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Synthesis of a boron modified phenolic resin

Abstract: *Phenolic resin has long been used as matrix for composites mainly because of its flame retardant behavior and high char yield after pyrolysis, which results in a self supporting structure. The addition of ceramic powders, such as SiC and B_4C, as fillers to the phenolic resin, results in better thermo-oxidative stability, but as drawbacks, it has poor homogeneity, adhesion and processing difficulties during molding of the composites. The addition of single elements, such as boron, silicon and phosphorus in the main backbone of the thermo-set resin is a new strategy to obtain special high performance resins, which results in higher mechanical properties, avoiding the drawbacks of simply adding fillers, which results in enhanced thermo-oxidative stability compared to conventional phenol-formaldehyde resins. Therefore, the product can have several applications, including the use as ablative thermal protection for thermo-structural composites. This work describes the preparation of a boron-modified phenolic resin (BPR) using salicyl alcohol and boric acid. The reaction was performed in refluxing toluene for a period of four hours, which produced a very high viscosity amber resin in 90% yield.The final structure of the compound, the boric acid double, substituted at the hydroxyl group of the aromatic ring, was determined with the help of the Infrared Spectroscopy, ^{1}H-NMR, TGA-DSC and boron elemental analysis. The absorption band of the group B-O at 1349 cm^{-1} can be visualized at the FT-IR spectrum. ^{1}H-NMR spectra showed peaks at 4.97-5.04 ppm and 3.60-3.90 ppm assigned to belong to CH_2OH groups from the alcohol. The elemental analysis was also performed for boron determination.The product has also been tested in carbon and silicon fibers composite for the use in thermal structure. The results of the tests showed composites with superior mechanical properties when compared with the conventional phenolic resin.*

Keywords: *Phenolic resin, Boron, Thermal protection, Oxidizing agents.*

LIST OF SYMBOLS

Ar-H	Aromatic protons
BPFR	Boron-containing phenol-formaldehyde resin
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetry
FT-IR	Fourier transform spectroscopy
GPC	Gel permeation chromatography
HMTA	Hexamethylenetetramine
ILSS	Interlaminar shear strength
Mn	Molecular weight (average number)
Mw	Molecular weight (average weight)
NMR	Nuclear magnetic resonance
OH	Hydroxyl group
PC	Polycarbonates
PF	Phenol formaldehyde resin
PPG	Polypropyleneglycol
PS	Polystyrene
TLC	Thin layer chromatrography
Tc	Critical temperature
Tg	Glass transition temperature
TG	Thermogravimetric analysis

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INTRODUCTION

Phenolic resin was the first synthetic polymer. The processing technique was carried out firstly by A. von Bayer, in 1872, and further patented by Leo H. Baekeland in 1907 (Knop and Pilato, 1985). Since then, thermo-set phenolics have wide industrial and commercial application (Whitehouse, Pritchett and Barnett, 1968). Due to their excellent ablative properties and structural integrity, they have been used as high performance thermal protection systems, such as nose caps and exit cones for rocket nozzles (Knop and Pilato, 1985; Segal, 1967; Schmidt and Graig, 1982). They also have widely use in thermal insulation materials, molding compounds, foundry, coating material, wood products industry and in many other composite materials (Casiraghi *et al*., 1980). Another application is the use as precursor of solid carbon materials as a matrix for heat resistant materials (Lenghaus, Qiao and Solomon, 2000), and also as adhesives

for production of wood agglomerates (Park *et al*., 1999). Another important application of phenolics is as a polymeric blend with other polymers, which produces materials with superior physical properties, such as tensile strength and modulus (Okoroafor, Villemaire and Agassant, 1992).

Phenolic resins are synthesized by the reaction of phenol with formaldehyde. These resins can be divided into two main groups according to reaction conditions that are used, such as pH of the catalyst and the formaldehyde/ phenol ratio. Formaldehyde has a functionality of two and phenol, of three. Phenol will react with the OH group at the para and at the two ortho position. The two meta positions are un-reactive. If the reaction proceeds with excess of one or two moles of formaldehyde, the final product is a thermo-set resin. If the reaction proceeds with excess of phenol, it has sufficient functionality, but not enough cross linking molecules to be thermo-set or thermoplastic resin.

Under acidic conditions, the reactions of phenol with formaldehyde with excess of phenol lead to the formation of novolac type resin (Fig. 1). The resole type resin is formed under alkaline conditions and excess of formaldehyde (Fig. 2).

The main difference between novolac and resole resins is the presence of the reactive methylol groups and, occasionally, dimethylene-ether linkage in the resoles instead of the condensation products linked with methylene bridges, as in the case of novolacs. Therefore, novolac resins are thermally cured by addition of a methylene cross linker – hexamethylenetetramine (HMTA) or paraformaldehyde. Resoles are cured only by application of heat.

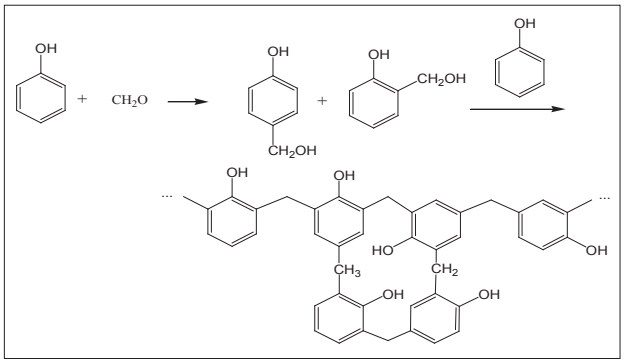


Figure 1: Structure of novolac resin.

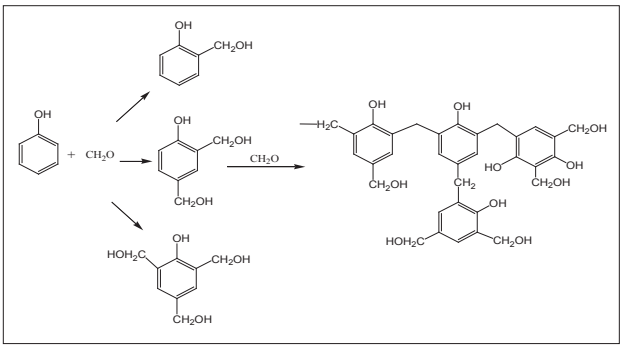


Figure 2: Structure of resole resin.

Phenol formaldehyde resins (PF) are characterized by their capability of forming hydrogen bonds with polymers containing carbonyl or carbonate groups (Fahrenholtz and Kwei, 1981), or forming covalent bonding if the polymer contains complementary hydroxyl groups. In addition, the phenyl ring structure of phenolic resin is capable of forming secondary bonding by π-π overlap, which is important for building these polymers.

The final properties of these materials depend on the synthesis and operating conditions. Details of the curing process are responsible for many of the physical and mechanical characteristics: the cure time and temperature influence, the resulting glass transition temperature (Tg) and the elastic modulus. Thus, structural information and explicit knowledge relevant to the curing process is important and essential for understanding and improving the synthesis process and the use of phenolic resins.

The most commercially available phenolic resin has the average molecular weight (M_w) in the range of 500 to 1000 $gmol^{-1}$. The molecular weight of phenolic resins depends on the formaldehyde/phenol ratio, the type of catalyst (acidic or alkaline), and the time and temperature of the reaction, but the most important factor for controlling the molecular weight of PF is the molar ratio. Figure 3 shows the resulting type of phenolic resin, resole or novolac, as a function of the formaldehyde/phenol ratio and molecular weight (Lemon, 1985).

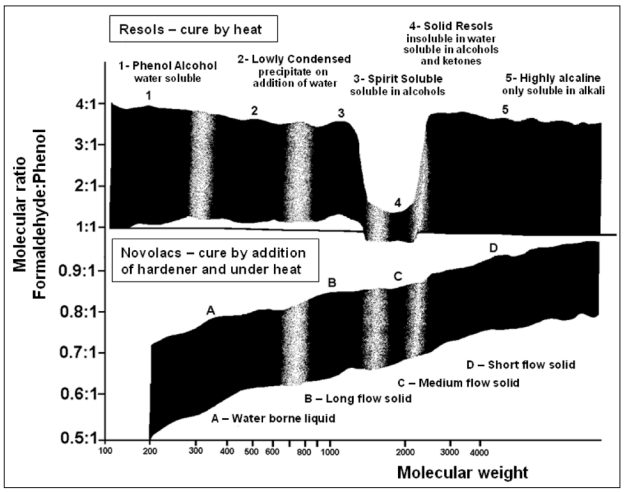


Figure 3: Curing graphic for phenolic resin forming novolac and resol (Lemon, 1985).

