Pyrolysis of municipal plastic waste: Chlorine distribution and formation of organic chlorinated compounds

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1. Introduction

It was anticipated that approximately155-265 Mt/y of municipal plastic waste (MPW) would be generated globally in 2060, therefore it is urgent to develop efficient and economical methods for MPW treatment (Cudjoe et al., 2023). Pyrolysis is considered the most promising MPW treatment technology and has attracted widespread attention (Faisal et al., 2023). In particular, pyrolytic oil emerges as the principal pyrolysis product has a significant potentiality in substitution of petrochemicals and fuel (Chang, 2023). However, organic chlorinated compounds are generated due to the presence of polyvinyl chloride (PVC) during MPW pyrolysis, which threatens the environment seriously (Ren et al., 2022). Besides, chlorine also has a significant impact on oil quality, and the maximum tolerance for chlorine is set at just 10 ppm by the petrochemical industry (Park et al., 2022). The composition of MPW is extremely complex, making it challenging to achieve accurate classification, and previous studies have rarely focused on actual MPW pyrolysis, which is unhelpful to the treatment of MPW (Snow et al., 2023; Lu et al., 2023). Therefore, it is urgent to study the chlorine release characteristics and the formation of organic chloride compounds during actual MPW pyrolysis for the regulation of chlorine-containing pollutants.

2. Material and methods

The fresh mixed waste was collected from the treatment plant in Shanghai, and then the waste plastics (included PE, PP, PS, PVC, and PET) were selected as the raw materials for this study. In the co-pyrolysis experiment, the pure PVC and PET powders were produced by Aladdin Co., Ltd. TG-FTIR was used to analyze the pyrolysis behavior of MPW, including weight loss and release characteristics of volatiles. The effect of temperature (300-500 °C) on chlorine thermal behavior was further investigated via a fixed bed reactor during MPW pyrolysis. The released HCl was captured by 0.2 M NaOH solution (500 mL). Combustion coupled ion chromatography (IC) method was used to determine the chlorine content of raw MPW, char and liquid products.

3. Results and discussion

The chlorine content in MPW was only 2.11%, which was significantly lower than the weight loss of stage II (10.52 %) (Fig. 1a). It was indicated that chlorine was mainly released in stage II in the form of HCl and organic chlorinated compounds during the pyrolysis of MPW. After MPW pyrolysis, chlorine was mainly distributed in gas and char, which were 74.34-82.89% and 10.17-21.29%, respectively (Fig. 1b).

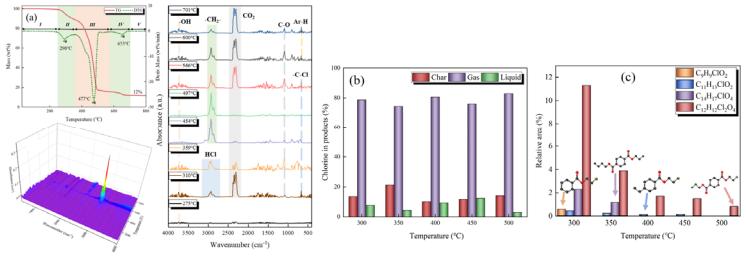

Fig.1. (a) TG-FTIR analysis, (b) chlorine distribution and (c) composition of organic chlorinated compounds.

There was 3.02-12.32% of chlorine distributed in liquid products. In addition, it was discovered that chlorine

release was inhibited due to the melting behavior at <350 °C. Apparently, the composition and relative content of organic chlorinated compounds exhibited a significant decrease with increasing temperature, which decreased from 14.55% (300 °C) to 0.80% (500 °C). Besides, it was observed that terephthalic acid, di(2-chloroethyl) ester was identified as the dominant organic chlorinated compounds with relative contents of 0.80-11.29%. Therefore, it was speculated that PET was the main contributor to the formation of organic chlorinated compounds during MPW pyrolysis.

The co-pyrolysis of PVC (50%) and PET (50%) was investigated to further elucidate the formation of chloroesters. It can be concluded that the decomposition temperature of PET was decreased from 390 °C to 308 °C due to the promotion of HCl during the co-pyrolysis. It was clear that terephthalic acid, di(2-chloroethyl) ester was the predominant organic chlorinated compound (58.08%), which was consistent with the result of MPW pyrolysis.

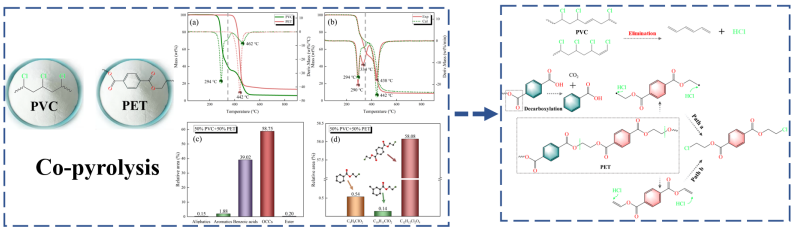

Fig. 2. Potential formation pathways of terephthalic acid, di(2-chloroethyl) ester.

4. Conclusion

This research studied the migration of chlorine during MPW pyrolysis. Chlorine was mainly released in stage II (241-353 °C) in the form of HCl and organic chlorinated compounds. As the temperature increased (300-500 °C), chlorine concentration (9988-838 ppm), relative content (14.55-0.80%) and types of organic chlorinated compounds were all reduced. Besides, terephthalic acid, di(2-chloroethyl) ester was dominant over other organic chlorinated compounds during the pyrolysis of MPW, and its generation was mainly attributed to the chlorination of micromolecule organics produced from the thermal decomposition of PET.

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