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Boron-containing novolac resins as flame retardant materials

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Abstract

Boron-containing novolac resins were prepared from novolac resins and bis(benzo-1,3,2-dioxaborolanyl)oxide and bis(4,4,5,5-tetramethyl-1,3,2-dioxa-borolanyl)oxide. The reaction of the model compound 2,6-dimethylphenol with these organoborates was complete but when the novolac resin was reacted, the degree of modification was moderate, even when there was an excess of boron compounds. The thermal degradation was investigated by TGA and pyrolysis, collecting volatiles which were investigated by GC–MS analysis, and the various compounds detected at different degradation temperatures were shown. The thermal degradation under air showed that the presence of boron is significant in the residue at high temperature. LOI values were high. Correlations between the high char yields and LOI values mean that the flame retardancy of the novolac resins improves when they are modified with bis(benzo-1,3,2-dioxaborolanyl)oxide.

Keywords: Flame retardant; Boron-containing; Novolac resin; Thermal degradation

1. Introduction

Although in the last decade there has been an increase in the number of hetero-elements used in flame retardants, the commercial market is still dominated by compounds containing halogens, notably chlorine and bromine. They are exceptionally efficient and may be incorporated as either additives or as reactives, but they do have such clear disadvantages as the generation of toxic and corrosive gases during thermal degradation. Recent developments in the chemistry of halogen-free flame retardant polymers involve polymers or reactive monomers that are inherently flame retarding such as those containing P, Si, B, N and other miscellaneous elements [1].

Boric acid and borate salts have been used as flame retardant additives since early 1800s, but they have been less studied than phosphorous, halogen and other compounds. The use of borates in enhancing the flame retardancy of polymeric materials was reported earlier in the 20th century [2,3]. Borates are effective flame retardants because impenetrable glass coatings form when they thermally degrade. The glass coatings form on the surface, and can contribute to the intumescent effect, because they exclude oxygen and prevent further propagation of combustion. The water of hydration is lost by endothermic decomposition and therefore both dilutes and cools, by absorbing the thermal energy from the flame (Scheme 1).

The flame retardant action of the boron-containing compounds on polymeric materials is chemical as well as physical. It was found that these inorganic boron compounds promote char formation in the burning process [4]. The mechanism involving the formation of the char is clearly related to the thermal action of boric acid with alcohol moieties [2]. The borate esters formed dehydrate further, probably by carbo-cation

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$$2H_3BO_3 \xrightarrow[-2H_2O]{120\text{-}130^{\circ}C} 2HBO_2 \xrightarrow[-H_2O]{260\text{-}270^{\circ}C} B_2O_3$$

Scheme 1. Dehydration process of boric acid.

mechanisms. Thus boron is found to exert its flame retardant action on polymeric materials at a temperature well below that of the normal pyrolysis of these materials.

However, additives have the disadvantage that they have to be used in relatively high concentrations (typically 30% by weight, or more) and this may affect the physical and mechanical properties of the polymers. Also, additives may be leached or may volatilised from the polymer during service [5]. The alternative strategy is to use reactive flame retardants, via copolymerisation or some other type of chemical modification (i.e. flame retardant groups that are inherently part of the polymer backbone or that are covalently attached as side groups to the polymer). The influence of boron-containing reactive groups on the flame retardancy of simple chain reaction polymers such as polystyrene and poly(vinyl alcohol) has been reported [6].

Phenolic resins are mainly used in reinforced thermoset moulding materials. Generally, they are used in combination with organic or inorganic fibres and fillers. These compounds possess remarkable thermal stability, flame retardancy and heat resistance properties [7]. The rapid growth of phenolic resin applications has prompted extensive research to improve their thermal properties. Moreover, for critical applications in the electric and electronic industries an improvement in the flame retardancy and thermo-oxidative resistance of phenolic resins would be desirable. In this respect, boron-containing phenol–formaldehyde resins (resoles) synthesized from boric acid, phenol and paraformaldehyde have been reported [8].

In this work, boron-containing novolac resins have been synthesized by chemically modifying a commercial novolac resin with bis(benzo-1,3,2-dioxaborolanyl)oxide and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)oxide to obtain various boron-modified novolac resins.

Various boron-modified novolacs have been characterized, their thermal properties were evaluated, and the effect of boron on the flame retardant properties were studied.

2. Experimental part

2.1. Materials

Boric acid (Panreac), catechol (Aldrich), pinacol (Aldrich), and 2,6-dimethylphenol (Aldrich) were used as received. Novolac resin was supplied by Aismalibar S.A. Toluene was dried by standard procedures.

