PYROLYSIS OF HALOGEN CONTAINING POLYMER MIXTURES

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Abstract

Thermal decomposition of various mixtures of acrylonitrile-butadiene-styrene copolymer containing brominated epoxy resin flame retardant (ABS-Br), polyethylene terephthalate (PET) and polyvinylchloride (PVC) has been studied in order to clarify the reactions between the components of mixed polymers. It was established that the decomposition rate curves (DTG) of the mixtures were different from the summed curves of the individual components indicating the interactions between the decomposition reactions of the polymer components. Both ABS and PET maximal rate of thermal decomposition decreases significantly in the presence of each other. The dehydrochlorination rate of PVC was sensitive for the presence of ABS or PET. More than 40 halogen containing molecules have been identified among the pyrolysis products of mixed samples. Brominated and chlorinated aromatic esters were detected from the mixtures containing PET and halogen-containing polymers. A series of chlorinated, brominated and both chlorinated and brominated phenols and bisphenol A molecules have been identified among the pyrolysis products of polymer mixtures containing flame retarded ABS and PVC.

Keywords: *ABS, PET, PVC, halogenated products, pyrolysis*

1. Introduction

Pyrolysis is a promising alternative for the recycling of plastic waste, because the process produces valuable chemicals or fuels. However, pyrolytic recycling of waste plastics require special attention due to their possible halogen content, since it should be accompanied with the elimination of halogenated products.

Polymer wastes generally contain various polymers together, in this way any component could affect the thermal decomposition reactions of the others.

PVC generally affects the decomposition of other polymers due to the catalytic effect of HCl released. Chlorinated organic compounds have been identified in the pyrolysis oil of the mixture of (PVC) and (PET)[1].

Brominated epoxy resin is a widely used flame retardant plastic, tetrabromobisphenol A is built in its polymer structure. The thermal decomposition of this polymer results in various bromobisphenols and bromophenols, in this way the involvement of brominated epoxy is also a potential source of environmental pollution[2]. Thermal degradation of PET, PVC and ABS-Br containing polymer mixtures was examined in a fixed bed reactor and significant effect was found in the yield of degradation products[3].

The detailed knowledge of halogenated products and their possible formation mechanism could help to find the proper way to eliminate these harmful materials from the pyrolysis oil, or to hinder their formation during pyrolysis procedures.

The aim of the present work is to investigate the thermal decomposition process of polymer mixtures that can be present in plastics waste. Thermogravimetry-mass spectrometry (TG/MS) technique was used to examine the changes in the overall thermal decomposition of polymers in their mixtures. The qualitative analysis of pyrolysis oil has been focused on the evolution of halogenated organic compounds, and has been studied by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS).

2. Materials and Methods

PET was obtained from Eastman Kodak Co., Ltd and PVC from Geon Chemical Co. Ltd. Japan. Commercially available ABS copolymer containing brominated epoxy oligomer flame retardant and Sb_2O_3 synergist (ABS-Br) (9.3 wt% Br and 3.8 wt% Sb) was used in the present investigation. The samples were mechanically mixed to simulate the situation in the municipal waste. Binary and ternary mixtures of the above polymer samples were examined using compositions of 1:1 or 1:1:1 by weight.

TG/MS measurements were performed on a modified Perkin-Elmer TGS-2 thermobalance and a HIDEN HAL 2/301 PIC quadrupole mass spectrometer. Typically 0.5-1 mg polymer samples were placed into the platinum sample pan and heated at a 10°C min^{-1} up to 600°C in argon atmosphere.

Py-GC/MS measurements were carried out in a CDS Pyroprobe 2000 equipped with a platinum coil and quartz sample tube. The pyrolyzer was coupled to an Agilent 6890/5973 GC/MS instrument. About 0.4 mg polymer

sample was pyrolyzed at 600°C for 20 s in a quartz tube using helium as a carrier gas.

