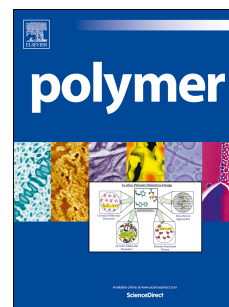# Accepted Manuscript

Prediction of thermosets flammability using a model based on group contributions

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Abstract

From a set of around 30 thermosets (polycyanurates, polybenzoxazines, epoxy and phtalonitrile resins) tested in pyrolysis-combustion flow calorimetry, the contributions to flammability of 14 new chemical groups are calculated using a method previously proposed and validated. The flammability properties include total heat release, heat release capacity and char content. The comparison between these groups allows drawing some consistent conclusions about the best structures in terms of flammability. Especially, the aromaticity, the number of covalent bonds between the considered chemical group and the neighboring groups and the presence of heteroatoms (O, N) in the structure are highlighted.

Keywords: polymer flammability, thermosets, pyrolysis-combustion flow calorimetry, Van Krevelen approach

Introduction

Predicting the fire performance of a material is a very difficult challenge because this performance

depends on many parameters, including the composition of the material but also test conditions: size, geometry and orientation of the sample, type of ignition (radiative or flaming), heat flux, air flow… Obviously the intrinsic flammability properties of the material are of primary importance to predict its fire behavior.

Pyrolysis-combustion flow calorimetry (PCFC) was developed over 20 years ago to assess some important properties of the combustion of a polymer, namely heat release capacity (HRC) and total heat release (THR) from a very small amount of material (few milligrams) [1]. Even if PCFC is not suitable for assessment of the overall reaction-to-fire of a polymer [2], attempts to correlate statistically the fire properties measured in PCFC to the rating in various other tests such as UL94 or some flame propagation tests [3, 4] have been explored.

Another way has been the prediction of the flammability of polymers in PCFC using a so-called Van Krevelen approach [5-7], i.e. the polymer structure is divided in simple groups having specific contributions to the properties being studied. The overall property of the polymer is the sum of these contributions multiplied by the molar or weight fraction of the corresponding groups. A first database of the contributions of thirty-eight groups has been proposed [6].

Pursuing this approach [8, 9], an improved model based on the additivity of the contributions [10] has been proposed. The contributions of thirty-one groups have been determined which the correct calculation of the flammability of around one hundred polymers. Most of the polymers studied in the previous work were elastomers or thermoplastics. Based on this model, the contributions to HRC and THR of around fifteen new groups from a set of twenty-eight thermosets structures, including epoxy resins, polybenzoxazines, polycyanurates and phtalonitrile resins have now been determined. Most of these new groups are linked to more than two other groups (crosslinker groups). One main objective of this work was to assess the influence of the number of chemical covalent bonds (called in this study bond number) on the flammability of these groups. Bond number is defined to be the number of covalent bonds linking the chemical moiety (group) to the mainchain of the polymer. Terminal monovalent atoms such as halogens and hydrogen are not included in the determination of bond number. Moreover, the contributions of molecular units to char formation were also established. This permits an assessment of the consistency of the calculation of the combustion parameters using the group contribution method. The comparison between the values calculated for the groups studied in this work and those studied previously is presented.

Methodology

All the polymers studied in this work are listed in Table 1.

All benzoxazine resins (numbered 1-7) were prepared using a solventless method derived from a previously procedure described [11]. Depending on the phenol/amine couple, the synthesis procedure may vary slightly but the general route can be summarized as follow: the phenol and amine in stoichiometric amount, were liquefied in a beaker heated at 120-140°C while paraformaldehyde in a 10% excess, was added to the blend under vigorous mechanical agitation to allow Mannich type condensation for formation of the benzoxazine ring. After 20-30 min, the crude

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resin product was degassed in an oven at 140°C and reduced pressure for 5-10min in order to remove the formed water and possible residual formaldehyde. A yellowish translucent vitrified resin was obtained and thermally polymerized without additional purification. The different benzoxazine resins are named according to the phenol and amine reagents used for the synthesis.

Polycyanurates used in this work (numbered 8-15) have previously been described [12]. These thermosets are crosslinked through the reaction of three cyanate ester groups to form cyanurates, i.e. oxygen-linked triazine rings. The combustion characteristics of these thermosets were determined using PCFC at the FAA laboratory. The values determined for heat release were generally consistent with those presented previously [12].

Four epoxy resins (numbered 16-19) have previously been developed and their flammability has been extensively evaluated using PCFC and cone calorimetry [13]. Other epoxy resins (numbered 21-25) have been prepared using various polyglycidyl ethers as epoxy monomers. They were kindly provided by Nagase and Cardolite. The hardener was a polyether amine (Jeffamine T403) supplied by Huntsman. The curing of epoxy/amine formulations was carried out with a ratio of 1 mole of epoxy group with 1 mole of active hydrogen from the amine. After weighting, reactants were mixed and vigorously stirred using a high speed mixer (IGT Testing Systems) with a stirring program (1'30 at 1000 rpm, 2'30 at 1750 rpm and 6 min at 2500 rpm). The mixture was then poured in a mold and heated at 80°C for 2h and 125°C for 3h in order to obtain sheets (15x15x0.1 cm^3). A last epoxy resin (numbered 20) was prepared using bisphenol A diglycidyl ether and Jeffamine D230.

The flammability of three phtalonitrile-based thermosets (numbered 26-28) has previously been assessed [5].

In order to complete the study, the flammability characteristics of two new thermoplastic polymers were also studied. These two polymers numbered 29 and 30 are poly(4-vinylphenol). Combustion parameters for these materials have previously been determined [5].

Table 1 –Experimental and calculated THR and HRC values for polymers studied.

N°	Polymer	Experimental value			Calculated value		
		THR (kJ/g)	HRC (J/g.K)	Char (g/g)	THR (kJ/g)	HRC (J/g.K)	Char (g/g)
1	Phenol and para-phenylenediamine based benzoxazine	10	88	0.6	10.2	109	0.56
2	Bisphenol A and aniline based benzoxazine	21.5	247	0.3	17.7	280	0.43
3	Chavicol and para-phenylenediamine based benzoxazine	14.8	173	0.48	13.8	189	0.54
4	Hydroquinone and furfurylamine based benzoxazine	3.4	30	0.65	4.7	46	0.6
5	Resorcinol and furfurylamine based benzoxazine	4.5	40	0.65	4.7	46	0.6
6	Bisphenol A and aminophenylacteylene based benzoxazine	10.5	135	0.6	12.7	146	0.59
7	Bisphenol A and propargylamine based benzoxazine	16.1	222	0.4	18.7	229	0.41

