

Temperature Dependent Pyrolytic Product Evolution Profile for Binary Mixtures of Low density polyethylene and Poly (ethylene terephthalate)

Ujwala Hujuri¹, Alope K. Ghoshal², and Sasidhar Gumma^{2*}

¹Department of Chemical Engineering, Assam Engineering College,
Guwahati, INDIA 781013

²Department of Chemical Engineering, Indian Institute of Technology
Guwahati, Guwahati, INDIA 781039
email: s.gumma@iitg.ernet.in

Abstract

The present work aims at evaluating temperature dependency of product evolution from pyrolysis of binary mixtures of low density polyethylene (LDPE), and polyethylene terephthalate (PET). Product distribution studies have been reported for three different mixture compositions (20:80, 50:50, and 80:20) in the temperature range of 300-600°C, for a wide range of hydrocarbon products (C5-C44) and the same has been explained with mechanistic pathways of decomposition. The pyrograms have been analyzed in terms of mole fractions of different products evolved at various pyrolysis temperatures. Enhancement in the production of lighter fractions also support this observation. The following reaction types are considered to explain the degradation mechanism of the mixtures: (a) heterolytic cleavage of PET to generate acid ends and olefin ends; (b) homolytic cleavage of LDPE to generate free radicals; (b) attack of these free radicals on PET fragmented chain; (c) intramolecular and intermolecular hydrogen transfer to form volatile products, oligomers and regeneration of radicals, acid-ends or, olefin-ends.

Keywords: pyrolysis; gas chromatography (GC); poly (ethylene terephthalate) (PET); low density polyethylene (LDPE)

1. Introduction

Pyrolysis of plastics results in the production of liquid and gaseous hydrocarbons, which have remarkable potential to be upgraded to fuels or petrochemical feedstock. Interaction between the constituent plastics is a very important aspect to be considered to examine the efficacy of any commercial pyrolysis process involving mixed plastics. This is due to the fact that interaction between the fragmented chains and radicals of the component plastics at the prevailing high temperature of pyrolysis might lead to a different product distribution from that of their single component pyrolysis. In our earlier study, interaction between the plastics was observed in their thermal decomposition experiments [1]. The concept behind the present investigation is to enumerate the interaction between LDPE and PET in terms of product evolution from their pyrolysis. In this study, we have carried out degradation of binary mixtures of LDPE and PET in a Thermo Gravimetric Analyzer (TGA) and analyzed the products in a Gas Chromatograph (GC) equipped with FID detector. We have monitored the product evolution (C5-C44) at five different temperatures from 300-600°C. 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%. LDPE was obtained from National Chemical Limited, Gujarat, India. It has a melt flow index of 5.13 and melting point of 126.9°C.

Binary degradation experiments for three different compositions (20:80, 50:50, 80:20) of the mixtures 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 (300, 400, degradation, T_{max} (temperature corresponding to the maximum rate of decomposition), 500 or 600°C), 1 ml of the evolved sample was collected and injected into the GC. Calibration of the GC was 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

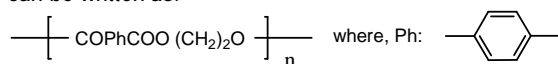
The characteristic T_{max} for the single plastics and their binary mixtures are listed in Table 1. PET is thermally less stable of the two, which could be due to the presence of two heterogeneous linkages between O and C in its backbone [1]. It can be seen that addition of PET

has resulted in an enhancement in the overall decomposition process.

