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Pyrolysis of mixed plastics used in the electronics industry[☆]

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Abstract

The pyrolysis of three plastics used by the electronics industry has been studied using pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS). The materials selected for this study were acrylonitrile–butadiene–styrene (ABS), polycarbonate (PC) and polyoxymethylene (POM). The selection was based upon the analysis of several pieces of electronic equipment, which had been the subject of laboratory studies. Each polymer was pyrolyzed at two pyrolysis temperatures (700 and 900°C) alone, together (side by side) with polyvinyl chloride (PVC) in a 50/50 co-pyrolysis experiment, and as an intimate chemical blend with PVC (50/50). In addition the three polymers were also pyrolyzed in the presence of copper powder to determine the role of copper contamination on the pyrolysis of each polymer. The results of the study suggest that both the presence of PVC and copper can influence the extent of degradation and the pyrolysis product distribution obtained when these polymers are pyrolyzed. However, no significant changes were noted that could drastically influence the value of the pyrolysis products. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Polymer pyrolysis; Py/GC/MS; ABS; PC; POM; PVC; Copper

1. Introduction

According to industrial estimates, 3.1 billion pounds of plastics are used each year in the production of computers and other electronic products [1]. Unfortu-

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nately as the equipment rapidly becomes obsolete little is recycled, with the majority being landfilled [2]. Data for Sweden indicates that 200 000 tonnes of these products are scrapped each year and the numbers are forecasted to increase [3]. Similar numbers have been estimated for other European countries [4]. While several companies have expressed interest in the recycling of their products at the end of their life, the problem has been one of establishing effective and efficient collection programs to deal with these materials [1].

To address these issues, several European countries are seriously considering the introduction of regulations that would make electronic manufacturers responsible for the ultimate disposition of their products [5,6]. The purpose of these ‘takeback’ regulations is to manage what happens to a product at the end of its useful life, thereby promoting the development of acceptable, economic and environmentally sound recycling and resource recovery technologies. When dealing with electronic equipment three basic strategies are currently being employed to divert the material from landfills [7].

- refurbishing/resale/donation of systems
- reclamation/reselling of components
- salvaging/recycling of materials

While each strategy has its merits, the success of the first two options depends upon the age of the equipment being processed. In the information technology sector it does not take long for the equipment to become obsolete and rapidly lose its resale value.

When dealing with plastic materials, the only economic choice appears to be the recovery of the polymeric materials used in the original construction. Unfortunately conventional mechanical recycling (e.g. melt reprocessing) the route of choice for the recycling of packaging materials (e.g. PET and HDPE) is not readily adaptable to plastics recovered from electronic equipment. This is due to the fact that in electronic equipment 15–20 different types of plastics may be used containing a variety of plasticizers, colorants, flame retardants and fillers [7]. In addition the material may have undergone degradation, or be contaminated with other materials, such as heavy metals, which potentially could make the material hazardous [2]. It is because of these barriers that the recycling of the plastic materials is not more widespread [1]. However, as new technologies evolve, markets are developed and infrastructure is established, this picture will change.

One of the technologies that could hasten this progress is ‘pyrolysis’. Because pyrolysis involves the thermal degradation of plastic materials in the absence of air it could yield valuable hydrocarbon products, while at the same time facilitating the recovery of the metal components. Because pyrolysis would degrade the polymeric materials used in plastics and release volatile organic compounds which could be removed from the solid waste, it would facilitate the recovery of both chemical hydrocarbons as well as metals embedded or mixed with the plastic waste stream.

In order to explore the feasibility of pyrolysis as a resource option for the mixed plastics found in waste electronic equipment, we have investigated the thermal degradation of a series of synthetic polymers commonly used in the electronics industry. In order to better reflect real life conditions these polymers have been

studied individually, as well as mixtures with other plastics or in the presence of copper contamination. The study was designed to determine the influence of material composition as well as contaminant impurities on the pyrolysis process and products of pyrolysis.

In previous studies, we have investigated the chemical degradation of mixtures of polymers used in the automotive industry [8–10], as well as the degradation of these materials in the presence of a variety of contaminants [11]. The studies with automotive plastics were conducted using mixtures of polypropylene (PP), acrylonitrile–butadiene–styrene (ABS), polyvinyl chloride (PVC), and polyurethane (PU) using dynamic thermogravimetry (TGA). The results suggested that polymers such as PVC and contaminants such as copper and iron oxide could influence the degradation behavior as measured by mass-loss measurements. However, the results provided no information on the products of pyrolysis, which could have implications on the value of recoverable resources. It was therefore decided to investigate the products of pyrolysis of synthetic polymer mixtures using pyrolysis/gas chromatography/mass spectrometry to elucidate the effects they may have on the products of pyrolysis.

2. Experimental

2.1. Materials

The polymer samples examined in this study are listed in Table 1, along with the source of each material. No specifications were reported regarding the composition of each sample, however, they were assumed to be additive free, with the exception of processing aids to facilitate subsequent compounding and processing. Each polymer was evaluated:

- as the individual polymer
- in a side by side combination with PVC (co-pyrolysis)
- as an intimate blend with PVC
- in a mixture with copper powder

The intimate blends of ABS/PVC and PC/PVC were produced by dissolving 1 g of each polymer in 100 ml of tetrahydrofuran (THF) at room temperature. The two solutions were combined and added dropwise to 1.2 l of rapidly stirred methanol, which resulted in the co-precipitation of a 50/50 mixture of the two polymers.

Table 1
Polymers evaluated in this study

Polymer	Abbreviation	Source
Acrylonitrile butadiene styrene	ABS	Dow, Magnum
Polyvinyl chloride	PVC	Goodrich, Geon 85796-1240
Bisphenol A polycarbonate	PC	Low viscosity GE Lexan ML4858
Polyoxymethylene	POM	Delrin Rod

The POM/PVC blend was similarly produced except that the two polymers were dissolved in N,N'-dimethylacetamide at 140°C. This approach to producing an intimate blend of the two polymers was thought to be better than melting the two polymers together, since any preliminary degradation associated with this chemical processing was avoided.

The copper contaminated mixtures were produced by first cryogenically grinding the polymer in a Wiley Laboratory Mill to a size less than 40 mesh. Fine copper powder was then added to the polymer to give a 5% by weight loading of the metal. The resulting mixture was then tumbled in a ball mill for 15 min to obtain thorough mixing.

2.2. The pyrolysis unit

All pyrolyses were carried out using a CDS AS-2500 Pyrolysis Autosampler, interfaced with a CDS Pyroprobe 2000 unit, working under 2000 PLUS software, version 3.0d. The interface was maintained at 250°C and the coil was programmed to heat to a set temperature, which was held for 10 s. All samples were weighed accurately (approximately 0.5 mg) into quartz auto sampler tubes (10A1-3015) which are 39 mm long with a 2 mm OD.