8	Bisphenol A cyanate ester based polycyanurate	16	277	0.36	16.2	272	0.40
9	Hexafluorobisphenol A cyanate ester based polycyanurate	2.6	58	0.43	8.9	108	0.32
10	Bisphenol E cyanate ester based polycyanurate	12.7	274	0.42	14.9	211	0.41
11	Bisphenol M cyanate ester based polycyanurate	21.7	380	0.26	22.4	464	0.31
12	Bisphenol C cyanate ester based polycyanurate	4.2	21	0.53	2.1	-47	0.56
13	Tetramethylbisphenol F cyanate ester based polycyanurate	14.6	202	0.35	14.6	242	0.44
14	Phenol Novolac cyanate ester based polycyanurate	7.1	93	0.59	7.9	105	0.53
15	Dicyclopentadienyl-bisphenol cyanate ester based polycyanurate	20.8	629	0.27	22.8	487	0.32
16	Bisphenol A diglycidyl ether and isophorone diamine based epoxy	27.5	490	0.09	24.2	434	0.22
17	Triglycidyl phloroglucinol and isophorone diamine based epoxy	18.3	481	0.28	19.5	449	0.26
18	Triglycidyl phloroglucinol and decane-1,10-diamine based epoxy	19.4	401	0.28	19.9	492	0.26
19	Triglycidyl phloroglucinol and difurfurylamine based epoxy	11.4	192	0.26	14.3	276	0.34
20	Bisphenol A diglycidyl ether and Jeffamine D230 based epoxy	26.8	542	0.05	22.7	411	0.21
21	Glycerol polyglycidyl ether and Jeffamine T403 based epoxy	20.7	451	0.02	21.1	435	0.11
22	Diglycerol polyglycidyl ether and Jeffamine T403 based epoxy	20.9	599	0.01	21.1	480	0.11
23	Sorbitol polyglycidyl ether and Jeffamine T403 based epoxy	19.7	449	0.05	20.5	461	0.10
24	Cardanol polyglycidyl ether and Jeffamine T403 based epoxy	32.7	613	0	27.8	622	0.19
25	Isosorbide polyglycidyl ether and Jeffamine T403 based epoxy	22.6	612	0.03	22.8	612	0.06
26	Bisphenol A phtalonitrile	5.9	40	0.74	5.7	70	0.62
27	Bisphenol AF6 phtalonitrile	2.8	9	0.64	2.8	-1	0.53
28	Biphenol phtalonitrile	3.5	15	0.79	2.4	-14	0.67
29	Poly(4-vinylphenol)	27.6	261	0.03	28.8	284	0.12
30	Polyvinylbutyral	26.9	806	0.10	27.1	857	0.11

The flammability of the polymers listed in Table 1 was analyzed using PCFC (from FTT, United Kingdom) under standard conditions, i.e. anaerobic pyrolysis from 25 to 750°C at 1 °C/s in nitrogen and complete combustion in an excess of oxygen at 900 °C [14]. O_2 and N_2 volume fractions in combustor were fixed at 0.2 and 0.8 respectively.

The THR corresponds to the area under the heat release peak. The HRC generally corresponds to the peak of heat release rate (pHRR) divided by the heating rate. However, in some cases, several peaks can be observed. In such a case, sumHRC may be considered. SumHRC is the sum of the HRR peaks after deconvolution carried out using the FTT software. In some cases, the deconvolution is easy because the different peaks do not overlap. In other cases, several peaks

overlap. When several peaks overlap, sumHRC was determined as previously described by summing the minimum number of Gaussian, Lorentzian, asymmetric Gaussian or Lorentzian, or asymmetric Gaussian–Lorentzian hybrid peaks needed to fit the HRR curve with an accuracy of at least 95% [6]. Obviously the choice of the number of peaks influences the sumHRC.

Equations 1 and 2 explain how the total heat release (THR) and heat release capacity (HRC) of a polymer can be calculated from its structure.

$$THR = \sum_i w_i \times THR_i \text{ (Equation 1)}$$

$$HRC = \sum_i w_i \times HRC_i \text{ (Equation 2)}$$

where THR_i and HRC_i reflect the contributions of the group i to THR and HRC respectively, and w_i the weight fraction of the group i in the polymer.

In the pioneering work [6], the contribution to char had also been calculated using the same method. Then the contributions to char were independently calculated and were not correlated to the contributions to THR. Previously, the contribution to char was only considered through an example [10]. In this work, the proposed method is extended. Indeed, it has been shown that the char composition is close to C_5H_2 in most cases [15]. The energy released by the complete pyrolysis and combustion of such char Δh_{char} is then 37.2 kJ/g. When the contribution to THR is significantly different from the heat of complete combustion (Δh), it would be possible to calculate the contribution to char (μ) according to Equation 3. Δh is calculated using Huggett's relation [16] considering the complete pyrolysis and combustion of the whole polymer structure. Nevertheless Δh is calculated without considering the oxidation of nitrogen atoms. Indeed, oxidation of nitrogen is believed to occur at much higher temperature [17].

$$\mu = \frac{\Delta h - THR}{\Delta h_{char}} \text{ (Equation 3)}$$

This method is simplistic because it considers that all the chars have the same composition. Nevertheless, its main advantage is that the contribution to char depends on the contribution to THR. In other words, it allows assessing the correctness of the calculated contribution to THR. Thus, to be suitable, the method must predict correctly the THR and the char content of the polymers from only one parameter: the contribution to THR.

More details about the method to build step-by-step the database of calculated group contributions are presented in a previous work [10]. Briefly, the groups are defined around a carbon atom or an aromatic ring. Different groups are created according to the number of covalent bonds with various elements as C, O, H, F, N… Two rules must be pointed out. First, when there are several possibilities to choose the groups constituting a molecule, the heaviest group is considered. For example, in polycyanurates, the structure is composed of an oxygen atom which links the triazine ring to a phenyl group. For this structure the oxygen atom is assigned to the triazine ring and not to the phenyl group. Second, the number of groups on the aromatic ring is taken into account but their exact position is neglected (ortho, para, meta).

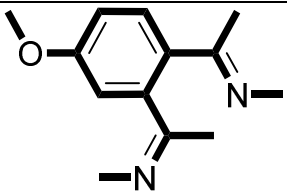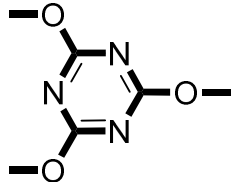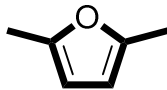**Results and discussion**

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The main results are presented in the following. Some additional results are shown in the supporting information.

The contributions to THR, HRC and char of 14 new chemical groups are listed in Table 2. Their heat of complete combustion (Δh) calculated using the Huggett's relation is also reported. Calculated THR, HRC and char content of polymers listed in Table 1 are compared to the experimental values in Figures 1, 2 and 3 respectively.

Note that some groups are present only in one polymer. Then their calculated contributions must be considered cautiously. Further polymers will have to be studied to better define these values. These groups are considered in this work only in order to compare the contributions of several groups belonging to a same series (for example the series of phenol groups).

Table 2 – New chemical groups present in the studied polymers and their contributions to THR, HRC and Char.

Groups	Molar mass (g/mol)	Polymers containing this group (from Table 1)	Contributions to			Δh (kJ/g)
			THR (kJ/g)	HRC (J/g.K)	Char (g/g)	
	29	22, 23, 25, 30	7	600	0.1	10.8
	28	1, 2, 3, 4, 5, 7, 16, 17, 18, 19, 21, 22, 23, 24, 25	19	200	0.1	22.5
	27	16, 17, 20	16	200	0.1	19.4
	90	1, 3, 6	0	0	0.88	32.6
	93	29	26	200	0.12	30.4
	92	1	8	-30	0.58	29.6
	91	2, 3, 6, 7	0	-300	0.77	28.8
	106	4, 5	-20	-400	1.12	21.8
	123	17, 18, 19	0	100	0.62	23.0

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(structure)	75	14, 15	25	700	0.27	34.9
(structure)	74	13	25	500	0.24	34.0
(structure)	143	26, 27, 28	-15	-500	0.97	21.3
(structure)	126	8, 9, 10, 11, 12, 13, 14, 15	-30	-1200	1.07	10.0
(structure)	66	4, 5, 19	3	-150	0.6	25.4

