

Composition of Products from the Pyrolysis of a Polypropylene/Polystyrene Mixture

Paul T. Williams* and Elizabeth A. Williams

Department of Fuel and Energy, The University of Leeds, Leeds LS2 9JT, UK

E-mail: p.t.williams@leeds.ac.uk FAX: +44-1132440572

Polystyrene (PS) and polypropylene (PP) were pyrolysed in a fixed bed reactor at 700 °C, in addition, a 1:1 mixture of PS/PP was pyrolysed to final temperatures of 500, 550, 600, 650 and 700 °C. The yield and composition of the derived oils and gases was determined in relation to pyrolysis temperature and compared with pyrolysis of the individual PS and PP. The main pyrolysis gases produced were hydrogen, methane, ethane, ethene, propane, propene, butane and butene. Gas yield was increased for the mixture and there was a marked increase in gas yield with increasing temperature of pyrolysis. The molecular weight range of the oils was influenced by the interaction of the PS and PP. Detailed analysis of the derived oils for PS and PS/PP showed that they contained high concentrations of styrene and styrene oligomers which decreased with increasing pyrolysis temperature. Other single ring compounds identified included, benzene, toluene, xylenes, indane and indene. Polycyclic aromatic hydrocarbons including naphthalene, fluorene, phenanthrene and their alkylated derivatives were also found in significant concentrations in the derived oils.

Introduction

Feedstock recycling of waste plastic has been proposed as a process to produce basic petrochemicals that can be used as feedstock to make virgin plastic or refined fuels [1-3]. Pyrolysis is a feedstock recycling process which shows considerable potential and involves the thermal degradation of the waste plastic in an inert atmosphere to produce an oil/wax with potential uses in the petrochemicals industry [4-8]. The process also produces a hydrocarbon rich gas with a high calorific value which may be used to provide the energy requirements for the pyrolysis process. The process has the advantage that mixed plastics can be used since all of the feedstock is reduced to petrochemicals. Polypropylene (PP) and polystyrene (PS) occur in high concentrations in municipal solid waste, they also occur as the main two plastics in the waste from large entertainment events. However, there are few data on how plastic types interact with each other in mixtures and the influence of pyrolysis process conditions on product yield and composition. In this paper, PS and PP and a 1:1 mixture of PS/PP have been pyrolysed in a fixed bed reactor and the yield and composition of the products determined.

Materials and Methods

The plastics used were polystyrene (PS) and polypropylene (PP) which were obtained from BP Chemicals Ltd., Grangemouth, UK and were virgin plastics of 2 - 5 mm diameter pellets. The plastic sample was placed in a crucible inside the fixed bed pyrolysis reactor.

The fixed bed pyrolysis reactor consisted of a 200 cm³ stainless steel reactor externally heated by an electric ring furnace and continuously purged with nitrogen [9]. The samples

were heated at a fixed heating rate of 25 °C min⁻¹ to the final pyrolysis temperature, which was 700 °C for PS and PP and 500, 550, 600, 650 and 700 °C for the PS/PP 1:1 mixture. The sample was held at the final temperature for one hour or until there was no significant yield of gas. The liquid oil/wax phase was trapped in a series of cold condensation traps. The gas effluent from the condenser system was collected in a 100 litre Teflon gas sample bag which was sealed and analysed immediately for a range of gases.

Gas analysis consisted of off-line packed column gas chromatography using three separate gas chromatographs which were used to analyse for, hydrocarbons up to C₄, hydrogen, carbon monoxide, nitrogen, oxygen and carbon dioxide [5,9].

The molecular weight (MW) distribution of the derived oil/wax samples was determined via size exclusion chromatography [5,9]. The calibration system used was based on polystyrene samples of low polydispersity in the MW range of 800 to 860 000, also included was benzene for low MW calibration. The detectors were an ultra-violet (uv) detector from Merck-Hitachi and a refractive index (RI) detector from Varian.

