THE EFFECT OF POLYETHYLENE TEREPHTHALATE (PET) ON PYROLYSIS OF BROMINATED FLAME RETARDANT CONTAINING HIGH IMPACT POLYSTYRENE (HIPS-Br)

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Abstract: Pyrolysis of brominated flame retardant containing high impact polystyrene (HIPS-Br) was performed in the presence of 1 wt% of polyethyelene terephtalate (PET). The brominated HIPS contained decabromo diphenyl oxide (DDO) as flame retardant with or without antimony trioxide (as synergist) 5 wt%. The pyrolysis experiment was performed in a pyrex glass reactor at 430^{o}C. The affect of PET on pyrolysis of HIPS-Br was confirmed from the analyses of pyrolysis products with gas chromatograph (TCD, FID, MSD, and ECD) and ion chromatography. The presence of PET had significant effect in material balance in particular of decreasing the products gas and increasing the residue. However, it lowered the degradation temperature in both the HIPS-Br samples with and without synergist.

1. Introduction

The use of electronic devices has proliferated in recent decades, and proportionately, the quantity of electronic devices, such as PCs, mobile telephones and entertainment electronics that are disposed of, is growing rapidly throughout the world. Electronic waste, or e-waste, is an emerging problem as well as a business opportunity of increasing significance, given the volumes of e-waste being generated and the content of both toxic and valuable materials in them. Plastics are the second largest component by weight representing approximately 21wt% of Waste Electronic and Electrical Equipment (WEEE). The enormous amount of mixed waste plastics is coming from various sectors including electrical and electronic appliances. Among the various available treatment methods, feedstock recycling has more advantageous. Feedstock recycling is a decomposition of plastics waste by means of physical-chemical treatment for obtaining the chemical feedstock. We have shown various catalysts/sorbents and reactions conditions for the production of halogen free hydrocarbons from the PVC mixed waste plastics by catalytic/sorptive and/or non-catalytic methods [1-3]. In recent years, much attention has been paid to the possibility of recycling plastics by pyrolysis and the introduction of the Waste Electronic and Electrical Equipment (WEEE) Directive by the European Union has inspired an increasing amount of research into using pyrolysis to recycle WEEE plastics. Unfortunately, WEEE plastics often contain toxic brominated flame retardants, which makes them particularly problematic to recycle.The waste plastics such as brominated high impact polystyrene (HIPS-Br) from the electric and electronic appliances along with the other polyolefins poses various problems than the chlorinated plastics due to the presence of inorganic compounds as synergist (Sb_2O_3 etc.,) and brominated flame retardants. In addition to the polyolefins, the small quantities of PET are also used in electric and electronic products. In the present investigation, we report the pyrolysis of HIPS-Br in the presence of PET to understand the affect of PET on the distribution of pyrolysis products and brominated hydrocarbons in pyrolysis products.

2. Experimental

High impact polystyrene (HIPS) with several types of flame retardant and synergist was chosen as it is one of the most commonly used plastics in electrical and electronic equipment. The HIPS contained either decabromodiphenyl oxide or decabromodiphenyl ethane flame retardant and either 5% or 0% antimony trioxide. The schematic experimental setup for the pyrolysis of mixed plastics has been given in fig. 1. Decabromo diphenyl ether with antimony trioxide shown as DDO-Sb(5) and Decabromo diphenyl ether without antimony trioxide shown as DDO-Sb(0). The detailed information on the samples and pyrolysis procedure has been given elsewhere [1-3].