2.3. Pyrolysis product analysis

Separation and analysis of the pyrolysis products were conducted using a Hewlett–Packard (HP) 5890 Series II gas chromatograph (GC) coupled to a HP 5972A series Mass Selective Detector (MSD). Separation were achieved using a 30 m × 0.25 mm, 250 µm coated J & W Scientific, DB-5 (crosslinked 5% phenyl methyl silicone) fused silica capillary column, operated in the split mode (100:1). The column was programmed from 45 to 250°C at 15°/min after an initial hold of 3 min at 45°C, and a final hold of 10 min at 250°C.

3. Results and discussion

3.1. The pyrolysis temperature

Because the polymers being studied have widely different thermal stability's, as indicated by TGA studies [8,12], the choice of an appropriate pyrolysis temperature for the study was initially determined based upon mass-loss experiments performed with the CDS pyrolysis unit using the individual polymers. The results of this analysis are presented in Fig. 1. From this data it can be seen that very little mass loss was noted with the polycarbonate sample at set temperatures below 700°C. Meanwhile, the other polymers showed appreciable mass loss at 700°C. Because of this apparent divergence in thermal stability of the polymers, it was decided to employ two pyrolysis set temperatures in this study, 700 and 900°C. However, it should be noted that the set temperatures employed in pyrolysis experiments of this

Fig. 1. Mass loss (%) of the polymers evaluated as a function of set pyrolysis temperature.

type can be, and frequently are, much higher than the actual pyrolysis temperatures experienced by the polymer samples [13,14]. This is due to the thermal shielding effects of the quartz tubes, which can result in actual temperatures being at least 120°C below those dialed in.

3.2. Pyrolysis of ABS

In the case of the pyrolysis of ABS/PVC 50/50 mixtures, as measured by TGA, it has been shown [9,10] that three distinct mass-loss regions can be detected. A low temperature decomposition centered around 283°C (5°C/min heating rate) can be attributed to the dehydrochlorination of the PVC. The degradation of the ABS, meanwhile, occurred around 409°C. Finally the polyenes, produced from the PVC by dehydrochlorination, degraded around 448°C.

Based upon the data presented in Fig. 1, it would appear that at set pyrolysis temperatures of 700 and 900°C the extent of degradation of both polymers will be high. The data presented in Table 2 confirms this finding, with observed mass losses being close to the values anticipated based upon the behavior of the pure polymers. Although, some slight increase in the extent of degradation appeared to be occurring with both the co-pyrolysis and blended experiments, the actual magnitude of these increases was not large. In a similar way it can be seen that copper, at a loading of 5% in ABS had no major effect on the extent of degradation of the ABS.

While ABS is a widely used polymer, with annual North American sales exceeding 1400 million pounds [15], little work has been published on its thermal degradation and degradation products. While the degradation kinetics and mechanism have been shown to be very much dependent upon the chemical structure of

the co-polymer [16,17], the types of products produced are those expected from the molecular structure, i.e. acetonitrile, acrylonitrile, benzene, toluene, styrene, benzonitrile, etc. [16,18,19].

Table 3 provides a listing of the major pyrolysis products detected in this study when a set pyrolysis temperature of 700°C was employed. As was noted by Shapi [18], styrene was the most abundant product produced, significantly higher than any other species detected. Other predominant products included: 2-propenenitrile, benzenebutanenitrile, along with a variety of other aromatic species. With respect to the other products, it is quite clear that a large number of nitrogen containing aromatics were produced, mainly as the nitriles. No HCN was detected under the pyrolysis conditions used in the study.

The addition of PVC to ABS produced some interesting changes in the pyrolysis products, although for the most part the changes were only slight and well within experimental variability. However, the yields of ethylbenzene, methylstyrene, toluene and 1,3-diphenylpropane all increased when pyrolyzed in the presence of PVC. All these increases were also greatest when the PVC was blended with ABS. The yield of 1,3-butadiene also increased when PVC was present, but the yields were almost identical irrespective of whether PVC was blended with ABS or not. In the meantime the yields of most of the nitrogen containing compounds, namely the aromatic nitriles, appear to be reduced in the presence of PVC especially with the intimate blends. However, in examining the data from ABS with PVC the pyrolysis products of PVC have also to be considered. Table 4 provides information on the pyrolysis of PVC under the same test conditions. The products listed in this table are very similar to those reported by McNeill et al. [20] who provided a detailed analysis of the pyrolysis products of PVC. Clearly this data indicates that a large percentage of the benzene detected from ABS/PVC mixtures is originating from PVC and it is difficult to determine if the blending of PVC and ABS is responsible for any increase in the yield of benzene. It should also be noted that while PVC also contributes to the yields of toluene and styrene, the numbers presented in Table 3 would suggest that some increases in the amounts of these two compounds are occurring. Based upon this data it would appear that the presence of PVC in ABS will reduce the yield of nitrile products while enhancing the formation of the aromatic hydrocarbons, toluene, styrene, ethylbenzene and methylstyrene.

Table 2

Mass loss data for the pyrolysis experiments

	ABS Experiments		PC Experiments		POM Experiments	
Set pyrolysis temperature	700°C	900°C	700°C	900°C	700°C	900°C
Polymer alone	54.8	86.9	0.15	51.5	86.5	98.8
PVC alone	64.5	71.9	64.5	71.9	64.5	71.9
Anticipated for 50/50 mix	59.7	79.4	31.8	61.7	75.5	85.5
Observed for 50/50 co-pyrolysis	58.8	83.3	33.5	67.2	81.7	87.3
Observed for 50/50 blend	67.5	80.6	39.8	73.5	90.0	92.7
Anticipated for 5% copper sample	52.1	82.5	0.14	48.9	82.1	93.9
Observed for 5% copper sample	53.4	82.7	1.42	54.4	69.1	82.3

Table 3
Pyrolysis products from the pyrolysis of ABS at 700°C^a

Retention time (min)	Compound	ABS Alone		50/50 Co-pyrolysis		50/50 Intimate blend		5% Addition of copper	
		Area (%)	TIC signal per mg of ABS ($\times 10^6$)	TIC signal per mg of ABS ($\times 10^6$)	% Change	TIC Signal per mg of ABS ($\times 10^6$)	% Change	TIC signal per mg of ABS ($\times 10^6$)	% Change
1.85	1,3-Butadiene	2.87	70.20	160.11	128.1	147.86	110.6	119.85	70.7
2.00	Acetonitrile	0.56	13.70	ND	ND	ND	ND	2.00	–85.4
2.09	2-Propenenitrile	11.07	270.78	338.60	25.0	457.81	69.1	458.85	69.5
2.94	Benzene	0.05	1.22	196.54	15963.9	309.22	25173.6	1.57	28.0
4.41	Toluene	3.52	86.10	136.74	58.8	231.25	168.6	163.87	90.3
5.49	Cyclohexene, 4-ethenyl-	1.26	30.82	30.09	–2.4	14.19	–54.0	50.28	63.1
5.92	Ethylbenzene	0.72	17.61	35.51	101.6	91.77	421.1	22.81	29.5
6.45	Styrene	42.61	1042.29	1249.12	19.8	1190.09	14.2	1884.51	80.8
7.36	Benzene, iso- cyanato-	0.64	15.66	ND	ND	24.18	54.4	40.50	158.7
7.67	α -Methyl- styrene	1.42	34.73	58.84	69.4	163.86	371.8	74.49	114.4
8.64	3-Hexenedini- trile	0.71	17.37	ND	ND	18.40	5.9	26.62	53.3
11.58	Benzenebu- tanenitrile	6.99	170.98	190.54	11.4	213.91	25.1	309.59	81.1
12.31	3-Phenyl-4- pentenenitrile	2.71	66.29	67.58	1.9	43.64	–34.2	128.02	93.1
14.28	1,3-Diphenyl- propane	1.16	28.37	35.73	25.9	59.60	110.1	50.28	77.2
14.80	1,4-Diphenyl- butene	3.04	74.36	74.95	0.8	38.97	–47.6	138.73	86.6
15.37	4-Phenyl-4- pentenenitrile	1.38	33.76	32.52	–3.6	29.96	–11.3	63.78	88.9

