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Scavenging of Halogen in Recycling of Halogen-Based Polymer Materials

Maria P. Luda[1]**, Giovanni Camino*[1]*, Alexander I. Balabanovich*[1]°*,*
Andreas Hornung[2]

1 Dipartimento di Chimica dell'Università Via P. Giuria 7 10125 Torino, Italy
2 Institut für Chemische Technik, Universität Karlsruhe Kaiserstrasse 12, 76131 Karlsruhe, Germany
°*Permanent address: Research Institute for Phys. Chem. Problems of Bielorussin State University ul. Leningradskaya 14, 220050 Minsk*

Summary: Pyrolytic recycling of materials for electronics and automotive is attractive because of the possibility of recovery of fuel and of precious metals from printed circuit. Due to the complexity of their composition an appropriate pre-treatment has to be performed in order to limit the evolution of dangerous halogen containing compounds which strongly impair the fuel quality. An advantageous pyrolysis approach implies the attempt of mineralisation of the organic bromine to the not volatile and harmless inorganic form using strong bases such as NaOH and KOH to reduce the amount of volatile and increasing the residue. The char stability is greatly variable depending on the substrate. $Mg(OH)_2$ and $Ca(OH)_2$ behave in a similar manner but to a lower extent. Carbonates and reducing agent such as LiAlH have been tested as well and their ability to scavenge bromine is discussed in terms of effectiveness and mechanism.

Introduction

Because of increasing use of plastics and rubber and their high visibility in wastes, polymer recycling has gained much attention in the last decades. A special branch of polymer recycling is that of mixed polymer waste. Examples for such type of waste are automotive shredder, polymer coated aluminium scrap and electronic scrap. Here the portion of polymers mingled together with other materials is often the minor part. Therefore, the polymer waste is often an undesired by-product that gives rise to appreciable problems because of the development of toxic products during the process of recycling [1]. Origin of toxics mostly comes from the use of halogenated fire retardants which were very widely used in the past because of their effectiveness. The content of halogen in forthcoming discarded computers and electronic devices is certainly decreasing, nowadays however, one have to cope with the relevant amount of fire retardant materials used in the past [2].

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There are many processes described in literature that deal with the usage of polymer fractions in various parts of foundry and cement industries and in several thermal waste treatment processes. However, it is not possible to use fraction containing electronic scrap or shredder fractions from automotive industry in the blast furnace due to the amount of halogens and metals as well as inert materials. The halogens accumulate in the cooling water systems followed by corrosion. The metals are leading to formation of alloys and the inert materials are changing the composition of the slag. The cement industries are essentially considering polymer fractions as a substitute for conventional fuel. Here, because of the alkaline conditions in the cement making process, the exhaust gases will contain only a minimum of pollutants. However, the process is limited by the amount of halogen input.

In spite of this, electronic scraps are an high value fraction due to content of noble metals and the possibility of energy recovering: even though problematic, recycling is attractive. In this contest thermal methods seem to be particularly promising. Some preliminary experimental results show that electronic scrap can be processed into halogens containing fractions, fuels with an amount of about 500 ppm halogens and residues with or nearly without halogens, depending on process parameters [3-6]. In particular, scavengers and catalysts are able to redirect pyrolysis course toward clean fuel and useful char formation. The purpose of this paper deals with the search for optimal pre-treatment of halogen scavenging.

Experimental Part

Materials

Octabromodiphenyl oxide, OBDPO, has been used as a model fire retardant. A model mixture of fire retardant high impact polystyrene, FR HIPS, has been prepared by mixing in a Brabender mixer 85% of HIPS with OBDPO (10%) and antimony trioxide Sb_2O_3 (5%). Fire retardance in this system is performed both by gas phase action [evolution of volatile $SbBr_3$ a powerful flame poison) and by condensedphase action [7-9].

Two sets of circuit board scrap, LP1 and LP2 were used. They came from computer circuit boards and from electronics for entertainment respectively. After manual separation of visible metal fragments, samples were powdered and carefully homogenised in a professional coffee mill at reduced grinding speed to avoid overheating. Selected scavengers were added to powdered samples and mixed by manual grinding in a mortar.