The correlation between the calculated and experimental THR is very satisfying with a slope close to 1 and a R^2 coefficient equal to 0.93 (Figure 1). The THR of only one polymer appears overestimated. Calculated THR of polymer 9 with a polycyanurate structure is 8.9 kJ/g versus 2.6 kJ/g for the experimental value. The reason for such a discrepancy is unclear.
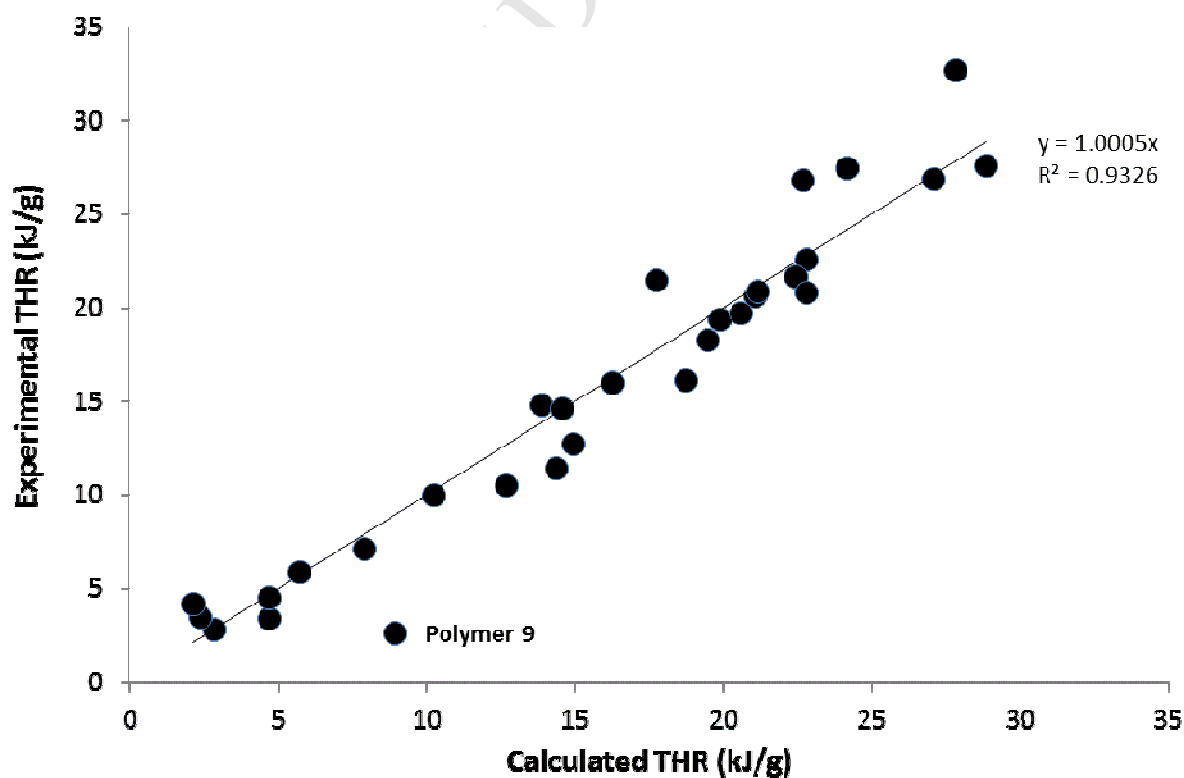

Figure 1 – Experimental versus calculated THR for 30 polymers.

HRC is also well predicted in all cases (Figure 2). The slope is 1 and the R^2 coefficient is close to 0.93. Interestingly, even the HRC of the polymers exhibiting the lowest values (like some polybenzoxazines, phtalonitriles and polycyanurates) are well estimated. In other words, in these polymers, the groups exhibiting high contributions to HRC (like CH_2) are well compensated by other groups exhibiting negative contributions to HRC. It has already been shown, some polymers had highly negative calculated HRC like copolymer ethylene-maleic anhydride [10]. So it had been concluded that the method was not suitable when the mass fraction of the groups exhibiting a negative contribution to HRC (i.e. a lowering effect on the HRC of neighboring groups) was too high. In the case of the copolymer ethylene-maleic anhydride the mass fraction of maleic anhydride (having negative contribution to HRC) exceeded 0.77. In the present study, the structure of the thermosets is more complex but the mass fraction of these groups is apparently low enough in all cases to allow the use of this method (max 0.65).
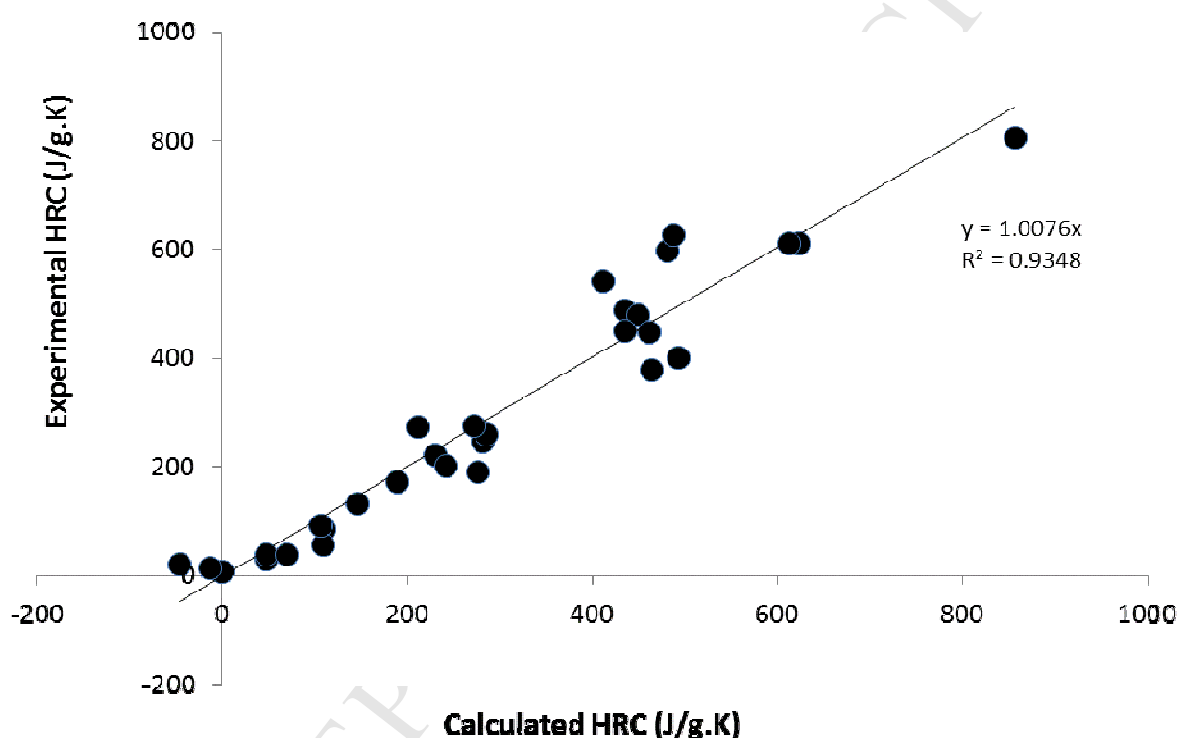

Figure 2 – Experimental versus calculated HRC for 30 polymers.