2.1.1. Synthesis of bis(benzo-1,3,2-dioxaborolanyl)-oxide (*a*) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)oxide (*b*)

In a 100 ml round bottom flask, a mixture of catechol (15.4 g, 0.14 mol) or pinacol (16.5 g, 0.14 mol), boric acid (8.7 g, 0.14 mol), and toluene (50 ml) was boiled for 4 h or 6 h with azeotropic removal of water using a Dean–Stark trap. The toluene was removed at low pressure and the product was purified by sublimation under vacuum. In this way, 16.9 g of (**a**) (95% yield) and 17.5 g of (**b**) (92% yield) were obtained as fine white powders.

(**a**) ^{1}H NMR ($CDCl_3$, δ, ppm): 7.24 (4H, dd), 7.13 (4H, dd). ^{13}C NMR ($CDCl_3$, δ, ppm): 147.5 (4C, s), 122.9 (4C, s), 112.5 (4C, s).

(**b**) ^{1}H NMR ($CDCl_3$, δ, ppm): 1.18 (24H, s). ^{13}C NMR ($CDCl_3$, δ, ppm): 82.7 (4C, s), 24.3 (8C, s).

2.1.2. Synthesis of 2-(2,6-dimethyl-phenoxy)-benzo-[1,3,2]dioxaborolane (*I*)

This boronic ester was prepared from 2,6-dimethylphenol (**c**) and (**a**) using molar ratios (1:1) and (2:1): that is to say, a molar ratio of (1:2) and (1:1) of the hydroxyl group to the boron atom, respectively.

In a 100 ml round bottom flask equipped with a Soxhlet, filled with molecular sieves 4A and a condenser with a tube containing calcium chloride (**c**) (6.1 g, 0.05 mol or 12.2 g, 0.1 mol) and (**a**) (12.7 g, 0.05 mol) in anhydrous toluene (50 ml) was stirred at reflux for 2 h or 4 h. After evaporation under reduced pressure, the product (**I**) was obtained as a brown oil.

^{1}H NMR ($CDCl_3$, δ, ppm): 7.00 (2H, dd), 6.97 (2H, d), 6.91 (2H, dd), 6.88 (1H, t), 2.14 (6H, s). ^{13}C NMR ($CDCl_3$, δ, ppm): 149.8 (1C, s), 147.7 (2C, s), 129.0 (2C, s), 124.5 (2C, s), 123.1 (2C, s), 122.8 (1C, s), 112.7 (2C, s), 16.6 (2C, s).

2.1.3. Synthesis of 2-(2,6-dimethyl-phenoxy)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (*II*)

Following a similar procedure but using (**c**) (6.1 g, 0.05 mol or 12.2 g, 0.1 mol) and (**b**) (13.5 g, 0.05 mol), product (**II**) was obtained after 8 h or 24 h as a brown oil.

^{1}H NMR ($CDCl_3$, δ, ppm): 6.99 (2H, d), 6.88 (1H, t), 2.20 (6H, s), 1.27 (12H, s). ^{13}C NMR ($CDCl_3$, δ, ppm): 150.5 (1C, s), 128.4 (2C, s), 123.4 (2C, s), 120.1 (1C, s), 83.3 (2C, s), 24.8 (4C, s), 16.8 (2C, s).

2.1.4. Synthesis of boron-modified phenolic resins

Commercial phenol novolac resin was modified with (**a**) and (**b**) using two molar ratios: (1:2) and (1:1) of the hydroxyl group to the boron atom, respectively, to give (**M-a**) and (**M-b**). These modifications were carried out in the same way as in the synthesis above, but in this case by adding dioxane to dissolve the novolac resin.

(**M-a**) ^{1}H NMR (DMSO-d_6, δ, ppm): 9.2–8.7 (m), 7.1–6.5 (m), 6.2 (s), 4.0–3.4 (m). ^{13}C NMR (DMSO-d_6, δ, ppm): 156–150 (s), 133–112 (d), 120 (d), 40–30 (t).

(**M-b**) ^{1}H NMR (DMSO-d_6, δ, ppm): 9.6–9.0 (m), 8.0 (s), 7.2–6.4 (m), 4.0–3.2 (m), 1.2 (m). ^{13}C NMR (DMSO-d_6, δ, ppm): 156–150 (s), 135–128 (d), 120 (d), 82 (s), 40–30 (t), 24 (q).

2.2. Instrumentation

The ^{1}H NMR (300 or 400 MHz) and ^{13}C NMR (75.4 or 100.6 MHz) spectra were obtained with a Varian Gemini 300- or 400-Hz spectrometer with a Fourier transform and DMSO-d_6 or $CDCl_3$ as solvent and TMS as an internal standard.

