

TEMPERATURE DEPENDENT PYROLYTIC PRODUCT EVOLUTION PROFILE FOR BINARY MIXTURES OF POLY (ETHYLENE TEREPHTHALATE) AND POLYPROPYLENE

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Abstract

Pyrolysis of mixed plastics is a very complex phenomenon, and the feed composition as well as the structure of the component plastics have a pronounced effect on their degradation products. Interaction between the fragmented chains and radicals of the component plastics at the prevailing high temperature of pyrolysis leads to a different product distribution from that of their single component pyrolysis. In the present work, detailed gas chromatographic studies on pyrolysis products of binary mixtures of poly (ethylene terephthalate) (PET) and polypropylene (PP) are reported in the temperature range of 300-600°C. The pyrograms have been analyzed in terms of mole fractions of different products evolved at various pyrolysis temperatures. Synergistic effects are evident from the fact that addition of PET to PP, enables its degradation at a relatively lower temperature. 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 PP 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: mixtures; gas chromatography (GC); poly (ethylene terephthalate) (PET); polypropylene (PP); pyrolysis

1. Introduction

A vast amount of work in plastics pyrolysis has been reported in the literature and research is continuously growing in search of innovative ways to narrow down product distribution to the desired range by appropriate selection of operating parameters, catalyst etc. Westerhout *et al.* observed that polymer mixtures behave quite similarly to pure polymers and claimed that additivity rule is the correct approach to the problem [1]. However, interactions between the component plastics cannot be completely ruled out. This is a very important aspect to be considered to examine the efficacy of any commercial pyrolysis process. The concept behind the present investigation is to enumerate the interaction between PET and PP in terms of product evolution from their pyrolysis. In this study, we have carried out degradation of binary mixtures of PET and PP in a Thermo Gravimetric Analyzer (TGA) and analyzed the products in a 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%. PP (Trade Name: Koylene ADL AS030N) was obtained from Indian Petrochemicals Corporation Limited, Vadodara, India. It has a melt flow index of 3.0, melting point of 175.6°C, heat of fusion of 62.38 J/g and a percentage crystallinity of 32.83.

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, 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 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.

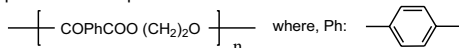
3. Results and Discussion

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 [2]. Difference between their thermal stability is not much; nonetheless addition of PET has resulted in an enhancement in the overall degradation process.

Table 1. T_{max} for the single and the mixed plastics

PP (%)	PET (%)	T_{max} (°C)
-	100	435
20	80	432
50	50	434
80	20	440
100	-	446

Figure 1 compares the evolution pattern of hydrocarbons obtained from single plastics with one of their binary mixtures (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:



PP is an aliphatic polymer having the repeat unit

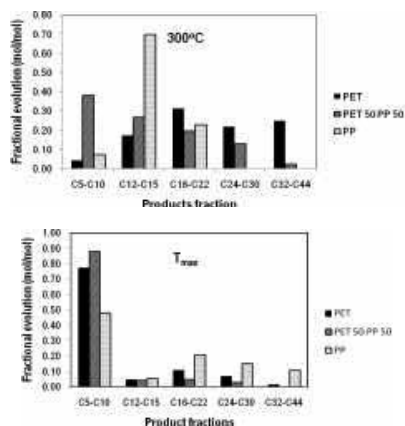
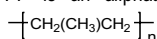
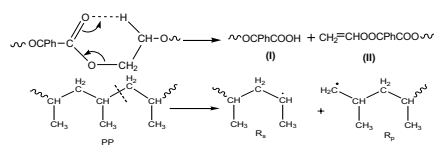


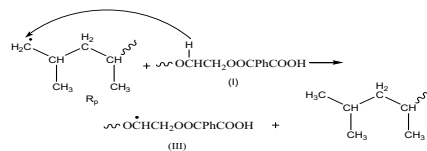
Fig. 1. Fractional evolution of the products for the plastics at 300°C and T_{max}

PET is a condensation polymer which essentially degrade by ionic (heterolytic) mechanism forming acid end(I) and olefin end (II); whereas, PP is an addition polymer which degrade by free radical mechanism resulting into a primary radical (R_p) and a secondary radical (R_s) (Scheme 1). R_p formed by random scission of PP 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 PP, 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) and 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 (C12 and above) are more in PET as compared to C5-C10 fraction, whereas C12-C15 is the major fraction for PP.

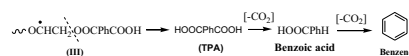
It is evident from the figure that evolution of C5-C10 hydrocarbons are enhanced in the mixture as compared to the single plastics. At T_{max} , relative yield of C5-C10 fraction is the highest for the mixture, which could be justified by the possible interaction between the radicals and the fragmented 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

The CSBR is suitable for obtaining high yields of liquid at moderate temperatures. Temperature has an important effect on product distribution by increasing the aromatization of the volatile fraction and the gas yield. Moreover, the quality of the solid fraction (adulterated carbon black) is improved by operating at high temperatures. The liquid fraction is of suitable quality for its use as fuel or it can be an interesting feedstock for a refinery, especially for the hydrocracking process. Pyrolysis oil contains interesting products in high concentrations depending on the operating conditions, such as limonene.

References

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