Techniques

The thermal decomposition was studied at a heating rate of 10°C/min under nitrogen flow by thermogravimetry using the TGA 2950 Du Pont system either in the normal mode (TG) or in the high resolution mode (HRTG; resoluton factor +5 or +6). Combination curves were calculated using Origin software.

Micro scale pyrolysis (500-1000mg of material) were performed under helium flow. The bottom part of the tube was heated up to desired temperature (heating rate 10°C/min) . Solid residues were analysed by FTIR (Perkin Elmer 2000). When appropriate, the residue was dissolved in water and filtrated. The filtrate was titrated with $AgNO_3$ 0.01N using Na_2CrO_4 as indicator.

Elemental analyses were carried out by a professional laboratory in Italy

Results and Discussion

Interaction with strong bases

OBDPO

OBDPO evaporates unaltered at 250°C when heated in quasi-isothermal HRTG mode (Figure 1, left , dashed line). In constant heating rate TG mode (10°C/min) OBDPO evaporates still unaltered between 250 and 340°C. (Figure 1, right, dashed line). When mixed with strong bases such as NaOH or KOH a residue is left which is much larger than expected on the basis of an additive behaviour. This is well demonstrated by comparing experimental and calculated thermograms. Calculated curve is a linear combination of the thermograms of the single components of the mixture, therefore it is representative of a non interacting comportment.

In order to investigate the nature of such an interaction the mixture OBDPO/NaOH 8/3 has been heated at 300°C in helium for 30 min in a microscale pyrolysis equipment. The IR of the water insoluble residue is shown in figure 2 (bottom spectrum) compared to that of original OBDPO (upper spectrum). The major difference is the appearance of a strong band at 1269 cm^{-1} which point out to the formation of Ph-O bonds.

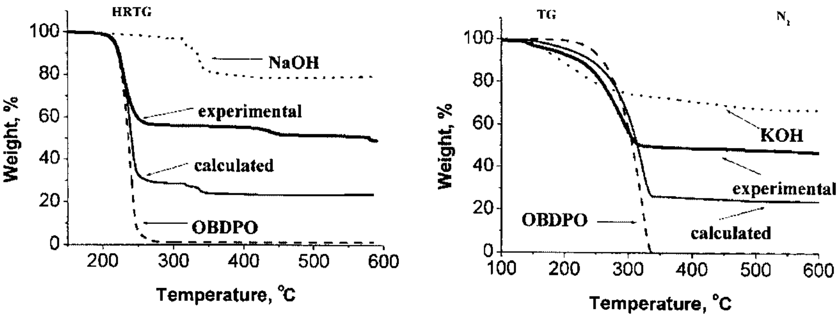


Figure 1. HRTG of OBDPO, NaOH, the mixture OBDPO/NaOH 8/3, and the correspondent calculated curve, Left; TG of OBDPO, KOH, the mixture OBDPO/KOH 16/9, and the correspondent calculated curve, right.

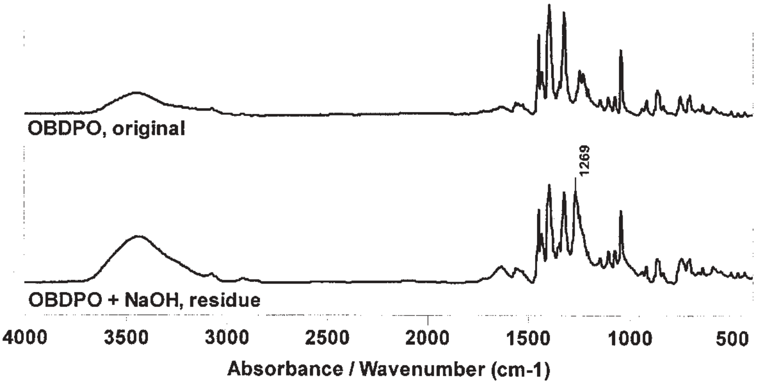
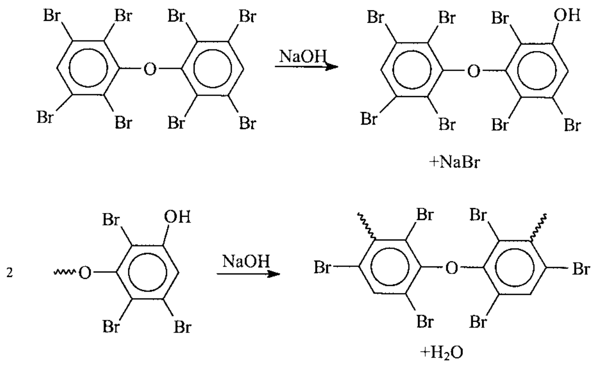


Figure 2. IR of original OBDPO (upper) and of the water insoluble residue of the thermal treatment at 300°C for 30 min of the mixture OBDPO/NaOH 8/3 (bottom).

