

Thermal degradation of complex polymer mixtures containing ABS-Br, PVC and PET

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INTRODUCTION

Polymer waste has continuously increasing amount that poses serious problems related to their treatment/recovery. Pyrolysis is one of the best methods to recover the material and energy content of polymer waste in addition to protecting the environment. This is obtained by breaking down polymers into petrochemical feedstock components from which they originate. Municipal plastic waste is a complex mixture of polymers (PE, PP, PS) and heteroatom containing polymers (PVC, ABS, PET). Moreover most flame retardants contained in polymer materials are based on polybrominated aromatic compounds. Big attention has to be paid to the formation of very toxic and corrosive halogen- and nitrogen- containing compounds during pyrolysis of polymer waste as their presence in pyrolysis oil make it not usable as fuel or hydrocarbon resource. In present investigation we report our results on pyrolysis of mixed polymers containing brominated ABS, PVC and PET, with special interest to determine the quantity and distribution of chlorine-, bromine-, nitrogen- and oxygen- containing compounds as a preliminary step in developing methods to decrease their quantity in pyrolysis oil.

EXPERIMENTAL

A mixture of HDPE, PP and PS hydrocarbonated polymers in 1:1:1 ratio (3P) was pyrolysed under atmospheric pressure by batch operation process at 450°C in the presence of brominated ABS (ABS-Br), PVC and PET. All polymers are commercially available ones. The composition of polymer mixtures is given in Table 1. As the total amount of plastics was of 10 g, adding PVC and PET was counterbalanced by decreasing the amount of PS in 3P mixture.

The thermal degradation of the mixed polymers was performed in a glass reactor as shown Figure 1. The reactor was purged before experiments by nitrogen gas flow of 30 ml/min for 10 min in order to remove air. Then nitrogen flow was stopped and the temperature was increased by a heating rate of 5 °C/min up to the final temperature of pyrolysis (450 °C).

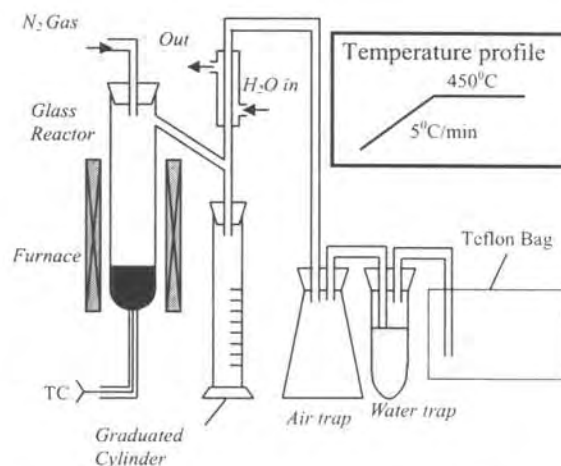


Figure 1: Schematic experimental setup for pyrolysis of polymer mixtures with ABS-Br, PVC and PET

The analysis of degradation products was performed with gas chromatographs equipped with TCD, FID, AED and MSD detectors.

RESULTS AND DISCUSSION

Table 1. Material balance from thermal degradation of mixed polymers (3P = HDPE:PP:PS) at 450°C

| Sample | Products yield (wt%) | | | | Oil | |
|--|----------------------|----|---|----|----------|------|
| | L | G | W | R | C_{np} | d |
| 3P(9g) + ABS-Br(1g) | 73 | 11 | 3 | 13 | 9.7 | 0.79 |
| 3P(8g) + ABS-Br(1g) + PVC(1g) | 62 | 20 | 4 | 14 | 9.4 | 0.76 |
| 3P(8g) + ABS-Br(1g) + PET (1g) | 59 | 19 | 9 | 13 | 9.8 | 0.78 |
| 3P(8g) + ABS-Br(0.5g) + PVC (1g) + PET(0.5g) | 52 | 22 | 6 | 20 | 9.5 | 0.79 |

L: liquid product (oil); G: gas product; W: wax; R: residue ($G = 100 - L - R - W$); C_{np} : average carbon number of liquid product; d: density (g/cm^3)

The material balance of mixed polymer pyrolysis and the global characteristics of oil products are presented in Table 1. The presence of either PVC or PET in polymer mixture decreases the amount of liquid products favouring the formation of gases and waxes while the residue amount is not affected. This could be explained by formation of gaseous HCl and CO/CO₂ in the first steps of thermal degradation of PVC and PET respectively. When both PVC and PET are in the

polymer mixture pyrolysis gives the lowest oil amount and the highest gas amount. The global characteristics of oil products are not essentially affected by the presence of PVC and/or PET; however the average carbon number seems to be slightly lowered by PVC.

