

RESEARCH ON SEPARATING BROMINATED FLAME RETARDANTS FROM WASTE TV HOUSING PLASTIC

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Abstract: The thermal stability and degradation kinetic of TV housing plastic and brominated flame retardants were studied by the means of thermogravimetry (TG) instruments, the effects of treatment temperature on the removal rate of Br were investigated by a tube furnace reactor under isothermal and vacuum. The results show that the weight loss of TV housing plastic was divided into two different stages, thermal degradation of brominated flame retardants mainly occurred at 290°C~ 350°C, the HIPS resin mainly occurred at 350°C~ 455°C. Over 90% of Br can be released from the TV housing plastic if the treatment temperature exceeds 280°C.

Keywords: TV set housing; high impact polystyrene; Brominated flame retardants

1. Introduction

TV housing is generally manufactured from high impact polystyrene(HIPS) or polystyrene(PS), styrene polymers is belong to flammable material type and easily cause a fire accident, Brominated flame retardants (Br-FR) such as Decabromodiphenyl ether(Deca-BDE), tetrabromo bisphenol-A or polybrominated epoxy resins in combination with Sb₂O₃ synergist are used in HIPS to prevent combustion during accidental fires[1,2]. In recent years there has been a growing concern in environmental pollution from waste electric and electronic equipment (WEEE), recycling of plastics from WEEE is an important subject not only from the point of waste treatment but also from the aspect of recovering valuable organic materials, so far, TV housing plastic was mainly recycled by the physical process. Unfortunately, the recycled plastics from waste TV have been banned to used for manufacturing new electrical equipments against duo to the presence of polybrominated diphenyl ether(PBDEs)[3], though the conversion of waste plastics into chemical fuel or feedstock is a good alternate technique for physical process, but material recycling of flame-retarded plastic wastes may result in the formation of toxic or harmful organobromine

compounds[4,5], which will influenced the further utilization of pyrolytic product. therefore, so it is very necessary to separate brominated flame retardants from TV housing plastic before recycling.

In this paper, the thermal stability of waste TV housing plastic was investigated, and the feasibility of separating Br from TV housing plastic under vacuum and isothermal is also discussed.

2. Experimental

2.1 Materials

The waste TV housing plastic used in this work was supplied by GuangDong ShuYe Environmental Technology Co.LTD, it was identified that housing plastic was manufactured from flame retarded HIPS resin containing 6.15 wt% of PBDEs (4%Deca-BDE, 0.18% nonabromodiphenyl ether, 1.97% octabromodiphenyl ether)and 2.05wt% of Sb₂O₃. The plastic sample was necessary to be crumbed into <0.85mm powders before used for the present experiments. Deca-BDE, commercial grade, was bought from Sino-Brom Compounds Co.,Ltd.

2.2 Apparatus and measurement procedure

Thermogravimetric(TG) experiments were carried out on a NETZSCH TG thermal system TG/DSC 409 in nitrogen atmosphere under a gas flow of 50 cm³ / min at a heating rate of 10°C / min from 30 to 800°C. Isothermal Thermogravimetric experiments were performed on the same TG instruments, temperature program was as fallow: heat temperature to 280 at 10°C / min and then held for 60 min with a N₂ carrier gas flow 50 cm³/min.

Thermal treatment experiments under isothermal and vacuum condition were performed in a quartz tube reactor, approximately 0.5g of the sample was used for each experiment and heated up to the set temperature at heating rate of 10°C/min, then held for 60 minutes. The pressure of reaction system was kept lower 5 kPa by a vacuum pump. The thermal gradation of the samples was studied by IR spectrum, PBDEs in the samples was separated by soxhlet's extraction with the mixture of toluene and isopropanol, then PBDEs extracted was determined by HPLC.

3. Results and discussion

3.1 Thermal stability of waste TV set housing plastic

The TG curve of waste TV housing plastic in nitrogen is shown in Fig.1,which is very similar to the TG curves obtained by E.Jakab[6] and Nona[7] with the mixture samples prepared from HIPS, Deca-BDE and Sb₂O₃. It could be seen in Fig.2 that the temperature range of weight loss was divided into two obvious different stages. The first stage is from 290°C to 350°C, which the weight loss is about 25%,The second stage is from 350°C to

455°C, which the weight loss reached 65%. The weight loss of the sample mainly occurred in the second stage, and the weight loss rate in the second stage was also faster than the first stage. The TG experimental results indicates that the TV housing plastic may contain two type of compounds with different thermal stability at least.

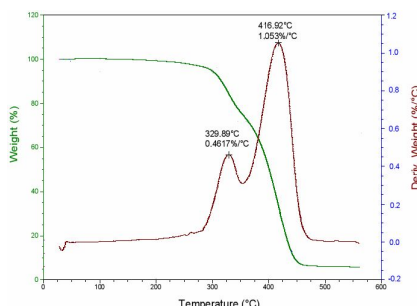


Fig. 1 TG and DTG curves of waste TV set housing material in N₂(10°C/min)

TV housing used for this present work was manufactured from HIPS, which is generally composed of polybutadiene (PB phase) and polystyrene (PS phase), However, Fig.2 shows that the TG curve of pure HIPS resin only display a single stage, this proved that two weight loss stages of TV housing plastic should not result from the different thermal stability of two phases of HIPS. The activation energies and reaction orders of the degradation reactions in the two stages can be calculated according to Friedman method by determining the TG curves under different heating rates, the calculating results listed in Tab. 1.