These experimental evidences can be interpreted on the basis of the mechanism depicted in scheme 1 which shows the formation of NaBr and aromatic esters, both responsible for the residue increase. However these reactions strongly compete with volatilisation of original OBDPO.



Scheme 1

FR HIPS

Interaction between NaOH and FR HIPS is well pointed out in figure 3, left. The first step of weight loss (250-350°C), which is mainly related to the evolution of volatile flame poison $SbBr_3$ [7,8] is nearly suppressed in the presence of NaOH. At the same time the residue increases. The occurrence of a preferential interaction of OBDPO with NaOH in comparison to Sb_2O_3 is strongly suggested by these data. The increase of the residue comes both by crosslinking reactions as seen for OBDPO/NaOH mixture (Scheme 1) and by avoiding antimony volatilisation.

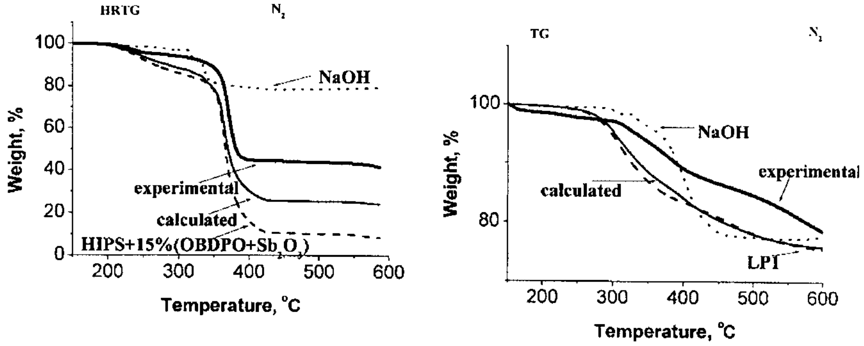


Figure 3. HRTG of FR HIPS; NaOH, the mixture FR HIPS/NaOH 78/22, and the correspondent calculated curve, left; TG LP1; NaOH, the mixture LP1/NaOH 83/17 and the correspondent calculated curve, right.

LP1

In order to clarify LP1 composition the IR on single pieces of these waste have been run. Aromatic polyester, epoxy resins polyamides and silicones have been recognised.

Their relative amount in whole LP1 waste can be highlighted from the IR of homogenised LP1 (figure 4, upper spectrum), in which aromatic polyester (1717, 1607, 1580, 1267 cm^{-1}), epoxy resins, ER, (1509, 1246, cm^{-1}) and silicon based polymers (1100, 467 cm^{-1}) can be envisaged. The spare pieces of polyamide have been also recognised prior of homogenisation which however are a minor fraction of the whole material. The complex nature of LP1 is highlighted by the continuous weight loss process.

The comparison between experimental and calculated thermogravimentric curves of figure 3, right, clearly point out at the occurrence of interaction NaOH/LP1; the weight loss is postponed to 50-100°C in the range 300-600°C. However, the residue time by time formed is not thermally stable. In order to investigate the nature of such an interaction LP1 has been treated 2 hours with NaOH at 300°C. Results on parallel heating on LP1 and on LP1/NaOH mixture are reported in table 1.