The most common catalyst of phenol-formaldehyde novolac resin synthesis is: sodium, potassium and lithium hydroxides, and rarely hydroxides of divalent metals (magnesium, calcium or barium) (Knop and Sheib, 1979; Knop and Pilato, 1985). Carbonates (Na) and oxides (Ca or Mg) can also be used as catalyst in the synthesis (Polish Patent 109 966, 1981; Polish Patent 150 036, 1990). Tertiary amines, in particular triethylamine, were claimed recently as the catalyst for the resole resin synthesis (Russina Patent 2 028 313, 1995; US Patent 4 045 398, 1977).

Knop (1979,1985) found that the substitution of phenol with formaldehyde in the ortho-position *versus* para-position increased in the following sequence of hydroxide catalyst metal: K < Na < Li < Ba < Sr < Ca < Mg. Grenier-Loustalot *et al*. (1996) concluded that the rate at which phenol disappeared from the reaction mixture depended on the metal valence in the hydroxide catalyst and on the size of the hydrated metal cation. Magnesium, calcium and barium hydroxides were found to be more effective catalyst than lithium, sodium or potassium hydroxides.

Although phenolic resin has good thermo-oxidative resistance, extensive research has been done to improve their thermal properties through modification of their structure with introduction of some elements, such as boron or phosphorus and even silicon.

The boron-containing phenol-formaldehyde resin (BPFR) is a modification of the phenolic resin. It is obtained with the introduction of boron in the main backbone of the phenolic resin. The BPFR resin has good heat-resistance, mechanical properties, electric properties and absorbance of neutron radiation (Abdalla, 2003). There are several works that describe the synthesis and applications of BPFR (America Patash Chem Corp, 1964; Gao and Liu, 1999; Gao and Liu, 2001). This resin is usually synthesized by the formaldehyde method, in which phenol borate synthesized from phenol and boric acid is followed by the reaction with poly-formaldehyde. Another popular method is the synthesis using the method of formalim (Gao and Liu, 1999), which consists in the reaction of phenol with formaldehyde to form the alcohol and then followed the reaction with boric acid.

MATERIALS AND EXPERIMENTAL

Materials

Solvents, boric acid and 2-hydroxy benzyl alcohol were purchased from Aldrich, Fluka or Merck, according to their required purity, price and availability. Butanediol, dichloromethane and epichlorhydrin were purified by distillation prior to use.

Experimental

Synthesis

Boric acid and 2-hydroxy benzyl alcohol in a ratio of 1:2 were dissolved in toluene and placed in a four-necked round bottom flask equipped with a stirrer, thermometer, condenser and a Dean Stark system, and stirred under reflux for the period of four hours. Over this period, the amount of water collect at the Dean Stark was according to the calculated amount, and also the total disappearance of the alcohol can be observed on the TLC plate. Then, the solvent was evaporated giving a high viscous amber product in 89.4% yield.

The reactions were performed by the use of the Dean Stark system with a heat controlled oil bath, and they were followed through the amount of water that were released during the reaction and also from thin layer chromatography.

^{1}H-NMR, ^{13}C-NMR analysis were conducted on a 300 MHz Brüker DPX spectrometer using methyl-d_6 sulfoxide as solvent. The proton and carbon chemical shifts are recorded in ppm and calibrated on the solvents as internal standard. Infrared spectroscopy has been recorded by a Magna-IR spectrometer 750 Fa. Thermo Nicolet (4000 to 400 cm^{-1}, 40 scans).

Resin characterization and composite processing and characterization

The characterization of boron-modified phenolic resin, uncured and cured, was performed by thermal (DSC and TG) and mechanical analysis. DSC analyses were carried out in a PerkinElmer Pyris 1 DSC analyser, at 20°C/min in N_2 (20 mL/min), mass of 11 mg in a tightly closed aluminium sample holder and gave information on the curing process, temperature and heat of the reaction and also the glass transition temperature for the cured resin. The glass transition was measured in the second heating.

TG/DTG analysis of uncured resin were carried out in a SDT-Q600 TA Instruments analyser, using alumina pans (11 mg), under nitrogen atmosphere (100 mL/min) and heating rate of 10ºC/min. TG/DTG curves under nitrogen or synthetic air (20 mL/min) of the cured boron-modified phenolic resin were produced at 10°C/min using a PerkinElmer Pyris 1 TG analyser and platinum pans (11 mg). TG/DTG/DTA curves were obtained with a Seiko TG/DTA 6200 analyser,

under synthetic air (20 mL/min) at 2.5 and 10°C/min, platinum pans (2 mg).

The rheological characterization of n on cured resin was performed on a Rheometrics SR5 rheometer by using a parallel plate measuring system. The rheological characterization helps to obtain viscosity profiles as a function of time, temperature and shear rate, which in turn can be used to define the processing window of the neat resin.

Thermal diffusivity measurements were carried out according to ASTM E1461-07 in the temperature range of 25 to 175°C. The thermal diffusivity of a material depends on its thermal conductivity, density and heat capacity according to Equation 1. The thermal diffusivity characterizes the heat transport in material during transient regime conditions.

$$Thermal\ diffusivity = \frac{\kappa}{\rho.Cp} \quad (1)$$

Where:
k = thermal conductivity;
ρ = density;
Cp = heat capacity.

A composite material was molded in the form of a plate by using a lab-scale autoclave. The composite was molded with silica fabric fiber (650 g/m^2) and the boron-modified phenolic resin. The cure schedule was made according to the cycle developed in this work. A 55% fiber volume fraction was measured in the silica fiber/resin composite.

The composite was characterized by interlaminar and Iosipescu shear tests. The interlaminar shear strength was measured according to ASTM D2344-06, using specimens with dimensions showed in Fig. 4. Accepted failure modes for interlaminar shear are characterized by tiny elongated cracks between laminae at the center of the specimen. The interlaminar shear strength is calculated according to the Equation 2.

$$\tau_{average} = \frac{3}{4} \cdot \frac{P_{rupture}}{A} \quad (2)$$

Where:
$\tau_{average}$: apparent interlaminar shear strengh (MPa);
$P_{rupture}$: ultimate load corresponding to the rupture of the sample (N);
A: cross section area calculated by W (width) x t (thickness) (mm^2).

The Iosipescu shear test was performed according to ASTM D5379-98. The strength and modulus of composite

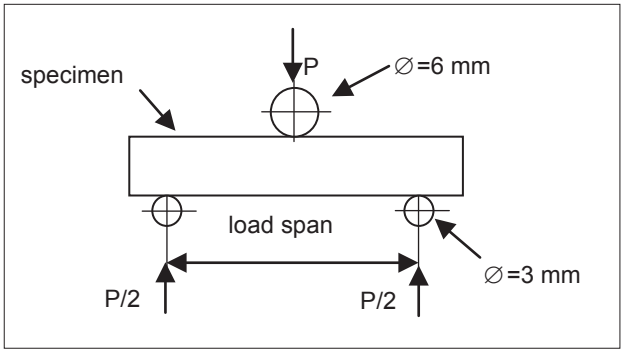


Figure 4: Dimensions of the specimens and its assembling on the equipment for performing the tests according to ASTM 2344-06.

specimen were measured in the direction 1-2 of the composite, as shown in Fig. 5. In this case, the loading is parallel to the stacked layers. The test jig used for the tests is showed in Fig. 6. Accepted Iosipescu shear failure modes are mainly between the V-notches.

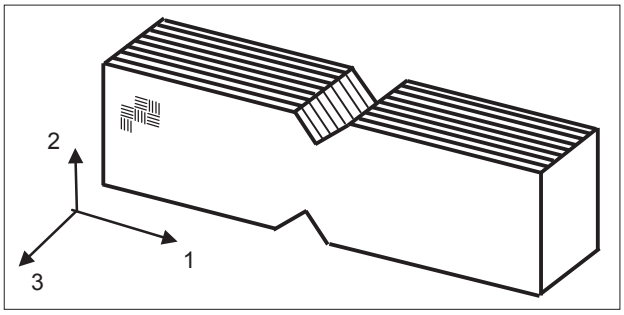


Figure 5: Specimen geometry for Iosipescu shear tests in the 1-2 plane.