Differences caused by PVC and especially by PET appear in the amount and distribution of N- and Br-content in pyrolysis oil, as shown in Figures 2 and 3.

The main part of the initial N amount in polymer mixture remains in the pyrolysis wax and residue due to the cyclisation of acrylonitrile units in ABS, this quantity increasing by the presence of PVC in the mixture. Less than 18 wt% from initial nitrogen goes in pyrolysis oil as mainly light aliphatic nitriles that appear in NP gram at n-C₅ – n-C₆ and aromatic nitriles appearing at n-C₁₄, 4-phenylbutyronitrile being the most important one (Figure 2).

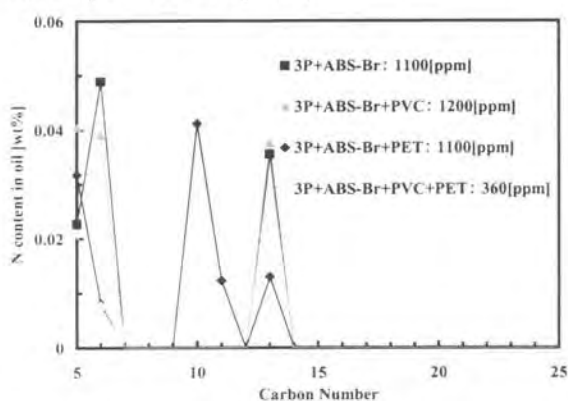


Figure 2. N-NP gram of pyrolysis oil from mixed polymers (3P = HDPE:PP:PS 1:1:1)

PVC in mixture slightly increases the amount of N in oil (from 1100 to 1200 ppm) that comes from light aliphatic nitriles at n-C₅. On the other hand PET decreases the amount of light aliphatic nitriles appearing at n-C₅ – n-C₆ and of 4-phenylbutyronitrile, the main N-containing compound at n-C₁₃ but new compounds are formed in high amounts in the region of n-C₁₀ – n-C₁₁ that might be amino derivatives; however the total N content in oil is not changed. The simultaneous presence of PVC and PET in polymer mixture strongly decreases the N content in oil due to mainly the absence of compounds in n-C₁₀ – n-C₁₁ region.

Pyrolysis of polymer mixture containing brominated ABS leads to oils with 1300 ppm of bromine that is distributed in three main peaks at n-C₇, n-C₉ and n-C₁₁ (Figure 3).

The presence of PVC increases the Br content (from 1300 to 1900 ppm) by formation of higher amounts of the compounds appearing in Br-NP gram after n-C₈ and formation of new ones at n-C₁₄ and n-C₁₆.

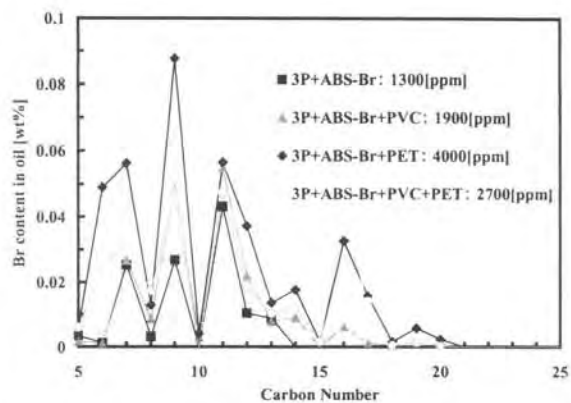


Figure 3. Br-NP gram of pyrolysis oil from mixed polymers (3P = HDPE:PP:PS)

PET has higher effect on the amount and distribution of Br in oil. All bromine- containing compounds increases in amount and new heavy ones are formed up to n-C₂₀ with a peak at n-C₁₆. The total amount of bromine in oil increases to 4000 ppm. Formation of heavy bromine- containing compounds is also favoured when polymer mixture contains both PET and PVC.

Chlorine is distributed in pyrolysis oil of polymer mixture containing PVC in peaks at n-C₆, n-C₈ and n-C₁₀₋₁₂. Its amount of 5000 ppm increases to 5300 when PET is also present. Most part of initial chlorine in PVC went out as hydrochloric acid and only 5.2 – 5.8 wt% went to liquid oil as organic chloride. Oxygen from PET remains in oil as light compounds at n-C₅ – n-C₉ with total amount of about 1300 ppm.

CONCLUSIONS

Pyrolysis at 450 °C of complex mixture of polymers containing HDPE, PP, PS, ABS-Br, PVC and PET leads to formation of N-, Br-, Cl- and O- containing compounds in oil with quantities and distribution depending on the individual or simultaneous presence of corresponding polymers in the mixture. Various catalysts were tested for reducing the amount of heteroatom- containing compounds and the results will be discussing during presentation.

REFERENCES

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