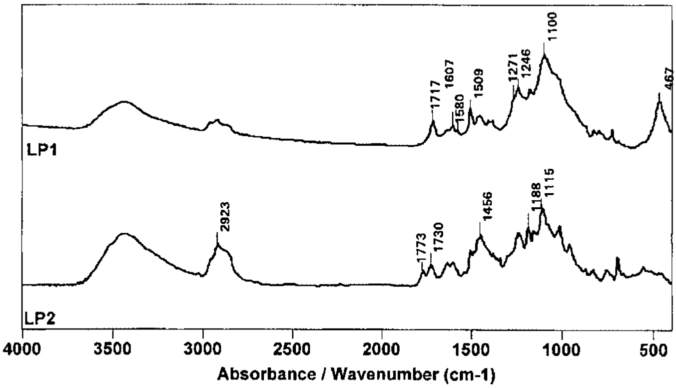


Figure 4. IR of homogenised powdered mixtures LP1 (upper) and LP2(bottom).

Table 1. Residue composition from thermolysis at 300°C for 2 hours of LP1 and LP2 in different experimental conditions.

	LP1	LP1 +NaOH 17%	LP2	LP2 +NaOH 17%
Cl initial	0.14%	0.12%	2.30%	1.91%
Br initial	3.7%[1]	3.2%[1]	2.22%	1.84%
Halogen, initial meq/g	0.5	0.41	0.94	0.78
Residue amount	82%	96%	77%	88%
Water soluble residue	1.4%	27%	1.1%	27%
Water soluble halogen	27%[2]	80.5%[2]	14.8%[2]	62.1%[2]

1: elemental analysis; % refers to the initial amount in the mixture

2 $AgNO_3$ titration; % refers to the initial amount of halogens(meq) in the mixture

The residue (96%) of the mixture is partially water soluble (27% of the initial sample, table 1). Titration with $AgNO_3$ of the soluble residue shows that 80.5% of the initial equivalents of halogen are converted to inorganic soluble salts. The IR of the residue (figure 5, upper spectrum) is dominated by the absorption of the carboxylate (1574, 1440 cm^{-1}), carbonate (1440 and 880 cm^{-1}) and possibly bicarbonate (1278 cm^{-1}) ions. All these absorption disappears as soon as the residue is washed with water (figure 5, spectrum in the middle). The structure of this residue shows similar features with that obtained by heating LP1 at 340°C without NaOH (Figure 5, bottom spectrum). However a new absorption occurs at 1037 cm^{-1}, which can be attributed to the ether groups formation.

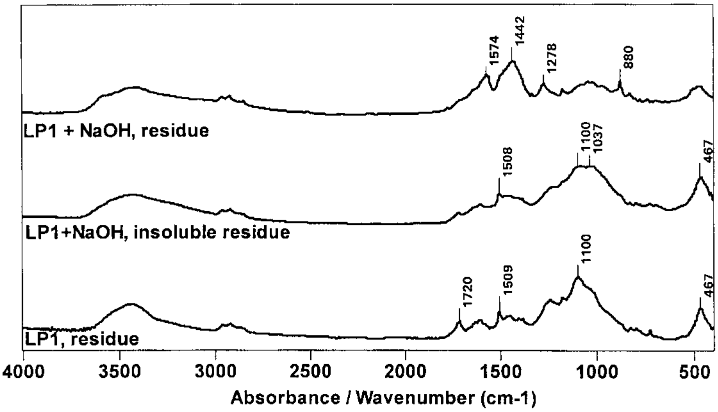
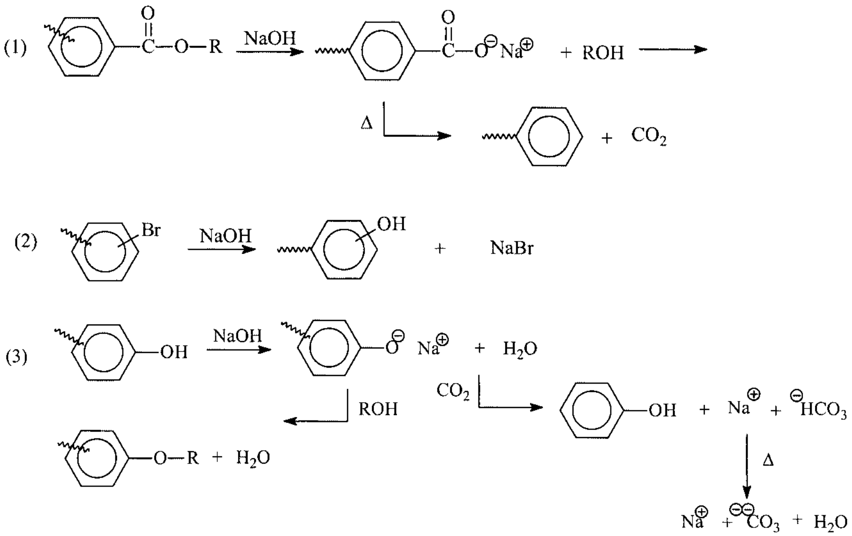


