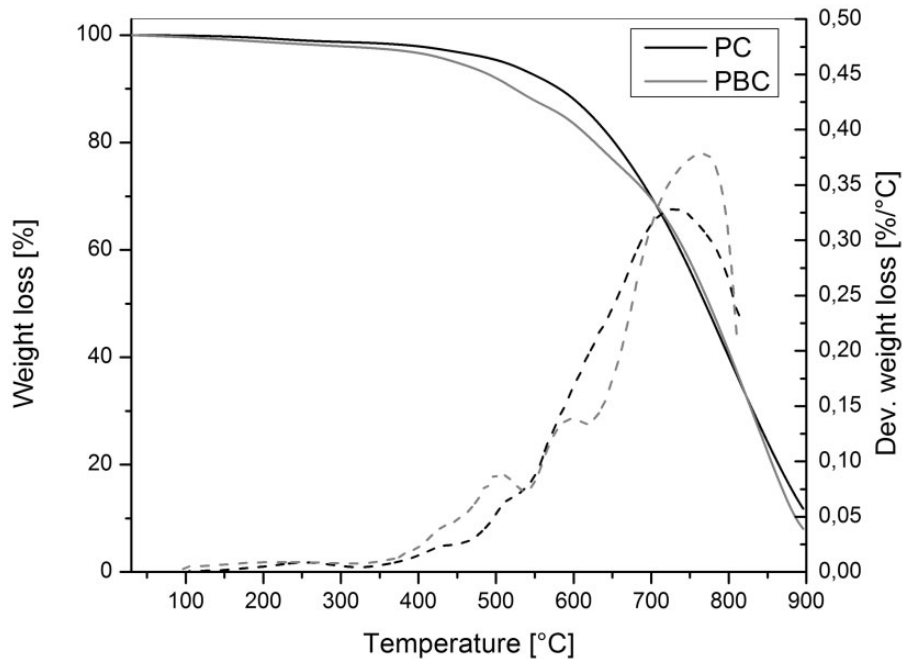
Figure 11. Thermogravimetric curves at 10°C/min of the composites in air.

Figure 12. Stress vs. strain curved obtained in the three-point bending test of the composites.

The difference in the final fiber content was due to the higher viscosity of the modified phenolic resin, which reduces the resin extraction of the bleeder during the processing, resulting in a higher resin content. The values obtained for the composites are in the range of the values that can be obtained for typical epoxy-carbon composites.[37]

In Figures 10 and 11, the thermal degradation of the composites is presented. The degradation under nitrogen atmosphere can be divided into three stages, between 150°C and 350°C, between 350°C and 500°C, and above 500°C. The first region can be associated with the evaporation of volatiles (water and free formaldehyde). The second and third regions correspond

to the thermal fragmentation with chain scissions of methylene bridges groups, scissions of phenolic groups and the char formation.[38] The addition of nanoclay did not change the degradation of the materials since mass losses occur at the same temperature in the both atmospheres. The residual mass of the unmodified composites is higher, which is associated with its higher carbon fiber content.

Regarding the mechanical properties, Figure 12 shows the stress versus strain curves for both materials. The average flexural modulus, strength and the standard deviations are summarized in Table 3. The results show a lower strength and flexural modulus of the composites in the case of clay-modified prepregs; since the mechanical strength is principally given by the carbon reinforcement, this can be due to the lower fiber content achieved during the manufacturing of the modified composites.

Conclusions

Resol-type phenolic resin was obtained with a formaldehyde-to-phenol molar ratio equal to 1.3 under basic conditions. Five percent of the modified nanoclay was added to the obtained resin. Only slight differences were observed in the kinetics of curing measured by FTIR between both systems.

Both resins were used to successfully produce carbon fiber/phenolic resin and carbon fiber/clay modified phenolic resin prepregs by vacuum bag molding. An important result is that nanoclay incorporation did not produce any difficulties in the processing.

When the prepregs obtained were analyzed, it was found that they had intermediate fiber volume content, near 45%, which is adequate for the processing of composite materials. It was also demonstrated that the addition of 5 wt% of modified bentonite to the phenolic resin did not significantly affect the prepregs stiffness but increased the tack, which was related to the increase in resin viscosity caused by the clay. Therefore, the processing parameters were not affected by the addition of clay, while some final characteristics of the prepregs were improved, which is a relevant and not previously reported behavior.

Finally, it was possible to process high-fiber-content composite materials based on the prepregs. The addition of clay was detrimental for the mechanical properties of the composites, but this is due to the higher viscosity of the matrix, which produces a lower degree of resin draining during composite processing and, as consequence, a material with lower fiber content. As the mechanical strength is principally given by the carbon reinforcement, modified composites showed less flexural modulus and strength.

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