Tab.1 Kinetic parameters of thermal degradation of TV housing plastic

temperature /K	Linear equation	Average activation energy $E/(kJ \cdot mol^{-1})$	Reaction order n
290~350	$y=-18.03x+26.29$	149.87	0.11
350~455	$y=-26.45x+35.25$	219.98	1.2

The kinetic study results in Tab.1 show that the activation energy and reaction order in two stages are different, this clearly indicates that the two weight loss stages are respectively controlled by the different chemical reaction mechanism. The activation energy in the first stage is significantly smaller than the second stage, thus it is deduced that the activation energy in the first stage may reflect the thermal degradation of lower thermostability compounds, and activation energy in the second stage may reflect higher thermostability compounds. It is known that C-C and C-H bond of HIPS are more stable than C-Br bond of brominated flame retardants, the experimental results from Nona[7] also showed that Deca-BDE can start to decompose at about 300 °C with the presence of Sb₂O₃.Therefore, it

can be concluded that weight loss in the first stage is mainly related to the evaporation of additives and flame retardants, and the weight loss in the second stage is mainly related to the degradation of more stable HIPS, the activation energy number of the later is also close to the activation energy of HIPS degradation in literatures published[8].

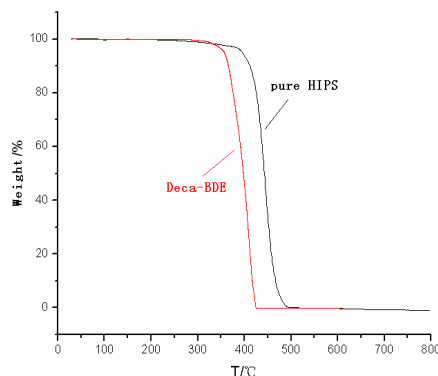


Fig. 2 TG curves of Deca-BDE and HIPS in N₂ (10°C/min)

Fig. 2. shows the initial weight loss temperature of Deca-BDE is lower about 50°C than pure HIPS, but the initial weight loss temperature of pure HIPS is higher than 350°C, whereas HIPS in the TV housing has started to degrade at below 350°C. there may be two reasons, the first is that the aging of HIPS reduced the thermal stability due to the long term service of TV set; the second is that the thermal chemical reaction of flame retardants change the degradation mechanism of HIPS and caused partly degrading of HIPS at a lower temperature. This shows that the degradation behavior of waste TV housing plastic is very different from pure HIPS resin.

2.2 The weight loss under isothermal conditions

The TG analysis of waste TV housing indicated that the decomposition temperature of Deca-BDE is lower than HIPS resin, if the thermal treatment temperature is controlled at below the decomposed temperature of HIPS, it is possible to separate Br from the waste TV housing plastic. The isothermal TG curves of pure HIPS, Deca-BDE and TV housing plastic at 280°C are shown in Fig.3. it could be seen from Fig.3 that the weight loss of the waste TV housing plastic reached about 14wt%, which obviously exceed about 2.5wt% of weight loss of pure HIPS, and was more closed to weight loss of Deca-BDE. the experimental results indicate Br-FR containing in TV housing can be prior to degrading of HIPS polymer matrix, that is to say, under the suitable isothermal condition, Br-FR can be first released from TV housing plastic, and it can be avoid severely degrading of HIPS at the same time.

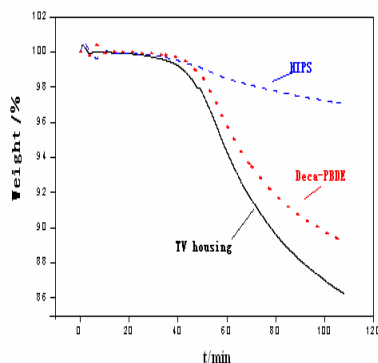


Fig.3 TG curves of virgin HIPS and waste TV housing material under isothermal condition at 280°C

2.3 Separating bromine from TV housing plastic

Polybrominated diphenyl ethers have the characteristics of high boiling point and low volatility, it is not easy to separate them from the polymer matrix by evaporating under atmospheric pressure, however, the evaporating of PBDEs can be accelerated in a vacuum condition. The removal rates of PDBEs at different temperature were investigated by a tube pyrolyzing furnace under vacuum, the experimental results are shown in Fig. 4.

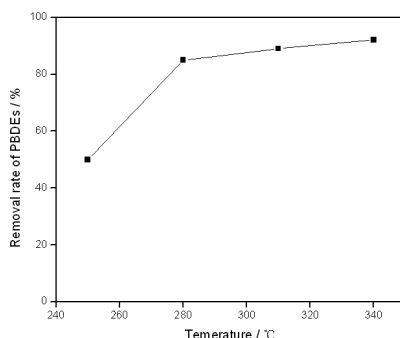


Fig.4 Removal rate of PBDEs in the housing plastic under isothermal condition and vacuum

The results show that both the releasing rate of PBDEs increased with elevating of the thermal treatment temperature, over 90wt% of PBDEs can be removed if the treatment temperature exceeds 280°C, but the weight loss of the samples will obviously increased when the thermal treatment temperature was higher than 300°C, Therefore the separating temperature should be controlled below 300°C to reduce decomposition extent of HIPS matrix.

3. Conclusion

(1) TG curve of the TV housing plastic was divided into two obvious different stages, the first stage(280°C~ 350°C) reflect the thermal degradation of of the flame retardants and

the small part of HIPS resin, which activation energy is about 150kJ/mol; the second stage (350°C~ 450°C) is associated with thermal degradation of HIPS , which activation energy is about 210kJ/mol.

(2) Over 90% of decabromodiphenyl ether can be firstly released from the waste TV housing plastic under isothermal (> 280°C) and vacuum(<5kPa), but HIPS matrix will suffer significant degradation if thermal treatment temperature is beyond 300°C.

Acknowledgements

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