Many thermosets listed in Table 1 exhibit significant charring ability (Figure 3). The char content of these polymers is quite correctly predicted in accordance with R^2 coefficient achieved (0.93). Nevertheless, it is to be noted that the intercept of the linear regression curve is slightly shifted from 0 to -0.1. This deviation can be explained by the contributions to char which are not calculated independently. They are calculated from the contributions to THR and Δh and considering that the char composition is fixed (Δh of the char is estimated equal to 37.2 kJ/g). This methodology is a simplistic approach. Therefore, many chemical groups exhibit a non-zero contribution to char (close to 0.1) like C, CH, CH_2 or CH_3, CHO… while these groups are present in many non-charring polymers. So the char content for some polymers can be slightly overestimated. Another reason for that apparent inconsistency (underestimation of THR) will be discussed later.
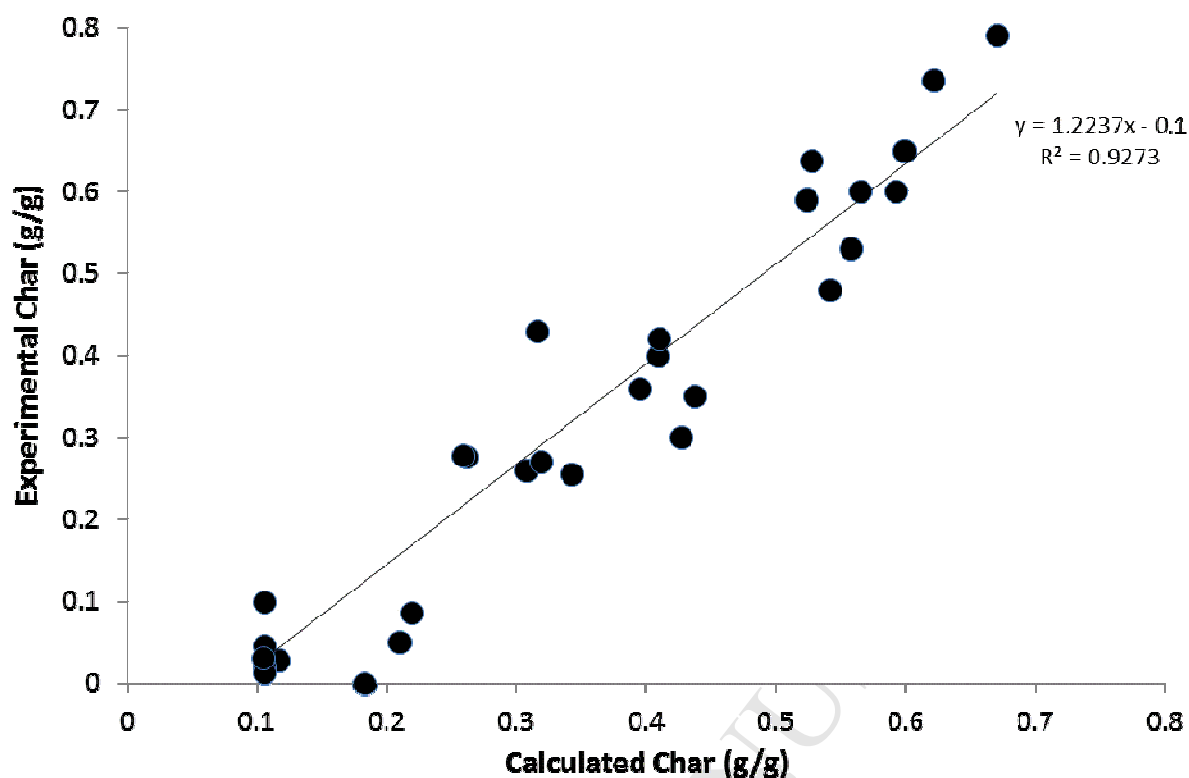
Figure 3 – Experimental versus calculated char for 30 polymers.

In order to understand the relations between the main flammability data of a polymer (namely HRC, THR, Δh and char content), it is interesting to plot these characteristic values of the groups two by two. Figures 4-6 represent these relations.

It was previously found that the contributions to HRC and to THR were roughly related for most groups with only few exceptions [10]. Most of the new calculated groups follow the same tendency (Figure 4). Only one group seems to exhibit a higher contribution to HRC in comparison to its contribution to THR: >CH-O-. This group is present in four polymers but its contribution to HRC is mainly driven by the HRC of polymer 30 (polyvinylbutyral). Its mass fraction in this polymer is 0.4 versus less than 0.1 in the four other polymers (epoxy resins 22, 23 and 25). Its contribution to HRC needs to be further assessed with more polymers. Three groups exhibit highly negative contributions to HRC and THR. These groups have a high number of covalent bonds with neighboring groups (bond number equal to 3, 4 or 5) and one contains a heterocyclic group.
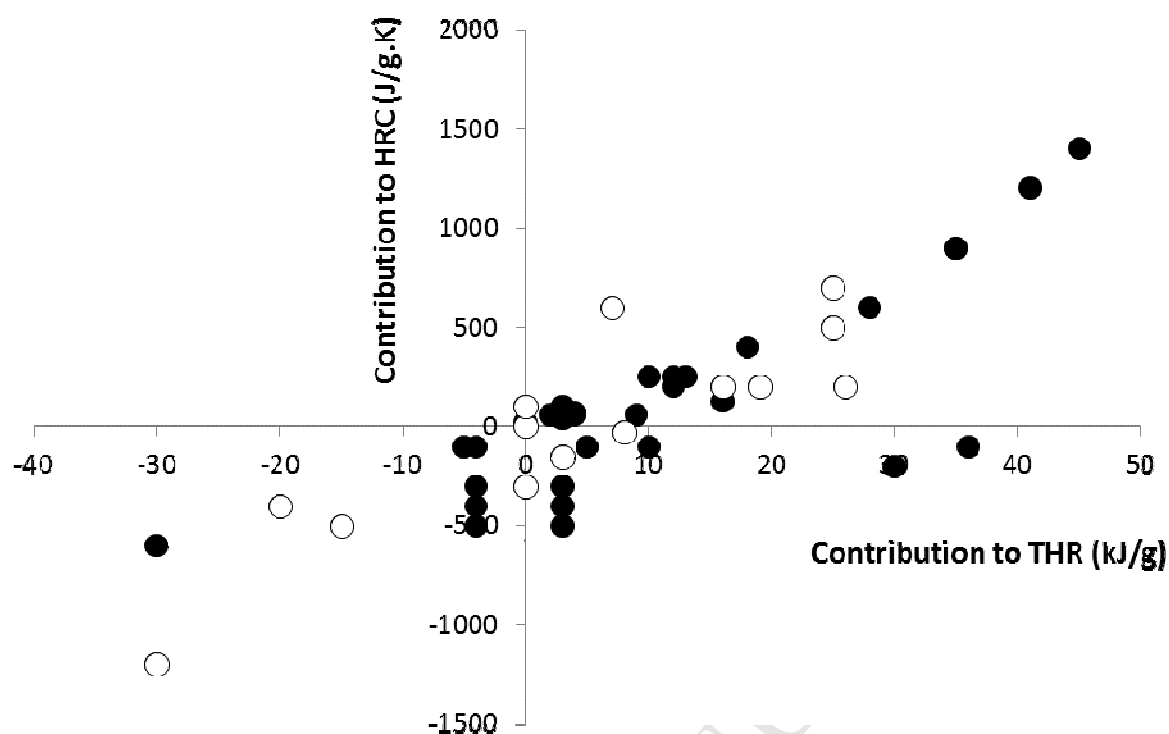
Figure 4 – Contribution to HRC versus contribution to THR for all groups studied in the present work (white circles) and in the previous work [10] (black circles).

Figure 5 shows the relation between the contribution to THR and Δh calculated using Huggett's relation. Most of the groups previously studied exhibited a clear relation between these two parameters. Indeed, most of them did not exhibit any ability to charring. The polymers studied were mainly non-charring thermoplastics [10]. On the contrary, in the present work, many groups exhibit a low contribution to THR in comparison to Δh, i.e. these groups have a significant contribution to char. This reflects the fact that these groups are present in charring thermosets: nine of them (mainly polybenzoxazines, polycyanurates and phtalonitriles, numbered 1, 4, 5, 6, 12, 14, 26, 27, 28) have char contents higher than 50%.

