Capture of hydrogen chloride by copyrolysis of polyvinyl chloride waste materials with steelmaking dust

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Abstract

Experimental study of pyrolysis of PVC based materials in presence of various amount of steelmaking dust was performed. The dust from steel manufacture employing zinc plated scrap contains considerable amount of zinc oxide and its utilization in metallurgy is quite complicated. However the dust can react with the hydrogen chloride released from the heated PVC in the temperature range 200-400°C. Material balance of the pyrolysis process was studied by thermogravimetry, and the data obtained were checked by comparison with the results of larger laboratory oven experiments. In excess of PVC, the amount of captured HCl stoichiometrically approximately corresponds to the content of ZnO; additional HCl is probably captured to FeCl₂. In excess of the dust, the captured amount of HCl approximates 100 %. The suggested copyrolysis seems to be a promising method to prevent formation of dangerous chlorinated organic compounds during the thermal treatment of the waste PVC. Furthermore, the obtained ZnCl₂ is a valuable material and the zinc depleted dust may be reused in metallurgy instead of the dumping.

Keywords: Waste PVC; Steelwork dust; Thermogravimetry; Pyrolysis; Zinc chloride

1. Introduction

Poly-(vinyl chloride), PVC, is one of the most popular synthetic polymers. With respect to its specific mechanical and electric properties, taking in account its environmental stability and resistance toward many chemicals, it is preferred in a great number of technologies. More than a half of the PVC production is targeted to building applications as window frames, sewage pipes, flooring. PVC is also used in packaging applications, in rainproof fabric, and it is superior material for electric cable insulation. Lifetime of PVC products is estimated to be 30-100 years and considering that the PVC mass production started in fiftieth of the 20th century, amount of the PVC waste rapidly increases (Mleziva, 2000; Vinyl Progress Report, 2010).

There are four essential ways of the PVC waste treatment, i.e. dumping, material recycling, chemical recycling and combustion. Dumping is the least recommended way, as dangerous pollutants may be released by a slow stepwise degradation. There are experiments with application of the waste PVC particles instead of gravel as a filler in concrete (Najjar et al., 2013; Siddique et al., 2008).

The material recycling is a commonly employed with well-defined PVC material, as the one rejected directly during the polymer processing. After the melting and granulation, this material may be processed like a virgin polymer (La Mantia, 1996; Braun, 2002; Sadat-Shojai and Bakhshandeh, 2011). Problems arise from a stepwise dehydrochlorination by heat and light, resulting in the formation of conjugated bonds, oxidation and branching (Starnes, 2002; Jian et al., 1990, 1991; Osawa and Aiba, 1982). Therefore, the re-melting is problematic, and postconsumer recycling is practically infeasible.

The aim of chemical recycling is to destroy the polymer chains with the yield of simple organic compounds, suitable as a feed for organic syntheses. Unlike the material recycling, it can be employed with more complex polymer feed. However, the polymer chain breaking processes, like pyrolysis, hydrogenation, or gasification require complex reactors and are also energetically demanding.

Combustion in proper furnace seems to be the simplest way which does not require any polymer feed separation. (La Mantia, 1996; Braun, 2002; Sadat-Shojai and Bakhshandeh, 2011). Nevertheless, the released hydrogen chloride and, in the presence of oxygen highly corrosive elementary chlorine, are precursors of a number of extremely toxic polychlorinated substances, e.g. the ones based on dibenzo-p-dioxines, dibenzofuranes, or polycyclic aromatic hydrocarbons (Everaert and Baeyens, 2002, Wang et al., 2003).

The pyrolysis is a more promising way of PVC recycling. However, it should be carefully controlled. The PVC decomposition takes place in two steps. In the range 200-360°C, hydrogen chloride is released with a minor amount of hydrocarbon gas. Later, in the range 360-500°C the polymer chains are cracked releasing hydrocarbon gases and tar. There are many papers devoted to the process under different conditions (Bhaskar et al., 2006; Czégény et al., 2012; Slapak et al., 2000; McNeill et al., 1995; Marongiu et al., 2003;
Matuschek et al., 2000; Miranda et al., 1999). Miranda et al. (1999) have examined production of hydrocarbons during the pyrolysis in vacuum equipment. Matuschek et al. (2000) have observed more degradation steps in the air atmosphere. The stage of hydrogen chloride release period has been observed in the same temperature range by all investigators. However, it is necessary to separate hydrogen chloride as soon as possible and at lower temperatures, to prevent formation of chlorinated organic compounds. All remaining organic compounds can be used as a fuel or as a reducing agents (Zevenhoven and Saed, 2000).