The oil/wax derived from the pyrolysis of the plastics were analysed in detail for their content of aromatic and aliphatic compounds. The oil/wax were separated by liquid chromatography into chemical class fractions followed by gas chromatography/flame ionisation detection and confirmation of identification by gas chromatography/mass spectrometry [5].

Results and Discussion

Table 1 shows the yield of products from the pyrolysis of PS, PP and a PS/PP mixture in relation to pyrolysis temperature, PP gave a light coloured waxy product, whereas PS produced a red/brown oil, the mixture gave a light yellow coloured oil. The amount of oil yield was high illustrating the potential of pyrolysis to produce a petrochemical feedstock.

Table 1. Product yield from the fixed bed pyrolysis of PS, PP and a PS/PP mixture in relation to final pyrolysis temperature (wt%).

Plastic/Temperature	Gas	Oil	Char
PS (700 °C)	2.33	83.77	3.50
PP (700 °C)	13.63	84.44	0.15
PS/PP (500 °C)	5.44	84.20	0.03
PS/PP (550 °C)	8.15	85.19	0.19
PS/PP (600 °C)	6.18	85.65	0.29
PS/PP (650 °C)	5.85	84.82	0.29
PS/PP (700 °C)	16.04	83.93	0.35

The mixture of PS/PP was a 1:1 mixture, consequently the gas yield (at 700 °C) would be expected to be the mean of the individual PS and PP pyrolysis gas yields, however, the results show that there was a clear interaction of the plastics to produce a much higher than expected gas yield. Koo *et al.* [6] pyrolysed mixtures of PS with a polyalkene plastic, HDPE and also showed evidence of interaction of the plastics.

PP produced a much higher gas yield than PS and table 2 shows that the main gases were, the alkene gases ethene, propene and butene, derived from the thermal degradation of the

polyalkene polymer chemical structure. The random scission process of the polymer during pyrolysis coupled with stabilisation of the resultant radical leads to the formation of carbon double bonds and hence this results in a tendency of the thermal degradation process to yield alkenes as the major product [10-12]. The alkane gases, methane, ethane, propane and butane were also present in significant concentrations, again formed as part of the random scission process of the thermal degradation of the polymer. PS gave a low total gas yield which consisted mainly of alkene gases, ethene, propene and butene and also methane. The PP/PS mixture gave gases somewhat higher than expected, producing higher concentrations of the alkene gases, most noticeably, butene. As the temperature of pyrolysis was increased, the concentrations of individual gases increased.

Table 2. Gas composition from the fixed bed pyrolysis of PS, PP and a PS/PP mixture in relation to final pyrolysis temperature (wt%).

Plastic/Temperature	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	C ₄ H ₁₀	C ₄ H ₈
PS (700 °C)	0.04	0.53	0.08	0.26	0.02	0.05	0.00	0.06
PP (700 °C)	0.05	0.93	1.45	3.52	1.00	3.53	0.23	1.29
PS/PP (500 °C)	0.04	0.18	0.38	0.21	0.15	2.56	0.06	0.98
PS/PP (550 °C)	0.04	0.38	0.38	0.23	0.19	2.77	0.06	1.26
PS/PP (600 °C)	0.04	0.19	0.31	0.25	0.18	2.39	0.06	1.16
PS/PP (650 °C)	0.05	0.24	0.48	0.32	0.16	2.91	0.07	0.92
PS/PP (700 °C)	0.19	1.11	1.12	2.82	0.69	2.81	0.21	5.26