Table 3 (Continued)

Retention time (min)	Compound	ABS Alone		50/50 Co-pyrolysis		50/50 Intimate blend		5% Addition of copper	
		Area (%)	TIC signal per mg of ABS ($\times 10^6$)	TIC signal per mg of ABS ($\times 10^6$)	% Change	TIC Signal per mg of ABS ($\times 10^6$)	% Change	TIC signal per mg of ABS ($\times 10^6$)	% Change
15.62	3-Phenyl-3-methyl-3-butenitrile	3.19	78.03	73.34	-6.0	59.34	-24.0	149.90	92.1
15.76	2-(2-Phenylethyl)-4-methylenepentanedinitrile	1.3	31.80	32.44	2.0	23.13	-27.3	58.19	83.0
17.49	4-Phenyl-2-methyl, 2,4-pentadienenitrile	2.36	57.73	63.77	10.5	52.44	-9.2	113.59	96.8
17.83	2-(2,4-Diphenylbutyl) propenenitrile	2.52	61.64	63.79	3.5	41.43	-32.8	124.30	101.6
18.04	5-Phenyl-5-hexenenitrile	5.14	125.73	128.16	1.9	101.34	-19.4	244.87	94.8
	Total of above	95.22	2329.19	2968.38	27.4	3312.38	42.2	4226.62	81.5

^a ND, denotes not detected.

Table 4
Pyrolysis products detected in the pyrolysis of PVC at 700 and 900°C

Retention time (min)	Compound	Experiments at 700°C		Experiments at 900°C	
		Area (%)	TIC Signal per mg PVC ($\times 10^6$)	Area (%)	TIC Signal per mg PVC ($\times 10^6$)
1.47	Carbon dioxide	0.37	5.91	0.37	6.21
1.74	Hydrochloric Acid	73.71	1170.46	65.37	1097.82
2.14	1,3-Cyclopentadiene	0.88	14.00	2.08	34.93
2.71	1,4-Cyclohexadiene	0.20	3.11	0.79	13.27
2.91	Benzene	11.21	178.05	11.42	191.79
3.52	2-Propenoic acid, 2-methyl-	2.15	34.21	2.03	34.09
4.40	Toluene	2.54	40.27	4.54	76.24
5.91	Ethylbenzene	0.34	5.44	0.59	9.91
6.04	p-Xylene	0.20	3.11	0.65	10.92
6.37	Styrene	0.63	9.95	1.17	19.65
6.41	Benzene, 1,3-dimethyl-	0.40	6.38	0.83	13.94
8.49	Indene	0.65	10.26	1.38	23.18
9.71	Benzene (1-methyl-2-cyclopropen-1-yl)-	0.54	8.55	0.95	15.95
9.89	Naphthalene, 1,2-dihydro-	0.58	9.17	0.71	11.92
10.11	Naphthalene	1.28	20.37	2.08	34.93
11.23	Naphthalene, 1-methyl-	0.40	6.38	0.74	12.43
11.40	Naphthalene, 2-methyl-	0.27	4.35	0.63	10.58
12.00	Naphthalene, 2-ethenyl-	0.44	7.00	0.59	9.91
16.30	Hexadecanoic acid	0.69	10.89	0.47	7.89
17.67	Octadecanoic acid	0.83	13.22	0.25	4.20
	Total	98.31	1561.08	97.64	1639.77

The addition of copper at a 5% loading appears to enhance the quantity of volatile products. Based upon the mass-loss data presented in Table 2, this result is rather surprising. However, it should be noted that the analysis presented in Table 3 considers only the volatile compounds that were separated by the GC system. Other higher molecular weight species may be formed in the absence of copper, but were not detected in our analytical system. When these experiments were conducted in the presence of copper, these species could be converted to lower molecular weight compounds, which can now be detected. While styrene is still the major pyrolysis product, the quantity of almost all the pyrolysis products detected increases when copper is present. The only exception was acetonitrile, which showed a decrease in yield.

The results of the ABS pyrolysis experiments conducted at the higher pyrolysis temperature of 900°C are presented in Table 5. On increasing the pyrolysis temperature from 700 to 900°C the measured total ion chromatogram (TIC) for all of the compounds detected increased by 60.4%, in close agreement with the increased mass loss of 58.6% reported in Table 2. Increasing the pyrolysis temperature from 700 to 900°C also resulted in an increase in the number of principal products detected from 34 to 45.

In comparing the pyrolysis product profile for ABS obtained at 700°C (Table 3) with the data obtained at 900°C (Table 5) some general trends can be noted. While the total product yield, as measured by the TIC peak areas, of all the compounds listed increased with pyrolysis temperature, the contribution of some compounds to the overall pyrolysis products increased while others decreased. The compounds, which increased their total contribution to the pyrolysis products (increased peak area %) were: acetonitrile, benzene, toluene, ethylbenzene, and methylstyrene and 3-hexenedinitrile. Meanwhile the contribution of the higher molecular weight phenyl-alkyl nitriles all appeared to be reduced when higher pyrolysis temperatures were employed.

When the role of PVC on the pyrolysis products of ABS was once again examined, the results obtained at 900°C, in many respects, resemble those obtained at 700°C. For example there were increases in the yields of benzene, toluene, ethylbenzene and methylstyrene. However, once again it should be noted that the degradation of PVC (Table 4) also contributes significantly to these species, especially at this higher pyrolysis temperature. For example, a significant portion of the benzene is coming from PVC and not from ABS. However, even allowing for the contributions from PVC, it would appear that some of the noted increases can be attributed to the influence of PVC on the degradation of ABS.

Also, as was noted at 700°C, PVC also appears to be causing a reduction in the yield of the majority of the nitrile species, nearly all of which show measurable decreases, especially when the two polymers were intimately blended together. These results suggest that reactions could be occurring between the two polymer systems, which may be linked to the presence of the HCl liberated from PVC and the subsequent loss of the nitrile functionality.