Calorimetric studies were carried out on a Mettler DSC821e thermal analyser with N_2 as the purge gas at scanning rates of 20 °C/min. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N_2 as a purge gas at scan rates of 10 °C/min.

The samples were degraded at different temperatures in an oven (Carbolite) connected to a condenser which collected different volatiles by means of a nitrogen flux. These condensed volatiles were dissolved in acetone and analysed by GC–MS, using a gas chromatograph HP5890 with capillary column Ultra 2 (crosslinked 5% PH ME siloxane) coupled to a mass spectrometer HP 5989 A.

Quantitative boron analyses were carried out by inductively coupled plasma (ICP) spectroscopy.

The limiting oxygen index (LOI) is the minimum concentration of oxygen determined in a flowing mixture of oxygen and nitrogen that will just support the flaming combustion of materials. LOI values were measured on a Stanton Redcroft instrument, provided with an oxygen analyser, on plaques of the polymers 100 × 6 × 4 mm prepared by compression moulding.

3. Results and discussion

We prepared two organic boron compounds: bis(benzo-1,3,2-dioxaborolanyl)oxide (**a**) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)oxide (**b**) by esterification of boric acid with catechol or pinacol [9]. These compounds, which act as boron-reagents, are very soluble in organic solvents such as toluene and dioxane, which make the reaction with hydroxyl groups easier. On the other hand, boric acid and borate salts are insoluble in organic solvents and yield partially cross-linked compounds when they react with polyhydroxylic compounds.

In order to study the reaction of the phenolic group with these boron-reagents we used 2,6-dimethylphenol as the model compound and two different OH:B molar ratios. In both cases, the incorporation of boron was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy.

Fig. 1 shows the scheme of the reaction with (**a**) and the ^{13}C NMR spectrum of the reaction mixture obtained with OH:B molar ratio (1:2).

The incorporation of boron from (**a**) to phenol was confirmed by the disappearance of the aromatic quaternary C–OH signal at 152.3 ppm and the appearance of three new aromatic quaternary carbon signals at 149.8, 148.1 and 147.9 ppm, all of which were assigned to the C–O–B due to two new compounds (**I**) and (**a**′). Moreover, two different groups of CH aromatic carbons can be distinguished. Taking into account their relative

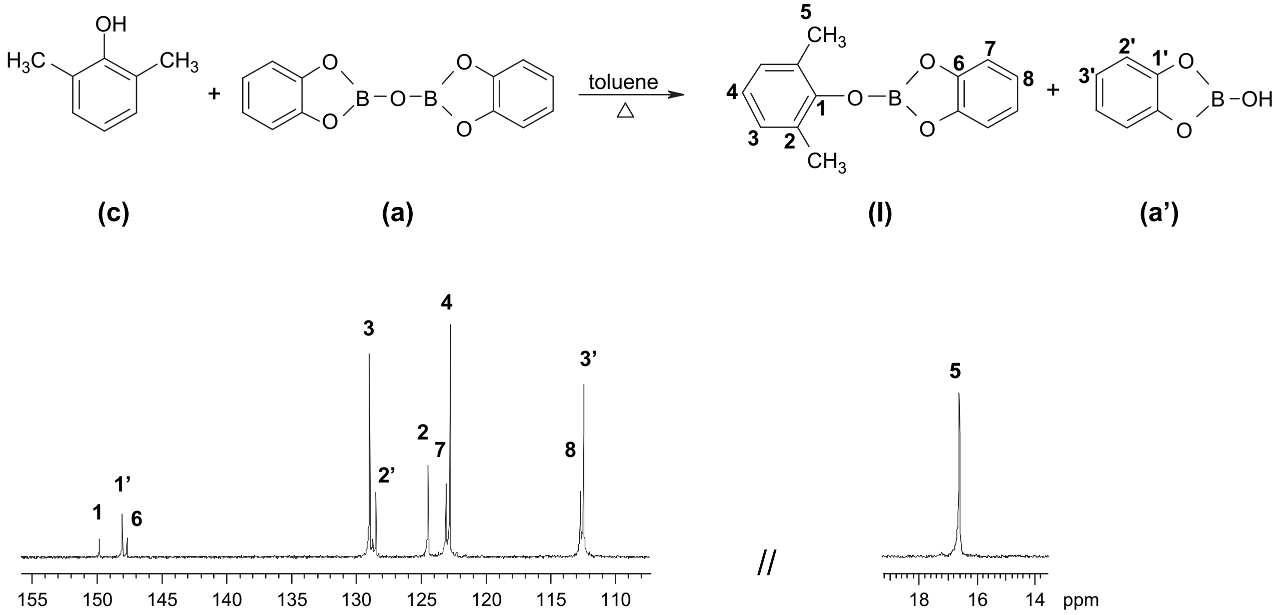

Fig. 1. ^{13}C NMR spectrum of the products obtained by reaction of 2,6-dimethylphenol and (**a**), molar ratio OH:B (1:2).