Figure 5. IR spectrum of the residue after heating in helium at 300°C for 2 hours the mixture LP1/NaOH (83/17), up; of the water insoluble residue, middle; and of the residue of LP1 after heating in nitrogen up to 340°C at 10°C/min., bottom.

A possible mechanism is proposed in scheme 2.

Organic carboxylates and aliphatic alcohols are formed by basic catalysed hydrolysis of polyesters. decarboxylation can also occur by heating (scheme 2, reactions 1). In such a strong basic entourage dehalogenation of aromatic structures takes places (scheme 2, reaction 2). Phenols sodium salts interact with water and CO_2 forming sodium bicarbonate which in turn can be converted to carbonate by heating. Eventually condensation of phenate and ROH leads to the ether formation shown by IR (reaction 3).

The amount of soluble residue depends on the balance between soluble carboxylates and NaBr formation, residual NaOH and condensation reactions.



Scheme 2

LP2

The main constituents of LP2 are polyolefines (2923, 1456 cm^{-1}), polyphenylenoxide, PPO, (1188 cm^{-1}), polycarbonates, PC, (1773 cm^{-1}) and polyesters (1730 cm^{-1}) possibly containing polyols (1115 cm^{-1}) (Figure 4, bottom spectum). Acrylonitrile based polymers (2238 cm^{-1}) have also been detected in spares pieces of LP2 as a minor fraction.

The same qualitative features described so far for LP1/NaOH interaction have been found for thermal treatment of LP2/NaOH mixture (table 1): the residue of LP2/NaOH mixture is partially water soluble and 62% of the initial amount of halogen (in equivalent) is transformed in water soluble salts.

Interaction with $Ca(OH)_2$ and $Mg(OH)_2$

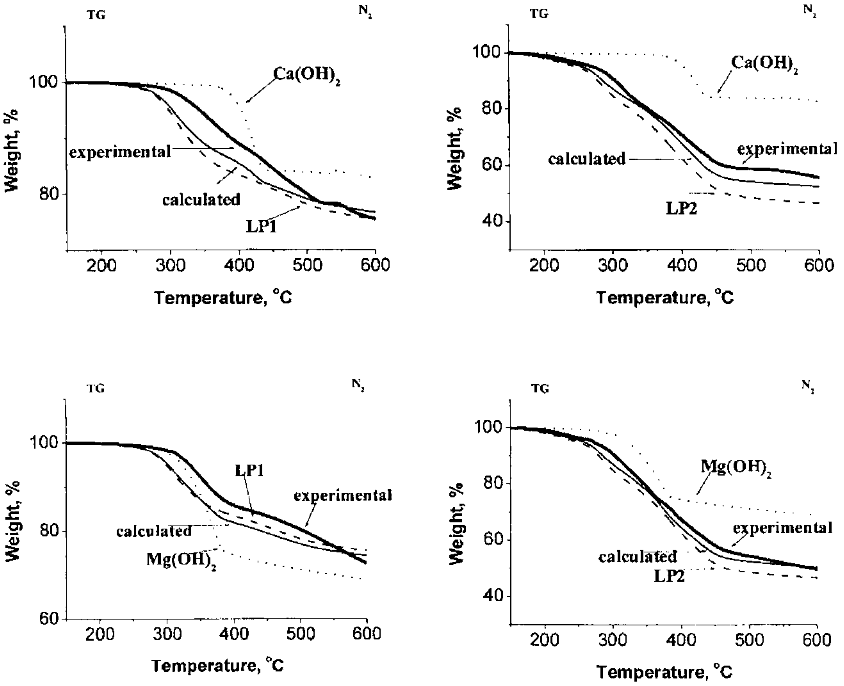


Figure 6. TG of LP1 and LP2 in mixture with 17% of $Ca(OH)_2$, first row, and with 17% of $Mg(OH)_2$, second row.