Figure 1 shows the molecular weight (MW) range of the oil/wax derived from the pyrolysis of PS, PP and a mixture of PS/PP at 700 °C final pyrolysis temperature. The results are shown for both RI and uv detectors. The use of two detectors enables more information to be obtained from the system. Whilst both detectors will detect the full range of hydrocarbons, whether aliphatic or aromatic, the uv may be tuned to an optimum wavelength to give an enhanced signal for aromatic compounds. The oil produced from PS gave a MW range from a nominal 60 to about 800 Da. whilst the wax from PP produced a MW range from 100 to 1200 Da. There were two distinct MW regions, peaking at about 100 Da and 150 Da. for PS and 130 Da. and 1000 Da. for PP. Both RI and uv detector responses were recorded, suggesting that a range of both aliphatic and aromatic compounds were present in the oil/wax. The mixture of PS/PP produced a MW distribution which was similar to that produced for PS alone. The interaction of PP with PS producing a distinct reduction in the MW range of the compounds produced for PP. This was also demonstrated by the physical appearance of the product which was a light wax for PP but an oil when PS and PP were pyrolysed together, again suggesting interaction of the two plastics. Table 3 shows the detailed analysis of the oil derived from pyrolysis of PS and the wax derived from PP. The oil from the pyrolysis of PS was a mainly aromatic product dominated by styrene and styrene oligomers. In addition, the oil/wax contained a significant proportion of benzene, toluene, xylenes and alkylated benzenes, indene and indane. Polycyclic aromatic hydrocarbons, including, naphthalene, fluorene and phenanthrene and their alkylated derivatives were also detected.

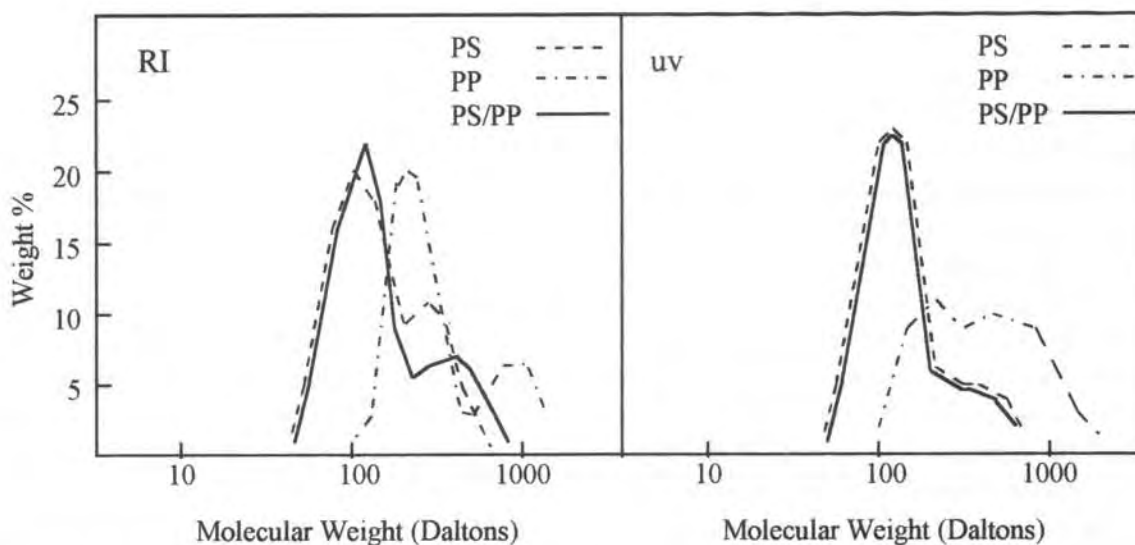


Figure 1. Molecular weight range of oil/wax derived from the pyrolysis of PS, PP and a mixture of PS/PP.

The wax derived from the pyrolysis of PP gave an almost exclusively aliphatic product consisting of a series of triplet peaks of alkanes, alkenes and alkadienes up to C_{53} . The molecular weight distribution of the oil/wax discussed previously has shown that much higher molecular weight compounds were present in the oil/wax but were unable to be analysed by the gas chromatography system. No aromatic compounds were detected. The pyrolysis of the PP/PS mixture resulted in an oil which was mainly aromatic, but also contained the characteristic alkanes, alkenes and dienes derived from PP pyrolysis. The dominant species were styrene and styrene oligomers. In addition, other aromatic compounds were present, for example, benzene, toluene, xylenes, and naphthalene, fluorene, and phenanthrene and their alkylated derivatives. There was evidence of interaction of the plastics as increased aromatic concentrations were found, in particular alkylated aromatic compounds. Koo *et al.* [6] also showed that mixing of a polyalkene plastic with PS resulted in a change in product composition compared to pyrolytic products from the individual plastics pyrolysed singly. The influence of increasing the pyrolysis temperature from 500 to 700 °C for the PS/PP mixture was to decrease the concentration of styrene and styrene oligomers and also toluene.