The relation between the contributions to THR and Δh for the non-charring groups is a straight line whose the intercept is not 0. According to this straight line, contribution to THR is -4 kJ/g when Δh is equal to 0 kJ/g. For example, polypropylene does not char but its THR was measured equal to 39.6 kJ/g while its heat of complete combustion is 44.9 kJ/g. It has been shown that the THR is slightly underestimated using PCFC because CO_2 generated by combustion modifies the volumetric flow rate and changes the thermal flowmeter calibration, leading to a small systematic error in the heat of combustion measurement [18, 19]. For O_2 fraction close to 0.2, the error on THR is about 5 % or less depending on the fuel composition. This underestimation may also explain why the poorer prediction of char contents (in comparison to the prediction of THR and HRC). A method has been proposed to correct THR knowing the polymer structure and the O_2 fraction in combustor. Nevertheless, while the present article is a continuation of a previous work, we have decided to use the raw data (i.e. without correction on THR).
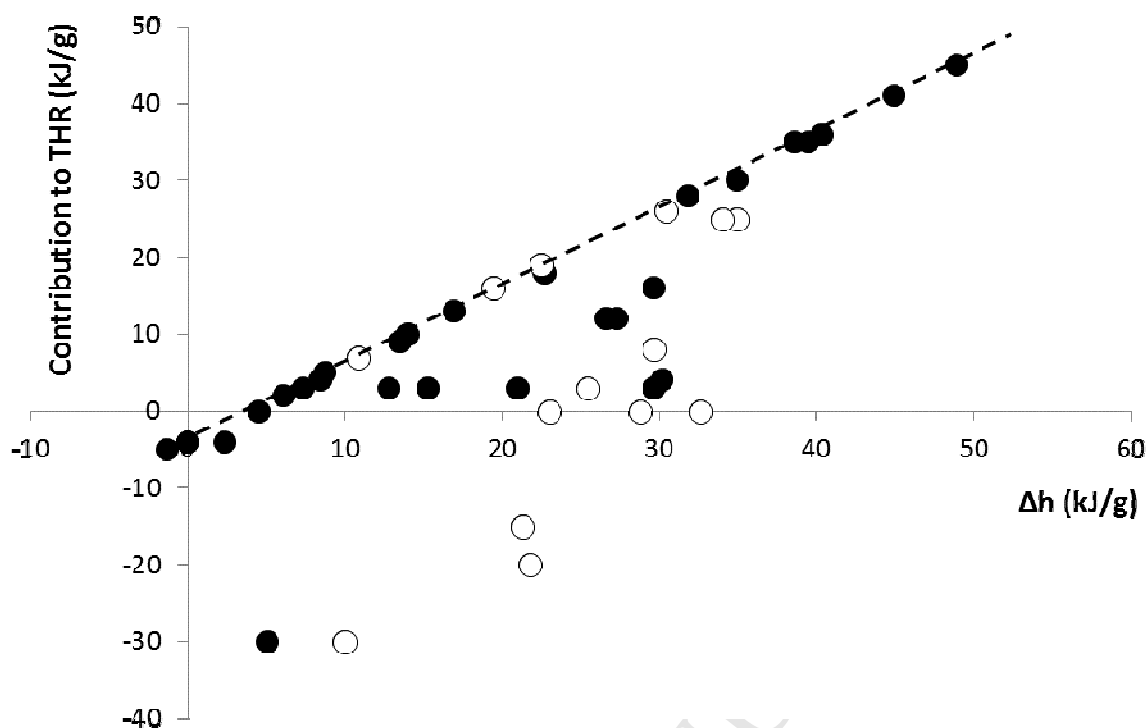
Figure 5 – Contribution to THR versus heat of complete combustion calculated using Huggett's relation for all groups studied in the present work (white circles) and in the previous work [10] (black circles).

The contributions to THR are plotted versus the contributions to char in Figure 6. As already noted the contribution to char is deduced from the difference between the contribution to THR and Δh and is never equal to 0. Some groups have a low contribution to THR and a non-significant contribution to char because their Δh is low (for example amide or ester groups). For a low contribution to char (close to 0.1) it is possible to find very different contributions to THR (from CH_2 group with a contribution to THR = 44 kJ/g to COO group with a contribution to THR = -4kJ/g). Nevertheless, the contribution to THR is lowering when the contribution to char increases. The contribution to THR does not exceed 20 kJ/g when the contribution to char is in the range 0.3-0.6 g/g. For contributions to char equal or higher than 0.6 g/g, the contribution to THR is very low or even negative. One group exhibits a contribution to char slightly higher than 1 g/g, i.e. this group may enhance the charring of neighboring groups.
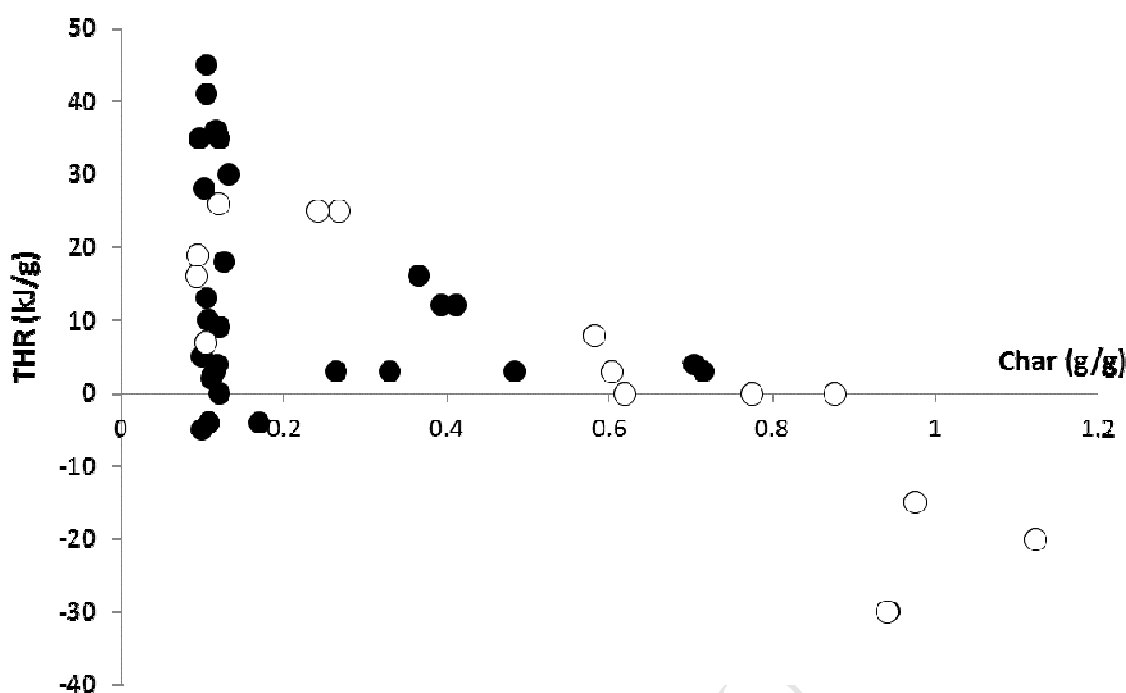
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Figure 6 – Contribution to THR versus contribution to char for all groups studied in the present work (white circles) and in the previous work [10] (black circles).

In order to compare more accurately the different groups, we have gathered them into three series: the first one does not contain aromatic rings, the second one contains aromatic rings and the third contains heterocyclic groups.

Figures 7 and 8 summarize the contributions to THR and HRC of the groups belonging to the first series. All of them have a similar contribution to char, close to 0.1, i.e. these groups are not able to char in comparison to the groups belonging to the two other series. This is obvious when considering the very low char content of aliphatic epoxy resins (numbered 21-25). The contribution to THR of these groups containing one carbon atom depends mainly on the nature of the atoms linked to this carbon. When this carbon atom is linked only to hydrogen or to others carbons, its contribution is very high (30 kJ/g or more). When this carbon atom is linked at least at one nitrogen or oxygen atom, the contribution to THR of the group is much lower. It can be found that the contribution to THR of similar groups is slightly decreasing when the bond number increases (i.e. when the number of hydrogen atoms in the group decreases).