Table1. T_{max} for the single and the mixed plastics

LDPE (%)	PET (%)	T_{max} (°C)
-	100	435
20	80	434
50	50	439
80	20	459
100	-	470

Figure 1 compares the evolution pattern of hydrocarbons obtained from the plastics (50:50 composition), as temperature changes from 300°C to T_{max} . It is worthwhile to see that T_{max} of the mixtures is a function of composition of the single plastics. The repeat unit of PET can be written as:



LDPE is an aliphatic polymer having the repeat unit

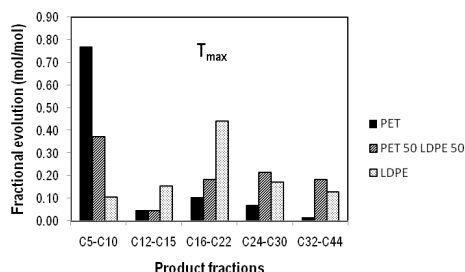
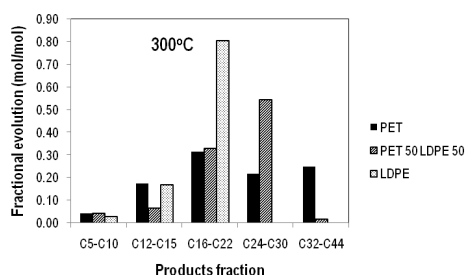
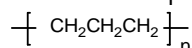


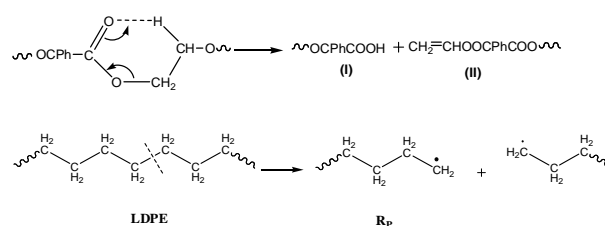
Fig.1. Fractional evolution of the products for the plastics at 300°C and T_{max}

PET is a condensation polymer which essentially decompose by ionic (heterolytic) mechanism forming acid end (I) and olefin end (II); whereas, LDPE is an addition polymer which decompose by free radical mechanism resulting into two primary radicals (R_p) (Scheme 1). R_p formed by random scission of LDPE might abstract a hydrogen from methylene group of the acid end, transferring the radical center to the PET fragmented chain (Scheme 2). Thus, PET can undergo radical reactions at a relatively lower temperature in presence of LDPE, which is otherwise possible only at a higher temperature (at or above 400°C). The radical (III), thus generated can undergo β -CH hydrogen transfer giving rise to terephthalic acid (TPA). Acid end, II is

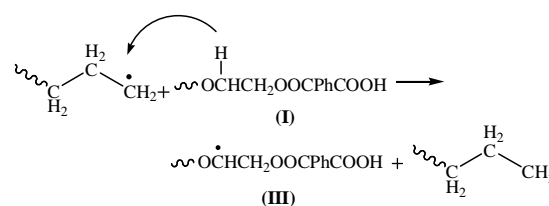
regenerated in the process. Decarboxylation of TPA leads to the formation of benzoic acid, which on subsequent decarboxylation gives benzene (Scheme 3).

At 300°C, relative yield of higher hydrocarbons (C16 and above) are more in PET as compared to C5-C10 fraction, whereas C16-C22 is the major fraction for LDPE.

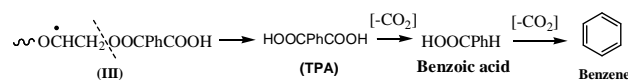
At T_{max} , yield of C5-C10 fraction is more in case of the mixture than that from LDPE alone, which could be justified by the possible interaction between the radicals and the fragmented chains of the constituent plastics in the mixture. The major products obtained from the mixtures are likely to be isopentane, pentene, benzene, benzoic acid and a host of other aliphatic and aromatic hydrocarbons.



Scheme 1



Scheme 2



Scheme 3

4. Conclusions

Pyrolysis of the binary mixtures of PET and LDPE is a function of temperature as well as the mixture composition. Proper selection of operating temperature and mixture composition is thus essential for efficient design of a pyrolysis procedure of a mixture to have desired yield of value added products.

References

- [1] Hujuri U., Ghoshal A.K., Gumma S., Modeling pyrolysis kinetics of plastic mixtures. *Polym. Degrad. Stab.* 93 (2008) 1832-1837.