Effect of Gamma irradiation on Tensile Strength and Pyrolysis Behavior of Polyvinyl Chloride

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Summary: Pyrolysis-Gas chromatography (Py.GC) technique has been used for the rapid characterization of polyvinyl chloride (PVC). The pyrolysis of the PVC starts as soon as the sample is inserted in the hot zone. The carrier gas rapidly swept the primary products from hot zone to the chromatographic column, so the secondary decomposition is largely eliminated and the pyrolysis products give accurate information about the nature,composition and structure of the polymeric material. The productions of hydrocarbons from PVC are monitored. The effect of the variation of temperature (600-800°C), sample size (0.5-3) mg, pyrolysis atmosphere Nitrogen and Helium, residence time (0.365-1.827) seconds and gamma irradiation on the distribution of products were studied. The effect of gamma irradiation on tensile strength was also studied. The observed products from PVC were Ethane/Ethene, Propane/Propene, 1,3-Butadiene, 1-Butene, Benzene and Toluene. The yield of these products showed an increase with an increase in temperature from 600-800°C. Gamma irradiation of PVC at doze rate higher than 1 KGry was to decrease the tensile strength and the yield of Ethane/Ethene, propane/propene, 1,3 Butadiene, and 1-Butene decrease, while the yield of Benzene and Toluene remains constant.

Introduction

Plastic based on polyvinyl chloride are present in large amount in domestic and industrial wastes and can cause serious pollution problem. Usually they are thrown of or some time incinerated in case of medical waste, their potential energy content is wasted. Therefore, Conversion of these plastics wastes to useful chemicals may be a promising solution to pollution problem and viable alternate to expensive chemicals [1-2]. The behaviors of macromolecules at high temperature have been studied for decades [3]. Prolysis gas chromatography and GC.MS is used for the identification of polymer and their fragments. At elevated temperature, large molecules dissociate to smaller suitable molecules that generally retain chemical information about the original material. The entire degradation pathway of any macromolecule is quite complex [4]. The overall process may be simplified by grouping the mechanism into three broad categories.

1) the molecule essentially revert back largely or almost exclusively to monomer

2) the molecule breaks apart into many smaller oligomeric fragments, including monomer, dimmer, trimmer, etc. and

3) little or no monomer is formed because the bond within the monomer unit are weaker than those holding the chain together.

In the last case, characteristic products are still formed from the polymer, but the process includes elimination of side groups along the chain, which generally show up as small molecules. Polyolefin such polyethylene and polypropylene generate many oligomers [5] creating a characteristic pattern that becomes readily recognizable. In case of polyethylene molecule, the oligomer products from it are normal hydrocarbons including alkanes, alkenes, and diene etc. The effect of having methyl group found in polypropylene is easily discerned in the pyrogram. Polyvinyl chloride loses HCL and then forms aliphatic and aromatic hydrocarbons [6]. Therefore no vinyl chloride monomer is detected.

Since these processes are the characteristic for the polymers involved, and are highly reproducible, it is easy to identify polymer based on the identity of its pyrolysis products. Even in the case of polymer blends, copolymer and composites material, the small molecule generated during pyrolysis can identify the original material [7-10]. Pyrolysis Gas Chromato-

graphy Mass Spectrometry have been used for the pyrolysis of polyvinyl chloride. In the first step there is loss of HCl leaving a conjugated polyene structure as a residue that can undergo further pyrolysis to yield a vast array of hydrocarbon. The most abundant products other than HCl is aliphatic hydrocarbon Benzene and Toluene [11]. Several investigators examined [12-14] the decomposition of PVC by Thermogravimetric analyzer and pyrolysis Gas Chromatography. Pyrolysis gas chromatography has an advantage in investigating the structure and composition of polymer like Polyethylene and Polypropylene, where formation of hydrocarbon and monomer is monitored [15-18].