On the contrary, the contribution to THR of CF_x groups decreases when the number of fluorine atoms increases (i.e. when the bond number decreases). This is due to the fact that the mass fraction of carbon in the group decreases when the number of fluorine atoms increases.
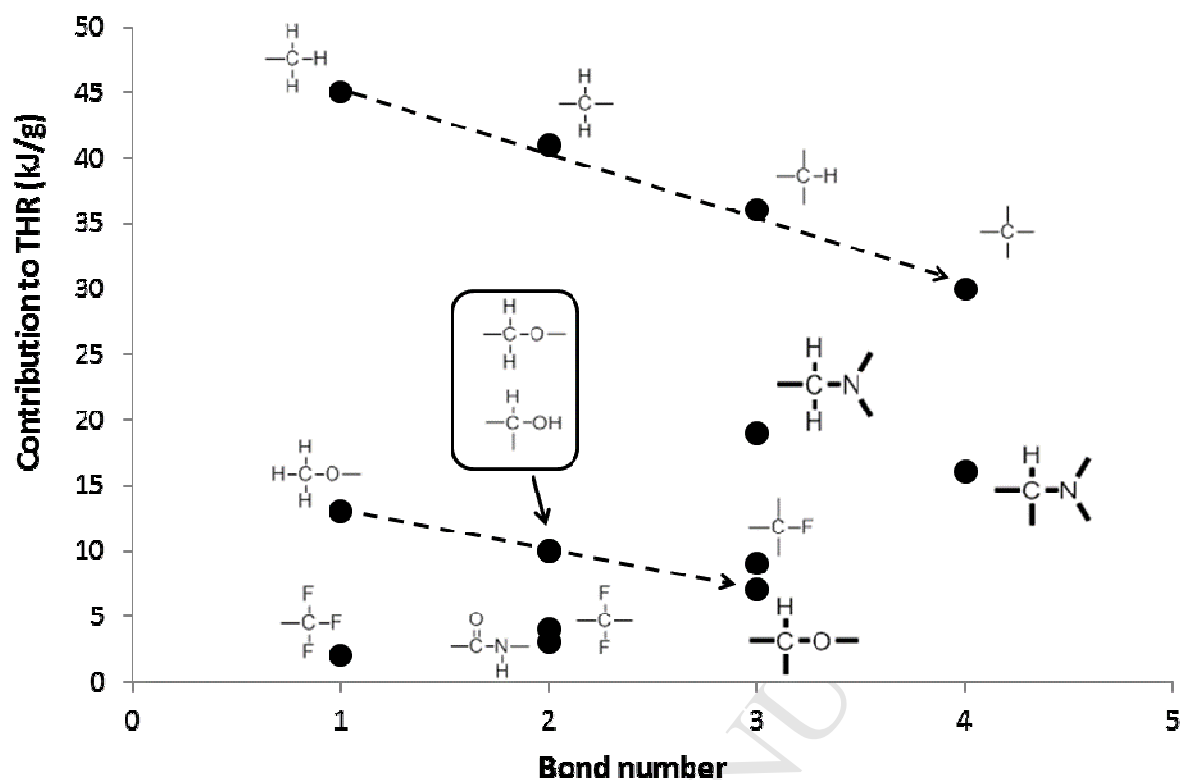
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Figure 7 – Contribution to THR versus bond number for non-aromatic groups studied in the present work (in bold) and in the previous work [10].

The contributions to HRC exhibit a quite similar tendency versus the bond number (Figure 8). The nature of the atoms linked to the carbon atom is the most important parameter. The contributions to HRC of all groups containing at least one nitrogen or oxygen atom are always lower than 250 J/g.K. Nevertheless the bond number is also influent, particularly for the groups containing only carbon and hydrogen atoms. Indeed, CH_3 and CH_2 exhibit a very high contribution to HRC while CH and C exhibits much lower contributions (see dotted line). Of course, CF_x have low contributions to HRC. This is also the case of the amide group.
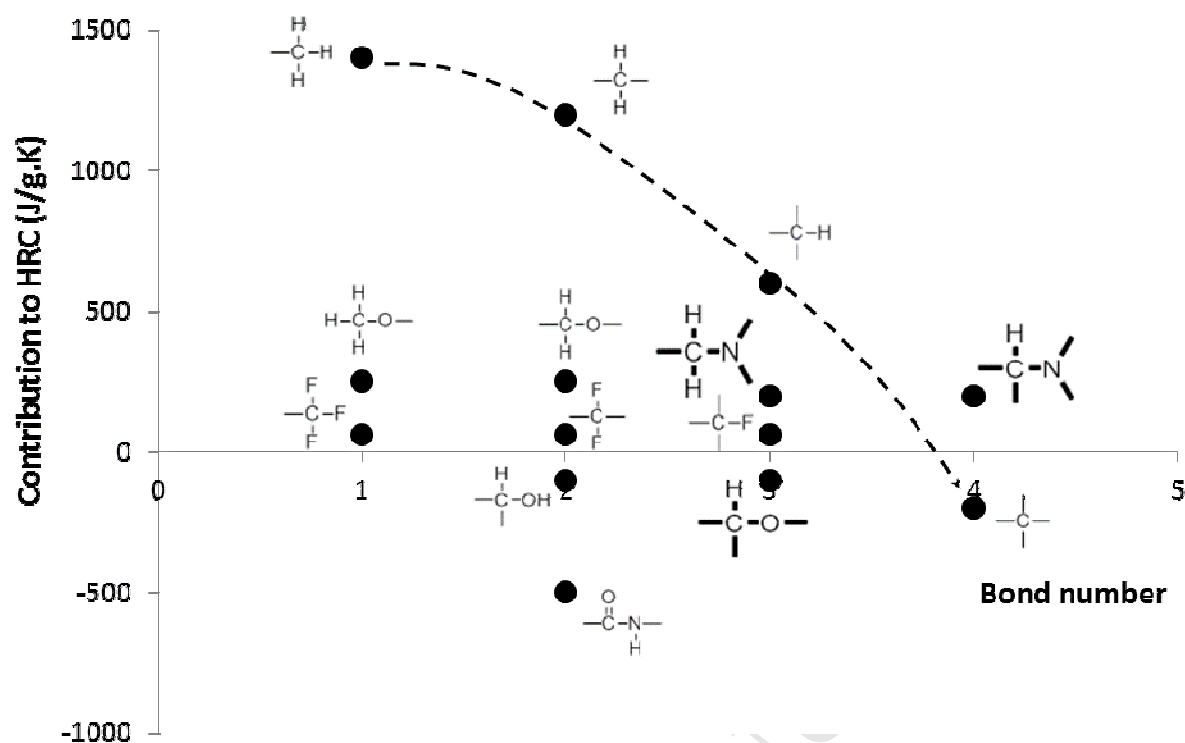
Figure 8 – Contribution to HRC versus bond number for non-aromatic groups studied in the present work (in bold) and in the previous work [10].