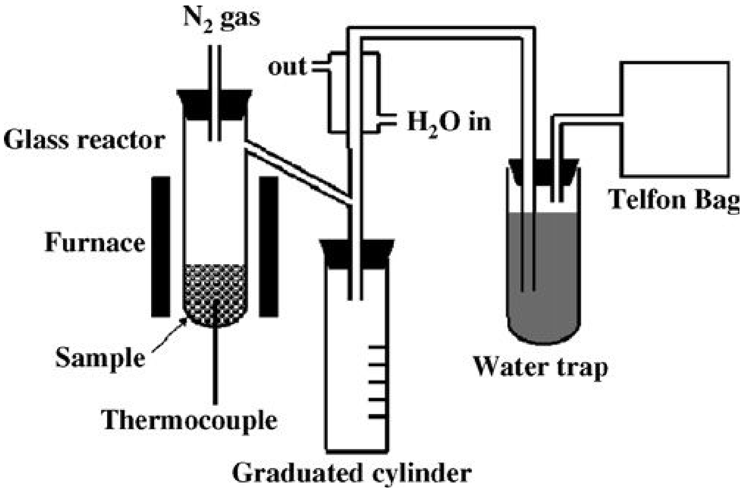

Fig. 1 Schematic experimental setup for the pyrolysis of mixed plastics

3. Results and Discussion

The pyrolysis of HIPS-Br, mixture of HIPS-Br and PET was performed at 430^{0}C using the experimental setup shown in fig. 1. The yield of pyrolysis products along with the properties of liquid products such as density, average carbon number (C_{np}) given in Tab. 1. It is obvious from tab. 1 that the yield of gaseous products decreased and yield of residue is increased in the presence of PET with the four HIPS-Br samples used in this study. There is no change in the yield of liquid products with the DDO and DDE type flame retardants with or without synergist (Sb_2O_3). The liquid products were characterized by a Normal Paraffin gram (NP-gram) proposed by Murata [4]. Briefly the C-NP gram of the liquid products obtained by analyzing their gas chromatogram obtained from GC-FID for liquid products and GC-TCD for gaseous products. The carbon numbers in the abscissa of the NP-gram are equivalent to retention time (from gas chromatogram) of the corresponding normal paraffin and the ordinate shows the weight percent of the corresponding hydrocarbons or weight percent of halogen content. The average carbon number which is obtained from the normal paraffin gram (C-NP) using the gas chromatograph of liquid products has no significant effect.

Tab. 1 Product Yields and Properties of Liquid Product from
HIPS-Br and HIPS-Br+PET mixtures at 430^{0}C

Sample plastics (10 g)	Yield of degradation products, wt%			Liquid properties	
	Liquid (L)	Gas (G)	Residue (R)	C_{np}	Density (g/mL)
DDO-Sb(5)	79	5	16	14	1.07
DDO-Sb(0)	77	11	12	16	0.95
PET/DDO-Sb(5)	76	4	20	14	1.07
PET/DDO-Sb(0)	77	9	14	14	0.99
DDE-Sb(5)	78	6	16	14	1.04
DDE-Sb(0)	77	12	12	14	0.95
PET/DDE-Sb(5)	76	5	19	13	1.06
PET/DDE-Sb(0)	77	9	13	14	0.97

PET: 0.1g ; DDO/DDE:9.9g

The liquid products was analysed by FT-IR and the representative IR spectra has been given in Fig.2. The general conclusions that can be drawn from the FT-IR analysis are, all of the oils had an aromatic content with C-H stretches present between 3010 and 3110 cm^{-1}. All the oils also had methyl and methylene groups present (C-H stretches at 2850 – 2970 cm^{-1}). Relatively large benzene ring substitution ring patterns are also present between 1660 - 2000 cm^{-1}. The antimony free oils have a peak present at 1629 cm^{-1} which is absent from the antimony containing oils. This is possibly related to the C=C stretch in aliphatic hydrocarbons. All the oils have a large stretch at 1602 cm^{-1} and 1494 cm^{-1} which is caused by the C=C stretches in benzene derivatives. The large stretch in all the oils at 1453 cm^{-1} is caused by methylene groups. The stretch around 1374 cm^{-1} is caused by C-CH$_3$ deformation although it is unclear whether 1, 2, or, 3 methyl group's area attached to a common carbon atom. Bonds at 909 and 991 cm^{-1} are present in all the antimony free oils but not in the antimony containing oils and were caused by C-H deformation in vinyl compounds. The strong bonds between 690 – 780 cm^{-1} can be assigned to C-H out-of-plane deformation in benzene derivatives, although the benzene substitution is unclear.