Hydrogen chloride in the presence of inorganic basic compounds is fixed to chloride salts and this is a common way of the chlorine separation. Usually basic oxides, hydroxides or carbonates are used for this purpose in laboratories. Borgianni et al. (2002) have suggested Na₂CO₃ to be more efficient than CaO and Ca(OH)₂. Jacksland et al. (2000) obtained reliable results with CaCO₃. Zhu et al. (2008) have compared application of CaO, Ca(OH)₂ a CaCO₃. Effects of various other oxides, as Fe₂O₃, ZnO, La₂O₃, Nd₂O₃, Co₂O₃, TiO₂; partly acting as catalysts, were also studied during the degradation of PVC (Blazso and Jakab, 1999; Terakado et al., 2009; Sivalingam and Madras, 2004; Iida and Goto, 1977; Masuda et al., 2006).

However, the best basic compounds are comparatively expensive and the chloride products are valueless, making this approach impractical for large scale application. Another option is to employ the waste metallurgy dust; major components of them are iron oxides, zinc oxide, zinc ferrite, and lime. The dust is usually captured by a wet scrubber in a form of a sludge. Content of iron and zinc in steelmaking dust depends on the ladle feed, and on the technology. Fe content may be within the range 20-73% and when zinc plated scrape is used, Zn content may be as high as 35%, and CaO content within 3-20%. Separation of particular metals is a complicated process, and when the zinc ferrite is present in the form of franklinite (Doronin and Svyazhin, 2011) most of the sludge is simply dumped.

Pyrolytic coprocessing of the dust with PVC produces different chlorides, zinc chloride being a valuable product. Lee and Song (2007) pelletized the dust from electric arc furnaces with PVC powder and released practically all zinc from it at 800-1000°C in a laboratory oven. To recover zinc, reaction of the steelmaking dust with gaseous hydrogen chloride at high temperature was studied (Wichterle et al., 2010; Cieslar, 2009). At the temperatures beyond 300°C, hydrogen chloride did not react with Fe(3) and ZnCl₂ was formed preferably (Cieslar, 2009). However, with respect to the high corrosiveness of HCl, the process has not been found to be industrially feasible.

The aim of our research was to investigate the utility of the metallurgy dust for hydrogen chloride capture. The main goal was to obtain chlorine free pyrolytic gases from PVC, with a secondary goal to reduce zinc content in the dust and extract it as zinc chloride.

2. Experimental

2.1. Materials

Four samples of PVC were studied experimentally. One was the virgin powdered polymer Neralit, three others were taken from typical PVC waste materials shredded to 1 mm particles. In the following text the abbreviations according the Tab.1 are used:

The PVC samples were mixed with the metallurgy dust, obtained by drying an arbitrary sample of centrifuged sludge collected from the emissions of tandem ovens of the steelwork Arcelor Mittal Steel Ostrava. Elementary composition of the dust, as determined by AAS, is presented in Chyba! Nenalezen zdroj odkazů.

1 g of the dust contains such amount of oxides that all hydrogen chloride formed from 0.285 g of pure PVC Present metal oxides in HCl environment can react to produce ZnCl₂, CaCl₂, CdCl₂ and FeCl₂ while Fe(III) prefers the oxide form in the temperature range 200-400°C, as obvious from

<table>
<thead>
<tr>
<th>Tab.1</th>
<th>PVC samples used.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbreviation</td>
<td>Origin of the PVC samples</td>
</tr>
<tr>
<td>V</td>
<td>Virgin polymer Neralit</td>
</tr>
<tr>
<td>WP</td>
<td>Sewadge piping</td>
</tr>
<tr>
<td>CR</td>
<td>Construction rod</td>
</tr>
<tr>
<td>CI</td>
<td>Electric cable insulation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Steelmaking-dust composition and chlorine required for the dissolution at 400°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)</td>
<td>Fe(III)</td>
</tr>
<tr>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>a)</td>
<td>53.49</td>
</tr>
<tr>
<td>b)</td>
<td>2.00</td>
</tr>
<tr>
<td>mol metal/100 g</td>
<td>0.036</td>
</tr>
<tr>
<td>mol Cl/100 g</td>
<td>0.072</td>
</tr>
</tbody>
</table>

a) - by elementary analysis
b) - Fe speciation estimated by RTG analysis; oxygen calculated
c) - in the chlorides stable at 400°C
Gibbs free energy data plotted in Fig. 1. Reduction Fe(III) → Fe(II) does not probably take place during the low-temperature PVC pyrolysis.

2.2. Procedure

Two kinds of experiments were completed. First, the mixture of PVC with various ratios of the dust were treated by thermogravimetric (TG) analysis to check the pyrolysis process. Then, laboratory scale experiments have been done to check the efficiency of chlorine capture during the process.