The aim of present work is to evaluate the effect of gamma irradiation on the yield of hydrocarbon using pyrolysis Gas Chromatography. The effect of gamma irradiation on tensile strength at room temperature is also studied.

Results and Discussion

To check the reproducibility of present pyrolysis-gas chromatographic procedure, three identical samples of PVC resin, of same quantity were pyrolysed at 700°C (typical prygram of sample is shown in Figure (1). The main pyrolysis products identified were Ethane/Ethene, Propane/Propene, 1,3-Butadiene, 1-Butene, Benzene and Toluene. The individual peak areas were observed for 0.5 mg of sample. The data was processed to obtain the arithmetic mean of percent peak area of each peak and this was used for calculating percent standard deviation. The results are shown in Table-1 which clearly indicates that percent standard deviation is high and greater variation in the product yield is observed. This level of precision although not completely satisfying, but is consistent and in some instances better than the work reported earlier [19] in their pyrolysis gas chromatography experiments for the characterization of polymer.

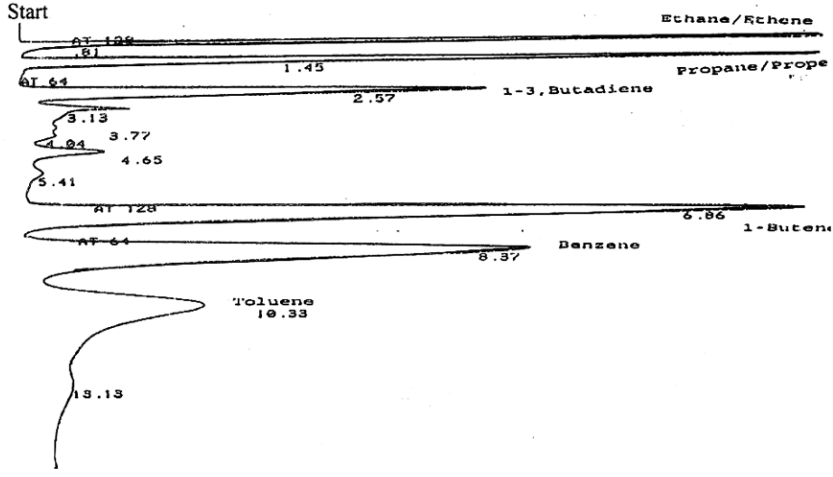

Fig. 1: Typical Pyrogram from the pyrolysis of Polyvinylchloride at 700°C.

Table-1: Precision of Pyrolysis of Polyvinyl Chloride at 700°C

Peak No.	Ethane / Ethene	Propane/ Propene	1,3,Butadiene	1-Butene	Benzene	Toluene
1	9.96	9.98	9.91	35.53	13.35	11.46
2.	8.09	9.33	7.76	34.34	14.18	12.09
3	8.66	12.00	8.04	38.15	13.91	10.11
Average peak Area (cm^3)	8.90	10.44	8.57	36.006	13.81	11.22
Standard deviation	0.9534	1.3923	1.1688	1.9492	0.4234	1.0115
% SD	10.7123	13.3362	13.6382	5.4135	3.0658	9.0151

To measure the variation in the yield of different pyrolysis products due to gas chromatographic detector, three injections of Toluene of 1µl each were made directly on to the injection port of gas chromatograph under the similar optimum conditions. The data given in Table-2 indicate that the percent standard deviation up to 2.38 can be taken as a maximum error in the reproducibility of gas-chromatographic detector and the value exceeding 2.38 can be attributed to the operational cum instrumental error.

Table-2: Reproducibility of Toluene Injection

No. of Run	Area (X)	Average of three runs	$[X-X]^2$	Average $[X-X]^2$	Strand deviation	%SD
1	12.95		.0784			
2	12.71	12.67	0.0016	0.1824	0.30199	2.38
3	12.35		0.1024			

Under identical condition as used for PVC resin, pyrolysis of PVC plastic yellow and red were carried out. The major products identified were the same as for PVC resin. . The total yield (total areas) of the products from each polymer was computed. The results are given in Table-1. A comparison of the result clearly illustrates that there is no significant change in the yield of pyrolysis products.