Once again the addition of copper to ABS resulted in an increase in the quantity of low molecular weight species. However, at this higher pyrolysis temperature

Table 5
Pyrolysis products from the pyrolysis of ABS at 900°C^a

Retention time (min)	Compound	ABS Alone		50/50 Co-pyrolysis		50/50 Intimate blend		5% Addition of copper	
		Area (%)	TIC signal per mg of ABS ($\times 10^6$)	TIC signal per mg of ABS ($\times 10^6$)	% Change	TIC signal per mg of ABS ($\times 10^6$)	% Change	TIC Signal per mg of ABS ($\times 10^6$)	% Change
1.82	1,3-Butadiene	2.62	109.06	272.20	149.6	205.08	88.0	244.77	124.4
1.98	Acetonitrile	0.95	39.54	106.98	170.5	100.89	155.1	46.40	17.3
2.07	2-Propenenitrile	11.44	476.19	580.32	21.9	568.75	19.4	736.53	54.7
2.41	2-Propenenitrile, 2-methyl-	0.81	33.72	102.00	202.5	145.04	330.2	75.10	122.7
2.93	Benzene	0.21	8.74	270.81	2998.0	301.79	3352.5	88.67	914.4
4.40	Toluene	3.99	166.08	444.73	167.8	408.81	146.1	370.28	122.9
5.49	Cyclohexene, 4-ethenyl-	0.81	33.72	22.00	−34.8	8.59	−74.5	45.73	35.6
5.93	Ethylbenzene	0.84	34.96	195.44	459.0	182.54	422.1	91.14	160.6
6.48	Styrene	40.49	1685.39	2046.91	21.5	1538.91	−8.7	2558.98	51.8
7.36	Benzene, isocyanato-	0.69	28.72	12.29	−57.2	15.45	−46.2	58.54	103.8
7.69	α -Methylstyrene	1.98	82.42	235.10	185.3	235.85	186.2	175.16	112.5
8.67	3-Hexenedinitrile	0.86	35.80	32.35	−9.6	22.32	−37.6	52.83	47.6
11.60	Benzenebutanenitrile	5.78	240.59	218.75	−9.1	216.00	−10.2	312.59	29.9
12.33	3-Phenyl-4-pentenitrile	2.70	112.39	86.68	−22.9	49.12	−56.3	149.93	33.4
14.29	1,3-Diphenylpropane	1.02	42.46	33.64	−20.8	54.93	29.4	56.44	32.9
14.81	1,4-Diphenylbutene	2.87	119.46	72.69	−39.2	34.03	−71.5	147.73	23.7
15.38	4-Phenyl-4-pentenitrile	0.92	38.29	61.20	59.8	26.90	−29.8	58.64	53.1

Table 5 (Continued)

Retention time (min)	Compound	ABS Alone		50/50 Co-pyrolysis		50/50 Intimate blend		5% Addition of copper	
		Area (%)	TIC signal per mg of ABS ($\times 10^6$)	TIC signal per mg of ABS ($\times 10^6$)	% Change	TIC signal per mg of ABS ($\times 10^6$)	% Change	TIC Signal per mg of ABS ($\times 10^6$)	% Change
15.63	3-Phenyl-3methyl-3-butenitrile	2.31	96.15	82.46	– 14.2	45.58	– 52.6	133.38	38.7
15.77	2-(2-Phenylethyl)-4-methylenepentanedinitrile	0.93	38.71	30.41	– 21.4	21.75	– 43.8	58.45	51.0
17.51	4-Phenyl-2-methyl-2,4-pentadienenitrile	1.85	77.01	68.72	– 10.8	41.99	– 45.5	103.10	33.9
17.85	2-(2,4-Diphenylbutyl)propenenitrile	1.87	77.84	67.05	– 13.9	30.86	– 60.3	112.80	44.9
18.06	5-Phenyl-5-hexenenitrile	3.82	159.01	139.17	– 12.5	79.52	– 50.0	213.28	34.1
	Total of above	89.76	3736.24	5181.88	38.7	4334.69	16.0	5890.45	57.7

^a ND, denotes not detected.

there appeared to be a change in the product distribution. For example, while the higher molecular weight (longer retention time) species all showed increases they all tended to be less than the overall percentage increase noted at this temperature. Meanwhile the increases in the lower molecular species (low retention times) showed TIC increases higher than the average. Consequently, it would appear that copper is promoting the degradation of ABS and leading to increased yields of the lower molecular weight species.

3.3. Pyrolysis of polycarbonate

The thermal decomposition of polycarbonates has received wide attention based upon information contained in the scientific literature and referenced in the paper by Montaudo and Puglisi [20], who list a total of 26 references dealing with the subject. These studies include investigations with aliphatic as well as aromatic polycarbonates. The polycarbonate used in the current investigation was based upon bisphenol A polycarbonate (BPA-PC) which is widely used in the electronics industry because of its desirable combination of toughness, and thermal stability. While there is some debate regarding the degradation mechanisms that occur in the pyrolysis of polycarbonates, the major volatile degradation products are carbon dioxide and phenolic compounds [21–23]. These same compounds were identified in the pyrolysis products obtained from the pyrolysis of the BPA-PC used in this study.

Tables 6 and 7 provide a listing of the major chemical compounds identified in this study. From these tables it can be clearly seen that the product yield is much lower at 700°C (TIC per mg PC) than the yield obtained at 900°C. This finding is in keeping with the mass-loss data observed in Fig. 1 and provided in Table 2. In terms of pyrolysis products it is clear that carbon dioxide, phenol, 4-methyl phenol and 4,4'-(1-methylethylidene) bisphenol (bisphenol A) are the major products of pyrolysis, especially at the higher pyrolysis temperatures. Interestingly, while diphenyl carbonate appears to constitute a major portion of the gases at 700°C, its concentration in the gases at 900°C remains relatively unchanged.

When PC is mixed with PVC and pyrolyzed at 700°C an interesting situation arises. Based upon the data presented in Fig. 1 and summarized in Table 2 very little degradation of the PC should be expected, while that for PVC should be almost complete. However, based upon the mass-loss data (Table 2), it is clear that at 700°C the presence of PVC with PC is resulting in an increased yield of volatile degradation products, 5.3% when co-pyrolyzed and 25% when pyrolyzed as a blend. These represent significant increases, since the degradation of PC is only expected to show a 0.15% mass loss at 700°C. This observation is in agreement with the finding of McNeill [24] who found that PVC is responsible for the destabilization of PC when blends are degraded. The presence of copper also appears to be responsible for a ten-fold increase in mass loss at 700°C. However, once again because of the small amount of degradation of PC at 700°C the actual increase is not exceptionally large.

