

TEMPERATURE DEPENDENT PYROLYTIC PRODUCT EVOLUTION PROFILE FOR POLY (ETHYLENE TEREPHTHALATE)

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Abstract

The structure and purity of the plastics used in the degradation experiments decide the type of products obtained therefrom. A concurrent study of products distribution and the underlying reaction mechanism of their degradation, helps one to understand the pyrolysis behavior of plastics better. In this work, a detailed gas chromatographic study of pyrolysis products of poly (ethylene terephthalate) (PET) is carried out in the temperature range of 200-600°C. The pyrograms have been analyzed in terms of mole fractions of different products evolved at various pyrolysis temperatures. At low temperatures (200-300°C), yield of lighter hydrocarbons (C5-C10) is low. It gradually increases until maximum decomposition temperature (446°C) and decreases thereafter. PET degradation can be explained by two possible routes viz., ionic and radical mechanism. At low temperature it proceeds mainly by ionic mechanism. The following reaction types are considered to explain its degradation mechanism: (a) heterolytic main chain cleavage to form olefin-end and acid-end structure; (b) intra or intermolecular ester-interchange reactions to yield cyclic oligomers; (c) intramolecular hydrogen transfer to form volatile products and regeneration of the acid-ends or, olefin-ends; (d) decarboxylation and intramolecular elimination of compounds like acetaldehyde and acetylene; and (e) hydrogen abstraction and acetylene addition (HACA) mechanism for the formation of polycyclic aromatic hydrocarbons (PAH).

Keywords: gas chromatography (GC); poly (ethylene terephthalate) (PET); product analysis; pyrolysis; thermogravimetric analysis (TGA)

1. Introduction

With the increase in consumption of PET in the packaging sector, there is a parallel increase in the volume of waste PET. This has triggered the importance of study of pyrolysis of PET, which can convert the plastic to valuable hydrocarbons. The structure of PET indicates possibility of production of significant amount of aromatic hydrocarbons as well as PAHs. Literature reports that decomposition of PET produces about the same quantities of gas and liquid with a proportion of solids around 10% [1,2]. The gases contain carbon oxides (nearly 90%) [1]. In the oils, benzene and toluene are the major products [2]. Montaudo *et al.* reported formation of cyclic oligomers by doing structural characterization of the products obtained by isothermal degradation of PET in the temperature range of 270-370°C [3].

In this study, we have carried out degradation of PET in a TGA and analyzed the product in a GC equipped with FID detector. We have monitored the product evolution (C5-C44) at six different temperatures from 200°C (where there is a negligible product formation) through 600°C (end of degradation). The GC results were used to study the product distribution and correlate the same with the decomposition mechanism.

2. Materials and Methods

PET used in the study was virgin PET (AS-40 bottle grade) supplied by South Asian Petrochem Limited, India. It has a melting point of 248.4°C, heat of fusion of 44.91 J/g and a percentage crystallinity of 39.05%.

Degradation experiments were carried out in a TGA in an inert environment at a heating rate of 10°C/min. Once the sample reached the desired temperature (200, 300, 400, 435 (maximum degradation temperature, T_{max}), 500 or 600°C), 1 ml of the evolved sample was collected and injected into the GC. Calibration of the GC is done using two reference petroleum standards (ASTM D3710 and ASTM D5442) containing 27 known hydrocarbons (C5-C44). Mole fractions of the eluent hydrocarbons were calculated using the response factors obtained from the calibration procedure.

3. Results and Discussion

A typical derivative thermogravimetric (DTG) curve for rate of degradation $\frac{d\alpha}{dT}$ of PET is shown in Figure 1. It is

evident from this figure that degradation of PET occurs over a wide temperature range, and T_{max} for PET is around 435°C.