Effect of Temperature

Thermal degradation of PVC was carried out over the temperature range 600-800°C with 0.5mg sample. The removal of HCl from the polymer leaves conjugated polyene structure of various length, which either recyclizes via intra or intermolecular interaction to give cyclic compounds like Benzene and Toluene or undergo random chain scission producing free radical to form various aliphatic hydrocarbons [11]. Table-3 shows the dependence of products yield on temperature. It is evident from the results that the yield of Ethane/Ethene, Propane/Propene, 1-Butene and Benzene increases with the rise in temperature while that of 1-3 Butadiene and Toluene increases first then decreases when the temperature is increased from 600 to 800°C. The results are consistent with the earlier work on PVC thermal degradation [16]

Effect of Sample Size

0.5-3mg of polymer samples were pyrolyzed at 700°C. The results are given in Table-4. An examination of the results indicate that there is a slight increase in the yield of lower hydrocarbons with an increase in the sample size, while the aromatic hydrocarbon i.e. Benzene and Toluene show a little decrease in their yield with increasing sample size. This study is comparable to those reported by Lattimer and Kroenke [11]

Effect of Pyrolysis Atmosphere

The effect of pyrolysis atmosphere on the composition and yield of pyrolysis products was

Table-3: Effect of temperature on the yield of products from thermal decomposition of PVC at 700°C

Pyrolysis Temp. °C	Percent products					
	Ethane / Ethene	Propane/ Propene	1,3, Butadiene	1-Butene	Benzene	Toluene
600	4.24	5.52	6.39	50.27	7.21	7.16
650	5.37	6.20	7.64	49.08	10.22	8.35
700	9.69	9.88	9.17	33.53	13.35	11.46
750	12.06	12.89	6.19	36.23	15.17	10.94
800	14.99	14.85	3.20	47.78	15.58	7.78

Table-4: Effect of sample size on the yield of products from thermal decomposition of PVC at 700°C

S.#	Samples Size (mg)	Percent products					
		Ethane/ Ethene	Propane/ Propene	1,3, Butadiene	1-Butene	Benzene	Toluene
1	0.5	8.09	9.33	7.76	34.14	14.18	12.09
2	1	9.68	9.88	9.16	33.53	13.35	11.45
3	1.5	11.23	12.09	9.93	36.90	12.99	11.87
4	2	13.52	13.20	12.76	37.53	13.57	13.07
5	2.5	15.98	16.61	13.98	40.11	14.69	12.52
6	3	15.81	16.00	14.62	40.75	15.14	12.32

Table-5: Effect of pyrolysis atmosphere on the yield of products from thermal decomposition of PVC at 700°C

S.#	Pyrolysis atmosphere	Percent Product					
		Ethane/ Ethene	Propane/ Propene	1,3, Butadiene	1-Butene	Benzene	Toluene
1.	Nitrogen	8.98	9.88	10.32	33.53	13.24	11.18
2.	Helium	9.56	10.02	9.65	34.71	12.68	11.46

investigated in Nitrogen and Helium atmosphere at 700°C. The results are reported in Table-5. It is obvious from these results that no significant changes occur in the composition and yield of major volatile products, when the carrier gas was changed from Nitrogen to Helium. However a slight difference was observed in the retention indices of the products in the chromatogram of the polymer in the atmospheres of Nitrogen and Helium.

Effect of Residence Time.

The effect of residence time on the distribution of products resulting from pyrolysis of Polyvinylchloride was carried out at 700°C. The residence time of the volatile products in the hot zone was varied for seconds by changing the flow rate of carrier gas from 20-100 ml/min. The results are presented in Table-6. The yield of all the products decreases with increase in the residence time indicating secondary decomposition. Lehmann and Brauer [20] in their study of polystyrene pyrolysis observed that the variation of flow rate of carrier gas between 45 and 75 ml/min did not alter the composition of the degradation products. However, at low flow rate i.e.<45 ml/min, they observed an appreciable amount of secondary decomposition products resulting from primary products.

