The Pyrolysis of Mixed Plastics, The Role of PVC: A Material of Concern or Convenience? †

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The pyrolysis of three engineering plastics used by the electronics industry has been studied using Pyrolysis/Gas Chromatography/Mass Spectrometry (Py/GC/MS). These materials acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC) and polyoxymethylene (POM) have been pyrolysed in the presence of polyvinyl chloride (PVC) to determine its effect upon the products of pyrolysis. The results of the study suggest that while hydrochloric acid is the major chlorinated product produced, other chlorinated hydrocarbons are also formed. The composition and yield of these chlorinated compounds are, however, very much dependant upon the other polymers present in the plastic mixture. The results of the study also suggest that the presence of PVC can influence the extent of degradation and the pyrolysis product distribution obtained from these three engineering polymers. The effect of PVC, although measurable, was not judged to be major in terms of significant changes. However the chlorinated pyrolysis products could influence the value of the pyrolysis oil and gases if they were to be used as fuels. In a separate series of experiments using an industrial mixed plastic waste stream which contained fillers such as calcium carbonate in addition to PVC it was noted that the HCI produced from the pyrolysis of PVC can be neutralized insitu. This leads to the production of inorganic chlorides, alleviating many of the concerns associated with HCI formation.

Introduction

Recycling is becoming an important part of the "Responsible Care" programs being adopted by many manufacturers of appliances, electronic equipment and automobiles to handle their products when they reach the end of their useful life [1]. These companies are starting to implement Product Stewardship Programs in which they accept responsibility for the ultimate fate of their products once they have served their useful purpose. While conventional mechanical recycling (e.g. melt processing) may be the process of choice, currently, there is no cost effective process for selectively collecting, sorting and reprocessing the mixed contaminated plastic materials contained in these wastes. Pyrolysis, however, provides an alternative technology for the recovery of the valuable hydrocarbons contained in this mixed contaminated plastic waste stream [2].

The aim of the present research work was to study the effect of PVC on the pyrolysis products of several common plastics used by the electronic and automobile industries. In addition, a mass balance of chlorine has been conducted on the pyrolysis of automobile shredder residue

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Materials and Method

The polymers investigated were Acrylonitrile/Butadiene/Styrene (ABS), Bisphenol-A Polycarbonate (PC), Polyoxymethylene (POM) along with Polyvinyl Chloride (PVC). An industrial mixed plastic waste stream known as automobile shredder residue (ASR) from an automobile shredding operation, was also evaluated.

Two types of experimental investigations were conducted:

(i) Pyrolysis/Gas Chromatography/Mass Spectrometry (Py/GC/MS) experiments of 1:1 blends of each polymer with PVC.

(ii) Batch scale pyrolysis of ASR using a laboratory screw kiln reactor in which a detailed chemical analysis of the pyrolysis products was carried out.

Experimental details are provided elsewhere [3,4].

Results and Discussions

Pyrolysis of PVC. Before examining the results of the blended samples with PVC it is first appropriate to examine the pyrolysis products from PVC alone. As would be expected hydrogen chloride (HCl) was the major chlorinated product with a measured peak area of 63.2%. Other major products of the pyrolysis included benzene (11.4%), toluene (4.5%), naphthalene (2.1%), 1,3 cyclopentadiene (2.1%) and 2-methyl, 2-propenoic acid (2.0%).

In addition, as reported by others [5], several organo chlorides were detected including: 3-chloro-1-butene; 2-chlorobutane; 1-chlorocyclopentene; chlorobenzene; 1-chlorohexane; benzyl chloride; 1-chloro octane; chloro-1-methyl-4-(1-methylethyl)-benzene; chloro diphenylmethane; 9-chlorofluorene and 4-chloro, 4'-hydroxy-biphenyl. However, it should be noted that the yields of these products were not large, all having peak areas less than 0.4%.

Having identified the chlorinated products from the pyrolysis of PVC under defined conditions the focus was turned to the influence of the other polymers on the production of chlorinated hydrocarbon pyrolysis products. In conducting these comparisons the differences in the actual measured total ion chromatograms (TIC's) for each species was used.

Pyrolysis of PVC/ABS Mixture. Several interesting observations were noted with respect to the pyrolysis data obtained with the PVC/ABS mixture. Based upon the TIC data, it was noted that the yield of HCl per mg of Cl in the PVC/ABS was very close to that observed with PVC alone, but the detectable amounts of the chlorinated aliphatic compounds were significantly reduced. However, the most striking observation was a significant increase in the number and amounts of the chlorinated aromatic species being produced. New chlorinated species included: 1-(chloroethenyl)-benzene; 4-chlorobutyl-benzene; trichlorvinyl -benzene and alpha-chloro-benzenebutanenitrile. These findings suggest that not only are new chlorinated compounds being produced during the pyrolysis of ABS, but also the extent of chlorination of pyrolysis products is increasing in the presence of PVC. These findings clearly increase concerns regarding the value of pyrolysis oils when a mixture of ABS and PVC are pyrolyzed.