Interestingly the second series also exhibits similar tendencies. The contribution to THR of aromatic groups without heteroatoms in their structure is always high, and decreases only slightly when the bond number increases (Figure 9). The groups containing at least one nitrogen or oxygen atom exhibit lower contributions to THR. But in this case, the bond number seems to be very influent. For example, considering only the groups containing one or two hydroxyl groups, the contribution to THR is 26, 8, 0, -20 kJ/g respectively for a bond number equal to 1, 2, 3 and 4.
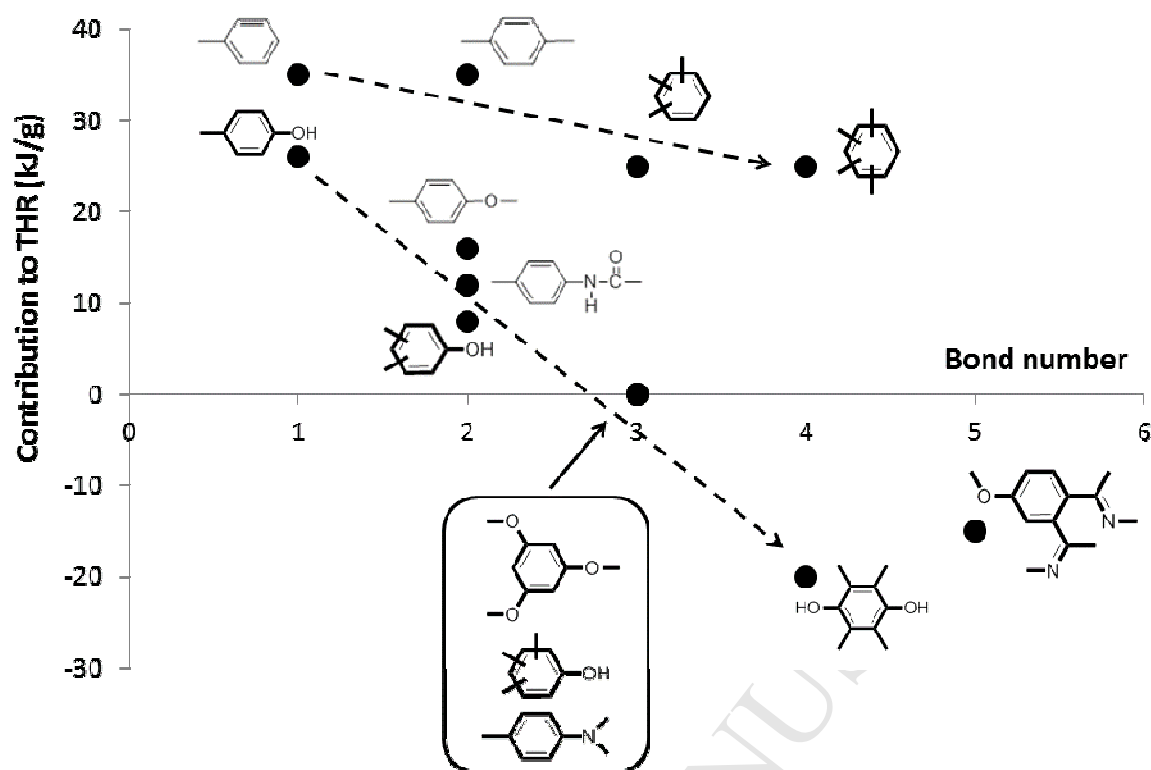
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Figure 9 – Contribution to THR versus bond number for groups containing an aromatic ring studied in the present work (in bold) and in the previous work [10].

Figure 10 shows the contributions to HRC of the groups belonging to the second series. Once again the most important parameter is the presence of oxygen or nitrogen atoms bonded to the aromatic ring. These groups exhibit much lower contribution to HRC in comparison to aromatic rings bonded only to carbon atoms. The bond number of these groups is also influent. Higher is the number of covalent bonds, lower is the contribution to HRC. The contribution to HRC may become highly negative for high bond number.
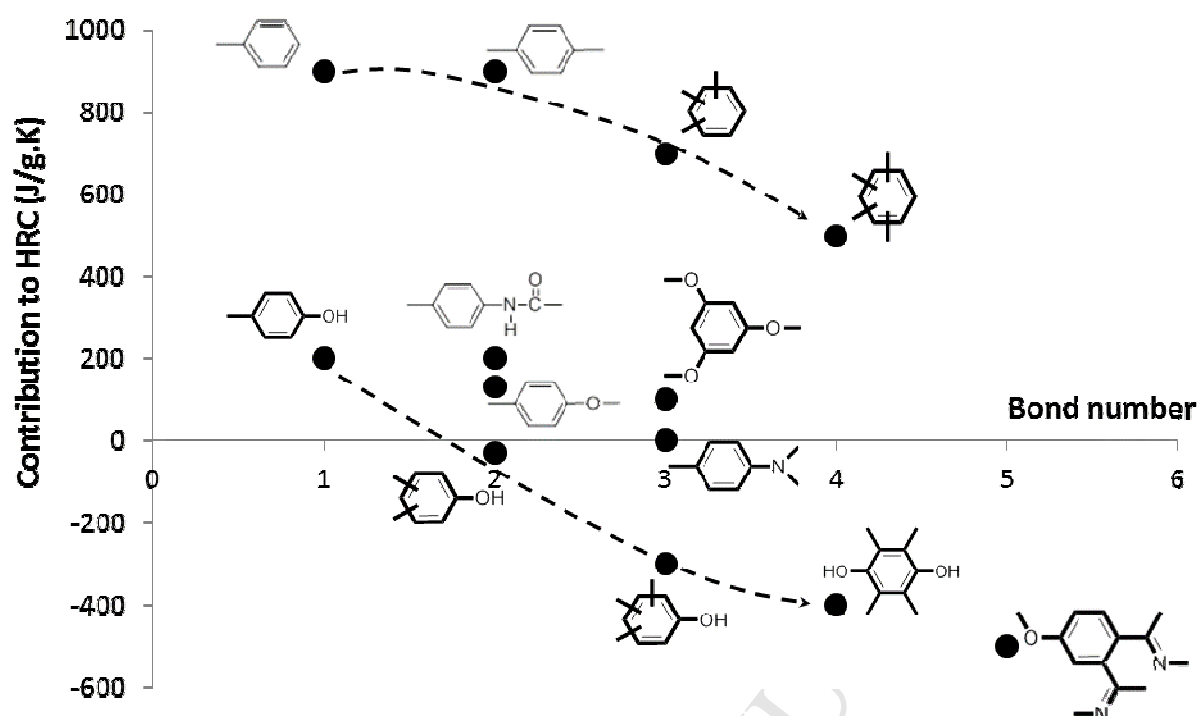
15

Figure 10 – Contribution to HRC versus bond number for groups containing an aromatic ring studied in the present work (in bold) and in the previous work [10].

Contrarily to groups belonging to the first series, the groups containing an aromatic ring have a significant contribution to char, at least when these rings are bonded to one oxygen or nitrogen atom (Figure 11). The aromatic groups without heteroatoms have a poor contribution to char.

Considering Figures 9 to 11, it can be seen that the phenol groups (aromatic groups carrying one or two hydroxyl functions) are very effective to reduce the flammability. For a given bond number, they exhibit lower contributions to THR and HRC and higher contribution to char. Phenols are well known as radical scavengers. Their ability to trap radicals may be related to the good contributions obtained for groups with phenol structures.
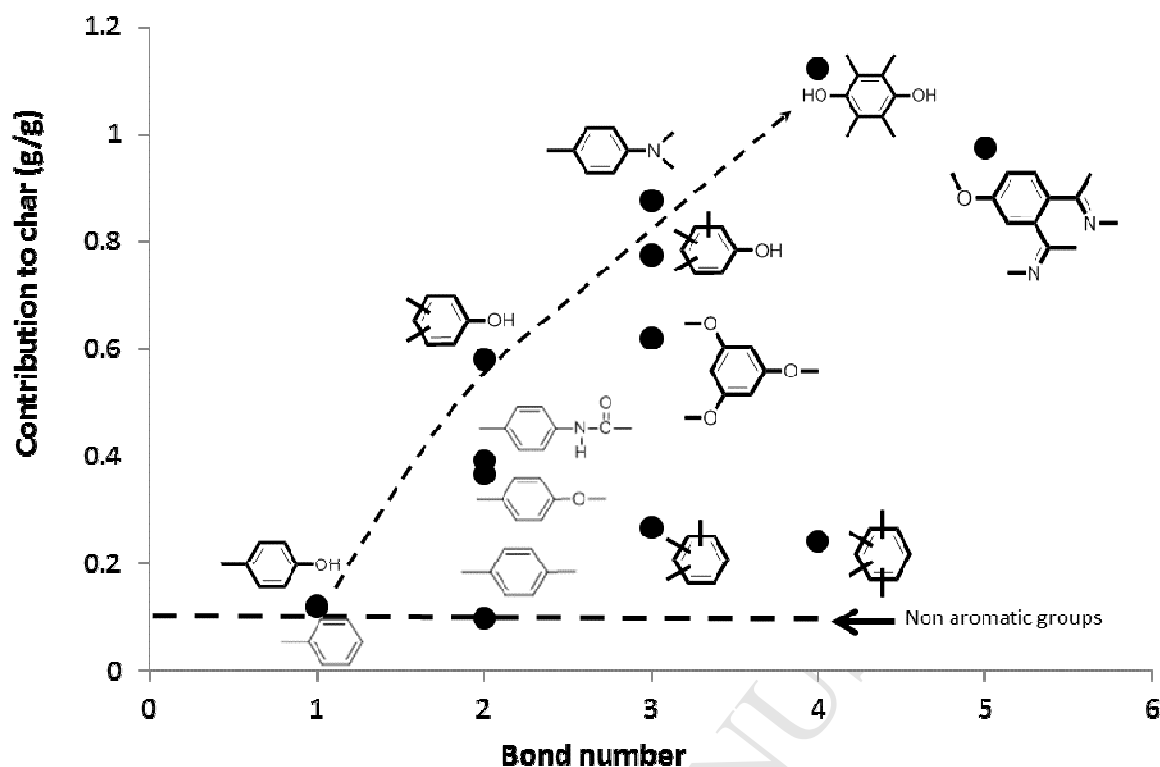
Figure 11 – Contribution to char versus bond number for groups containing an aromatic ring studied in the present work (in bold) and in the previous work [10].