2.3. Thermoanalytical experiments

Setsys Evolution (Setaram) thermoanalytical apparatus was used for all experiments. The device was interconnected with mass spectrometry (MS) detector (QMG 700, Pfeifer) through Supersonic system (Setaram) for analysis of released gases.

TG measurements were used for preliminary testing of thermal behavior of pure samples and for pyrolysis of mixtures of PVC containing samples and the sludge. The mixtures were prepared by direct weighing of the components to TG crucible and homogenization (intensive shaking of the crucible covered with a lid).

All thermoanalytical experiments were carried out in opened alumina crucibles with heating rate 10 K/min in the range 20 – 500 °C. The furnace was purged with argon (200 ml/min, 25 min) before the experiments to ensure inert atmosphere, the measurements were performed under argon flow of 20 ml/min.

HCl in evolved gases was detected as MS signal with m/z = 36 (in multi-ion detection mode of measurement).

2.4. Laboratory scale experiments

The batch was prepared for any experiment by mixing 4 grams of particular PVC sample with the dust in mass ratios 1:1 to 1:4; for PVC-V the ratio 1:6 was used as well. The mixture was transferred to the corundum crucible and heated in an electric furnace. The rate of heating was programmed to the slope equivalent with the previous TG experiments; i.e. 10 K/min within the range 20-400°C, which corresponds to complete release of HCl. After the cooling, the solid residuum was crushed and leached by water and chloride content in the extract was analyzed by the argentometric titration, using potassium chromate as an indicator.

Other experiments were performed at 400°C with PVC samples under the nitrogen stream to determine the released HCl captured in a bubble trap with NaOH solution, again using the argentometric titration.

3. Results and discussion

3.1. Thermal behavior of PVC containing samples

Thermal decomposition of the PVC samples is presented by thermogravimetry curves in Fig. 2 together with the MS results for HCl. The data are consistent with a two-stage decomposition; one step occurs within the interval 200-370°C, where practically all HCl is released (Slapak et al., 2000; McNeill et al., 1995; Marongiu et al., 2003; Matuschek et al., 2000; Miranda et al., 1999). Observed difference in the behavior of pure and technical PVC is likely due to differences in various fillers, softeners and other additives.

Average mass change during pyrolysis of pure PVC-V sample in temperature interval 200 – 370°C was found to be 62.0±1.2 % (95% confidence interval, 8 measurements). The value is higher than stoichiometric content of HCl in (C₂H₃Cl)n (58.4 %), the difference (3.6 %) can be attributed to slow cracking of the structure and release of volatile hydrocarbons (process immediately following HCl elimination at higher temperatures). The loss of mass for all pure samples under the same conditions is shown in Chyba! Nenalezen zdroj odkazů.

3.2. TG analysis of mixtures with sludge
Thermal decomposition curves for PVC-V mixed in various mass ratios with the metallurgy dust are presented in Fig. 3. Percentage of the remaining mass is related to the input mass of PVC samples. The observed decrease of the mass loss is likely due to the capture of HCl in the dust. Significant decrease of the temperature at which the decomposition starts is probably due to the catalytic action of the metallic oxides contained in the dust, as mentioned by Terakado et al. (2009) and Sivalingam and Madras (2004).

Main quantitative results of thermogravimetry analysis for all samples are also presented in Table 3.

Thermal decomposition curves for PVC-V mixed in various mass ratios with the metallurgy dust are presented in Fig. 3. Percentage of the remaining mass is related to the input mass of PVC samples. The observed decrease of the mass loss is likely due to the capture of HCl in the dust. Significant decrease of the temperature at which the decomposition starts is probably due to the catalytic action of the metallic oxides contained in the dust, as mentioned by Terakado et al. (2009) and Sivalingam and Madras (2004).

By combining of the above equations, the hydrogen chloride mass captured, $m(HCl_C)$, can be determined on the basis of two decomposition experiments as

$$m(HCl_C) = 1.328 \Delta m_0 - \Delta m$$

where $m(HCl_E)$ and $m(C_mH_n)$ are the masses of the released HCl and hydrocarbons, respectively. In contrast, in the presence of an excess of the dust the total mass change $\Delta m$ of the feed during the thermal treatment in given temperature range should take into consideration also the mass of HCl captured into the dust $m(HCl_C)$, and corresponding mass of water $m(H_2O)$ formed by the reaction

$$2HCl + O^2- = 2Cl^- + H_2O$$

and released immediately as a vapor. By using stoichiometry, we can calculate

$$m(H_2O) = \frac{18.02}{2 \times 36.46} m(HCl_C)$$

The mass change in presence of the dust is

$$\Delta m = m(HCl_E) - m(HCl_C) + m(C_mH_n) + m(H_2O)$$

3.3. Laboratory oven experiments

During the laboratory oven tests, the released hydrogen chloride was absorbed in a trap, and its mass was determined by titration. Accordingly, the amount of released hydrocarbons from the samples in the absence of the dust was calculated, as presented in Tab. 4.