Table 3. Compounds identified in PS and PP oil/wax.

Plastic/Temperature	Compounds Identified
PS (700 °C)	styrene, styrene dimer, benzene, toluene, xylene, indane, indene, biphenyl, C_1 - C_4 - naphthalene, acenaphthene, fluorene, pyrene C_1 - C_2 - fluorene, phenanthrene, C_1 - phenanthrene, chrysene
PP (700 °C)	C_8 - C_{53} diene, C_8 - C_{53} alke-1-ene, C_8 - C_{53} alkane

The oil/wax derived from the pyrolysis of PS, PP and the mixture of PS/PP has the potential to provide a feedstock for the petrochemical industry. The pure aliphatic wax produced from PP may be used as a feedstock for a conventional steam cracker in the production of ethene and other alkenes used to produce plastic polymers [5]. The use of the derived pyrolysis wax for the steam cracker process depends on their purity with highly aromatic feedstocks being less desirable since they are thought to lead to increasing coking rates in the process. The wax produced from PP pyrolysis showed no aromatic compounds present. The pyrolysis of PS produced a high conversion to styrene and other single ring aromatic compounds. These aromatic compounds have a significant commercial value and are used in a wide variety of applications. The mixture of PS/PP produced an oil which contained a range of aliphatic and aromatic compounds which may represent a difficult mixture to process and consequently limited commercial potential. In addition, the oil from PS and the oil from the mixture of PS/PP contained polycyclic aromatic hydrocarbons some of which have been shown to be biologically hazardous and which may represent potential difficulties in handling and processing the oils.

Conclusions

The pyrolysis of PS, PP and a mixture of PS/PP produces potentially valuable process feedstocks. PP pyrolysis produced an aliphatic wax with no aromatic compounds, suitable for processing to produce virgin plastics. PP produced a highly aromatic oil containing significant concentrations of single ring aromatic compounds from PS. The PS/PP mixture contained both aliphatic and aromatic compounds representing a difficult and complex mixture to process commercially. The oils from PS and the mixed PS/PP contain polycyclic aromatic hydrocarbons which represent a potential adverse impact on the process and the environment. There was evidence of interaction of the plastics in the mixture, producing changes in composition of the oil and gases.

References

1. Williams, P.T., *Waste Treatment and Disposal*, John Wiley and Sons, Chichester, UK, 1998
2. Lee, M. *Chemistry in Britain*, Royal Society of Chemistry, July, 1995, 515.
3. Kaminsky W., Kim, J-S., ., *J.Anal.Appl.Pyrol.*, 1999, **51**, 127-134.
4. Scott D.S., Czernik S.R., Piskorz J. and Radlein D., *Energy & Fuels*, 1990, **4**, 407-411.
5. Williams P.T. and Williams E.A., *J.Anal.Appl.Pyrol.*, 1999, **51**, 107-126.
6. Koo J.K., Kim S.W. and Seo Y.H., *Resources, Conserv. Recycl.*, 1991, **5**, 365-382.
7. Kaminsky W., *J. Anal. Appl. Pyrol.*, 1985, **8**, 439-448.
8. Conesa J.A., Font R.F., Marcilla A. and Garcia A.N., *Energy & Fuels*, 1994, **8**, 1238-1246.
9. Williams E.A. and Williams P.T., *J.ChemTech.Biotechnol.*, 1997, **70**, 9-20.
10. Wampler T.P., *J. Anal. Appl. Pyrol.*, 1989, **5**, 187-195.
11. Shalaby S.W., In, *Thermal Characterisation of Polymer Materials*, Turin E.A. (Ed.), Academic Press, New York, 237-264, 1981.
12. Driver W.E., *Plastics, Chemistry and Technology*, Van Nostrand Reinhold Company, Germany, 1979.