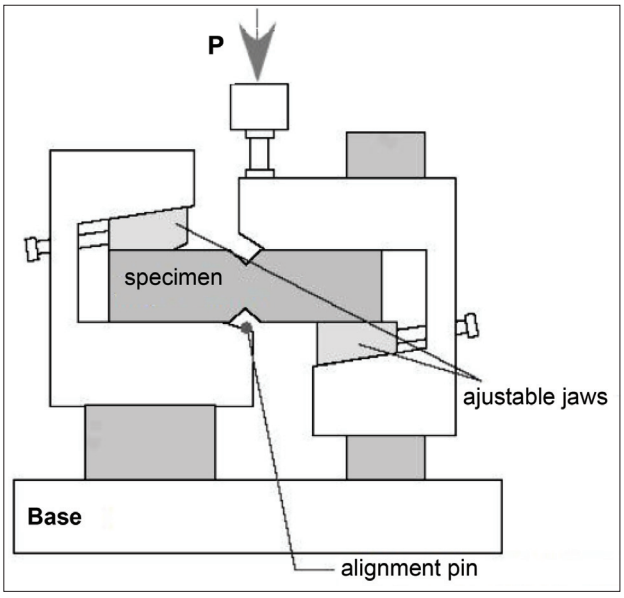


Figure 6: Test jig for Iosipescu shear test, according to ASTM D5379-98.

The Iosipescu shear strength can be calculated by the Equation 3:

$$\tau = \frac{P_{ultimate}}{A} \quad (3)$$

Where:
τ: the aparent average shear strength, in MPa;
$P_{ultimate}$: the ultimate load of the sample at rupture – N;
A: the cross section area of the specimen (width x thickness), between the V-notches (mm^2).

RESULTS AND DISCUSSION

Structure of boron modified phenolic resin

According to the literature (Xu, 1976; Tu and Wei, 1981; Heefel *et al*., 1975), the initial condensation product of salicyl alcohol and boric acid consists mainly of phenol borate and some salicyl alcohol borate as shown in Fig. 7.

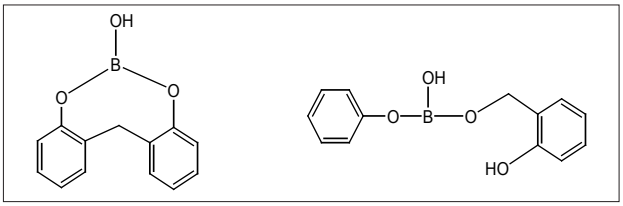


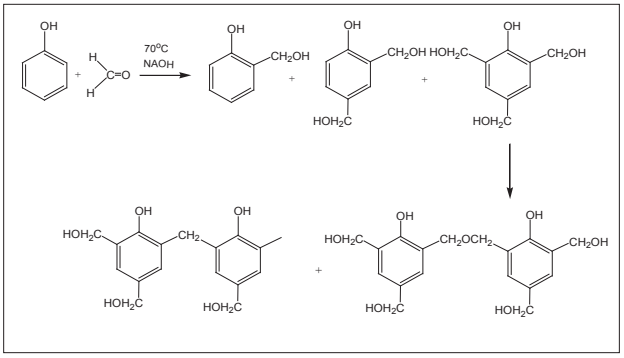
Figure 7: Condensation products from the reaction of salicyl alcohol and boric acid.

In this work, the synthesis has been done using the Formalin (Gao and Liu, 1999) method, that consists in the initial formation of salicyl alcohol (reaction of phenol with formaldehyde) that followed the reaction with boric acid. However, the reaction of phenol with formaldehyde produced a mixture of several compounds as shown in Scheme 1 (Abdalla, Ludwick and Mitchell, 2003).

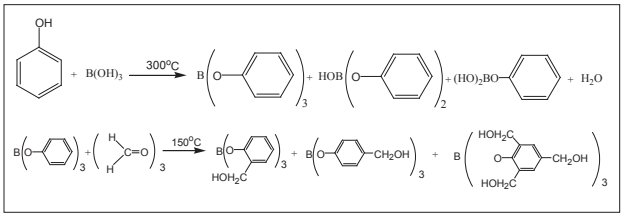
This mixture is difficult to separate, causing problems to follow the subsequent reaction to obtain the desired monomer.

Hirohata *et al*. (Hirohata, Misaki and Yoshii, 1987) used the strategy of the reaction of phenol with boric acid followed reaction with formaldehyde. However, this also leads to a mixture of several compounds that is very difficult to separate, as shown in Scheme 2.

However, it has been proved (Gao and Liu, 1999) that the reaction of salicyl alcohol with boric acid proceeded with the ratio of 50% in 50 minutes, while the reaction of phenol was only 4% in 150 minutes. Therefore, it is evident that the condensation product has salicyl alcohol groups attached to oxygen of boric acid (Scheme 3).

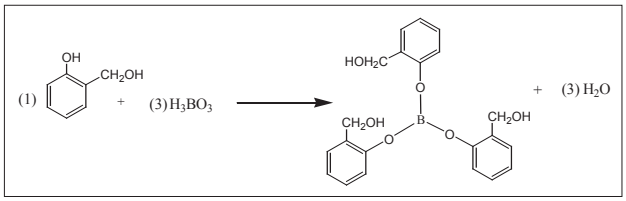


Scheme 1: Method for the synthesis of salicyl alcohol.



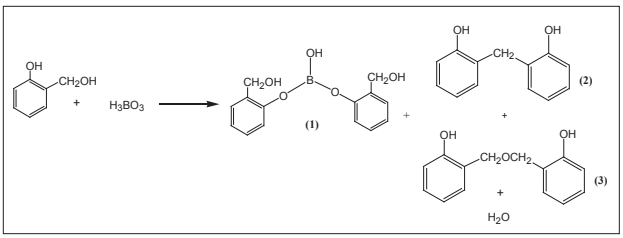
Scheme 2: Method for synthesis of BPFR resin.

Several attempts has been done to obtain the boron resin using the formalin method, however, it was not possible to get a monomer free from side compounds and therefore the following reaction to get BPFR resin did not proceed. The alternative proposed in this project was to get the monomer starting from the available pure alcohol and reaction with boric acid. Then, the reaction was performed according to Scheme 3.



Scheme 3: Synthesis of BPFR monomer.

In order to replace the three OH groups at boric acid to alcohol, the molar ratio of 3:1 (alcohol:acid) was used, which would produce the compound shown in Scheme 4. As it has been described at experimental part, the reaction was performed in toluene at 120°C. However, the resulting compound has only two OH groups replaced by the alcohol. The third group could not be replaced, and this might be due to steric hindrance. After four hours, the reaction is finished, as it can be visualized from the water that is formed and collected at the Dean Stark. When the reaction was left longer (approximately 12 hours), it was verified the formation of side compounds, resulted from the reaction of the methylol groups that condense with each other forming methylene and ether linkages, as shown is Scheme 4.



Scheme 4: Synthesis of boron resin.

When the reaction is interrupted after four hours, the product is only the compound resulting from the condensation of boric acid with salicylic acid (Knop and Pilato, 1985), an amber and high-viscous compound. The non reacted salicylic acid precipitated as white solid.

Analysis of the boron modified phenolic resin

Figure 8 shows the FT-IR spectrum of the boron resin. The main bands are in agreement with the bands coming from boron and the alcohol. The region at 3400-3300 cm^{-1} shows characteristic bands for alcohol and acid. The band at 1592 cm^{-1} belongs to the alcohol. Boric acid has a strong and characteristic band at 1480 cm^{-1} and the alcohol has several bands between 1482 and 1417 cm^{-1}. Therefore, the bands that were observed between 1493 and 1421 cm^{-1} belong to both acid and alcohol. The bands at 1395 and 1234 cm^{-1} belong only to alcohol, since these bands are not present in the acid, and the band at 1350 and 1300 cm^{-1} (BO) refers to the acid. The strong band at 1200 cm^{-1} and the remaining bands at 700 cm^{-1} refer to alcohol and acid (Smith, 1999).

In general, the ^{1}H-NMR and ^{13}CNMR spectra of the BPFR resins are always complicated to analyze, which reflects the complexity of the boron containing system. The ^{1}H-NMR spectrum is shown in Fig. 9. The wide resonance lines (multiplets) at the region of 6.89-7.19 ppm refer to the aromatic protons (Ar-H). The resonances at the region of 4.97-5.04 ppm and 3.60-3.90 ppm are assigned to the methylene groups (CH_2OH) and ether linkages (CH_2OR). The peaks at the region of 2.5 ppm are assigned to the OH groups that come from boric acid and salicylic alcohol.