intensities and chemical shifts, and by comparing them with the starting compounds, we can assign both groups of signals to the compounds mentioned (see Fig. 1).

Fig. 2 shows the ^{1}H NMR spectrum of the reaction mixture of the phenol and (**b**). The disappearance of the phenolic proton (at 4.6 ppm) and the unshielding of aromatic protons in meta and para positions and the methyl protons of (**II**) can be seen. Moreover, the presence of a signal at around 5 ppm confirms the presence of (**b**′).

Although in both cases the phenol completely reacted with (**a**) and (**b**), these boron compounds showed considerably different reactivities. Thus, reaction with (**a**) was complete after 2 h for OH:B molar ratio (1:2) and after 4 h for OH:B molar ratio (1:1). On the other hand, the reaction with (**b**) took 8 h for the OH:B molar ratio (1:2) and 24 h for the OH:B molar ratio (1:1) to be completed. This behaviour can be rationalized by taking into account the higher Lewis acidity of the boron aromatic compound [10].

The novolac resins were modified with (**a**) and (**b**) with the same two molar ratios. Structures (**M-a**) and (**M-b**) were obtained with different degrees of modification (Fig. 3).

At first, the novolac resin reacted with a boron equivalent (OH:B molar ratio (1:1)). The spectrum of the raw material obtained by reacting the resin with (**a**), see A) in Fig. 3, shows the typical pattern of a novolac resin with a lower intensity in the corresponding signal of the phenol hydroxyl which indicates a partial reaction with the boron compound. The same characteristic was observed in the spectrum of the raw material obtained from the resin and (**b**).

Moreover, a signal was detected corresponding to the OH linked to the boron in (**a**′) or (**b**′), which is the leaving group formed after the OH phenolic attacks one of the two boron sites in the molecule. This signal appears at 8 ppm in spectrum A) in Fig. 3. To eliminate these secondary compounds, the raw materials were heated for 2 h under vacuum at 110 °C to allow them to sublimate. The analysis of these sublimates confirmed the structure of (**a**′) and (**b**′).

The spectra of the purified resins show that the above boron compounds had completely disappeared, as can be seen in spectrum B) (Fig. 3).

The degree of modification of the novolac resin, calculated by ^{1}H NMR and boron elemental analysis,