Effect of Irradiation

In order to check the effect of irradiation on the yield of pyrolysis products and structures the PVC samples were irradiated by gamma-irradiation with Co^{60} source at doze rate 1KGry, 2KGry, 3KGry, 4KGry, and 5KGry. The observed pyrolysis products from both unirradiated and irradiated PVC samples were Ethene/Ethane/Propane/Propene, 1-3 Butadiene, 1-Butene, Benzene and Toluene. A comparison of the yield of various products from both unirradiated and irradiated PVC samples are given in Table-7. The results show that the irradiation of PVC at doze rate of 1KGry for 33.5 min has no effect on the yields and composition of these products indicating that exposure of PVC polymers to irradiation of 1 KGry for 33.5 min has no effect on the structure of polymer. However, the variation in the yields of pyrolysis product was observed, when the doze rate was increased from 1KGry to 5KGry. There is increase in the yield of Ethane/Ethene, Propane-/Propene 1, 3, Butadiene and 1-Butene, while the yield of Benzene and Toluene remain constant. The higher the yield of lower molecular weight product could be due to to the acceleration of random chain scission reaction by the high doze rate irradiation

Table-6: Effect of residence time on the yield of products from thermal decomposition of PVC at 700°C

S.#	Residence Time in Hot Zone (second)	Percent Products					
		Ethane/ Ethene	Propane/ Propene	1,3, Butadiene	1-Butene	Benzene	Toluene
1.	0.365	14.71	13.98	12.10	47.65	18.32	12.92
2.	0.457	13.05	13.19	11.78	45.40	17.47	12.37
3.	0.522	12.32	12.31	11.11	41.37	16.85	11.99
4.	0.731	10.21	11.43	10.21	37.52	16.01	11.23
5.	1.218	9.69	9.88	9.17	36.23	15.12	10.94
6.	1.827	8.78	7.88	8.40	31.61	13.61	8.13

Table-7: Effect of Gamma irradiation on yield of products from thermal decomposition of PVC at 700°C

S.#	Irradiation Doze rate	Percent Products					
		Ethane/ Ethene	Propane/ Propene	1-3, Butadiene	1-Butene	Benzene	Toluene
1.	Unirradiated	9.56	10.02	8.82	34.71	13.68	11.18
2.	1 KGry	8.76	8.57	8.63	33.53	14.18	12.09
3.	2 KGry	9.09	9.88	9.76	36.90	13.35	11.31
4.	3 KGry	10.33	11.23	10.16	38.10	12.39	11.45
5.	4 KGry	13.09	13.52	12.76	38.55	12.01	10.99
6.	5 KGry	15.81	16.00	15.81	39.68	11.33	11.54

Table-8: Effect of Color on the yield of products from thermal decomposition of PVC at 700°C

S.#	PVC Colour	Percent Products					
		Ethane/ Ethene	Propane/ Propene	1-3, Butadiene	1-Butene	Benzene	Toluene
1.	Resin	8.35	9.84	9.17	33.53	10.35	11.46
2.	Yellow	7.33	12.92	10.09	48.60	9.09	10.12
3.	Red	8.54	14.01	10.82	44.05	10.01	10.05

Effect of Colour

To observe the effect of colour on the yield of pyrolysis products, the PVC samples of resin, yellow, and red plastic were decomposed at 700°C. The carrier gas flow rate was 50 ml/min. The results are presented in Table-8. From the results it is clear that the yield of Ethane/Ethene, 1,3-Butadiene, Benzene and Toluene are the same both for coloured plastic and PVC resin. The yield of Propane/Propene and 1-Butene are higher from colour PVC as compared to PVC resin.