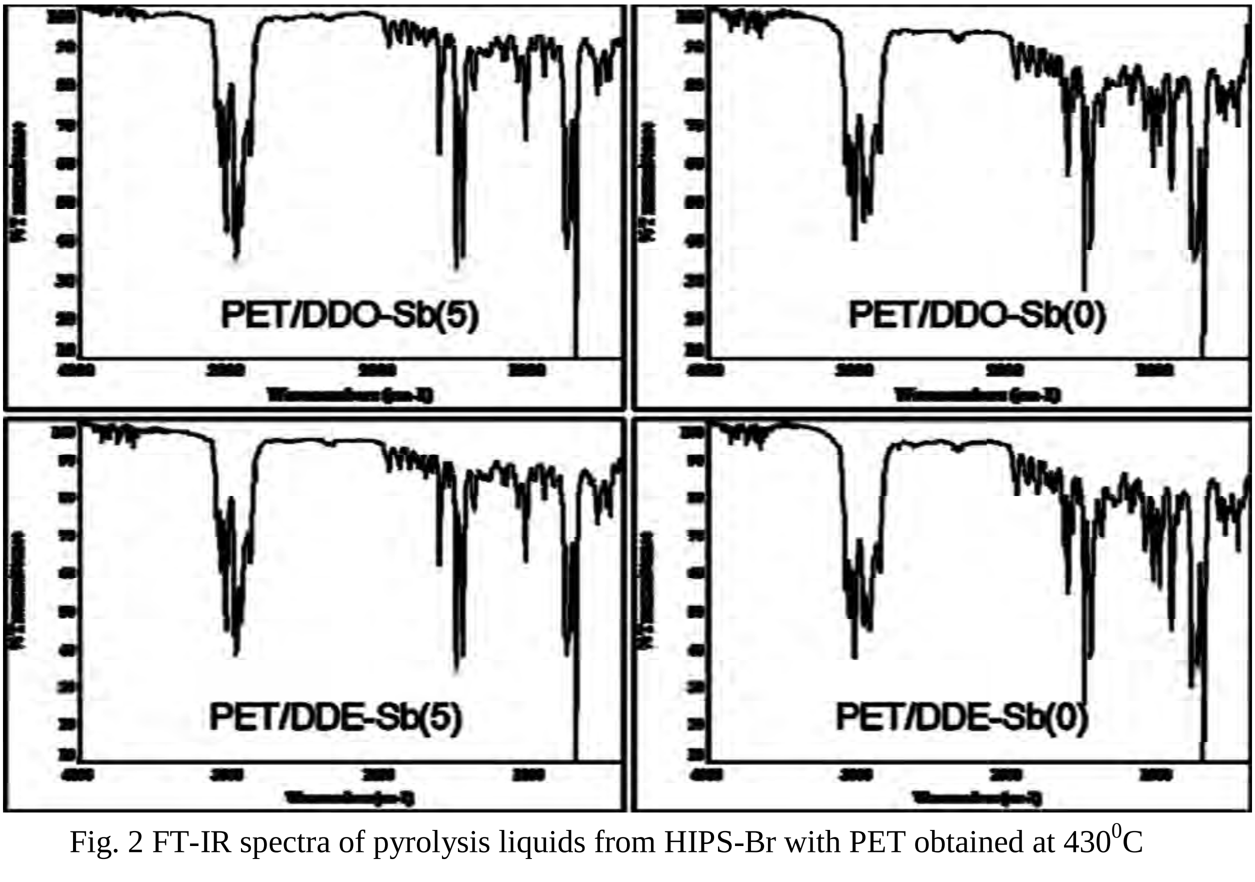

Fig. 2 FT-IR spectra of pyrolysis liquids from HIPS-Br with PET obtained at 430^{0}C

The detailed characterization of brominated hydrocarbons and congenerers of flame retardant species etc were analysed by GC-ECD and qualitative analysis by GC-MS etc. The quantitative analysis of bromine in pyrolysis residue was done by ionchromatograph.

4. Conclusions

The affect of PET (1 wt%) on the pyrolysis of HIPS-Br (99 wt%) was performed using fixed bed reactor at 430^0C and found that the yield of pyrolysis products (gas and solid) significantly changed. The qualitative analysis of liquid products indicated that the distribution hydrocarbons were different with the presence of PET.

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