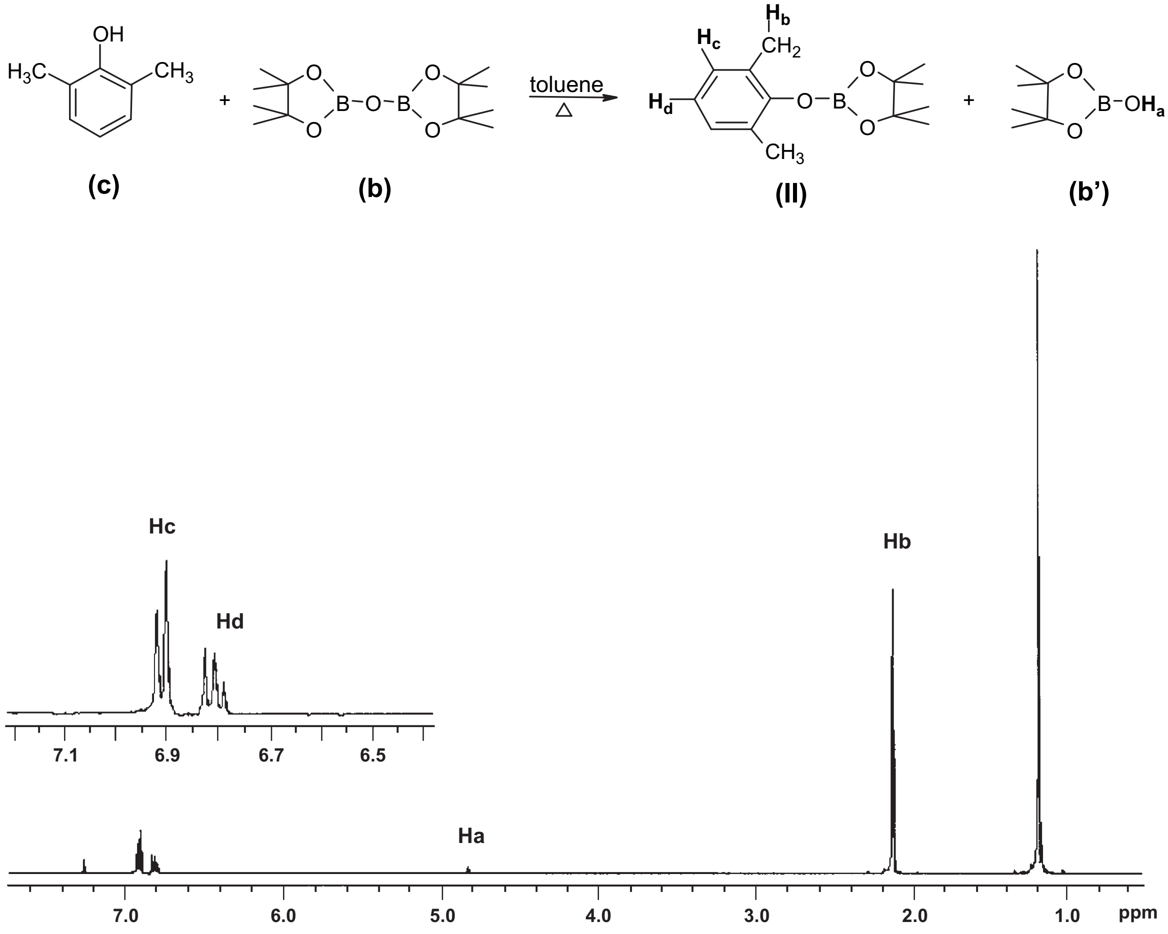

Fig. 2. ^{1}H NMR spectrum of the products obtained by reaction of 2,6-dimethylphenol and (**b**), molar ratio OH:B (1:2).