Pyrolysis of PVC/PC Mixture. The changes noted in the pyrolysis products obtained with the PVC/PC mixture were not nearly as large as those obtained with the PVC/ABS mixture. This may, in part, be due to the large differences in the thermal stability of PVC and PC. For example the liberation of HCl from PVC is likely to occur prior to the degradation of the PC, resulting in decreased opportunities for product interactions. However, the production of measurable quantities of 5-chloro-2-benzofuran (0.38%) when PVC/PC mixtures are pyrolysed should be viewed with concern, since potentially it could be a precursor to the production of chlorinated dibenzodioxines and dibenzofurans. However, in this study, the possible formation of these compounds was not investigated.

Pyrolysis of PVC/POM Mixture. In the case of the POM/PVC mixture, the pyrolysis data once again suggested that the number and quantity of the chlorinated hydrocarbons were increasing when PVC was pyrolyzed in the presence of POM. Once again, several new chlorinated products were formed as the result of the reactions of HCl with POM pyrolysis products. New chlorinated products included: oxybis chloro methane; 4-chlorotetrahydro-2H-pyran; 1,4-dichloro, 2,5-dimethoxy-benzene and 4-chloro, 4'-methoxy-biphenyl. While the majority of these new species were only detected as traces (< 0.05%), the oxybis-chloro-methane was detected with a peak area percentage of 0.46%. However, as was noted in the case of PVC/ABS mixtures, there was a significant increase in the number of chlorinated hydrocarbons that could be attributed to the reaction of HCl with the pyrolysis products from POM.

Pyrolysis of an ASR Waste System. The pyrolysis of the ASR in a laboratory screw kiln reactor was carried out using a pyrolysis temperature of 700°C and a totals solids residence time of 3.4 min. Using these conditions a 70% conversion of the organic faction (41.6% of the ASR) of the feed was obtained. Three pyrolysis product fractions (gas, liquid, residue), were collected and analyzed for their chlorine content and the results are summarized in Table 1.

Table 1

Chlorine Distribution in the Pyrolysis Products from ASR

	Yield (%)	Chlorine Species	Chlorine in Fraction (%)
ASR	100	from PVC	0.56
Pyro-Gas	18	HCl	<0.0001
		RCl	0.03
Pyro-Liquid	7	Cl^-	0.003
		RCl	0.02
Solid Residue	68	Cl^-	0.567
		RCl	0

From this data, it can be seen that virtually no gaseous HCl was detected in the pyrolysis gas. While some inorganic chlorine was detected in the pyro-liquid, the majority of the chlorine present in the original ASR appears to have been converted into inorganic chlorides, which end up in the solid residue. This observation suggests that during pyrolysis, the HCl released from the PVC reacts with inorganic fillers such as calcium carbonate to form inorganic chlorides. Thus the pyrolysis of a mixed plastic waste streams, in which fillers are present, can be expected to have low releases of HCl. Unfortunately, as was noted in the pyrolysis of PVC mixtures, HCl also reacts with the organic pyrolysis products forming a wide range of chlorinated hydrocarbons which were detected in both the pyrolysis gas and the pyrolysis liquid. These species included aliphatic and aromatic species such as: chloromethane; 3-chloro-1-propene; 3-chloro-1,5,-hexadiene; 4-chloro-cyclohexene; chlorobenzene; 5-chloro-2-methyl benzofuran and 2-chlorophenol. Although the actual concentrations may be small, just their presence in the pyro-gas and pyro-liquid raise concerns, especially if these fractions are to be used directly as fuels where dioxin formation becomes a distinct possibility.

Conclusions

The pyrolysis of PVC containing wastes can lead to the formation of chlorinated hydrocarbons. The presence of these species in both the pyro-oil and pyro-gas will influence the value of these products and the economics of the process. Although the concentrations of these species in the final product may be low it appears that their composition and concentrations are very much dependent upon the chemical composition of polymers within the mixture.

In all cases, the major chlorinated pyrolysis product was HCl, formed as a result of the dehydrochlorination of PVC. While this could be a major problem when dealing with certain plastic waste streams, the presence of plastics with inorganic fillers such as calcium carbonate may help to alleviate the problem. Under these specific conditions the filler present in the plastic may neutralize the HCl, and precipitate the chlorine as an inorganic chloride thereby helping to neutralize subsequent reactions and help alleviate potential corrosion problems. The problem of the possible formation of chloro hydrocarbons remains, and if pyrolysis products are to be used as fuels, the possibility of the formation of dioxins and dibenzofurans must be investigated.

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