Supposing that all chlorine contained in the sample had been released in the form of HCl, content of pure PVC in these materials was estimated, as shown also in Tab. 4. For 100% virgin PVC, the error of such estimation is less than 3%.

Primary results of the measurements in the presence of the dust are given in Tab. 5.
3.4. Products of PVC materials pyrolysis
According to the experiments, practically all chlorine has been released from PVC. Proximate composition of the products is shown in Fig. 4. The amount of volatile organic compounds is considerably higher for the CI sample, likely due to the presence of softeners in the cable insulations.

3.5. Efficiency of HCl capture in the metallurgy dust
By stoichiometry, 1 g of the dust at 200-400°C is capable to trap HCl contained in 0.35 g PVC in form of ZnCl$_2$ and other chlorides.

When all obtained data were plotted as the efficiency of HCl capture versus the mass ratio of the dust to the pure PVC for all measured systems, we have obtained the graph shown in Fig. 5. Interestingly, our data indicate that at lower ratios of the dust additional HCl is captured as FeCl$_2$, while at higher ratios practically all HCl is captured.

4. Conclusion
Metallurgy dust from the steel processing that employs zinc plated scrap contains some amount of zinc oxide. Here we demonstrate its use for the abatement of hydrogen chloride from pyrolyzed polymeric PVC based technical materials. The produced zinc chloride can be further used as a suitable raw material for zinc recycling.

The laboratory pyrolysis employed in our study enabled determination of the content of pure PVC in the complex polymeric materials. Thermogravimetry turned out to be a simple method for investigation of the polymers decomposition both in the absence and in the presence of solid oxide materials added to facilitate fast transformation of the released hydrogen chloride to the inorganic form. Evidently, the dust was capable to capture more HCl, than corresponds to the amount of Zn present. We suppose that under these conditions additional HCl reacts with Fe(II) oxides. In excess of the dust, more than 90 % of chlorine was captured. We estimate that the residence time of HCl inside the fixed bed of the dust was about 1 s. We anticipate that in more efficient reactors (e.g. with countercurrent moving bed) the residence time will be longer and the conversion will be even higher.

Presented results indicate that by synergy of two waste materials – waste PVC and metallurgy dust –

Table 4
Balance of PVC decomposition samples characteristics 200 – 370°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass change TG (%)</th>
<th>Released HCl LO (%)</th>
<th>Released hydrocarbons %</th>
<th>PVC estimate %</th>
<th>PVC actual %</th>
<th>Moles Cl in 100 g of the sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>62.0</td>
<td>55.1</td>
<td>6.9</td>
<td>97.1</td>
<td>100</td>
<td>1.510</td>
</tr>
<tr>
<td>WP</td>
<td>49.3</td>
<td>48.0</td>
<td>1.3</td>
<td>84.6</td>
<td>-</td>
<td>1.316</td>
</tr>
<tr>
<td>CR</td>
<td>55.8</td>
<td>46.6</td>
<td>9.3</td>
<td>82.0</td>
<td>-</td>
<td>1.276</td>
</tr>
<tr>
<td>CI</td>
<td>60.6</td>
<td>28.9</td>
<td>31.7</td>
<td>51.0</td>
<td>-</td>
<td>0.794</td>
</tr>
</tbody>
</table>

Table 5
Composition of laboratory oven experiment mixture and mass of captured HCl.
Mass of the PVC based material was 4 g and different amount of the dust was added.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass ratio dust : sample</th>
<th>Mass of HCl captured, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>1</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.91</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1.91</td>
</tr>
<tr>
<td>WP</td>
<td>1</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.63</td>
</tr>
<tr>
<td>CR</td>
<td>1</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.65</td>
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<tr>
<td>CI</td>
<td>1</td>
<td>1.15</td>
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<tr>
<td></td>
<td>2</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.17</td>
</tr>
</tbody>
</table>

Fig. 5. Captured portion of HCl as a function of the mass ratio of the dust to the recalculated mass of pure PVC in the samples.
TG - estimated by thermogravimetry experiments
LO – estimated by the laboratory oven pyrolysis
two useful product may be obtained: zinc chloride and chlorine free organic residuum, which can be safely combusted.

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Abbreviations
LO Laboratory oven
PVC Poly-(vinyl chloride). (Detailed specification of PVC materials by Table 1).
TG Thermogravimetry

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http://www.vinylplus.eu/en_GB/resources/publications/resources-progress-reports/pr-vinyl-2010-archive