Figure 12 shows the contributions to HRC and to char for six heterocyclic rings considered in the present article and in a previous work [10]. Pendant pyridine group is the only group exhibiting very high contributions to THR (28 kJ/g) and HRC (600 J/g.K) without significant contribution to char. This is very different when the pyridine cycle is in the mainchain (low contributions to THR and HRC and high contribution to char). In our opinion, this is related to the delocalization of electron density along the whole chain. Five-atom rings (furan, maleimide and maleic anhydride) exhibit low contributions to HRC, similar contributions to THR (3 kJ/g) but various contributions to char. From this point of view, furan is more effective to increase charring. Nevertheless, keep in mind that the contributions of furan group were calculated from a series of thermosets while the contributions to maleimide and maleic anhydride were calculated from a series of thermoplastics and in some cases, these groups are pendant groups. Finally oxygen-linked triazine group with a higher bond number (3) exhibits the lowest contributions to THR and HRC and the highest contribution to char.
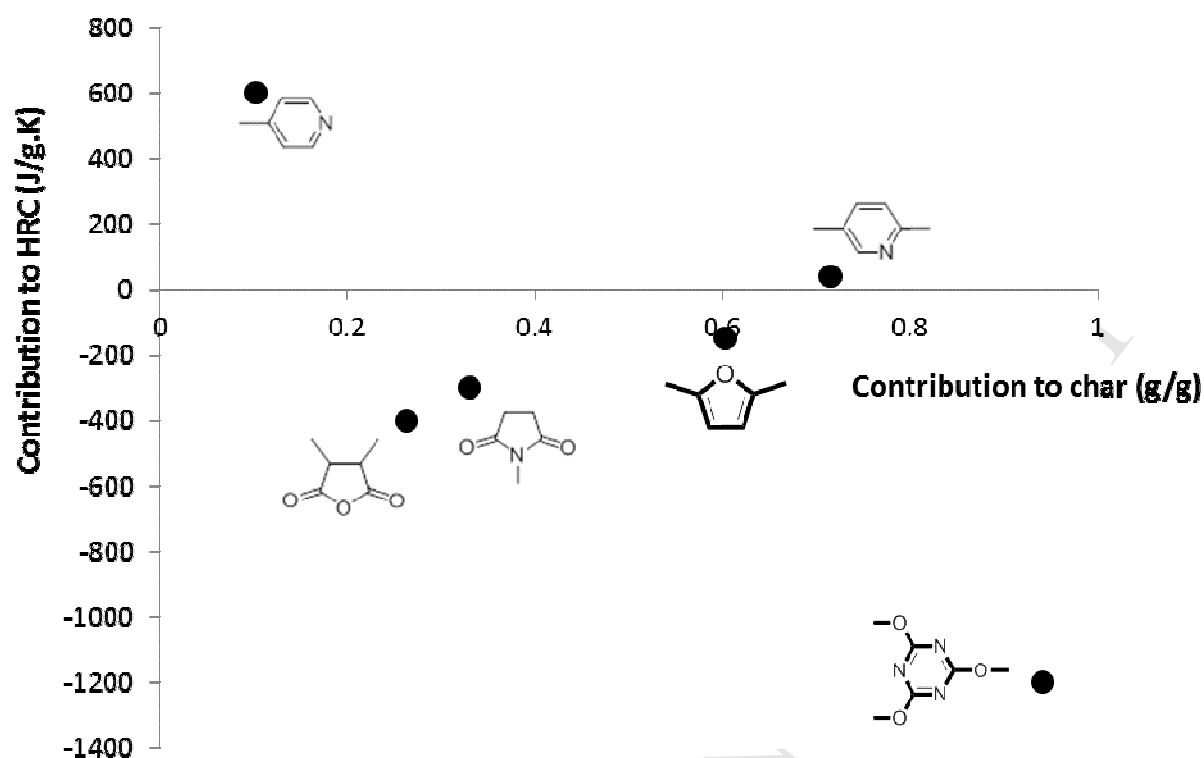
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Figure 12 – Contribution to HRC versus contribution to char for heterocyclic groups studied in the present work (in bold) and in the previous work [10]

Conclusion

The contributions of 14 new groups have been calculated using a method previously described from a series of 30 polymers (mainly thermosets). A reasonable agreement between the calculated and experimental properties (heat release capacity, total heat release and char content) has been found in all cases, except one polymer, the polymer 9 with a polycyanurate structure concerning the total heat release.

Three main parameters seem to control the contribution to flammability of the groups. The first one is the aromaticity. Charring is observed only for some aromatic groups. The second and the most influent parameter is the presence of one (or more) oxygen or nitrogen atom in the structure of these groups. The third one is the bond number, i.e. the number of bonds between the considered group and the neighboring groups. If concerted reactions leading to char formation are more likely to occur when the number of backbone bonds that must be broken is large (e.g., a cage effect), a higher bond number will result in higher char and lower HRC. But of course, while other parameters also affect, the influence of bond number must be properly assessed by considering "homologous" structures. These three parameters may explain the very high flame retardancy of some thermosets, in particular some benzoxazine and phtalonitrile-based resins. Their structures contain groups based on an aromatic ring linked to one oxygen atom and whose the bond number is 4 or 5. The properties of the best polycyanurate resins (from the point of view of flammability) are rather related to the presence of halogenated groups. Epoxy resins exhibit higher flammability properties.

While aromatic structures without heteroatoms are highly flammable even with a high bond number, phenolic groups seem to be particularly effective to reduce the flammability, probably because these groups are radical scavengers.

Henceforth, the contributions of approximately 45 groups have been calculated from a set of more than 135 polymers. Even if some of them need to be confirmed by testing additional polymers, we think that this database may allow predicting correctly the flammability of new polymeric structures.

Among the other parameters influencing the flame retardancy, it is noteworthy to mention the groups containing some key elements. Especially, polymers containing phosphorus-based groups should exhibit high flame retardancy. Nevertheless, in previous works, it has been shown that the contributions of some phosphorus-based groups seem to depend on the neighboring groups. Future work will investigate this specific issue.

Acknowledgements

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The flammability of new chemical groups from 30 thermosets is assessed using PCFC.

A group contribution method is used to calculate the contributions to heat release.

Aromaticity, presence of heteroatoms and bond number influence the flammability.