The elemental analysis of the resin showed 66.49% carbon, 5.36% hydrogen, 13.96% oxygen and 4.46% boron. The calculation of the percentage value of boron that can be present in a resin (pre-polymer), obtained from boric acid reaction, gave a value of about 4%. The calculation was carried out based on the compound resulted from the reaction of boric acid with two molecules of salicyl alcohol (Fig. 10a). The difference resulted from the measured elemental analysis was about 10%, which might be from the small amount of product containing methylol group condensation that started to form (Fig. 10b), which presents higher content of boron.

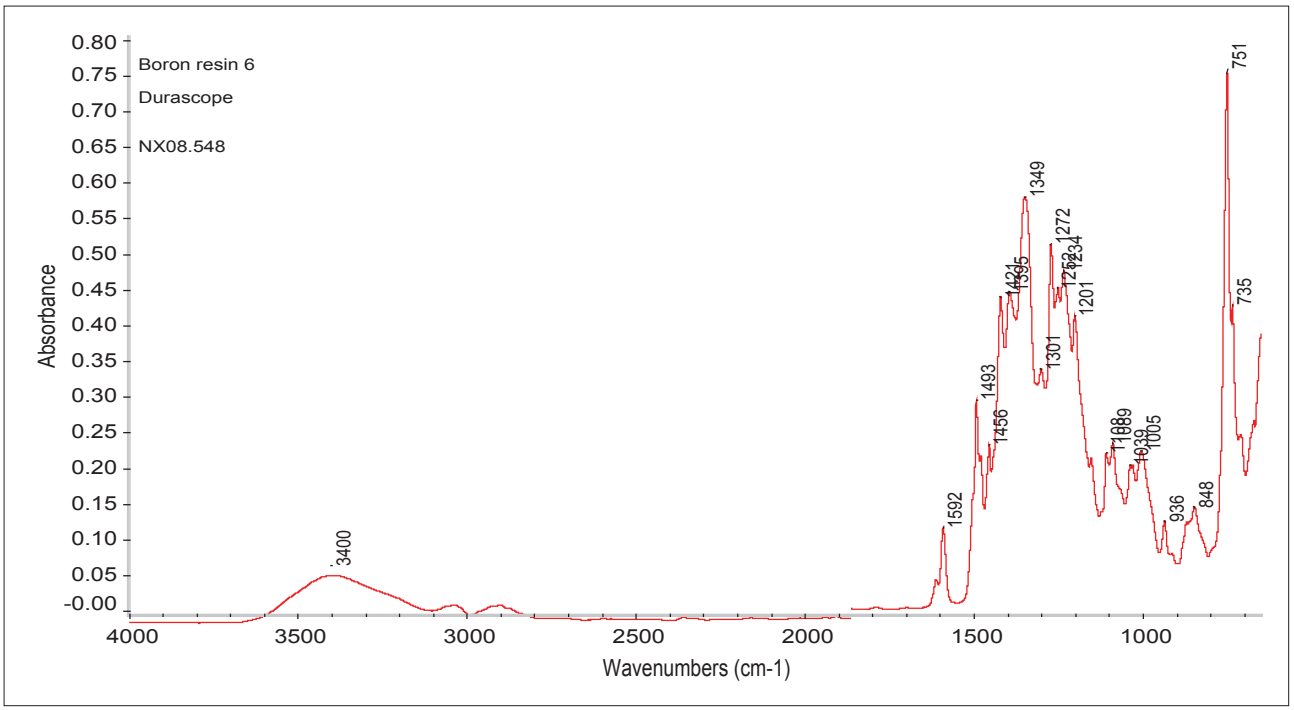


Figure 8: Fourier transform spectroscopy (FT-IR) for boron resin.

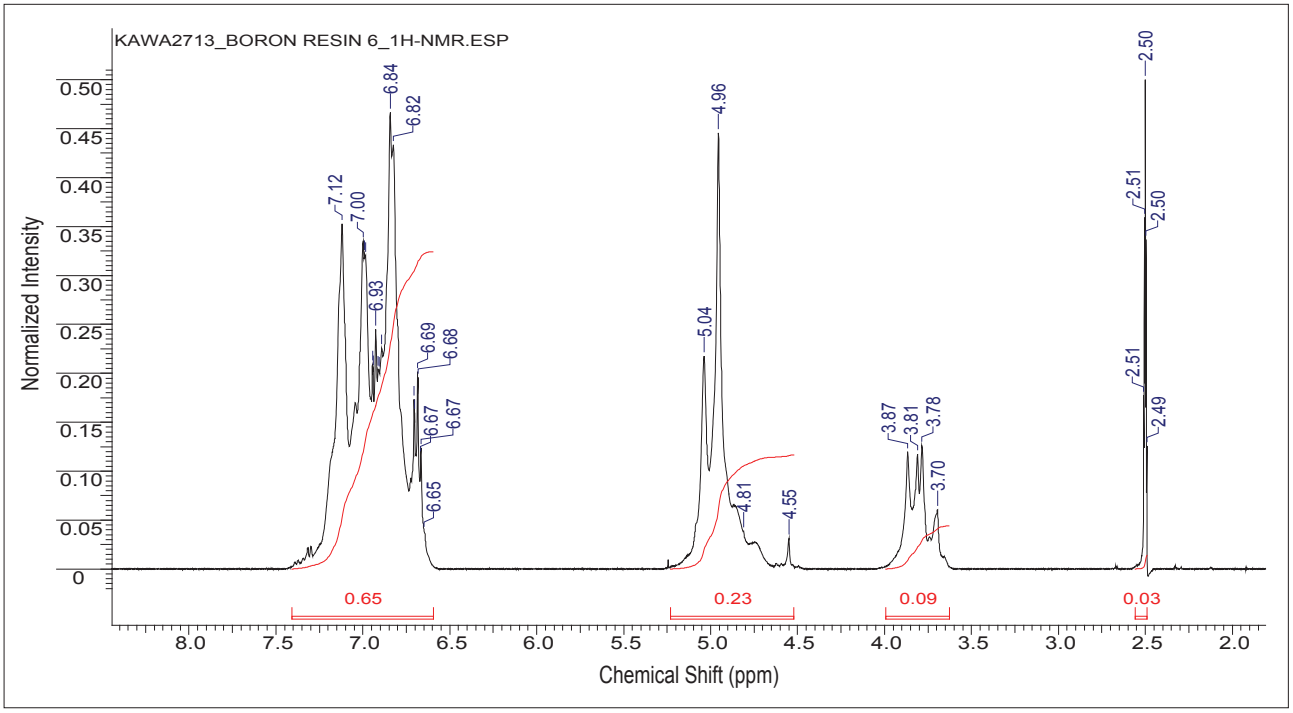


Figure 9: ^{1}H-NMR of boron resin.

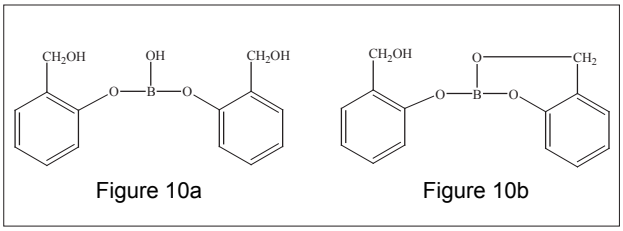


Figure 10: (a) Molecules of salicyl alcohol (b) product containing methylol group condensation.

Differential scanning calorimetry analysis

With differential scanning calorimetry (DSC) measurement is possible to get a thermal profile of the investigated sample under the conditions of thermal dynamic or isothermal scanning. The results of the measurements produce the knowledge of the reaction behavior, the beginning, the end and at which point the reaction reach its maximum peak. It also gives the heat of reaction and the glass transition temperature when operated under dynamic scanning.

Figure 11 shows the DSC curve of the boron phenolic resin. The reaction starts at around 205°C, with a peak in 224°C, and ends at 260°C. The heat of reaction is approximately 120 J/g.The Tg at DSC from cured samples is shown in Fig. 12. The value of Tg for the boron phenolic resin is approximately 266.4°C, which is superior to the commercial phenolic resin that has a value of 130°C.

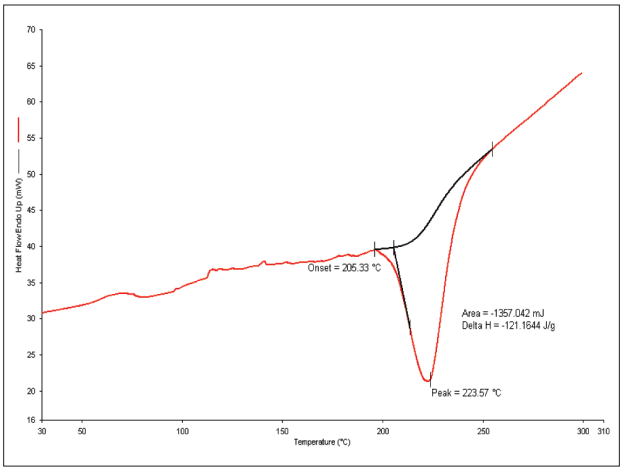


Figure 11: DSC curve of the boron resin at 20°C/min in N_2, 20 mL/min, mass of 11 mg in a tightly closed aluminium sample holder.