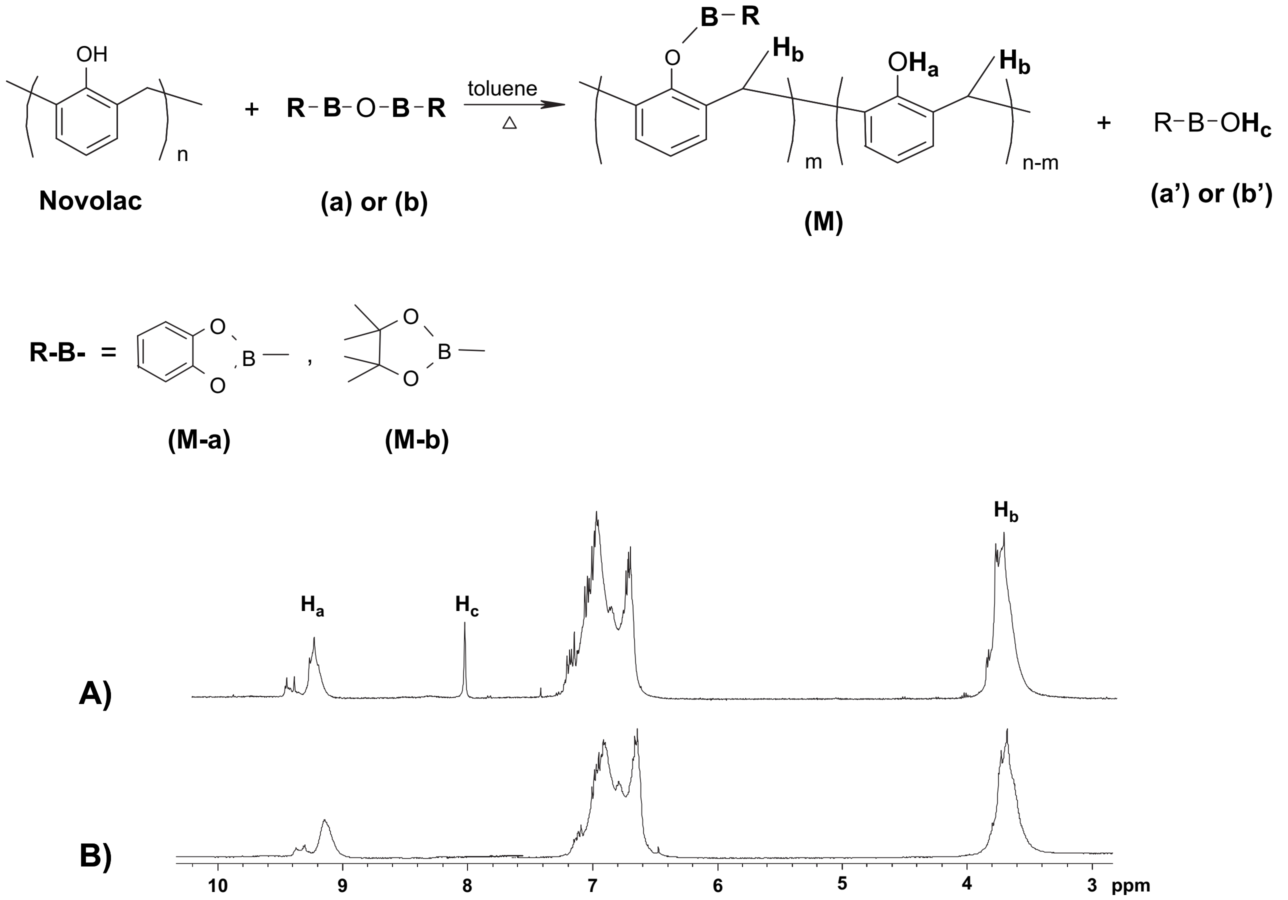

Fig. 3. Modification of novolac resins with organoborate compounds. ^{1}H NMR spectra of raw material from reaction of novolac with (**a**) (A); after heating 2 h at 110 °C (B).

was about 65% for (**M-a**) and 45% for (**M-b**) proving that all the boron compounds did not react with the OH phenolic. These results confirm the higher reactivity of the aromatic boron compound, as observed in the model reactions.

In order to increase the degree of modification the reaction was carried out in a OH:B molar ratio (1:2), but the increase was only slight.

The T_g values were determined by DSC plots (Table 1). As can be observed, the T_g values of pinacol derivative resins are lower than those of unmodified resins, due to the greater mobility of the molecule because of decreasing of intramolecular hydrogen bonding in the novolac resin. On the other hand, for catechol derivative resins the presence of an aromatic moiety increases the rigidity and the T_g values increase.

Table 1
T_g values from DSC plots of boron modified novolac resins

Polymer	Novolac	**M-a**[a]	**M-a**[b]	**M-b**[a]	**M-b**[b]
T_g(°C)	79	84	88	63	65

[a] Molar ratio OH:B (1:1).
[b] Molar ratio OH:B (1:2).

To determine the thermal stability of the polymers, thermogravimetric analysis was carried out under nitrogen and air. The boron-free and boron-modified novolac resins, which contain different amounts of boron, were investigated by TGA. Fig. 4 shows TGA curves and Table 2 gives TGA data for the weight loss with temperature. The temperatures of 10% loss weight of all modified novolac resins show a decrease to compare with the unmodified novolac resin, but these temperatures are lower for the samples with higher boron contents (that is to say, the catechol derivative resins). This degradation of boron-modified resins occurs before indicating that the first degradation steps may correspond to the loss of the catechol or pinacol moieties. The second maximum weight loss rate (T_{max}) observed in the boron-modified novolacs is lower for the catechol derivatives than that for the pinacol derivatives under nitrogen and air, which seems to indicate that the catechol moieties are released more easily than pinacol moieties. It must also be related to the higher boron content of the catechol derivative novolacs. Under air, a third step in the weight loss rate appears at higher temperatures, about 640 °C, corresponding to the thermo-oxidative degradation.