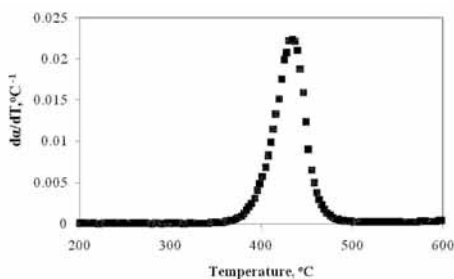
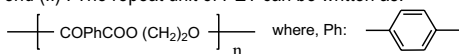


Fig. 1. DTG curve for PET

GC analysis reveals a change in the evolution pattern of hydrocarbons with temperature (Figure 2). PET falls under the category of condensation polymers, decomposition pathways of which are dominated by the polarity and reactivity of the functional groups, and at low temperature it essentially degrades by ionic (heterolytic) mechanism (scheme 1) forming acid end(I) and olefin end (II). The repeat unit of PET can be written as:



As depicted in Figure 2, at low temperature (200-300°C), C5-C10 produced is insignificant, which could be attributed to the extra stability of PET due to resonance stabilized structures in the chain backbone. The higher

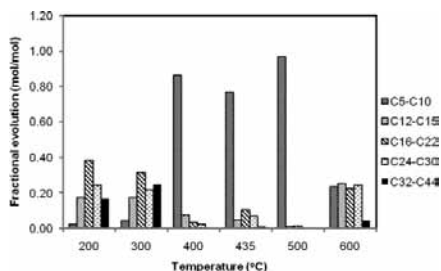
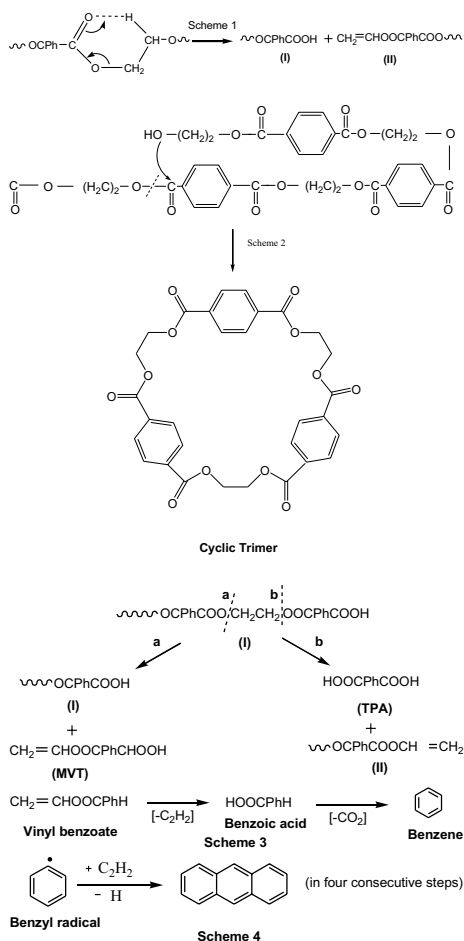


Fig.2. Temperature dependency of the evolved products (C5-C44) from PET

hydrocarbons detected might correspond to the linear and cyclic dimers (C20) and trimers (C30), which could be present in the PET chain. Moreover, intramolecular ester exchange reactions might also lead to their formation (scheme 2). As the temperature approaches T_{max} , significant evolution of C5-C10 is observed. Given the structure of PET, benzene, toluene, terephthalic acid (TPA), monovinyl terephthalate (MVT) would be the major products, formed by β -CH hydrogen transfer (scheme 3). Beyond 500°C, relative yield of first three fractions is more or less the same, while C32-C44 fraction is almost insignificant. In all the TGA experiments, a black residue is obtained, which could be due to the formation of PAHs, which are fused aromatic rings. Their formation is likely at high temperature (at or above 400°C) by HACA mechanism (scheme 4).



4. Conclusions

Products obtained from pyrolysis of PET range from simple acetylene molecules to complex PAHs. Its thermal degradation mainly occurs by ionic mechanism. However, at high temperature radical reactions are likely to occur. Temperature plays a crucial role. At T_{max} , maximum evolution of volatiles are observed. Benzene, MVT, TPA are the major products obtained at T_{max} .

References

- [1] Williams P.T. and Williams E.A. Recycling of plastic waste by pyrolysis. J. Inst. Energy 71 (1998) 81-93.
- [2] Kaminsky W. and Sinn H. In: Brandrup B.M.; Menges G. (eds). Recycling and Recovery of Plastics, pp. 434, Munich: Hansen, 1996.
- [3] Samperi F., Puglisi C., Rossana A., Montaudo G. Thermal degradation of poly(ethylene terephthalate) at the processing temperature. Polym. Degrad. Stab. 83 (2004) 3-10.