Table 1 summarized the results obtained from the isothermal cure showed in Fig. 10. These curves give the possibility to calculate the partial heat of reaction, which subsequently could be used for determining the rate of conversion of the ongoing curing reaction.

Thermogravimetric analysis

The thermogravimetric (TG) analysis is an important thermal analysis that shows the thermal stability of the

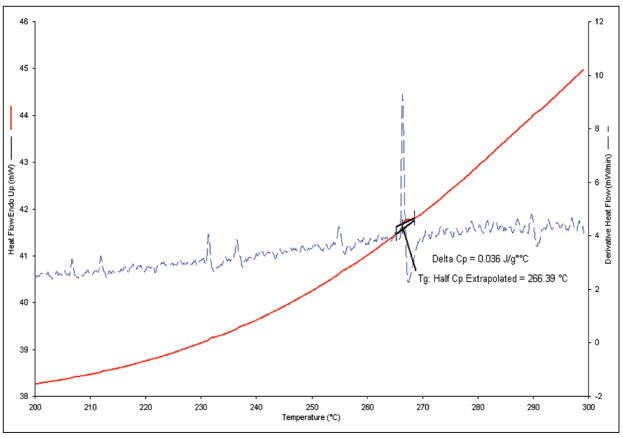


Figure 12: DSC analysis for determining glass transition temperature of boron resin after DSC curing. The red line is the specific heat curve.

materials. Also, the profile of decomposition process and yield of the material associated with the thermal treatment can be obtained.

The TG curve of a uncured boron-modified phenolic resin is shown in Fig. 13. It shows two stages of weight loss. The first stage started around room temperature and continued until 250°C, with 12.5 ± 0.3% of weight loss, which is related to the curing reaction. In the second stage, 250-790°C, the weight loss was 25.7 ± 0.2%, which was due to the decomposition of the polymer, leaving a carbonaceous residue equal to 61.9 ± 0.4% of the initial mass.

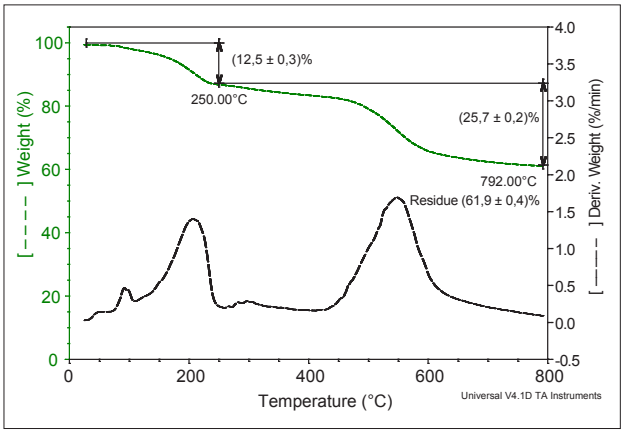


Figure 13: TG and DTG curves of uncured boron resin (nitrogen, 10°C/min).

Figures 14 and 15 show the TG analysis for a cured boron-modified phenolic resin in nitrogen atmosphere and synthetic air atmosphere, respectively. In nitrogen, the material showed a maximum weight loss of 5% up to 500°C, when an inflexion begins until, approximately, 600°C. Up to 800°C, the material showed a weight loss around 25%, which results in a significant yield of 75%. As a comparison, condensation cure phenolic resins show a carbon yield of 45% tested under similar conditions. In synthetic air, the material showed a similar behavior, but with a weight loss of 10% up to 500°C, and 27% up to 800°C, shows an yield of 72%.

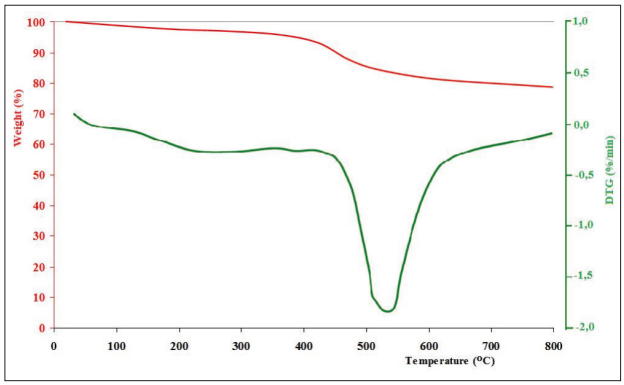


Figure 14: TG of the cured boron-modified phenolic resin in nitrogen (20 mL/min). Heating rate = 10°C/min; sample weight = 12 mg.

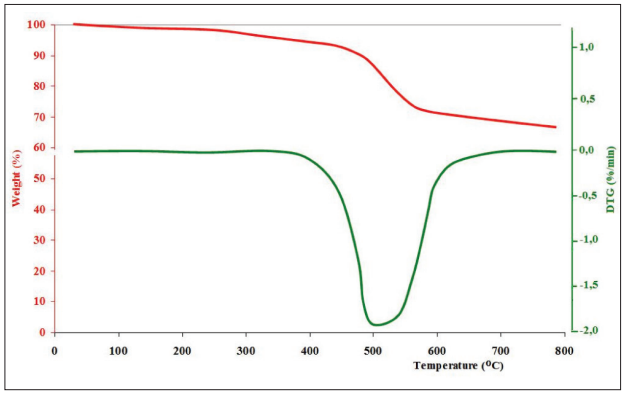


Figure 15: TG of cured boron-modified phenolic resin in synthetic air (20 mL/min). Heating rate = 10°C/min; sample weight = 11.6 mg.

The controlled degradation mechanism under pyrolysis of phenol formaldehyde type resins has been described elsewhere in many works during the last four decades (Costa *et al.*, 1997; Serio *et al.*, 1991). The structural changes are mainly monitored by thermogravimetry coupled with mass spectroscopy and FT-IR. In inert atmosphere and temperatures above 350°C, there is mainly evolution of water and unreacted oligomers (Costa *et al.*, 1997). Up to 500°C, the polymer network remains essentially unaffected, whereas above 500°C dramatic changes can be noticed, leading to the collapse of the network and formation of polyaromatic domains (Costa *et al.*, 1997; Clayton, Fabish and Lagedrost, 1969).

According to Costa (Costa *et al*., 1997), air oxidation takes place in lower temperatures (~300°C) than when the resin was heated in an inert atmosphere. This was confirmed in the present work for the boron-modified phenolic resin (Figs. 14 and 15). Although similar morphology rearrangements can take place, in the presence of an oxidizing atmosphere, oxidative degradation is not an important pyrolysis pathway, as mentioned by Costa *et al*. (1997).

In the case of the boron-modified phenolic resin, an hyperbranched structure can take place after curing, which increases the carbon yield (~80%/mass in nitrogen at 800°C) in the air in relation to the conventional phenol formaldehyde resin (~45%/mass in nitrogen at 800°C) (Costa *et al*., 1997).

On the other hand, Liu *et al*. (2007) studied the pyrolysis and the structure of hyperbranched polyborate modified phenolic resin using thermogravimetry. The resin was prepared by mixing resole with boric acid in acetone. The yield in weight loss obtained by thermogravimetry was found to be ~75%/mass in nitrogen up to 800°C, which is similar to the result found in the present work (Fig. 14).

The thermogravimetric studies performed on the boron-modified phenolic resin show the outstanding performance of this material in oxidizing environment (Fig. 16) in relation to the commercial phenolic resin (Fig. 17). Boron has been used as an oxidation resistant material for carbon materials, as a surface coating or as a mixture in the formulation of the carbon material (Castro, 1991; McKee, 1991). So, it is possible that the B-C linkages formed in the resin during charring can enhance oxidation resistance during temperature excursion.

Figures 16 and 17 show curing process for boron phenolic resin comparatively to CR2830 phenol-formaldehyde resin at different heating rate in synthetic air. The results can prove the superior thermal properties of the boron-modified phenolic resin when compared with the commercial phenolic resin that are in current use at the institute in the thermal protection of the Rocket program. Additionally, the high yield (~70%/mass at 700°C) of the resulting carbon from boron-modified resin, compared to the commercial phenolic resin, is a significant result for decreasing the processing time for Carbon/Carbon composite, which consequently reduces the number of cycles required for the pyrolysis/impregnation processes.