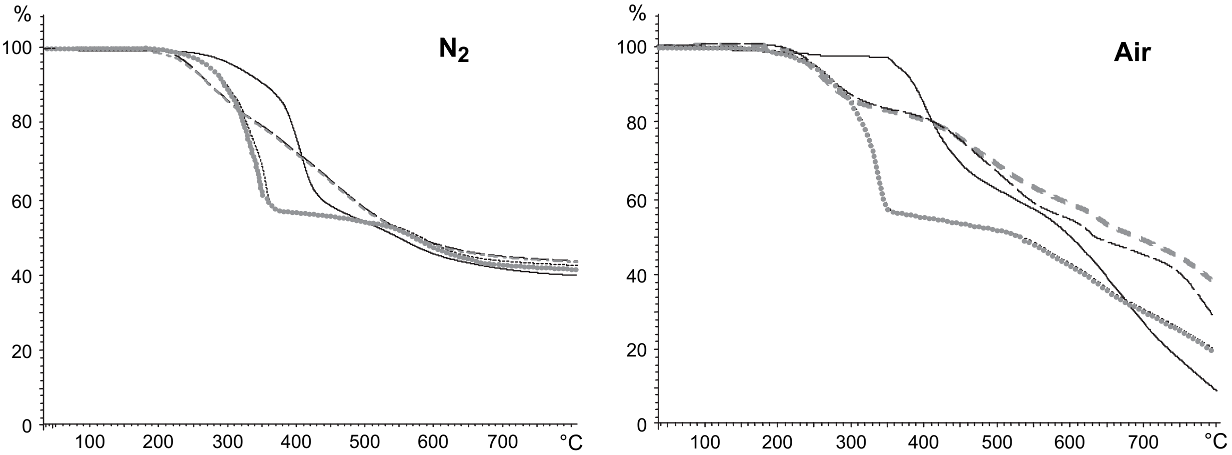

Fig. 4. TGA plots (10 °C/min, N_2, air) of novolac (—); **M-a**[a] (– –); **M-a**[b] (— —); **M-b**[a] (···); **M-b**[b] (····).

The char yields at 800 °C are also collected. Char yield is correlated to the polymer's flame retardancy [11] but it should be pointed out that in our case the experimental char yield under nitrogen does not show significant differences among the boron-containing and boron-free novolacs. Differences are observed under air. While the char yield for unmodified novolacs is practically non-existent, the boron-modified novolac shows char yields that increase with the boron content, thus the boron plays a role in the char formation. Because char yield has been correlated to flame retardancy, these resins were expected to have good flame retardant properties.

The thermal degradation of novolac resins has been studied by pyrolysis–gas chromatography at 770 °C [12]. It was shown that, as is generally thought, the decomposition of phenol–formaldehyde resins consists of breaking the bonds between aromatic rings and methylene bridges. Thus, the main degradation products are phenol and its methyl derivatives, as well as small amounts of simple aromatic hydrocarbons [13]. Moreover, as well as the pyrolysis products of novolac resins mentioned above as low volatility compounds, such as naphthalene, methylnaphthalene, biphenyl, dibenzofuran, fluorene, phenanthrene, xanthene and anthracene were also detected [14].

To study the different weight losses of the boron-modified novolac resins and the unmodified resins, we studied the thermal degradation of the resins using an oven, under nitrogen, connected to a condenser that allowed us to collect volatiles by heating at different controlled temperatures. These temperatures were chosen by observing the degradation steps in TGA plots and in all cases the experiments were performed for 2 h. Thus, boron-free novolac was heated at 360 °C and the GC–MS analysis identified phenols, hydroxybenzylphenols and mono- and dimethyl derivatives. When it was heated at 550 °C the following were mainly detected: phenol, *o*-cresol, *p*-cresol, 2,6-dimethylphenol, 2,4-dimethylphenol, *o*-xylene, *p*-xylene and, to a lesser extent, flourene and xanthene. These last compounds can be created in a cyclisation reaction involving hydroxyl or methyl groups in an ortho position to methylene bridges. The presence of these polynuclear aromatics suggests that some dehydration and dehydrogenation occurs. The boron-containing novolac catechol derivative (**M-a**) was heated at 310, 360 and 550 °C and all the above mentioned compounds were detected. At the lowest temperature, catechol was also detected. The boron-containing novolac pinacol derivative (**M-b**) was heated at 300, 340 and 570 °C and, likewise, all the above

Table 2
TGA data and LOI values of boron modified novolac resins

Polymer	Boron (%)	LOI (% O_2 v/v)	TGA nitrogen			TGA air		
			$T_{10\%}$ (°C)	T_{max} (°C)	Residue 800 °C (%)	$T_{10\%}$ (°C)	T_{max} (°C)	Residue 800 °C (%)
Novolac	–	24.6	357	398/548	40	385	402/664	7
M-a[a]	3.4	38.0	273	380/453	44	285	266/469/623	31
M-a[b]	3.8	38.2	271	375/451	44	274	254/463/640	38
M-b[a]	2.3	24.8	294	348/584	43	283	338/567/641	21
M-b[b]	2.4	24.8	296	345/579	42	280	336/568/640	20

[a] Molar ratio OH:B (1:1).

[b] Molar ratio OH:B (1:2).