Table 6
Pyrolysis products from the pyrolysis of polycarbonate at 700°C^a

Compound	PC Alone		Co-pyrolysis		Intimate blend		5% Copper	
	Area (%)	TIC per mg PC (x 10 ⁶)	TIC per mg PC (x 10 ⁶)	% Change	TIC per mg PC (x 10 ⁶)	% Change	TIC per mg PC (x 10 ⁶)	% Change
Carbon dioxide	20.52	8.54	ND	ND	ND	ND	18.01	110.9
Benzene	ND	ND	183.36	–	201.44	–	ND	ND
Toluene	ND	ND	38.55	–	30.20	–	ND	ND
<i>P</i> -xylene	ND	ND	3.24	–	3.50	–	ND	ND
Styrene	1.29	0.54	9.13	1589.0	9.81	1715.1	ND	ND
Phenol	35.61	14.82	46.72	215.3	52.68	255.5	34.19	130.8
Phenol, 2-methyl-	0.41	0.17	ND	ND	ND	ND	ND	ND
Phenol, 4-methyl-	1.42	0.58	8.74	1407.2	6.23	975.0	2.14	269.4
Phenol, 4-ethyl-	1.12	0.47	7.77	1553.3	7.66	1528.9	1.08	129.3
Phenol, 4-vinyl-	0.81	0.34	2.32	581.5	1.82	436.5	1.37	301.5
Phenol, 4-(1-methylethyl)-	0.96	0.40	8.35	1988.3	10.82	2605.7	1.44	259.6
Phenol, 4-propyl-	ND	ND	1.24		1.24		ND	ND
Phenol, 4-(1-methylvinyl)-	2.32	0.97	21.76	2150.6	7.89	715.7	3.30	240.9
Diphenyl carbonate	20.19	8.40	7.23	–13.9	6.09	–27.5	16.57	97.2
Phenyl, 4-methylphenyl (methylethylidene)-	0.67	0.28	5.33	1803.7	5.58	1893.1	1.16	313.6
Carbonic acid, 4-methylphenyl, phenyl ester	ND	ND	1.40	–	ND	ND	0.24	–
Phenyl, (1-methylethylidene) bis-	ND	ND	ND	ND	ND	ND	ND	ND
Phenol, 4-(1-methyl-1-phenylethyl)-	1.44	0.60	11.66	1842.6	9.47	1477.7	2.61	335.5
Phenylene oxide, 4-(1-methylvinyl)-	1.0	0.41	5.57	1258.4	1.88	359.3	0.86	109.7
Phenol, 4,4'-methylene bis-	0.49	0.21	ND	ND	ND	ND	0.09	–56.3
Dibenzofuran, 3-methyl-	0.38	0.16	2.37	1380.5	ND	ND	0.09	–45.2
Anthrone	0.87	0.36	ND	ND	ND	ND	1.73	380.1
Phenol, 4,4'-(1-methylethylidene) bis-	6.73	2.80	49.89	1682.5	44.32	1483.3	12.53	347.7
Total	96.23	36.06	414.64	1049.7	400.64	1010.9	97.40	170.1

^a ND, denotes not detected.

Table 7
Pyrolysis products from the pyrolysis of polycarbonate at 900°C^a

Compound	PC Alone		Co-pyrolysis		Intimate blend		5% Copper	
	Area (%)	TIC per mg PC ($\times 10^6$)	TIC per mg PC ($\times 10^6$)	% Change	TIC per mg PC ($\times 10^6$)	% Change	TIC per mg PC ($\times 10^6$)	% Change
Carbon dioxide	20.93	484.10	502.59	3.8	409.01	−15.5	622.81	28.7
Benzene	0.93	21.51	168.52	683.5	372.87	1633.4	107.60	400.2
Toluene	1.10	25.44	59.68	134.6	118.01	363.8	103.66	307.4
<i>p</i> -xylene	0.34	8.33	14.01	68.2	16.52	98.3	15.18	82.2
Styrene	0.19	4.56	23.89	423.6	38.14	736.2	34.15	648.7
Phenol	10.90	252.11	336.14	33.3	270.80	7.4	548.05	117.4
Phenol, 2-methyl-	0.48	11.10	11.50	3.6	52.97	377.2	48.60	337.7
Phenol, 4-methyl-	14.36	332.14	170.36	−48.7	195.65	−41.1	442.08	33.1
Phenol, 4-ethyl-	7.71	178.33	113.74	−36.2	122.19	−31.5	72.66	−59.3
Phenol, 4-vinyl-	4.30	99.46	21.83	−78.0	28.37	−71.5	259.40	160.8
Phenol, 4-(1-methylethyl)-	2.42	55.97	94.29	68.4	67.73	21.0	20.41	−63.5
Phenol, 4-propyl-	0.47	10.87	5.14	−52.7	0.51	−95.3	8.52	−21.7
Phenol, 4-(1-methylvinyl)-	3.13	72.39	58.78	−18.8	39.91	−44.9	203.94	181.7
Diphenyl carbonate	0.45	10.41	12.67	21.7	4.31	−58.6	23.26	123.4
<i>p</i> -Hydroxybiphenyl	0.25	5.96	6.31	5.9	21.27	257.0	54.11	808.2
Phenyl, 4-methylphenyl(-methylethylidene)-	1.03	23.82	20.62	−13.4	15.08	−36.7	28.70	20.5
Phenol, 4-(phenyl-methyl)-	0.38	8.79	4.05	−53.9	13.73	56.2	38.89	342.2
Carbonic acid, 4-methylphenyl, phenyl ester	0.34	8.25	5.73	−30.5	7.68	−6.9	6.80	−17.5
Phenyl, (1-methylethylidene) bis-	0.49	11.33	17.92	58.1	18.55	63.7	76.70	576.8

Table 7 (Continued)

Compound	PC Alone		Co-pyrolysis		Intimate blend		5% Copper	
	Area (%)	TIC per mg PC ($\times 10^6$)	TIC per mg PC ($\times 10^6$)	% Change	TIC per mg PC ($\times 10^6$)	% Change	TIC per mg PC ($\times 10^6$)	% Change
Phenol, 4-(1-methyl-1-phenylethyl)-	1.31	30.30	62.82	107.3	57.58	90.1	33.89	11.9
Benzofuran, 2,3-dihydro-2-methyl-4-phenyl-	0.59	13.65	12.28	−10.0	6.70	−50.9	29.45	115.8
Phenylene oxide, 4-(1-methylvinyl)-	1.10	25.44	19.26	−24.3	12.80	−49.7	52.07	104.7
Phenol, 4,4'-methylene bis-	0.90	20.82	8.81	−57.7	19.53	−6.2	62.21	198.8
Dibenzofuran, 3-methyl-	1.97	45.56	51.33	12.6	68.88	51.2	11.22	−75.4
Anthrone	0.35	8.19	11.42	39.4	6.82	−16.7	31.82	288.6
Phenol, 4,4'-(1-methylethylidene) bis-	21.84	505.15	621.13	23.0	617.25	22.2	733.18	45.1
Total	97.91	2273.99	2434.84	7.1	2602.93	14.5	3669.36	61

^a ND, denotes not detected.