Results of thermal diffusivity

Figure 18 shows the curve of thermal diffusivity for boron phenolic resin. The majority of the polymers have thermal

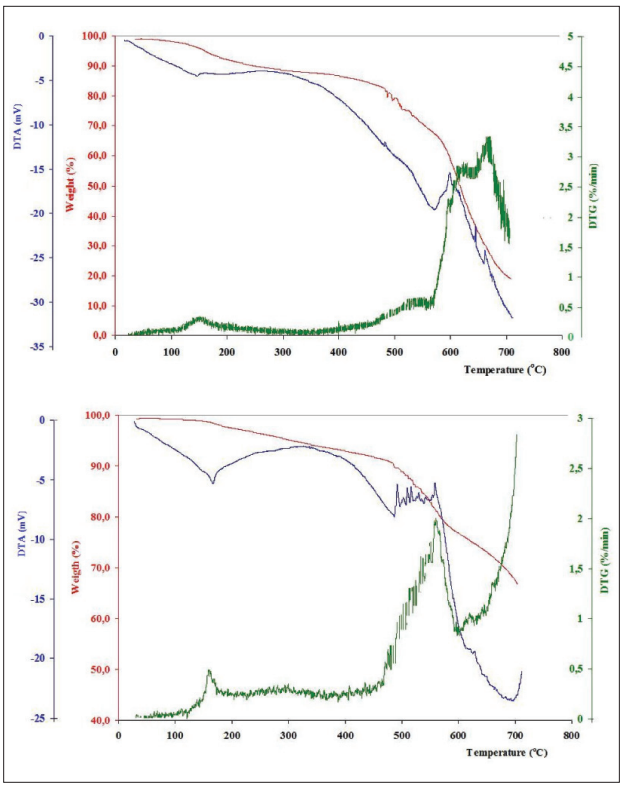


Figure 16: TG/DTA curves for the cured boron-modified phenolic resin. (A) Rate of heating of 2.5°C/min, in synthetic air, weight of the sample = 2.184 mg; (B) Rate of heating of 10°C/min, in synthetic air, weight of the sample = 2.2669 mg.

diffusivity in the range of 1.0 x 10^{-7} and 1.5 x 10^{-7} m^2/s at room temperature (Santos, Mummery and Wallwork, 2005). Thermal diffusivity of unfilled phenolic resin is hardly found in literature. Besides, thermal properties of unfilled polymer materials are given by their thermal conductivity. Anyway, the thermal conductivity of an unfilled phenolic resin at 25°C is 0.21 W/m.K and increases to 0.28 W/m.K at 316°C (US Army Armament Research, Development, and Engineering Center, 1991). The specific heat of a typical phenolic resin is ~1.2 kJ/kg.K and the density is ~1250 kg/m^3 – this results in a thermal diffusivity of ~0.14 mm^2/s at 25°C, which agrees reasonably with the result found for the boron-modified phenolic resin (Fig. 18). At temperatures higher than 200°C, phenolic resin undergoes morphological changes and the thermal conductivity at 316°C can only be taken as a reference.

Rheological characterization

Figure 19 shows results of the storage shear modulus (G'), loss modulus (G"), Tan δ and viscosity (η) as a function of shear stress (τ).

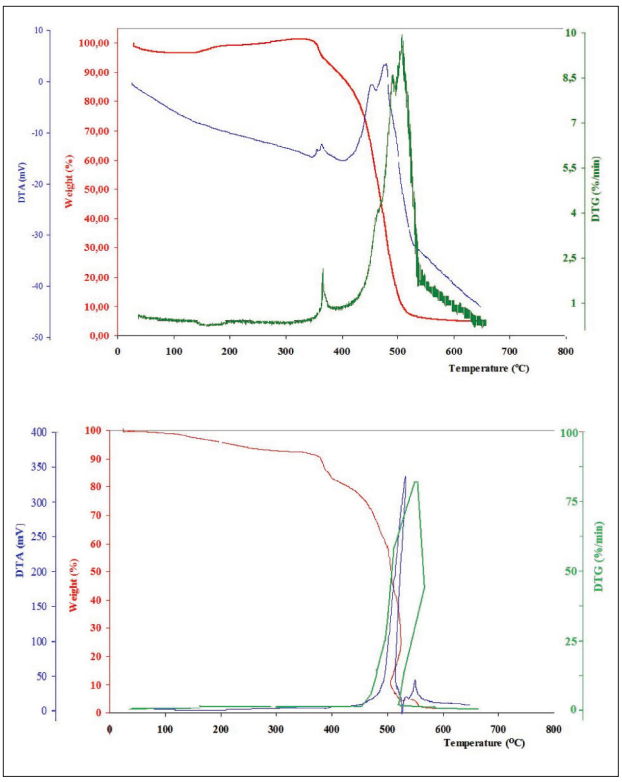


Figure 17: TG/DTA curves for a cured CR2830 phenol-formaldehyde resin. (A) Rate of heating of 2.5°C/min, in synthetic air, weight of the sample = 2.432 mg; (B) Rate of heating of 10°C/min, in synthetic air, weight of the sample = 2.206 mg.

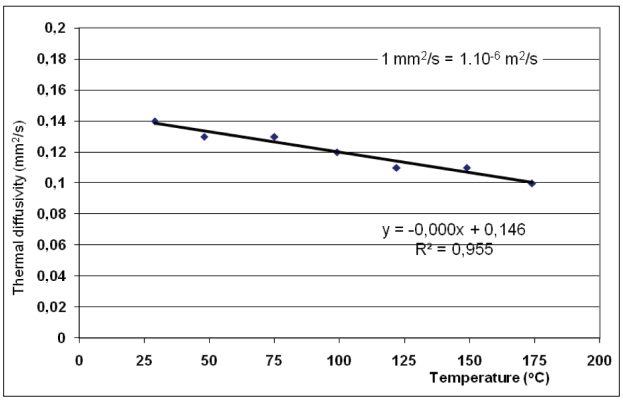


Figure 18: Thermal diffusivity as a function of temperature for the cured boron-modified phenolic resin.

The shear stress defines the conditions for testing the neat resin, which corresponds to the near newtonian behavior related to the storage shear modulus. For the phenolic boron resin, the chosen value for shear stress was 6 Pa, which corresponds to the region of maximum G'. This value was kept constant for all the other tests.

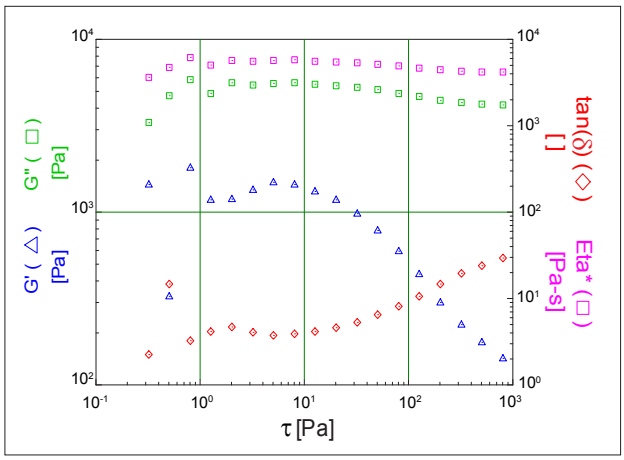


Figure 19: Elastic modulus (G'), loss modulus (G"), tan δ and viscosity (η) *versus* shear stress for boron phenolic resin at room temperature (25°C).

Figure 20 shows the plot of viscosity (η) as a function of temperature for the boron-modified phenolic resin. It can be seen that the minimum viscosity of the resin reach a value lower than 20 Pa at 60°C, keeping it constant up to approximately 200°C. This indicates that, in this range of temperature, the cure reaction is latent. This consequently results in benefits for processing as, for instance, a longer pot life for the resin. In this range of temperature (60-200°C), is not temperature dependent, which characterizes a polymer that contains mainly olygomers.