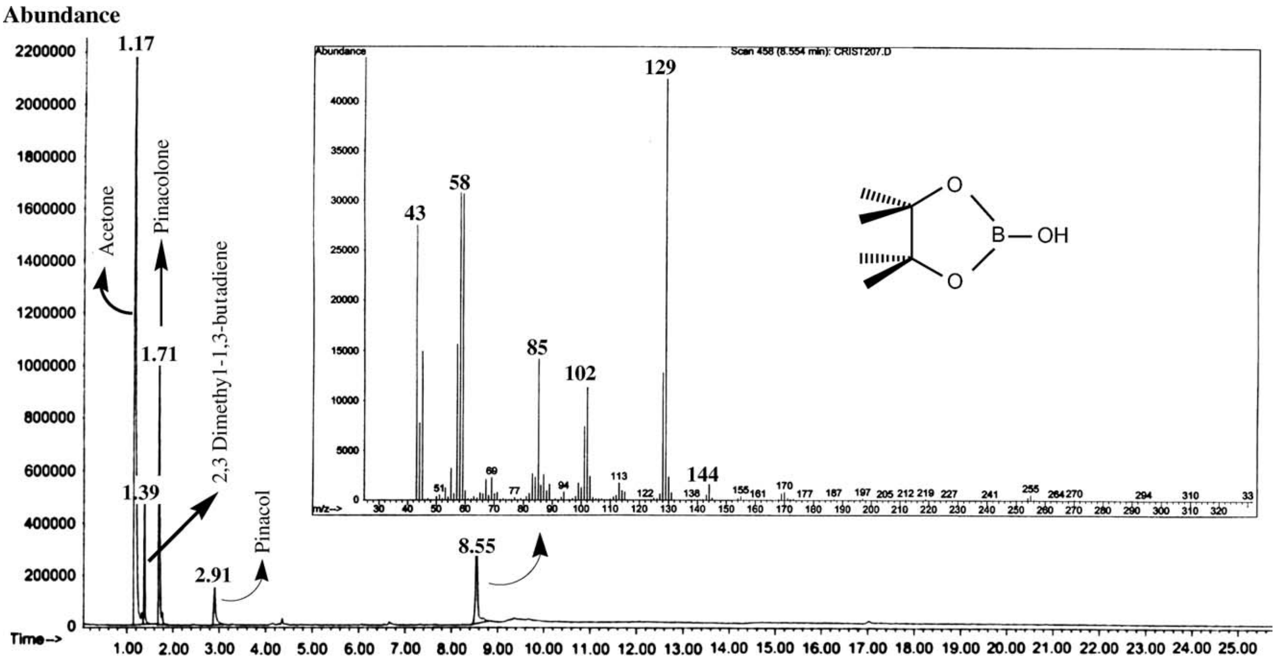

Fig. 5. GC of volatiles at 300 °C of **M-b** and MS of (**b′**).

compounds were detected. However, in this case at the lowest temperature was detected pinacol; pinacolone, due to the pinacolinic rearrangement from pinacol; 2,3-dimethyl-1,3-butadiene, from di-dehydration of pinacol and 2-hydroxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**b′**). Fig. 5 shows the separation by GC of the above compounds and the mass spectrum of (**b′**). In this case the base peak corresponds to $[M\text{-}15]^+$, due to the most significant methyl fragmentation of (**b′**) and the molecular peak, at 144 is observed but with low abundance. The release of this boron compound (**b′**) could explain why the char yield for the pinacol derivative novolacs under air is lower than that of catechol derivative novolacs. This suggests that the presence of boron is significant in the residue at high temperature.

The LOI value, which can be taken as an indicator to evaluate the polymer's flame retardancy of the boron-modified resins and unmodified novolac were also measured and given in Table 2. As can be seen, the LOI values of pinacol derivative resins are similar to those of boron-free novolac resins, which are because of the boron loss observed in the thermal degradation GC–MS analysis. Therefore, the amount of boron in the char could be very low. However, the catechol derivative resins have higher LOI values as a consequence of the higher boron content and char yields. This behaviour is in accordance with the mechanism of improved fire performance via boron modification. This retarded-degradation phenomenon forms an insulating protective layer, a glass coating that can contribute to the intumescent effect which prevents the combustible gases from transferring to the surface of the materials, increases thermal stability at higher temperatures and improves fire resistance.

4. Conclusion

The two organoborate derivatives of catechol and pinacol enabled a novolac resin to be partially modified by introducing boron as reactive. The reaction of the model compound 2,6-dimethylphenol with these organoborates was complete but when the novolac resin was reacted, the degree of modification was moderate, even when there was an excess of boron compounds. The thermal degradation under air showed that the presence of boron is significant in the residue at high temperature. Correlations between the high char yields and LOI values mean that the flame retardancy of the novolac resins improves when they are modified with bis(benzo-1,3,2-dioxaborolanyl)oxide.

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