The analysis of the volatile degradation products produced for PC in the presence of PVC and copper at the 700°C pyrolysis temperature are presented in Table 6. Based upon the results contained in this table it is clear that there is an increase in the volatile products from PC when pyrolysis is carried out in the presence of PVC. However, when comparing the yields of the individual species it should be noted, once again, that allowance has to be made for the contribution of some products from the pyrolysis of PVC. For example, as was noted in the case of the ABS/PVC study, benzene, toluene, *p*-xylene, styrene are all products of the degradation of PVC (Table 4). However, it is clear that PVC is promoting the formation of phenols, with all phenolic products showing substantial increases due to the presence of PVC. Based upon the data presented in Table 6, it would appear that the yield of the majority of the products is independent of whether PVC and PC are co-pyrolyzed or pyrolyzed as an intimate blend. However, there does appear to be an exception to this case. While the yields of phenol, 4-vinyl phenol, 4-(1-methylvinyl)phenol and 4-(1-methylvinyl)phenylene oxide, all increased in the presence of PVC, when PVC was intimately blended with PVC the increases were measurably less than when the materials were co-pyrolyzed. This suggests that secondary reactions could occur in the case of these vinyl species prior to their release. These reactions were much less likely in the co-pyrolysis experiments. It should also be noted that PVC also resulted in a slight reduction in the yield of diphenyl carbonate, both when PVC was co-pyrolyzed and intimately blended with PC.

The influence of copper on the pyrolysis of PC appears to be less dramatic than that observed with PVC. However, there does appear to be an approximate three-fold increase in all products when copper was present. The only two exceptions being 4,4'-methylene bisphenol, and 3-methyldibenzofuran. However, both these compounds are minor constituents in the total pyrolysis products.

At a pyrolysis temperature of 900°C, mass-loss data for PC (Table 2) indicated that appreciable volatilization occurred, resulting in a 51.5% mass loss. Based upon the mass-loss data presented in Table 2 it would appear that the presence of PVC, once again, increased the mass loss resulting in the production of more volatile pyrolysis products. It would also appear that when PVC was intimately blended with PC, higher yields of volatile products were achieved. Interestingly however, when copper was added to PC the mass loss appeared to be reduced slightly, suggesting a retardation of volatile pyrolysis product formation. How this translates into the volatile pyrolysis product distribution is presented in Table 7.

Once again it was noted that there was a substantial increase in the yields of benzene, toluene, xylene and styrene which in part can be attributed to the degradation of PVC (Table 4). Consequently the yields of these species, which can originate from PVC, need to be balanced with the changes noted in the other products which appear to change due to the presence of PVC. Generally, however, it would appear that the yields of most of the alkyl phenols (4-methyl, ethyl, propyl, vinyl etc.) decreased in the presence of PVC (the 2-methyl, and 2-propyl appear to be exceptions) while certain other species such as *p*-hydroxybiphenyl appeared to increase. Although generalization is difficult, it would appear that the presence of

PVC as an intimate blend with PC has a slightly greater effect than when it is co-pyrolyzed with PVC.

The addition of copper to PC, appeared to have a significant impact on the yield of several pyrolysis products when the pyrolysis was conducted at 900°C. At this pyrolysis temperature the total yield of pyrolysis products appeared to have increased significantly over values obtained in the absence of copper. This finding seems strange in light of the small increased mass loss noted in Table 2. It should be noted, however, that some species such as 4-ethylphenol, 4-isopropylphenol, 4-propylphenol and 3-methyldibenzofuran show reduced yields due to the presence of copper. However, their contribution to the total pyrolysis products was not large.

3.4. Pyrolysis of polyoxymethylene (POM)

The thermal degradation of polyoxymethylene has been studied in detail by several researchers [25–29], and it has been shown to occur mainly at the polymer chain ends leading principally to formaldehyde as the predominant product. However, because some, although few, random chain scission reactions can occur at the higher pyrolysis temperatures employed in this study, a whole range of oligomers as well as substituted trioxanes are to be expected.

Table 8 provides a listing of the compounds detected in this study, along with the principal ions detected which were used to identify the compounds. However, before examining the yields of the specific pyrolysis products, the mass losses on pyrolysis should be examined.

In terms of the mass-loss data presented in Fig. 1, the degradation of POM and PVC are not as widely different as the other polymers ABS and PC. Consequently both polymers exhibited large mass losses at 700 as well as 900°C. These mass losses are presented in Table 2 for the two sets of pyrolysis conditions used in this study. Even at a pyrolysis temperature of 700°C the mass loss of POM was over 86%, not much less than the 98.8% observed at 900°C. However, despite these high mass losses, the presence of PVC appeared to increase the yield of pyrolysis products anticipated based upon the simple addition of the two components. It should also be noted that the increased mass loss was also greatest when PVC was intimately blended with POM.

While POM/PVC samples showed augmented degradation, the presence of copper at 5% in POM appeared to have the reverse effect. Both at 700 and 900°C the presence of copper appeared to substantially reduce the mass losses of POM on pyrolysis.

The pyrolysis products from POM at 700°C are listed in Table 9. As already mentioned, the major product of the pyrolysis of POM was formaldehyde which accounted for over 93% of the detected volatile products. The only other two species of any significance (over 1%) were dimethylformaldehyde and formic acid. All the other compounds detected were less than 1%, and consisted of a wide variety of low molecular methoxy oligomers as well as 1,3,5-trioxanes with methoxy substituents.