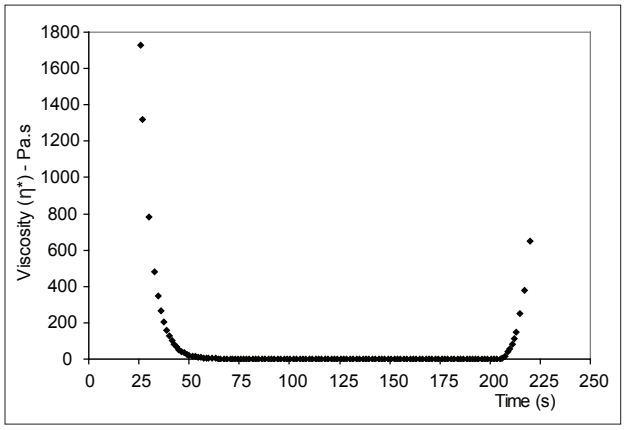


Figure 20: Dynamic scanning at the rate of 5°C/min for shear elastic modulus (G'), shear loss modulus (G"), tan δ and viscosity (η) at frequency of 1 rad/s and shear stress of 6 Pa.

Figure 21 shows graphics of viscosity as a function of time for the boron-modified phenolic resin at isotherm temperatures of 160, 180 and 200°C. In this case, it can be seen that cure reactions start at 20 minutes, 13 minutes and 5 minutes, respectively.

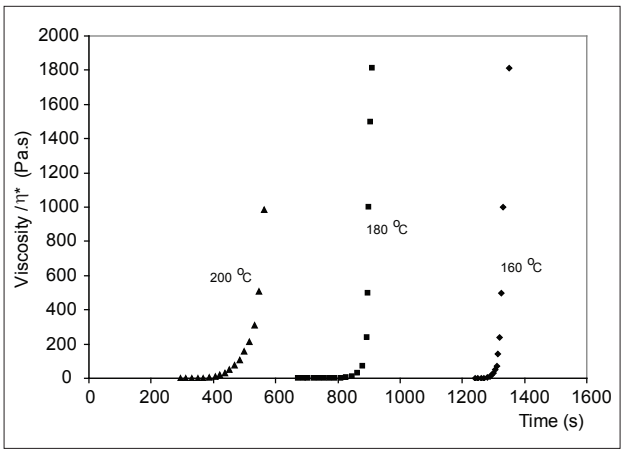


Figure 21: Viscosity as a function of time at temperature isotherms of 160°C, 180°C and 200°C for the boron-modified phenol resin.

For composite processing, results of viscosity as a function of time and temperature are important, since they can define the schedule of the curing cycle. Figure 22 shows the curing cycle that has been proposed for curing composites made with the boron-modified phenolic resin matrix. The curing process started at a heating rate of 3°C/min up to 160°C. After 60°C, the material exhibits adequate flow, which allows the wetting of the reinforcing fibers. After ~30 minutes at 160°C, pressure of 0,7 MPa and vacuum are applied to the molding system, for compaction of the layers. After 1 hour at 160°C, the curing proceeds up to 220°C.

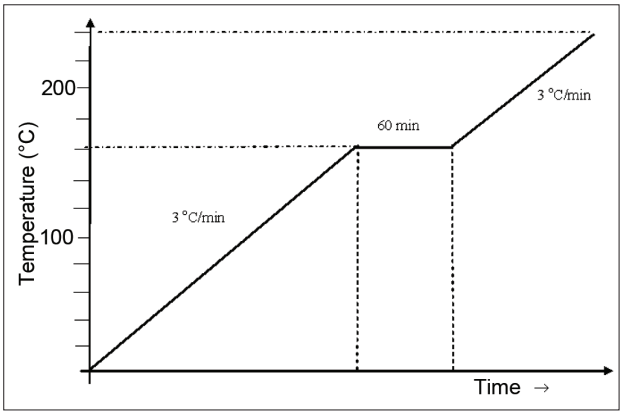


Figure 22: Curing cycle proposed for the boron-modified phenolic resin for composite preparation.

Results of interlaminar shear strength

Figure 23 shows the interlaminar shear stress (ILSS) as a function of deflection for boron-modified phenolic resin composite and silica fiber, and Fig. 24 shows comparative results of composites made from commercial phenolic resin and silica fibers.

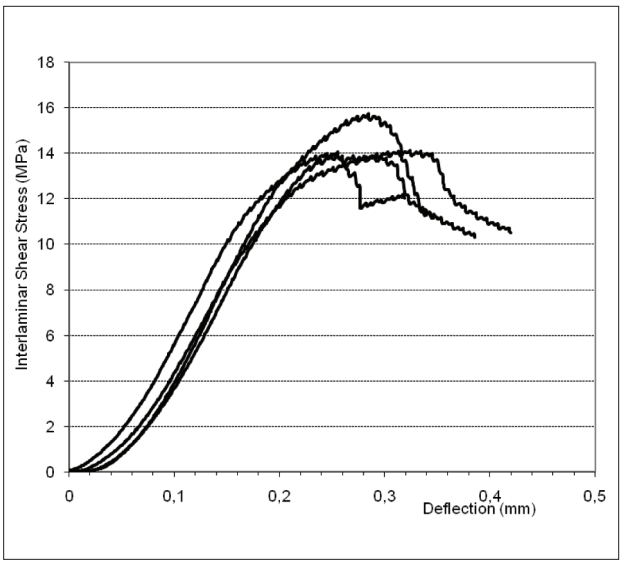


Figure 23: ILSS as a function of deflection for boron-modified phenolic resin composite/silicon fiber.

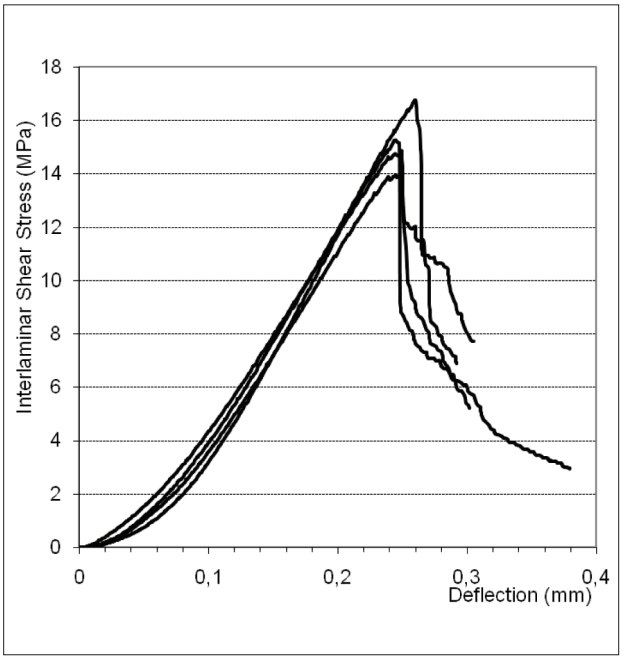


Figure 24: Comparative results of a ILSS as a function of deflection for composites made from commercial phenolic resin (CR 2830) and silica.

The results showed that there is no evidence of significant differences in the average values of ILSS for both materials, although there is a gently failure mode of the composite made with commercial phenolic resin in relation to the composite made with boron-modified phenolic resin. This is not a surprise, since interlaminar shear properties are a matrix dominated property.

Results of Iosipescu shear test

The value of the Iosipescu shear strength is around 25 MPa, corresponding to a deformation closer to 1.5%. The shear modulus (G_{12}), calculated at the limit of 20 MPa, was approximately 3.5 GPa, which is a value close to many other polymer composite systems. Figure 25 shows the Iosipescu shear strengh as a function of shear strain for the boron-modified/phenolic resin. Figure 26 shows a representative Iosipescu composite specimen after the test. It can be observed that the failure region is located between the V-notches, which is a representative and valid failure mode for Iosipescu shear.

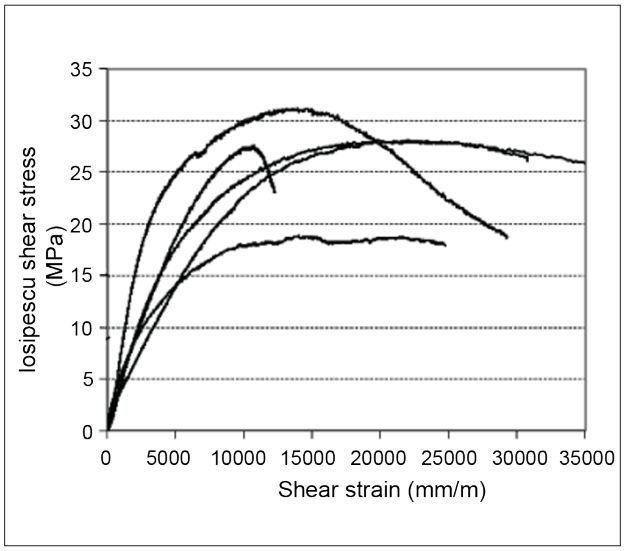


Figure 25: Iosipescu shear stress as a function of shear strain for a boron-modified phenolic resin/sílica fiber composite.