Effect of irradiation on Tensile Strength

To study the effect of irradiation on tensile strength the irradiated PVC samples were tested by Universal testing machine. A comparison of the results from both irradiated and unirradiated PVC samples are shown in Table-9. The results show that the irradiation of PVC at doze rate of 1KGry for 33.5 min has slight effect on the tensile strength indicating that exposure of PVC polymers to irradiation of 1 KGry for 33.5 min has slight effect on the structure of polymer. However, the variation in tensile strength was observed, when the doze rate was increased from 1KGry to 5KGry. The tensile strength and modulus at 100% strain decrease by increasing the doze rate from 1KGry to 5KGry.

Table-9: Effect of Gamma irradiation on tensile strength of PVC

S.#	Irradiation	Tensile Strength MPa			
	Doze rate	Yellow	% at Elongation	Red	% at Elongation
1.	Unirradiated	15.4	385	15.8	382
2.	1 KGry	14.9	369	14.6	364
3.	2 KGry	13.7	361	17.7	352
4.	3 KGry	12.8	342	12.6	336
5.	4 KGry	11.3	309	11.3	302
6.	5 KGry	9.2	286	9.5	278

Experimental

Apparatus

Pyrolyzer used for pyrolysis as PyR-2A Shimadzu GC.7AG Gas Chromatograph, which was attached to spectraphysic Data jet integrator. The furnace temperature was recorded on Shimadzu R 112 bench type automatic balancing recorder. The full scales of the recorder indicate 1000°C.Tensile properties were measured on Model (Instron) 4301 Universal Testing Machine.

Material

PVC used in the present study were in powder form and were commercially available. The PVC resin and plastic form were collected from prim star Industry Hayat Abad, Peshawar NWFP. Standard PVC sample was purchased from BDH limited Poel, England. PVC low molecular weight B.P. = 100°C, Viscosity 0.725, mol.wt app, 100,000, Toluene, Benzene BDH. Methane, Ethane, Ethene, Propane, Propene, Butane, 1-Butene, 1-3 Butane were purchased from Aldrich Company limited.

Procedure

A Shamadizu PYR-2A Pyrolyzer was directly coupled to Shamadizu GC-7AG gas chromatograph equipped with flame ionization detector. Polymer sample 0.5 mg was pyrolyzed at temperature range 500-800°C for 30 second. The temperature of interface between the pyrolyzer and gas chromatograph was maintained at 250°C. The analytical column was a stainless steel tube (6ft x ¼ "), which was packed with Porapak Q (80-100 mesh). The initial temperature of column was maintained at 50°C and programmed to increase at the rate of 32°C/min up to 230°C. The Nitrogen carrier gas flow rate was 50ml/min. The recording of pyrogram were carried out by Data jet integrator. Identification of the products was done by comparing the retention times of the peaks in pyrogram with those of the standard pure compounds. Following gas chromatographic condition were employed for the analysis of volatile products, resulting from PVC (Poly vinyl chloride).

- Carrier Gas = Nitrogen
- Flow rate of carrier = 50 ml/min
- Air pressure = 0.5 Kg/cm^2
- Hydrogen preserve = 1 Kg/ cm^2
- Injection port temp. = 170°C
- Range = 10^3
- Column = (6ft x 1/8 inch) porapak Q
- Detector = FID
- Column Temp. = 50-230°C@32^{0}C/min
- Pyrolysis temp. = 600 – 800°C
- Pyrolysis time = 30 second

Conclusions

Pyrolysis Gas Chromatography system allowed qualitative and quantitative estimation pf hydrocarbon products from PVC sample. The yield and composition of these products are characteristic of individual PVC sample and strongly depends upon the reaction condition. Comparison of the yield of hydrocarbon from unirradaited and irradiated sample indicate that increase in the yield of lower hydrocarbon was observed, when the doze rate is increased from 1KGry to 5KGry and also resulting decrease in tensile strength.

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