Table 8
Pyrolysis products detected in the pyrolysis of polyoxymethylene

Retention time (min)	Reference code	Structure/compound	Mol. Wt.	Principal ions						
1.73	1	CH ₂ O	30	30	29	28				
1.96	2	CHOOH	46	29	46	45	44	28	30	
2.02	3	CH ₃ OCH ₂ OCH ₃	76	45	29	75	28	31	61	
2.14	4	CH ₃ OCH ₂ OH	62	61	31	29	33	30	45	
2.20	5	CHOCH ₂ OH	60	31	29	32	28	60	42	
2.28	6	CHOCH ₂ OCH ₃	74	45	29	28	43	60	74	
2.31	7	CH ₃ COOH	60	28	43	45	36	60	32	
2.37	8	CH ₃ OCH ₂ CH ₂ OCH ₃	90	45	29	28	30	43	60	
2.46	9	CHOOCH ₂ CH ₃	74	28	32	73	32	29	44	
2.57	10	CHOOCH ₂ OCH ₃	90	45	29	31	61	47	89	
2.62	11	CH ₃ CH ₂ OCH ₂ OH	76	45	28	31	29	61	75	
2.64	12	Furan, tetrahydro-	72	42	28	41	72	71	36	
2.94	13	CH ₃ CH ₂ OCH ₂ OH	74	28	29	32	59	43	74	
3.24	14	1,3,5-Trioxane, methyl-	102	31	61	89	29	32	102	
3.40	15	CH ₂ CHCH ₂ CH ₂ CH ₂ OCH ₃	100	55	28	27	32	29	99	
3.51	16	CH ₃ OCH ₂ OCH ₂ OCH ₃	106	45	28	75	29	32	105	
3.59	17	CH ₂ C(CH ₃)COOCH ₃	100	41	69	39	100	59	85	
3.63	18	CHOCH ₂ OCH ₂ CH ₃	88	28	45	32	43	61	87	
3.65	19	ClCH ₂ OCH ₂ Cl	115	79	49	81	51	29	113	
3.76	20	CHOCH ₂ CH ₂ OCH ₂ CH ₃	102	56	28	41	31	73	91	
4.31	21	CHOCH ₂ OCH ₂ OH	90	31	60	28	44	43	75	
4.82	22	1,3-Dioxolane, 4-ethyl-	102	42	71	41	27	31	102	
5.00	23	CHOOCH ₂ OCH ₂ OCH ₃	120	45	28	31	74	61	119	
6.34	24	1,3,5-Trioxane	90	61	89					
6.67	25	HOCH ₂ OCH ₂ OCH ₂ OCH ₂ OH	108	61	91	108	89	55	79	
6.83	26	3-Furanol, tetrahydro-	88	70	57	88	73	60	55	
7.06	27	ClCH ₂ OCH ₂ OCH ₂ Cl	145	79	81	51	109	115	145	
7.68	28	1,3,5-Trioxane, methoxy-	120	61	75	89	74	103	119	
7.86	29	Furan, tetrahydro-2-methoxy-	102	57	87	88	71	54	72	
8.55	30	CHOOCH ₂ CHCHCH ₂ OCHO	144	54	72	87	100	108	55	
8.81	31	1,3,5-Trioxane, hydroxy, methoxy	136	89	61	75	77	105	135	
9.26	32	CH ₃ CHCHCH ₂ OCH ₂ OCH ₂ OH	132	55	71	101	58	117	131	

Table 8 (Continued)

Retention time (min)	Reference code	Structure/compound	Mol. Wt.	Principal ions						
9.80	33	1,3,5-Trioxane, dimethoxy	150	61	75	89	105	119	149	
10.46	34	$\text{CH}_2\text{CHCH}_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{OH}$	132	55	101	71	84	61	131	
10.69	35	3,4,-dimethylpyran	114	55	56	113	85	84	67	
10.75	36	$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_3$	136	75	105	61	91	135	78	
11.17	37	Hindered Phenol Stabilizer		135	150	91	77	159	174	
11.58	38	1,3,5-Trioxane,[methoxy,] ₃	180	89	75	61	105	91	179	
12.42	39	1,3,5-Trioxane,[methoxy,] ₂ hydroxy	166	75	89	61	105	135	165	
12.64	40	Hindered Phenol Stabilizer		177	149	192	91	161	193	
12.78	41	$\text{CH}_3\text{CHCHCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_3$	178	101	55	75	131	71	177	
13.16	42	1,3,5-Trioxane,[methoxy,] ₃	180	89	75	61	105	91	121	
13.91	43	1,3,5-Trioxane,[methoxy,] ₃ hydroxy	196	75	105	89	61	135	195	
14.02	44	$[\text{CH}_3\text{CHCHCH}_2\text{OCH}_2\text{OCH}_2]_2\text{O}$	246	55	73	101	71	89	246	
14.24	45	$\text{CH}_3\text{CHCHCH}_2\text{OCH}_2\text{OCH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$	192	101	55	75	131	105	192	
14.59	46	1,3,5-Trioxane,[methoxy,] ₄	210	89	61	75	105	121	135	
15.26	47	1,3,5-Trioxane,[methoxy,] ₃ hydroxy	196	75	105	89	135	61	165	
15.89	48	1,3,5-Trioxane,[methoxy,] ₄	210	89	75	61	105	121	213	
16.50	49	1,3,5-Trioxane,[methoxy,] ₇ hydroxy	316	75	105	135	61	89	316	
16.78	50	$[\text{CH}_3\text{CHCHCH}_2\text{OCH}_2\text{OCH}_3\text{OCH}_2\text{OCHCH}_2]_2$	280	101	55	131	75	105	280	
17.08	51	1,3,5-Trioxane,[methoxy,] ₇ hydroxy	316	61	89	75	105	121	316	
17.73	52	1,3,5-Trioxane,[methoxy,] ₄ hydroxy	226	75	105	135	61	165	225	
18.09	53	$\text{CH}_3\text{CHCHCH}_2[\text{OCH}_2]\text{CH}_3$	222	101	55	75	131	161	221	
18.48	54	1,3,5-Trioxane,[methoxy,] ₆ hydroxy	276	61	89	91	119	151	277	

Table 9
Pyrolysis products from the pyrolysis of POM at 700°C

Retention time (min)	Compd. no.	POM alone		50/50 Co-pyrolysis		50/50 Intimate blend		5% Addition of copper	
		Area (%)	TIC signal per mg of POM ($\times 10^6$)	TIC signal per mg of POM ($\times 10^6$)	% Change	TIC signal per mg of POM ($\times 10^6$)	% Change	TIC signal per mg of POM ($\times 10^6$)	% Change
1.76	1	93.19	3799.01	1720.22	–54.7	1811.92	–52.3	3280.56	–13.6
2.02	3							65.35	
2.17	4	0.81	33.11					79.59	140.4
2.21	5			28.46				46.85	
2.31	7	1.35	34.97						
2.37	8							46.66	
2.59	10	1.64	66.83						
2.62	11					35.11		109.54	
2.97	13	0.14	5.65					34.34	507.5
3.24	14			10.88		53.16			
3.40	15					15.36			
3.51	16	0.12	4.95					27.62	458.2
3.59	17					191.78			
3.63	18	0.09	3.77	90.27	2291.9	66.11	1651.7		
3.71	20							17.70	
4.32	21	0.43	17.40					16.88	–3.0
4.81	22					345.08		35.77	
5.00	23	0.16	6.72					4.55	–32.3
6.34	24	0.04	1.48					2.91	96.0
6.67	25	0.06	2.39	15.27	538.3	36.70	1434.2	1.39	–41.9
6.80	26							1.48	
7.06	27			6.95		8.76			
7.68	28	0.05	2.02					2.80	38.3
7.86	29							9.72	
8.55	30							11.87	
8.81	31	0.08	3.07					2.70	–12.1
9.26	32					5.66		3.08	

Table 9 (Continued)