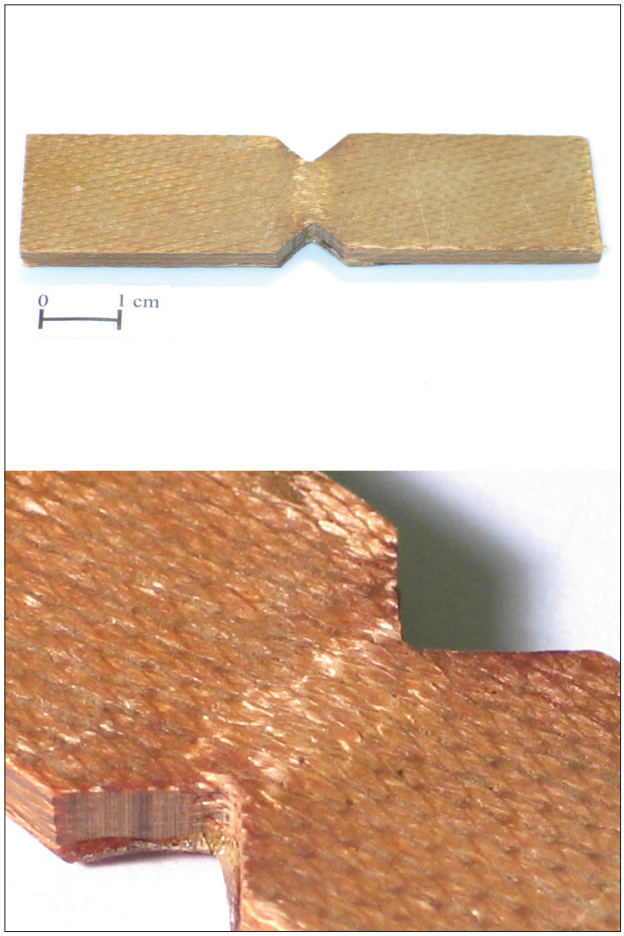


Figure 26: View of the failure in the central V-notch region of the Iosipescu specimen of boron-modified phenolic resin/silica fiber.

CONCLUSIONS

A boron-modified phenolic resin was prepared from the reaction of salicyl alcohol and boric acid using the ratio alcohol:acid of 2:1. The resulting compound has been fully characterized by NMR, IR, DSC, TG and elemental analysis, and it showed properties that indicate promising processing applications.

It has been cured as composite with silica, and the results were compared with cured commercial phenolic resin. The results of TG of boron phenolic resin showed clearly a superior thermal performance when compared with the commercial ones, that are in use at the Brazilian space program.

From DSC analysis it is also possible to see the superiority of the boron resin, comparing to the commercial phenolic resin.

ILSS and shear resistance Iosipescu tests have been done in silica fiber and boron phenolic resin composite. ILSS was ~16 MPa for silica fiber/phenolic resin and silica fiber/boron-modified phenolic. The in-plane V-notch Iosipescu shear for silica fiber reinforced with boron-modified phenolic resin was 25 MPa.

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REFERENCES

Abdalla, M.O., Ludwick, A., Mitchell, T., 2003, "Boron-modified phenolic resin for high performance applications", Polymer, Vol. 44, pp. 7353-7359.

America Patash Chem Corp., 1964, "British patent 957611"..

Ancelotti Jr., A.C., 2006, "Efeitos da porosidade na resistência ao cisalhamento e nas propriedades dinâmicas de compósitos de fibra de carbono/resina epóxi", Master of Science dissertation, Intituto Tecnológico de Aeronáutica, São José dos Campos, SP, Brazil.

Bonner, J.G., Hope, P.S., 1993, "Compatibilities and reactive blending". In: Folkes, M.J., Hope, P.S., "Polymer blends and alloys", Blackie Academic and Professional, London, pp.46-74.

Casiraghi, G., *et al*., 1980, "Selective Reactions between Phenols and Formaldehyde. A Superior Synthesis of Salicyl Alcohols", Synthesis, Vol. 2, pp. 124-125.

Castro, L.D., 1991, "Inhibition of Oxidation of Carbon Materials". PhD Thesis, University of Bath, UK.

Clayton, W.A., Fabish, T.J., Lagedrost, J.F., 1969, "Thermal Conductivity of Phenolic Chars. Technical Report AFML-TR-69-313", Air Force Materials Laboratory, Wright Air Force Base, Ohio-USA.

Costa, L., *et al*., 1997, "Structure-charring relationship in phenol-formaldehyde type resins". Polymer Degradation and Stability, Vol. 56, No 1, pp. 23-35. doi: 10.1016/S0141-3910(96)00171-1.

Fahrenholtz, S.R., Kwei, T.K., 1981, "Compatibility of polymer mixtures containing novolac resins", Macromolecules, Vol. 14, pp. 1076-1079.

Gao, J.G., Liu, Y.F., Yang, L.T., 1999, "Thermal stability of boron-containing phenolformaldehyde resin"Polymer Degradation and Stability, Vol. 63, pp. 19-22.

Gao, J.G., Liu, Y.F., Yang, F.L., 2001, "Structure and properties of boron-containing bisphenol-A formaldehyde resin", European Polymer Journal, Vol. 37, pp. 207-210.

Grenier-Loustalot, M.F., *et al*., 1996, "Phenolic resins .2. Influence of catalyst type on reaction mechanisms and kinetics", Polymer, Vol. 37, No 8, pp. 1363-1369.

Hirohata, T., Misaki, T., Yoshii, T.M., 1987, "Improvement of flame retardance and heat resistance of bromine, chlorine and boron modified phenolic resins", J Soc Mater Sci Jpn (Engl Transl), Vol. 36, No 401, pp. 184-188.

Knop, A., Sheib, W., 1979, "Chemistry and application of phenolic resins", Springer-Verlag, Berlin.

Knop, A., Pilato, L.A., 1985, "Phenolic resins", Springer-Verlag, Berlin.

Lemon, P.H.R.B., 1985, "Phenol formaldehyde polymers for the bonding of refractories", Brit. Ceram. Trans. J., Vol. 84, Nº. 2, pp. 53-56.

Lenghaus, K., Qiao, G.G., Solomon, D.H., 2000, "Model studies of the curing of resole phenol-formaldehyde resins. Part I.The behaviour of ortho quinone methide in a curing resin", Polymer, Vol. 41, No.6, pp. 1973-1979.

McKee, D.W., 1991, "Oxidation protection of carbon materials", In: Thrower, P.A., editor, "Chemistry and physics of carbon", Vol. 23, pp. 173-232.

Liu, C.L., *et al*., 2007, "Evolution of microstructure and properties of phenolic fibers during carbonization", Materials Science and Engineering A, Vol. 459, No 1-2, pp. 347-354.

Okoroafor, E.U., Villemaire, J.P., Agassant, J.F.,1992, "The viscosity of immiscible polymer blends:influences of the interphase and deformability", Polymer, Vol. 33, No 24, pp. 5264-5271.

Park, B.D., *et al*., "Polymer", 1999, Vol. 40, Nº 7, pp. 1689-1699

Santos, W.N., Mummery, P., Wallwork, A., 2005, "Thermal diffusivity of polymers by the laser flash technique", Polymer testing, Vol. 24, No 5, pp. 628-634.

Schmidt, D.L., Graig, R.D., 1982, "Advanced Carbon Fabric-Phenolic for Thermal Protection Application", AFWAL US, AFWAL-TR-81-4136, USA.

Segal, C.L., 1967, "High Temperature Polymers", Marcel Dekker, New York.

Serio, M.A., *et al*., 1991, "Pyrolysis of phenol-formaldehyde resin: experiments and modeling". ACS Div. Fuel Chem. Prepr., Vol. 36, No 2, p. 664.

Smith, A.L, 1999, "Infrared Spectroscopy", John Wiley & Sons, Hoboken, NJ, USA.

US Army Armament Research, Development, and Engineering Center, SMCAR-BAC-S, 1991, "Military Handbook 754 (AR) Plastic Matrix Composites with Continuous Fiber Reinforcement", Picatinny Arsenal, Dover, NJ, USA.

United States Patent and Trademark Office 4 045 398, 1977 .

Whitehouse, A.A.K., Pritchett, E.G.K., Barnett, G., 1968, "Phenolic Resins", Iliffe Books Ltd., London; American Elsevier, New York.