$Ca(OH)_2$ and $Mg(OH)_2$ are weaker bases than NaOH and their ability as halogen scavenger is greatly reduced. This is in agreement with the nucloephylic character of aromatic substitution in scheme 1 and 2 which require strong nucleophylic agents and activated substrates. They are ineffective with OBDPO and very poorly effective with LP2 in which calculated and experimental thermograms nearly overlap (Fig. 6, right column). In LP1, degradation is postponed to 20-40°C in the presence of these bases but the residue is not stable at the temperature at which is formed and eventually a smaller residue is left (Fig. 6 left column). Thus, $Ca(OH)_2$ and $Mg(OH)_2$ are able to interact only with more reactive species which comes from degradation of LP1 (eg. HBr or aliphatic bromine containing products) (10) and therefore might be reactive in aggregation with agents catalysing HBr formation. Investigation on the volatile degradation products is currently in progress in order to elucidate this point.

Interaction with $CaCO_3$

$CaCO_3$ interact very poorly with OBDPO and LP2 and better with LP1 (figure 7, left) and FR HIPS. The same conclusion discussed so far for weaker bases $Ca(OH)_2$ and $Mg(OH)_2$ can be drawn in this case. For example it is clearly imaginable that, if HBr is evolved during thermal degradation, it will react immediately with $CaCO_3$ forming $CaBr_2$.

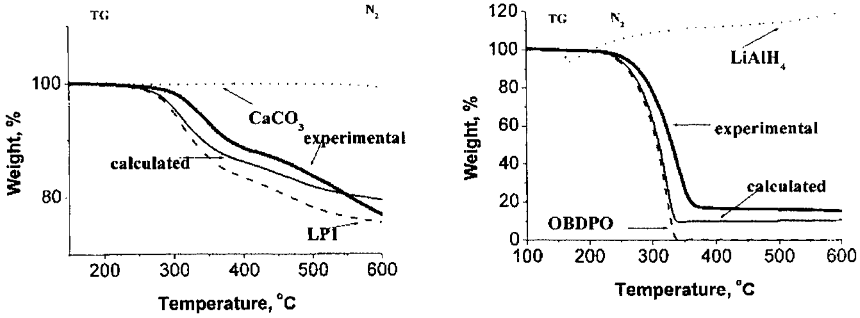


Figure 7. Thermograms of LP1 in mixture with 17% of $CaCO_3$. (left) and of OBDPO in mixture with 9% of $LiAlH_4$.

Interaction with reducing agents

TG of stoichiometric mixture of $LiAlH_4$/OBDPO shows that interaction between them occurs (Figure 7, right): the residue left at 350°C fits with the stoichiometry reported by Brown at al [11]

$$\text{Ar-Br} + 2\ LiAlH_4 \rightarrow 2\ \text{Ar-H (volatile)} + \text{LiBr (unvolatile)} + \text{Li}\ Al_2H_7\ \text{(unvolatile)}$$

Evaluation of the degradation products will help in clarifying whether this mechanism really occur or not. If this is the case, this reaction will produce very clean fuel whereas the residue is fully inorganic. However the difficulties arising from $LiAlH_4$ manipulation in industrial environment and costs will prevent from using this agent as a scavenger despite its possible large effectiveness.

Conclusions

Compounds of different chemical classes have been tested as halogen scavenger for clean pyrolysis of real electronic scraps and model mixtures.

Strong bases such as NaOH and KOH are highly effective by leaving at a reasonably low temperature a large residue containing mineral halogens. Therefore, this residue is suitable for a second-step-pyrolysis at higher temperatures to get a large amount of clean fuel. However, strong bases can be aggressive for the recycling implants.

Weaker bases and $CaCO_3$ are able to capture only reactive species evolved during degradation such as HBr or aliphatic halides and, therefore, can only be useful for scavenging halogen from reactive substrates; reducing agent can be very effective in principle but costs and environmental consideration prevent their large employ.

Investigations are in progress to fully define the interaction mechanism by analysis of volatile products of thermal treatment and to find less aggressive substitute for strong bases. In this view, a mixture $Na_2CO_3/Ca(OH)_2$ which should form *in situ* NaOH is actually under investigation.

Acknowledgement

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