Retention time (min)	Compd. no.	POM alone		50/50 Co-pyrolysis		50/50 Intimate blend		5% Addition of copper	
		Area (%)	TIC signal per mg of POM ($\times 10^6$)	TIC signal per mg of POM ($\times 10^6$)	% Change	TIC signal per mg of POM ($\times 10^6$)	% Change	TIC signal per mg of POM ($\times 10^6$)	% Change
9.80	33	0.06	2.28					2.23	−2.1
10.46	34							3.71	
10.69	35	0.23	9.49						
10.75	36	0.09	3.59					2.91	−18.9
11.17	37							2.29	
11.58	38	0.06	2.64					3.08	16.8
12.47	39	0.08	3.42					3.84	12.2
12.64	40							4.55	
12.78	41							2.77	
13.16	42	0.07	2.93					3.78	28.8
13.91	43	0.10	3.96					4.37	10.5
14.02	44	0.01	0.29					4.23	1334.5
14.24	45							3.92	
14.59	46	0.08	3.32					2.43	−26.6
15.26	47	0.05	2.08					3.13	51.0
15.89	48	0.05	1.89					3.72	97.2
16.50	49	0.05	2.08					4.41	112.1
16.78	50							3.11	
17.08	51	0.03	1.40					3.39	141.9
17.73	52	0.05	2.11					4.57	116.3
18.09	53							4.21	
18.48	54	0.03	1.13					3.14	177.6
Total		99.20	4024.00	1896	−52.9	2570	−36.1	3875	−3.7

When POM was pyrolyzed in the presence of PVC, the first observation was the apparent reduction in the chemical species detected that could be attributed to POM. The large reduction in the yield of formaldehyde was especially noticeable based upon the data presented in Table 9. Interestingly, while the number of methoxy oligomers detected have decreased when POM was pyrolysed in the presence of PVC, the yield of several compounds such as species # 17, 18, 22 and 25 showed substantial increases. These increases meant that they became relatively important species in the pyrolysis product profile. Meanwhile other species such as formic acid and dimethoxyformaldehyde were no longer detected.

The addition of copper to POM appeared to have almost no effect on the pyrolysis process, with the possible exception that several additional compounds were detected in the pyrolysis gases although in small amounts. The exception was the formation of ethoxymethanol (compound # 11) which was detected at the 2.8% level and after formaldehyde, was the most abundant species. There was also a three-fold increase in methoxy methanol (compound # 4) making this the third most abundant compound detected.

When the pyrolysis experiments were conducted at the higher pyrolysis temperature of 900°C the results (Table 10) were very much a reflection of those obtained at 700°C. This was not too surprising considering the differences in the extent of thermal degradation at these two temperatures. Once again, as was obtained at 700°C, formaldehyde was the major product, responsible for close to 90% of the volatile species. Once again the reduction in formaldehyde was somewhat surprising, as was the reduction in the total TIC signal noted at this higher pyrolysis temperature. One explanation, which needs to be explored, is the possible formation of secondary degradation products of higher molecular weight which were not detected by our Py/GC/MS approach. In terms of the influence of PVC on the degradation products, the results were similar to those obtained at 700°C. For example the yields of compounds # 17, 18, 22 and 25 were once again enhanced with the largest yields being obtained when the two polymers were intimately blended together.

In the case of copper, once again, the effects noted were not large. While the actual relative amounts of several species changed significantly, the concentrations of the majority of the species were exceedingly small and as a result their overall impact on the value of the pyrolysis products was not expected to be large.

4. Conclusion

Because the thermal degradation of PVC involves the formation of HCl, as a result of dehydrochlorination, it is to be expected that the degradation of polymers sensitive to acid catalysis may be influenced when co-pyrolyzed in the presence of PVC. In this study we have shown that the thermal stability of the polymers ABS, PC and POM are all decreased when pyrolyzed in the presence of PVC, resulting in greater mass losses. It has also been shown that PVC can influence the pyrolysis products profile of these polymers. However, under the conditions used in this

Table 10
Pyrolysis products from the pyrolysis of POM at 900°C

Retention time (min)	Compd. no.	POM alone		50/50 Co-pyrolysis		50/50 Intimate blend		5% Addition of Copper	
		Area (%)	TIC signal per mg of POM ($\times 10^6$)	TIC signal per mg of POM ($\times 10^6$)	% Change	TIC signal per mg of POM ($\times 10^6$)	% Change	TIC signal per mg of POM ($\times 10^6$)	% Change
1.73	1	89.67	2964.54	1443.96	– 51.29	1620.30	– 45.34	2875.92	– 2.99
1.96	2	0.48	15.77					19.48	23.51
2.02	3	0.23	7.75						
2.14	4	3.47	114.74					126.26	10.04
2.20	5	0.69	22.88						
2.28	6								
2.31	7			34.60					
2.37	8	1.11	36.55					24.39	– 33.29
2.46	9	0.16	5.55					5.35	– 3.71
2.57	10	0.87	28.92					33.17	14.68
2.62	11	0.67	22.29			46.61	109.08	38.63	73.25
2.94	12	0.29	9.66					15.78	63.29
2.94	13			23.06		67.91			
3.24	14					10.89			
3.40	15								
3.51	16	0.31	10.09					11.46	13.65
3.59	17					163.76			
3.63	18	0.12	3.88	25.44	555.31	40.35	939.31		
3.65	19							15.24	1472.50
3.76	20	0.03	0.97					11.37	5.24
4.31	21	0.33	10.81					21.68	
4.82	22					325.77		10.05	28.72
5.00	23	0.24	7.80					10.52	309.57
6.34	24	0.08	2.57					1.82	42.38
6.67	25	0.04	1.28	5.28	312.34	30.93	2314.05	0.92	– 1.09
6.83	26	0.03	0.93						
7.06	27			4.03		5.91		3.88	273.16

Table 10 (Continued)

Retention time (min)	Compd. no.	POM alone		50/50 Co-pyrolysis			50/50 Intimate blend		5% Addition of Copper		
		Area (%)	TIC signal per mg of POM ($\times 10^6$)	TIC signal per mg of POM ($\times 10^6$)	% Change		TIC signal per mg of POM ($\times 10^6$)	% Change	TIC signal per mg of POM ($\times 10^6$)	% Change	
7.68	28	0.03	1.04						10.06		
7.86	29								10.92		
8.55	30								2.74	16.18	
8.81	31	0.07	2.36						1.49		
9.26	32						2.84		3.26	191.66	
9.80	33	0.03	1.12						2.45		
10.46	34								1.52	−62.76	
10.69	35	0.12	4.07						3.03	6.18	
10.75	36	0.09	2.85						2.23		
11.17	37								5.52	333.69	
11.58	38	0.04	1.27						4.15	37.61	
12.42	39	0.09	3.01						4.22		
12.64	40								2.34		
12.78	41								4.24	201.66	
13.16	42	0.04	1.40						4.70	40.46	
13.91	43	0.11	3.35						3.17	1303.89	
14.02	44	0.01	0.23						3.25		
14.24	45								5.71	262.42	
14.59	46	0.05	1.58						3.36	95.79	
15.26	47	0.05	1.72						4.69	507.31	
15.89	48	0.02	0.77						3.94	150.71	
16.50	49	0.05	1.57						3.23		
16.78	50								4.62	556.27	
17.08	51	0.02	0.70						4.57	257.92	
17.73	52	0.04	1.28						4.86		
18.09	53								4.49		
18.48	54										
Total		99.67	3295.32	1536.36	−53.38		2315.33	−29.74	3334.66	1.19	

study no significant changes were noted that could drastically influence the value of the pyrolysis products.

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