3. Results and Discussion

3.1 TG/MS study

Thermogravimetry/mass spectrometry is a suitable method for the examination of thermal decomposition and analysis of the decomposition products under slow heating rate. Binary and ternary mixtures of ABS-Br, PET and PVC were examined. The thermal decompositions of pure ABS-Br, PET and the second decomposition step of PVC are overlapping and occur in a temperature range of 350 and 500 °C.

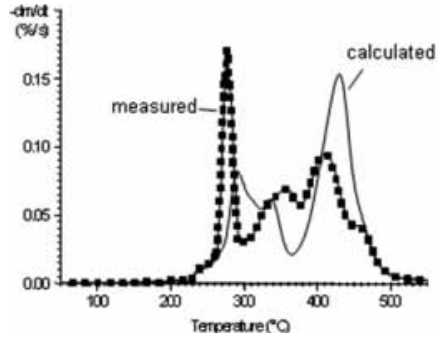

Fig. 1. Differential thermogravimetric (DTG) curve of the ABS-Br – PVC - PET polymer mixture (mass ratio 1:1:1) in comparison with the calculated curve (sum of the individual polymer curves).

The DTG curve of the 1:1:1 mixture of the three polymers (Fig. 1) is strikingly different from the summed curve of the individual DTG curves of the polymers. As the shape of DTG and mass spectrometric curves (not shown here) indicate the decomposition of all three polymer components were influenced by the presence of other polymers at a different rate. The first peak of PVC becomes sharper and the maxima shifted to slightly lower temperature indicating an enhanced dehydrochlorination rate. The maximal rate of decomposition of both ABS-Br and PET are shifted to a lower temperature by some 20°C. It seems that the second PVC peak (scission of the polyene chains) at around 460°C is not much affected by the presence of other materials.

3.2 Formation of halogenated organic products

In order to identify the evolved bromine and chlorine containing molecules, Py-GC/MS experiments were carried out at 600°C. Under Py-GC/MS experiments the heating rate is high, the thermal decomposition of all the components proceeds simultaneously.

More than 40 chlorine and/or bromine containing molecules have been identified among the pyrolysis products of mixed samples.

In the pyrolysis products of mixtures containing both ABS-Br and PVC the yield of bromophenol and dibromophenol are slightly decreased, while bromochlorophenols, dibromochlorophenols and chlorophenol appear among the products. Analogously to the phenolic products, a series of chlorinated, brominated and both brominated and chlorinated bisphenol A molecules have been identified (Figure 2.).

Chlorination and bromination of the PET decomposition products also occurs. The relative amount of bromoethane, chloroethane, bromobenzene and chlorobenzene radically increase in the presence of PET. Parallel formation of chlorine and bromine containing ester type molecules could be observed. It was found that the halogenation occurs mainly on the ethylene groups, but not on the aromatic rings. More chlorinated esters are formed than brominated or mixed halogenated esters, but it can be explained by the fact that the chlorine content of PVC is higher than the bromine content of ABS.

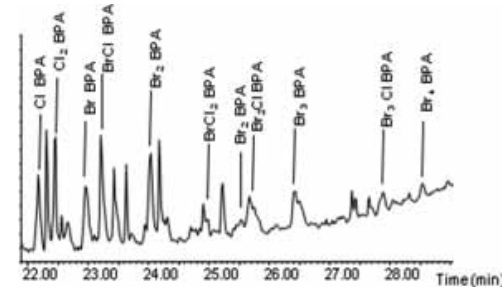

Fig. 2. Total ion chromatogram of the mixture of brominated epoxy oligomer containing ABS-Br - PVC (1:1) in a range of halogenated bisphenol A (BPA) elution.

4. Conclusions

It can be concluded that all the three polymers influence the decomposition of each other and significant amount of various chlorinated and brominated products are released during the decomposition of the mixture. The results provided useful information about the changes in the thermal stability, in the composition of pyrolysis oil, and enhance the understanding of the chemical reactions taking place during pyrolytic waste elimination procedures.

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